BEYOND CURRENT RESEARCH TRENDS IN CO_2 UTILIZATION

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BEYOND CURRENT RESEARCH TRENDS IN CO_2 UTILIZATION

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EDITORIAL
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Editorial: Beyond Current Research Trends in CO_2 Utilization

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Editorial on the Research Topic

Beyond Current Research Trends in CO_2 Utilization

The Carbon Circular Economy-CCE is a key component of the strategy for sustainable, climate-neutral growth of our society. CCE encompasses carbon management in all its forms and fields of application (energy sector, all manufacturing sectors including the chemical industry, agriculture and related practices, civil life) for an efficient reduction strategy that minimizes the emission of greenhouse gases (GHGs), and CO_2 in particular, in all anthropic activities.

Carbon Dioxide emissions reduction is under particular pressure these days as CO_2 is considered the origin of climate change. In our opinion, the protagonist of the extreme events we are observing of late (tornados, floodings and fires, desertification, and rising oceans) is the inefficient use we make of fossil-C that causes over 65% of the energy to be released in the form of heat to the atmosphere, in addition to too high emissions of all GHGs, including water vapor.

The reduction of CO_2 emissions can be achieved primarily by reducing the consumption of fossil-C, and by changing primary energy sources or adopting a Nature-like strategy: the recycling of carbon.

The use of Renewable Carbon is a major attitude shift, and this stopping the linear model of taking fossil-C (formed over millions of years) and releasing CO_2 (a spent form of carbon). Human intelligence must discover ways to develop a man-made Carbon Cycle, that can complement the natural one, one even more efficient in terms of rate and selectivity of processes. Vegetal plants make what they need, and a man-made carbon cycle can make what humans need: energy products, or alternatively molecular compounds necessary for everyday life, or else other materials. Nature uses the sun to power the synthetic processes; we can use sun, wind, hydropower, geothermal energy-SWHG, all C-free, perennial sources, to power synthetic processes. We call SWHG sources perennial as have always existed and will continue to exist in the future for as long as our planet does. We prefer to reserve the term *renewable* for biomass.

The cost of the change is high, as all technologies based on C-free perennial energy sources and even on renewable energy sources (biomass) are more costly than technologies based on fossil-C, and less efficient. Over two hundred years of Chemical Industry based on fossil-C has developed efficient syntheses for a single target product. Technologies based on perennial energies are much younger and need to develop and mature.

However, carbon recycling can be performed by Nature-based systems (growing any kind of biomass) or by man-made systems, e.g., by converting CO_2 into chemicals, materials, and fuels. Biomass-based products are already on the market, CO_2 based products must be developed in a legal frame and become accepted by the public. This will take time and education.

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Nevertheless, it is time to implement CO_2 utilization if we wish to reduce the use of fossil-C. Biomass alone cannot satisfy the needs of human beings (being limited by growth rate and amount). Complementing biomass with industrial processes may help to find a valid solution.

This Research Topic is devoted to making the point on what we do with CO_2 and what we could do if perennial energy sources were available at a low cost. Most likely, by 2050 innovative synthetic strategies based on CO_2 will be performing at high efficiency.

In Chapter 1 (Aresta and Dibenedetto), a perspective on future utilization of CO_2 is outlined, highlighting barriers and ways to get around them. Any use of CO_2 requires its availability: therefore, Chapter 2 (Wang and Song) makes the point on established techniques for CO_2-capture and discusses the capture from air, where CO_2 is present at a low concentration (410 ppm at present), but will guarantee its availability forever (fossil-C availability is finite). Chapter 3 (Baciocchi and Costa) presents a way to fix CO_2 into materials that have a long lifetime: such materials are like natural rocks that sequester $CO_{2,}$ and the technology does not integrate into the circular economy: it is more functional to the linear economy for carbon dioxide sequestration. Chapter 4 (Zhang et al.) discusses the conversion of CO_2 into methanol, a chemical with rich chemistry and an energy product at the same time (usable if fuel cells and mixed with gasoline in cars). Chapter 5 (Centi et al.) is a complementary aspect of methanol synthesis as it makes a point on the economics of methanol production. As mentioned above, fossil-C substitution will raise costs issues as today fossil-C is a cheap source of raw materials and processes are optimized for both investment and operational costs, CAPEX and OPEX, respectively. Chapter 6 (Bogaerts and Centi) presents plasma technology for CO_2 conversion, highlighting how fluctuating renewable energy can be used and stored as chemical energy. Chapter 7 (Tomishige et al.) exemplifies the use of CO_2 in the production of large market chemicals, namely organic carbonates that may find application in several sectors such as solvents, raw materials, monomers for polymers, a medium in lithium batteries, etc. Chapter 8 (Kondaveeti et al.) introduces new systems for CO_2 conversion, e.g., biosystems coupled to electricity. This is an attractive new area that can contribute to CO_2 utilization on a large scale making a variety of products according to the bio-system (microorganism) used. Chapter 9 (Gerotto et al.) makes light on the organisms in Nature which convert CO_2 the fastest: microalgae, a fascinating world that has a great potential for application in the synthesis of fuels or chemicals or materials. Finally, Chapter 10 (Kumar et al.) opens a window on the use of biomass highlighting problems that are around when one wishes to use such raw materials as a source of chemicals or energy.

All together, this book presents interesting aspects of the potential of carbon recycling, and the difficulties that one encounters when facing such stimulating and innovative technology, barriers to full exploitation of the strategy, and how to go around them.

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All authors listed have made a substantial, direct, and intellectual contribution to the work and approved it for publication.

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REVIEW
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Advanced Routes of Biological and Bio-electrocatalytic Carbon Dioxide (CO_2) Mitigation Toward Carbon Neutrality

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Changes in the environment due to multiple factors, such as combustion of fossil fuels, heating, transportation, deforestation, etc., have led to more greenhouse gases in the atmosphere, which eventually led to a rise in global temperatures. Carbon dioxide (CO_2) is the major factor for the rapid rise in global temperature. One of the most encouraging technological advances to address global warming is to transform CO_2 into value-added commodities that offer a win–win strategy. In this regard, intensive research has been pursued around the world for development of feasible systems in product recovery or product synthesis from CO_2-rich industrial emissions. We envision that the biological CO_2 reduction or conversion process can be beneficial for developing carbon-neutral technologies. The integration of CO_2-emitting industrial technologies with CO_2-converting biological systems can be helpful in achieving sustainable value-added products with no or minimal loss of energy and materials that are assuring for improved economics. The CO_2-converting bioprocesses can be directly integrated with the processes emitting a high amount of CO_2. This symbiotic integration can make the whole process carbon neutral. Herein, this review highlights an insight on research activities of biological CO_2 mitigation using photo catalysts (algae and photo bacteria), an anaerobic biocatalyst (bacteria), gas fermentation, and an enzymatic catalyst. Perspectives and challenges of these technologies are discussed.

Keywords: CO_2 capture and utilization, algae, bioenergy, greenhouse gases (GHG), gas fermentation, microbial electrosynthesis (MES), CO_2 reduction pathways

INTRODUCTION

Expansion of industries and world population are leading to an increase in the release of greenhouse gases, resulting in accelerated global warming (Kumar et al., 2016; Effendi and Ng, 2019; Youn et al., 2019). The higher levels of carbon dioxide (CO_2) emissions into the environment have become a major contributor to global warming (**Figure 1A**). Both reduction in CO_2 emission and capture of CO_2 are critical to reduce global warming (Benhelal et al., 2013). In this regard, carbon capture, sequestration, and utilization have proven to be efficient options for decreasing the atmospheric CO_2, which can be regarded as a waste-to-energy process (Liu et al., 2016). This energy process can be either fuel generation or chemical and material production. Several industrial technologies have been developed and are operational, such as the alkaline adsorption process (CO_2 capture), mineralization process, landfill process (CO_2 sequestration), urea synthesis, methanol production, phenol carboxylation, epoxide carboxylation, and pyrrole carboxylation (CO_2 utilization) (Shi et al., 2015; Liu et al., 2016). Global research on biological CO_2 conversion for renewable and sustainable energy generation is increasing at a rapid pace in diversified research disciplines (**Figure 1B**). In addition, many bench laboratory-scale or pilot-scale technologies are also being developed to increase the performance of CO_2 capture, sequestration, and utilization toward value addition (Shi et al., 2015).

Capture and transformation of CO_2 to value-added products, such as biofuel, are of special interest, and several countries have been developing policies by providing subsidies and legislative incentives. For instance, the Renewable Energy Directive (RED) under the European Union (EU) is moving toward a vision of 2020, which is targeting the generation of 10% of the energy required for the transportation sector that should be replaced with renewable biofuels (Chang et al., 2016; Sadhukhan et al., 2016). Likewise, in the United States, the Renewable Fuel Standard is targeted at increasing biofuel generation by 36% with a vision of 2022 (Rana et al., 2011). About 58% of biofuel generation is mainly from second- (e.g., organic waste, plant waste) and third-generation (e.g., algae biomass) biofuels.

Biological, chemical, photo-chemical, electrochemical, and enzymatic technologies have been developed for fixing and conversion of CO_2 to renewable energy generation (Benemann, 1997; Bond et al., 2001). However, a majority of the processes are linked with high energy input, which is making the process economically unfavorable. Among these methods, a biological system for CO_2 utilization using bacteria as a catalyst, which is of low cost and self-regenerative, is of particular interest and importance (Benemann, 1993; Jiang et al., 2019). Hence, the

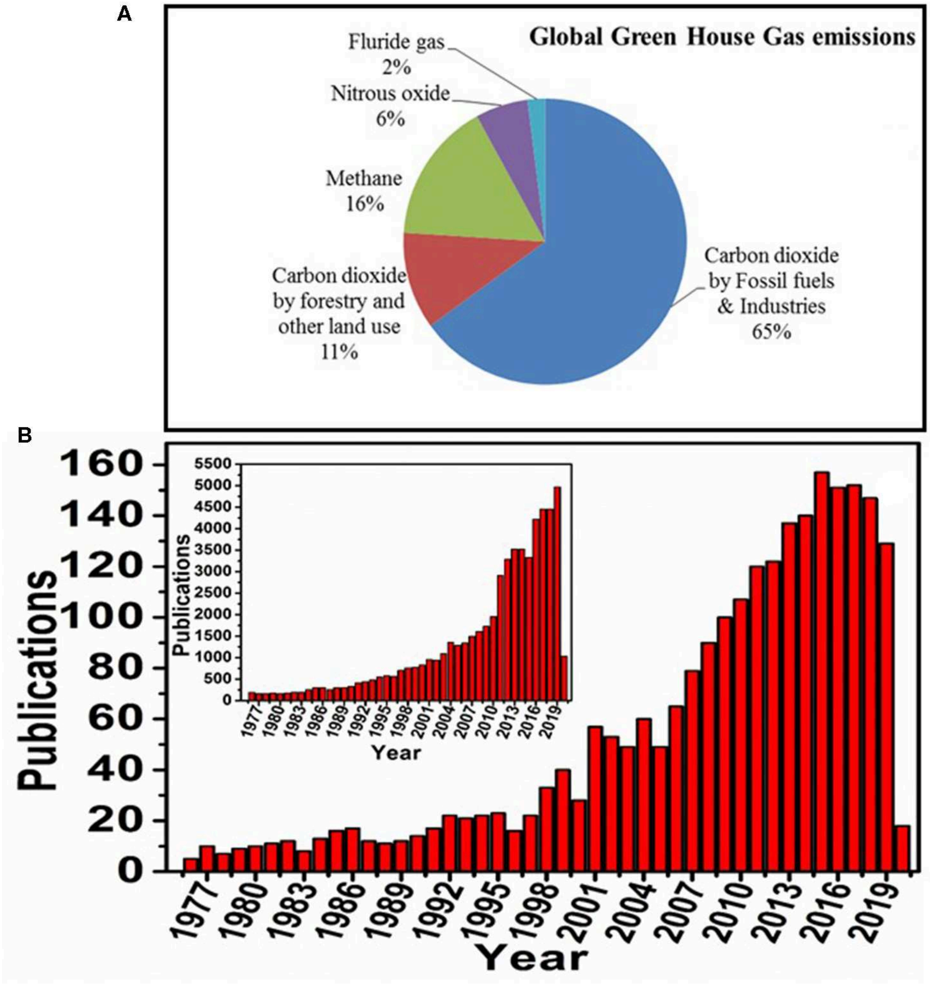


FIGURE 1 | (A) Graphical representation of global greenhouse gas emissions (source: https://tinyurl.com/EPA-GHG-Data), **(B)** number of articles published on biological conversion of CO_2 to value-added production (source: Scopus; key words: Biological carbon dioxide reduction or Biological carbon dioxide conversion, as on date: 21/04/2020). Inset figure exhibits the number of published articles on carbon dioxide reduction or carbon dioxide conversion irrespective of field.

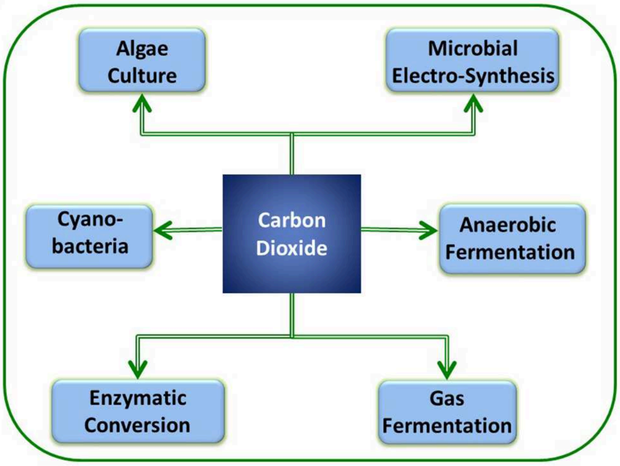


FIGURE 2 | Various biological processes that have potential for CO_2 sequestration along with sustainable bioenergy/chemical production.

potential of numerous biological CO_2 utilization methods to decrease the atmospheric CO_2 should be investigated further with an energy-neutral and biorefinery approach (Venkata Mohan et al., 2016; Hou et al., 2019). The petroleum refinery approach has been well-known for a long time for energy generation. However, the use of a CO_2 biorefinery approach is exciting and offers a sustainable and eco-friendly process (Packer, 2009; Venkata Mohan et al., 2016). Nonetheless, this area of biological CO_2 utilization research is obstructed with several questions regarding its efficiency, establishment cost, and fulfilling of current and future energy demands. Despite these criticisms, the research on utility of CO_2 should be increased toward a carbon-neutral footprint and energy neutrality. Therefore, the major objective of this review is to highlight the biological CO_2 utilization methods that can be implemented to generate bio-based products and elaborate on the biology of sequestration methods of different systems/microbes.

BIOLOGICAL MITIGATION OF CO_2

Photosynthetic CO_2 Reduction

Recently, several researchers have concentrated on sequestration of CO_2 using light energy to generate value-added products, including fuels, chemicals, and other materials. Most of the photosynthetic biological systems include oxygenic or oxygenic photosynthesis routes (Hunt et al., 2010). Below, we discuss the CO_2 reduction using algae and photosynthetic bacteria (**Figure 2**). Algae cultivation for CO_2 conversion provides numerous advantages and liabilities that are documented in **Table 1**.

CO_2 Sequestration/Assimilation Using Algae

In the past decade, several studies have proven that CO_2 mitigation with algae is found to be a sustainable process with simultaneous generation of high calorific products, such as biodiesel, pigments, fatty acids, etc. (Chisti, 2007; Demirbas, 2010) (**Table 2**). The potential utilization of algae is mainly attributed to its wide distribution, high biomass production, capability to adjust in adverse conditions, swift carbon uptake and utilization, and capability to generate value-added products (**Figure 3**). Both macro and micro algae have the capability to metabolize inorganic carbon by a photoautotrophic mechanism using carbonic anhydrase enzyme (CAE) (Clarens et al., 2010). The generated $NADH_2$ from the electron transport chain combines with the RuBisCo (Ribulose-1,5-bisphosphate carboxylase/oxygenase, provided by CAE) and helps in carbohydrate generation from CO_2 and provides the reducing power in the Calvin cycle for glucose synthesis (Shi et al., 2015).

Selection of suitable microalgae for CO_2 fixation

It is known that a higher concentration (generally greater than 5%) of CO_2 adversely impacts the growth and production rate in most microalgae (Clarens et al., 2010). Therefore, numerous research studies are being carried out to isolate a suitable algal strain for direct and efficient conversion of industrial CO_2 into products such as agar and alginate, etc. (**Table 3**). The criteria for selection is not only tolerance of CO_2, temperature, and toxic compounds, but also for attaining high growth rates and maximum cell densities (Kratz and Myers, 1955; Allen and Stanier, 1968).

Freshwater microalgae *Chlorella* HA-1 exhibited a maximum growth rate when it was evaluated at 5 and 10% of CO_2 (Watanabe et al., 1992). However, the growth was inhibited with further increases in CO_2 concentration up to 20%. This study proposed that *Chlorella* HA-1 can be used to treat industrial flue gas with a maximum CO_2 concentration of 10% (Watanabe et al., 1992). This strain exhibited a variation in response with a change in temperature and pH. *Chlorococcum littorale* culture isolated from a saline water pond was able to show an almost similar growth rate from 5 to 60% of CO_2, which is a much higher CO_2 concentration than in flue gas (20%). When the CO_2 concentration was boosted to 70%, a decrease in growth rate was identified. As this strain exhibits high growth at high CO_2 concentrations, it can be readily applied for industrial flues gases (Kodama et al., 1993). There were also several other strains of micro algae that have exhibited a high growth rate in adverse conditions, such as extreme pH and temperature (Kumar et al., 2011). The most industrially applicable algal product is lipids, which can be used as a source for biofuel productions (e.g., biodiesel) (Silva et al., 2014). Therefore, the assortment of strains for generation of high lipid generation and augmenting the culture conditions, such as light, temperature, and pH, are vital to enhance the productivity (Csavina et al., 2011; Georgianna and Mayfield, 2012). The unoptimized pH, during algae growth, can affect the distribution of carbon species and carbon availability. Also, at extreme pH, it can directly affect the metabolic activity of algae.

Flue gases from fossil fuel power plants and industries discharge elevated strengths of CO_2, varying from 10 to 20%, along with a biologically significant amount of NOx and SOx. The dosing of flue gases to algae ponds has shown to increase biomass yields by 3-fold and high energy generation (Hanagata et al.,

TABLE 1 | Diversified advantages and liabilities of algae based biofuels systems.

Advantages	Liabilities
Sustainable, renewable, and environmental friendly	Utilization of fossil fuel for process in small quantities
Low carbon to high carbon sources namely carbohydrates, lipids, and proteins	Indefinite availability of sustainable algae resources for biofuel generation
High value feedstock as a replacement to terrestrial biomass	Lack of origin and source certification for global monitoring and control of algae fuel
Non-toxic and non-edible	Regionally constrained market structures for biofuels
Diversification of fuel and energy generation	Production costs for operation of algae biofuel plant
Conservation of fossil fuel, High CO_2 capture, energy conversion through photosynthesis	Economics of process need to be improved
High productivity and yields with rapid growth rates	Harmful algae blooms in global waters
Easily cultured, readily, and rapidly bioengineered	Utilization of arable land
Easy adaptability at various climatic conditions	Unclear utilization of type of waste materials
Can grow almost everywhere such as ponds, wastelands etc.,	May cause Neurotoxic problems
Restoration of contaminated areas and ponds with quick bioremediation with degradable sources	Limited expertise in optimization of industrial biofuel generation

TABLE 2 | Products from algae using CO_2 as a substrate and their applications.

Products	Applications	References
Agar	Food ingredient, brewing agents, biological/microbiological applications	Lee et al., 2017
Alginate (Kerogen)	Medical, paper, and cosmetic	Petersen et al., 2008
Antioxidants (Fucoxanthin)	Preservative in food, chemical, and cosmetic industries	Foo et al., 2017
Beta carotene and Carotenoids	Supplement in vitamin C and precursor for vitamin A	Fernando et al., 2016
Biobutanol, bioethanol, biodiesel, biomethane, biohydrogen,	Bioenergy and Biofuels	Xia et al., 2016
Biochar	Combustion and agriculture	Nautiyal et al., 2016
Biosorbents	Ion exchange materials that have the capacity in binding toxic heavy metals	Bulgariu and Bulgariu, 2016
Chemicals	Medical and industrial application	Trivedi et al., 2015
Cosmetics	Water binding material, antioxidants, and skin food	Wang et al., 2015
Digester residue	Compost and Vermi-compost	Vassilev and Vassileva, 2016
Feed	Animal and biological feedstock	Wang C. et al., 2015; Mark Ibekwe et al., 2017
Fertilizers	Rich in N,P and K minerals, as fertilizer	Rengasamy et al., 2016
Food	Juices, sauce, noodles, beverages, cheese, etc.,	Vigani et al., 2015
Preservatives	Food industry	Kerdudo et al., 2016; Lowe and LaLiberte, 2017
Pharmaceutical (Omega 3 and Omega 6)	Pharma industry	El Gamal, 2010; Samarakoon and Jeon, 2012
Pigments (phycocyanin, phycoerythrin)	Synthesized pigments can be helpful in textile industry	Venil et al., 2013; Holkar et al., 2016; Li et al., 2017

1992; Maeda et al., 1995). Fortunately, the benefits in injecting the flue gas to algae growth can be more helpful than the growth impacts attributed in the photorespiration process at high CO_2 concentrations. Recent studies have shown that direct submission of flue gases into algal ponds exhibited a 30% increase in biomass yields over using the equivalent concentration of CO_2 (Tsuzuki et al., 1990; Singh and Singh, 2014). This might be due to the existence of additional nutrients (oxides of nitrogen and sulfur) present in flue gas. This competence of CO_2 encapsulation by algae can vary according to the algae physiology, pond chemistry, and temperature. About 80 to 99% of CO_2 capture can be obtained under optimized conditions with gas residence times as short as 2 s (Keffer and Kleinheinz, 2002; Lee and Lee, 2003). For a 200 MW/h power plant, it has been noted that 3,600 acres of algae pond would be required to capture 80% of the plant's CO_2 emissions during the daylight hours, assuming a productivity rate of 20 g dry biomass/m^2/d. Therefore, locating the algae ponds next to CO_2 point suppliers provides numerous potential low-cost and energy-saving advantages (Sayre, 2010) with a minimal carbon footprint.

Challenges in using algae for CO_2 capturing/sequestration

On an industrial scale, algae are typically growing in photo bioreactors, open ponds, or raceway ponds (Wang, 2014). The use of open ponds can be simpler in architecture and operation. However, these are limited with a large surface area necessity, elevated cultivation cost, high chance of contamination, and low productivity. Photo bioreactors with closed systems have been

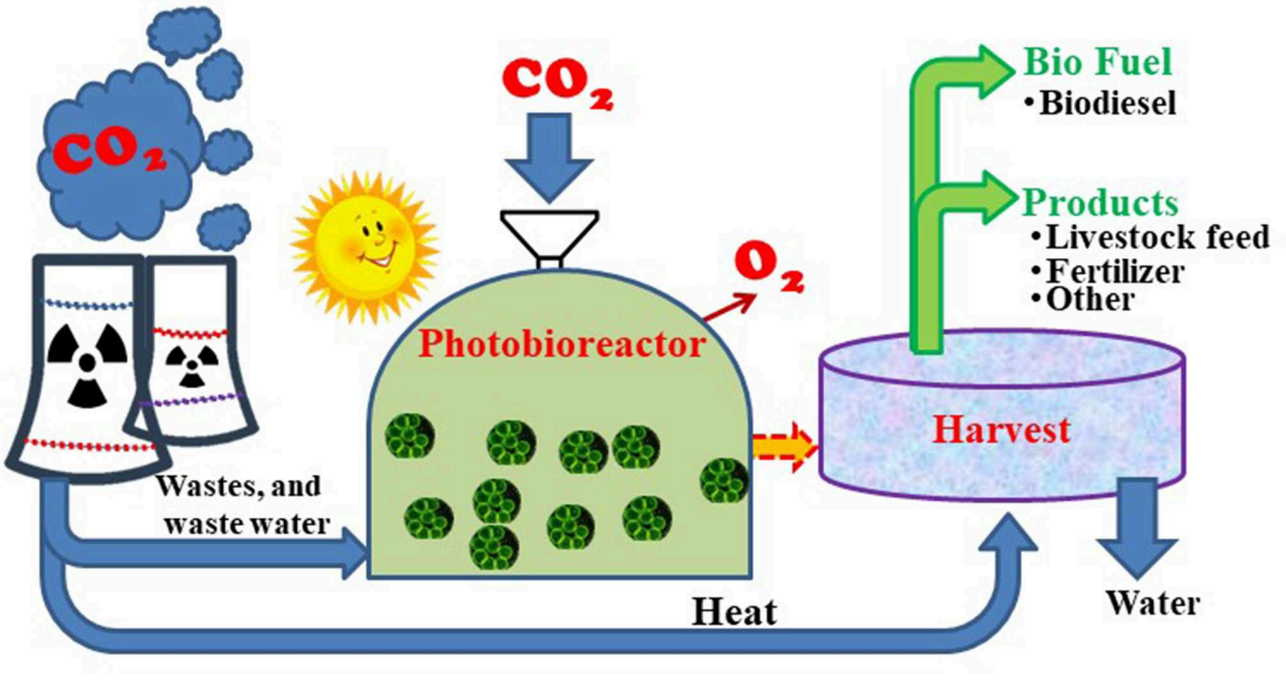


FIGURE 3 | Carbon dioxide capture by microalgae for biomass and value-added product formation.

proposed to overcome the above limitations (Li et al., 2014). A detailed review study published by Kumar et al. (2011) provided great aspects in the design of photo bioreactors and challenges noticed in industrial algae growth. Flue gas compositions are made up of different types of gases along with CO_2, which is viable for the growth of few algae. However, high temperatures, fluctuating flue gas composition, and the presence of sulfur and nitrogen can be toxic to some algal strains. Therefore, the selection of suitable algal processes and strains is needed. One of the other key aspects that play a crucial role in algae development is light intensity (Sorokin and Krauss, 1958). Insufficient light can lead to poor growth, and an increase in light intensity can also show adverse effects on the growth, known as photo inhibition (Xu et al., 2016). The mixing of cell cultures requires an extensive amount of energy input and constitutes a major portion of operational costs (Cloot, 1994). Stirring of cultures is important to reduce the mass transfer limitations occurring in photo bioreactors, which also favorably helps to eliminate oxygen accumulation. Several other advancements have been made to overcome the challenges that are discussed.

In general, the CO_2 uptake/capture with algae is calculated based on carbon concentration in influent and effluent (Anbalagan et al., 2017). However, it is difficult to consider that whole CO_2 uptake is carried out by algae and is utilized for its growth. But the carbon content in biomass can deliver a more precise value on the quantity of CO_2 consumption by algae. This scenario can only be useful if the provided culture media does not have an additional organic carbon source, other than inorganic carbon, such as bicarbonate or CO_2. Based on the following, CO_2 capture by algae can be calculated as

$$R_{CO2} = P.C_{CO2}\frac{M_{CO2}}{M_C}$$

where R_{CO2} is the fixation rate of CO_2 concentration (g.l^{-1} d^{-1}), P is the production of biomass concentration per day (g.l^{-1} d^{-1}), C_{CO2} is increase in carbon content of algae biomass from CO_2 utilization, M_{CO2} is the molecular weight of CO_2, and M_C is the molecular mass of carbon (de Morais and Costa, 2007a).

Tang et al. (2011) analyzed the carbon content and calculated the rate of CO_2 biofixation for different algae species that were grown in modified Blue-Green 11 (BG11) medium. In this study, they calculated the carbon capture rate by varying the CO_2 concentration from 0.03 to 50%. The carbon content in biomass was found to be around 50%, whereas the CO_2 fixation was in the range of 0.105 to 0.288 g. l^{-1} d^{-1}.

Commercialization of microalgal technologies

To commercialize products from microalgal technologies, a designed biorefinery in a circular loop was found to be a sustainable option. A self-sustainable biorefinery (SSB) model of microalgae maximizes resource utilization along with zero waste discharge (Venkata Mohan et al., 2020). Utilization of defatted or de-oiled microalgal biomass (DMB) for other processes also helps to develop sustainable biorefineries. DMB can be used as a substrate for other biofuel generation, such as biomethane, biohydrogen, and bioethanol (Maurya et al., 2016). Thermochemical liquefaction, pyrolysis, and gasification are non-biological processes in which DMB can be used as substrate

TABLE 3 | Summary of diverse algal species for CO_2 fixation and conversion rates.

Type of algae	Conversion of CO_2 (μmol/ g of CO_2/h)	References
Nannochloris sp.	57–569	Negoro et al., 1991
Phaeodactylum tricornutum	27–267	Negoro et al., 1991
Chlorella sp.	125–1,246	Sakai et al., 1995
Synechocystis	142–142	Kurano et al., 1995
Chlorella vulgaris	7–3,352	Scragg et al., 2002; Fan et al., 2008
Scenedesmus sp.	44–436	Jin et al., 2006; Yoo et al., 2010
Spirulina sp.	37–373	de Morais and Costa, 2007a,b
Anabaena sp.	137–1,373	González López et al., 2009
Euglena gracilis	36–362	Chae et al., 2006
Microcystic sp.	46–493	Jin et al., 2006
Botryococcus braunii	1,100	Murakami and Ikenouchi, 1997
Synechocystis aquatilis	1,500	Murakami and Ikenouchi, 1997
Dunaliella tertiolecta	272–313	Kishimoto et al., 1994; Sydney et al., 2010

to produce fuels and chemicals (Sarkar et al., 2015; Maurya et al., 2016). Compared to conventional methods, the microalgae industry is concerned about the two fundamental hurdles, which can be identified as low productivity and high costs (Maurya et al., 2016). Subjecting residual biomass or DMB (post lipid extraction) in various fields improves the economic feasibility and commercialization of algal bioprocesses (Singh et al., 2011; Rashid et al., 2013). The biomass of microalgae can be used as inoculum for new processes that reduce the maintenance of parent cultures. This helps in sustainable operation of microalgal bioreactors (Sarkar et al., 2015). Apart from utilizing DMB in fuel and chemical production, it can also be used as feed supplement and biofertilizer. DMB is rich in protein and essential amino acids that could be utilized as livestock and aquaculture feeds or as a dietary supplement. DMB has also been tested to replace fishmeal from wild fish caught in an ocean environment. Thus, it can mitigate ocean resource depletion (Zhang and Kendall, 2019). In wastewater treatment, DMB can be used as an active biosorbent to remove dyes/color and heavy metals (Maurya et al., 2016). During the extraction of lipids from algal biomass, the biomass used to rupture, which has a higher surface area than the raw biomass. This helps for the efficient functioning of DMB as an active biosorbent (Dong et al., 2016).

Bioenergy production with carbon capture and storage (CCS) plays a crucial role in CO_2 mitigation. Combination of bioenergy production and CCS help to keep CO_2 in geological reservoirs. Algae have high potential to store CO_2 as biomass, which is due to high photosynthetic efficiencies and high biomass yields (Moreira and Pires, 2016). Microalgal cultivation was designated as a negative emission technology (NET), which can reduce the impacts of ocean acidification and anthropogenic climate change (Moreira and Pires, 2016). Since the scope of microalgae is versatile and possesses the expansive possibility of microalgae cultivation with a self-sustainability approach, it is designated as a blue-bioeconomy.

Autotrophic lipid/biodiesel generation using algae

World energy is mainly dependent on electricity and fuel segments. Still, both segments are needed to implement substantial carbon-neutral techniques to reach international legislated standards in regard to the CO_2 emissions target (International Energy Agency, 2019). Currently, 38% of the world's energy is generated in the form of electricity from fossil fuels, and still, these sectors are pursuing research in development of low-range carbon emission technologies, such as solar, wind, geothermal, hydroelectricity, etc. On the contrary, transportation fuels account for larger consumption (Dudley, 2018). Despite the significance of fuels, CO_2-neutral biodiesel, bioethanol, and biohydrogen are still being less used due to several concerns in biofuel production and environmental limitations. In this aspect, second-generation biomass, such as using lignocellulose and algae for fuels, have tremendous potential in a clean energy market with a value of US$500 billion by 2050 (Schenk et al., 2008). Furthermore, based on several research studies, it is well-known that microalgae biofuel production systems exhibit high net energy balance, high water efficiency, and less land requirement in comparison to first-generation biofuels (plant biomass) (Benedetti et al., 2018).

In consideration of oil extracted from plant biomass vs. algal biomass, palm oil can generate a maximum of 4–5 vs. 30 ton/ha/yr, thus yielding a 5-fold higher product in comparison to a plant crop during similar posttreatment of biomass (Benedetti et al., 2018). In terms of area, algae are known to generate about 15–300 times more oil for biodiesel (Schenk et al., 2008). In contrast to crop plants' single harvesting process, algae allows multiple harvesting cycles in the same duration with high yield and greater light and CO_2 capture efficiencies.

Different oil concentrations are noted with various algae species, which is due to differences in the amount of protein/carbohydrates/fats. For instance, *S. maxima* has about 60∼70% w/w proteins, *Porphyidium cruentum* generates around 57% proteins, and *Scenedesmus dimorphus* generates up to 40% w/w of lipids (Nigam and Singh, 2011; Venkata Mohan et al., 2011) (**Table 4**). In a few species of algae, such as *Botryococcus braunii* and *Chlorella protothecoides*, terpenoid hydrocarbons and lipids are noted, which can be further converted to short-chain hydrocarbons, similar to that of crude oil (Carlsson and Bowles, 2007). On the basis of prevalence of lipids or sugars, algae can be a wonderful substrate for biodiesel or bioalcohol, respectively (Kondaveeti et al., 2014a). Therefore, algae can be a great resource as a biofuel substrate under certain conditions. Several studies have employed different strategies for increasing lipid concentration of algae, such as temperature, CO_2 concentration, light strength/intensity, nutrient starvation, metal, and salinity stress. It is well-known that adequate light intensity helps in overproduction of microalgae lipids. This might be because a sufficient amount of light is beneficial for storing an excess of photo assimilates, which can be further transformed

TABLE 4 | Generation of biomass by pure microalgae cultures at specific CO_2 concentrations.

Algae type	Concentration of CO_2 supply (%)	Generated biomass (g/l/d)	References
Chlorella vulgaris	0.03–6	0.21	Chinnasamy et al., 2009; Bhola et al., 2011
Chlorococcum littorale	N/A	9.2	Chen et al., 2009
Scenedesmus obliquus	5–15	1.14–2.3	de Morais and Costa, 2007c; Kaewkannetra et al., 2012
Spirulina platensis	10	2.91	Ramanan et al., 2010
Nannochloropsis oculata	2–15	0.37–0.48	Chiu et al., 2009
Chlorella sp. KR-1	10–70	0.6–0.7	Sung et al., 1999

into chemical energy (Zhu et al., 2016). The *Nannochloropsis* species of algae experienced the maximum accumulation of lipids (47% of dry weight) under light intensity of 51,800 lux (Zhu et al., 2016). In another study with *Scenedesmus abundans* by Mandotra et al. (2016) and Zhu et al. (2016), they noticed a 32.7% increase in lipid accumulation with an upsurge in light intensity from 3,000 to 6,000 lux. When light intensity of 5,000 and 3,000 lux were maintained, the lipid content was found to be 27 and 21%, respectively. It is recognized that higher lipid concentration is noted at maximum photosynthetic efficiency, which occurs at the light saturation point (Zhu et al., 2016). Hence, the extreme light intensity can cause photo inhibition, leading to damage of algal photo systems and, thus, reducing lipid accumulation. In the case of temperature, the optimal value for higher lipid generation achieved does vary from species to species. *C. vulgaris*, a microalgal species, achieved a maximum lipid concentration at 25°C. The decrease in external temperature led to an obvious decrease in lipids (Converti et al., 2009). Microalgae species *S. obliquus* had a lipid concentration of 18 and 40% of dry weight when the temperature was at 20 and 27.5°C, respectively (Xin et al., 2011). This suggests that an increase in temperature can increase total lipid content. However, this does not mean that all types of lipids experience an increase in concentration. A recent review by Zhu et al. (2016) provides detailed strategies for lipid enhancement.

Biodiesel is being developed as one of the most vital biofuels as basically all industrialized vehicles used for agriculture, transportation, and trade are diesel/fossil fuel–based. With an increase in algae biodiesel production, several studies had endeavored to calculate the cost of oilgae (algae oil) from large farms. Studies by Benemann and Oswald (1996) reported that the cost of oilgae would ranging from US$39 to US$69 per barrel from 4 Km^2 open ponds either by using pure CO_2 or flue gas from coal power stations with productivity in a range of 30 to 60 $g/m^2/day$ with a 50% algal lipid yield (Benemann and Oswald, 1996). In recent studies, it is noted that the production of oil from algae would cost around US$66–153 per barrel (Nagarajan et al., 2013). Companies generating oilgae are not optimistic in terms of production cost. Seambiotic Ltd. calculated that the cost of dried algae would be US$0.34 per kg with a productivity and total lipid content of 20 $g/m^2/d$ and 8∼40%, respectively. Presuming the standard yield of lipid to be 24% without any additional cost, this would be equals to US$1.42 per kg for lipid extractions, which is equal to US$209 per barrel. With an increase in yield of lipids to 40%, the lipid extraction would cost around US$0.85 per kg, which is equal to US$126 per barrel, which points to an increase in lipid concentration decreasing oil prices. Accounting for inflation in crude oil prices in 2017, the oil prices seem to be stabilizing around US$51 per barrel (https://www.eia.gov/todayinenergy/prices.php, 2017). These estimates suggest that oilgae diesel production needs to be further improved to be economically viable and to compete with conventional fuels. However, the industrial production of biodiesel using algae is at early stages, and there is much scope for decrease in cost and increase in performance.

Reduction of CO_2 Using Photosynthetic Cyanobacteria

Most types of photosynthetic bacteria derive energy from ATP, which helps in the conversion of CO_2 to biomass and other products (Hatch and Slack, 1970). In comparison to eukaryotic plants and algae, photosynthetic bacteria have simpler photosystems due to the presence of pigments on their cytoplasm rather than specialized organelles (Pfennig, 1967). Photosynthetic bacteria are classified as five phyla: cyanobacteria, proteobacteria, chlorobi, choloflexi, and firmicutes (Pfennig, 1967). Cyanobacteria are capable of fixing atmospheric nitrogen and carbon. Similar to algae, they are distinct and broadly distributed and exist as biofilms or as suspended planktonic cells. Several scientists believe that cyanobacteria played a decisive role in atmospheric formation by decreasing CO_2 concentration and increasing oxygen (**Figure 1**) (Kasting and Siefert, 2002). In the present days also, cyanobacteria are found to be a key player by accounting for 20∼30% of Earth's photosynthetic activity. Owing to their simpler nature, cyanobacteria are the most efficient in atmospheric carbon utilization over algae (Berman-Frank et al., 2003). However, cyanobacteria are still limited in biomass yield as compared to algae without any structural or genetic modifications.

In recent years, the production of ethanol using microbes has gained considerable attention. In general, the biomass from photosynthetic microbes is collected and subsequently converted to biofuel by solventogenesis. This process was found to be inefficient due to lower conversion efficiency (Lau et al., 2015). Thus, intense research is being carried out on direct conversion of CO_2 to fuel by photosynthetic bacteria. Although few cyanobacterial species are capable of generating ethanol in smaller concentrations as a product in biological fermentation, it is required to boost production rates as an economically viable process. Dexter and Fu (2009) made an attempt to generate ethanol by introducing the genes of pyruvate decarboxylate (pdc) and alcohol dehydrogenase II (adh) from *Z. mobilis* into the chromosomes of *Synechocuystis* sp. PCC6803, which achieved 550 mg/l of ethanol. Acetyl Co A-dependent 1-butanol production by *Synechococcus elongates* demonstrates its capability in generation of butanol through an autotrophic mechanism (Kusakabe et al., 2013). This species was metabolically engineered to generate isopropanol by using CO_2 and light to generate 26.5 mg/l of product following 9 days of cultivation (Kusakabe et al., 2013), whereas *Clostridium beijerinckii* generated 1.5 g/l through a heterotrophic mechanism (Chen and Hiu, 1986). These studies suggest that usage of genetically modified bacteria can be a viable advancement to increase product formation by employing CO_2 as an electron source rather than organics. Butanol is considered to be a better alternative to gasoline in contrast to ethanol as it exhibits higher energy density, less volatility, and low corrosivity (García et al., 2011; Zhang et al., 2018). Current advances in metabolic engineering of cyanobacteria for the generation of solvents from CO_2 were critically reviewed elsewhere (Quintana et al., 2011).

Cyanobacterial species, such as *Anabaena*, *Aphanocapsa*, *Calothrix*, *Microcystis*, *Nostoc*, and *Oscillatoria*, are equipped for the generation of hydrogen by using a photosynthetic autotrophic mechanism (Lambert and Smith, 1977; Lau et al., 2015). Filamentous cyanobacteria generate H_2 as a by-product during nitrogen fixation under N_2-limiting conditions. Additionally, cyanobacteria can generate H_2 by reversible activity of the hydrogenases enzyme. In general, these species are equipped to use bidirectional or reversible hydrogenase enzymes to oxidize oxygen to generate hydrogen. The enhancement in hydrogen generation can be achieved by blocking the pathways that use the hydrogenases for a reduction reaction (Tamagnini et al., 2002).

Cyanobacteria are also known to produce alkanes and alkenes, which have a desirable property for industrial application (Lau et al., 2015). Among these enzymes, acyl-acyl carrier protein reductase and aldehyde decarbonylases are the key enzymes noted for efficient conversion of fatty acids of metabolic intermediates to alkanes and alkenes (Schirmer et al., 2010). Additionally, due to similarity to algae metabolism, cyanobacteria are well-known for their effluent treatment of wastewaters that are rich in nitrogen and phosphorus contaminants.

Value-Added Products Using Algae and Cyanobacteria

Apart from the biodiesel and fuels, algae are well-known for their usage in the food industry. The commercial products of algal powders are sold in the health and food industries. Algal products, such as unsaturated fatty acids and polysaccharides from microalgae and seaweed provide a dietary fiber and health benefits. The carotenoids that present in algae serve as antioxidants and vitamin A. In the textile industry, several algal products (pigments) are used as coloring agents. In aquatic fields, algae are used as feedstock in fish, shrimp, and other seafood that are grown in enclosed environments. Carotenoids, such as astaxanthin, beta-carotene, bixin, and fucoxanthin, are used in the cosmetic and pharmaceutical industries (Hudek et al., 2014).

Anaerobic Fermentation of CO_2 for Value Addition

The increase in fossil fuel consumption is leading to a shortage of fuels and increase in energy prices. In order to reimburse energy consumption from the past few decades, research has been gaining attention on renewable energy sources with a prime focus on using inorganic carbon such as CO_2 as a substrate (Chang et al., 2016). The policy is to replace the fossil fuel with renewable energy sources and simultaneously decrease global carbon emissions. One of these renewable products includes CH_4 generation, which can be an assurance of chemical storage of energy (Villano et al., 2010). In several cases, anaerobic methane generation is productive and is frequently used in electricity generation and as a heat energy source (combustion process). Additionally, it can be used in the generation of biodiesel, methanol, and a few other hydrocarbons, such as ethanol and butanol (Ge et al., 2014; Zakaria and Kamarudin, 2016; Wang et al., 2017). In general, methane is generated in two ways: through biotic and abiotic pathways. Abiotic pathways include the catalytic conversion or thermal split of kerogen (Lawton and Rosenzweig, 2016). Biogenic methane generation is abundantly noticed from anaerobic digestion and from dairy farms. In fact, 20% of global natural gas is being produced from methanogens (Wang et al., 2017).

Methanogenic microbes are obligate anaerobes, which are under the Euryarchaeota phyla belonging to the Archaea domain. These obligate anaerobes have the capability of sequestering the CO_2 under optimized specific conditions (Zeikus, 1977; Strong et al., 2016). In gas fermentation, CO_2 sequestration is carried out by hydrogenotrophic methanogens with the help of gamma- and zeta-type carbonic anhydrase enzymes. The CO_2 can be digested with different forms of chemicals, such as bicarbonate, carboxylic acids, alcohols, and biogas with their respective enzymes. However, acetyl CoA is the central mediator molecule in several microbial processes for product synthesis. Methanogenic and acetogenic bacteria are frequently found in a pair when CO_2 is the reduction medium (Kuramochi et al., 2013; Shi et al., 2015). In conventional anaerobic digestion, the difference in operational conditions affects the behavior and fate of both acetogenic and hydrogenotrophic methanotrophs. Under optimized conditions, the acetogenic bacterium transforms the acetic acid to H_2 and CO_2, which is followed by the conversion to methane via acetate (Equation 1) or the indirect conversion of H_2 and CO_2 (Equation 2) by hydrogenotrophic methanogenic bacterial cells (Jiang et al., 2013; Bian et al., 2018).

$$CH_3COOH \rightarrow CO_2 + CH_4 \tag{1}$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \tag{2}$$

For efficient and stable performance in the transformation of CO_2 and H_2 to CH_4 by hydrogenotrophic methanogens, a continuous supplement of molecular hydrogen is required. Based on several studies, the key parameters that control hydrogenotrophic methanogenic activity were identified as pressure, redox conditions, temperature, headspace gas composition, hydraulic retention time, and pH (Rabaey et al., 2009; Lee et al., 2012). Scherer et al. (2000) analyzed the degradation of organics in municipal gray water under thermophilic and mesophilic environments using a lab-scale continuous mode of operation for biogas generation. The most probable number (MPN) technique illustrated that hydrogenotrophic methanogens (H_2-CO_2 utilizers) were in a range of 10^8 to 10^{10}/g total solids (TS), which seems to dominate the acetogenic methanotrophs by a factor of 10 to 10,000, due to short hydraulic retention time (HRT). Similarly, Ahring et al. (2001) noted that hydrogenotrophic methanogens exhibited higher specific methanogenic activity at 65°C. Although these studies prove that the presence of hydrogenotrophic methanogens can enhance methane formation, it is unclear whether enhanced methane formation is by direct or indirect conversion under practical conditions. Thus, future research in methane production should be encouraged toward the CO_2-utilizing metabolic pathways that control the symbiotic relationship among acetoclastic and hydrogenotrophic methanotrophs along with acidogenic bacteria.

Gas Fermentation of CO_2 to Products

The preceding advances in bio-energy generation have raised a feed vs. fuel debate. In this regard, gas fermentation looks to be a promising technology, in which gaseous substrates (CO_2) are converted to biochemicals. Also, many industrial processes generate large amounts of carbon gases, which are left unused. Thereby, utilization of CO_2 as a feedstock toward value-added products can shut down the feed vs. fuel debate. As aforementioned, conversion scenarios indicate that CO_2-rich waste gases can be a suitable substrate for gas fermentation. Several microbes have the ability to utilize CO_2 as a carbon source. Among these several microbes, acetogenic bacterium is mostly being studied and shows a capability for industrial applications. These bacterial species are equipped to convert CO_2 and CO by making use of the Wood–Ljungdahl pathway (WLP). Different acetogenic bacteria can naturally generate ethanol or butanol and some other goods of industrial interest, such as 2-oxobutyrate, hexanol, PHA, vitamin B12, polymers, and their precursors for other products.

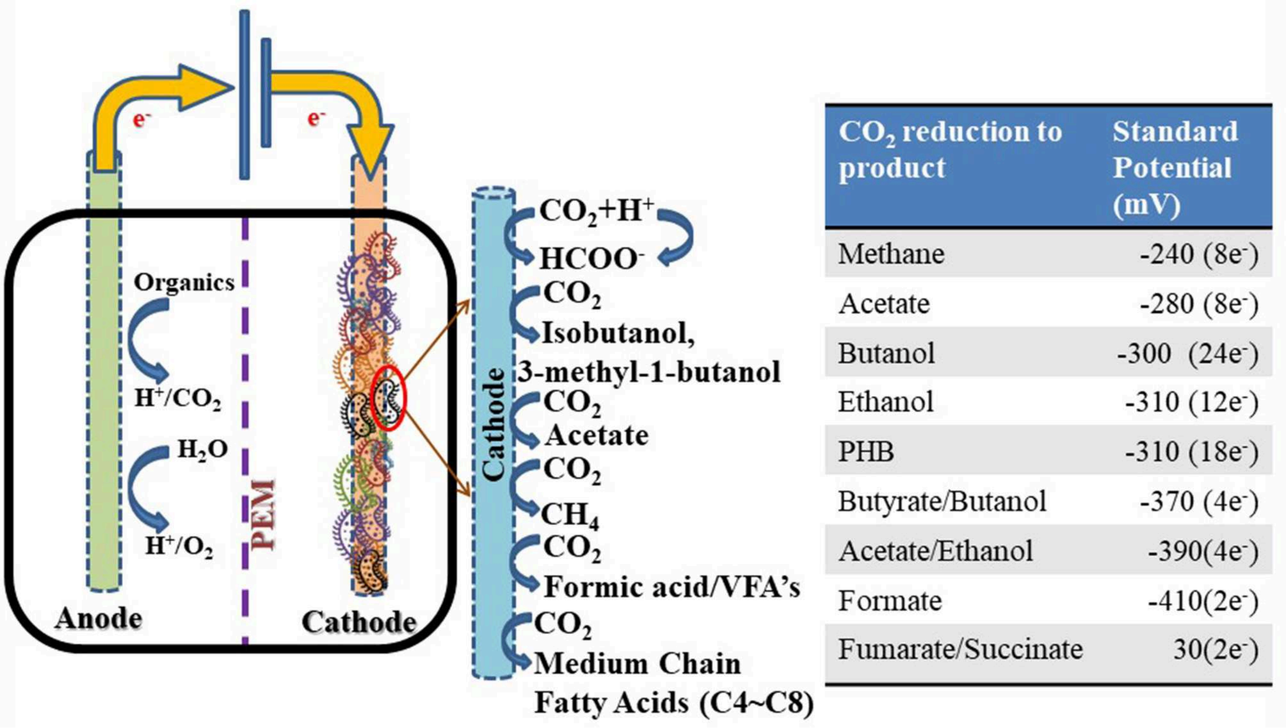
In a recent study by Kim et al. (2016) acetate was noted as an end product in a multistage gas fermentation process by using steel mill off-gas as a feedstock. In the initial stage of fermentation, CO was transformed to CO_2 and H_2 by *Thermococcus onnurineus*. Later, the mixture of CO, CO_2, and H_2 were converted to acetate by *Thermoanaerobacter kivui* and resulted in a maximum generation rate of 0.33 mmol/l/h. When the initial step was absent, *T. kivui* was unable to generate acetate due to CO inhibition and lack of CO_2 as a substrate. Acetate formations in the multistep process also can be employed for the production of ethanol and other value-added products. Richter et al. (2013) operated a two-stage system for generation of ethanol with CO_2 as a feedstock by using *C. ljungdahlii*. The first stage of the reactor was employed for acetate; then the broth containing acetate was transferred to a second fermenter by lowering the pH for efficient conversion of acetate to ethanol. The production rate and maximum concentrations of ethanol were noted as 0.37 g/l/h and 450 mM, respectively. Different types of clostridium strains were tested in similar systems, and it was noted that *C. ljungdahlii* PETC was the most optimal producer for ethanol (Martin et al., 2016). Hu et al. (2016) developed a two-stage system for generation of longer chain fatty acids (C_{16}-C_{18}). This was carried out by *M. thermoacetica* in the first stage for acetate formation with syngas as a feedstock. The effluent broth was subjected to an aerobic reactor containing genetically modified *Yarrowia lipolytica*. The system could generate up to 18 g/l of C_{16}-C_{18} lipids at a rate of 0.19 g/l/h. The system proves the conversion of carbon in syngas to complex substrates with a multistage system.

To generate value-added products by an integration approach along with biological processes, chemical processes are also feasible. Lanzatech, in association with invista and SK innovation (http://greenchemicalsblog.com/2014/06/05/invista-and-lanzatech-expand-collaboration/; http://www.invista.com/en/news/pr-invista-and-lanzatech-make-breakthrough-for-bio-derived-butadiene-production.html), proposed production of 1, 3-butadiene in a two-step process, which is combination of biological and chemical steps. The recent review published by Liew et al. (2016) gives an excellent overview on the advances of synthetic biology on syngas-fermenting bacteria. However, we speculate that these technologies are limited by low concentration of substrate uptake, productivity, and selectivity in terms of product formation in comparison to current technologies.

Bioelectrochemical Conversion of CO_2 to Fuels and Chemicals

Bioelectrochemical systems (BES), such as microbial electrosynthesis (MES), microbial electrolysis cells (MECs), and microbial fuel cells (MFCs), are gaining importance in the field of renewable energy due to their promising approach for converting waste to energy (Kondaveeti et al., 2017; Mohanakrishna et al., 2020). In general, MFCs generate electricity from organics, whereas MES synthesizes value-added chemicals from CO_2 via electrogenic fermenting cathode microbes (biocathode) by using the cathode electrode as a sole electron source (**Figure 4**) (Logan, 2008). Nonetheless, MES is more beneficial in comparison to MFCs due to its capability in taking CO_2 and slashing the greenhouse gases. In addition, MES is interesting because of energy storage in the form of chemical production (e.g., hydrogen, alcohols, and C_1-C_6 medium chain fatty acids) for sustainability and decrease in dependency on non-renewable sources, such as fossil fuels (Rabaey et al., 2009).

The bioelectrochemical conversion of organics, such as acetate, in the anode of MFCs generates CO_2, protons, and electrons. The generated electrons move toward the cathode through an external circuit. The protons are diffused toward the cathode through a separator, typically a proton exchange membrane (PEM, e.g., Nafion-117) or cation exchange membrane (CEM). On the cathode, the diffused protons and electrons are combined together to form water by using O_2 as an electron acceptor (cathodic reduction reaction). The potential



CO_2 reduction to product	Standard Potential (mV)
Methane	-240 ($8e^-$)
Acetate	-280 ($8e^-$)
Butanol	-300 ($24e^-$)
Ethanol	-310 ($12e^-$)
PHB	-310 ($18e^-$)
Butyrate/Butanol	-370 ($4e^-$)
Acetate/Ethanol	-390($4e^-$)
Formate	-410($2e^-$)
Fumarate/Succinate	30($2e^-$)

FIGURE 4 | Schematic representation of microbial electrosynthesis system toward CO_2 reduction for value-added product formation and their corresponding standard potentials.

disparity between the anode and cathode are captured as voltage. When an external electron acceptor, such as O_2, is absent, the diffused protons are converted to H_2 with the help of minimal external voltage (0.2 V), which was termed as MEC. The initial discovery for generation of hydrogen by modifying MFC to MEC was reported by the B.E. Logan group at Penn State University (Logan, 2008). MEC operations are more economic over MFC due to the ecologically beneficial production of valuable products, such as H_2. By the same process, the microbes at biocathodes can shuttle the e^- from the electrode for the reduction of CO_2 to value-added products. This can be achieved by using an anaerobic biotic anode with an electrogenic biocatalyst using organics or with an abiotic anode with an electrolysis process by applying additional potential. The bioprocess for value-added product formation was carried out by numerous metabolic pathways, such as the Calvin Benson cycle or the WLP (Rabaey and Rozendal, 2010; ElMekawy et al., 2016).

MES is capable of generating basic value-added products, such as H_2, acetate, and oxobutyrate (Kadier et al., 2020). These products can be directly used as fuels or can be used further to generate high carbon fuels or bioplastics. Initially, Nevin et al. (2010) stated reduction of CO_2 to acetate in small concentrations by operating MES at −0.6 V by using an acetogenic *Sporomusaovata* ascathodic biocatalyst (Nevin et al., 2010) and renewable energy (solar energy) as an external power source. This study also evidenced smaller amounts of oxobutyrate production (**Table 5**). Further, in 2011, acetate at a production rate of 0.05 mM/d was achieved using mixed cultures (Nevin et al., 2011). In other studies using *S. ovata*, the production rates were 2.3-fold higher using a nickel nanoparticle-coated cathode over a plain graphite cathode (1.13 mM/d) (Zhang et al., 2013). Mohanakrishna et al. (2015) reported an acetate generation rate of 4.1g/l by using enriched single chamber MES with VITO-activated carbon electrodes. Similarly, in other studies from the same group, they analyzed acetate formation by using bicarbonate and CO_2 as a substrate by varying the poised cathode potentials (−0.6 and −0.8 V vs. Ag/AgCl). Interestingly, in this study, they noted that MES operation with CO_2 at −0.8 V generated a higher acetate concentration of around 5.1 g/l. However, decreasing poised potentials (−0.6 V) during MES operation with bicarbonate exhibited maximum acetate concentrations of around 4.1 g/l (Mohanakrishna et al., 2016). Batlle-Vilanova et al. (2016) operated continuous mode MES for CO_2 reduction and noted an acetate production rate of 0.98 mM.l/d. Marshall et al. (2013) reported the highest acetate generation (17.25 mM/d) from CO_2 by using MES (−0.79 V) with a carbon bed cathode and enriched cultures from methonogenic bacteria and H_2. MES operation with a simultaneous production and extraction mechanism for acetate from CO_2 were operated by Gildemyn et al. (2015). In this study, the maximum concentration of acetate formation was noted as 13.5 g/l, which is found to be the highest to date, whereas the highest production rate of 0.78 g/l/h was registered by LaBelle and May (2017). This might be due to the ceasing

TABLE 5 | Bio electrochemical generation of solvents and biofuels from CO_2 under various operational and nutritional conditions.

Reactor	Substrate	Applied energy (voltage or current)	Operational condition	Dominant catalyst (microbes or enzymes)	Products	References
H-Type double chamber	$CaCO_3$	+0.5 to −0.5 V (vs. Ag/AgCl)	Batch type; Anaerobic Fermentation	*Clostridium Sporogenes BE01*	Butanol, Ethanol, Fatty acids, Hydrogen	Gottumukkala et al., 2015
Double Chamber Fuel cell	Butyraldehyde + TRIS-HCl buffer	−0.6 V (vs. Ag/AgCl)	Batch type; Enzymatic Fuel cell	Alcohol dehydrogenase enzymes	Butanol	Schlager et al., 2015
H-Type double chamber	P2 electron carriers in medium + Glucose	−0.7 V (vs. Ag/AgCl)	Batch type; Anaerobic Fermentation	*Clostridium beijerinckii IB4*	Acetone, Butanol, Ethanol production and butanol as primary product	He et al., 2016
Two compartment Cell	CAB medium with electron carrier in buffer	−2.5 V poised at cathode	Batch type; Electrochemical cell	*Clostridium Acetobutylicum ATCC 4259*	Butanol and Acetone	Kim and Kim, 1988
H-Type double chamber	CO_2 injection +DSMZ medium	−0.6 V (vs. Ag/AgCl)	Continuous mode operation	*Sporomusa, Geobacter, Clostridium, Morella*	Acetate, Formate, Butyrate, Propanol, Ethanol and 2-oxobutyrate	Lovley and Nevin, 2018
H-Type double chamber	CO_2 (No organics in media)	−0.8 V(vs. SHE)	Batch type; Electrochemical cell	*Clostridium* species+ Carboxydotrophic mixed culture	Ethanol, Butanol, acetate, butyrate	Puig et al., 2015
H-Type double chamber	Modified P 2 Medium + SMM medium	1.32 V as Applied voltage	Batch type; Electrochemical cell	*C. pasteurianum*	Butanol and by products as solvents and acids	Khosravanipour Mostafazadeh et al., 2016
Double chamber	CO_2	−0.55 V (vs. NHE)	Batch type; Electrochemical cell	N/A	CH_4	Van Eerten-Jansen et al., 2012

of acetate oxidation at the cathode by employing simultaneous production and extraction techniques. All these studies pointed out that, during long-term operation, the oxidation of acetate to methane is one of the major limitations. This can be controlled by employing a chemical treatment process, such as by using BESA (2-Bromoethanesulfonic acid) or employing pH shock treatment (Mohanakrishna et al., 2015, 2016; ElMekawy et al., 2016). The variation in acetate production might be due to differences in applied voltage, operational environment, reactor configuration, electrode type, biofilm activity, and type of bio-electrocatalyst at the cathode.

Compared to pure culture of *C. ljungdahlii*, enriched mixed culture results showed a higher acetate (1.3 mM/d) production rate at −1.1 V, which has hydrogen-generating potential (Bajracharya et al., 2015). This study also evidenced methane production and suggests an increase in CO_2 reduction by using mixed cultures by supplementing H_2. The supplementation of H_2 can be obtained by maintaining higher negative cathode potentials for the reduction of protons to H_2. However, generated H_2 can leak from the reactors, thereby restricting the CO_2-reduction process, which, in turn, decreases current and product formation. This complication can be overcome by using high gas absorption electrodes (e.g., platinum single crystal electrode) in order to decrease H_2 leakage (Will, 1965; Wang Q. et al., 2015). Several pure cultures, such as *Clostridia*, *Moorella*, and *Sporomusa*, are proven for direct conversion of CO_2 by accepting electrons from a poised cathode electrode at −0.6 V (Nevin et al., 2010; Bajracharya et al., 2015); however, these are still limited for practical applications due to strict operational conditions.

In MES, acetate is one of the primary products noticed from the reduction of CO_2 (Mohanakrishna et al., 2016; Modestra and Mohan, 2017). However, its autotrophic production is not economically desirable due to lower yields and little commercial value. In this aspect, researchers have further explored the possibility of higher value-added product generation (Rabaey and Rozendal, 2010; Arends et al., 2017). In this facet, acetic and butyric acids were converted to bioalcohols using a poised biocathode at −0.65 V (Steinbusch et al., 2010; Sharma et al., 2013b). In this study, total alcohol production of 13.5 mM was achieved. Ethanol, butanol, propanol, and acetone were noticed as major alcohols along with propionic and caproic acids (Sharma et al., 2013a). Similarly, Kondaveeti et al. operated a BES and transformed the VFAs from anaerobic digester effluent to bioalcohols by varying applied voltage. Electron mediators, such as neutral red, helped for increasing product formation at higher redox potentials (Kondaveeti and Min, 2015). Ethanol and butanol are the major alcohols noticed at the applied voltage of 2 V (Cathode potential, −0.9 V). Likewise, Steinbusch et al. (2010) operated a microbial electrosynthesis system with various mediators [methyl viologen (MV), neutral red (NR), anthraquinone-2,6-disulfonate (AQDS)] and noted a maximum yield of 13.5 mM of ethanol by using MV. In other studies pursued by Van Eerten-Jansen et al. (2013), a reduction in acetate to Caproate (6.8 mM) and butyrate (3 mM) were noticed in MES with cathode poised potential of −0.9 V. Recently, Vassilev et al. (2019) operated a dual cathode MES system for concurrent acetogenesis and solventogenesis followed by carbon chain elongation. This type of system can assist in operational cost reduction with a simultaneous increase in productivity due to the utilization of off-gas. All previous studies are found to be interesting in terms of product formation; however, these systems are still limited by selectivity of product formation and extraction of product using cheaper processes (del Pilar Anzola Rojas et al., 2018; Li et al., 2018; Vassilev et al., 2018). Most of the product extraction studies of MES include integrated membrane separation with an anion and cation exchange membrane or sequential operation. However, the operation of such processes can be expensive as they often need to be changed because of fouling during longer operation. The research in this regard needs to be pursued to increase the production rate and decrease operational costs for product extraction and selectivity of product formation.

In the past few years, research on generation of methane from CO_2 using bioelectrochemical techniques has increased significantly. It has been noted that the optimized electrode potential (direct electron donor) for direct conversion of CO_2 to methane was found to be around −0.6 to −0.7 V vs. Ag/AgCl (Cheng et al., 2009; Villano et al., 2010; ElMekawy et al., 2016; Bajracharya et al., 2017). Villano et al. (2010) reported that, using −1.0 V of applied external potential, 96% of the obtained current was captured in the form of methane. Based on current and obtained abiotic hydrogen, it was noted that CH_4 was produced directly from electrons derived from a cathode electrode rather than using the hydrogen gas. Alternatively, they also have suggested that some amount of methane generation is by hydrogenophilic methanogens by consuming H_2 from abiotic water reduction. The performances of biocathodes were further tested by inoculating with methanogenic culture. These cultures were greatly able to reduce the inorganic carbon to methane (0.055 mmol/d for mg/VSS) with 80% electron capture efficiency (Villano et al., 2010). The standard theoretical potential for the reduction of CO_2 to CH_4 is −0.44 V vs. Ag/AgCl. The required energy for this cathodic reaction can be achieved from the bioanode (organic oxidation) process. However, in practical operation, these can be greatly limited with over-potentials. These over-potentials can be reduced by implementing biocathode systems. In another study, Villano et al. (2013) demonstrated a double chamber MEC for methane generation with anode potential of −0.397 V vs. Ag/AgCl by using acetate as an energy source. Simultaneously, a cathode was constantly supplemented along with CO_2 and N_2 for pH correction and carbonate supply. It was reported that a 94% reduction in acetate at the anode chamber with 91% of coulombic efficiency, which proves that the generated current was mainly from methane production. Yasin et al. operated an enriched activated sludge system to generate methane from CO_2. In this system, in the presence of CO_2 and H_2, they noticed a 70-fold increase in methane generation after 72 h of operation. The complete utilization of CO_2 was noticed after 96 h of incubation under supplementation of CO_2 and H_2 as carbon and electron sources, respectively (Mohd Yasin et al., 2015). Based on a recent study by Xenia et al., the microbial electrosynthesis cells were proven to be economical and sustainable with CO_2 as a substrate for product formation, such as methanol, ethanol, and formate (Christodoulou et al., 2017).

OTHER CO_2-UTILIZING BACTERIA

β-Proteobacteria

Proteobacteria are Gram-negative bacteria, mainly composed of lipopolysaccharides in their outer membrane. These are found to be a geologically, environmentally, and evolutionarily important group of microorganisms. The members of this bacterial phylum exhibit an enormous metabolic diversity. Most of these bacteria have an industrial, medical, and agricultural significance (Sezenna, 2011). The photosynthetic proteobacteria are known as purple bacteria, concerning their reddish pigments. One of the most common and well-known photosynthetic β-proteobacteria is *Ralstonia eutropha*. This bacterium can grow on variable carbon environments, such as heterotrophic, autotrophic, and mixotrophic. In the absence of a heterotrophic carbon environment as an electron source, this bacterium has proven to utilize hydrogen as an energy source for fixing CO_2 via the Calvin–Bassham cycle (CBB) (**Figure 5**) (Jajesniak et al., 2014).

R. eutrohpa is a convenient photosynthetic bacterium to handle because of its aerobic H_2 oxidizing capabilities over obligate anaerobes to generate chemicals and other value-added products. This fascinating interest in *R. eutrohpa* has led to generation of bioplastics (PHAs/poly hydroxyalkanoates) by storing carbon in cytoplasm. PHAs are generally composed of PHB (poly 3-hydroxybutyrate) and PHBV (poly 3-hydroxybutyrate-co-3-hydroxyvalerate) (Luengo et al., 2003; Jajesniak et al., 2014). These bioplastics are gaining high importance due to credentials such as biodegradability over conventional plastics and their green synthesis with CO_2 sink. These polymers with desired length can be pursued with genetic modifications (Reinecke and Steinbüchel, 2009). Few studies are pursued in genetic modification of *R. eutropha* for the generation of products with variable properties (mechanical strength) and production yield. Voss et al. modified *R. eutropha* and generated a cyanophycin, a protein-like polymer, with an increased production quantity (Voss and Steinbüchel, 2006). A few other studies have synthesized several useful compounds, such as ferulic acid (precursor to vanillin biotransformation) and 2 methyl citric acid, by genetic modification (Overhage et al., 2002; Ewering et al., 2006). The limitation in these studies is use of organic carbon as an energy source rather than inorganic CO_2. Beller et al. engineered *R. eutropha* and generated methyl ketones of diesel range with productivity in a range of 50–180 mg/l by using CO_2 and H_2 as energy and electron sources, respectively (Müller et al., 2013). In a previous study, Li et al. (2012) described an integrated approach for production of isobutanol and 3-methyl-1-butanol by using a microbial electrochemical process. In this system, initially, CO_2 was converted to formate

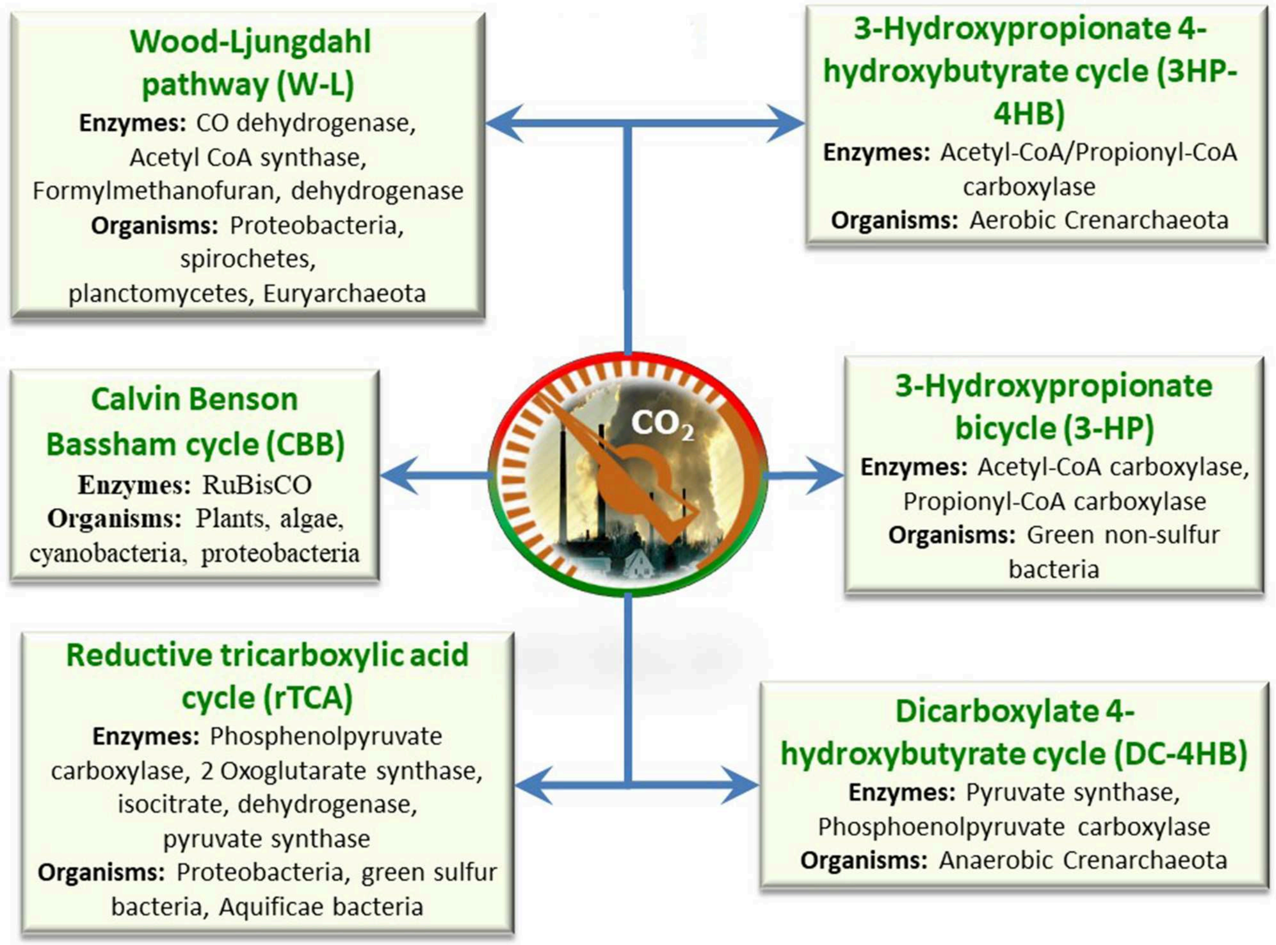


FIGURE 5 | Various biological pathways for CO_2 metabolism in microbes for carbon fixation.

and tailed by isobutanol and 3-methyl-1-butanol generation. This system achieved a final concentration of 850 and 570 mg/l of isobutanol and 3-methyl-1-butanol, respectively.

Idenolla species is another type of photosynthetic bacteria similar to *R. eutropha* in generation of polymers by using CO_2. An additional superiority of *Idenolla* over *R. eutropha* is the generation of products using carbon monoxide (CO) as an energy source. These bacterial species have an additional advantage by synthesizing products from exhaust gas (Tanaka et al., 2011).

Clostridia

Most clostridia are anaerobic and Gram-positive bacteria. They are found to have great importance in (i) human and animal health and physiology, (ii) anaerobic mortification of simple and complex carbohydrates, (iii) the carbon cycle, and (iv) bioremediation/degradation of complex organic chemicals (Kondaveeti et al., 2014b). Many strains of clostridia are capable of autotrophic fixation of CO_2 or CO by using H_2 as an electron donor (Willey et al., 2014). Clostridia also can use simple chain organic carbon molecules, such as formate or methanol, as an energy source. They can achieve this by the WLP pathway in which two molecules of CO_2 are scaled down to generate one molecule of Acetyl-CoA with CO or H_2 being used as a reducing proportionate (Tracy et al., 2012).

Additionally, *Clostridium* species provide many fascinating characteristics for biotechnological utilization: (i) ability to use simple as well as complex substrates such as H_2, CO_2, and CO; (ii) equipped with diversified pathways for generation of value-added products; and (iii) tolerant to toxic metabolites and substrates. However, as they are strictly anaerobic, the cultivation of *Clostridium* is very difficult (Willey et al., 2014). Normal atmospheric and facultative conditions are lethal to *Clostridium* species. Early work with *Clostridium* was mostly carried out for the production of acetic acid and other related products. The synthetic biology/genetic modification of Clostridium are being pursued at a slow pace due to their difficulty in lack of genetic tools as found in *R. eutropha.* However, the repertoires of genetic tools are applicable for *Clostridium* with development in plasmid DNA and chromosomal manipulation technologies (Tracy et al., 2012). The uses of mobile group II introns are generally targeted for gene disruption and genetic engineering of *Clostridium.* Cooksley et al. (2012) demonstrated a

ClosTron application through genetic engineering in *Clostridium acetobutylicum* for acetone-butanol-ethanol (ABE) fermentation and for expression of cellulosome. Leang et al. (2012) employed double crossover homologous recombination technology and an improved electroporation protocol to the process in a proof-of-concept gene deletion study on the species of *C. ljundahlii*. Likewise, recent studies by the D.R. Lovley group demonstrated introduction of foreign genes and deletion of certain genes in *C. ljungdahlii* to enhance the production of biocommodities. Here, deletion of the ethanol-production pathway led to an increase in acetate production. The homolog recombination method described in their study can be applicable for the introduction of desired metabolic genes or reporters into the chromosomes of *C. Ljungdahlii* (Leang et al., 2012; Ueki et al., 2014).

Archaea

Archaea are generally found in abnormal ecological niches, such as high and low temperatures, acidic and high-saline environments, and anaerobic atmospheres. The hydrogenotrophic methanogens of Archaea use H_2 as an energy carrier and CO_2 as a carbon source for CH_4 generation. Furthermore, several strains of Archaea belonging to the haloarchael group are equipped with a metabolic pathway for accumulation of PHA from CO_2. As most of the Archaea are thermophilic in nature, this becomes an excellent source of the carbonic anhydrases (CA) enzyme, which is thermo stable and convenient for industrial CO_2 capture and a platform for gas fermentation (Willey et al., 2014). The recognition of genetic tools for Archaea might enhance the product yield in the gas fermentation process. Recently, genetic reengineering of Archaea for valuable product formation has been rising. Keller et al. (2013) reported a heterologous expression of five genes from a carbon fixation pathway in *Metallosphaera sedula* into hyper theromophilic *Pyrococcus furious*, which grows on organic carbon at 100°C. Engineered *P. furious* is capable of incorporating CO_2 for generation of 3-hydroxypropionte-4-hydroxybutyrate (3BHP) at an optimum condition of *M. sedula*; i.e., at 70°C. This temperature-dependent strategy for generation of valuable product formations is established in the work of Basen et al. (2012).

KEY ROLE OF ENZYMES IN MICROBIAL CELLS FOR CONVERSION OF CO_2

Adaptation of CO_2 to value-added products in the microbial kingdom has been found with six different pathways, such as WLP, Calvin Benson Bassham cycle, reductive tricarboxylic acid cycle (reductive/reverse TCA cycle), dicarboxylate 4-hydroxybutyrate cycle, 3-hydroxypropionate bicycle, and 3-hydroxypropionate 4-hydroxybutyrate cycle. These pathways are not found in every species, but specific pathways are found in specific organisms (**Figure 5**). Among these, the first three routes were found to be dominant for CO_2 conversion, and these are discussed in detail.

Calvin Cycle for the Phototrophic Reduction of CO_2

The Calvin cycle is one of the important biochemical cycles in photosynthetic organisms, which are capable of incorporating CO_2 into carbon metabolism. Thus, this metabolic function is dominant for CO_2 reduction in nature. In general, three key enzymes and three vital steps of the CO_2 process are noticed in the Calvin cycle (Venkata Mohan et al., 2016). The steps are known for CO_2 fixation, CO_2 reduction, and regeneration of CO_2. In the first step, the 1-5, bisphosphate ribulose bis-phosphate carboxylase (RuBisCo) catalyzes the reaction between CO_2 and 1-5, bisphosphate ribulose, and this process generates 3-phosphoglycerate (Shi et al., 2015). Later, 3-phosphoglycerate is further converted to 1,3-diphosphoglycerate by accepting inorganic phosphate (Pi) from ATP and further reduced to 3-phosphate glyceraldehyde with the help of the phosphoglyceraldehyde dehydrogenase enzyme. In the final step, phosphate glyceraldehyde is further transformed to 5-phosphate ribulose via a series of enzymatic reactions following further with its activation by phosphoribulokinase in ATP-dependent condensation to synthesize 1-5, bisphosphate ribulose for CO_2 collection for further cycles (Willey et al., 2014). One sixth of 3-phosphate glyceraldehyde is transformed as sugars, fatty acids, amino acids, etc.

Reverse TCA (Tricarboxylic Acid Cycle) Cycle

The reverse TCA (rTCA) cycle is known as the reductive citric acid cycle (reverse Krebs cycle), which basically runs in the reverse pathway. In this cycle, CO_2 and water are converted to carbon compounds (Lehninger et al., 2005). The reductive TCA cycle was first identified in anaerobic *Chloorbium limicola*, a green photoautotrophic sulfur-reducing bacteria. It was also identified in another thermophilic bacterium that uses hydrogen and sulfur as an energy source. The reverse TCA cycle contains four steps of carboxylation, in which, initially, succinyl-CoA is reductively carboxylated with CO_2 by α-Ketoglutarate synthase/2-oxoglutarate synthase (ΔGo, +19 kJ/mol; first step) to generate α-Ketoglutarate/2-oxoglutarate by utilizing two equivalents of reduced ferrodoxin. Next, α-Ketoglutarate/2-oxoglutarate along with CO_2 is converted to isocitrate (ΔGo, +8 kJ/mol; second step) by using isocitrate dehydrogenase and NADPH. Further, isocitrate is converted to citrate by a cleavage mechanism, followed by oxaloacetate and acetate-CoA by ATP citrate lyase. The terminal compounds are carboxylated with CO_2, which requires a pyruvate synthase enzyme (ΔGo, +19 kJ/mol). The synthesized pyruvate is activated by pyruvate kinase to yield phosphoenolpyruvate (PEP), which is further converted to bicarbonate by a carboxylation mechanism (ΔGo, −24 kJ/mol). As an outcome, oxaloacetate is generated and finally converted to succinyl-CoA by a series of enzymes (Venkata Mohan et al., 2016).

Reverse Acetyl-CoA Cycle

The reverse acetyl-CoA pathway is predominantly found in strict acetogenic (Eubacteria) and methanogenic (Euryarchaeota) bacteria. This route was suggested by Ljungdahl and Wood (2013), and it was named after them (Garrett and Grisham, 2008). Unlike the Calvin and reductive TCA cycles, the reductive acetyl-CoA is a non-cyclic route. In this route, initially, CO_2 is converted to formate by using NADH-dependent formate dehydrogenase ($F_{ate}DH$) (ΔGo +22 kJ/mol). Later, formate is apprehended by tetrahydrofolate and reduced into a methyl group by generating methyl-H4 folate. Methyltransferase transfers the methyl group of methyl-H4 folate to the cobalt center of hetero dimeric corrinoid iron sulfur protein, thus generating methylated corrinoid protein. Further, CO dehydrogenase (CODH) functions to convert CO_2 into CO via acetyl CoA synthase accepting the methyl group from CH_3-Co^{III} and converts CO, CoASH, and methyl groups to acetyl CoA (Mohanakrishna et al., 2015; Shi et al., 2015). As noted in the above enzymatic reaction, the autotrophic mechanism is by either CO_2 or bicarbonate as the carbon source. This mainly depends on the specific enzyme in a specific CO_2 fixation/conversion reaction. The attribute difference is noted in carbon source, and a fast-reliable conversion of CO_2 to bicarbonate is required.

SYNTHETIC BIOLOGY IN THE CONVERSION OF CO_2

Direct use of microbes in generation of value-added products is typically hindered by several characteristics/properties, such as low product yield, expensive cultivation condition, and inadequate growth rate. In this aspect, synthetic biology has gained importance due to its interest in product formation by altering biochemical pathways or by introduction of heterologous pathways into microbes for favorable features (Ferry et al., 2012). With consideration of recent advances in metabolic and protein engineering, the synthetic biology proves to be an excellent tool for boosting up biological process and to improve economic viability. In this section, *E. coli* is given special attention as it is the most often used microbe in the field of synthetic biology (Sawitzke et al., 2007).

Genetic Engineering for CO_2 Conversion

Despite being heterotrophic in nature, the Gram-negative *E. coli* gained its place at the table of genetic engineering due to its simple cultivation, low cost, easy transformation, fermentation, and high production for new technologies, which include using CO_2 as a carbon source (Willey et al., 2014). Zhuang et al. utilized different fermentation conditions for heterologous expression of RuBisCo and phosphoribulokinase (PRK) in *E. coli* (Zhuang and Li, 2013). In this study, they noticed a 67-mg CO_2/mole arabinose/l/h as the CO_2 fixation rate by a 15% decrease in CO_2 reduction during the fermentation process. Heterologous expression of carbonic anhydrase (CA) in *E. coli* is extensively reported. CA expression of *Methanobacterium thermoautotrophicum* in periplasm of *E. coli* resulted in a whole cell biocatalyst for CO_2 hydration. These systems successfully hydrated the CO_2 with a catalytic efficiency and productivity similar to free enzymes (Patel et al., 2013). The smaller difference observed in productivity might be due to mass transport limitations. In the presence of $CaCl_2$ and $CaCO_3$, a 50∼70% increase in carbon precipitation is noticed in comparison to operation without calcium (carbonate and chloride) components (Jo et al., 2013). Despite using free enzymes, whole cell utilization provides additional advantages such as (i) an increase in stability (100% in mortality activity after 24 h of use) and (ii) by passing the protein purification (whole cells are isolated and recycled). Similarly, as *M. thermoautotrophicum*, the periplasmic expression of CA is noticed in *Neisseria gonorrhoeae* (Jo et al., 2013). These advances noted in *E. coli* are not confined in the expression of individual enzymes. Bonacci et al. (2012) studied the expression of efficient carboxysomes from *Halothiobacillus neapolitanus* and encoded 10 genes in *E. coli* and noted that these bacteria are capable of carbon fixation. Further, they noticed an *in vitro* CO_2 fixation mechanism by using expressed carboxysomes with a sucrose gradient centrifugation as a purification step.

Synthetic biology of *E. coli* has provided a possibility of encoding photo bacterial genetics for the generation of value-added products. For instance, brown algae are well-known feedstock for the generation of carbon-neutral biofuel. However, from the point of economic industrial viability, these are limited by their inability to utilize alginate. Wargacki et al. (2012) reported the DNA fragments in *Vibrio splendidus* that are responsible for secretion of enzymes that are capable of utilization of alginate. This enzyme expression in *E. coli* resulted in a bacterial platform that is capable of metabolizing alginate with a yield of 0.281 weight ethanol/dry weight of microalgae that is equivalent to 80% of the theoretical basis of total polysaccharide composition. Along with several bacterial species, *Saccharomyces cerevisiae* also gained attention in conversion of CO_2 to value-added products. However, it has been limited with low productivity as compared to *E. coli*.

FUTURE PROSPECTS

The concepts of green and biological energy and/or chemical generation have been settling firmly in academia and industrial aspects, especially in utilizing CO_2 (Kuk et al., 2019). These processes guide the development of environmentally friendly products by optimized design concepts. The existing carbon capture technologies require huge land areas, large volumes, high energy, and expensive catalysts, and they also consume chemicals (ElMekawy et al., 2016). Therefore, based on reviewing the biological processes here, we suggest that biological systems align perfectly with green chemistry platforms for sustainable carbon capture and sequestration. The importance of biological processes for chemical generation using CO_2 as a carbon source is increasing rapidly (Venkata Mohan et al., 2016). From an economic point of view, all the biological processes for chemical/fuel production cannot be an industrially viable process. However, in consideration of carbon-neutral green energy generation, challenges, and their improvements, the biological adaptation of CO_2 utilization seems to be promising. The integration of a biological CO_2-mitigation process with conventional wastewater treatment technologies can minimize the economics related to waste remediation (Sadhukhan et al., 2016). Concurrently, process integration can be beneficial in generating sustainable energy or fuels with a minimum carbon footprint. Yet the conversion of low concentrated waste organics into fuels or chemical commodities is required to achieve selective product formation with use of biocatalytic technology by economic evaluation, mathematical modeling, optimization, and integration of energy-efficient processes (ElMekawy et al., 2016; Sadhukhan et al., 2016). In this regard, the MES technology has proven to be a potential approach for conversion of CO_2 to chemicals and fuels.

Moreover, the scaling up of MES is an advancement to MFC that produces high-value products. Likewise, it has the capability to become an alternative to fossil fuels and also to eliminate the food vs. fuel debate. However, there are few constraints that should be solved, for instance, the low electron intake by bacteria at the cathode and low productivity, stability, selectivity, etc. The synergistic effects of the substrate, electrode materials, and bacterial cell should be studied and well-understood for up-scaling. The conventional anaerobic fermentation system necessitates ∼3 kg of glucose for production of 1 kg of butanol, which seems to be non-optimal in spite of existing large-scale processes (He et al., 2016). In this regard, alcohol generation in MES using organic-rich wastewater seems to be a promising choice (Rabaey and Rozendal, 2010). More specifically, influence of current and electrical potential on the microbial metabolism and microbial strains related to electro fermentation or MES are required to consider for industrial application (Mohanakrishna et al., 2016). Microbial carbon capture is likely to be a standalone process that could be competitive to conventional technologies. Therefore, coupling of biological CO_2 processes with chemical processes, such as gasification and water gas shift reaction, could be beneficial. Complex biomass sources, such as

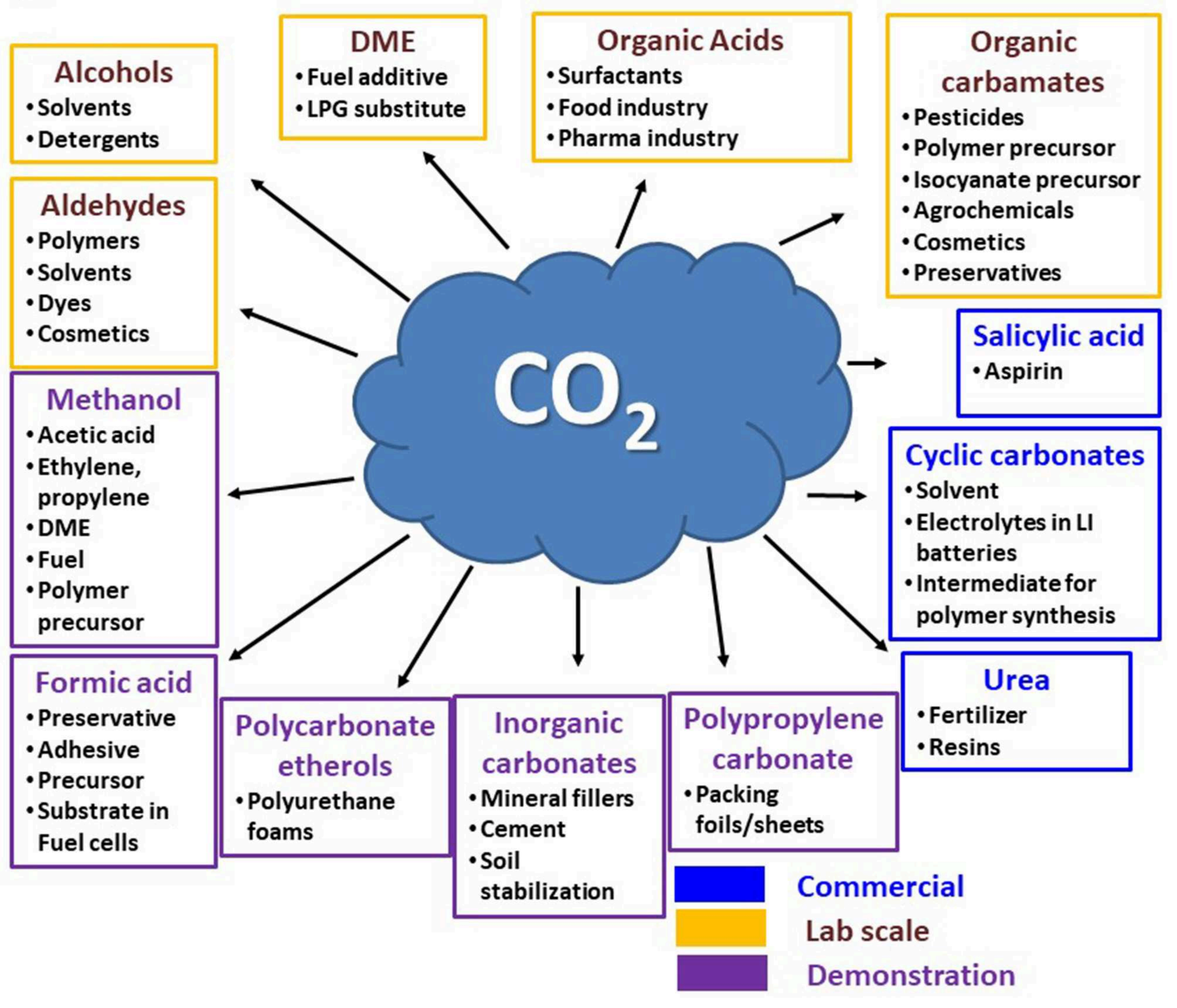


FIGURE 6 | CO_2 conversion to target products and their position of implementation. Redrawn from (Bioenergy, IEA – 2020; ISBN 978-1-910154-69-4).

cellulosic, wood, and straw materials, cannot be easily degraded or fermented. A good alternative is biomass gasification, which converts carbonaceous compounds into syngas through partial oxidation. H_2 and CO_2 in syngas also can be utilized by microbes for product formation. The conversion of syngas to products with a higher productivity rate can be achieved with bioelectrochemical and photobiological processes (Jiang et al., 2013). Further research would be required in order to enhance biofuel generation with low energy utilization and a minimal amount of toxic by-product generation (Rabaey and Rozendal, 2010; Mohanakrishna et al., 2015; ElMekawy et al., 2016; Venkata Mohan et al., 2016).

In terms of biotechnology of CO_2 utilization, algae and cyanobacteria have gained importance due to enhanced biomass generation for a feedstock and transesterification process. However, β-proteobacteria, clostridia, archaea, and other bacterial species can overtake the photosynthetic microbes due to rigorous research and efforts (Wang et al., 2012). Nonetheless, in utilization of various microbes for successful bioprocess development, one needs to pay attention to vital necessities, such as (i) suitable and appropriate strain selection for higher lipid generation (e.g., cell growth, autotrophic carbon fixation rate, product type and yield), (ii) supplementation minerals/chemical in CO_2 fixation, (iii) operation parameters (gas concentration, composition, etc.), (iv) type of bioprocess operation (batch or continuous), and (v) reactor configuration (CSTR, fixed bed reactor, membrane reactor) (Li et al., 2014). A few decisive factors in biological processes and engineering of carbon capture and utilization include (i) safety (especially during the H_2 utilization as electron donor/source), (ii) type of product selectivity and formation (concerning the purification and extraction economy), (iii) optimized operational conditions, and (iv) an increase in productivity by amplifying the cell density, etc.

In overview, the earlier described bioelectrochemical reaction pathways using CO_2 as the feedstock are based on H_2 as a reaction companion, whereas algae can transform CO_2 into value-added products, such as omega fatty acids, proteins, and amino acids and can simultaneously reduce pollutants. Likewise, other technologies, such as enzymes (e.g., formate dehydrogenase) can utilize/transform CO_2 by providing necessary energy. **Figure 6** provides an overview of different CO_2-based product formation pathways and their current status of employment. Apart from urea, the leading CO_2-based product formations from other industrial processes involve the production of cyclic carbonates and salicylic acids, which are being produced at about 0.1 million tons/year (technology readiness level (TRL): 9) (Bazzanella and Ausfelder, 2017). The poly (propylene) carbonate and polycarbonate etherols are extensively produced polymers in industries using CO_2 as a building block. Novomer incorporation from the United States and Covestro (former Bayer Material Science) are dynamic in this area with large-scale operations (TRL7-9). DNV (Det Norske Veritas) from Norway has constructed a pilot-scale operation plant for formic acid generation with a capability of 1 kg/day via electrochemical CO_2 reduction. Similarly, Mantra Energy Alternative Limited from Vancouver, British Columbia, Canada, is constructing a plant for 100 kg/day formic acid generation (TRL7) by electro-reduction of CO_2 (Bazzanella and Ausfelder, 2017). Mineral carbonation, also known as carbon mineralization, is already being used in smaller and semi-commercial plants for various purposes, such as treatment of industrial waste, polluted soil, and generation of cement-like building materials (TRL7-9). There are several other processes being researched at lab scale with significantly lower TRL. Among these, one approach is noteworthy to point out because of its huge potential in the direct synthesis of dimethyl ether (DME) from CO_2. This method allows a CO_2 reduction of 0.125 t CO_2 /t DME, which is known to be higher in comparison to the state-of-the-art process with an intermediation of methanol equivalent to a 30% reduction. There is more production pathways research that involves direct production of sodium acrylate from ethylene and CO_2 or electrocatalytic conversion of CO_2 to ethylene (Alexis Bazzanella, 2017).

One of the crucial parameters to be considered for commercialization of CO_2 reduction via biological routes is the CO_2 that is stoichiometrically converted per ton of product. Based on earlier studies, acetic acid, ethanol, succinic acid, and caproic acid have stoichiometric production of 1.47, 1.91, 1.49, and 2.28 t CO_2/t, respectively. These chemicals (acetic acid, ethanol, succinic acid, and caproic acid) have a projected market value of 16.4 (Acumen Research Consulting, 2019), 54.63 (Coherent Market Insights, 2017), 0.237 (Markets Markets, 2019), and 0.27 (Market Study Report, 2019) billion dollars by 2026. Moreover, these products, such as acetate, can be used as building blocks for higher valued product generation, such as ethyl acetate, with a projected market value of 95 billion dollars by 2024 (Global Market Insights, 2018). Also, the combination of ethanol and other compounds (e.g., volatile fatty acids) can be used for a carbon chain elongation reaction. On the basis of these projected market values, the mitigation of CO_2 to product formation can be beneficial. However, these biological approaches need a further life cycle assessment (LCA) in order to compare benchmarks with the state-of-the-art production, considering energy aspects, etc.

In order to implement innovative biological ideas on a commercial scale and to reach the visionary target, consideration of the following aspects can be beneficial: (i) high-performing conversion technology on the level of CO_2 upstream: The technology should ideally cope with given impurities and/or CO_2 gas concentrations of their client's CO_2 waste streams at minimal pretreatment costs. CO_2 conversion process: convert CO_2 in an efficient way (total CO_2 conversion and selectivity toward product of interest) at an appreciable productivity (space–time yield) toward product in order to minimize investment and operational costs and obtain a techno-economic feasible route. Downstream: obtain high product titers and high product selectivity in order to reduce further downstream processing steps or costs. (ii) Local value chains fit for given CO_2-to-product pathway via biological route. (iii) Legislation for the end product in case of high-volume application (ethanol, fuels) (Carr, 2005).

Indeed, some of the major challenges of CO_2 reduction are the availability of renewable energy to sufficiently supply the potential biological CO_2 conversion strategies (via green H_2 production), location, and transport of product. In this regard, low potential photovoltaic energy prices in the Middle East, Southern Europe, and North Africa would enable the production of liquid CO_2 fuels that can be easily transported to Europe, for instance. This enables the creation of new value chains and business cases of interest. As energy prices are high today and scales are small, we need high-value product routes or high volume that is supported by proper legislation. In the future, at low energy prices and larger scale, the challenge would be the energy supply in the most ambitious scenario, in which the full potential for given chemical/fuels is valorized via the CO_2 route (Tahvonen et al., 1994; Illing et al., 2018).

CONCLUSIONS

This report has overviewed and discussed potential applications of biological processes for CO_2 fixation with generation of value-added products. Despite achieving some progress, there is still a need for finding suitable processes or microbial strains for CO_2 mitigation. For instance, the productivity of microbial CO_2 sequestration should be more than 3-fold higher than traditional CO_2 technologies, which seems to be a daunting goal with current methods. Thus, the combination of industrial processes with microbial CO_2 mitigation can be sustainable and economically viable for reduction of CO_2. The metabolism of CO_2 conversion by algae and photosynthetic processes can be equally viable as chemical and electrochemical technologies. Furthermore, market analysis and commercialization need to be further discussed by considering the real field application. Bioelectrochemical CO_2 conversion and photo biological processes for value-added product synthesis seems to be an economical and sustainable approach toward future technological development and commercialization. However, integration of suitable CO_2-converting processes with CO_2-generating processes helps for the development of a CO_2-based bio-refinery that may lead to carbon-neutral industrialization.

AUTHOR CONTRIBUTIONS

SK: inception of review concept, major write-up part of the review. IA-R: editing of review and supervision and Co-Lead PI of the project. GM: involved in writing two sections of the manuscript, editing of review and supervision. MB: involved in writing future prospective of the CO_2 transformation/reduction section of the review. DP: editing of review and supervision. All authors contributed to the article and approved the submitted version.

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REFERENCES

Acumen Research and Consulting (2019). *Acetic Acid Market Value to Reach US 16.4 Billion by 2026*. Available online at: https://www.acumenresearchandconsulting.com/acetic-acid-market (accessed February 15, 2020).

Ahring, B. K., Ibrahim, A. A., and Mladenovska, Z. (2001). Effect of temperature increase from 55 to 65°C on performance and microbial population dynamics of an anaerobic reactor treating cattle manure. *Water Res.* 35, 2446–2452. doi: 10.1016/S0043-1354(00)00526-1

Alexis Bazzanella, D. K. (2017). *Technologies for Sustainabilityand Climate Protection –Chemical Processes and Use of CO_2*. Available online at: https://dechema.de/en/energyandclimate_CO2_Buch_engl.pdf (accessed February 15, 2020).

Allen, M. M., and Stanier, R. Y. (1968). Selective isolation of blue-green algae from water and soil. *Microbiology* 51, 203–209. doi: 10.1099/00221287-51-2-203

Anbalagan, A., Toledo-Cervantes, A., Posadas, E., Rojo, E. M., Lebrero, R., González-Sánchez, A., et al. (2017). Continuous photosynthetic abatement of CO_2 and volatile organic compounds from exhaust gas coupled to wastewater treatment: evaluation of tubular algal-bacterial photobioreactor. *J. CO_2 Util.* 21, 353–359. doi: 10.1016/j.jcou.2017.07.016

Arends, J. B. A., Patil, S. A., Roume, H., and Rabaey, K. (2017). Continuous long-term electricity-driven bioproduction of carboxylates and isopropanol from CO_2 with a mixed microbial community. *J. CO_2 Util.* 20, 141–149. doi: 10.1016/j.jcou.2017.04.014

Bajracharya, S., Ter Heijne, A., Dominguez Benetton, X., Vanbroekhoven, K., Buisman, C. J. N., Strik, D. P. B. T. B., et al. (2015). Carbon dioxide reduction by mixed and pure cultures in microbial electrosynthesis using an assembly of graphite felt and stainless steel as a cathode. *Bioresour. Technol.* 195, 14–24. doi: 10.1016/j.biortech.2015.05.081

Bajracharya, S., Yuliasni, R., Vanbroekhoven, K., Buisman, C. J. N., Strik, D. P. B. T. B., and Pant, D. (2017). Long-term operation of microbial electrosynthesis cell reducing CO_2 to multi-carbon chemicals with a mixed culture avoiding methanogenesis. *Bioelectrochemistry* 113, 26–34. doi: 10.1016/j.bioelechem.2016.09.001

Basen, M., Sun, J., and Adams, M. W. W. (2012). Engineering a hyperthermophilic archaeon for temperature-dependent product formation. *MBio* 3, e00053–e00012. doi: 10.1128/mBio.00053-12

Batlle-Vilanova, P., Puig, S., Gonzalez-Olmos, R., Balaguer, M. D., and Colprim, J. (2016). Continuous acetate production through microbial electrosynthesis from CO_2 with microbial mixed culture. *J. Chem. Technol. Biotechnol.* 91, 921–927. doi: 10.1002/jctb.4657

Bazzanella, A., and Ausfelder, F. (2017). *Low Carbon Energy and Feedstock for the European Chemical Industry*. Frankfurt am Main: DECHEMA; Gesellschaft für Chemische Technik und Biotechnologie eV.

Benedetti, M., Vecchi, V., Barera, S., and Dall'Osto, L. (2018). Biomass from microalgae: the potential of domestication towards sustainable biofactories. *Microb. Cell Fact.* 17:173. doi: 10.1186/s12934-018-1019-3

Benemann, J. R. (1993). Utilization of carbon dioxide from fossil fuel-burning power plants with biological systems. *Energy Convers. Manage.* 34, 999–1004. doi: 10.1016/0196-8904(93)90047-E

Benemann, J. R. (1997). CO_2 mitigation with microalgae systems. *Energy Convers. Manage.* 38(Suppl.), S475–S479. doi: 10.1016/S0196-8904(96)00313-5

Benemann, J. R., and Oswald, W. J. (1996). *Systems and Economic Analysis of Microalgae Ponds for Conversion of CO {sub 2} to Biomass*. Final report. Berkeley, CA: California Univ., Dept. of Civil Engineering. doi: 10.2172/493389

Benhelal, E., Zahedi, G., Shamsaei, E., and Bahadori, A. (2013). Global strategies and potentials to curb CO_2 emissions in cement industry. *J. Clean. Prod.* 51, 142–161. doi: 10.1016/j.jclepro.2012.10.049

Berman-Frank, I., Lundgren, P., and Falkowski, P. (2003). Nitrogen fixation and photosynthetic oxygen evolution in cyanobacteria.

Res. Microbiol. 154, 157–164. doi: 10.1016/S0923-2508(03)00029-9

Bhola, V., Desikan, R., Santosh, S. K., Subburamu, K., Sanniyasi, E., and Bux, F. (2011). Effects of parameters affecting biomass yield and thermal behaviour of *Chlorella vulgaris*. *J. Biosci. Bioeng.* 111, 377–382. doi: 10.1016/j.jbiosc.2010.11.006

Bian, B., Alqahtani, M. F., Katuri, K. P., Liu, D., Bajracharya, S., Lai, Z., et al. (2018). Porous nickel hollow fiber cathodes coated with CNTs for efficient microbial electrosynthesis of acetate from CO_2 using *Sporomusa ovata*. *J. Mater. Chem. A* 6, 17201–17211. doi: 10.1039/C8TA05322G

Bonacci, W., Teng, P. K., Afonso, B., Niederholtmeyer, H., Grob, P., Silver, P. A., et al. (2012). Modularity of a carbon-fixing protein organelle. *Proc. Natl. Acad. Sci. U.S.A.* 109, 478–483. doi: 10.1073/pnas.1108557109

Bond, G. M., Stringer, J., Brandvold, D. K., Simsek, F. A., Medina, M-G., and Egeland, G. (2001). Development of integrated system for biomimetic CO_2 sequestration using the enzyme carbonic anhydrase. *Energy Fuels* 15, 309–316. doi: 10.1021/ef000246p

Bulgariu, D., and Bulgariu, L. (2016). Potential use of alkaline treated algae waste biomass as sustainable biosorbent for clean recovery of cadmium(II) from aqueous media: batch and column studies. *J. Clean. Prod. 112*, 4525–4533. doi: 10.1016/j.jclepro.2015.05.124

Carlsson, A. S., and Bowles, D. J. (2007). *Micro- and Macro-algae: Utility for Industrial Applications : Outputs from the EPOBIO Project.* Speen; Newbury, UK: CPL Press.

Carr, M. (2005). Energy bill boosts industrial biotechnology; sweeping new legislation looks to bioproducts and biofuels to cut peak oil-dependency. *Ind. Biotechnol.* 1, 142–143. doi: 10.1089/ind.2005.1.142

Chae, S. R., Hwang, E. J., and Shin, H. S. (2006). Single cell protein production of *Euglena gracilis* and carbon dioxide fixation in an innovative photo-bioreactor. *Bioresour. Technol.* 97, 322–329. doi: 10.1016/j.biortech.2005.02.037

Chang, X., Wang, T., and Gong, J. (2016). CO_2 photo-reduction: insights into CO_2 activation and reaction on surfaces of photocatalysts. *Energy Environ. Sci.* 9, 2177–2196. doi: 10.1039/C6EE00383D

Chen, J-S., and Hiu, S. F. (1986). Acetone-butanol-isopropanol production by *Clostridiumbeijerinckii* (synonym,clostridiumbutylicum). *Biotechnol. Lett.* 8, 371–376. doi: 10.1007/BF01040869

Chen, W., Zhang, C., Song, L., Sommerfeld, M., and Hu, Q. (2009). A high throughput Nile red method for quantitative measurement of neutral lipids in microalgae. *J. Microbiol. Methods* 77, 41–47. doi: 10.1016/j.mimet.2009.01.001

Cheng, S., Xing, D., Call, D. F., and Logan, B. E. (2009). Direct biological conversion of electrical current into methane by electromethanogenesis. *Environ. Sci. Technol.* 43, 3953–3958. doi: 10.1021/es803531g

Chinnasamy, S., Ramakrishnan, B., Bhatnagar, A., and Das, K. C. (2009). Biomass production potential of a wastewater alga *Chlorella vulgaris* ARC 1 under elevated levels of CO(2) and temperature. *Int. J. Mol. Sci.* 10, 518–532. doi: 10.3390/ijms10020518

Chisti, Y. (2007). Biodiesel from microalgae. *Biotechnol. Adv.* 25, 294–306. doi: 10.1016/j.biotechadv.2007.02.001

Chiu, S-Y., Kao, C-Y., Tsai, M-T., Ong, S-C., Chen, C-H., and Lin, C-S. (2009). Lipid accumulation and CO_2 utilization of Nannochloropsis oculata in response to CO_2 aeration. *Bioresour. Technol.* 100, 833–838. doi: 10.1016/j.biortech.2008.06.061

Christodoulou, X., Okoroafor, T., Parry, S., and Velasquez-Orta, S. B. (2017). The use of carbon dioxide in microbial electrosynthesis: advancements, sustainability and economic feasibility. *J. CO_2 Util.* 18(Suppl. C), 390–399. doi: 10.1016/j.jcou.2017.01.027

Clarens, A. F., Resurreccion, E. P., White, M. A., and Colosi, L. M. (2010). Environmental life cycle comparison of algae to other bioenergy feedstocks. *Environ. Sci. Technol.* 44, 1813–1819. doi: 10.1021/es902838n

Cloot, A. (1994). Effect of light intensity variations on the rate of photosynthesis of algae: a dynamical approach. *Math. Comput. Model.* 19, 23–33. doi: 10.1016/0895-7177(94)90038-8

Coherent Market Insights (2017). *Global Ethanol Market to Surpass US 54.63 Billion by 2026, Attributed to Increasing Production of Renewable Fuels.* Available online at: https://www.coherentmarketinsights.com/press-release/global-ethanol-market-to-surpass-us-531-billion-by-2025-fuelled-by-increased-production-of-renewable-fuels-314. (accessed February 15, 2020).

Converti, A., Casazza, A. A., Ortiz, E. Y., Perego, P., and Del Borghi, M. (2009). Effect of temperature and nitrogen concentration on the growth and lipid content of *Nannochloropsis oculata* and *Chlorella vulgaris* for biodiesel production. *Chem. Eng. Process. Process Intensific.* 48, 1146–1151. doi: 10.1016/j.cep.2009.03.006

Cooksley, C. M., Zhang, Y., Wang, H., Redl, S., Winzer, K., and Minton, N. P. (2012). Targeted mutagenesis of the *Clostridium acetobutylicum* acetone–butanol–ethanol fermentation pathway. *Metab. Eng.* 14, 630–641. doi: 10.1016/j.ymben.2012.09.001

Csavina, J. L., Stuart, B. J., Guy Riefler, R., and Vis, M. L. (2011). Growth optimization of algae for biodiesel production. *J. Appl. Microbiol.* 111, 312–318. doi: 10.1111/j.1365-2672.2011.05064.x

de Morais, M. G., and Costa, J. A. V. (2007a). Biofixation of carbon dioxide by *Spirulina* sp. and *Scenedesmus obliquus* cultivated in a three-stage serial tubular photobioreactor. *J. Biotechnol.* 129, 439–445. doi: 10.1016/j.jbiotec.2007.01.009

de Morais, M. G., and Costa, J. A. V. (2007b). Carbon dioxide fixation by *Chlorella kessleri*, *C. vulgaris, Scenedesmus obliquus* and *Spirulina* sp. cultivated in flasks and vertical tubular photobioreactors. *Biotechnol. Lett.* 29, 1349–1352. doi: 10.1007/s10529-007-9394-6

de Morais, M. G., and Costa, J. A. V. (2007c). Isolation and selection of microalgae from coal fired thermoelectric power plant for biofixation of carbon dioxide. *Energy Convers. Manage.* 48, 2169–2173. doi: 10.1016/j.enconman.2006.12.011

del Pilar Anzola Rojas, M., Zaiat, M., Gonzalez, E. R., De Wever, H., and Pant, D. (2018). Effect of the electric supply interruption on a microbial electrosynthesis system converting inorganic carbon into acetate. *Bioresour. Technol.* 266, 203–210. doi: 10.1016/j.biortech.2018.06.074

Demirbas, A. (2010). Use of algae as biofuel sources. *Energy Convers. Manage.* 51, 2738–2749. doi: 10.1016/j.enconman.2010.06.010

Dexter, J., and Fu, P. (2009). Metabolic engineering of cyanobacteria for ethanol production. *Energy Environ. Sci.* 2, 857–864. doi: 10.1039/b811937f

Dong, T., Knoshaug, E. P., Pienkos, P. T., and Laurens, L. M. L. (2016). Lipid recovery from wet oleaginous microbial biomass for biofuel production: a critical review. *Appl. Energy* 177, 879–895. doi: 10.1016/j.apenergy.2016.06.002

Dudley, B. (2018). *BP Statistical Review of World Energy.* London: BP Statistical Review.

Effendi, S. S. W., and Ng, I. S. (2019). The prospective and potential of carbonic anhydrase for carbon dioxide sequestration: a critical review. *Process Biochem.* 87, 55–65. doi: 10.1016/j.procbio.2019.08.018

El Gamal, A. A. (2010). Biological importance of marine algae. *Saudi Pharm. J.* 18, 1–25. doi: 10.1016/j.jsps.2009.12.001

ElMekawy, A., Hegab, H. M., Mohanakrishna, G., Elbaz, A. F., Bulut, M., and Pant, D. (2016). Technological advances in CO_2 conversion electro-biorefinery: a step toward commercialization. *Bioresour. Technol.* 215, 357–370. doi: 10.1016/j.biortech.2016.03.023

Ewering, C., Heuser, F., Benölken, J. K., Brämer, C. O., and Steinbüchel, A. (2006). Metabolic engineering of strains of *Ralstonia eutropha* and *Pseudomonas putida* for biotechnological production of 2-methylcitric acid. *Metab. Eng.* 8, 587–602. doi: 10.1016/j.ymben.2006.05.007

Fan, L-H., Zhang, Y-T., Zhang, L., and Chen, H-L. (2008). Evaluation of a membrane-sparged helical tubular photobioreactor for carbon dioxide biofixation by *Chlorella vulgaris*. *J. Membr. Sci.* 325, 336–345. doi: 10.1016/j.memsci.2008.07.044

Fernando, I. P. S., Nah, J-W., and Jeon, Y-J. (2016). Potential anti-inflammatory natural products from marine algae. *Environ. Toxicol. Pharmacol.* 48, 22–30. doi: 10.1016/j.etap.2016.09.023

Ferry, M. S., Hasty, J., and Cookson, N. A. (2012). Synthetic biology approaches to biofuel production. *Biofuels* 3, 9-12. doi: 10.4155/bfs.11.151

Foo, S. C., Yusoff, F. M., Ismail, M., Basri, M., Yau, S. K., Khong, N. M. H., et al. (2017). Antioxidant capacities of fucoxanthin-producing algae as influenced by their carotenoid and phenolic contents. *J. Biotechnol.* 241, 175–183. doi: 10.1016/j.jbiotec.2016.11.026

García, V., Päkkilä, J., Ojamo, H., Muurinen, E., and Keiski, R. L. (2011). Challenges in biobutanol production: how to improve the efficiency? *Renew. Sustain. Energy Rev.* 15, 964–980. doi: 10.1016/j.rser.2010.11.008

Garrett, R. H., and Grisham, C. M. (2008). *Biochemistry.* Boston, MA: Cengage Learning.

Ge, X., Yang, L., Sheets, J. P., Yu, Z., and Li, Y. (2014). Biological conversion of methane to liquid fuels: status and opportunities. *Biotechnol. Adv.* 32, 1460–1475. doi: 10.1016/j.biotechadv.2014.09.004

Georgianna, D. R., and Mayfield, S. P. (2012). Exploiting diversity and synthetic biology for the production of algal biofuels. *Nature* 488, 329–335. doi: 10.1038/nature11479

Gildemyn, S., Verbeeck, K., Slabbinck, R., Andersen, S. J., Prévoteau, A., and Rabaey, K. (2015). Integrated production, extraction, and concentration of acetic acid from CO_2 through microbial electrosynthesis. *Environ. Sci. Technol. Lett.* 2, 325–328. doi: 10.1021/acs.estlett.5b00212

Global Market Insights (2018). *Ethyl Acetate Market size, Industry Analysis Report, Regional Outlook, Application Development Potential, Price Trends, Competitive Market Share and Forecast, 2019 - 2025*. Available online at: https://www.gminsights.com/industry-analysis/ethyl-acetate-market (accessed February 15, 2020).

González López, C. V., Acién Fernández, F. G., Fernández Sevilla, J. M., Sánchez Fernández, J. F., Cerón García, M. C., and Molina Grima, E. (2009). Utilization of the cyanobacteria *Anabaena* sp. ATCC 33047 in CO_2 removal processes. *Bioresour. Technol.* 100, 5904–5910. doi: 10.1016/j.biortech.2009.04.070

Gottumukkala, L. D., Sukumaran, R. K., Mohan, S. V., Valappil, S. K., Sarkar, O., and Pandey, A. (2015). Rice straw hydrolysate to fuel and volatile fatty acid conversion by *Clostridium sporogenes* BE01: bio-electrochemical analysis of the electron transport mediators involved. *Green Chem.* 17, 3047–3058. doi: 10.1039/C5GC00310E

Hanagata, N., Takeuchi, T., Fukuju, Y., Barnes, D. J., and Karube, I. (1992). Tolerance of microalgae to high CO_2 and high temperature. *Phytochemistry* 31, 3345–3348. doi: 10.1016/0031-9422(92)83682-O

Hatch, M., and Slack, C. (1970). Photosynthetic CO_2-fixation pathways. *Annu. Rev. Plant Physiol.* 21, 141–162. doi: 10.1146/annurev.pp.21.060170.001041

He, A. Y., Yin, C. Y., Xu, H., Kong, X. P., Xue, J. W., Zhu, J., et al. (2016). Enhanced butanol production in a microbial electrolysis cell by *Clostridium beijerinckii* IB4. *Bioprocess Biosyst. Eng.* 39, 245–254. doi: 10.1007/s00449-015-1508-2

Holkar, C. R., Jadhav, A. J., Pinjari, D. V., Mahamuni, N. M., and Pandit, A. B. (2016). A critical review on textile wastewater treatments: possible approaches. *J. Environ. Manage.* 182, 351–366. doi: 10.1016/j.jenvman.2016.07.090

Hou, X., Huang, L., Zhou, P., Tian, F., Tao, Y., and Li Puma, G. (2019). Electrosynthesis of acetate from inorganic carbon (HCO3−) with simultaneous hydrogen production and Cd(II) removal in multifunctional microbial electrosynthesis systems (MES). *J. Hazard Mater.* 371, 463–473. doi: 10.1016/j.jhazmat.2019.03.028

Hu, P., Chakraborty, S., Kumar, A., Woolston, B., Liu, H., Emerson, D., et al. (2016). Integrated bioprocess for conversion of gaseous substrates to liquids. *Proc. Natl. Acad. Sci. U.S.A.* 113, 3773–3778. doi: 10.1073/pnas.1516867113

Hudek, K., Davis, L. C., Ibbini, J., and Erickson, L. (2014). "Commercial products from algae," in *Algal Biorefineries: Volume 1: Cultivation of Cells and Products,* eds R. Bajpai, A. Prokop, and M. Zappi (Dordrecht: Springer Netherlands), 275–295. doi: 10.1007/978-94-007-7494-0_11

Hunt, A. J., Sin, E. H. K., Marriott, R., and Clark, J. H. (2010). Generation, capture, and utilization of industrial carbon dioxide. *ChemSusChem* 3, 306–322. doi: 10.1002/cssc.200900169

Illing, L., Natelson, R., Resch, M., Rowe, I., and Babson, D. (2018). *Rewiring the Carbon Economy: Engineered Carbon Reduction Listening Day Summary Report*. USDOE Office of Energy Efficiency and Renewable Energy (EERE), Washington, DC. doi: 10.2172/1419624

International Energy Agency (2019). *CO_2 Status Report*. Paris, France: IEA (International Energy Agency).

Jajesniak, P., Ali, H. E., and Wong, T. S. (2014). Carbon dioxide capture and utilization using biological systems: opportunities and challenges. *J. Bioprocess. Biotech.* 4:1. doi: 10.4172/2155-9821.1000155

Jiang, Y., May, H. D., Lu, L., Liang, P., Huang, X., and Ren, Z. J. (2019). Carbon dioxide and organic waste valorization by microbial electrosynthesis and electro-fermentation. *Water Res.* 149, 42–55. doi: 10.1016/j.watres.2018.10.092

Jiang, Y., Su, M., Zhang, Y., Zhan, G., Tao, Y., and Li, D. (2013). Bioelectrochemical systems for simultaneously production of methane and acetate from carbon dioxide at relatively high rate. *Int. J. Hydrogen Energy* 38, 3497–3502. doi: 10.1016/j.ijhydene.2012.12.107

Jin, H-F., Lim, B-R., and Lee, K. (2006). Influence of nitrate feeding on carbon dioxide fixation by microalgae. *J. Environ. Sci. Health A Toxicol. Hazard Substain. Environ. Eng.* 41, 2813–2824. doi: 10.1080/10934520600967928

Jo, B. H., Kim, I. G., Seo, J. H., Kang, D. G., and Cha, H. J. (2013). Engineered *Escherichia coli* with periplasmic carbonic anhydrase as a biocatalyst for CO_2 sequestration. *Appl. Environ. Microbiol.* 79, 6697–6705. doi: 10.1128/AEM.02400-13

Kadier, A., Jain, P., Lai, B., Kalil, M. S., Kondaveeti, S., Alabbosh, K. F. S., et al. (2020). Biorefinery perspectives of microbial electrolysis cells (MECs) for hydrogen and valuable chemicals production through wastewater treatment. *Biofuel Res. J.* 7, 1128–1142. doi: 10.18331/BRJ2020.7.1.5

Kaewkannetra, P., Enmak, P., and Chiu, T. (2012). The effect of CO_2 and salinity on the cultivation of scenedesmus obliquus for biodiesel production. *Biotechnol. Bioprocess Eng.* 17, 591–597. doi: 10.1007/s12257-011-0533-5

Kasting, J. F., and Siefert, J. L. (2002). Life and the evolution of earth's atmosphere. *Science* 296, 1066–1068. doi: 10.1126/science.1071184

Keffer, J. E., and Kleinheinz, G. T. (2002). Use of *Chlorella vulgaris* for CO_2 mitigation in a photobioreactor. *J. Ind. Microbiol. Biotechnol.* 29, 275–280. doi: 10.1038/sj.jim.7000313

Keller, M. W., Schut, G. J., Lipscomb, G. L., Menon, A. L., Iwuchukwu, I. J., Leuko, T. T., et al. (2013). Exploiting microbial hyperthermophilicity to produce an industrial chemical, using hydrogen and carbon dioxide. *Proc. Natl. Acad. Sci. U.S.A.* 110, 5840–5845. doi: 10.1073/pnas.1222607110

Kerdudo, A., Burger, P., Merck, F., Dingas, A., Rolland, Y., Michel, T., et al. (2016). Development of a natural ingredient – natural preservative: a case study. *Comptes Rendus Chimie* 19, 1077–1089. doi: 10.1016/j.crci.2016.06.004

Khosravanipour Mostafazadeh, A., Drogui, P., Brar, S. K., Tyagi, R. D., Le Bihan, Y., Buelna, G., et al. (2016). Enhancement of biobutanol production by electromicrobial glucose conversion in a dual chamber fermentation cell using *C. pasteurianum*. *Energy Convers. Manage.* 130, 165–175. doi: 10.1016/j.enconman.2016.10.050

Kim, T. S., and Kim, B. H. (1988). Electron flow shift in *Clostridium acetobutylicum* fermentation by electrochemically introduced reducing equivalent. *Biotechnol. Lett.* 10, 123–128. doi: 10.1007/BF01024638

Kim, T. W., Bae, S. S., Lee, J. W., Lee, S-M., Lee, J-H., Lee, H. S., et al. (2016). A biological process effective for the conversion of CO-containing industrial waste gas to acetate. *Bioresour. Technol.* 211, 792–796. doi: 10.1016/j.biortech.2016.04.038

Kishimoto, M., Okakura, T., Nagashima, H., Minowa, T., Yokoyama, S-Y., and Yamaberi, K. (1994). CO_2 fixation and oil production using micro-algae. *J. Ferment. Bioeng.* 78, 479–482. doi: 10.1016/0922-338X(94)90052-3

Kodama, M., Ikemoto, H., and Miyachi, S. (1993). A new species of highly CO_2 tolerant fast growing marine microalga suitable for high-density culture. *J. Mar. Biotechnol.* 1, 21–25.

Kondaveeti, S., Choi, K. S., Kakarla, R., and Min, B. (2014a). Microalgae *Scenedesmus obliquus* as renewable biomass feedstock for electricity generation in microbial fuel cells (MFCs). *Front. Environ. Sci. Eng.* 8, 784–791. doi: 10.1007/s11783-013-0590-4

Kondaveeti, S., Kakarla, R., Kim, H. S., Kim, B-G., and Min, B. (2017). The performance and long-term stability of low-cost separators in single-chamber bottle-type microbial fuel cells. *Environ. Technol.* 39, 288–297. doi: 10.1080/09593330.2017.1299223

Kondaveeti, S., Lee, S-H., Park, H-D., and Min, B. (2014b). Bacterial communities in a bioelectrochemical denitrification system: the effects of supplemental electron acceptors. *Water Res.* 51, 25–36. doi: 10.1016/j.watres.2013.12.023

Kondaveeti, S., and Min, B. (2015). Bioelectrochemical reduction of volatile fatty acids in anaerobic digestion effluent for the production of biofuels. *Water Res.* 87, 137–144. doi: 10.1016/j.watres.2015.09.011

Kratz, W. A., and Myers, J. (1955). Nutrition and growth of several blue-green algae. *Am. J. Bot.* 42, 282–287. doi: 10.1002/j.1537-2197.1955.tb11120.x

Kuk, S. K., Ham, Y., Gopinath, K., Boonmongkolras, P., Lee, Y., Lee, Y. W., et al. (2019). CO_2 reduction: continuous 3D titanium nitride nanoshell structure for solar-driven unbiased biocatalytic CO_2 reduction. *Adv. Energy Mater.* 9:1970097. doi: 10.1002/aenm.201970097

Kumar, B., Brian, J. P., Atla, V., Kumari, S., Bertram, K. A., White, R. T., et al. (2016). New trends in the development of heterogeneous catalysts for electrochemical CO_2 reduction. *Catal. Today* 270, 19–30. doi: 10.1016/j.cattod.2016.02.006

Kumar, K., Dasgupta, C. N., Nayak, B., Lindblad, P., and Das, D. (2011). Development of suitable photobioreactors for CO_2 sequestration addressing global warming using green algae and cyanobacteria. *Bioresour. Technol.* 102, 4945–4953. doi: 10.1016/j.biortech.2011.01.054

Kuramochi, Y., Fu, Q., Kobayashi, H., Ikarashi, M., Wakayama, T., Kawaguchi, H., et al. (2013). Electromethanogenic CO_2 conversion by subsurface-reservoir microorganisms. *Energy Procedia* 37, 7014–7020. doi: 10.1016/j.egypro.2013.06.636

Kurano, N., Ikemoto, H., Miyashita, H., Hasegawa, T., Hata, H., and Miyachi, S. (1995). Fixation and utilization of carbon dioxide by microalgal photosynthesis. *Energy Convers. Manage.* 36, 689–692. doi: 10.1016/0196-8904(95)00099-Y

Kusakabe, T., Tatsuke, T., Tsuruno, K., Hirokawa, Y., Atsumi, S., Liao, J. C., et al. (2013). Engineering a synthetic pathway in cyanobacteria for isopropanol production directly from carbon dioxide and light. *Metab. Eng.* 20, 101–108. doi: 10.1016/j.ymben.2013.09.007

LaBelle, E. V., and May, H. D. (2017). Energy efficiency and productivity enhancement of microbial electrosynthesis of acetate. *Front. Microbiol.* 8:756. doi: 10.3389/fmicb.2017.00756

Lambert, G. R., and Smith, G. D. (1977). Hydrogen formation by marine blue—green algae. *FEBS Lett.* 83, 159–162. doi: 10.1016/0014-5793(77)80664-9

Lau, N-S., Matsui, M., and Abdullah, A. A-A. (2015). Cyanobacteria: photoautotrophic microbial factories for the sustainable synthesis of industrial products. *Biomed. Res. Int.* 2015:754934. doi: 10.1155/2015/754934

Lawton, T. J., and Rosenzweig, A. C. (2016). Biocatalysts for methane conversion: big progress on breaking a small substrate. *Curr. Opin. Chem. Biol.* 35, 142–149. doi: 10.1016/j.cbpa.2016.10.001

Leang, C., Ueki, T., Nevin, K. P., and Lovley, D. R. (2012). A genetic system for *Clostridium ljungdahlii*: a chassis for autotrophic production of biocommodities and a model homoacetogen. *Appl. Environ. Microbiol.* 79, 1102–1109. doi: 10.1128/AEM.02891-12

Lee, J. C., Kim, J. H., Chang, W. S., and Pak, D. (2012). Biological conversion of CO_2 to CH_4 using hydrogenotrophic methanogen in a fixed bed reactor. *J. Chem. Technol. Biotechnol.* 87, 844–847. doi: 10.1002/jctb.3787

Lee, J-S., and Lee, J-P. (2003). Review of advances in biological CO_2 mitigation technology. *Biotechnol. Bioprocess Eng.* 8:354. doi: 10.1007/BF02949279

Lee, W-K., Lim, Y-Y., Leow, A. T-C., Namasivayam, P., Ong Abdullah, J., and Ho, C-L. (2017). Biosynthesis of agar in red seaweeds: a review. *Carbohydr. Polym.* 164, 23–30. doi: 10.1016/j.carbpol.2017.01.078

Lehninger, A. L., Nelson, D. L., and Cox, M. M. (2005). *Lehninger Principles of Biochemistry.* New York, NY: W. H. Freeman.

Li, H., Opgenorth, P. H., Wernick, D. G., Rogers, S., Wu, T-Y., Higashide, W., et al. (2012). Integrated electromicrobial conversion of CO_2 to higher alcohols. *Science* 335:1596. doi: 10.1126/science.1217643

Li, J., He, J., and Huang, Y. (2017). Role of alginate in antibacterial finishing of textiles. *Int. J. Biol. Macromol.* 94, 466–473. doi: 10.1016/j.ijbiomac.2016.10.054

Li, K., An, X., Park, K. H., Khraisheh, M., and Tang, J. (2014). A critical review of CO_2 photoconversion: catalysts and reactors. *Catal. Today* 224, 3–12. doi: 10.1016/j.cattod.2013.12.006

Li, X., Angelidaki, I., and Zhang, Y. (2018). Salinity-gradient energy driven microbial electrosynthesis of value-added chemicals from CO_2 reduction. *Water Res.* 142, 396–404. doi: 10.1016/j.watres.2018.06.013

Liew, F., Martin, M. E., Tappel, R. C., Heijstra, B. D., Mihalcea, C., and Köpke, M. (2016). Gas fermentation—a flexible platform for commercial scale production of low-carbon-fuels and chemicals from waste and renewable feedstocks. *Front. Microbiol.* 7:694. doi: 10.3389/fmicb.2016.00694

Liu, M., Pang, Y., Zhang, B., De Luna, P., Voznyy, O., Xu, J., et al. (2016). Enhanced electrocatalytic CO_2 reduction via field-induced reagent concentration. *Nature* 537, 382–386. doi: 10.1038/nature19060

Ljungdahl, L., and Wood, H. G. (1965). Incorporation of C^{14} From Carbon Dioxide into Sugar Phosphates, Carboxylic Acids, and Amino Acids by Clostridium thermoaceticum. *J. Bacteriol.* 89, 1055–1064.

Logan, B. E. (2008). *Microbial Fuel Cells.* Hoboken, NJ: John Wiley and sons, Inc.

Lovley, D. R., and Nevin, K. (2018). *Microbial Production of Multi-carbon Chemicals and Fuels from Water and Carbon Dioxide Using Electric Current.* U.S. Patent, 9856449. Available online at: https://tinyurl.com/yahnawoc

Lowe, R. L., and LaLiberte, G. D. (2017). "Chapter 11 - benthic stream algae: distribution and structure," in *Methods in Stream Ecology, 3rd Edn, Vol. 1*. (Boston, MA: Academic Press), 193–221. doi: 10.1016/B978-0-12-416558-8.00011-1

Luengo, J. M., Garcia, B., Sandoval, A., Naharro, G., and Olivera, E. A. R. (2003). Bioplastics from microorganisms. *Curr. Opin. Microbiol.* 6, 251–260. doi: 10.1016/S1369-5274(03)00040-7

Maeda, K., Owada, M., Kimura, N., Omata, K., and Karube, I. (1995). CO_2 fixation from the flue gas on coal-fired thermal power plant by microalgae. *Energy Convers. Manage.* 36, 717–720. doi: 10.1016/0196-8904(95)00105-M

Mandotra, S., Kumar, P., Suseela, M., Nayaka, S., and Ramteke, P. (2016). Evaluation of fatty acid profile and biodiesel properties of microalga *Scenedesmus abundans* under the influence of phosphorus, pH and light intensities. *Bioresour. Technol.* 201, 222–229. doi: 10.1016/j.biortech.2015.11.042

Mark Ibekwe, A., Murinda, S. E., Murry, M. A., Schwartz, G., and Lundquist, T. (2017). Microbial community structures in high rate algae ponds for bioconversion of agricultural wastes from livestock industry for feed production. *Sci. Total Environ.* 580, 1185–1196. doi: 10.1016/j.scitotenv.2016.12.076

Market Study Report (2019). *Capric Acid Market Size is Expected to Exhibit 270 million USD by 2024.* Available online at: https://www.marketwatch.com/press-release/capric-acid-market-size-is-expected-to-exhibit-270-million-usd-by-2024-2019-09-05 (accessed February 15, 2020).

Markets and Markets (2019). *Succinic Acid Market worth $237.8 million by 2027.* Available online at: https://www.marketsandmarkets.com/PressReleases/succinic-acid.asp (accessed February 15, 2020).

Marshall, C. W., LaBelle, E. V., and May, H. D. (2013). Production of fuels and chemicals from waste by microbiomes. *Curr. Opin. Biotechnol.* 24, 391–397. doi: 10.1016/j.copbio.2013.03.016

Martin, M. E., Richter, H., Saha, S., and Angenent, L. T. (2016). Traits of selected *Clostridium strains* for syngas fermentation to ethanol. *Biotechnol. Bioeng.* 113, 531–539. doi: 10.1002/bit.25827

Maurya, R., Paliwal, C., Ghosh, T., Pancha, I., Chokshi, K., Mitra, M., et al. (2016). Applications of de-oiled microalgal biomass towards development of sustainable biorefinery. *Bioresour. Technol.* 214, 787–796. doi: 10.1016/j.biortech.2016.04.115

Modestra, J. A., and Mohan, S. V. (2017). Microbial electrosynthesis of carboxylic acids through CO_2 reduction with selectively enriched biocatalyst: microbial dynamics. *J. CO_2 Util.* 20, 190–199. doi: 10.1016/j.jcou.2017.05.011

Mohanakrishna, G., Abu Reesh, I. M., Vanbroekhoven, K., and Pant, D. (2020). Microbial electrosynthesis feasibility evaluation at high bicarbonate concentrations with enriched homoacetogenic biocathode. *Sci. Total Environ.* 715:137003. doi: 10.1016/j.scitotenv.2020.137003

Mohanakrishna, G., Seelam, J. S., Vanbroekhoven, K., and Pant, D. (2015). An enriched electroactive homoacetogenic biocathode for the microbial electrosynthesis of acetate through carbon dioxide reduction. *Faraday Discuss.* 183, 445–462. doi: 10.1039/C5FD00041F

Mohanakrishna, G., Vanbroekhoven, K., and Pant, D. (2016). Imperative role of applied potential and inorganic carbon source on acetate production through microbial electrosynthesis. *J. CO_2 Util.* 15(Suppl. C), 57–64. doi: 10.1016/j.jcou.2016.03.003

Mohd Yasin, N. H., Maeda, T., Hu, A., Yu, C-P., and Wood, T. K. (2015). CO_2 sequestration by methanogens in activated sludge for methane production. *Appl. Energy* 142, 426–434. doi: 10.1016/j.apenergy.2014.12.069

Moreira, D., and Pires, J. C. M. (2016). Atmospheric CO_2 capture by algae: negative carbon dioxide emission path. *Bioresour. Technol.* 215, 371–379. doi: 10.1016/j.biortech.2016.03.060

Müller, J., MacEachran, D., Burd, H., Sathitsuksanoh, N., Bi, C., Yeh, Y-C., et al. (2013). Engineering of *Ralstonia eutropha* H16 for autotrophic and heterotrophic production of methyl ketones. *Appl. Environ. Microbiol.* 79, 4433–4439. doi: 10.1128/AEM.00973-13

Murakami, M., and Ikenouchi, M. (1997). The biological CO_2 fixation and utilization project by rite (2) — screening and breeding of microalgae with high capability in fixing CO_2 —. *Energy Convers. Manage.* 38(Suppl.), S493–S497. doi: 10.1016/S0196-8904(96)00316-0

Nagarajan, S., Chou, S. K., Cao, S., Wu, C., and Zhou, Z. (2013). An updated comprehensive techno-economic analysis of algae biodiesel.

Bioresour. Technol. 145, 150–156. doi: 10.1016/j.biortech.2012.11.108

Nautiyal, P., Subramanian, K. A., and Dastidar, M. G. (2016). Adsorptive removal of dye using biochar derived from residual algae after *in-situ* transesterification: alternate use of waste of biodiesel industry. *J. Environ. Manage.* 182, 187–197. doi: 10.1016/j.jenvman.2016.07.063

Negoro, M., Shioji, N., Miyamoto, K., and Micira, Y. (1991). Growth of microalgae in high CO_2 gas and effects of SOX and NOX. *Appl. Biochem. Biotechnol.* 28, 877–886. doi: 10.1007/BF02922657

Nevin, K. P., Hensley, S. A., Franks, A. E., Summers, Z. M., Ou, J., Woodard, T. L., et al. (2011). Electrosynthesis of organic compounds from carbon dioxide is catalyzed by a diversity of acetogenic microorganisms. *Appl. Environ. Microbiol.* 77, 2882–2886. doi: 10.1128/AEM.02642-10

Nevin, K. P., Woodard, T. L., Franks, A. E., Summers, Z. M., and Lovley, D. R. (2010). Microbial electrosynthesis: feeding microbes electricity to convert carbon dioxide and water to multicarbon extracellular organic compounds. *mBio* 1:e00103-10. doi: 10.1128/mBio.00103-10

Nigam, P. S., and Singh, A. (2011). Production of liquid biofuels from renewable resources. *Prog. Energy Combust. Sci.* 37, 52–68. doi: 10.1016/j.pecs.2010.01.003

Overhage, J., Steinbüchel, A., and Priefert, H. (2002). Biotransformation of eugenol to ferulic acid by a recombinant strain of *Ralstonia eutropha* H16. *Appl. Environ. Microbiol.* 68, 4315–4321. doi: 10.1128/AEM.68.9.4315-4321.2002

Packer, M. (2009). Algal capture of carbon dioxide; biomass generation as a tool for greenhouse gas mitigation with reference to New Zealand energy strategy and policy. *Energy Policy* 37, 3428–3437. doi: 10.1016/j.enpol.2008.12.025

Patel, T. N., Park, A-H. A., and Banta, S. (2013). Periplasmic expression of carbonic anhydrase in *Escherichia coli*: a new biocatalyst for CO_2 hydration. *Biotechnol. Bioeng.* 110, 1865–1873. doi: 10.1002/bit.24863

Petersen, H. I., Rosenberg, P., and Nytoft, H. P. (2008). Oxygen groups in coals and alginite-rich kerogen revisited. *Int. J. Coal Geol.* 74, 93–113. doi: 10.1016/j.coal.2007.11.007

Pfennig, N. (1967). Photosynthetic bacteria. *Annu. Rev. Microbiol.* 21, 285–324. doi: 10.1146/annurev.mi.21.100167.001441

Puig, S., Batlle-Vilanova, R.G. P., Dolors Balaguer, M., and Colprim, J. (2015). Microbial electrosynthesis of C_2-C_4 platform chemicals from carbon dioxide. *ACS Sustain. Chem. Eng.* 6, 8485–8493.

Quintana, N., Van der Kooy, F., Van de Rhee, M. D., Voshol, G. P., and Verpoorte, R. (2011). Renewable energy from cyanobacteria: energy production optimization by metabolic pathway engineering. *Appl. Microbiol. Biotechnol.* 91, 471–490. doi: 10.1007/s00253-011-3394-0

Rabaey, K., Angenent, L., Schroder, U., and Keller, J. (2009). *Bioelectrochemical Systems.* London: IWA Publishing.

Rabaey, K., and Rozendal, R. A. (2010). Microbial electrosynthesis — revisiting the electrical route for microbial production. *Nat. Rev. Microbiol.* 8, 706–716. doi: 10.1038/nrmicro2422

Ramanan, R., Kannan, K., Deshkar, A., Yadav, R., and Chakrabarti, T. (2010). Enhanced algal CO_2 sequestration through calcite deposition by *Chlorella* sp. and *Spirulina platensis* in a mini-raceway pond. *Bioresour. Technol.* 101, 2616–2622. doi: 10.1016/j.biortech.2009.10.061

Rana, D., Kim, Y., Matsuura, T., and Arafat, H. A. (2011). Development of antifouling thin-film-composite membranes for seawater desalination. *J. Membr. Sci.* 367, 110–118. doi: 10.1016/j.memsci.2010.10.050

Rashid, N., Rehman, M. S. U., and Han, J-I. (2013). Recycling and reuse of spent microalgal biomass for sustainable biofuels. *Biochem. Eng. J.* 75, 101–107. doi: 10.1016/j.bej.2013.04.001

Reinecke, F., and Steinbüchel, A. (2009). *Ralstonia eutropha* strain H16 as model organism for PHA metabolism and for biotechnological production of technically interesting biopolymers. *J. Mol. Microbiol. Biotechnol.* 16, 91–108. doi: 10.1159/000142897

Rengasamy, K. R. R., Kulkarni, M. G., Papenfus, H. B., and Van Staden, J. (2016). Quantification of plant growth biostimulants, phloroglucinol and eckol, in four commercial seaweed liquid fertilizers and some by-products. *Algal Res.* 20, 57–60. doi: 10.1016/j.algal.2016.09.017

Richter, H., Martin, M. E., and Angenent, L. T. (2013). A two-stage continuous fermentation system for conversion of syngas into ethanol. *Energies* 6, 3987–4000. doi: 10.3390/en6083987

Sadhukhan, J., Lloyd, J. R., Scott, K., Premier, G. C., Yu, E. H., Curtis, T., et al. (2016). A critical review of integration analysis of microbial electrosynthesis (MES) systems with waste biorefineries for the production of biofuel and chemical from reuse of CO_2. *Renew. Sustain. Energy Rev.* 56, 116–132. doi: 10.1016/j.rser.2015.11.015

Sakai, N., Sakamoto, Y., Kishimoto, N., Chihara, M., and Karube, I. (1995). Chlorella strains from hot springs tolerant to high temperature and high CO_2. *Energy Convers. Manage.* 36, 693–696. doi: 10.1016/0196-8904(95)00100-R

Samarakoon, K., and Jeon, Y-J. (2012). Bio-functionalities of proteins derived from marine algae — a review. *Food Res. Int.* 48, 948–960. doi: 10.1016/j.foodres.2012.03.013

Sarkar, O., Agarwal, M., Naresh Kumar, A., and Venkata Mohan, S. (2015). Retrofitting hetrotrophically cultivated algae biomass as pyrolytic feedstock for biogas, bio-char and bio-oil production encompassing biorefinery. *Bioresour. Technol.* 178, 132–138. doi: 10.1016/j.biortech.2014.09.070

Sawitzke, J. A., Thomason, L. C., Costantino, N., Bubunenko, M., Datta, S., and Court, D. L. (2007). Recombineering: *in vivo* genetic engineering in *E. coli*, *S. enterica*, and Beyond. *Methods Enzymol.* 421, 171–199. doi: 10.1016/S0076-6879(06)21015-2

Sayre, R. (2010). Microalgae: the potential for carbon capture. *Bioscience* 60, 722–727. doi: 10.1525/bio.2010.60.9.9

Schenk, P. M., Thomas-Hall, S. R., Stephens, E., Marx, U. C., Mussgnug, J. H., Posten, C., et al. (2008). Second generation biofuels: high-efficiency microalgae for biodiesel production. *Bioenergy Res.* 1, 20–43. doi: 10.1007/s12155-008-9008-8

Scherer, P. A., Vollmer, G-R., Fakhouri, T., and Martensen, S. (2000). Development of a methanogenic process to degrade exhaustively the organic fraction of municipal "grey waste" under thermophilic and hyperthermophilic conditions. *Water Sci. Technol.* 41, 83–91. doi: 10.2166/wst.2000.0059

Schirmer, A., Rude, M. A., Li, X., Popova, E., and Del Cardayre, S. B. (2010). Microbial biosynthesis of alkanes. *Science* 329, 559–562. doi: 10.1126/science.1187936

Schlager, S., Neugebauer, H., Haberbauer, M., Hinterberger, G., and Sariciftci, N. S. (2015). Direct electrochemical addressing of immobilized alcohol dehydrogenase for the heterogeneous bioelectrocatalytic reduction of butyraldehyde to butanol. *ChemCatChem* 7, 967–971. doi: 10.1002/cctc.201402932

Scragg, A. H., Illman, A. M., Carden, A., and Shales, S. W. (2002). Growth of microalgae with increased calorific values in a tubular bioreactor. *Biomass Bioenergy* 23, 67–73. doi: 10.1016/S0961-9534(02)00028-4

Sezenna, M. L. (2011). *Proteobacteria: Phylogeny, Metabolic Diversity and Ecological Effects.* New York, NY: Nova Science.

Sharma, M., Aryal, N., Sarma, P. M., Vanbroekhoven, K., Lal, B., Benetton, X. D., et al. (2013a). Bioelectrocatalyzed reduction of acetic and butyric acids via direct electron transfer using a mixed culture of sulfate-reducers drives electrosynthesis of alcohols and acetone. *Chem. Commun.* 49, 6495–6497. doi: 10.1039/c3cc42570c

Sharma, M., Jain, P., Varanasi, J. L., Lal, B., Rodríguez, J., Lema, J. M., et al. (2013b). Enhanced performance of sulfate reducing bacteria based biocathode using stainless steel mesh on activated carbon fabric electrode. *Bioresour. Technol.* 150, 172–180. doi: 10.1016/j.biortech.2013.09.069

Shi, J., Jiang, Y., Jiang, Z., Wang, X., Wang, X., Zhang, S., et al. (2015). Enzymatic conversion of carbon dioxide. *Chem. Soc. Rev.* 44, 5981–6000. doi: 10.1039/C5CS00182J

Silva, C., Soliman, E., Cameron, G., Fabiano, L. A., Seider, W. D., Dunlop, E. H., et al. (2014). Commercial-scale biodiesel production from algae. *Ind. Eng. Chem. Res.* 53, 5311–5324. doi: 10.1021/ie403273b

Singh, A., Nigam, P. S., and Murphy, J. D. (2011). Mechanism and challenges in commercialisation of algal biofuels. *Bioresour. Technol.* 102, 26–34. doi: 10.1016/j.biortech.2010.06.057

Singh, S. P., and Singh, P. (2014). Effect of CO_2 concentration on algal growth: a review. *Renew. Sustain. Energy Rev.* 38, 172–179. doi: 10.1016/j.rser.2014.05.043

Sorokin, C., and Krauss, R. W. (1958). The effects of light intensity on the growth rates of green algae. *Plant Physiol.* 33, 109–113. doi: 10.1104/pp.33.2.109

Steinbusch, K. J. J., Hamelers, H. V. M., Schaap, J. D., Kampman, C., and Buisman, C. J. N. (2010). Bioelectrochemical ethanol production through mediated acetate reduction by mixed cultures. *Environ. Sci. Technol.* 44, 513–517. doi: 10.1021/es902371e

Strong, P. J., Kalyuzhnaya, M., Silverman, J., and Clarke, W. P. (2016). A methanotroph-based biorefinery: potential scenarios for generating multiple products from a single fermentation. *Bioresour. Technol.* 215, 314–323. doi: 10.1016/j.biortech.2016.04.099

Sung, K. D., Lee, J. S., Shin, C. S., and Park, S. C. (1999). Isolation of a new highly CO_2 tolerant fresh water microalga Chlorella SP. KR-1. *Renew. Energy* 16, 1019–1022. doi: 10.1016/S0960-1481(98)00362-0

Sydney, E. B., Sturm, W., de Carvalho, J. C., Thomaz-Soccol, V., Larroche, C., Pandey, A., et al. (2010). Potential carbon dioxide fixation by industrially important microalgae. *Bioresour. Technol.* 101, 5892–5896. doi: 10.1016/j.biortech.2010.02.088

Tahvonen, O., Von Storch, H., and Storch, J-S. (1994). Economic efficiency of CO_2 reduction programs. *Clim. Res.* 4, 127–141. doi: 10.3354/cr004127

Tamagnini, P., Axelsson, R., Lindberg, P., Oxelfelt, F., Wünschiers, R., and Lindblad, P. (2002). Hydrogenases and hydrogen metabolism of cyanobacteria. *Microbiol. Mol. Biol. Rev.* 66, 1–20. doi: 10.1128/MMBR.66.1.1-20.2002

Tanaka, K., Miyawaki, K., Yamaguchi, A., Khosravi-Darani, K., and Matsusaki, H. (2011). Cell growth and P(3HB) accumulation from CO_2 of a carbon monoxide-tolerant hydrogen-oxidizing bacterium, *Ideonella* sp. O-1. *Appl. Microbiol. Biotechnol.* 92, 1161–1169. doi: 10.1007/s00253-011-3420-2

Tang, D., Han, W., Li, P., Miao, X., and Zhong, J. (2011). CO_2 biofixation and fatty acid composition of *Scenedesmus obliquus* and *Chlorella pyrenoidosa* in response to different CO_2 levels. *Bioresour. Technol.* 102, 3071–3076. doi: 10.1016/j.biortech.2010.10.047

Tracy, B. P., Jones, S. W., Fast, A. G., Indurthi, D. C., and Papoutsakis, E. T. (2012). Clostridia: the importance of their exceptional substrate and metabolite diversity for biofuel and biorefinery applications. *Curr. Opin. Biotechnol.* 23, 364–381. doi: 10.1016/j.copbio.2011.10.008

Trivedi, J., Aila, M., Bangwal, D. P., Kaul, S., and Garg, M. O. (2015). Algae based biorefinery—how to make sense? *Renew. Sustain. Energy Rev.* 47, 295–307. doi: 10.1016/j.rser.2015.03.052

Tsuzuki, M., Ohnuma, E., Sato, N., Takaku, T., and Kawaguchi, A. (1990). Effects of CO_2 concentration during growth on fatty acid composition in microalgae. *Plant Physiol.* 93, 851–856. doi: 10.1104/pp.93.3.851

Ueki, T., Nevin, K. P., Woodard, T. L., and Lovley, D. R. (2014). Converting carbon dioxide to butyrate with an engineered strain of *Clostridium ljungdahlii. mBio* 5:e01636-14. doi: 10.1128/mBio.01636-14

Van Eerten-Jansen, M. C. A. A., Heijne, A. T., Buisman, C. J. N., and Hamelers, H. V. M. (2012). Microbial electrolysis cells for production of methane from CO_2: long-term performance and perspectives. *Int. J. Energy Res.* 36, 809–819. doi: 10.1002/er.1954

Van Eerten-Jansen, M. C. A. A., Ter Heijne, A., Grootscholten, T. I. M., Steinbusch, K. J. J., Sleutels, T. H. J. A., Hamelers, H. V. M., et al. (2013). Bioelectrochemical production of caproate and caprylate from acetate by mixed cultures. *ACS Sustain. Chem. Eng.* 1, 513–518. doi: 10.1021/sc300168z

Vassilev, I., Hernandez, P. A., Batlle-Vilanova, P., Freguia, S., Krömer, J. O., Keller, J., et al. (2018). Microbial electrosynthesis of isobutyric, butyric, caproic acids, and corresponding alcohols from carbon dioxide. *ACS Sustain. Chem. Eng.* 6, 8485–8493. doi: 10.1021/acssuschemeng.8b00739

Vassilev, I., Kracke, F., Freguia, S., Keller, J., Krömer, J. O., Ledezma, P., et al. (2019). Microbial electrosynthesis system with dual biocathode arrangement for simultaneous acetogenesis, solventogenesis and carbon chain elongation. *Chem. Commun.* 55, 4351–4354. doi: 10.1039/C9CC00208A

Vassilev, S. V., and Vassileva, C. G. (2016). Composition, properties and challenges of algae biomass for biofuel application: an overview. *Fuel* 181, 1–33. doi: 10.1016/j.fuel.2016.04.106

Venil, C. K., Zakaria, Z. A., and Ahmad, W. A. (2013). Bacterial pigments and their applications. *Process Biochem.* 48, 1065–1079. doi: 10.1016/j.procbio.2013.06.006

Venkata Mohan, S., Hemalatha, M., Chakraborty, D., Chatterjee, S., Ranadheer, P., and Kona, R. (2020). Algal biorefinery models with self-sustainable closed loop approach: trends and prospective for blue-bioeconomy. *Bioresour. Technol.* 295:122128. doi: 10.1016/j.biortech.2019.122128

Venkata Mohan, S., Modestra, J. A., Amulya, K., Butti, S. K., and Velvizhi, G. (2016). A circular bioeconomy with biobased products from CO_2 sequestration. *Trends Biotechnol.* 34, 506–519. doi: 10.1016/j.tibtech.2016.02.012

Venkata Mohan, S., Prathima Devi, M., Mohanakrishna, G., Amarnath, N., Lenin Babu, M., and Sarma, P. N. (2011). Potential of mixed microalgae to harness biodiesel from ecological water-bodies with simultaneous treatment. *Bioresour. Technol.* 102, 1109–1117. doi: 10.1016/j.biortech.2010.08.103

Vigani, M., Parisi, C., Rodríguez-Cerezo, E., Barbosa, M. J., Sijtsma, L., Ploeg, M., et al. (2015). Food and feed products from micro-algae: market opportunities and challenges for the EU. *Trends Food Sci. Technol.* 42, 81–92. doi: 10.1016/j.tifs.2014.12.004

Villano, M., Aulenta, F., Ciucci, C., Ferri, T., Giuliano, A., and Majone, M. (2010). Bioelectrochemical reduction of CO_2 to CH_4 via direct and indirect extracellular electron transfer by a hydrogenophilic methanogenic culture. *Bioresour. Technol.* 101, 3085–3090. doi: 10.1016/j.biortech.2009.12.077

Villano, M., Scardala, S., Aulenta, F., and Majone, M. (2013). Carbon and nitrogen removal and enhanced methane production in a microbial electrolysis cell. *Bioresour. Technol.* 130, 366–371. doi: 10.1016/j.biortech.2012.11.080

Voss, I., and Steinbüchel, A. (2006). Application of a KDPG-aldolase gene-dependent addiction system for enhanced production of cyanophycin in *Ralstonia eutropha* strain H16. *Metab. Eng.* 8, 66–78. doi: 10.1016/j.ymben.2005.09.003

Wang, B., Albarracín-Suazo, S., Pagán-Torres, Y., and Nikolla, E. (2017). Advances in methane conversion processes. *Catal. Today* 285, 147–158. doi: 10.1016/j.cattod.2017.01.023

Wang, B., Wang, J., Zhang, W., and Meldrum, D. R. (2012). Application of synthetic biology in cyanobacteria and algae. *Front. Microbiol.* 3:344. doi: 10.3389/fmicb.2012.00344

Wang, C., Scott Buchanan, J., Kliewer, W. R., and Qian, K. (2015). Water-washing to reduce metals in oils extracted from nannochloropsis algae for potential FCC feedstock. *Fuel* 155, 63–67. doi: 10.1016/j.fuel.2015.03.074

Wang, H-M. D., Chen, C-C., Huynh, P., and Chang, J-S. (2015). Exploring the potential of using algae in cosmetics. *Bioresour. Technol.* 184, 355–362. doi: 10.1016/j.biortech.2014.12.001

Wang, Q., Dong, H., Yu, H., and Yu, H. (2015). Enhanced performance of gas diffusion electrode for electrochemical reduction of carbon dioxide to formate by adding polytetrafluoroethylene into catalyst layer. *J. Power Sources* 279, 1–5. doi: 10.1016/j.jpowsour.2014.12.118

Wang, W-N. (2014). Comparison of CO_2 photoreduction systems: a review. *Aerosol Air Qual. Res.* 14, 533–549. doi: 10.4209/aaqr.2013.09.0283

Wargacki, A. J., Leonard, E., Win, M. N., Regitsky, D. D., Santos, C. N. S., Kim, P. B., et al. (2012). An engineered microbial platform for direct biofuel production from brown macroalgae. *Science* 335, 308–313. doi: 10.1126/science.1214547

Watanabe, Y., Ohmura, N., and Saiki, H. (1992). Isolation and determination of cultural characteristics of microalgae which functions under CO_2 enriched atmosphere. *Energy Convers. Manage.* 33, 545–552. doi: 10.1016/0196-8904(92)90054-Z

Will, F. G. (1965). Hydrogen adsorption on platinum single crystal electrodes I. Isotherms and heats of adsorption. *J. Electrochem. Soc.* 112, 451–455. doi: 10.1149/1.2423567

Willey, J. M., Sherwood, L. M., and Woolverton, C. J. (2014). *Prescott's Microbiology*. New York, NY: McGraw-Hill Education.

Xia, A., Jacob, A., Tabassum, M. R., Herrmann, C., and Murphy, J. D. (2016). Production of hydrogen, ethanol and volatile fatty acids through co-fermentation of macro- and micro-algae. *Bioresour. Technol.* 205, 118–125. doi: 10.1016/j.biortech.2016.01.025

Xin, L., Hong-Ying, H., and Yu-Ping, Z. (2011). Growth and lipid accumulation properties of a freshwater microalga *Scenedesmus* sp. under different cultivation temperature. *Bioresour. Technol.* 102, 3098–3102. doi: 10.1016/j.biortech.2010.10.055

Xu, Y., Ibrahim, I. M., and Harvey, P. J. (2016). The influence of photoperiod and light intensity on the growth and photosynthesis of *Dunaliella salina* (chlorophyta) CCAP 19/30. *Plant Physiol. Biochem.* 106, 305–315. doi: 10.1016/j.plaphy.2016.05.021

Yoo, C., Jun, S-Y., Lee, J-Y., Ahn, C-Y., and Oh, H-M. (2010). Selection of microalgae for lipid production under high levels carbon dioxide. *Bioresour. Technol.* 101(Suppl. 1), S71–S74. doi: 10.1016/j.biortech.2009.03.030

Youn, M. H., Park, K. T., Lee, Y. H., Kang, S-P., Lee, S. M., Kim, S. S., et al. (2019). Carbon dioxide sequestration process for the cement industry. *J. CO_2 Util.* 34, 325–334. doi: 10.1016/j.jcou.2019.07.023

Zakaria, Z., and Kamarudin, S. K. (2016). Direct conversion technologies of methane to methanol: an overview. *Renew. Sustain. Energy Rev.* 65, 250–261. doi: 10.1016/j.rser.2016.05.082

Zeikus, J. (1977). The biology of methanogenic bacteria. *Bacteriol. Rev.* 41, 514–541. doi: 10.1128/MMBR.41.2.514-541.1977

Zhang, L., Singh, R. D. S., Guo, Z., Li, J., Chen, F., et al. (2018). An artificial synthetic pathway for acetoin, 2,3-butanediol, and 2-butanol production from ethanol using cell free multi-enzyme catalysis. *Green Chem.* 20, 230–242. doi: 10.1039/C7GC02898A

Zhang, T., Nie, H., Bain, T. S., Lu, H., Cui, M., Snoeyenbos-West, O. L., et al. (2013). Improved cathode materials for microbial electrosynthesis. *Energy Environ. Sci.* 6, 217–224. doi: 10.1039/C2EE23350A

Zhang, Y., and Kendall, A. (2019). Consequential analysis of algal biofuels: benefits to ocean resources. *J. Clean. Prod.* 231, 35–42. doi: 10.1016/j.jclepro.2019.05.057

Zhu, L. D., Li, Z. H., and Hiltunen, E. (2016). Strategies for lipid production improvement in microalgae as a biodiesel feedstock. *Biomed. Res. Int.* 2016:8792548. doi: 10.1155/2016/8792548

Zhuang, Z-Y., and Li, S-Y. (2013). Rubisco-based engineered *Escherichia coli* for *in situ* carbon dioxide recycling. *Bioresour. Technol.* 150, 79–88. doi: 10.1016/j.biortech.2013.09.116

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REVIEW
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Reaction of CO_2 With Alcohols to Linear-, Cyclic-, and Poly-Carbonates Using CeO_2-Based Catalysts

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Reaction of CO_2 with alcohols to organic carbonates is one of non-reductive CO_2 conversion methods. The catalysts are needed for this reaction, at the same time, effective H_2O removal methods are also needed because the yield of organic carbonates is strongly limited by the equilibrium. The development of heterogeneous catalysts for the synthesis of dimethyl carbonate from CO_2 and methanol, which is a model and typical reaction, is described. This is because heterogeneous catalysts are more suitable to the practical process than homogeneous catalysts from the viewpoint of the separation of catalysts from the products and the reusability of the catalysts. One of the reported heterogeneous catalysts is CeO_2, and it has been also reported that the combination of dimethyl carbonate synthesis from CO_2 and methanol with the hydration of nitriles such as 2-cyanopyridine, where both reactions are catalyzed by CeO_2, enabled high yield of the carbonate. In addition, the combination of CeO_2 catalyst + nitriles can be applied to the synthesis of a variety of linear-, cyclic (five- and six-membered ring)-, and poly-carbonates from CO_2 and corresponding alcohols.

Keywords: carbon dioxide, ceria, alcohol, carbonate, equilibrium shift, nitrile hydration

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INTRODUCTION

Much attention has been recently paid to chemical utilization of CO_2, although the chemicals produced from CO_2 are so limited at present. Generally speaking, it is not easy to decrease the net CO_2 emission in the production of a chemical from CO_2 because of the CO_2 emission due to the separation and purification of CO_2. On the other hand, it is possible that the CO_2 emission from the CO_2-based chemical production becomes smaller than that from conventional production methods. This can be connected to the replacement of the conventional method by CO_2-based one.

Chemical utilization of CO_2 can be divided into two categories: one is reductive conversion of CO_2 and the other is non-reductive conversion of CO_2. One of typical methods for reductive conversion of CO_2 is the hydrogenation of CO_2. In most cases of the CO_2 hydrogenation, the production of renewable hydrogen is required for the decrease in the CO_2 emission and it is thought that the development of the feasible production method for hydrogen from renewable resources needs more time. In contrast, non-reductive conversion of CO_2 does not need the renewable hydrogen.

One of the non-reductive conversions of CO_2 includes the synthesis of organic carbonates, carbamates, and ureas from CO_2, and alcohols, and/or amines. The synthesis of organic carbonates, carbamates, and ureas is possible from phosgene, and alcohols, and/or amines. Much higher reactivity of phosgene than CO_2 enables no equilibrium limitation of these reactions and also connected to the non-catalytic reactions. In contrast, the synthesis of organic carbonates, carbamates, and ureas from CO_2, and alcohols, and/or amines is commonly reversible reactions and can be limited by the equilibrium. At the same time, much lower reactivity of CO_2 than phosgene requires effective catalysts. It has been reported that CeO_2-based catalysts are effective to the synthesis of organic carbonates, carbamates, and ureas from CO_2, and alcohols, and/or amines (Tamura et al., 2014; Tomishige et al., 2019, 2020). The product yield at the equilibrium is strongly influenced by the substrates such as alcohols and amines. As is known, the equilibrium limitation of the synthesis of organic carbonates from CO_2 and alcohols is usually much more serious than that of the synthesis of carbamates and ureas. Therefore, the shift of the equilibrium is very important for high product yield in the synthesis of organic carbonates from CO_2 and alcohols. Recently, it is found that the combination of the synthesis of organic carbonates from CO_2 and alcohols with the hydration of nitriles to amides is effective to the shift of the equilibrium to the product side (Honda et al., 2014a). The present review mainly mentions the synthesis of the organic carbonates such as linear-, cyclic, and poly-carbonates from CO_2, and corresponding alcohols combined with the hydration of the nitriles over CeO_2 as a heterogeneous catalyst comparing to other related catalysts, organic dehydrants, and so on. First, various synthesis routes of organic carbonates are introduced, and challenging subjects such as the low equilibrium level, and the catalyst development are mentioned. Next, we mention the method for the removal of H_2O in the synthesis of organic carbonates from CO_2 and alcohols to shift the equilibrium since the production of target organic carbonates in higher yield is important and can enhance the impact. Then, various examples of catalyst development for the reaction are shown and compared, indicating that CeO_2 can be regarded as one of promising heterogeneous catalysts in terms of the catalytic activity such as the formation rate of organic carbonates. Another superiority of CeO_2 is that the combination of the synthesis of DMC synthesis from CO_2 and methanol with the hydration of nitriles over CeO_2 enhanced the DMC yield remarkably, and the applicability of this system is also mentioned in this review.

SYNTHESIS ROUTES OF ORGANIC CARBONATES

A variety of synthesis routes of organic carbonates have been considered, and we would like to compare the routes from the thermodynamic viewpoint. This can clarify the thermodynamic difficulty level of the routes, and this is a fundamental aspect before the development of catalysts for each reaction. In this chapter, synthesis routes of organic carbonates are divided into three categories: non-CO_2-based route, indirect CO_2-based route, and direct CO_2-based route.

Table 1 lists the energy change in carbonate formation reactions and their related reactions calculated by DFT for the evaluation of the severity of the equilibrium limitation and part of calculation was carried out for this article and some calculation has been described in our previous review (Tomishige et al., 2019). We adopted the DFT calculations because it is generally difficult to collect all the thermodynamic data such as formation enthalpy and so on regarding various substrates and products. The experimental data of the heat of reaction are also shown in **Table 1** for representative entries. Although the obtained values can be different from the experimentally determined ones, the comparison of the obtained values can be suggestive. In particular, we have to be careful that all the substrate and product molecules are present in the gas phase. The negative and large energy change means that the reaction is highly exothermic and the positive and large one means that the reaction is highly endothermic. Since these values are almost the same to enthalpy change, the equilibrium is also affected by entropy change, especially when the number of molecules is changed in the reaction. Comparison between reactions with different changes in the number of molecules should be careful because the entropy term is much different between such reactions. Since the standard entropy (S^0) of liquid alcohols is about 150 J mol^{-1} K^{-1}, the difference in the number of reactant alcohol molecules by one corresponds to about 60 kJ mol^{-1} difference in free energy at 400 K.

Non-CO_2-Based Synthesis Route of Linear Organic Carbonates

Phosgene method is the most typical one for the synthesis of the linear organic carbonates from alcohols (Equation 1).

$$COCl_2 + 2ROH + 2NaOH \rightarrow (RO)_2CO + 2NaCl + 2H_2O \quad (1)$$

The problem of this method is the toxicity of phosgene and large amount of byproduct NaCl. The formation of DMC from phosgene and methanol is highly exothermic even when the product HCl is not neutralized (**Table 1**, Entry 1). This behavior is explained by the high energy state of phosgene itself, which is also connected to high reactivity of phosgene. It should be noted that the exothermicity becomes much larger considering the reaction of HCl with NaOH for the neutralization (**Table 1**, Entry 2). Totally, the high energy state and high reactivity of phosgene enables the practical production of organic carbonates by the reaction with alcohols, and this reaction can proceed without any catalysts.

Transesterification of linear organic carbonates with alcohols is applied to the synthesis of other organic carbonates, for example, DMC is the simplest linear organic carbonate and transesterification of DMC with other alcohols gives various organic carbonates (Equation 2) (Ono, 1997). High yield of the target carbonates will be obtained by large excess of DMC. This reaction has been also applied to the production of diphenyl carbonate, which can be rather endothermic due to the high energy of diphenyl carbonate (**Table 1**, Entry 7) (Ono, 1997).

$$(CH_3O)_2CO + 2R'OH \rightarrow (R'O)_2CO + 2CH_3OH \quad (2)$$

If DMC can be produced by CO_2-based routes, this route can be also categorized to indirect CO_2-based ones.

TABLE 1 | Summary of energy changes for related reactions for the synthesis of organic carbonates by DFT calculation (calculated at B3LYP/6-311++G(d,p) level theory with Gaussian 16 program package (Gaussian, Inc.) and the reference experimental data.

Entry	Name of reaction	Reaction equation	Energy changes ΔE (kJ/mol)
1	Phosgene method	$2MeOH + COCl_2 \rightarrow (MeO)_2CO + 2HCl$	−116.0
1′[a]	Phosgene method (DEC, experimental data)	$2EtOH(g) + COCl_2(g) \rightarrow (EtO)_2CO(g) + 2HCl(g)$	−135 (ΔH^0)
2[a]	HCl neutralization (experimental data)	$HCl(g) + NaOH(s) \rightarrow H_2O(g) + NaCl(s)$	−135 (ΔH^0)
3	Urea synthesis	$2NH_3 + CO_2 \rightarrow CO(NH_2)_2 + H_2O$	+10.3
4	Urea methanolysis	$CO(NH_2)_2 + 2MeOH \rightarrow (MeO)_2CO + 2NH_3$	−7.0
4′[a]	Urea ethanolysis (experimental data)	$CO(NH_2)_2(g) + 2EtOH(g) \rightarrow (EtO)_2CO(g) + 2NH_3(g)$	−26 (ΔH^0)
5	Ethylene oxide carboxylation	$C_2H_4O + CO_2 \rightarrow (C_2H_4)O_2CO$	−53.5
6	Ethylene carbonate transesterification	$(C_2H_4)O_2CO + 2MeOH \rightarrow (MeO)_2CO + HOC_2H_4OH$	−51.1
6′[a]	Ethylene carbonate transesterification (DEC, experimental data)	$(C_2H_4)O_2CO + 2EtOH \rightarrow (EtO)_2CO + HOC_2H_4OH$	−57 (ΔH^0)
7	DMC transesterification with phenol	$(MeO)_2CO + 2PhOH \rightarrow (PhO)_2CO + 2MeOH$	+65.9
8	DMC synthesis	$2MeOH + CO_2 \rightarrow (MeO)_2CO + H_2O$	+3.3
9	DME formation	$2MeOH \rightarrow CH_3OCH_3 + H_2O$	−14.8
9′[a]	Diethyl ether formation (experimental data)	$2EtOH(g) \rightarrow CH_3OCH_3(g) + H_2O(g)$	−26 (ΔH^0)
10	DEC synthesis	$2EtOH + CO_2 \rightarrow (EtO)_2CO + H_2O$	+5.4
10′[a]	DEC synthesis (experimental data)	$2EtOH(g) + CO_2(g) \rightarrow (EtO)_2CO(g) + H_2O(g)$	−18 (ΔH^0)
11	DnPrC synthesis	$2nPrOH + CO_2 \rightarrow (nPrO)_2CO + H_2O$	+5.6
12	DiPrC synthesis	$2iPrOH + CO_2 \rightarrow (iPrO)_2CO + H_2O$	+9.6
13	DPC synthesis	$2PhOH + CO_2 \rightarrow (PhO)_2CO + H_2O$	+69.2
13′[a]	DPC synthesis (experimental data)	$2PhOH(g) + CO_2(g) \rightarrow (PhO)_2CO(g) + H_2O(g)$	+33 (ΔH^0)
14	Ethylene glycol carboxylation	$HOCH_2CH_2OH + CO_2 \rightarrow (C_2H_4)O_2CO + H_2O$	+54.4
14′[a]	Ethylene glycol carboxylation (experimental data)	$HOCH_2CH_2OH(g) + CO_2(g) \rightarrow (C_2H_4)O_2CO(g) + H_2O(g)$	+39 (ΔH^0)
15	Propylene glycol carboxylation	$CH_3CHOHCH_2OH + CO_2 \rightarrow CH_3(C_2H_3)O_2CO + H_2O$	+49.2
16	(*R*, *R*)-2,3-Butanediol carboxylation	$CH_3CHOHCHOHCH_3 + CO_2 \rightarrow (C_4H_8)O_2CO + H_2O$	+41.1
17	(*R*, *S*)-2,3-Butanediol carboxylation	$CH_3CHOHCHOHCH_3 + CO_2 \rightarrow (C_4H_8)O_2CO + H_2O$	+46.2
18	1,3-Propanediol carboxylation	$HOCH_2CH_2CH_2OH + CO_2 \rightarrow (C_3H_6)O_2CO + H_2O$	+68.1
19	1,3-Butanediol carboxylation	$CH_3CHOHCH_2CH_2OH + CO_2 \rightarrow CH_3(C_3H_5)O_2CO + H_2O$	+64.6
20	(*R*, *R*)-2,4-Pentanediol carboxylation	$CH_3CHOHCH_2CHOHCH_3 + CO_2 \rightarrow (C_5H_{10})O_2CO + H_2O$	+62.5
21	(*R*, *S*)-2,4-Pentanediol carboxylation	$CH_3CHOHCH_2CHOHCH_3 + CO_2 \rightarrow (C_5H_{10})O_2CO + H_2O$	+61.4
22	1,4-Butanediol carboxylation	$HOCH_2CH_2CH_2CH_2OH + CO_2 \rightarrow (C_4H_8)O_2CO + H_2O$	+78.6
23	Ethylene carbonate ring opening (chain extension)	$(C_2H_4)O_2CO + HO[COO(CH_2)_2O]_2H \rightarrow HO[COO(CH_2)_2O]_3H$	−29.6
24	Propan-1,3-diyl carbonate ring opening (chain extension)	$(C_3H_6)O_2CO + HO[COO(CH_2)_3O]_2H \rightarrow HO[COO(CH_2)_3O]_3H$	−46.4
25	Butan-1,4-diyl carbonate ring opening (chain extension)	$(C_4H_8)O_2CO + HO[COO(CH_2)_4O]_2H \rightarrow HO[COO(CH_2)_4O]_3H$	−59.5
26	Ethylene glycol carboxylation to polycarbonate	$HOCH_2CH_2OH + CO_2 + HO[COO(CH_2)_2O]_2H \rightarrow HO[COO(CH_2)_2O]_3H + H_2O$	+24.8
27	1,3-Propanediol carboxylation to polycarbonate	$HOCH_2CH_2CH_2OH + CO_2 + HO[COO(CH_2)_3O]_2H \rightarrow HO[COO(CH_2)_3O]_3H + H_2O$	+21.7
28	1,4-Butanediol carboxylation to polycarbonate	$HOCH_2CH_2CH_2CH_2OH + CO_2 + HO[COO(CH_2)_4O]_2H \rightarrow HO[COO(CH_2)_4O]_3H + H_2O$	+19.1
29	2,2-Dimethoxypropane (DMP) hydrolysis	$CH_3C(OMe)_2CH_3 + H_2O \rightarrow CH_3COCH_3 + 2MeOH$	+14.7
30	Overall of the combination of DMC synthesis with DMP hydrolysis	$CH_3C(OMe)_2CH_3 + CO_2 \rightarrow (MeO)_2CO + CH_3COCH_3$	+18.0
31	Trimethoxymethane (TMM) hydrolysis	$HC(OMe)_3 + H_2O \rightarrow HCOOMe + 2MeOH$	−15.6
32	Overall of the combination of DMC synthesis with TMM hydrolysis	$HC(OMe)_3 + CO_2 \rightarrow (MeO)_2CO + HCOOMe$	−12.3
33	Trimethoxyethane hydrolysis	$CH_3C(OMe)_3 + H_2O \rightarrow CH_3COOMe + 2MeOH$	−41.0
34	Methyl trichloroacetate hydrolysis	$CCl_3COOMe + H_2O \rightarrow CCl_3COOH + MeOH$	+15.7
35	Methyl acetate hydrolysis	$CH_3COOMe + H_2O \rightarrow CH_3COOH + MeOH$	+9.2
36	Methyl formate hydrolysis	$HCOOMe + H_2O \rightarrow HCOOH + MeOH$	+11.8
37	1,2-Epoxybutane hydration	$C_2H_5C_2H_3O + H_2O \rightarrow C_2H_5CH(OH)CH_2OH$	−101.3

(Continued)

TABLE 1 | Continued

Entry	Name of reaction	Reaction equation	Energy changes ΔE (kJ/mol)
38	1,2-Epoxybutane+methanol	$C_2H_5C_2H_3O + CH_3OH \rightarrow C_2H_5CH(OH)CH_2OCH_3$	−114.4
39	1,2-Epoxybutane+methanol	$C_2H_5C_2H_3O + CH_3OH \rightarrow C_2H_5CH(OCH_3)CH_2OH$	−103.4
40	Styrene oxide hydration	$PhC_2H_3O + H_2O \rightarrow PhCH(OH)CH_2OH$	−98.8
41	Styrene oxide + methanol	$PhC_2H_3O + CH_3OH \rightarrow PhCH(OH)CH_2OCH_3$	−109.1
42	Styrene oxide + methanol	$PhC_2H_3O + CH_3OH \rightarrow PhCH(OCH_3)CH_2OH$	−109.4
43	Cyclohexene oxide hydration	$C_6H_{10}O + H_2O \rightarrow$ *trans*-1,2-$C_6H_{10}(OH)_2$	−103.2
44	Cyclohexene oxide + methanol	$C_6H_{10}O + CH_3OH \rightarrow$ *trans*-1,2-$C_6H_{10}(OH)(OCH_3)$	−111.0
45	Acetonitrile hydration	$MeCN + H_2O \rightarrow MeCONH_2$	−89.2
45′[a]	Acetonitrile hydration (experimental data)	$MeCN(g) + H_2O(g) \rightarrow MeCONH_2(g)$	−71 (ΔH^0)
46	Methanol addition to acetonitrile	$CH_3CN + CH_3OH \rightarrow CH_3C(OCH_3)=NH$	−42.8
47	Benzonitrile hydration	$PhCN + H_2O \rightarrow PhCONH_2$	−89.3
48	Methanol addition to benzonitrile	$PhCN + CH_3OH \rightarrow PhC(OCH_3)=NH$	−41.0
49	2-Cyanopyridine hydration	$C_5H_4N\text{-}CN + H_2O \rightarrow C_5H_4N\text{-}CONH_2$	−123.1
50	Methanol addition to 2-cyanopyridine	$(C_5H_4N)CN + CH_3OH \rightarrow (C_5H_4N)C(OCH_3)=NH$	−65.7
51	2-Furonitrile hydration	$C_4H_3O\text{-}CN + H_2O \rightarrow C_4H_3O\text{-}CONH_2$	−111.1
52	Methanol addition to 2-furonitrile	$C_4H_3O\text{-}CN + CH_3OH \rightarrow (C_4H_3O)C(OCH_3)=NH$	−60.7
53	Acetoamide methanolysis	$CH_3CONH_2 + CH_3OH \rightarrow CH_3COOCH_3 + NH_3$	−10.1
54	Benzamide methanolysis	$PhCONH_2 + CH_3OH \rightarrow PhCOOCH_3 + NH_3$	−14.6
55	Picolinamide methanolysis	$C_5H_4N\text{-}CONH_2 + CH_3OH \rightarrow C_5H_4N\text{-}COOCH_3 + NH_3$	+18.0
56	2-Furamide methanolysis	$C_4H_3O\text{-}CONH_2 + CH_3OH \rightarrow C_4H_3O\text{-}COOCH_3 + NH_3$	+0.9

[a] *The reaction enthalpies are originated from NIST Chemistry WebBook (https://webbook.nist.gov/chemistry/).*

Indirect CO_2-Based Synthesis Route of Organic Carbonates

The most typical CO_2-based chemical in the industry is the production of urea from CO_2 and NH_3 (Equation 3).

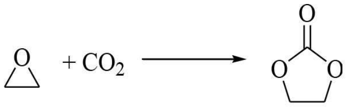
$$CO_2 + 2NH_3 \rightarrow (NH_2)_2CO + H_2O \tag{3}$$

As listed in **Table 1**, Entry 3, the reaction seems to be endothermic, however, the reaction can be exothermic if $(NH_2)_2CO$ is obtained as solid. Methanolysis of urea (**Table 1**, Entry 4) can give DMC as below (Equation 4). The overall reaction including Equations 2, 3 is regarded as indirect CO_2-based DMC synthesis.

$$2CH_3OH + (NH_2)_2CO \rightarrow (CH_3O)_2CO + 2NH_3 \tag{4}$$

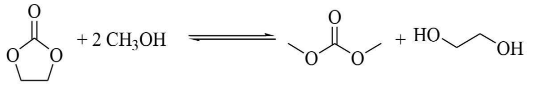
An example of the reports on alcoholysis of urea in supercritical methanol shows that 98% urea-based yield of DMC was obtained at 538 K, the molar ratio of methanol/urea of 14, and 9.2 MPa (Hou et al., 2014). Although the large excess of methanol is necessary for high DMC yield, the equilibrium of Equation 4 is not serious judging from high DMC yield. One of the merits of this process is that ammonia evolved in this synthesis route (Equation 4) can be recycled back to urea by reacting it with CO_2 (Equation 3). This method has been also applied to the synthesis of diethyl carbonate (DEC), glycerol carbonate, propylene carbonate, ethylene carbonate and so on (Shukla and Srivastava, 2017).

Another approach for the DMC synthesis is the transesterification of ethylene carbonate with methanol. Ethylene carbonate can be produced by the reaction of CO_2 with ethylene oxide (**Table 1**, Entry 5). The energy change of Equation 5 represents the exothermic reaction, which can be due to the high energy of ethylene oxide.



(5)

DMC can be synthesized by the transesterification of ethylene carbonate with methanol (Equation 6) (**Table 1**, Entry 7).



(6)

High DMC yield (93%) has been reported in Equation 6, for example, at 333 K and the molar ratio of methanol/ethylene carbonate of 16 (Liu et al., 2013). There have been a lot of reports on the transesterification of ethylene carbonate as summarized in a previous review (Santos et al., 2014). These reactions have been applied to non-phosgene route for the production of polycarbonate via diphenyl carbonate (**Table 1**, Entry 6) developed by Asahi Kasei Corporation (Fukuoka et al., 2003). The overall reaction including Equations 4, 5 is also regarded as indirect CO_2-based DMC synthesis. This process can be very effective when ethylene oxide is available and ethylene glycol can be consumed by other processes such as the production of polyethylene terephthalate.

Direct CO_2-based Synthesis Route of Linear Organic Carbonates

The direct synthesis of linear organic carbonates from CO_2 and corresponding alcohols is described in Equation 7.

$$2ROH + CO_2 \rightarrow (RO)_2CO + H_2O \tag{7}$$

It has been well-known that this reaction is strongly limited by the equilibrium. Another important point is the selectivity to organic carbonates. A possible side reaction is the formation of ethers (Equation 8).

$$2ROH \rightarrow ROR + H_2O \tag{8}$$

The energy changes of DMC synthesis from CO_2 and methanol (Entry 8) and dimethyl ether (DME) formation from methanol (Entry 9) are also listed in **Table 1**. The comparison between the energy changes of DMC synthesis and DME formation indicates that the equilibrium limitation of DMC synthesis is much more serious than that of DME and the formation of DME is more favorable than the DMC synthesis from the thermodynamic viewpoint. The formation of H_2O with DME can suppress the DMC synthesis. Therefore, very high selectivity to DMC is required in the catalytic performance.

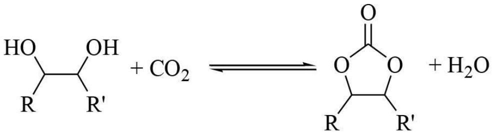
Regarding the catalysts for the DMC synthesis from CO_2 and methanol, homogeneous Sn alkoxide was firstly reported to be effective as mentioned in our previous review (Honda et al., 2014a). Regarding the heterogeneous catalysts for direct DMC synthesis from CO_2 and methanol, it has been firstly reported that ZrO_2-based oxides are effective catalysts (Tomishige et al., 1999, 2000; Ikeda et al., 2000, 2001), and then CeO_2-based oxides have been found to be effective catalysts giving almost 100% selectivity to DMC (Tomishige et al., 2001; Yoshida et al., 2006). In particular, heterogeneous CeO_2 catalysts have been utilized to the direct CO_2-based synthesis route in various organic carbonates, therefore, the experimental determination of the equilibrium level of the reaction over CeO_2 is mentioned here. The equilibrium limitation of DMC and diethyl carbonate (DEC) was investigated on CeO_2 catalyst (Yoshida et al., 2006). The amount of DMC and DEC was 0.66 and 0.41 mmol, respectively, using 0.1 g CeO_2 at 403 K under CH_3OH or C_2H_5OH: CO_2 = 200: 200 mmol, where the equilibrium yield of DMC and DEC is calculated to be as low as 0.7 and 0.4%, respectively. This tendency is also supported by the data in **Table 1**, Entries 8 and 10, and suggests that higher primary alcohols give lower equilibrium yield of corresponding organic carbonates, although the difference between methanol, and ethanol can be rather smaller than that between ethanol and *n*-propyl alcohol. The serious equilibrium limitation of the direct synthesis of organic carbonates from CO_2 and corresponding alcohols has been also supported by other reports. The thermodynamic calculation on the effect of the CO_2 pressure showed that very high pressure of CO_2 such as more than 2.41×10^4 MPa is required in order to progress the reaction spontaneously (Leino et al., 2010). Prof. Urakawa described that methanol conversion increased with the reaction pressure but it reached the level of ca. 1% at even 40 MPa without dehydrating agents (Bansode and Urakawa, 2014). These indicate that the pressurized CO_2 is not suitable to the equilibrium shift to the product side in the reaction of CO_2 with methanol to DMC.

Another important behavior is the reaction of CO_2 with secondary alcohols such as isopropanol and phenol (**Table 1**, Entries 12 and 13), suggesting higher level of difficulty in the synthesis of di-isopropyl carbonate and diphenyl carbonate. The formation of di-isopropyl carbonate using CeO_2 was unfavorable in the reaction of CO_2+aniline+2-propanol+2-cyanopyridine compared to the formation of DMC in the reaction of CO_2+aniline+methanol+2-cyanopyridine (Tamura et al., 2018a; Gu et al., 2019a). In fact, the energy change between CO_2+primary alcohols and CO_2+2-propanol is not so different, however, the reactivity of 2-propanol seems to be much lower than that of primary alcohols over CeO_2 catalyst, which may not be controlled by thermodynamics but by kinetics. Further investigation is necessary for low reactivity of secondary monoalcohol such as 2-propanol over CeO_2 catalyst.

Direct CO_2-Based Synthesis Route of Cyclic- and Poly-Carbonates

Cyclic carbonates and polycarbonates can be synthesized by the reaction of urea with diols, the transesterification of DMC with diols, and so on, which are similar reactions as described above and can be categorized to indirect CO_2-based synthesis route of cyclic carbonates. In this section, direct synthesis of cyclic carbonates and polycarbonates from CO_2 and corresponding diols.

Five membered ring carbonates can be synthesized by the reaction of CO_2 and 1,2-diols such as ethylene glycol, propylene glycol and so on (Equation 9, **Table 1**, Entries 14-17).

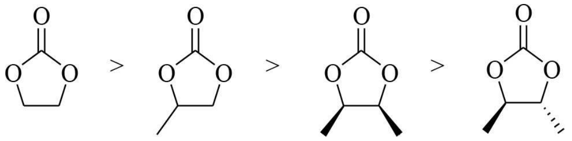


(9)

The selective formation of ethylene carbonate and propylene carbonate from CO_2 and corresponding diols catalyzed by CeO_2-based catalysts has been demonstrated (Tomishige et al., 2004a,b). An example of the equilibrium level of the synthesis of propylene carbonate from propylene glycol has been reported to be around 2% propylene glycol-based yield of propylene carbonate at 403 K and propylene glycol: CO_2: CH_3CN (solvent) = 100: 200: 120 mmol using CeO_2-ZrO_2 (Ce/(Ce+Zr)) = 0.33) catalyst (Tomishige et al., 2004a,b), which seems to be similar to or a little higher equilibrium level of DMC synthesis from

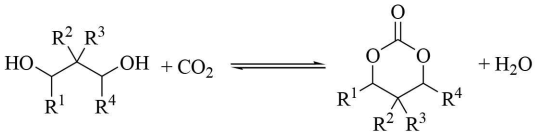
CO_2 and methanol. The level of difficulty in the synthesis of propylene carbonate may be comparable to that in the synthesis of DMC. The energy change of the synthesis of propylene carbonate is clearly higher than that of the synthesis of DMC. The inconsistency of the level of difficulty obtained from experimental results and the calculated energy changes may be explained by the difference in the number of molecules. In the case of DMC synthesis, the number of molecules is decreased from three as reactants to two as products, in contrast, in the case of propylene carbonate synthesis, the number of molecules is not changed during the reaction (two as reactants and two as products).

Therefore, it is not suitable to compare the energy change in the dialkyl carbonate synthesis (**Table 1**, Entries 8, 10–13) and the five membered ring carbonate synthesis (**Table 1**, Entries 14–17), on the other hand, the energy changes of five membered ring carbonate synthesis from CO_2 and 1,2-diols can be compared in **Table 1**, Entries 14–17. The order of the energy change is as follows.



The comparison suggests that methyl group binding with five membered ring carbonate structure can decrease the energy change, probably by the electron donating properties of methyl group. The difference in the energy change of the carbonate from (*R*, *R*)-2,3-butanediol and (*R*, *S*)-2,3-butanediol can be explained by conformation of the two neighboring methyl groups.

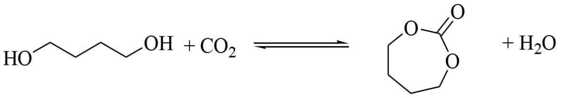
Six membered ring carbonates can be synthesized by the reaction of CO_2 and 1,3-diols such as 1,3-propanediol, 1,3-butanediol, and 2,4-pentanediol (**Table 1**, Entries 18–21) (Equation 10).



(10)

The energy change of the synthesis of six membered ring carbonates is clearly positive and larger than that that of the synthesis of five membered ring carbonates (**Table 1**, Entries 14–17). This can be interpreted by the difference in the stability of the ring structure. This tendency can also be related to high reactivity of six membered ring carbonates, for example, in the ring-opening polymerization (Honda and Abe, 2018; Tamura et al., 2018b). High reactivity in the ring-opening polymerization makes the synthesis of the reaction of CO_2 and 1,3-diols more difficult. The energy change of the carbonate from (*R*, *R*)-2,4-pentanediol and (*R*, *S*)-2,4-pentanediol is relatively small (**Table 1**, Entries 20, 21), which can be explained by the longer distance between the two methyl groups. Without dehydrating agents, six membered ring carbonate synthesis is very difficult, however, it has been reported that six membered ring carbonates can be synthesized from 1,3-diols using CeO_2 and 2-cyanopyridine as mentioned below (Honda et al., 2014b).

The energy change of seven membered ring carbonate formation from CO_2 and 1,4-butanediol (Equation 11) is clearly positive and higher than that of five or six membered ring carbonates from CO_2 and corresponding diols, which can be due to much lower stability of seven membered ring carbonates (**Table 1**, Entry 22).



(11)

The energy change of ring opening polymerization of five, six and seven membered ring carbonates is estimated by the reaction of the cyclic carbonates and its dimer, and the obtained results are also listed in **Table 1**. The values of the energy change are negative, and the order of the absolute values is as follows: five<six<seven. This tendency can be explained by the stability of the ring structure and it also corresponds to the reactivity of cyclic carbonates. The energy change of ring opening polymerization of five-, six-, and seven-membered ring carbonates are also listed in **Table 1**, Entries 23–25. The energy change is negative and larger and the order is five<six<seven, and this order can be connected to the order of the reactivity in the ring opening polymerization.

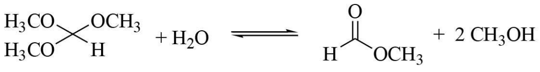
The energy change of the direct synthesis of polycarbonates from CO_2 and α,ω-diols (**Table 1**, Entries 26–28) can be calculated from that of the carboxylation of the diol (**Table 1**, Entries 14, 18, 22) and the ring-opening polymerization of the ring carbonate (**Table 1**, Entries 23, 24, 25), and the results are also listed in **Table 1**. The copolymerization of CO_2 and 1,4-butanediol is more preferable to that of CO_2 and 1,3-propanediol or ethylene glycol, although the equilibrium level of the formation of polycarbonate is so serious and the removal of H_2O is necessary for high yield of the polycarbonate.

REMOVAL OF H_2O IN THE SYNTHESIS OF CARBONATES FROM CO_2 AND ALCOHOLS

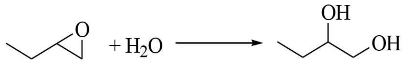
One of the common problems in the reaction of CO_2 and alcohols is the very low equilibrium yield of the target organic carbonates. The problem of the low yield of organic carbonates at the equilibrium cannot be solved by the catalyst development. Instead, the approach for the equilibrium shift to the product side is required, and one of the possible methods to shift the equilibrium is the removal of H_2O, one of which is the utilization of organic dehydrants. As mentioned above, very low equilibrium yield of the carbonates means very low H_2O concentration in the reactor. Therefore, the organic dehydrant can react with low concentration of H_2O selectively under the reaction conditions like the presence of large amount of alcohol substrates. There have been various reports on the carbonate synthesis from CO_2 and alcohols using organic dehydrants, for example, 2,2-dimethoxypropane (DMP) (Tomishige and Kunimori, 2002; Choi et al., 2008), 1,1,1-trimethoxymethane (TMM) (Zhang et al., 2011), butylene oxide (Leino et al., 2011, 2013), nitriles (Honda et al., 2009, 2010, 2011a, 2013, 2014c), and so on.

The reaction equations of organic dehydrants such as DMP (Equation 12), TMM (Equation 13), Butylene oxide (Equation 14), nitriles (Equation 15) are shown below.

(12)



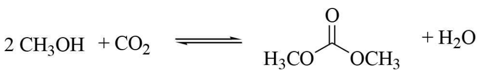
(13)



(14)

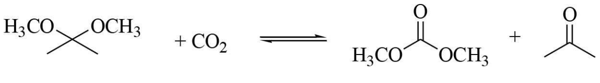
$$RCN + H_2O \rightarrow RCONH_2 \tag{15}$$

One of advantages of DMP and TMM in the synthesis of DMC from CO_2 and methanol is that methanol is the hydration product. At the same time, this can be disadvantage in the synthesis of organic carbonates from CO_2 and other alcohols than methanol. This is because it is not easy to get the acetal of acetone or methyl formate containing the corresponding alcohols. The energy change of DMP is positive (**Table 1**, Entry 29) and that of TMM is negative (**Table 1**, Entry 31), and this suggests that TMM can be a stronger dehydrant than DMP. The addition of DMP to the DMC synthesis from CO_2 and methanol clearly enhanced the yield of DMC above the equilibrium level in the reaction of CO_2+methanol, however, the yield of DMC is limited again to the equilibrium level in the reaction of CO_2+methanol+DMP (Equations 16–18). In particular, in the reaction of CO_2+methanol+DMP, the overall reaction (Equation 18) is the sum of the DMC synthesis from CO_2 and methanol (Equation 16) and the hydration of DMP (Equation 17). Methanol is not consumed or formed in the overall reaction (DMP+CO_2 to DMC and acetone; Equation 18), which is also reversible and limited by the equilibrium (**Table 1**, Entry 30) (Tomishige and Kunimori, 2002).



(16)

(17)

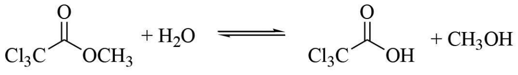


(18)

The overall reaction of the combination of DMC synthesis and TMM hydrolysis is similar to the case of DMP. An important point is that the hydrolysis of TMM is more thermodynamically favorable than that of DMP (**Table 1**, Entries 30 and 32). The yield of DMC using TMM can be clearly higher than that using DMP. The effect of TMM addition to the synthesis of DMC from CO_2 and methanol over $Ce_{0.5}Zr_{0.5}O_2$ has been reported (Zhang et al., 2011). Another possible dehydrant is 1,1,1-trimethoxyethane, where the hydrolysis of 1,1,1-trimethoxyethane gives methyl acetate and methanol (**Table 1**, Entry 33). 1,1,1-Trimethoxyethane can be a stronger dehydrant than TMM in terms of the energy change of the hydrolysis.

In the utilization of DMP, TMM, and 1,1,1-trimethoxyethane, acetone, methyl formate, and methyl acetate, which are produced from the hydrolysis, had better be regenerated to corresponding acetals. However, the regeneration to acetals with methanol is the reverse reaction of the hydrolysis acetals. This means that the stronger dehydrants can be more difficult to be regenerated. The energy balance between the hydrolysis and the acetalization can be important for the system construction including DMC synthesis and the regeneration of the dehydrants.

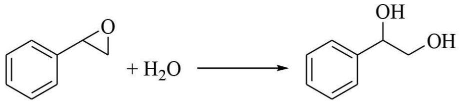
Recently, ester has been attempted to be used as a dehydrant, although the example is a little limited. The combination of DMC synthesis from CO_2 and methanol with the hydrolysis of methyl trichloroacetate has been reported (Marciniak et al., 2019). The reaction formula of the hydrolysis of methyl trichloroacetate is shown below and the energy change of this reaction is also listed in **Table 1**, Entry 34.



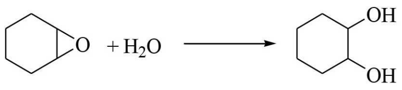
(19)

For the reference, the energy change of the hydrolysis of methyl acetate and methyl formate is also listed in **Table 1**, Entries 35 and 36. Judging from the energy change, it seems that methyl acetate or methyl formate can be more suitable dehydrants than methyl trichloroacetate. When the esters are used as a dehydrant, the produced carboxylic acids can decrease the catalytic activity of CeO_2 because of the interaction between the carboxylic group and CeO_2 is rather strong. It seems that it is not easy to obtain high alcohol-based carbonate yield because the amount of produced acids is very large at high methanol conversion.

Epoxides such as 1,2-epoxybutane (butylene oxide), styrene oxide (Equation 20) and cyclohexene oxide (Equation 21) have been used as a dehydrant in DMC synthesis from CO_2 and methanol or ethanol (Leino et al., 2011, 2013, 2018; Tamboli et al., 2018), and hydration of epoxides above are shown below and the energy change is listed in **Table 1**, Entries 37, 40, 43. In the case of epoxides, the selective reaction of epoxides with H_2O is not easy. In the combination of DMC synthesis with hydration of epoxides, the reaction of epoxides with methanol can proceed in a parallel way. Therefore, the energy change of epoxides with methanol is also listed in **Table 1** (Entries 38, 39, 41, 42, 44). The difference in the energy change of the reaction of epoxides with H_2O and methanol can be important because this can be connected to the selectivity of the H_2O removal. However, the difference in the energy change is rather small, suggesting that the reaction of epoxides with methanol can proceed more preferably than the reaction of epoxide with H_2O, in particular, considering much higher concentration of methanol than that of H_2O in the combination of DMC synthesis from CO_2 and methanol with hydration of epoxides. Therefore, the selectivity of the H_2O removal is not so high, as a result, the yield of DMC is not so high and larger amount of epoxides than the stoichiometry of H_2O removal is required.

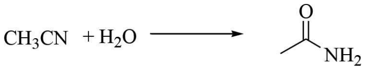


(20)

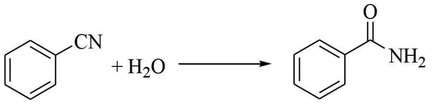


(21)

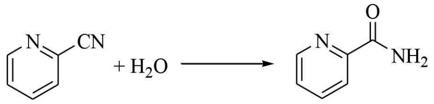
Nitriles such as acetonitrile (Equation 22), benzonitrile (Equation 23), 2-cyanopyridine (Equation 24), and 2-furonitrile (Equation 25) have been used as a dehydrant in DMC synthesis from CO_2 and methanol (Honda et al., 2009, 2010, 2011a, 2014c), and the reaction formulae of nitrile hydration are shown below.



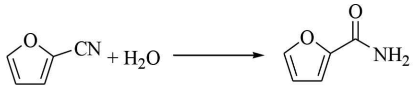
(22)



(23)



(24)



(25)

In the combination of DMC synthesis with hydration of nitriles, the reaction of nitriles with methanol may proceed in a parallel way. Here, the energy change of nitriles with H_2O and methanol is listed in **Table 1**, Entries 45–52. The difference in the energy change of the reaction of nitrile with H_2O and methanol is clearly larger than the case of the reaction of epoxides. This supports that the reaction of nitriles with H_2O can proceed more preferably than the reaction of nitriles with methanol. The difference between epoxides and nitriles can be explained by the stabilization with keto–enol tautomerism after H_2O addition to nitriles to give corresponding amides. In fact, the product in the reaction of nitriles with methanol was not detected in the combination of DMC synthesis from CO_2 and methanol with hydration of nitriles. Therefore, the selectivity of the H_2O removal can be very high, therefore, the yield of DMC is high and the stoichiometric amount of nitrile can be enough for H_2O removal.

Another side reaction in the combination of DMC from CO_2 and methanol with the hydration of nitriles is methanolysis of amides ($R\text{-}CONH_2 + CH_3OH \rightarrow RCOOCH_3 + NH_3$). The energy change of the methanolysis of picolinamide is positive and that of acetamide and benzamide is negative (**Table 1**, Entries 53–55). This means that the loss of picolinamide by the methanolysis can be suppressed. In particular, if NH_3 is formed by the methanolysis of amides, NH_3 can react with DMC to give methyl carbamate causing the decrease of the DMC yield.

HETEROGENEOUS CATALYSTS FOR THE SYNTHESIS OF ORGANIC CARBONATES FROM CO_2 AND ALCOHOLS

A variety of effective catalysts have been reported for the synthesis of organic carbonates from CO_2 and alcohols, mainly DMC from CO_2 and methanol. The catalysts can be divided into two categories: homogeneous and heterogeneous catalysts. Typical homogeneous catalysts are Sn alkoxides, Zn acetate, ionic liquids, inorganic, or organic base, and so on, which have been introduced in previous reviews (Honda et al., 2014a; Huang et al., 2015; Chaemchuen et al., 2019). The present review is focusing on the recent progress on heterogeneous catalysts. The most typical heterogeneous catalysts are CeO_2-based materials, which have been mentioned in the very recent review (Tomishige et al., 2020). Therefore, the recent progress on the development of heterogeneous catalysts except for CeO_2-based ones is focused in this review article, and the heterogeneous catalysts are divided into three categories: oxide catalysts, supported metal catalysts, and other catalysts including metal-organic framework (MOF). In addition, the recent reports on the catalyst development are summarized in **Table 2**.

Oxide Catalysts

The development of oxide catalysts for the synthesis of DMC from CO_2 and methanol probably started with the reports on the finding ZrO_2 as an effective heterogeneous catalyst (Tomishige et al., 1999, 2000). It has been also reported that the modification of ZrO_2 with H_3PO_4 enhanced the catalytic activity (Ikeda et al., 2000, 2001). Next, CeO_2-ZrO_2 solid solution catalysts were tested as a derivative of ZrO_2-based materials, and they showed clearly higher catalytic activity than ZrO_2 (Tomishige et al., 2001; Tomishige and Kunimori, 2002). At this time, we also tested pure CeO_2 as one of the reference catalysts of CeO_2-ZrO_2 solid solution and recognized that CeO_2 itself exhibited high catalytic activity in the DMC synthesis from CO_2 and methanol as a heterogeneous catalyst (Yoshida et al., 2006). The catalytic activity per surface area of this pure CeO_2 was almost comparable to that of CeO_2-ZrO_2. Based on these results, we have studied the application of pure CeO_2 for the synthesis of organic carbonates, carbamates, and ureas from CO_2 with alcohols, and/or amines (Honda et al., 2011b; Tamura et al., 2013a,b, 2016a, 2018a; Gu et al., 2019a).

Table 2 lists the catalytic performance of heterogeneous catalysts for the organic carbonate synthesis from CO_2 and alcohols. The results of our reports on ZrO_2- and CeO_2-based catalysts are also listed (**Table 2**, Entries 1–4), which can be regarding as a kind of standards in the organic carbonate synthesis from CO_2 and alcohols. As mentioned above, the reaction of CO_2 with alcohols to the corresponding organic

TABLE 2 | Summary of dialkyl carbonate synthesis systems from ROH and CO_2 using heterogeneous catalysts.

Entry	Catalyst	Catalyst surface area [m^2 g^{-1}]	Catalyst amount [*g*]	*R*	Amount of ROH [mmol], (flow rate [mmol h^{-1}])	CO_2 pressure or amount	Dehydrating agent (amount [mmol])	Temp. [*K*]	Time [*h*]	Carbonate amount [mmol] ([mmol h^{-1}])	Equilibrium limit of carbonate formation [mmol]	Carbonate formation rate [mmol g_{cat}^{-1} h^{-1}]	References
1	ZrO_2	100	0.5	Me	192	200 mmol		423	2	0.1	0.4	0.1	Tomishige et al., 1999, 2000
2	H_3PO_4/ZrO_2 (P/Zr = 0.05)	220	0.5	Me	192	200 mmol		383	2	0.5	0.7	0.12	Ikeda et al., 2000, 2001
3a	CeO_2-ZrO_2 (Ce/(Ce+Zr) = 0.2)	20	0.5	Me	192	200 mmol		383	2	0.7	0.78	0.7	Tomishige et al., 2001; Tomishige and Kunimori, 2002
3b	CeO_2-ZrO_2 (Ce/(Ce+Zr) = 0.2)	20	0.1	Et	200	200 mmol		383	2	0.1	0.4	0.5	Tomishige et al., 2001; Tomishige and Kunimori, 2002
3c	CeO_2-ZrO_2 (Ce/(Ce+Zr) = 0.2)	20	0.5	Me	192	200 mmol	DMP (30)	383	4	1.2	7	0.6	Tomishige and Kunimori, 2002
4a	CeO_2	80	0.01	Me	192	200 mmol		403	2	0.22	0.7	11	Yoshida et al., 2006
4b	CeO_2	80	0.17	Me	200	0.5 MPa	CH_3CN (600)	423	2	2	100^a	5.9	Honda et al., 2009, 2010
4c	CeO_2	80	0.17	Me	100	0.5 MPa	PhCN (300)	423	2	4.7	50^a	14	Honda et al., 2011a
4d	CeO_2	80	0.01	Me	200	5 MPa		393	0-2	0.0-0.046	0.7	2.3	Honda et al., 2014c
4e	CeO_2	80	0.01	Me	200	5 MPa	2PyCN (10)	393	0-2	0.5-2.0	$10+0.7^b$	75	Honda et al., 2014c
4f	CeO_2	80	0.17	Me	200	5 MPa	2PyCN (100)	393	2	61	100^a	180	Honda et al., 2013
5a	ZrO_2, 3A molecular sieve	54, 677	0.5, 0.1	Et	340	7 MPa	Molecular sieve 3A	423	2	0.36	n.r.	0.36	Zhang et al., 2014
5b	ZrO_2	54	0.5	Et	340	7 MPa		423	2	0.15	n.r.	0.15	Zhang et al., 2014
6a	$Fe_{0.7}Zr_{0.3}O_y$	87	1.0	Me	375	5 MPa		383	4	0.44	n.r.	0.11	Li et al., 2017
6b	ZrO_2	20	1.0	Me	375	5 MPa		383	4	0.12	n.r.	0.03	Li et al., 2017

(Continued)

TABLE 2 | Continued

Entry	Catalyst	Catalyst surface area [m^2 g^{-1}]	Catalyst amount [*g*]	*R*	Amount of ROH [mmol], (flow rate [mmol h^{-1}])	CO_2 pressure or amount	Dehydrating agent (amount [mmol])	Temp. [*K*]	Time [*h*]	Carbonate amount [mmol] ([mmol h^{-1}])	Equilibrium limit of carbonate formation [mmol]	Carbonate formation rate [mmol g_{cat}^{-1} h^{-1}]	References
6c	Fe_2O_3	5	1.0	Me	375	5 MPa		383	4	0.04	n.r.	0.01	Li et al., 2017
7	ZrO_2	168	0.05	Me	150	4.8 MPa		433	5	0.16	0.3	0.6	Akune et al., 2018
8	Y_2O_3	14	1.0	Me	625	8 MPa		363	6	1.0	n.r.	0.17	Sun et al., 2020
9	Hydrotalcite (Mg:Al:P=22:7:3)	85	0.25	Me	0.52 mmol h^{-1}	0.1 MPa		423	-	0.005 mmol h^{-1}	n.r.	0.02	Ghorbel et al., 2015
10a	Graphene oxide immobilized Cu phthalocyanine tetrasulphonamide (GO-CuPcS, Cu 2.4 wt%)	22	0.2	Me	150	2.5 MPa	DCC (*N*, *N*'-dicyclohexylcarbodiimide) (The amount was not shown.)	383	2.5	10	(DCC amount was not shown.)	20	Kumar et al., 2014
10b	GO-CuPcS Cu 2.4 wt%	22	0.2	Me	150	2.5 MPa		383	2.5	4.1	n.r.	8.2	Kumar et al., 2014
11	Cu-Ni/ZIF8 (total 5 wt%, Cu:Ni = 1:1)	272	0.5	Me	450	2.0 MPa		383	4	4.4	n.r.	2.2	Poungsombate et al., 2017
12a	V doped Cu-Ni/AC (30 wt%Cu, 14 wt%Ni, 11 wt%V, Cu:Ni:V = 2:1:1)	292	1–1.5	Me	74	5.0 MPa		443	Flow	3.0	n.r.	3.0 (if the catalyst amount is 1 g)	Chiang et al., 2019
12b	Cu-Ni/AC (33 wt%Cu, 15 wt%Ni, Cu:Ni = 2:1)	507	1-1.5	Me	74	5.0 MPa		443	Flow	2.3	n.r.	2.3 (if the catalyst amount is 1 g)	Chiang et al., 2019
13	Cu-Ni/AC (Cu:Ni = 2:1, 15 wt% (NiO+CuO)	692	0.5	Me	1.3	1.3 MPa		363	Flow		n.r.	0.03 (Calculated from the TOF value)	Arbeláez-Pérez et al., 2020
14	SnO_2 (Zn, Cu, K)/Al_2O_3 (14.5 mol% SnO_2, 1.2 mol% $CuCl_2$, 1.2 mol% $ZnCl_2$, 6 mol% KF)	150 (γ-Al_2O_3)	0.25 g (0.3 mmol Sn)	Me	7.4	1.6 MPa		403	4	0.66	n.r.	0.66	Greish et al., 2016
15	Graphene oxide immobilized $Cs_2Mo_6Br_{14}$ (Mo: 0.15 mmol g-cat^{-1}, 1.4 wt%)	130	0.5	Me	120	2.5 MPa		383	3.5	6.0	n.r.	3.4	Kumar et al., 2015
16	Titanium-based zeolitic thiophene-benzimidazolate framework (Ti-ZTBF)	811	0.15	Me	120	0.2 MPa		373	?	9.6	n.r.	?	Verma et al., 2017

(Continued)

TABLE 2 | Continued

Entry	Catalyst	Catalyst surface area [m^2 g^{-1}]	Catalyst amount [*g*]	*R*	Amount of ROH [mmol], (flow rate [mmol h^{-1}])	CO_2 pressure or amount	Dehydrating agent (amount [mmol])	Temp. [*K*]	Time [*h*]	Carbonate amount [mmol] ([mmol h^{-1}])	Equilibrium limit of carbonate formation [mmol]	Carbonate formation rate [mmol g_{cat}^{-1} h^{-1}]	References
17	Trifluoroacetic acid (TFA) modulated metal-organic frameworks UiO-66: $[Zr_6O_4(OH)_4](BDC)_{4.0}(CF_3COO)_{1.7}$	1480	0.5	Me	200	200 mmol		393	1	0.084	n.r.	0.17	Xuan et al., 2018
18a	MOF-808-4 ($[Zr_6O_4(OH)_4]$ $(BTC)_{1.5}$ $(HCOO)_{3.5}$)	1370	0.5	Me	200	12 MPa		413	4	0.12	n.r.	0.06	Xuan et al., 2019
18b	MOF-808-4 ($[Zr_6O_4(OH)_4]$ $(BTC)_{1.5}$ $(HCOO)_{3.5}$)	1370	0.5	Me	200	12 MPa	TMM (1,1,1-trimethoxymethane) (100)	413	4	3.3	100	1.6	Xuan et al., 2019
18c	MOF-808-4 ($[Zr_6O_4(OH)_4]$ $(BTC)_{1.5}$ $(HCOO)_{3.5}$)	1370	0.5	Me	200	12 MPa	TMM (1,1,1-trimethoxymethane) (100)	413	48	21.5	100	0.9	Xuan et al., 2019
18d	MOF-808-4 ($[Zr_6O_4(OH)_4]$ $(BTC)_{1.5}$ $(HCOO)_{3.5}$)	1370	0.5	Me	200	12 MPa	2-PyCN (100?)	413	48	34.3	100?	1.4	Xuan et al., 2019

2PyCN, 2-cyanopyridine; DMP, 2,2-dimethoxypropane; TMM, 1,1,1-trimethoxymethane; BO, 1,2-epoxybutane; n.r., not reported.

[a] Quantitative formation from alcohol is assumed because stoichiometric or excess amount of strong dehydrating agent was used. [b] Dehydrating agent is assumed to work quantitatively, and additional formation of the same amount to the case without dehydrating agent is assumed.

carbonates is limited by the equilibrium, therefore, one of the important factors regarding the catalytic performance is the catalytic activity, for example, per gram catalyst. Based on this policy, we selected the data, which can be far from the equilibrium level, from each report if possible. At the same time, we also list the BET surface area of the catalysts. In **Table 2**, the formation rates of the carbonates are described and this enables the estimation of the catalytic activity per surface area, which is a crucial index for the catalyst design of metal oxides.

Other ZrO_2-based catalysts have been studied (**Table 2**, Entries 5–7) and the activity seems to be comparable to that in previous reports (Zhang et al., 2014; Li et al., 2017; Akune et al., 2018). It has been recently reported that Y_2O_3 was an effective catalyst for the DMC synthesis from CO_2 and methanol (**Table 2**, Entry 8), and it is characteristic that Y_2O_3 has some activity at lower reaction temperature (363 K) than usual (for example, 383–423 K) (Sun et al., 2020). Unfortunately, the formation rate of DMC is not determined on Y_2O_3 precisely, and the formation rate can be clearly higher than the estimated value. however, considering the low BET surface area, Y_2O_3 may have high potential. The further development of Y_2O_3 may be promising and it is important to make clear the difference between Y_2O_3 and CeO_2 catalysts. It has been also reported that DMC synthesis is catalyzed by phosphoric acid intercalated Mg-Al hydrotalcite-like compounds (Ghorbel et al., 2015), although the catalytic activity is not so high (**Table 2**, Entry 9).

Supported Metal Catalysts

The most typical supported metal catalysts for DMC synthesis are Cu-Ni bimetallic catalysts, and related catalysts have been reported to show the activity in the synthesis of DMC from CO_2 and methanol. It has been reported that copper phthalocyanine tetrasulphonamide (Cu-PcS) showed catalytic activity as a homogeneous catalyst in the DMC synthesis from CO_2 and methanol with high selectivity. The Cu-PcS complex was immobilized on graphene oxide (GO Cu-PcS) and this was demonstrated to be a heterogeneous and recyclable catalyst for the selective synthesis of DMC from CO_2 and methanol, in particular, in the presence of *N*, *N*'-dicyclohexylcarbodiimide (DCC). The catalytic activity per g-cat of this heterogeneous catalyst is rather high (**Table 2**, Entry 10) (Kumar et al., 2014). Unfortunately, the amount of DCC is not shown, therefore, the highest yield of DMC in the presence of DCC cannot be calculated. It should be noted that the activity of heterogeneous GO Cu-PcS was comparable to that of homogeneous Cu-PcS.

ZIF-8 supported Cu-Ni catalyst showed the activity in the DMC synthesis from CO_2 and methanol (**Table 2**, Entry 11) (Poungsombate et al., 2017). The reported methanol conversion is relatively high (12.8%), which may be higher than the equilibrium level of methanol conversion. ZIF-8 may have a role on the H_2O removal and the shift of the equilibrium. V doped Cu-Ni/AC (30 wt% Cu, 14 wt% Ni, 11 wt% V, Cu:Ni:V = 2:1:1) was investigated in DMC synthesis from CO_2 and methanol (**Table 2**, Entry 12) (Chiang et al., 2019). From the results of the reaction time profiles, it seems that the catalyst system has some induction period, although the reduction pretreatment was carried out before the reaction. The formation rate of DMC on V doped Cu-Ni/AC is rather high, and the effect of V is remarkable. However, the role of each catalyst component (Cu, Ni, V) is not clarified. Cu-Ni/AC (Cu:Ni = 2:1, 15 wt% (CuO+NiO) showed much higher activity than monometallic Cu/AC and Ni/AC catalysts in the DMC synthesis from CO_2 and methanol, suggesting the strong synergy between Cu and Ni species (**Table 2**, Entry 13) (Arbeláez-Pérez et al., 2020). The activity is rather low due to the low reaction temperature (363 K). It is suggested that the Cu^0/NiO_x interface may be the catalytically active species. The selectivity of DMC formation is about 80%, and the byproducts were dimethyl ether and CO. It has been reported that SnO_2 (Zn, Cu, K)/Al_2O_3 (14.5 mol% SnO_2, 1.2 mol% $CuCl_2$, 1.2 mol% $ZnCl_2$, 6 mol% KF) catalyst gave high yield of DMC (17.8%) in high selectivity (about 99%) (**Table 2**, Entry 14) (Greish et al., 2016). This yield of DMC seems to be higher than the equilibrium level. The reaction time profiles of DMC on this catalyst is complicated: 3.2, 12.7, and 17.8% at 1, 2, and 4 h, respectively. At the initial stage, the activation of the catalyst may be necessary. Another important point is that the substrate to catalyst ratio is rather low (0.3 ml methanol to 0.25 g-catalyst), and high yield of DMC may be due to this low ratio. It has been reported that graphene oxide immobilized $Cs_2Mo_6Br_{14}$ (Mo: 0.15 mmol g-cat^{-1}, 1.4 wt%) exhibited rather high catalytic activity in the DMC synthesis from CO_2 and methanol and the catalyst reusability was also demonstrated (**Table 2**, Entry 15) (Kumar et al., 2015). The yield of DMC seems to be higher than the equilibrium level, and the GO may have a role on the H_2O removal and the shift of the equilibrium. An interesting point is the utilization of Mo species as a catalytically active species for the DMC synthesis. It is very important to elucidate the reaction mechanism of DMC formation on Mo species, which will be able to expand the active elements for the DMC synthesis.

Other Catalysts Including Metal-Organic Framework (MOF)

Titanium-based zeolitic thiophene-benzimidazolate framework (Ti-ZTBF) derived from Ti(IV) isobutoxide and 2-(thophen-2-yl)-1-((thiophen-2-yl)methyl)-1*H*-benzo[*d*]imidazole is an effective and recyclable heterogeneous catalyst for the DMC synthesis from CO_2 and methanol (**Table 2**, Entry 16) (Verma et al., 2017). The 16% yield of DMC seems to be higher than the equilibrium, and ZTBT may have a role of H_2O removal from the reaction system. Unfortunately, the activity cannot be calculated because of the lack of the reaction time.

UiO-66 is a class of Zr-based MOFs typically constructed with Zr_6 cluster and terephthalic acid (BDC) linker, and a series of trifluoroacetic acid (TFA) modulated metal-organic frameworks UiO-66 catalysts were synthesized and applied to the DMC synthesis from CO_2 and methanol (**Table 2**, Entry 17) (Xuan et al., 2018). This MOF has the catalytic activity of DMC formation, however, the activity is not high. The reusability of the catalyst was verified.

A series of metal-organic frameworks MOF-808-X (6-connected) were synthesized by regulating the $ZrOCl_2 \cdot 8H_2O$/1,3,5-benzenetricarboxylic acid (BTC) molar ratio (X) and they were applied to DMC synthesis from CO_2 and CH_3OH with 1,1,1-trimethoxymethane (TMM) or 2-cyanopyridine as a dehydrating agent (**Table 2**, Entry 17) (Xuan et al., 2019). It was reported that MOF-808-4 ($[Zr_6O_4(OH)_4]$ $(BTC)_{1.5}$ $(HCOO)_{3.5}$) was an effective and recyclable heterogeneous catalyst, and the combination of the hydration of TMM and 2-cyanopyridine increased the DMC yield remarkably. The formation rate of DMC on this MOF is not so high as that on CeO_2 in the presence of 2-cyanopyridine.

The comparison in **Table 2** indicates that CeO_2 showed higher catalytic activity (carbonate formation rate / mmol g-cat^{-1} h^{-1}) in the DMC synthesis from CO_2 and methanol without the addition of dehydrating agents than other catalysts (**Table 2**, Entry 4a) and that CeO_2 showed higher catalytic activity in the reaction in the presence of dehydrating agents than other catalysts (**Table 2**, Entry 4f). In addition, the reports on the applicability of heterogeneous catalysts except for CeO_2 catalysts to the direct CO_2-based synthesis routes of organic carbonates except for DMC are so limited. Based on the superiority of CeO_2 from the viewpoint of high formation rate and the broad scope, we focused on CeO_2 in this review.

Unique Properties of CeO_2 as a Heterogeneous Catalyst

As mentioned above, CeO_2 is one of effective catalysts in the DMC synthesis from CO_2 and methanol, and at the same time, broad applicability of CeO_2 catalysts to the synthesis of other linear-, cyclic-, poly-carbonates have been reported than that of other catalysts. Here, we would like to mention the reasons for this uniqueness of CeO_2. The formation of DMC and H_2O from CO_2 and methanol is thought to be acid-base-catalyzed reaction. When strongly acidic catalysts are used for the reaction of CO_2 and methanol, the main product can be DME. It is clear that strongly acidic catalysts are not suitable to DMC synthesis from CO_2 and methanol. Strongly basic catalysts such as MgO are not suitable to the DMC synthesis, which can be explained by the poisoning by CO_2. It is characteristic that CeO_2 has medium acidic and medium basic bifunctional properties. It has been known that ZrO_2 has similar acidic and basic bifunctional properties in the field of heterogeneous catalysis, although the oxides with acid-base bifunctionality are so limited. The basicity of CeO_2 is stronger than that of ZrO_2, and the acidity of CeO_2 is weaker than that of ZrO_2 (Tomishige et al., 2004a). These acid-base bifunctionality can be explained by rather large ionic radius and high oxidation state (+4). In particular, cerium is unique in the lanthanoid elements from the viewpoint of the stability of Ce^{4+}. As is known, cations with +3 of lanthanoid tends to be more stable, in contrast, Ce^{4+} is more stable than the 4+ cations of other lanthanoids. Higher oxidation state can be connected to higher Lewis acidity. As a result, CeO_2 can have medium acidic and medium basic bifunctional properties. Modification of CeO_2 with the additive such as Nb^{5+} and Al^{3+} has been also attempted for the improvement of the catalytic performance of CeO_2 (Aresta et al., 2010; Dibenedetto et al., 2012).

The most important properties of CeO_2 as a catalytic function is redox properties between Ce^{4+} and Ce^{3+}. In most cases, CeO_2 works as a redox catalyst at clearly higher temperature than that for the organic carbonate synthesis. In the case of DMC synthesis from CO_2 and methanol, methanol is not oxidized with CeO_2 at all, although benzyl alcohol can be oxidized with CeO_2 at similar reaction temperature range (Tamura and Tomishige, 2015). The formation of Ce^{3+} is connected to the oxide ion defect on CeO_2 surface, it has been reported that the oxide ion defects can have some function in the synthesis of DMC from methanol and CO_2, however, which cannot be demonstrated clearly. If only the oxide ion defect can be the catalytically active site for DMC synthesis from CO_2 and methanol, the catalytic activity is strongly dependent on the number of the oxide ion defect. Generally, the activity of CeO_2 with more oxide ion defect may be a little higher compared to that of CeO_2 with less oxide ion defect. This kind of behaviors suggests that the main active site on the CeO_2 surface, although the oxide ion defect may have higher activity. At present, the structure of catalytically active site and the reaction mechanism are under debated. Further investigation by means of *in-situ* spectroscopic studies and theoretical approach is necessary. Various CeO_2-based materials in the direct CO_2-based synthesis routes of organic carbonates from corresponding alcohols have been compared in the recent review (Tomishige et al., 2020).

HYDRATION OF NITRILES: SUITABLE TO H_2O REMOVAL IN DMC SYNTHESIS FROM CO_2 AND METHANOL OVER CERIA

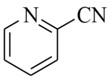
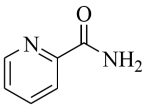
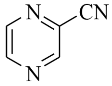
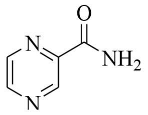
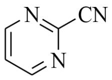
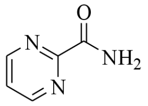
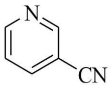
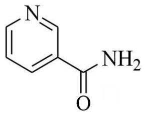
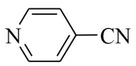
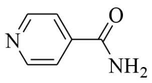
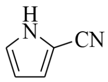
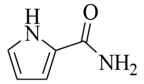
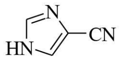
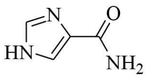
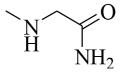
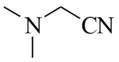
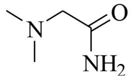
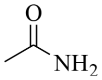
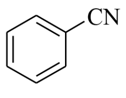
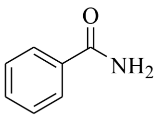
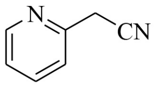
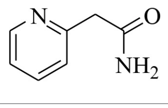
Development of heterogeneous catalysts for the reaction of CO_2 with alcohols has been carried out mainly using DMC or DEC synthesis from CO_2 and methanol or ethanol. The previous chapter shows that CeO_2 is one of promising heterogeneous catalysts. In the above chapter of removal of H_2O in the synthesis of carbonates from CO_2 and alcohols, various reactions for H_2O removal are listed. Among them, nitrile hydration is also catalyzed by CeO_2 and it can be combined with DMC synthesis from CO_2 and methanol. It has been found that the combination of DMC synthesis from CO_2 and methanol with the hydration of nitriles, in particular, 2-cyanopyridine drastically shifted the equilibrium of the DMC formation (**Table 2**, Entry 4f, Honda et al., 2013). The effect of the nitrile addition from the viewpoint of H_2O removal was strongly dependent on the type of nitriles. **Table 3** lists the DMC synthesis from CO_2 and methanol over CeO_2 catalyst in the presence of various nitriles, and the energy change of hydration of nitriles, the addition of methanol to nitriles, and the methanolysis of amides are also listed in **Table 3** (Honda et al., 2014c). Energy changes of the hydration of nitriles are more negative than that of methanol addition to nitriles in the case of all the nitriles. This indicates that the hydration of nitriles proceeds more preferably than methanol addition to nitriles in all the cases. It seems that the combination of DMC synthesis from CO_2 and methanol with nitrile hydration can be effective to the equilibrium shift of DMC synthesis from the thermodynamic viewpoint. Energy change of the methanolysis is strongly dependent on the amides in the range of positive values to negative ones. From the viewpoint of the regeneration of nitriles by the dehydration of amides, the methanolysis of amides, which is regarded as a side reaction to esters and NH_3, should be suppressed. Therefore, positive and larger energy change of the methanolysis of amides is better. It should be noted that three nitriles, 2-cyanopyridine, cyanopyradine, and 2-cyano-1,3-pyrimidine, promoted the formation of DMC remarkably (**Table 3**, Entries 1-3). The effect of other nitriles than these three nitriles on the formation rate of DMC is not so significant. The energy change of hydration of nitriles is not so different, which cannot explain the reactivity tendency. The explanation is as follows. These three nitriles have cyano group at the 2nd position of pyridine ring as a common structure. The investigation of the interaction between 2-cyanopyridine (**Table 3**, Entry 1) and CeO_2 surface suggests that the nitrogen on the pyridine ring is coordinated to surface Ce^{4+} and the lattice oxide ion is coordinated to C atom in cyano group, resulting in the strongly basic nitrogen species in cyano group as illustrated in **Figure 1A** (Tamura et al., 2015, 2017). It is interpreted that this strongly basic species can activate alcohols to enhance the catalytic activity in the presence of 2-cyanopyridine on CeO_2.

On the other hand, it has been also reported that the hydration of acetonitrile and benzonitrile (Entries 10, 11) can shift the equilibrium of DMC synthesis from CO_2 and methanol, although the formation rate of DMC was not promoted so significantly (**Table 3**, Entries 10,11) (Honda et al., 2010, 2011a). In addition, it has been recently reported that CeO_2 + 2-furonitrile was effective for the direct synthesis of alternating polycarbonates from CO_2 and α,ω-diols (Gu et al., 2019b). The comparison between 2-cyanopyridine and 2-furonitrile in the DMC synthesis from CO_2 and methanol over CeO_2 is listed in **Table 4** (Gu et al., unpublished data). The addition of 2-furonitrile also enhanced the yield of DMC with high selectivity, which was comparable to the case of 2-cyanopyridine, although the formation rate of DMC in the presence of 2-cyanopyridine is clearly higher than that in the presence of 2-furonitrile as listed in **Table 3**, Entries 1 and 13. According to the DFT calculations, the adsorption of 2-cyanopyridine on CeO_2 (111) surface is stronger than that of 2-furonitrile (**Figure 1B**), which can be connected to higher formation rate of DMC in the presence of 2-cyanopyridine. Another possible demerit of 2-furonitrile is the methanolysis of the amide, which is related to lower energy change of methanolysis of 2-furamide than that of picolinamide. However, the methanolysis of 2-furamide was suppressed sufficiently.

SYNTHESIS OF VARIOUS ORGANIC CARBONATES FROM CO_2 AND CORRESPONDING ALCOHOLS BY USING CEO_2 AND HYDRATION OF NITRILES

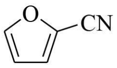
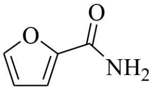
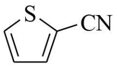
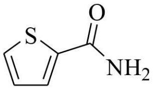
Various kinds of organic carbonates like cyclic- and poly-carbonates are recognized as value-added chemicals. The above chapters show that DMC can be synthesized from CO_2 and methanol in high yield beyond the equilibrium level by the combination with the hydration of nitriles, in other words, the finding of CeO_2 as the effective catalyst and nitriles as the effective dehydrating agent enables the direct synthesis of DMC from CO_2 and methanol in high yield. As introduced

TABLE 3 | DMC synthesis from CO_2 and methanol over CeO_2 with various nitriles (Honda et al., 2014c).

Entry	Nitrile	Amide	Amount of DMC / mmol	Amount of reacted nitrile/ mmol	Amount of amide/ mmol	Energy change of hydration of nitrile / kJ mol^{-1}	Energy change of addition of methanol to nitrile / kJ mol^{-1}	Energy change of methanolysis of amide / kJ mol^{-1}
1			1.4	1.6	1.5	−123.1	−65.3	+18.0
2			3.2	3.6	0.4	−123.5	−68.8	+13.5
3			1.8	2.5	0.2	−111.9	−62.7	+15.5
4			0.04	1.1	1.0	−90.9	−45.8	−16.9
5			0.04	1.0	0.9	−94.9	−48.2	−13.0
6			0.05	0.9	0.03	−108.0	−52.9	−9.1
7			0.00	0.2	0.0	−116.5	−60.7	−1.5
8			0.00	0.6	0.0	−111.1	−58.4	+1.0
9			0.03	1.0	0.0	−108.9	−56.5	+8.3
10	CH_3CN		0.03	0.3	0.0	−89.2	−42.8	−10.1
11			0.03	0.1	0.0	−89.3	−41.0	−14.6
12			0.00	0.0	0.0	−104.9	−47.2	+8.3

(Continued)

TABLE 3 | Continued

Entry	Nitrile	Amide	Amount of DMC / mmol	Amount of reacted nitrile/ mmol	Amount of amide/ mmol	Energy change of hydration of nitrile / kJ mol^{-1}	Energy change of addition of methanol to nitrile / kJ mol^{-1}	Energy change of methanolysis of amide / kJ mol^{-1}
13			0.03	0.5	0.1	−111.1	−60.7	+0.9
14			0.01	0.2	0.0	−94.2	−45.5	−14.6
15	None	-	0.02	-	-	-	-	-

Reaction conditions: CeO_2 0.01 g, CH_3OH: nitrile, 200 mmol: 10 mmol, CO_2 5 MPa, 393 K, 1 h.

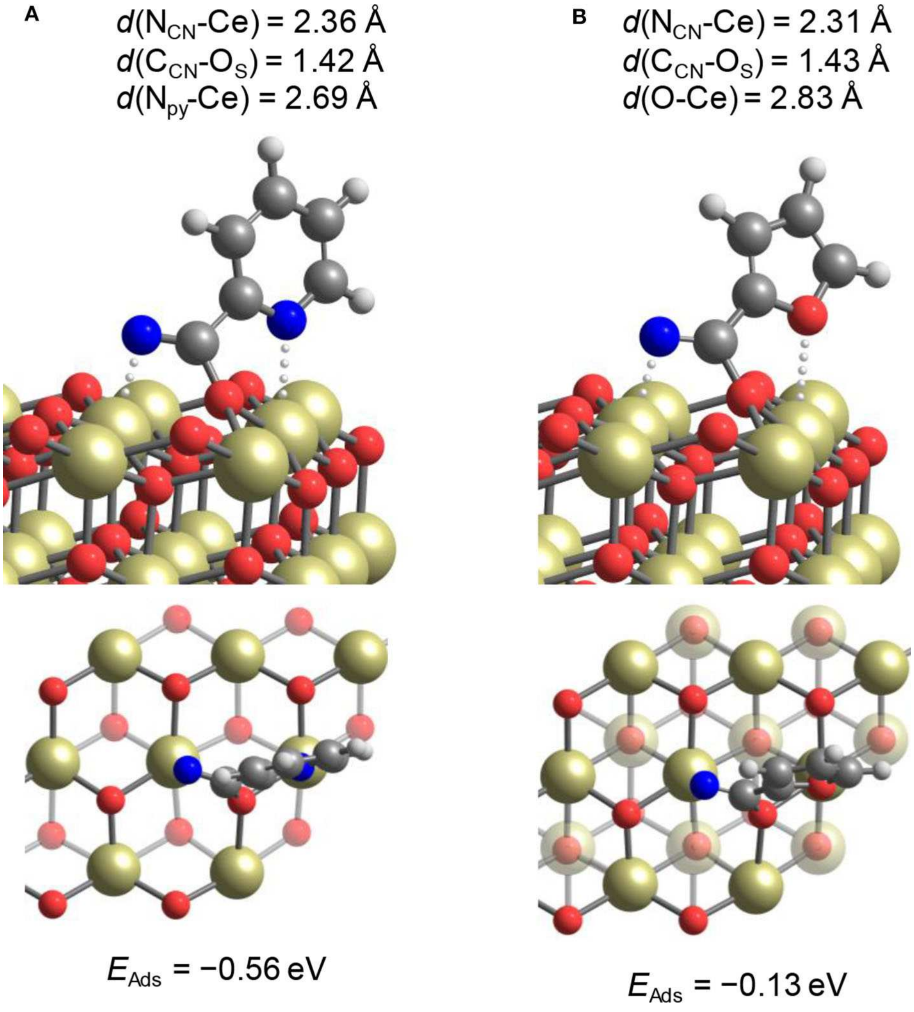
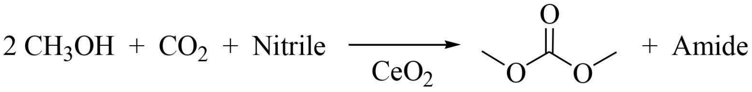
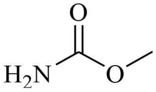
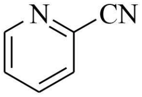
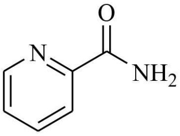
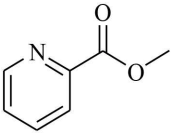
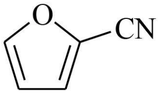
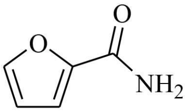
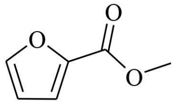


FIGURE 1 | Adsorption structures of **(A)** 2-cyanopyridine and **(B)** 2-furonitrile on the $CeO_2(111)$ surface (Gu et al., 2019b). (Reprint with permission by American Chemical Society). The atoms are color coded as follows: gray, H; dark gray, C; blue, N; red O; dark yellow, Ce.

TABLE 4 | Comparison between 2-cyanopyridine and 2-furonitrile in DMC synthesis from CO_2 and methanol on CeO_2 (Gu et al., unpublished data).



Nitrile	Amount of DMC/ mmol	Amount of methyl carbamate/ mmol 	Amount of amide / mmol	Amount of ester / mmol
	19.2	1.0	 21.0	 1.2
	18.5	0.17	 20.2	 0.22

Reaction conditions: CeO_2 0.34 g, CH_3OH: nitrile, 50 mmol: 25 mmol, CO_2 5 MPa, 393 K, 24 h.

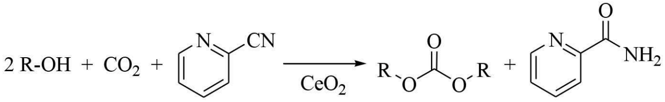
above, various kinds of catalysts and dehydrating methods have been developed, however, the methods whose broad applicability has been demonstrated are so limited. Therefore, in this chapter, the applicability of the method using CeO_2 catalyst and nitrile hydration to the direct synthesis of linear-, cyclic-, and poly-carbonates from CO_2 and corresponding alcohols is mentioned.

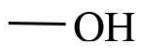
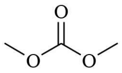
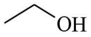
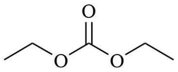
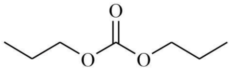
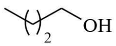
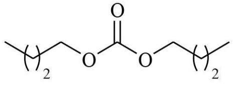
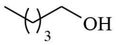
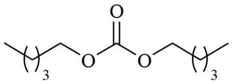
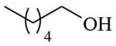
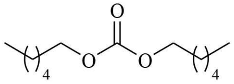
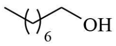
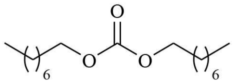
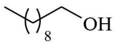
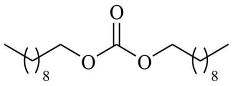
Table 5 lists the synthesis of linear carbonates from CO_2 and corresponding monoalcohols using CeO_2 and 2-cyanopyridine. Various linear primary alcohols can be converted to corresponding dialkyl carbonates in high yield (around 90%) and the stoichiometric amount of picolinamide was detected (Entries 1–8) (Honda et al., 2014c).

The synthesis of linear carbonates from unsaturated alcohols was also possible to some extent (**Table 5**, Entries 9, 10). The yield of the carbonates from branched primary alcohol (**Table 5**, Entries 11, 13), benzyl alcohol (**Table 5**, Entry 12), and secondary alcohol (**Table 5**, Entry 14) is not so high. Energy change of the carbonate formation calculated by DFT is also listed in **Table 5**. The energy change is not so dependent on the alcohols and its absolute values are clearly smaller than that of hydration of 2-cyanopyridine. Therefore, the difficulty of the reaction is not controlled by the thermodynamics, and CeO_2 does not seem to be good at converting the alcohols with large steric hindrance. Low reactivity of secondary alcohol such as 2-propanol (**Table 5**, Entry 14) is utilized to the carbamate synthesis from aniline, CO_2, and 2-propanol using CeO_2 + 2-cyanopyridine (Gu et al., 2019a). Here, it is very important to suppress the carbonate formation of alcohols, which can be connected to excess consumption of alcohols and 2-cyanopyridine. Actually, the carbamate synthesis from aniline, CO_2, and methanol gave a large amount of DMC and excess picolinamide (Tamura et al., 2018a).

Table 6 lists the synthesis of cyclic carbonates from CO_2 and corresponding diols using CeO_2 and 2-cyanopyridine (Honda et al., 2014b). 1,2-Diols (**Table 6**, Entries 1–6) gave the corresponding five-membered ring carbonates in high yield. 1,2-Cyclopentanediol and 1,4-anhydroerythirtiol showed rather different reactivity, however, the corresponding five-membered ring carbonates were obtained in high yield (Entries 7, 8). The yield of the six-membered ring carbonates from CO_2 and 1,3-diols (**Table 6**, Entries 9–12) tends to be clearly lower than the case of the synthesis of five-membered ring carbonates. For example, in the case of 1,3-propanediol (**Table 6**, Entry 9), the formation of cooligomers of CO_2 and 1,3-propanediol was detected and this can explain the difference between the amount of the reacted 1,3-propanediol and that of the six-membered ring carbonate (Tomishige et al., 2019). The six-member ring carbonates in the case of Entries 13 and 14 (**Table 6**) were obtained in high yield, probably because of the suppression of the formation of cooligomers of CO_2 and the diols. In this study, the synthesis of glycerol carbonate from CO_2 and glycerol using CeO_2 and 2-cyanopyridine was attempted, however, our yield of glycerol carbonate under similar reaction conditions was much lower than the case of other five- and six-membered ring carbonates as listed in **Table 6**, therefore, the result was not reported and we thought that the synthesis of glycerol carbonate is not so easy. On the other hand, this problem was solved to some extent. In the following study after our report, high yield (78.9%) of glycerol carbonate was reported using large amount of CeO_2 (1.72 g, Ce 10 mmol) and dimethyl formamide as a solvent as summarized in **Scheme 1** (Liu et al., 2016). In **Table 6**, the amount of substrates is clearly higher than that of CeO_2 catalyst, meaning the formation of the carbonates proceeds catalytically. On the other hand, in the synthesis of glycerol carbonate, large amount of CeO_2 is very crucial for high yield. The amount of

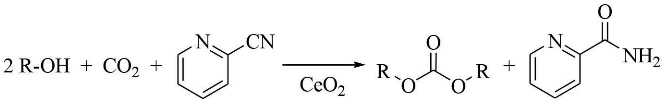
TABLE 5 | Synthesis of linear carbonates from CO_2 and corresponding monoalcohols using CeO_2 and 2-cyanopyridine (Honda et al., 2014c).

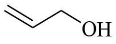
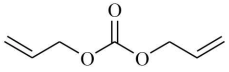
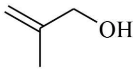
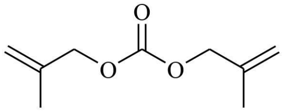
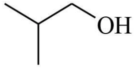
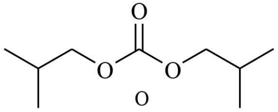
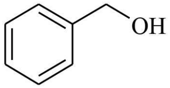
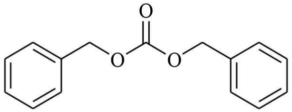
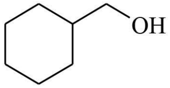
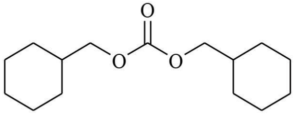
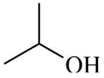
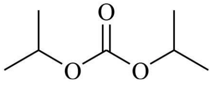


Entry	Alcohol	Carbonate	Temp. / K	Time / h	Amount of reacted alcohol / mmol	Amount of carbonate / mmol	Amount of reacted 2-cyanopyridine / mmol	Amount of picolinamide / mmol	Energy change of carbonate formation / kJ mol^{-1} ^{a}
1			393	16	19.4	9.6	11	10	3.3
2			393	24	18.6	9.1	11	10	5.4
3			393	24	18.4	9.1	10	10	5.6
4			393	24	17.4	8.7	9.7	9.5	5.6
5			383	48	17.2	8.6	9.0	8.6	5.6
6			383	48	17.0	8.5	9.7	9.4	5.6
7			393	48	17.4	8.7	9.9	9.6	5.8
8			403	24	18.2	9.0	9.7	9.0	5.8

(Continued)

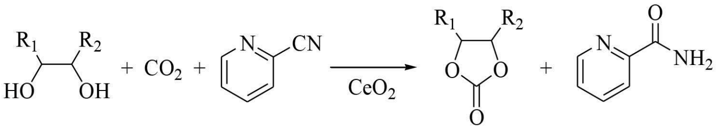
TABLE 5 | Continued

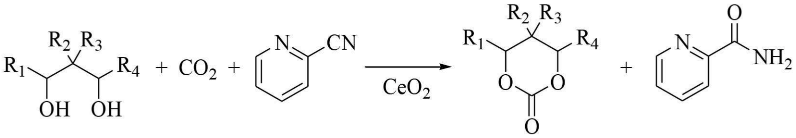


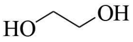
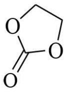
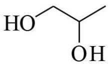
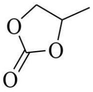
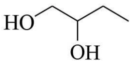
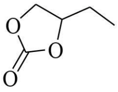
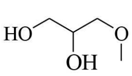
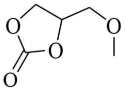
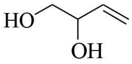
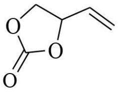
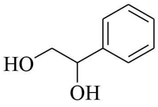
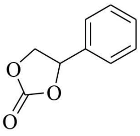
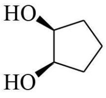
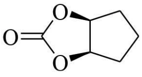
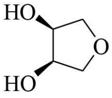
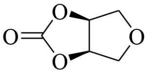
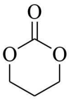
Entry	Alcohol	Carbonate	Temp. / K	Time / h	Amount of reacted alcohol / mmol	Amount of carbonate / mmol	Amount of reacted 2-cyanopyridine / mmol	Amount of picolinamide / mmol	Energy change of carbonate formation / kJ mol^{-1} [a]
9			393	48	15.2	7.6	9.5	9.4	7.4
10			393	24	10.2	5.1	6.3	6.3	6.9
11			393	48	13.2	6.0	7.8	7.0	5.9
12			403	48	17.8	7.4	8.5	8.0	8.3
13			423	48	13.6	4.9	14	6.5	4.8
14			403	48	7.6	3.3	5.2	4.4	9.6

Reaction conditions: CeO_2 0.34 g, Alcohol: 2-Cyanopyridine, 20 mmol: 100 mmol, CO_2 5 MPa.
[a] *DFT: B3LYP/6-311++G(d,p).*

TABLE 6 | Synthesis of cyclic carbonates from CO_2 and corresponding diols using CeO_2 and 2-cyanopyridine (Honda et al., 2014b).

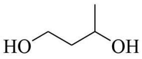
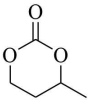
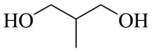
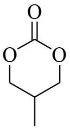
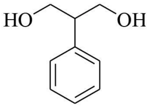
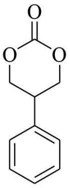
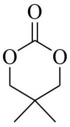
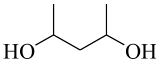
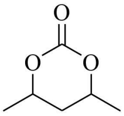




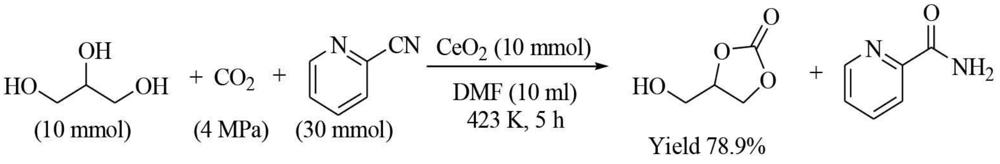
Entry	Diol	Carbonate	Temp. / K	Time/ h	Amount of reacted diol /mmol	Amount of carbonate/ mmol	Amount of reacted 2-cyanopyridine / mmol	Amount of picolinamide / mmol
1			403	1	10	10	10	10
2			413	1	10	9.9	11	10
3			413	1	10	10	12	11
4			423	2	10	9.7	11	11
5			433	1	7.2	6.7	10	8.3
6			453	48	9.6	9.5	12	10
7			403	1	10	10	11	11
8			443	8	10	10	11	10
9[a]			413	1	8.6	5.8	15	10

(Continued)

TABLE 6 | Continued

Entry	Diol	Carbonate	Temp. / K	Time/ h	Amount of reacted diol /mmol	Amount of carbonate/ mmol	Amount of reacted 2-cyanopyridine / mmol	Amount of picolinamide / mmol
10			413	1	10	8.4	13	11
11			433	1	9.5	7.3	11	10
12			443	2	6.7	6.2	7	7.1
13			423	2	9.6	9.5	11	10
14			443	8	9.7	9.7	11	10

Reaction conditions: CeO_2 0.34 g, diol/2-cyanopyridine, 10 mmol/100 mmol, CO_2 5 MPa.
[a] 2-cyanopyridine 200 mmol.

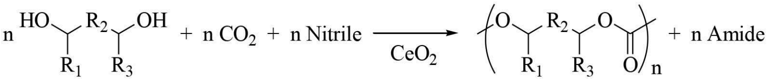


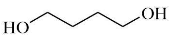
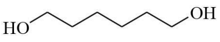
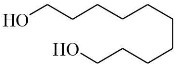
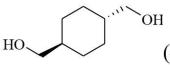
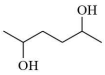
SCHEME 1 | Glycerol carbonate synthesis from CO_2 and glycerol using CeO_2 and 2-cyanopyridine (Liu et al., 2016).

glycerol carbonate was comparable to the amount of CeO_2, and this reaction may proceed non-catalytically, suggesting that CeO_2 can be deactivated rapidly. The reason for the necessity of large amount of CeO_2 should be elucidated for further development of the glycerol carbonate synthesis.

The system of CeO_2 + nitriles has been also applied to the direct copolymerization of CO_2 and diols. It has been recently demonstrated that the copolymerization of CO_2 and diols using CeO_2 catalyst and 2-cyanopyridine promotor, providing the alternating cooligomers in high diol-based yield (up to 99%) and selectivity (up to >99%). This catalyst system is applicable to various diols including linear C4-C10 α,ω-diols to provide high yields of the corresponding cooligomers, which cannot be obtained by conventional methods such as copolymerization of CO_2 and cyclic ethers and ring-opening polymerization of cyclic carbonates (Tamura et al., 2016b). In addition, the reaction of CO_2 with 1,4-butanediol in the presence of 2-cyanopyridine was studied by using CeO_2 with different morphologies such as nanorods (79 m^2 g^{-1}), nanocubes (18 m^2 g^{-1}), nanoparticles (59 m^2 g^{-1}), and submicroparticles (5 m^2 g^{-1}) (Gong et al., 2020). CeO_2 nanorods catalyst was more effective than CeO_2 with other different morphologies. The catalytic performance of CeO_2 nanorods from the viewpoint of activity, selectivity, and polymerization degree was actually comparable to that in our previous report (Tamura et al., 2016b). In contrast, the effect of nitrile was more remarkable. The synthesis of alternating

TABLE 7 | Comparison between 2-cyanopyridine and 2-furonitrile in copolymerization of CO_2 and diols on CeO_2 (Gu et al., 2019b).



Entry	Diol	Nitrile	Conv. / %	Selectivity/ %			Reacted nitrile / mmol	Amount of amide / mmol	M_n^b / g mol^{-1}	M_w/M_n^b	DP^c
				Polymer	Monoester^a	Cyclic carbonate					
1a		2-Furonitrile	>99	99	1	<1	8.0	7.6	2300	1.3	20
1b		2-Cyanopyridine	>99	93	<1	7	9.6	9.0	1100	1.3	9
2a		2-Furonitrile	99	>99	<1	<1	10	7.8	2600	1.4	18
2b		2-Cyanopyridine	>99	>99	<1	<1	13	8.1	1200	1.3	9
3a		2-Furonitrile	97	99	1	<1	10	7.2	2600	1.3	13
3b		2-Cyanopyridine	96	>99	<1	<1	9.2	7.7	1800	1.2	9
4a		2-Furonitrile	90	>99	<1	<1	9.1	6.2	1700	1.3	10
4b	(48 h)	2-Cyanopyridine	42	98	2	<1	7.7	3.2	600	1.2	4
5a		2-Furonitrile	17	97	<1	3	4.4	1.4	500	1.0	3
5b		2-Cyanopyridine	15	86	<1	14	3.3	1.7	500	1.0	3

Reaction conditions: CeO_2 0.17 g, diol 10 mmol, nitrile 50 mmol, CO_2 5 MPa (at r.t.), 403 K, 24 h.

[a] *Produced from amide and diol.*

[b] *Determined by SEC using polystyrene as a standard and THF as eluent.*

[c] *Degree of polymerization.*

polycarbonates with higher molecular weight from CO_2 and diols by using the catalyst system of CeO_2 + 2-furonitrile than the case of CeO_2 + 2-cyanopyridine (Gu et al., 2019b). **Table 7** lists the comparison between 2-cyanopyridine and 2-furonitrile in the copolymerization of CO_2 and diols over CeO_2 catalyst under the similar reaction conditions. It is clear that 2-furonitrile is more effective than 2-cyanopyridine, from the viewpoint of the polymerization, although the reaction rate on CeO_2 + 2-furonitrile is clearly lower than that of CeO_2 + 2-cyanopyridine as shown above in the case of DMC synthesis. The effectiveness of 2-furonitrile is explained by two factors. First, the reactivity of 2-furamide, which is produced by the hydration of 2-furonitrile, with OH groups of polycarbonate diols leads to low selectivity of the ester-capped polycarbonates and this can increase the polymerization degree. The other is the weak adsorption of 2-furonitrile on CeO_2, decreasing the steric hindrance at the active sites of CeO_2 and enabling the reaction of longer diols, such as polycarbonate diols (Gu et al., 2019b).

SUMMARY AND OUTLOOK

The direct synthesis of organic carbonates from CO_2 and alcohols is a challenging subject, which includes two key issues: development of catalysts and H_2O removal. This article is dealing with CeO_2 catalyst and the combination with the nitrile hydration mainly. A variety of heterogeneous catalysts have been developed for the organic carbonates from CO_2 and alcohols. In these studies, methanol has been used as an alcohol and the application of each heterogeneous catalyst to wide scope of alcohols is hardly demonstrated. In contrast, it is demonstrated that CeO_2 is applicable to the carbamate synthesis from CO_2, alcohols, amines, and the urea synthesis from CO_2 and amines as well as linear-, cyclic- and polycarbonates from CO_2 and alcohols. It is recommended that the applicability and the limitation of the catalysts should be demonstrated in each study. These results can be very useful for further development of catalysts and H_2O removal methods. At present, the system of CeO_2 + nitriles has limitation in the synthesis of organic carbonates from CO_2 and alcohols: examples of reactions not achieved include the linear carbonate formation from CO_2 and secondary alcohols, the synthesis of diphenyl carbonate from CO_2 and phenol, the synthesis of seven-membered ring carbonate from CO_2 and diols, the synthesis of polycarbonate with higher molecular weight, and so on. Moreover, the dehydration of picolinamide to 2-cyanopyridine is very important from the practical viewpoint. At present, the researches on the dehydration of picolinamide is so limited, and the catalyst development is essential. It is may be possible to replace 2-cyanopyridine by other nitriles or organic dehydrating agents with easier regeneration ability. As mentioned above, 2-furonitrile is one of the candidates, however, the dehydration of 2-furamide is not investigated.

The evaluation of the catalytic performance in the organic carbonate synthesis from CO_2 and alcohols using fixed bed flow reactors is more important from the practical viewpoint. This can give the information on the catalyst deactivation profiles, which can be also connected to the further development of catalysts. This kind of studies have been conducted recently

(Stoian et al., 2017, 2018), where the visual inspection was combined with IR and Raman spectroscopic studies to identify the origin of the catalyst deactivation and establish an efficient catalyst reactivation protocol.

Process design for the synthesis of carbonates from CO_2 and alcohols and the evaluation of the process by techno-economic and CO_2 emission assessment are necessary. We feel that this kind of study on non-reductive CO_2 conversion including the synthesis of organic carbonates is increased steadily. It will be more important to develop the catalytic system on the basis of the suggestions from the studies on the process design and techno-economic analysis.

AUTHOR CONTRIBUTIONS

KT made manuscript design and wrote the paper. YG summarized the literature. YN carried out DFT calculation and made discussion in theoretical view. MT made discussion in view of materials chemistry. All authors contributed to the article and approved the submitted version.

REFERENCES

Akune, T., Morita, Y., Shirakawa, S., Katagiri, K., and Inumaru, K. (2018). ZrO_2 nanocrystals as catalyst for synthesis of dimethyl carbonate from methanol and carbon dioxide: catalytic activity and elucidation of active sites. *Langmuir* 34, 23–29. doi: 10.1021/acs.langmuir.7b01294

Arbeláez-Pérez, O. F., Domínguez-Cardozo, S., Orrego-Romero, A. F., Villa-Holguín, A. L., and Bustamante, F. (2020). Gas phase synthesis of dimethyl carbonate from CO_2 and CH_3OH over Cu-Ni/AC. A kinetic study. *Revista Facultad de Ingeniería Universidad de Antioquia*. 95, 88–99. doi: 10.17533/udea.redin.20190941

Aresta, M., Dibenedetto, A., Pastore, C., Angelini, A., Aresta, B., and Papai, I. (2010). Influence of Al_2O_3 on the performance of CeO_2 used as catalyst in the direct carboxylation of methanol to dimethyl carbonate and the elucidation of the reaction mechanism. *J. Catal.* 269, 44–52. doi: 10.1016/j.jcat.2009.10.014

Bansode, A., and Urakawa, A. (2014). Continuous DMC synthesis from CO_2 and methanol over a CeO_2 catalyst in a fixed bed reactor in the presence of a dehydrating agent. *ACS Catal.* 4, 3877–3880. doi: 10.1021/cs501221q

Chaemchuen, S., Semyonov, O. V., Dingemans, J., Xu, W., Zhuiykov, S., Khan, A., et al. (2019). Progress on catalyst development for direct synthesis of dimethyl carbonate from CO_2 and methanol. *Chem. Africa* 2, 533–549. doi: 10.1007/s42250-019-00082-x

Chiang, C.-L., Lin, K.-S., and Yu, S.-H. (2019). Improvement of dimethyl carbonate formation via methanol carbonation over vanadium-doped Cu–Ni/AC catalyst. *J. Taiwan Inst. Chem. Eng.* 98, 132–149. doi: 10.1016/j.jtice.2018.08.001

Choi, J. C., Kohno, K., Ohshima, Y., Yasuda, H., and Sakakura, T. (2008). Tin- or titanium-catalyzed dimethyl carbonate synthesis from carbon dioxide and methanol: large promotion by a small amount of triflate salts. *Catal. Commun.* 9, 1630–1633. doi: 10.1016/j.catcom.2008.01.013

Dibenedetto, A., Aresta, M., Angelini, A., Ethiraj, J., and Aresta, B. M. (2012). Synthesis, characterization, and use of Nb^V/Ce^{IV}-mixed oxides in the direct carboxylation of ethanol by using pervaporation membranes for water removal. *Chem. Eur. J.* 18, 10324–10334. doi: 10.1002/chem.201201561

Fukuoka, S., Kawamura, M., Komiya, K., Tojo, M., Hachiya, H., Hasegawa, K., et al. (2003). A novel non-phosgene polycarbonate production process using by-product CO_2 as starting material. *Green Chem*. 5, 497–507. doi: 10.1039/B304963A

Ghorbel, S. B., Medina, F., Ghorbel, A., and Segarra, A. M. (2015). Phosphoric acid intercalated Mg–Al hydrotalcite-like compounds for catalytic carboxylation reaction of methanol in a continuous system. *Appl. Catal. A*. 493, 142–148. doi: 10.1016/j.apcata.2015.01.004

Gong, Z.-J., Li, Y.-R., Wu, H.-L., Lin, S. D., and Yu, W.-Y. (2020). Direct copolymerization of carbon dioxide and 1,4-butanediol enhanced by ceria nanorod catalyst. *Appl. Catal. B* 265:118524. doi: 10.1016/j.apcatb.2019.118524

Greish, A. A., Finashina, E. D., Tkachenko, O. P., Shuvalova, E. V., and Kustov, L. M. (2016). Synthesis of dimethyl carbonate from methanol and CO_2 on the SnO_2/Al_2O_3-based catalyst. *Mendeleev Commun.* 26, 497–499. doi: 10.1016/j.mencom.2016.11.012

Gu, Y., Matsuda, K., Nakayama, A., Tamura, M., Nakagawa, Y., and Tomishige, K. (2019b). Direct synthesis of alternating polycarbonates from CO_2 and diols by using a catalyst system of CeO_2 and 2-furonitrile. *ACS Sustain. Chem. Eng.* 7, 6304–6315. doi: 10.1021/acssuschemeng.8b06870

Gu, Y., Miura, A., Tamura, M., Nakagawa, Y., and Tomishige, K. (2019a). Highly efficient synthesis of alkyl *N*-arylcarbamates from CO_2, anilines, and branched alcohols with a catalyst system of CeO_2 and 2-cyanopyridine. *ACS Sustain. Chem. Eng.* 7, 16795–16802. doi: 10.1021/acssuschemeng.9b04318

Honda, M., and Abe, H. (2018). Development of a $H_3PW_{12}O_{40}/CeO_2$ catalyst for bulk ring-opening polymerization of a cyclic carbonate. *Green Chem.* 20, 4995–5006. doi: 10.1039/C8GC01909F

Honda, M., Kuno, S., Begum, N., Fujimoto, K., Suzuki, K., Nakagawa, Y., et al. (2010). Catalytic synthesis of dialkyl carbonate from low pressure CO_2 and alcohols combined with acetonitrile hydration catalyzed by CeO_2. *Appl. Catal. A* 384, 165–170. doi: 10.1016/j.apcata.2010.06.033

Honda, M., Kuno, S., Sonehara, S., Fujimoto, K., Suzuki, K., Nakagawa, Y., et al. (2011a). Tandem carboxylation-hydration reaction system from methanol, CO_2 and benzonitrile to dimethyl carbonate and benzamide catalyzed by CeO_2. *ChemCatChem* 3, 365–370. doi: 10.1002/cctc.201000339

Honda, M., Sonehara, S., Yasuda, H., Nakagawa, Y., and Tomishige, K. (2011b). Heterogeneous CeO_2 catalyst for the one-pot synthesis of organic carbamates from amines, CO_2 and alcohols. *Green Chem.* 13, 3406–3413. doi: 10.1039/c1gc15646b

Honda, M., Suzuki, A., Noorjahan, B., Fujimoto, K., Suzuki, K., and Tomishige, K. (2009). Low pressure CO_2 to dimethyl carbonate by the reaction with methanol promoted by acetonitrile hydration. *Chem. Commun.* 4596–4598. doi: 10.1039/b909610h

Honda, M., Tamura, M., Nakagawa, Y., Nakao, K., Suzuki, K., and Tomishige, K. (2014c). Organic carbonate synthesis from CO_2 and alcohol over CeO_2 with 2-cyanopyridine: scope and mechanistic studies. *J. Catal.* 318, 95–107. doi: 10.1016/j.jcat.2014.07.022

Honda, M., Tamura, M., Nakagawa, Y., Sonehara, S., Suzuki, K., Fujimoto, K., et al. (2013). Ceria-catalyzed conversion of carbon dioxide into dimethyl carbonate with 2-cyanopyridine. *ChemSusChem* 6, 1341–1344. doi: 10.1002/cssc.201300229

Honda, M., Tamura, M., Nakagawa, Y., and Tomishige, K. (2014a). Catalytic CO_2 conversion to organic carbonates with alcohols in combination with dehydration system. *Catal. Sci. Technol.* 4, 2830–2845. doi: 10.1039/C4CY00557K

Honda, M., Tamura, M., Nakao, K., Suzuki, K., Nakagawa, Y., and Tomishige, K. (2014b). Direct cyclic carbonate synthesis from CO_2 and diol over carboxylation/hydration cascade catalyst of CeO_2 with 2-cyanopyridine. *ACS Catal.* 4, 1893–1896. doi: 10.1021/cs500301d

Hou, Z. Q., Luo, L. G., Liu, K., Liu, C. Z., Wang, Y. Y., and Dai, L. Y. (2014). High-yield synthesis of dimethyl carbonate from the direct alcoholysis of urea in supercritical methanol. *Chem. Eng. J.* 236, 415–418. doi: 10.1016/j.cej.2013.09.024

Huang, S. Y., Yan, B., Wang, S. P., and Ma, X. B. (2015). Recent advances in dialkyl carbonates synthesis and applications. *Chem. Soc. Rev.* 44, 3079–3116. doi: 10.1039/C4CS00374H

Ikeda, Y., Asadullah, M., Fujimoto, K., and Tomishige, K. (2001). Structure of the active sites on H_3PO_4/ZrO_2 catalysts for dimethyl carbonate synthesis from methanol and carbon dioxide. *J. Phys. Chem. B* 105, 10653–10658. doi: 10.1021/jp0121522

Ikeda, Y., Sakaihori, T., Tomishige, K., and Fujimoto, K. (2000). Promoting effect of phosphoric acid on zirconia catalysts in selective synthesis of dimethyl carbonate from methanol and carbon dioxide. *Catal. Lett.* 66, 59–62. doi: 10.1023/A:1019043422050

Kumar, S., Khatri, O. P., Cordier, S., Boukherroub, R., and Jain, S. L. (2015). Graphene oxide supported molybdenum cluster: first heterogenized homogeneous catalyst for the synthesis of dimethyl carbonate from CO_2 and methanol. *Chem. Eur. J.* 21, 3488–3494. doi: 10.1002/chem.201404949

Kumar, S., Kumar, P., and Jain, S. L. (2014). Graphene oxide immobilized copper phthalocyanine tetrasulphonamide: the first heterogenized homogeneous catalyst for dimethyl carbonate synthesis from CO_2 and methanol. *J. Mater. Chem. A* 2, 18861–18866. doi: 10.1039/C4TA03420A

Leino, E., Kumar, N., Mäki-Arvela, P., Rautio, A.-R., Dahl, J., Roine, J., et al. (2018). Synthesis and characterization of ceria-supported catalysts for carbon dioxide transformation to diethyl carbonate. *Catal. Today* 306, 128–137. doi: 10.1016/j.cattod.2017.01.016

Leino, E., Mäki-Arvela, P., Eränen, K., Tenho, M., Murzin, D. Y., et al. (2011). Enhanced yields of diethyl carbonate via one-pot synthesis from ethanol, carbon dioxide and butylene oxide over cerium (IV) oxide. *Chem. Eng. J.* 176–177, 124–133. doi: 10.1016/j.cej.2011.07.054

Leino, E., Mäki-Arvela, P., Eta, V., Kumar, N., and Demoisson, F., Samikannu, A., et al. (2013). The influence of various synthesis methods on the catalytic activity of cerium oxide in one-pot synthesis of diethyl carbonate starting from CO_2, ethanol and butylene oxide. *Catal. Today* 210, 47–54. doi: 10.1016/j.cattod.2013.02.011

Leino, E., Mäki-Arvela, P., Eta, V., Murzin, D. Y., Salmi, T., and Mikkola, J.-P. (2010). Conventional synthesis methods of short-chain dialkylcarbonates and novel production technology via direct route from alcohol and waste CO_2. *Appl. Catal. A* 383, 1–13. doi: 10.1016/j.apcata.2010.05.046

Li, A.-X., Pu, Y.-F., Li, F., Luo, J., Zhao, N., and Xiao, F.-K. (2017). Synthesis of dimethyl carbonate from methanol and CO_2 over Fe–Zr mixed oxides. *J. CO_2 Util.* 19, 33–39. doi: 10.1016/j.jcou.2017.02.016

Liu, J., Guo, H. T., Zhou, Q. B., Wang, J. Y., Lin, B. K., Zhang, H. B., et al. (2013). Highly efficient enzymatic preparation for dimethyl carbonate catalyzed by lipase from penicillium expansum immobilized on CMC–PVA film. *J. Mol. Catal. B* 96, 96–102. doi: 10.1016/j.molcatb.2013.06.013

Liu, J. X., Li, Y. M., Zhang, J., and He, D. H. (2016). Glycerol carbonylation with CO_2 to glycerol carbonate over CeO_2 catalyst and the influence of CeO_2 preparation methods and reaction parameters. *Appl. Catal. A* 513, 9–18. doi: 10.1016/j.apcata.2015.12.030

Marciniak, A. A., Alves, O. C., Appel, L. G., and Mota, C. J. A. (2019). Synthesis of dimethyl carbonate from CO_2 and methanol over CeO_2: role of copper as dopant and the use of methyl trichloroacetate as dehydrating agent. *J. Catal.* 371, 88–95. doi: 10.1016/j.jcat.2019.01.035

Ono, Y. (1997). Catalysis in the production and reactions of dimethyl carbonate, an environmentally benign building block. *Appl. Catal. A*. 155, 133–166. doi: 10.1016/S0926-860X(96)00402-4

Poungsombate, A., Imyen, T., Dittanet, P., Embley, B., and Kongkachuichay, P. (2017). Direct synthesis of dimethyl carbonate from CO_2 and methanol by supported bimetallic Cu–Ni/ZIF-8 MOF catalysts. *J. Taiwan Inst. Chem. Eng.* 80, 16–24. doi: 10.1016/j.jtice.2017.07.019

Santos, B. A. V., Silva, V. M. T. M., Loureiro, J. M., and Rodrigues, A. E. (2014). Review for the direct synthesis of dimethyl carbonate. *ChemBioEng Rev.* 1, 214–229. doi: 10.1002/cben.201400020

Shukla, K., and Srivastava, V. C. (2017). Synthesis of organic carbonates from alcoholysis of urea: a review. *Catal. Rev. Sci. Eng.* 59, 1–43. doi: 10.1080/01614940.2016.1263088

Stoian, D., Bansode, A., Medina, F., and Urakawa, A. (2017). Catalysis under microscope: Unraveling the mechanism of catalyst de- and re-activation in the continuous dimethyl carbonate synthesis from CO_2 and methanol in the presence of a dehydrating agent. *Catal. Today* 283, 2–10. doi: 10.1016/j.cattod.2016.03.038

Stoian, D., Medina, F., and Urakawa, A. (2018). Improving the stability of CeO_2 catalyst by rare earth metal promotion and molecular insights in the dimethyl carbonate synthesis from CO_2 and methanol with 2-cyanopyridine. *ACS Catal.* 8, 3181–3193. doi: 10.1021/acscatal.7b04198

Sun, W., Zheng, L., Wang, Y.-Q., Li, D.-D., Liu, Z.-R., Wu, L., et al. (2020). A study for thermodynamics and experiment on direct synthesis of dimethyl carbonate from carbon dioxide and methanol over yttrium oxide. *Ind. Eng. Chem. Res.* 59, 4281–4290. doi: 10.1021/acs.iecr.9b06092

Tamboli, A. H., Chaugule, A. A., Gosavi, S. W., and Kim, H. (2018). $Ce_xZr_{1--x}O_2$ solid solutions for catalytic synthesis of dimethyl carbonate from CO_2: reaction mechanism and the effect of catalyst morphology on catalytic activity. *Fuel*. 216, 245–254. doi: 10.1016/j.fuel.2017.12.008

Tamura, M., Honda, M., Nakagawa, Y., and Tomishige, K. (2014). Direct conversion of CO_2 with diols, aminoalcohols and diamines to cyclic carbonates, cyclic carbamates and cyclic ureas using heterogeneous catalysts. *J. Chem. Technol. Biotechnol.* 89, 19–33. doi: 10.1002/jctb.4209

Tamura, M., Honda, M., Noro, K., Nakagawa, Y., and Tomishige, K. (2013a). Heterogeneous CeO_2-catalyzed selective synthesis of cyclic carbamates from CO_2 and aminoalcohols in acetonitrile solvent. *J. Catal.* 305, 191–203. doi: 10.1016/j.jcat.2013.05.013

Tamura, M., Ito, K., Honda, M., Nakagawa, Y., Sugimoto, H., and Tomishige, K. (2016b). Direct copolymerization of CO_2 and diols. *Sci. Rep.* 6:24038. doi: 10.1038/srep24038

Tamura, M., Ito, K., Nakagawa, Y., and Tomishige, K. (2016a). CeO_2-catalyzed direct synthesis of dialkylureas from CO_2 and amines. *J. Catal.* 343, 75–85. doi: 10.1016/j.jcat.2015.11.015

Tamura, M., Kishi, R., Nakagawa, Y., and Tomishige, K. (2015). Self-assembled hybrid metal oxide base catalysts prepared by simply mixing with organic modifiers. *Nat. Commun.* 6:8580. doi: 10.1038/ncomms9580

Tamura, M., Kishi, R., Nakayama, A., Nakagawa, Y., Hasegawa, J.-,y., and Tomishige, K. (2017). Formation of a new, strongly basic nitrogen anion by metal oxide modification. *J. Am. Chem. Soc.* 139, 11857–11867. doi: 10.1021/jacs.7b05227

Tamura, M., Matsuda, K., Nakagawa, Y., and Tomishige, K. (2018b). Ring-opening polymerization of trimethylene carbonate to poly(trimethylene carbonate) diol over a heterogeneous high-temperature calcined CeO_2 catalyst. *Chem. Commun.* 54, 14017–14020. doi: 10.1039/C8CC08405J

Tamura, M., Miura, A., Honda, M., Gu, Y., Nakagawa, Y., and Tomishige, K. (2018a). Direct catalytic synthesis of *N*-arylcarbamates from CO_2, anilines and alcohols. *ChemCatChem*. 10, 4821–4825. doi: 10.1002/cctc.201801443

Tamura, M., Noro, K., Honda, M., Nakagawa, Y., and Tomishige, K. (2013b). Highly efficient synthesis of cyclic ureas from CO_2 and diamines by a pure CeO_2 catalyst using a 2-propanol solvent. *Green Chem.* 15, 1567–1577. doi: 10.1039/c3gc40495a

Tamura, M., and Tomishige, K. (2015). Redox properties of CeO_2 at low temperature: the direct synthesis of imines from alcohol and amine. *Angew. Chem. Int. Ed.* 54, 864–867. doi: 10.1002/anie.201409601

Tomishige, K., Furusawa, Y., Ikeda, Y., Asadullah, M., and Fujimoto, K. (2001). CeO_2-ZrO_2 solid solution catalyst for selective synthesis of dimethyl carbonate from methanol and carbon dioxide. *Catal. Lett.* 76, 71–74. doi: 10.1023/A:1016711722721

Tomishige, K., Gu, Y., Chang, T., Tamura, M., and Nakagawa, Y. (2020). Catalytic function of CeO_2 in non-reductive conversion of CO_2 with alcohols. *Mater. Today Sustain.* 9:100035. doi: 10.1016/j.mtsust.2020.100035

Tomishige, K., Ikeda, Y., Sakaihori, T., and Fujimoto, K. (2000). Catalytic properties and structure of zirconia catalysts for direct synthesis of dimethyl carbonate from methanol and carbon dioxide. *J. Catal.* 192, 355–362. doi: 10.1006/jcat.2000.2854

Tomishige, K., and Kunimori, K. (2002). Catalytic and direct synthesis of dimethyl carbonate starting from carbon dioxide using CeO_2-ZrO_2 solid solution heterogeneous catalyst: effect of H_2O removal from the reaction system. *Appl. Catal. A* 237, 103–109. doi: 10.1016/S0926-860X(02)00322-8

Tomishige, K., Sakaihori, T., Ikeda, Y., and Fujimoto, K. (1999). A novel method of direct synthesis of dimethyl carbonate from methanol and carbon dioxide catalyzed by zirconia. *Catal. Lett.* 58, 225–229. doi: 10.1023/A:1019098405444

Tomishige, K., Tamura, M., and Nakagawa, Y. (2019). CO_2 Conversion with alcohols and amines into carbonates, ureas, and carbamates over CeO_2 catalyst in the presence and absence of 2-cyanopyridine. *Chem. Rec.* 19, 1354–1379. doi: 10.1002/tcr.201800117

Tomishige, K., Yasuda, H., Yoshida, Y., Nurunnabi, M., Li, B. T., and Kunimori, K. (2004a). Catalytic performance and properties of ceria based catalysts for cyclic carbonate synthesis from glycol and carbon dioxide. *Green Chem.* 6, 206–214. doi: 10.1039/b401215a

Tomishige, K., Yasuda, H., Yoshida, Y., Nurunnabi, M., Li, B. T., and Kunimori, K. (2004b). Novel route to propylene carbonate: selective synthesis from propylene glycol and carbon dioxide. *Catal. Lett.* 95, 45–49. doi: 10.1023/B:CATL.0000023720.39110.4e

Verma, S., Baig, R. B. N., Nadagouda, M. N., and Varma, R. S. (2017). Fixation of carbon dioxide into dimethyl carbonate over titanium-based zeolitic thiophenebenzimidazolate framework. *Sci. Rep.* 7:655. doi: 10.1038/s41598-017-00736-1

Xuan, K., Pu, Y.-F., Li, F., Li, A.-X., Luo, J., Li, L., et al. (2018). Direct synthesis of dimethyl carbonate from CO_2 and methanol over trifluoroacetic acid modulated UiO-66. *J. CO_2 Util.* 27, 272–282. doi: 10.1016/j.jcou.2018.08.002

Xuan, K., Pu, Y.-F., Li, F., Luo, J., Zhao, N., and Xiao, F.-K. (2019). Metal-organic frameworks MOF-808-X as highly efficient catalysts for direct synthesis of dimethyl carbonate from CO_2 and methanol. *Chin. J. Catal.* 40, 553–566. doi: 10.1016/S1872-2067(19)63291-2

Yoshida, Y., Arai, Y., Kado, S., Kunimori, K., and Tomishige, K. (2006). Direct synthesis of organic carbonates from the reaction of CO_2 with methanol and ethanol over CeO_2 catalysts. *Catal. Today* 115, 95–101. doi: 10.1016/j.cattod.2006.02.027

Zhang, X.-Z., Jia,. D.-D., Zhang, J., and Sun, Y.-Y. (2014). Direct synthesis of diethyl carbonate from CO_2 and ethanol catalyzed by ZrO_2/molecular sieve. *Catal. Lett.* 144, 2144–2150. doi: 10.1007/s10562-014-1403-5

Zhang, Z.-F., Liu, Z.-W., Lu, J., and Liu, Z.-T. (2011). Synthesis of dimethyl carbonate from carbon dioxide and methanol over $Ce_xZr_{1-x}O_2$ and [EMIM]Br/$Ce_{0.5}Zr_{0.5}O_2$. *Ind. Eng. Chem. Res.* 50, 1981–1988. doi: 10.1021/ie102017j

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REVIEW
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Plasma Technology for CO_2 Conversion: A Personal Perspective on Prospects and Gaps

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There is increasing interest in plasma technology for CO_2 conversion because it can operate at mild conditions and it can store fluctuating renewable electricity into value-added compounds and renewable fuels. This perspective paper aims to provide a view on the future for non-specialists who want to understand the role of plasma technology in the new scenario for sustainable and low-carbon energy and chemistry. Thus, it is prepared to give a personal view on future opportunities and challenges. First, we introduce the current state-of-the-art and the potential of plasma-based CO_2 conversion. Subsequently, we discuss the challenges to overcome the current limitations and to apply plasma technology on a large scale. The final section discusses the general context and the potential benefits of plasma-based CO_2 conversion for our life and the impact on climate change. It also includes a brief analysis on the future scenario for energy and chemical production, and how plasma technology may realize new paths for CO_2 utilization.

Keywords: plasma, plasma catalysis, dielectric barrier discharge, microwave plasma, gliding arc, CO_2 conversion, dry reforming, energy efficiency

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INTRODUCTION

Plasma, also called the "fourth state of matter," is an ionized gas consisting of electrons, various types of ions, radicals, excited atoms, and molecules, besides neutral ground state molecules. Thus, it is a very reactive environment, making it of interest for many applications (Bogaerts et al., 2002). Plasma is created by applying electricity to a gas. The light electrons are heated by the applied electric field, and they activate the gas molecules by excitation, ionization, and dissociation, creating the above-mentioned reactive species and allowing chemical reactions to occur at mild conditions (ambient temperature and pressure). This makes plasma of particular interest for CO_2 conversion because the electrons can activate the CO_2 molecules, giving rise to new products without the need to heat the entire gas (Fridman, 2008; Snoeckx and Bogaerts, 2017). Thus, plasma technology can provide an energy-efficient method for CO_2 conversion, as discussed in section on Potential of plasma technology to reduce CO_2 emissions, although more research is needed to overcome current limitations, as will be discussed in section What Is Needed to Overcome Current Limitations of Plasma-Based CO_2 Conversion?

This perspective paper, like the others in this special issue, is not written as a classical review for specialists, but rather to provide to non-specialists an understanding of the background for this technology, the prospects and gaps, and the role of plasma technology in the new scenario for sustainable and low-carbon energy and chemistry. Therefore, it does not enter too much into mechanistic and other specialized aspects, but rather aims to give a bird's-eye overview of the field and the problems to be overcome in order to pass from lab-scale to industrial application. In fact, although plasma technologies are already applied commercially for a few sectors like waste incineration, their use in CO_2 conversion to fuels and chemicals, and in general for the conversion of small molecules such as CO_2, CH_4, H_2O, and N_2, is still mainly at the laboratory scale. Nevertheless, this is a crucial aspect for the future of sustainable energy and chemistry, from a circular economy to energy/chemistry based on perennial (renewable) sources rather than on fossil fuels (Lanzafame et al., 2017a; Centi et al., 2019; Centi and Perathoner, 2020). As a consequence, it is necessary that non-specialists understand the possible contribution of plasma technologies to address this challenge.

Although this paper provides a status on the use of non-thermal plasma for CO_2 conversion, we do not aim to give a systematic review of the state-of-the-art, and we refer to recent reviews on the topic (Snoeckx and Bogaerts, 2017; Chen et al., 2018; Puliyalil et al., 2018; Qin et al., 2018; Debek et al., 2019). Rather, we aim to give a glimpse about possibilities and issues in this area from our personal perspective. For this reason, the paper is largely based on our own results, put in a general perspective, and also provides some background information on the technology, as plasma technology is not yet well-known by the scientific community.

The general question is why plasma technology is relevant for CO_2 conversion in view of the future of energy and chemistry from a sustainable, low-carbon perspective. These aspects will be discussed in section Benefits for Our Life and Impact on Climate Change, but are briefly introduced here in relation to competitive technologies. There are two overarching topics when discussing the future of energy and chemistry, particularly in regions such as Europe, where there are political commitments about the reduction of CO_2 and other greenhouse gas (GHG) emissions (now with a target of 50% reduction for the year 2030), and where large initiatives such as the European Green Deal planning, a global investment of over 1 trillion Euro, are put into action with goals such as: (i) closing the carbon cycle (as part of circular economy) of CO_2 emissions and putting them back in use as carbon sources, and (ii) using renewable (perennial) energy sources (RES) rather than deriving from fossil fuels.

Being low but not lowest in thermodynamic energy content, CO_2 should react with other compounds to form chemicals with even lower thermodynamic energy level (inorganic carbonates) or react with higher energy level compounds to form chemicals/fuels with higher thermodynamic energy. The second route can involve either chemicals produced according to current routes (for example, reaction of CO_2 with epoxides to form cyclic carbonates) or produced through the use of RES, such as H_2, by electrolysis using electrical energy produced from wind or photovoltaic panels. The second option is preferable because it introduces RES in the energy/chemistry value chain, and thus reduces the dependence on fossil fuels and CO_2 emissions (Centi and Perathoner, 2010; Perathoner and Centi, 2014; Ampelli et al., 2015).

There are two main options for converting CO_2 to chemicals/fuels by using RES. The first, already developed at demonstration plants, is the production of H_2 by electrolyzers followed by the catalytic conversion of CO_2 to different products, from methane (power-to-X, Centi and Perathoner, 2020) to methanol or hydrocarbons. The second is the direct CO_2 conversion in electrocatalytic reactors (with the electrical energy produced from a separate RES unit) or in photoelectrocatalytic (PEC) reactors, where the solar cell is integrated into the electrocatalytic cell (García de Arquer et al., 2020). Although the latter is still the more challenging, it provides two main advantages: (i) it greatly reduces several of the energy losses due to coupling different components, and (ii) it avoids energy losses related to the overpotential in forming H_2 (from H^+/e^- which are the effective primary products in water electrolysis) and in using H_2. In the current approach, electrolysis followed by thermal catalytic conversion, the overall efficiency is limited by the different steps operating at different conditions and having different dynamics. For example, in coupling H_2 (produced in electrolyzers) to a second stage of catalytic conversion of CO_2 to methane or methanol (the two most common examples of power-to-X technologies), there is the need to compress and heat H_2, and there are severe issues in handling the different dynamics of the process and heat integration, and costs are relatively high.

This is thus considered the first generation, today at the stage of pilot/demo scale, and can achieve application depending on cost of renewable electrical energy, carbon taxes (or subsidies), and other aspects. However, moving to the second and third generation processes, which are those where the generation of H_2 equivalent (H^+/e^-) and CO_2 conversion are integrated in a single electrocatalytic device or when the photogeneration stage of the current/potential for water oxidation (i.e., H_2O to $O_2 + H^+/e^-$) is integrated in a single PEC device, can increase process efficiency and lower the costs around 15–20% and up to 25–30%, respectively (Perathoner and Centi, 2019).

In addition to these possibilities, direct photocatalytic conversion of CO_2 to chemicals/fuels is possible. Although attractive, the main issues are the low productivity and the combined (in a single compartment) formation of products of reduction (methane or methanol from CO_2) and oxidation (O_2 derived from water), creating issues of safety (explosivity) and costs of separation. Although many researchers have worked on this approach, the exploitability of the results still appears rather distant. A different alternative is the use of solar radiation, not to generate charge separation and thus photoinduced electrical currents or reactions, but simply to provide the heat for running thermal reactions. This is the concept of concentrated solar power (CSP) plants. For example, by thermal heating at high temperature (above about 1,200°C), metal oxides may be reduced, which react then at lower

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Abbreviations: APGD, atmospheric pressure glow discharge; CCS, carbon capture and storage; DBD, dielectric barrier discharge; DRM, dry reforming of methane; DVP, dual-vortex plasmatron; EOR, enhanced oil recovery; ERC, European Research Council; GA, gliding arc; GAP, GA plasmatron; GDP, gross domestic product; molec, molecule; MW, microwave; PEC, photoelectro-chemical or -catalytic; RES, renewable energy sources; RF, radio-frequency; SEI, specific energy input; VDF, vibrational distribution function; VT, vibrational-translational; VV, vibrational-vibrational.

temperatures (800–900°C) with CO_2 or H_2O to generate CO and H_2, respectively. Notwithstanding intense research, the many issues on productivity, stability, and costs (Centi and Perathoner, 2010) have strongly hindered development beyond pilot units, and current interest on this route is decreasing.

The different possibilities of using RES in CO_2 conversion technologies have been discussed in detail by Navarrete et al. (2017). In summary, electrocatalytic and (in a longer-term perspective) PEC approaches appear as the more promising routes in competition with plasma. Currently the major issue with the electrocatalytic route is to realizing high current densities together with high Faradaic efficiencies (FE) to the target compound. As a rough indication, current densities should be above 100 mA/cm^2 and FE > 90%. This is currently feasible only with formic acid, which is a $2e^-$ reduction of CO_2. More challenging reactions such as methanol formation, which is a 6e- reduction, have still significantly lower performances. Some results have been also reported with higher current densities. For example, García de Arquer et al. (2020) reported current densities up to 1 A in the reduction of CO_2 to ethylene, but at low FE (45%) and using as electrolyte 7 M KOH (pH ≈ 15), which creates severe problems with materials stability. Zheng et al. (2019) reported high current densities (around 80 mA/cm^2) and high FE (above 90%) to CO in a 10 × 10 cm electrode cell, but with performances lowering in 6 h tests, thus indicating stability issues. In addition, CO must be further converted by catalytic routes in the presence of H_2 (from renewable sources), so the effective advantage with respect to direct catalytic conversion of CO_2 is not very evident.

It is out of scope here to discuss in more detail other approaches to convert CO_2 by using RES, but these examples indicate how there is continuous progress in these alternative routes, though the results are still far from the possibility of application, at least in the short run. Therefore, when comparing plasma technology with these alternative possibilities, we need to keep in mind that it is an area still under fast development and thus not well-consolidated to allow a reliable comparison and indication of which route is the most promising, even if attempts have been made (Liu M. et al., 2019).

Plasma, as will be discussed in more detail in the following sections, has some advantages: (i) plasma is generated by electricity and can simply be switched on/off, allowing storage of fluctuating energy; (ii) the reaction occurs virtually in the entire volume of the reactor (although mainly confined at the discharges), as in thermal catalysis (i.e., the reactions occur on the catalyst, but it occupies a significant fraction of the volume of the reactor), while for electro- and photo-catalytic processes the reaction is on the surface of the electrode (thus, to simplify, a 3D vs. 2D approach); (iii) it is a relatively low cost technology in comparison with photo- and electro-catalytic routes requiring more sophisticated and costly devices and materials. On the other hand, as will be clarified later, the complexity of the phenomena in plasma chemistry and physics, and even more when coupled with a solid catalyst, require further progress in understanding to achieve high productivity, energy efficiency, and energy selectivity. Scalability of the technology is another challenge in exploiting the potential of plasma technology for industrial applications.

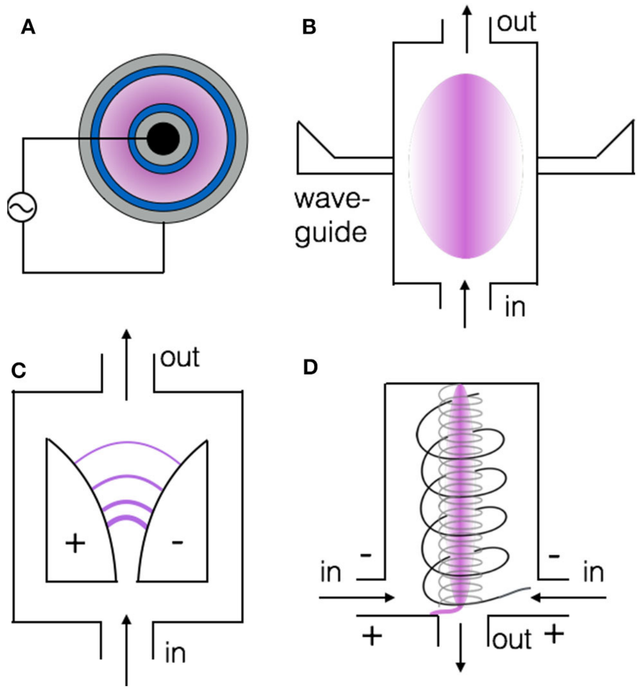

FIGURE 1 | Schematic picture of the three most common plasma reactors for CO_2 conversion, i.e., dielectric barrier discharge (DBD) **(A)**, microwave (MW) plasma **(B)**, and gliding arc (GA) discharge, in classical configuration **(C)**, and cylindrical geometry, called gliding arc plasmatron (GAP) **(D)**. The plasma is each time presented in purple. Adopted from Bogaerts and Neyts (2018) with permission.

THE POTENTIAL OF PLASMA TECHNOLOGY TO REDUCE CO_2 EMISSIONS

Different Plasma Types—Different Performance

Different types of plasmas are being investigated for CO_2 conversion, including dielectric barrier discharges (DBDs), microwave (MW) plasmas, gliding arc (GA) plasmas, atmospheric pressure glow discharges (APGDs), nanosecond-pulsed discharges, and corona and spark discharges. They differ in the way the electricity is applied and the actual value of the applied electric field, reactor configuration, pressure, power, etc. These differences manifest themselves in their performance toward CO_2 conversion, as discussed in detail by Snoeckx and Bogaerts (2017).

The three most common plasma types for CO_2 conversion are DBD, MW, and GA plasma, and they are depicted in **Figure 1** (Bogaerts and Neyts, 2018). A DBD (**Figure 1A**) is created by applying an electric field between two electrodes, of which at least one is covered by a dielectric barrier. The two electrodes can be parallel plates, but for CO_2 conversion, a cylindrical configuration in which the two electrodes are concentric cylinders (see **Figure 1A**), is more appropriate because it minimizes the amount of gas bypassing the plasma region. A DBD operates at atmospheric pressure and (near)

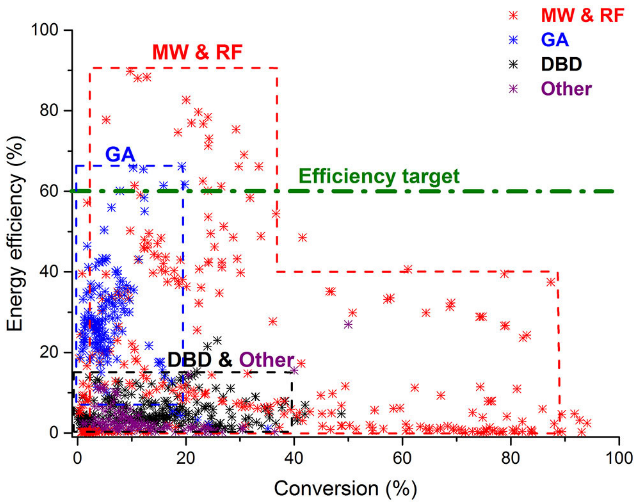

FIGURE 2 | Comparison of all data from literature for CO_2 splitting in different plasma reactors, illustrating the energy efficiency as a function of conversion. The 60% efficiency target is also indicated. Adopted from Snoeckx and Bogaerts (2017) with permission.

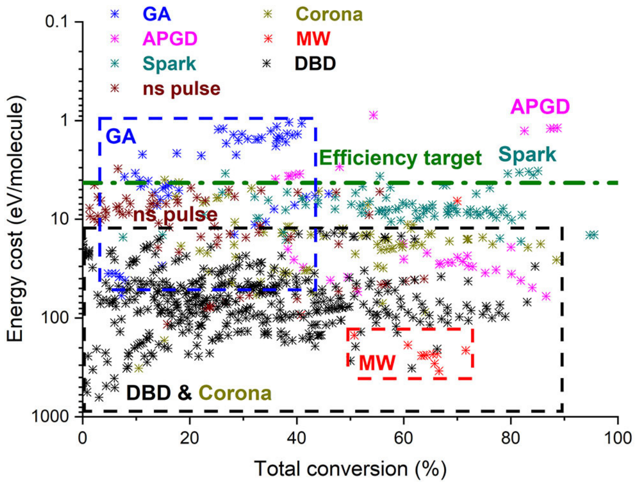

FIGURE 3 | Comparison of all data from literature for DRM in different plasma reactors, illustrating the energy cost as a function of conversion. The target energy cost of 4.27 eV/molec for syngas production (corresponding to 60% efficiency target) is also indicated. The y-axis is reversed to allow easier comparison with **Figure 2**. Adopted from Snoeckx and Bogaerts (2017) with permission.

room temperature. It has a simple design, making it easy for upscaling and commercial applications, as demonstrated a few decades ago for ozone synthesis (Kogelschatz, 2003). Moreover, the simple design allows also easy implementation of catalyst materials inside the plasma in order to better control the selective production of value-added compounds. Indeed, as mentioned in the introduction, plasma is very reactive, producing a plethora of different species, but the latter can react toward many different compounds. Therefore, if the selective production of specific molecules is targeted, plasma should be combined with catalysts, yielding so-called plasma catalysis (Neyts et al., 2015). Most studies on plasma catalysis have indeed been reported with DBD plasma reactors in a packed-bed configuration, where packing beads (of a few mm diameter) are typically coated by catalyst materials. A DBD reactor provides reasonable conversion but is not energy efficient compared to other plasma types, as shown in **Figures 2**, **3** below (Snoeckx and Bogaerts, 2017). The reason will be explained in next section.

A MW plasma arises when applying MW power to a quartz tube filled with gas (**Figure 1B**). It can operate in a pressure range from a few mbar up to 1 bar, but typically the CO_2 conversion and corresponding energy efficiency are better at reduced pressure (ca. 100–200 mbar) than at atmospheric pressure, for the reason explained in next section. Indeed, energy efficiencies up to 80% and even 90% (for CO_2 conversions around 20 or 10%, respectively) have been reported for MW plasmas at 100–200 mbar under subsonic and supersonic flow conditions, respectively (Legasov et al., 1978; Asisov et al., 1983; Fridman, 2008), although it must be realized that these record values have not been reproduced since then. The gas temperature can easily rise to above 3,000 K at (sub)atmospheric pressure. For this reason, catalyst materials cannot be easily implemented inside a MW plasma, but they can be placed after the plasma reactor (so-called "post-plasma catalysis"), although not many studies have reported on MW-plasma catalysis yet.

In a classical GA plasma, also called "2D GA plasma," an electric potential difference is applied between two flat diverging electrodes (see **Figure 1C**). An arc is created at the shortest interelectrode distance, and as a result of the gas flow it glides along the surface of the electrodes toward larger interelectrode distances until it extinguishes, and a new arc is created again at the shortest distance. A GA plasma typically operates at atmospheric pressure, and exhibits quite good energy efficiency (see **Figures 2**, **3**); the reason will be explained in next section. However, the conversion is limited (typically about 10%), because of the limited residence time of the gas inside the arc plasma. Indeed, the gas flow rate must be high enough for the arc to glide along the electrodes.

To overcome the limitation of short residence time, several 3D GA plasma configurations have been developed, such as the rotating GA and the GA-Plasmatron (GAP), in which the reactor is cylindrical and the gas typically enters the reactor tangentially, leading to a vortex gas flow (see **Figure 1D**) (Nunnally et al., 2011). When the outlet diameter is considerably smaller than the reactor diameter, the gas first flows upwards in an outer vortex, creating an isolating effect from the hot plasma arc in the center (see below) toward the walls. Once the gas reaches the end of the reactor it has lost some speed due to friction and inertia, and moves downwards in a smaller inner (reverse) vortex, before it leaves the reactor (see **Figure 1D**). The inner vortex flow causes stabilization of the arc in the center of the reactor, and in the ideal case, all the gas within the inner vortex passes through the arc for optimal conversion. Indeed, the arc itself is hot (around 3,000 K), causing nearly complete conversion, mainly due to thermal reactions (see next section). In reality, however, only a limited fraction of the gas actually passes through the arc, thus limiting the overall conversion to about 10%. Thus, reactor design improvements are needed to further enhance the performance, as will be discussed in section What Is Needed to Overcome Current Limitations of Plasma-Based CO_2 Conversion? Like in the MW plasma, catalysts cannot easily be implemented inside the plasma reactor due to the high temperature, but placing a catalyst bed after a GA plasma reactor has provided spectacular results in terms of enhanced conversion and energy efficiency (Li et al., 2016).

Figure 2 presents an overview of the energy efficiency vs. CO_2 conversion, based on all data collected from literature, for different plasma reactor types (Snoeckx and Bogaerts, 2017). Note that the energy efficiency is calculated as the product of conversion and reaction enthalpy, divided by the specific energy input (SEI), which is equal to plasma power over gas flow rate. As mentioned above, MW plasmas [as well as some radiofrequency (RF) plasmas] yield the best energy efficiency, even up to 80 and 90% (for a conversion of 10%), but these record values were all obtained at reduced pressure (100–200 mbar) and in special configurations (e.g., supersonic expansion) (Legasov et al., 1978; Asisov et al., 1983; Fridman, 2008), and have not been reproduced since then. Likewise, Silva et al. reported conversions of 50–80%, but at corresponding energy efficiencies of 10% (Silva et al., 2014), and again at reduced pressure (1–10 mbar). At (sub)atmospheric pressure, yielding temperatures of 3,000 K and above, the best energy efficiencies achieved were around 40–50 %, for a conversion around 10–20% at 100–200 mbar (den Harder et al., 2017), and up to 600 mbar (Bongers et al., 2017). Vice versa, conversion values up to 80% have also been reported for energy efficiencies of 20%, in quenching experiments at 200 mbar (Bongers et al., 2017). GA plasmas at atmospheric pressure have typical energy efficiencies around 20–40%, but for limited conversions up to 10% (Nunnally et al., 2011; Ramakers et al., 2017), although some configurations have resulted in energy efficiencies above 60% (Snoeckx and Bogaerts, 2017).

Note that an efficiency target of 60% (cf. green dashed line in **Figure 2**) was defined by Snoeckx and Bogaerts (2017) based on two criteria: (i) the comparison with electrochemical water splitting, being the main competitor of plasma conversion for storing renewable energy, and reaching commercial energy efficiencies of 65–75%; and (ii) the comparison with other novel technologies for CO_2 conversion, which directly use solar energy (e.g., solar thermochemical conversion), and for which a solar-to-fuel conversion efficiency of 20% was stated to be industrially competitive. Based on a solar panel efficiency of 25%, plasma-based CO_2 conversion at an energy efficiency of 60–80% would thus give rise to a competitive solar-to-fuel efficiency of 15–20%.

It is clear from **Figure 2** that several of the (reduced pressure) MW (& RF) plasma results and a few of the (atmospheric pressure) GA plasma results obtained in literature are already above this efficiency target. The DBD results, on the other hand, are clearly below the efficiency target, with energy efficiencies up to maximum ca. 10%, albeit at reasonable conversion values up to 40%.

A similar collection of data is presented in **Figure 3** for dry reforming of methane (DRM) (Snoeckx and Bogaerts, 2017). The combined conversion of CH_4 and CO_2 allows the production of other compounds besides CO and O_2, such as syngas (CO/H_2), higher hydrocarbons, and oxygenates. Note that the y-axis in this figure does not present the energy efficiency, but the energy cost, showing the highest values at the bottom and the lowest (i.e., best) values at the top of the axis, to allow easy comparison with **Figure 2**. Indeed, the energy efficiency could not be determined from all data points in literature because it is only possible when reporting all products formed, which was often not the case. The energy cost is determined as the ratio of SEI over conversion, so it can be defined even if not all products are identified. Note that an efficiency target of 4.27 eV/molec was determined by Snoeckx and Bogaerts (2017) (cf. green dashed line in **Figure 3**) based on the formation of syngas (corresponding to the 60% energy efficiency target).

The best results are now obtained in GA plasmas, with several data points already above the efficiency target, showing energy costs down to almost 1 eV/molec for conversions up to 40% (Li et al., 2016; Cleiren et al., 2017; Slaets et al., 2020). MW plasmas, on the other hand, have not been extensively studied yet for DRM, and the few results found in literature exhibit a very high energy cost. This is quite surprising in view of the very promising results for CO_2 splitting (cf. **Figure 2**), and it indicates the need for more research to exploit the potential of MW plasmas for DRM as well. Most results have been obtained in DBD reactors, often in combination with catalysis (packed bed DBDs), but they are again characterized by high energy costs, making them not competitive with other technologies. However, it should be noted that the efficiency target is based on the formation of syngas. If more valuable products, such as olefins or oxygenates, could selectively be formed, the efficiency target would not be so strict to be competitive with other technologies, where these products would be formed in a two-step process. This means that DBD plasmas, in spite of their low energy efficiency, could be still of interest for their easy implementation of catalysts, but only if suitable catalysts can be designed that selectively produce these value-added compounds in a one-step process in the DBD plasma. This will be further discussed in section What Is Needed to Overcome Current Limitations of Plasma-Based CO_2 Conversion? Finally, **Figure 3** also shows the results obtained in some other plasma types, such as corona, ns-pulsed, and spark discharges, as well as APGDs. APGDs especially provided very promising results, with energy costs down to 1 eV/molec at conversions up to 80–90%. However, the data points are limited, and clearly more research is needed to verify these results and to further improve the capabilities of the APGD and other plasma types for DRM.

Besides CH_4, H_2O or H_2 can also be added as H-sources to produce value-added compounds from CO_2. However, only very limited data are reported in literature for the combined CO_2/H_2O or CO_2/H_2 conversion (see **Figure 4**). Note that in this case, no efficiency target could be defined. Indeed, the latter requires knowledge on all products formed, and they are generally not all reported in literature for CO_2/H_2O or CO_2/H_2 mixtures. It is clear from this figure that the values reported for energy cost

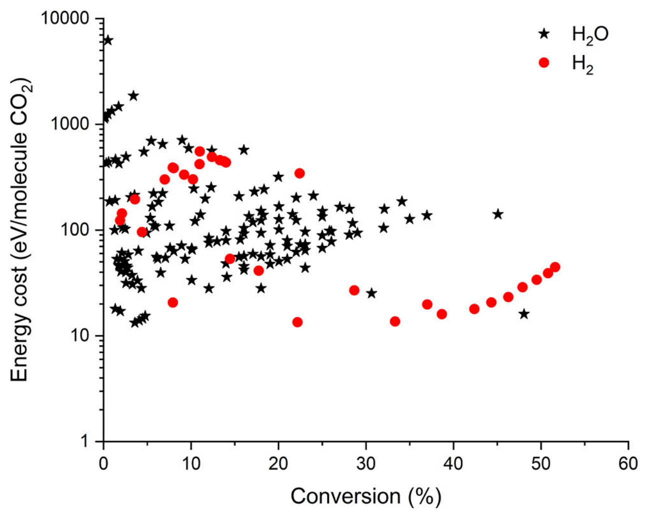

FIGURE 4 | Comparison of all data from literature for the combined CO_2 + H_2O (*) and the combined CO_2 + H_2 (•) conversion in different plasma reactors, illustrating the energy cost per converted CO_2 molecule as a function of conversion. Some data are recalculated from the original references, to account for (among others) dilution effects.

and conversion in these gas mixtures are not yet competitive with those obtained already for DRM (cf. **Figure 3**). The reason for this is the (virtual) absence of CH_3 and CH_2 radicals in these gas mixtures, which would contribute to the CO_2 conversion, as predicted by numerical simulations (De Bie et al., 2016). Moreover, the fact that CHO is formed ($H + CO + M \rightarrow CHO + M$), which can form CO_2 again ($CHO + O \rightarrow CO_2 + H$), as well as the recombination of CO with OH radicals, again forming CO_2, both limit the CO_2 conversion, as will be discussed in section What Is Needed to Overcome Current Limitations of Plasma-Based CO_2 Conversion? Nevertheless, the combined conversion of CO_2 and H_2O would be of great interest, as H_2O is the cheapest H-source. Therefore, more research should be performed to explore the possibilities and overcome the current limitations of the combined plasma-based CO_2/H_2O conversion.

Different Dissociation Mechanisms in Different Plasma Types

It is clear from **Figures 2**, **3** that MW plasmas (especially at reduced pressure, and in case of CO_2 conversion) and GA plasmas exhibit much better energy efficiency than DBD reactors. In earlier work (e.g., Fridman, 2008) this was attributed to the role of vibrational excitation in MW and GA plasmas, although more recent insights point toward thermal conversion in these plasmas at practical operating conditions (see below).

In the past decade, many papers, both experimental (e.g., Silva et al., 2014, 2017; Klarenaar et al., 2017, 2018, 2019; Stewig et al., 2020; Terraz et al., 2020; van den Bekerom et al., 2020) and computational (e.g., Kozák and Bogaerts, 2014, 2015; Pietanza et al., 2015, 2017a,b, 2018a,b, 2020; Berthelot and Bogaerts, 2016, 2018; Capitelli et al., 2017, Heijkers and Bogaerts, 2017; Grofulović et al., 2018; Silva et al., 2018; Vermeiren and Bogaerts, 2018, 2019; Kotov and Koelman, 2019; Terraz et al., 2020), focused on the role of the vibrational kinetics in plasmas, but mainly at low pressure conditions (few mbar up to a few hundred mbar). Most of these studies revealed the importance of the vibrational kinetics at specific conditions (low gas temperature, low pressure) and their contribution to a high energy efficiency.

It is generally assumed that the electric field applied in MW and GA plasmas is lower than in DBD plasmas, resulting in somewhat lower electron energy (or temperature) that is more suitable for electron-impact vibrational excitation of the CO_2 molecules compared to electronic excitation, ionization, or dissociation. This is illustrated in **Figure 5**, which plots the fraction of electron energy transferred to different CO_2 vibrational levels and the sum of all these levels, as well as the fraction of electron energy transferred to electronic excitation, ionization, and dissociation as a function of the reduced electric field (E/n) (Snoeckx and Bogaerts, 2017). The reduced electric field (E/n) is the ratio of electric field (E) over gas number density (n), and is usually expressed in Townsend (1 Td = 10^{-21} V m²). It is an important measure to distinguish the operating conditions of different plasma types. A DBD exhibits a reduced electric field around 200 Td and above, whereas MW and GA plasmas (and some other plasma types, such as APGD) typically operate around 50–100 Td (Bongers et al., 2017; Pietanza et al., 2020; van den Bekerom et al., 2020), although a recent model for determining the reduced electric field in CO_2 MW plasma derived by the principle of impedance matching (Groen et al., 2019) predicted somewhat higher E/n values, i.e., 10–60 Td for the so-called contracted regime (higher pressure and power), but 80–180 Td for the so-called diffuse regime (lower pressure and power). As depicted in **Figure 5**, for reduced electric fields around 200 Td and above, the largest part of the electron energy (70–80%) goes to electronic excitation, while limited amounts are spent for dissociation and ionization (ca. 5%; rising with E/n), and vibrational excitation (10% of less). On the other hand, around 50–100 Td, the electron energy is too low for electron impact ionization and dissociation because their cross sections have higher thresholds, and to some extent it is also too low for electronic excitation. Hence, only 10% of the electron energy is spent for electronic excitation, while up to 90% goes into vibrational excitation, which has lower energy thresholds. If MW and GA plasmas can operate at E/n values around 50 Td, vibrational excitation is indeed the dominant electron energy loss process. Pietanza et al. (2020) predicted values of 25–42 Td for a MW plasma in the contracted regime, and 48–50 Td in the diffuse regime. Bongers et al. (2017) reported somewhat higher values in practice (70–80 Td), attributed to the high gas temperature causing a lower gas density. These values are already a bit too high for the most efficient electron energy transfer to the vibrational levels (van den Bekerom et al., 2020), but as seen in **Figure 5**, electron impact vibrational excitation is still the most important electron energy loss process up to E/n of 100 Td.

Furthermore, it is generally accepted that vibrational excitation yields energy-efficient CO_2 conversion because it provides the most efficient CO_2 dissociation path. This is

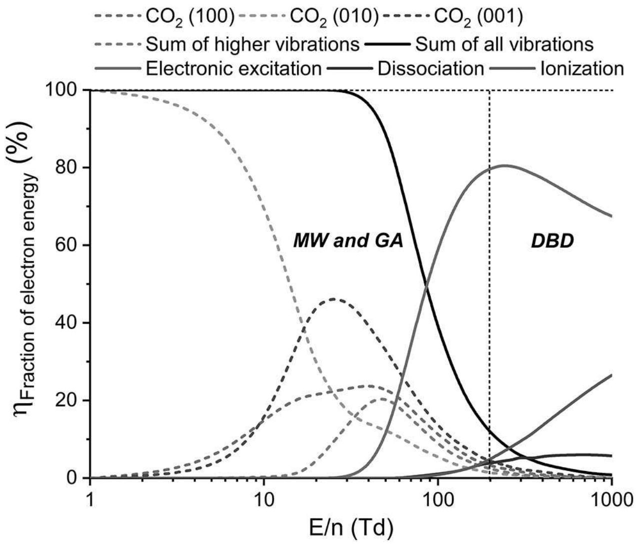

FIGURE 5 | Fraction of electron energy used for different electron impact reactions with CO_2, i.e., vibrational and electronic excitation, ionization and dissociation, as a function of the reduced electric field (E/n), calculated from the respective cross sections. The E/n regions characteristic for MW and GA plasma and for DBD plasma are indicated. Adopted from Snoeckx and Bogaerts (2017) with permission.

illustrated in **Figure 6**, which schematically illustrates some CO_2 electronic and vibrational levels (Bogaerts et al., 2015). Direct electron impact dissociation requires electron energies of at least 7 eV, as it proceeds through a dissociative electronically excited state. Knowing that theoretically, only 5.5 eV is required for C=O bond-breaking, it means that the extra energy is simply wasted. This process occurs in DBD plasmas (cf. **Figure 5**), explaining their lower energy efficiency (see previous section). In contrast, vibrational excitation requires significantly less energy, and once the lowest vibrational levels are populated, they can gradually populate the higher levels by vibrational-vibrational (VV) collisions, which gives rise to dissociation (cf. **Figure 6**). This process is called "ladder-climbing," and requires just the minimum amount of 5.5 eV for bond-breaking. It thus provides a more efficient dissociation pathway. If this process can be exploit ed, for instance in MW and GA plasmas at specific conditions (e.g., reduced pressure or power pulsing, cf. next section), this can explain the higher energy efficiency in these plasma types.

However, the vibrationally excited molecules can also lose their energy upon collision with ground state molecules, called vibrational-translational (VT) relaxation. This process depopulates the vibrational levels, and is thus detrimental for energy-efficient CO_2 conversion by the vibrational ladder climbing pathway. In addition, this process also heats up the gas molecules, and the rate coefficients for VT relaxation rise with higher gas temperature, further speeding up this vibrational depopulation process.

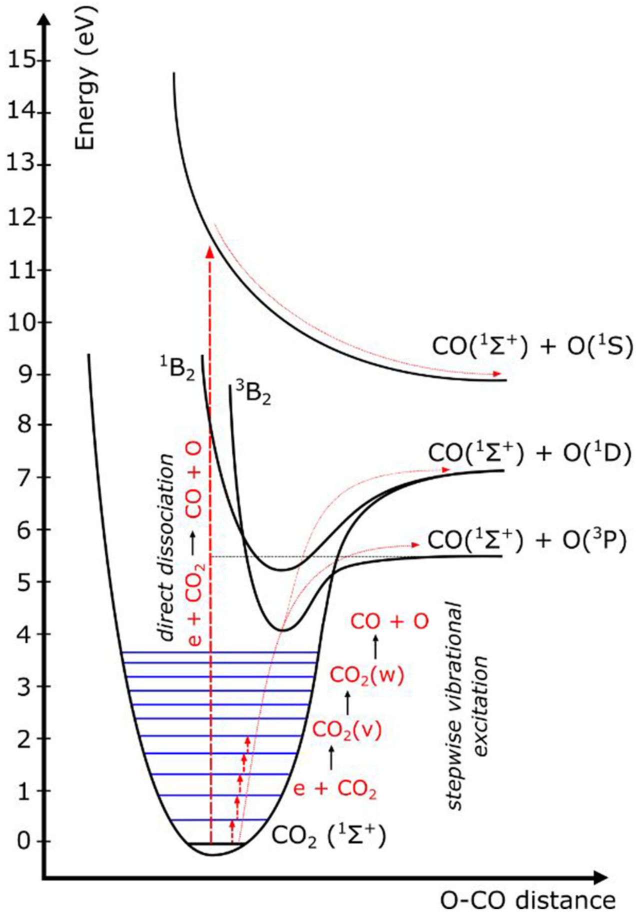

FIGURE 6 | Schematic picture of some CO_2 electronic and vibrational levels, showing that direct electronic excitation–dissociation (as occurs in DBD plasmas) requires much more energy than stepwise vibrational excitation, or vibrational ladder climbing, which is stated to be important in MW and GA plasmas at specific conditions, and which may explain their higher energy efficiency.

In practice, VT relaxation appears quite important in both MW plasmas at (sub)atmospheric pressure and GA plasmas, explaining their high gas temperature (3,000 K or higher; cf. section Different Plasma Types—Different Performance). Therefore, this type of plasmas is called "warm plasmas," as their temperature is in between those of non-thermal plasmas such as DBD, which operate at (or slightly above) room temperature, and thermal plasmas, where the gas temperature reaches 10,000 K, comparable to the electron temperature. In MW and GA plasmas, the electron temperature is still higher than the gas temperature (hence, they are not really thermal plasmas), but the vibrational and gas temperature are often close to each other (i.e., VT equilibrium), so they can also be considered as quasi-thermal plasmas. For this reason, the CO_2 conversion proceeds mainly by thermal reactions in MW and GA plasmas at practical operating conditions (van Rooij et al., 2015; Berthelot and Bogaerts, 2017; Bongers et al., 2017; den Harder et al., 2017; Heijkers and Bogaerts, 2017; Kotov and Koelman, 2019; van den Bekerom et al., 2019; Wolf et al., 2019, 2020).

WHAT IS NEEDED TO OVERCOME CURRENT LIMITATIONS OF PLASMA-BASED CO_2 CONVERSION?

Although the results obtained for both CO_2 splitting and DRM are already very promising (see **Figures 2**, **3**), and the performance of various plasma types is competitive with other emerging technologies (Snoeckx and Bogaerts, 2017), plasma-based CO_2 conversion is up to now only performed on lab-scale and is not yet implemented in industrial processes. We believe that further improvements are needed in terms of (i) energy efficiency, (ii) conversion, and/or (iii) selectivity toward value-added compounds, before plasma reactors should be scaled up and implemented commercially.

Improving the Energy Efficiency

As mentioned in the previous section, CO_2 conversion by vibrational excitation, followed by VV relaxation to the highest levels, is in theory the most energy-efficient CO_2 dissociation process. Therefore, a lot of experimental and modeling papers mainly focused on the vibrational pathway as the most energy-efficient CO_2 dissociation process (see references in previous section). This vibrational pathway requires strong VT non-equilibrium, i.e., much higher vibrational levels than gas (translational) temperature, or in other words, a strong overpopulation of the higher vibrational levels, compared to a thermal vibrational distribution function (VDF). Such behavior can be exploited under specific conditions, e.g., MW plasmas at low pressure and supersonic expansion (Asisov et al., 1983) or pulsed MW plasmas at low pressure, depending on the pulse on-off times, as demonstrated both computationally and experimentally (Vermeiren and Bogaerts, 2019; van den Bekerom et al., 2020). Generally, modeling has revealed that this VT non-equilibrium can be realized in plasmas at low pressure, high power density, and low gas temperature (Berthelot and Bogaerts, 2017); see below.

It should be noted, however, that although the high energy efficiencies reported for low pressure MW plasmas in the 1980s (i.e., up to 80% for subsonic flow, and even up to 90% for supersonic flow conditions; e.g., Legasov et al., 1978; Asisov et al., 1983) were theoretically explained by vibrational excitation followed by vibrational ladder climbing, as depicted in **Figure 6**, none of the experimental or computational studies mentioned in previous section could reproduce or mimic these high energy efficiencies up to now.

Berthelot and Bogaerts (2018) modeled the different energy transfers in a low pressure (100 mbar) CO_2 plasma for various conditions of reduced electric field, gas temperature, and ionization degree. At the most optimal conditions for energy-efficient CO_2 conversion, a low reduced electric field (10 Td) and a low gas temperature (300 K), the model predicted a maximum conversion and energy efficiency of 32 and 47%, respectively. This is clearly lower than the record values of 80%, reported in the 1980s for low pressure subsonic MW plasmas (Legasov et al., 1978). Likewise, Vermeiren and Bogaerts (2019) were not able to predict the record energy efficiency of 90% for a MW plasma at 100 mbar and supersonic flow conditions (Asisov et al., 1983). The major limiting factor in the energy efficiency was pinpointed as the high activation energy of the reaction $CO_2 + O \rightarrow CO + O_2$ (Berthelot and Bogaerts, 2018). Assuming that this activation energy can be entirely overcome, by either sufficient CO_2 vibrational energy or kinetic energy of the collision partners, the model could predict an energy efficiency of up to 86% in the ideal scenario (Berthelot and Bogaerts, 2018). Note that the reason why it was not 100% is due to other losses in the kinetics of CO_2 conversion, i.e., the fact that not all electron energy will go to vibrational excitation of CO_2, but some fraction is also spent to the dissociation products (CO and O_2). However, as mentioned, this maximum energy efficiency could not be realized in the model at practical operating conditions, where the vibrational overpopulation was not strong enough, even at ideal conditions.

On the other hand, more recent experiments reveal energy efficiencies close to 50% for (sub)atmospheric MW plasmas (van Rooij et al., 2015; Bongers et al., 2017; den Harder et al., 2017), around 30% for atmospheric pressure GA plasmas for CO_2 conversion (Nunnally et al., 2011; Ramakers et al., 2017), and even up to 70–80% for DRM (i.e., energy cost of a few eV/molec) (Li et al., 2016; Cleiren et al., 2017; Slaets et al., 2020). These efficiencies, however, are all correlated to the high temperatures in the MW and GA plasmas, pointing toward the dominance of thermal conversion.

It was indeed demonstrated, both experimentally (e.g., van Rooij et al., 2015; Bongers et al., 2017; den Harder et al., 2017; van den Bekerom et al., 2019; Wolf et al., 2019, 2020) and computationally (e.g., Berthelot and Bogaerts, 2017; Heijkers and Bogaerts, 2017; Kotov and Koelman, 2019), that in practice, the vibrational non-equilibrium is not the leading mechanism in (sub)atmospheric MW or GA CO_2 plasmas, and that the CO_2 conversion is thermal, although Pietanza et al. (2020) suggested to act with caution on this assumption, as their model still showed clear deviations from equilibrium, even at temperatures of 3,500–5,500 K.

In previous modeling (e.g., Berthelot and Bogaerts, 2017; Heijkers and Bogaerts, 2017; Sun et al., 2017; Kotov and Koelman, 2019) and experiments (e.g., Bongers et al., 2017), suggestions were provided on how the vibration-induced pathway could be exploited to optimize the energy efficiency at practical MW and GA conditions. For instance, Bongers et al. (2017) studied CO_2 dissociation in a vortex-stabilized MW plasma reactor in a wide range of conditions regarding MW field, residence time, quenching, and vortex configuration. They reported that the gas temperature was above 4,000 K, confirming dominant thermal CO_2 dissociation, and they suggested strategies to enhance the conversion and energy efficiency. At that time, the general aim was still to exploit the VT non-equilibrium for maximum energy efficiency. The authors claimed that the temperature during the plasma must be as low as possible to reduce vibrational energy losses via VT relaxation, and they suggested that future experiments should focus on reducing the reduced electric field values to maximize the vibrational excitation, e.g., by increasing the MW cavity dimensions, and on reducing the gas temperature by lowering the temperature of the injected gas.

However, in recent years, there is growing insight that optimizing the vibration-induced dissociation pathway may not be the most realistic strategy. In fact, experiments indicate that thermal CO_2 conversion gives rise to quite high energy efficiencies (up to 40–50%) (van Rooij et al., 2015; Bongers et al., 2017; den Harder et al., 2017; van den Bekerom et al., 2019; Wolf et al., 2019, 2020). Indeed, the rate coefficients of thermal reactions increase with gas temperature, thus enhancing the conversion. It was claimed (Wolf, 2020) that temperatures around 3,000–4,000 K are optimal for thermal conversion, to realize significant CO_2 conversion at limited thermal losses. Thus, it may be wiser to focus on how to improve the energy efficiency beyond the thermal equilibrium limit instead of trying to exploit the VT non-equilibrium (van den Bekerom et al., 2019).

In the following, we first give some suggestions on how VT non-equilibrium could be exploited in theory, as this paper is meant as a perspective to give indications how to "fly toward the future" (i.e., imagine what we do not have today), but as these suggestions might not be easy to realize in practical plasma reactors, we also discuss how the energy efficiency of thermal CO_2 conversion could be further improved.

(a) Exploiting VT Non-equilibrium

Computer modeling has demonstrated that a strong VT non-equilibrium can be realized under the conditions of (i) reduced electric field values (E/n) around 50 Td (or lower), providing the most suitable electron energy for vibrational excitation; (ii) sufficient power density to create enough electrons available for vibrational excitation; (iii) low gas pressure; and (iv) low gas temperature, to limit the process of VT relaxation (Berthelot and Bogaerts, 2017). We will now discuss these different conditions one by one.

First, as shown in **Figure 5** above, a reduced electric field around 50 Td is ideal for vibration-induced dissociation. While this value (or slightly higher) is reported for MW and GA plasmas, which may explain their higher energy efficiency (see section Different Dissociation Mechanisms in Different Plasma Types), DBD plasmas operate at higher E/n values. Thus, it would be of great interest if the reduced electric field in DBD plasmas could be lowered to values below 100 Td.

In theory, this can be realized in two ways: by lowering the applied electric field (E) or increasing the gas number density (*n*). The applied electric field is determined by the power supply, so applying lower power to a DBD may be beneficial, although the power must still be high enough to create a stable plasma. In addition, a lower power does not necessarily create a lower electric field, as a DBD plasma (operating in reactive gases, such as CO_2, CH_4, etc.) is typically filamentary. Hence, a lower power may also manifest itself in less filaments instead of a lower electric field in these filaments (Peeters et al., 2015; Ozkan et al., 2016). Thus, it would not be straightforward to control the electric field values in a DBD plasma.

In addition, CO_2 conversion is most often performed in packed bed DBDs, in the context of plasma catalysis. Modeling has revealed that the electric field is typically enhanced at the contact points between the packing beads, resulting in a higher electron energy (Van Laer and Bogaerts, 2016). This can give rise to more electron impact electronic excitation, ionization, and dissociation for the same applied power as in a non-packed DBD reactor, explaining the higher energy efficiency of CO_2 conversion in a packed bed DBD than in a non-packed reactor, at least when the effect is not compensated by the shorter residence time of the gas in the reactor due to the presence of the packing (Mei et al., 2015; Van Laer and Bogaerts, 2015; Zeng et al., 2015; Michielsen et al., 2017; Uytdenhouwen et al., 2018). However, the enhanced electron energy will give rise to less vibrational excitation, hence this effect is the opposite of exploiting conditions for enhancing the vibration-induced dissociation pathway. In other words, it is not clear whether a lower electric field, which is more suitable for vibrational excitation, can effectively be realized in a DBD.

Recent modeling, albeit in N_2 plasma, has however indicated that vibrational excitation may be important in DBD, mainly in between the microdischarge filaments (so-called afterglows, characterized by lower E/n), and even inside the filaments, depending on how the power is distributed among the filaments and the afterglows (van 't Veer et al., 2020). Because it would be highly beneficial to realize VT non-equilibrium in DBD plasmas operating in CO_2 as well, the effect of power introduction (and distribution) in DBD plasmas should be thoroughly investigated and verified experimentally, with the aim to optimize the E/n and thus the role of vibration-induced dissociation.

On the other hand, as mentioned above, the reduced electric field can also be lowered by a higher gas number density, and this should be easier to realize, i.e., by applying a higher gas pressure (above 1 bar). This was for instance demonstrated by Belov et al. (2017), resulting in a higher CO_2 conversion at 1.5 bar compared to 1 bar (30% vs. 25%). However, a further increase in pressure did not result in a higher CO_2 conversion because other effects play a role as well, as the higher pressure also resulted in more intense but fewer microdischarge filaments. In general, however, it is not the number of filaments that defines the efficiency, but their characteristics (in terms of average electric field and thus average electron energy). Thus, more intense filaments, with higher electric field, would give rise to less vibrational excitation. In addition, it should be realized that a higher pressure (or gas number density) would increase VT relaxation, but we expect this to be less critical as the gas temperature in DBD plasmas is typically not much above room temperature, and the rate coefficients of VT relaxation rise with temperature, so this process is probably not critical at typical DBD temperatures. A more obvious problem would be that a higher gas number density would also increase the required electric field strength to ignite and sustain the discharge, and thus the net E/n may be the same, as the higher electric field (E) would compensate for the higher gas number density (n).

Second, another way to enhance vibration-induced dissociation could be to apply a higher power density in MW or GA plasmas, as this will produce more electrons, which can give rise to more electron impact vibrational excitation, leading to a more pronounced overpopulation of the higher vibrational levels as predicted by modeling (Berthelot and Bogaerts, 2017). As illustrated in **Figure 7**, at low gas temperature (300 K), the

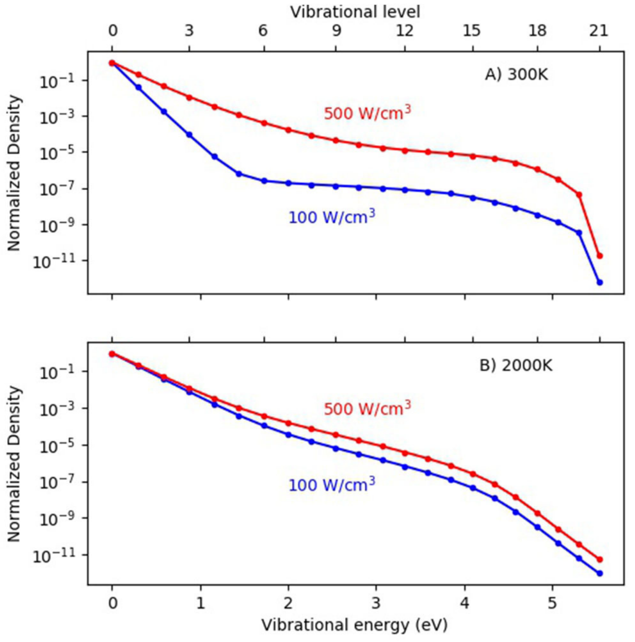

FIGURE 7 | Calculated vibrational distribution functions (VDFs) in a MW plasma, for a gas temperature of 300 K **(A)** and 2,000 K **(B)** and a pressure of 100 mbar, at two different power densities. Adopted from Berthelot and Bogaerts (2017) with permission.

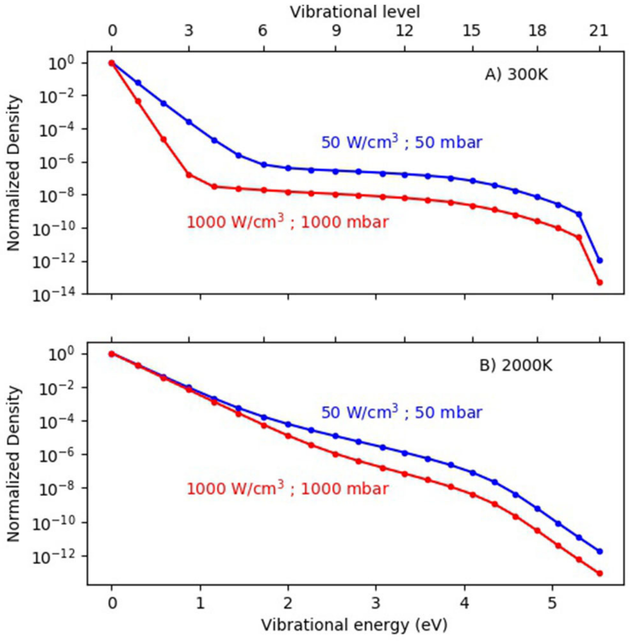

FIGURE 8 | Calculated vibrational distribution functions (VDFs) in a MW plasma, for a gas temperature of 300 K **(A)** and 2,000 K **(B)**, at two different pressures and power densities. Adopted from Berthelot and Bogaerts (2017) with permission.

VDF is clearly non-thermal, with strong overpopulation of the higher vibrational levels, especially at high power density. At 2,000 K, the effect of power density is less pronounced, but still the VDF is higher at higher power density. However, it must be mentioned that a higher power density will not only enhance the vibrational excitation, but also electronic excitation, ionization, and dissociation, which are not beneficial for energy-efficient CO_2 conversion. Even more, a higher power density will enhance the electron temperature, thereby promoting electronic excitation, ionization, and dissociation, above vibrational excitation. In addition, a higher power density will enhance the gas temperature, leading to more VT relaxation, which is detrimental for vibration-induced dissociation. Thus, in the ideal case of strong VT non-equilibrium, a high power density must be accompanied by a controlled (low) gas temperature (see also below). This is, however, very difficult to realize in practice. Note that the VDFs plotted in **Figure 7** were obtained from non-self-consistent model calculations to evaluate the effect of individual parameters. The gas temperature was fixed, and was thus not rising with power, as would be expected from self-consistent calculations.

Third, a lower gas pressure will give rise to less VT relaxation due to a lower number density of gas molecules, and thus it will also result in a more pronounced overpopulation of the higher vibrational levels, as again predicted by modeling (see **Figure 8**; Berthelot and Bogaerts, 2017). This will yield a larger contribution of the vibrational dissociation pathway, and thus more energy-efficient CO_2 conversion, as claimed already back in the 1980s, for low pressure MW plasmas (Legasov et al., 1978; Asisov et al., 1983; Fridman, 2008). This also explains why most studies on the vibrational kinetics in CO_2 plasmas (both experimental and computational) in the last decade were performed at reduced pressure (see references in section Different Dissociation Mechanisms in Different Plasma Types). However, a low pressure is less valuable for industrial processes, and the additional cost of pumping should also be accounted for in determining the overall energy cost or energy efficiency of the process.

Fourth, a lower gas temperature will also limit VT relaxation, and thus promote the VT non-equilibrium, as mentioned above. However, it should be realized that the gas temperature in the plasma typically follows from the applied power and the various chemical reactions, and cannot easily be controlled. A reduced pressure typically gives rise to a lower gas temperature due to reduced VT relaxation (see above), but operation at atmospheric pressure is preferable from industrial perspective, as discussed above. Gas cooling could be applied, but it would also increase the overall energy cost.

A promising way to control the gas temperature is by applying pulsed power with a suitable duty cycle. Model calculations have revealed that the ideal pulse-on time is around 40–100 µs, with a pulse-off time of 100 ms and above, at a reduced pressure of 100 mbar (see **Figure 9**; Vermeiren and Bogaerts, 2019). Indeed, the pulse-on time should be long enough to reach a high vibrational temperature (i.e., allowing enough time for the VDF to build up to the highest levels), but not too long to

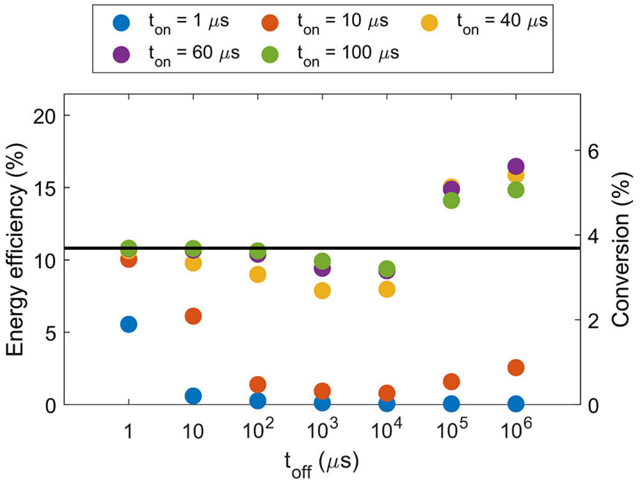

FIGURE 9 | Calculated energy efficiency and conversion in a pulsed MW plasma, as a function of interpulse time (t_{off}), for five different pulse-on times (t_{on}), at an SEI of 1 eV/molec and a pressure of 100 mbar. The horizontal line represents the conversion and energy efficiency of a continuous plasma at the same SEI value. Adopted from Vermeiren and Bogaerts (2019) with permission.

avoid having the gas temperature rise as well. The characteristic timescale for VV relaxation is indeed much shorter than for VT relaxation, at least at temperatures below 2,500 K, and thus the vibrational temperature rises faster than the gas temperature (Vermeiren and Bogaerts, 2019). In addition, the pulse-off time should be long enough so that the gas temperature can cool down again before the next pulse starts, although it should be realized that for too long pulse-off time, the CO_2 gas would not experience enough pulses within its residence time in the plasma for sufficient dissociation.

van den Bekerom et al. (2019) performed very interesting experiments on a 100 µs pulsed MW plasma in CO_2 at 25 mbar, 2.45 GHz, and up to 600 W peak power. The duty cycle was kept below 1% to ensure a low gas temperature at the discharge onset. Raman and Rayleigh scattering yielded space- and time-resolved vibrational, rotational, and gas temperatures. During the first 40 µs, the authors found a significant inter-vibrational non-equilibrium, with the temperature of the symmetric stretch and bending modes around 750 K and the temperature of the asymmetric stretch mode (generally known to be important for vibration-induced dissociation of CO_2) around 1,150 K. In addition, they observed a maximum rotational-vibrational non-equilibrium after 60 µs, in which the rotational temperature was about half the vibrational temperature of the asymmetric stretch mode (1,150 K). The rotational and translational temperatures were found to be in equilibrium at all times. Thus, in agreement with the model predictions of Vermeiren and Bogaerts (2019), the authors reported a VT non-equilibrium for the entire pulse duration (100 µs) in this 25 mbar pulsed MW plasma with small duty cycle (below 1%), albeit less predominant than often assumed.

Finally, another way to limit the gas heating, which causes at the same time a pressure drop, can be realized by using a Laval nozzle, yielding supersonic expansion of the gas. In this way, the inlet and outlet pressure can still be atmospheric (or above), being compatible with industrial operations. Modeling has indeed predicted that supersonic expansion leads to a pronounced non-equilibrium VDF (see **Figure 10**, Vermeiren and Bogaerts, 2018), hence promoting vibration-induced dissociation, but the gas pressure and temperature rise again after the shockwave and the VDF becomes thermal (cf. **Figure 10**), thus limiting the overall enhancement in energy efficiency. However, if the supersonic expansion region could be extended over a longer distance, the vibrational dissociation pathway could be further enhanced, thus improving the energy efficiency. As mentioned in section Different Plasma Types—Different Performance, the best energy efficiency ever reported for plasma-based CO_2 conversion, 90%, was for a MW plasma with supersonic expansion back in 1983 (Asisov et al., 1983), but these results have never been reproduced since then, as they are probably critically dependent on the exact operating conditions. Therefore, more experiments should be performed to optimize the conditions and plasma reactor/Laval nozzle design in order to maximize the supersonic region, and to reach the highest possible CO_2 conversion and energy efficiency.

(b) Improving the Energy Efficiency of Thermal CO_2 Conversion

The above suggestions to improve the energy efficiency by promoting the vibrational dissociation pathway are not straightforward to realize in practice. Indeed, recent insights based on both modeling and experiments have revealed that the CO_2 conversion in (sub)atmospheric pressure MW and GA plasmas proceeds by thermal reactions (van Rooij et al., 2015; Berthelot and Bogaerts, 2017; Bongers et al., 2017; den Harder et al., 2017; Heijkers and Bogaerts, 2017; Kotov and Koelman, 2019; van den Bekerom et al., 2019; Wolf et al., 2019, 2020), and this can also give rise to quite high energy efficiencies (up to 40–50%). As explained above, the rate coefficients of the thermal reactions between various plasma species rise upon higher gas temperature, thus enhancing the conversion. Temperatures around 3,000–4,000 K should be optimal for thermal conversion to realize significant CO_2 conversion and still limit thermal losses (Wolf et al., 2020). In this section, we provide some suggestions how to further improve the energy efficiency of thermal CO_2 conversion beyond the thermal equilibrium limits of 45–50%.

A limitation for energy-efficient CO_2 conversion at thermal conditions is the backward (recombination) reaction of CO with O atoms or O_2 molecules forming CO_2 again, as these recombination reactions also become faster at higher temperature. Fast quenching (cooling) of the gas after passing through the plasma reactor can limit these backward reactions, and should therefore be extensively investigated. Yang et al. (2018) demonstrated the effects of supersonic quenching for a thermal CO_2 plasma. The supporting computational fluid dynamics calculations revealed a fast quenching rate of 10^7 K/s, causing the gas temperature to drop from above 3,000 K to 1,000 K. The quenching method was based on (i) adiabatic expansion of the gas in a converging nozzle, yielding acceleration to sonic speed, or conversion of thermal energy into convective

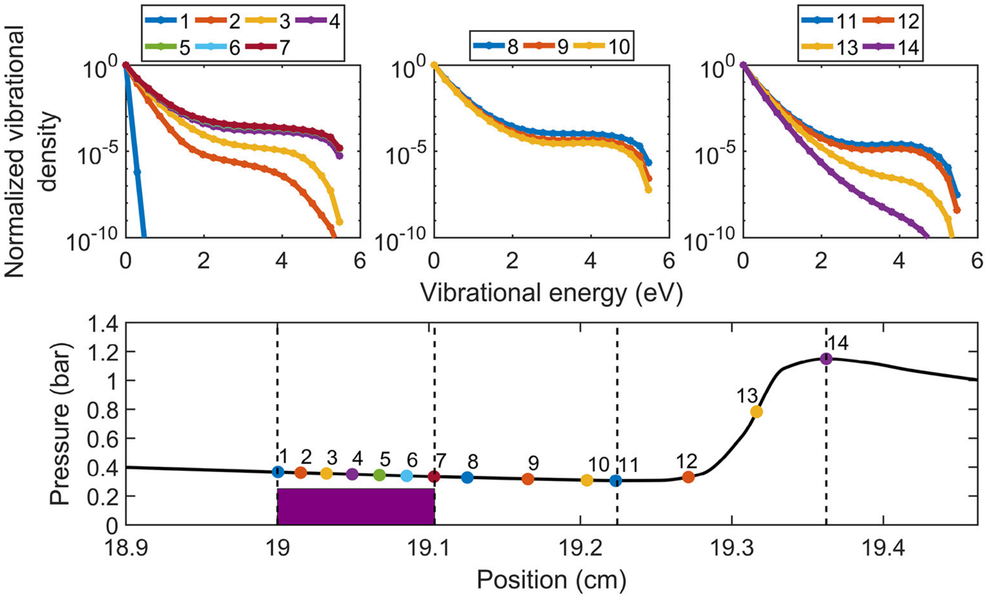

FIGURE 10 | Calculated evolution of the VDF in a MW plasma with Laval nozzle for supersonic expansion, for different axial positions, as indicated in the lower panel, showing the pressure evolution as a function of position in the supersonic expansion region and shock wave, for an SEI of 0.2 eV/molec, an inlet and outlet pressure of 2 and 1 bar, respectively. Adopted from Vermeiren and Bogaerts (2018) with permission.

kinetic energy, followed by (ii) a cooling tube in which strong eddies are formed, greatly enhancing the heat transfer between the inverse-flowing fluid and the cooling tube. This quenching prevents the reverse reactions, enhancing the CO_2 conversion and energy efficiency (so-called ideal quenching).

In addition, a beneficial side-effect of the quenching would be if the heat removed from the outflowing gas mixture due to the quenching/cooling process can be recovered to preheat the incoming gas so that the plasma power will not be used for initial heating the gas, and can be directly used for the conversion. We believe this could also improve the overall efficiency.

Another possibility to avoid the backward (recombination) reactions, in order to enhance the conversion and energy efficiency, may be the fast removal of the O atoms from the mixture. This was demonstrated by modeling in a classical GA plasma (Sun et al., 2017), but also experimentally for a thermal arc plasma (Liu P. et al., 2019), using a carbon bed after the plasma reactor, reporting a CO_2 conversion of 67–94% with corresponding energy efficiency of about 70%, much higher than ever observed in other (non-thermal or warm) plasmas. Likewise, Mori et al. integrated a solid oxide electrolysis cell (SOEC) into a plasma reactor to remove the O atoms, and thus avoid the recombination reaction. They demonstrated this concept for a DBD and showed significant enhancement of the CO_2 conversion, even up to 100% at 700°C (Mori et al., 2016).

Vice versa, yet another interesting idea to enhance the conversion and energy efficiency above the thermal equilibrium limit exploits the O atoms, formed by CO_2 splitting, to react with another CO_2 molecule ($CO_2 + O \rightarrow CO + O_2$) instead of recombining with CO. This is called "super-ideal quenching," and makes full use of the dissociation products. As mentioned above, however, this reaction has a significant energy barrier, which was pinpointed as the major limiting factor for energy-efficient CO_2 conversion, not only in thermal conversion, but also in case of vibration-induced dissociation; cf. above (Berthelot and Bogaerts, 2018). Thus, conditions should be explored to enhance this reaction, e.g., by vibrational excitation of CO_2, because the latter could reduce the energy barrier of this reaction.

As discussed before, the theoretically highest energy efficiency, induced by the vibrational pathway at VT non-equilibrium conditions, may not (easily) be realized in (sub)atmospheric MW and GA plasmas. However, in case of thermal CO_2 conversion, we can focus on the cooler regions outside the hot plasma zone in order to exploit the vibrationally excited CO_2 molecules to overcome the high energy barrier of the recombination with O atoms (super-ideal quenching), thus enhancing the CO_2 conversion above the thermal limit.

van den Bekerom et al. (2019) studied in detail the gas heating dynamics and their relation to the CO_2 dissociation efficiency in a pulsed CO_2 MW plasma at a pressure range of 30–160 mbar, and duty cycle of 20–100%. They reported rotational (or gas) temperatures up to 3,000 K in the core, with a cool edge temperature around 500 K. After the pulse, the gas cooled down convectively, but it was found to remain overall too hot for strong overpopulation of the vibrational modes (still 2,200 K in the core). Because the CO_2 dissociation was observed to scale with the observed peak rotational temperature, the authors concluded that thermal processes dominate.

They explained the separation between hot core and cool edge by the tangential gas injection yielding a swirl flow, causing recirculation zones with closed flow lines where the gas can only enter or exit by diffusion. This transport barrier is thought to be responsible for the steep temperature gradient between hot plasma core and cool edge, with only the hot core being heated by the MW power. This core temperature is stated to rise rapidly until equilibrium is reached between input MW power and diffusion. Note that other papers by different researchers also reported similar behavior. Typically, three different operating regimes could be distinguished for (sub)atmospheric MW plasmas (i.e., diffuse and two different constricted modes) depending on pressure (e.g., den Harder et al., 2017) and the constricted regimes were studied in detail by Wolf et al. (2019, 2020), who also confirmed the dominance of thermal dissociation.

van den Bekerom et al. (2019) discussed in detail how to increase the energy efficiency beyond the thermal equilibrium limit, focusing on the role of the edge region around the hot plasma core. Indeed, the gas that diffuses out of the hot core arrives in the stream of cold gas in the edge region, where it is subject to fast quenching. This means that the backward (recombination) reactions of CO and O to form CO_2 again are strongly diminished by the drop in temperature, and the high temperature CO_2 conversion remains frozen (ideal quenching).

In addition, although at thermal conditions there is no overpopulation of the CO_2 vibrational levels (i.e., the VDF follows a Boltzmann distribution), a significant amount of energy is still stored in the vibrational levels because of the high temperature in the core. When the hot CO_2 molecules diffuse out of the core, a VT non-equilibrium can be established because VT relaxation is much slower in the cooler edge.

If the quenching is fast enough, the O atoms do not recombine into CO or O_2, but survive and can react in the cold gas stream with the vibrationally excited CO_2 molecules to produce additional CO. The recycling of O atoms through reaction with vibrationally excited CO_2 molecules was also suggested by Silva et al. (2017) in a MW post-discharge. As mentioned above, this reaction has a high activation energy, but it may indeed be overcome by either hot O atoms or the vibrationally excited CO_2 molecules (Berthelot and Bogaerts, 2018). This super-ideal quenching may explain the energy efficiencies above the thermal equilibrium limits reported in the 1980s (Legasov et al., 1978; Asisov et al., 1983).

van den Bekerom et al. (2019) concluded that the research focus should shift from the core—which is in thermal equilibrium at the high temperature—to the cooler edge region, to investigate how effective is the latter in quenching products from the hot core to further enhance the energy efficiency above the thermal equilibrium limit. Although this study was applied to reduced pressure MW plasmas, the same concept may be valid to GA plasmas, where the hot arc region (ca. 3,000 K; Trenchev et al., 2017) is surrounded by cooler gas. Thus, the above suggestions should also be explored in detail for GA plasmas.

Likewise, besides unreacted CO_2 coming from the hot plasma, adding extra CO_2 in the post-conversion cooling zone could also be beneficial because (i) the cold CO_2 gas can enhance the cooling rate and suppress the back-reaction by dilution, and (ii) it can enhance CO formation upon reaction with O atoms.

In general, we may conclude that the conditions outside the hot plasma zone or the post-discharge recombination kinetics, rather than the plasma condition itself, are the key for optimization of energy-efficient CO_2 conversion. Maybe these phenomena will be able to explain the record energy efficiencies observed in the 1980s (Legasov et al., 1978; Asisov et al., 1983).

Improving the Conversion

The above suggestions to improve the energy efficiency will at the same time enhance the conversion as well. In addition, we believe the conversion can be further improved by smart plasma reactor design, i.e., by increasing the number of molecules passing through the active plasma region. Modeling has indeed identified this fraction as the limiting factor for the conversion in GA plasmas. This is the case both in classical GA reactors (Sun et al., 2017), but also in the GAP, because the arc plasma is not filling the entire plasma reactor but is only located in the center, thus not all of the gas will pass through the plasma (Ramakers et al., 2017; Trenchev et al., 2017). Furthermore, it can also be a limiting factor in MW plasmas at atmospheric pressure or in APGDs due to plasma contraction in the center (Trenchev et al., 2019; van den Bekerom et al., 2019; Wolf et al., 2019, 2020). Thus, even if the conversion is close to 100% inside the plasma, if only a certain fraction of the gas passes through the plasma, the latter determines and limits the overall conversion in the reactor, unless significant thermal conversion still occurs in the region around the plasma if the latter is still at high enough temperature, as demonstrated for DRM (Cleiren et al., 2017; Slaets et al., 2020), or the edge region contributes to further conversion by the reaction of O atoms with unreacted CO_2, as discussed in the previous section (van den Bekerom et al., 2019).

Major efforts are needed to enhance the processed gas fraction by smart reactor design, including gas inlet/outlet design. An example is shown in **Figure 11**, for CO_2 conversion in the GAP with different gas outlet diameters (Ramakers et al., 2017). As explained in section Different Plasma Types—Different Performance above, the gas enters the reactor tangentially, and when the reactor diameter is larger than the outlet diameter, the gas flows initially in an outer vortex toward the upper end of the reactor, after which it follows a reverse vortex with smaller diameter toward the outlet (see **Figure 1D** above). In the ideal scenario, this reverse vortex coincides with the arc in the middle of the reactor to maximize the conversion. **Figure 11** indeed illustrates that the reactor with the smallest outlet diameter yields the best conversion and energy efficiency, much greater than when the outlet diameter is the same as the reactor diameter, as the latter does not allow a reverse vortex gas flow to take place. Nevertheless, even for the smallest outlet diameter, the gas fraction that passes through the arc is still quite limited, and this explains the rather low overall CO_2 conversion in this reactor. In addition, the gas temperature is quite high (∼3,000 K; Trenchev et al., 2017) due to a hot cathode spot, which also causes severe electrode degradation. This clearly stresses the need for further reactor design improvements.

Figure 12A presents an innovative electrode design to improve the conversion capability of the GAP reactor by elongating the arc in two directions to increase the residence time of the gas inside the arc and to actively cool the cathode spot by rotation of the arc and gas convection. This novel reactor, called dual-vortex (GA) plasmatron (DVP), yields strong

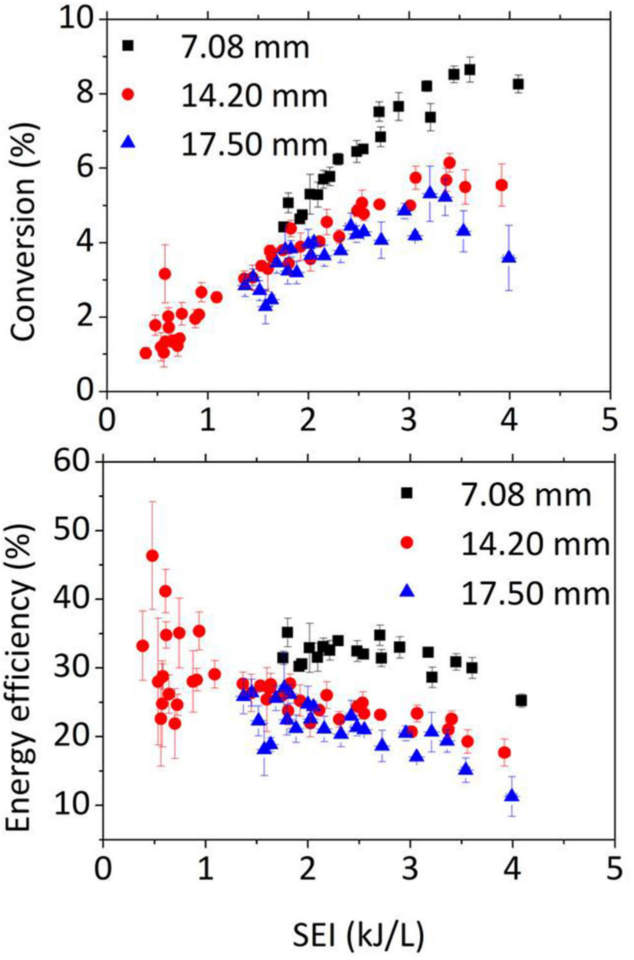

FIGURE 11 | Measured conversion and energy efficiency as a function of SEI, in a gliding arc plasmatron (GAP) at atmospheric pressure, for three different reactor outlet diameters, as indicated by the legend. Adopted from Ramakers et al. (2017) with permission.

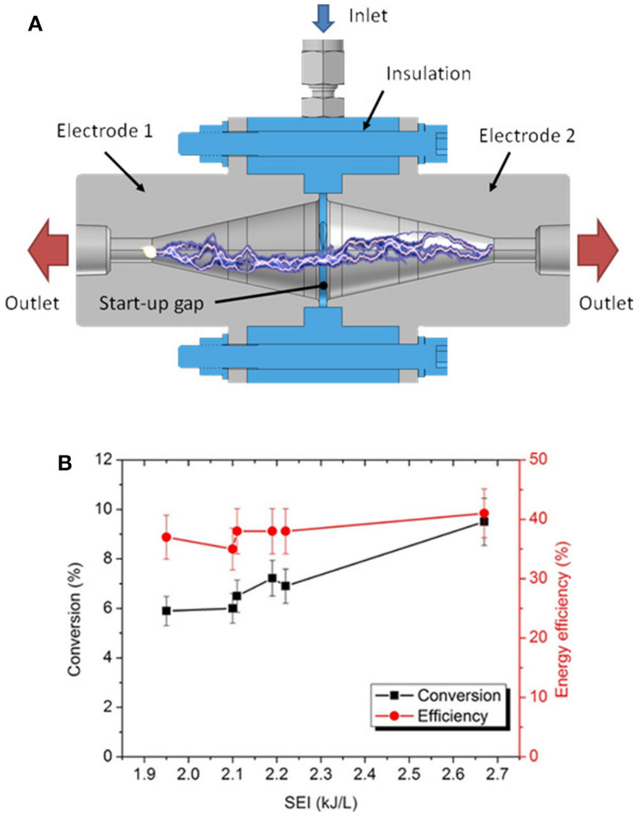

FIGURE 12 | Schematic illustration of the dual-vortex plasmatron (DVP) design **(A)**, and conversion and energy efficiency obtained in this setup, at atmospheric pressure, as a function of the SEI **(B)**. Adopted from Trenchev and Bogaerts (2020) with permission.

rotational gas flow up to the electrode outlets, as demonstrated from fluid dynamics simulations (Trenchev and Bogaerts, 2020). This allows rotating the cathode (or anode) hot spots, reducing electrode damage. The CO_2 conversion was found to be around 9%, with a corresponding energy efficiency up to 41%, for a gas flow rate of 10 L/min and a plasma power of 446 W, yielding a specific energy input of 2.7 kJ/L (**Figure 12B**). It should be noted that the conversion obtained in this study was still limited, attributed to the power supply, which did not yield a stable plasma at gas flow rates above 12.5 L/min. In addition, no stable plasma could be obtained for SEI values between 2.2 and 2.7 kJ/L (cf. **Figure 12B**). Model calculations predicted that a higher flow rate of 20 L/min would greatly reduce the gas temperature, due to strong turbulent heat transfer. While the conversion is thermal in this GA plasma, a lower temperature might shift it to the non-equilibrium regime, where the vibrational pathway of CO_2 dissociation could be promoted (see discussion in section Improving the Energy Efficiency). However, it is also very likely that the temperature would still be high enough for thermal conversion to dominate. On the other hand, a lower temperature could further cool the cathode spot, and thus reduce electrode degradation, which would be beneficial. Future work will thus require building a novel power supply to produce higher power values and to allow stable plasma operation at higher flow rates in order to evaluate whether this can further enhance the performance of the DVP.

Another example of plasma reactor design improvement to enhance the CO_2 conversion based on fluid dynamics simulations is given in **Figure 13** for an APGD reactor (Trenchev et al., 2019). The basic APGD reactor has a pin-to-plate design with simple gas inlet, as illustrated in **Figure 13A**. It exhibits an overall CO_2 conversion of only 3–4.5% (see **Figure 13D**), which could be explained by modeling, as the plasma was confined to the center of the reactor. The conversion inside the plasma was calculated to be 75%, but the overall conversion was much lower due to the limited fraction of gas passing through the plasma. The energy efficiency is around 30% (see **Figure 13D**), and modeling indicated that the conversion is thermal, and the VDF is Boltzmann-distributed.

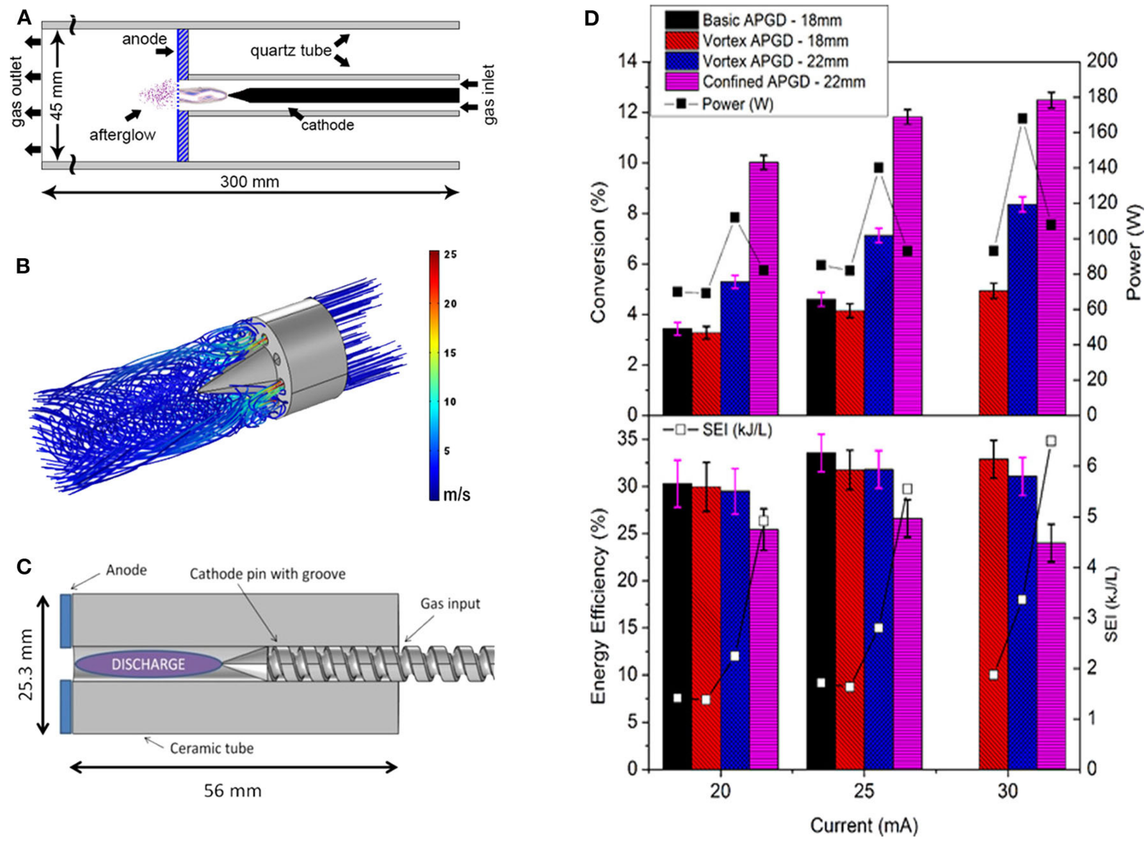

FIGURE 13 | Schematic illustration of the basic **(A)**, vortex **(B)**, and confined **(C)** APGD designs, as well as **(D)** conversion and energy efficiency obtained in these setups, at atmospheric pressure, at three different currents. The plasma power and corresponding SEI are also illustrated in **(D)**. Adopted from Trenchev et al. (2019) with permission.

Figure 13B illustrates calculated gas flow pathlines from fluid dynamics simulations in a modified setup by employing a vortex flow generator. This vortex flow reduces the cathode temperature due to turbulence, and thus enables operation at higher power with longer interelectrode distance (22 mm instead of 18 mm in the basic design) without melting. In addition, the turbulence allows somewhat more gas to pass through the plasma. Both effects lead to a longer residence time of the gas in the plasma and to a higher conversion of about 8% at the longer interelectrode distance of 22 mm (**Figure 13D**). The high gas temperature again yields a thermal VDF, with an energy efficiency around 30%.

To further enhance the gas fraction passing through the plasma, a "confined" configuration was designed, based on a ceramic tube with inner radius of 2.5 mm (i.e., equal to the plasma radius, predicted by the model) that fits precisely with the cathode pin (see **Figure 13C**). By means of a spiral groove in the cathode pin, the gas could be guided into the tube. In addition, the groove yielded cooling of the cathode pin, preventing it from melting, so that again a higher power could be used. This confined design makes sure that the plasma fills the entire reactor, and thus all the gas molecules pass through the plasma, resulting in a higher conversion of up to 12.5%. The downside is that the plasma is now in direct contact with the walls, resulting in heat losses and loss of plasma species toward the walls. Therefore, the energy efficiency is slightly lower than in the basic and vortex flow APGD, ca. 26%. However, the conversion enhancement is much more prominent, being three times higher than in the basic APGD and one and a half to two times higher than in the vortex flow design. Further improvements should be possible by keeping the concept of the confined configuration in combination with turbulence and reducing the heat losses toward the walls. Fluid dynamics simulations will be very useful to further guide the experimental reactor design improvements.

Improving the Selectivity

Finally, besides improving the conversion and energy efficiency, there is significant room for improvement in the field of plasma catalysis for the selective production of value-added compounds. Indeed, as mentioned in section Different Plasma Types—Different Performance, plasma is very reactive, but therefore it is not selective in the production of targeted compounds. If high value products, such as olefins and oxygenates, could be selectively formed in a one-step process by plasma catalysis, the high energy cost of current DBD reactors would be less of a limitation because in classical DRM, syngas also needs to be further converted into higher value products, by Fischer-Tropsch or methanol synthesis, which also adds to the overall energy cost of production. In the past, plasma catalysis experiments mainly used thermal catalysts, which are not necessarily most suitable for combination with plasma. Indeed, plasma is characterized by many reactive species, such as vibrationally and electronically excited molecules, radicals, ions, and electrons, which will affect the catalytic reactions. Therefore, special catalysts must be designed and tailored to the plasma environment to fully exploit the potential of plasma catalysis.

While in conventional heterogeneous catalysis, reactants chemisorb and follow some surface-mediated reaction path that ultimately determines the products formed and their formation rates; plasma causes external activation of the reactants, providing extra possibilities. Thus, other research questions should be answered, e.g., how can the catalyst interact with these highly reactive/energetic plasma species without simply quenching them, and how can it provide a selective path of transformation? A further complication is that the plasma may also transform the catalyst, both structurally and compositionally, and it may modify intrinsic surface reaction rates and/or pathways through for instance charging or electric field effects.

For plasma-catalytic NH_3 synthesis, microkinetic modeling demonstrated the effect of plasma-induced (vibrational) excitation of N_2 molecules, for enhanced NH_3 production at conditions that are thermally inaccessible, and also predicted that the optimal catalytic material (the "peak" in the so-called volcano plot) was shifted to materials with lower N binding energy, consistent with experimental observations (Mehta et al., 2018). This indicates that plasma-activation of N_2, e.g., by vibrational excitation, can overcome typical classical NH_3 synthesis scaling relations. In other words, the plasma can overcome the usual constraints of catalysts to have a low activation energy for N_2 dissociation and at the same time a weak interaction with surface intermediates, needed for easy desorption. Hence, this illustrates the great potential of plasma-catalytic NH_3 synthesis. Similar effects were recently predicted by microkinetic modeling for non-oxidative methane coupling by plasma catalysis, showing the role of both vibrational excitation and plasma radicals in enhancing plasma-catalytic reactions (Engelmann et al., 2020), and we may expect similar behavior for plasma-catalytic CO_2 conversion with a H-source (e.g., CH_4, H_2O, or H_2) as well. Mehta et al. recently reviewed the impact of plasma-catalytic DRM, highlighting the potential of plasma catalysis to allow chemical conversion at lower temperatures where thermally no conversion is expected (Mehta et al., 2019).

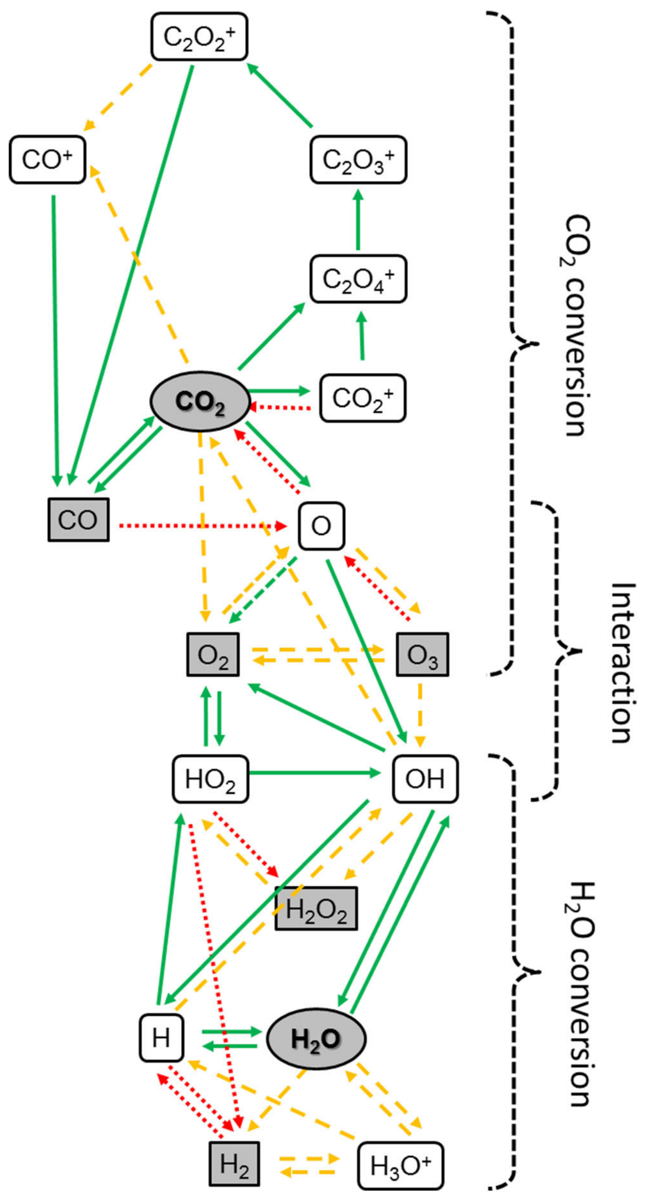

FIGURE 14 | Main reaction pathways for CO_2 and H_2O conversion in a DBD plasma. The arrow lines denote the formation rates of the species, with full green lines being formation rates over 10^{17} $cm^{-3} \cdot s^{-1}$, orange dashed lines between 10^{17} and 10^{16} $cm^{-3} \cdot s^{-1}$ and red dotted lines between 10^{16} and 10^{15} $cm^{-3} \cdot s^{-1}$. Adopted from Snoeckx et al. (2017) with permission.

Besides the beneficial effects of plasma activation for enhanced catalytic reactions, catalysts may in turn also help to overcome current limitations in plasma-based CO_2 conversion. This can be illustrated for the combined CO_2/H_2O conversion, where 1–2% of H_2O addition already result in much lower CO_2 conversion, corresponding to a much lower energy efficiency, than for pure CO_2 conversion. In addition, H_2 and CO were detected as the main products, and virtually no oxygenates were formed (Snoeckx et al., 2017). Indeed, modeling revealed that too many steps would be needed in plasma-based conversion without catalysts, all these steps require H atoms, and the latter react predominantly with OH into H_2O or with O_2 into HO_2, which again produces H_2O, as demonstrated in **Figure 14**. This also explains the low amount of H_2O conversion in plasma. In addition, the OH radicals exhibit a fast reaction with CO into CO_2, as predicted in the model, and this explains why the CO_2 conversion is significantly lower upon H_2O addition. Thus, it is clear that catalysts are needed to enable that CO and H_2 formed in the plasma react into oxygenates. More specifically, the binding of the reactants at the catalyst surface must proceed faster than the recombination of OH with H atoms into H_2O, as well as of OH with CO into CO_2.

By combining a CO_2/H_2 DBD with $CuO/ZnO/Al_2O_3$ catalyst, Eliasson et al. (1998) obtained a methanol yield and selectivity more than ten times higher than without catalyst. We may expect similar effects for a CO_2/H_2O DBD because it also forms a $CO/CO_2/H_2$ mixture. Furthermore, a CO_2/H_2O MW plasma with NiO/TiO_2 catalysts resulted in a rise in CO_2 conversion (up to 48%), with energy cost of 14.5 eV/molec (Chen et al., 2017) (cf. best data point in **Figure 4** above). This was explained by the fact that CO_2 molecules adsorb at oxygen vacancies in the catalyst surface, which lowers the threshold for dissociative electron attachment of CO_2 into adsorbed O atoms at the vacancies and CO molecules. Subsequently, the O atoms can recombine with gas phase O atoms or OH radicals into O_2 (and H atoms). Thus, the catalyst lets the O atoms or OH radicals from the plasma react into O_2, with help of surface-adsorbed O atoms, before they would react into CO_2 and H_2O, which is stated to be the major problem in CO_2/H_2O plasmas without catalysts. Nevertheless, the catalyst in this work could only improve the CO_2 conversion and energy cost, but did not allow the selective production of oxygenates.

Clearly, major research efforts are needed, including *in situ* and *operando* surface characterization and carefully designed experiments to isolate specific contributions from plasma and catalyst, as well as microkinetic modeling, to improve our insights in the mutual interactions between plasma and catalysts, for rational design of specific catalysts. Achieving control over the selectivity is clearly frontier research. It requires to go beyond the current approach in considering how to realize the synergy between plasma and catalysis. This is the objective of the ERC Synergy grant SCOPE (810182).

BENEFITS FOR OUR LIFE AND IMPACT ON CLIMATE CHANGE

After having introduced the general aspects and current prospects and gaps in plasma technology for CO_2 conversion, and having shortly compared plasma technology with the alternative technologies for CO_2 conversion (introduction, further aspects in the other contributions to this special issue), the aim of this section is to put plasma technology in the general context of the changing scenario of energy and chemistry transition. This is a complementary section to the other sections that will only in part discuss the specific case of plasma, because it is aimed to give a window on the future to understand better the directions, aims, and challenges of plasma technology beyond the technical aspects.

In general, the chemical and the process industries are crucial components of most of the value chains that allow a considerable improvement in the quality of life realized in the last century by delivering the goods and services needed to our society. The materials produced were enabling factors in many relevant societal aspects, including housing, mobility, communication, health, and food. Last but not least, these industries are crucial to create prosperity. The process industry sector in Europe, for example, creates many jobs (currently 6.3 million directly and 19 million indirectly) and contributes to the GDP (€565 billion/year); it drives innovation, and develops solutions for societal problems (European Commission, 2018). On the other hand, there is a loss of competitiveness in some geographical areas, such as Europe, in favor of emerging areas, such as Asia, and at the same time an increasing social pressure to reduce the environmental impact of this sector. In a globalized world, some of the old economic instruments such as depreciation are no longer valid, and thus there is increasing awareness that different approaches have to be pursued.

The European Green Deal, launched in December 2019 as a large initiative aimed to mobilize over one trillion Euro resources in the next decade, aims to transform the European Union into a modern, resource-efficient, and competitive economy. Thus, the aim is to use the environmental challenge (no net GHG emissions by 2050) to create innovation and industrial competitiveness, and thus combine the three faces of sustainability (economy, social growth, and environmental preservation). This is possible by a revolutionary rather than evolutionary approach, having science and technology at the core and as drivers for development. With the new targets in GHG emissions indicated at political level, disruptive technologies are needed, rather than a continuation of ongoing initiatives. Plasma technology for CO_2 utilization has many of the characteristics required, even if significant improvements are still necessary, as discussed in the previous sections, before it can pass from lab to industrial scale, or from idea to innovation. Although this is currently valid for Europe, it will likely be a drag effect on other parts of the world, with sustainability, rather than globalization, being put at the core of the strategic agenda.

The chemical and process industries always operated at the intersection of energy and resources, with the nexus between energy and chemical production being a relevant factor for the common development (Abate et al., 2015a). The ongoing energy transition (Gielen et al., 2019) has major implications on the structure of the chemical production and process industry. Together with the increasing evidence that renewable energy sources (RES) are now already the cheaper and more sustainable energy source (International Renewable Energy Agency - IRENA, 2019), and will become even more so in the near future, this allows us to predict a radical change in the actual production of chemicals and energy production, with RES becoming the backbone of our society in substitution of fossil fuels (Lanzafame et al., 2017a,b; Perathoner and Centi, 2019). This also has major implications in terms of technological perspectives (Centi and Čejka, 2019; Centi et al., 2019), because it requires developing new disruptive technologies that allow the direct use of RES for chemical production and chemical energy storage, and to close the carbon cycle. This is the reason for interest in plasma chemistry. Although it is an area known for a long time already, with many sub-sectors of application (from preparation of materials to surface treatments), the application in sectors such as chemical synthesis and energy vectors production has been limited. For a long time, it remained a niche sector, while in more recent years, an expansion of research beyond the more traditional applications can be observed. As a simple example, journals such as *Green Chemistry,* which were in the past reluctant to consider plasma chemistry as part of the portfolio of relevant technologies for green chemistry, are now open to plasma chemistry (Slaets et al., 2020). The changing scenario in chemistry asks for new technologies, and plasma technology for CO_2 conversion is one of the areas with great potential to contribute to this challenge.

Value chains will thus evolve to meet new societal demands such as climate change mitigation and prosperity, and to achieve these ambitious targets, an unprecedented wave of transformative innovation is needed. It was commented above how the "Green Deal" program in the EU is expected to enable innovation and competitiveness at the same time. Substituting current technologies based on fossil fuels with those based on RES and alternative carbon raw materials, including waste CO_2 (preferably from biogenic resources, such as fermentation and biogas processes), is a key element in this direction. This is the reason for interest in plasma technology. Even if still many challenges exist, in terms of combining an improved energy efficiency and conversion with high selectivity, and the use of more realistic operating conditions (high pressure, the presence of complex mixtures and water vapor, among other aspects), plasma technology offers also many elements of interest over alternative solutions, as commented on in the introduction.

Plasma technology, together with other technologies allowing the direct use of RES in chemical transformations (primarily electro- and photo-catalysis; Perathoner and Centi, 2019), is thus part of this technological wave of change, and in general part of the crucial technologies to convert waste CO_2 into fuels and chemicals as a more efficient and impactful way (up to an order of magnitude more effective) to store CO_2 in a more or less permanent way. Therefore, plasma technology is one of the technologies under development to contribute to substitution of the use of fossil fuels (Schlögl et al., 2018).

Next to biomass and waste, CO_2 is an alternative valuable source of carbon available in Europe and worldwide. It may be argued that the use of CO_2 would extend the use of fossil fuels, but this is true only in the outdated version of carbon capture and storage (CCS) where captured CO_2 is used for underground storage, for example in enhanced oil recovery (EOR) methods to stimulate further the extraction of oil in exhausted fields. In this case, CCS is even negative to meet societal demand of a more sustainable and low-carbon future. However, CO_2 utilization from biogenic sources together with RES has instead not only a larger impact (up to one order to magnitude) in terms of effective reduction of CO_2 equivalent emissions, but it is also a relevant way to boost the use of biomass by increasing economics and reducing the carbon footprint (Abate et al., 2015b). Thus, technologies for biogenic CO_2 conversion play a relevant role in the development of the new concept of e-refinery, and the new model of distributed (small-scale) production of energy and chemical products for a novel sustainable model of development.

Biogenic CO_2 resources also are present in emissions from municipal or agricultural/forestry waste combustion. To valorize these CO_2 resources is not only necessary to close the carbon-cycle and push a circular economy, but it can become necessary if the carbon taxes on CO_2 emissions will increase in the future, a realistic possibility considering political commitments to GHG reduction at least in some areas, such as Europe. In all of these cases, it is necessary to have technologies that are efficient at relatively small-scale with low cost of investment. Thus, new solutions with these characteristics that can take advantage of coupling with local RES availability are searched. This is another general motivation for plasma technology for CO_2 conversion.

In case of fermentation and biogas production, highly concentrated CO_2 streams are produced, which need only minor purification, and thus these streams can be directly transformed. A different case is, for example, the conversion of CO_2 present in flue gas of biomass waste combustion (e.g., from forest or agriculture production). In this case, recovery of CO_2 from the fuel gas is needed, but this is still a costly process (also from an energetic perspective). While improved technologies to recover CO_2 from flue gas are under development (Song et al., 2018), CO_2 capture will still remain an energy- and cost-intensive process. Thus, the possibility to directly use diluted concentrations of CO_2 (in the 10–30% range) would be of interest. In plasma-based CO_2 conversion, the concentration of CO_2 may not be a critical issue, but the presence of other components, like H_2O, which negatively affects the performance as commented above, is a critical issue. On the other hand, other admixtures, such as N_2, are not detrimental for CO_2 conversion, and can even enhance the conversion by chemical reactions with N_2 electronically or vibrationally excited levels (Snoeckx et al., 2016; Ramakers et al., 2019). Nevertheless, in general, from an application point of view, the development of plasma-based CO_2 conversion able to operate directly on fuel gas could be an important objective, although challenging.

This is just one example, but others can be indicated (in terms of reactor characteristics, issues related to downstream processing, safety, reliability of operations, possibility of management of fluctuations in space-velocity, temperature, and compositions, etc.) that have been considered only to a limited extent up to now, with research focused mainly on scientific rather than at technological aspects, with a view on the constraints and requirements from the application side. Putting plasma technology in this general context, as made here, also aims to focus attention on these aspects.

A general observation from this general perspective, which emerges from literature, as evidenced in the previous sections, is that there is a very large variability of the results obtained, which greatly depend on reactor typology, experimental conditions, fluid dynamics, etc. The variability in results is largely beyond that present in many other fields, for example, thermal catalysis. There are scientific motivations, as partly discussed in previous sections, but in general this variability indicates the complexity of the various factors, which can only partly be controlled. This has also major consequences for the scaling up of the results and the industrial exploitability. Today, for example, in terms of modeling a thermal catalytic fixed-bed reactor, a very simple model based on a plug-flow reactor gives a precision in terms of scalability higher than 15–20%, which is acceptable in most cases. When better precision is necessary, there are well-established reactor models which consider the presence of the catalyst, mass/heat transfer limitations, etc. Virtually, it is possible to scale-up a fixed-bed catalytic reactor from lab-scale to industrial-scale when enough precise data on the kinetics are available. Only for more complicated situations, such as for fluidized or circulating catalytic beds, or in the presence of multiphase operations, would modeling require intermediate steps of development. This is not valid for plasma technology, where upscaling is still largely empirical, like it was in the field of heterogeneous catalysis up to two to three decades ago for industrial reactor development.

Scale-up of plasma-based CO_2 conversion is thus a major issue to realize its potential social impact. The most straightforward way is by placing a large number of plasma reactors in parallel, as demonstrated already for ozone synthesis in DBD plasma reactors (Kogelschatz, 2003). However, before numbering up, current lab-scale plasma reactors may also be scaled up in size to some extent, to allow higher flow rates and power. Nevertheless, if the plasma is still confined in the center (see discussion in section Improving the Conversion), a larger reactor might lead to a larger number of molecules that may not pass through the active plasma region, therefore still limiting the conversion. As discussed above, the reactor configuration has an important effect on the performance and energy efficiency already on a lab-scale. Upscaling may thus be very difficult due to the complexity of having reliable and scalable models of plasma reactors. Although advanced modeling of the process is significantly contributing to a better understanding and control of the phenomena, the industrial realization of plasma technology for CO_2 remains a great challenge, requiring large effort.

Transferability of the results is another challenge, which requires attention to push plasma technology for CO_2 conversion (and in general for chemical synthesis) out of the specific field of interest and become one of the backbone technologies for energy/chemistry transition. Results on the comparison between CO_2 splitting and DRM reactions (**Figures 2**, **3**) are instructive and reveal again the great dependence on feed composition, besides other aspects (type of reaction, other experimental conditions, typology of experiments). While in heterogeneous catalysis some general criteria are available and allow to restrict at least the field of investigation, the complexity of plasma, and even more if combined with a catalyst, makes it not easy to predict what could be expected. Some of the background chemical and physical motivations have been discussed in the previous sections, and significant improvements have been made in the last decade. However, it still remains a challenge to predict the results for new types of applications, among which nitrogen fixation has to be mentioned for its large impact in terms of developing novel solutions for sustainable ammonia and fertilizers production (Gorbanev et al., 2020). This is an example of an area in which the developments in plasma technology are currently ahead of those obtained by, for example, electrocatalysis (Chen et al., 2020).

In conclusion, plasma-based CO_2 conversion may have a large and positive impact on the societal objective of a sustainable and low carbon future, but its industrial implementation still requires it to solve various aspects, for which only a knowledge-based approach can be effective to solve the complex phenomena discussed in the previous sections.

CONCLUSIONS

The purpose of this perspective paper is to explain why plasma may be promising for CO_2 conversion into value-added compounds, as well as to present the current gaps and perspectives to solve them. We briefly presented the most common plasma types and their performance in terms of conversion and energy efficiency, and we explained the underlying reasons for their different performance. Subsequently, we discussed the major limitations and steps to be taken for further improvement. Finally, we gave a brief general presentation of the general context and relevance of this technology to achieve societal goals, particularly for sustainability and climate change mitigation. The objective was to indicate, starting from these windows into the future, some of the existing challenges that need attention from an application perspective, and explain why plasma technology is relevant for our future.

In general, plasma technology is quite promising for CO_2 conversion because of (i) its high process versatility, allowing different kinds of reactions to be carried out (e.g., pure CO_2 splitting, as well as CO_2 conversion in the presence of a H-source, such as CH_4, H_2 or H_2O); (ii) its low investment and operating costs; (iii) the fact that it does not require the use of rare earth metals; (iv) that it can be applied in a very modular setting, as plasma reactors scale up linearly with the plant output, allowing on-demand production; and (v) that it can be very easily combined with (various kinds of) renewable electricity. Moreover, as plasma can easily be switched on/off, it is highly suitable for the conversion of intermittent renewable energy into base chemicals or fuels, for peak shaving and grid stabilization.

However, more research is needed to further improve the capabilities of plasma-based CO_2 conversion in terms of (i) energy efficiency, (ii) conversion, and (iii) product selectivity. The energy efficiency largely depends on the type of plasma reactor and operating conditions. The highest theoretical energy efficiency can be reached when the reduced electric field is around 50 Td or below, combined with a high plasma power to maximize vibrational excitation (as this provides theoretically the most energy-efficient dissociation pathway) with a low gas temperature (to minimize vibrational losses upon collision with other gas molecules, i.e., VT relaxation), or in other words, a strong VT non-equilibrium. The latter can also be achieved at low gas pressure, but that is less compatible with industrial operations. On the other hand, both experiments and modeling in recent years have revealed that in GA and MW plasmas at (sub)atmospheric pressure, the CO_2 conversion proceeds mainly by thermal reactions, and the vibrational distribution is in equilibrium with the gas temperature (VT equilibrium) due to the high gas temperature (around 3,000 K or more). Nevertheless, these conditions still give rise to high energy efficiency if the backward (recombination) reactions of CO with O or O_2 can be avoided by rapid quenching of the gas after the plasma reactor. In addition, if the O atoms can react with another CO_2 molecule, instead of recombining with CO or O, the conversion and thus energy efficiency can be further enhanced beyond the thermal equilibrium limit (super-ideal quenching).

Furthermore, the conversion should be enhanced by increasing the fraction of gas treated by the plasma, i.e., by smart reactor design (including gas inlet/outlet), based on fluid dynamics simulations. Finally, there is still much room for improvement in terms of product selectivity because plasma is very reactive, but not selective for the production of targeted compounds, which may require post-reaction separation steps, adding to the overall energy cost of the process. Therefore, when targeting specific compounds, plasma needs to be combined with catalysts. However, more insight in the plasma-catalyst interactions is crucial for designing catalysts most suited to the plasma environment.

From technological and application point of view, important issues may be the scalability and the use of complex gas mixtures, rather than pure feed of CO_2 or CO_2/CH_4. For example, the role of H_2O in reducing the efficiency in CO_2 transformation has been highlighted. But this also opens a window of opportunity because, for example, light-induced transformation of H_2O over semiconductors may well be integrated with current plasma-based CO_2 conversion technology. This is an area starting to be investigated, but it is still largely unexplored, in terms of realizing an effective synergy of operation. In general terms, the combination of catalysis with CO_2 plasma has to pass from a mainly phenomenological approach to a knowledge-based and innovative approach, based on exploiting all possible synergies. This is the objective of the ERC Synergy grant SCOPE (810182). While the science of catalysis can be considered well-established (Čejka et al., 2018) and there are good bases for applications to new fields as well, such as the use of renewable resources (Centi and Perathoner, 2009; Čejka et al., 2018; Centi and Čejka, 2019), plasma technology is still not at the same level, and still has to be promoted to be considered as an integral and relevant part of the roadmaps on the future challenges in this area (Lanzafame et al., 2017b).

In conclusion, plasma technology for CO_2 conversion has a large potential impact, but the complex phenomena present indicate the need of more disruptive approaches, based on integrated and multidisciplinary collaborations, to explore new ways of combining the potential of plasma with other methodologies, such as the mentioned combination with light-induced transformations on solid catalysts, using a knowledge-based approach. Modeling integrated with advanced design of plasma reactors and of nanostructured catalysts, as highlighted in the previous sections, are the keys to realize these challenges.

AUTHOR CONTRIBUTIONS

Potential of plasma technology to reduce CO_2 emission, What is needed to overcome current limitations of plasma-based CO_2 conversion?, and Conclusions are written by AB, while section Benefits for our life and impact on climate change is written by GC, and both wrote section Introduction. Both authors approved the other sections.

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REFERENCES

Abate, S., Centi, G., Lanzafame, P., and Perathoner, S. (2015a). The energy-chemistry nexus: a vision of the future from sustainability perspective. *J. Energy Chem*. 24, 535–547. doi: 10.1016/j.jechem.2015.08.005

Abate, S., Lanzafame, P., Perathoner, S., and Centi, G. (2015b). New sustainable model of biorefineries: biofactories and challenges of integrating bio-and solar refineries. *ChemSusChem* 8, 2854–2866. doi: 10.1002/cssc.201500277

Ampelli, C., Perathoner, S., and Centi, G. (2015). CO_2 utilization: an enabling element to move to a resource- and energy-efficient chemical and fuel production. *Philos. Trans. R Soc. A Math. Phys. Eng. Sci.* 373:20140177. doi: 10.1098/rsta.2014.0177

Asisov, R. I., Vakar, A. K., Jivotov, V. K., Krotov, M. F., Zinoviev, O. A., Potapkin, B. V., et al. (1983). Non-equilibrium plasma-chemical process of CO_2 decomposition in a supersonic microwave discharge. *Proc. USSR Acad. Sci*. 271, 94–97.

Belov, I., Paulussen, S., and Bogaerts, A. (2017). Pressure as an additional control handle for non-thermal atmospheric plasma processes. *Plasma Proc. Polym*. 14:e1700046. doi: 10.1002/ppap.201700046

Berthelot, A., and Bogaerts, A. (2016). Modeling of plasma-based CO_2 conversion: lumping of the vibrational levels. *Plasma Sources Sci. Technol*. 25:045022. doi: 10.1088/0963-0252/25/4/045022

Berthelot, A., and Bogaerts, A. (2017). Modeling of CO_2 splitting in a microwave plasma: how to improve the conversion and energy efficiency? *J. Phys. Chem. C* 121, 8236–8251. doi: 10.1021/acs.jpcc.6b12840

Berthelot, A., and Bogaerts, A. (2018). Pinpointing energy losses in plasma-based CO_2 conversion. *J. CO_2 Util*. 24, 479–499. doi: 10.1016/j.jcou.2018.02.011

Bogaerts, A., Kozák, T., Van Laer, K., and Snoeckx, R. (2015). Plasma-based conversion of CO_2: current status and future challenges. *Faraday Discuss*. 183, 217–232. doi: 10.1039/C5FD00053J

Bogaerts, A., and Neyts, E. (2018). Plasma technology: an emerging technology for energy storage. *ACS Energy Lett.* 3, 1013–1027. doi: 10.1021/acsenergylett.8b00184

Bogaerts, A., Neyts, E., Gijbels, R., and van der Mullen, J. J. A. M. (2002). Gas discharge plasmas and their applications. *Spectrochim. Acta B* 57, 609–658. doi: 10.1016/S0584-8547(01)00406-2

Bongers, W., Bouwmeester, H., Wolf, B., Peeters, F., Welzel, S., van den Bekerom, D., et al. (2017). Plasma-driven dissociation of CO_2 for fuel synthesis. *Plasma Processes Polym*. 14:1600126. doi: 10.1002/ppap.201600126

Capitelli, M., Colonna, G., D'Ammando, G., and Pietanza, L. D. (2017). Self-consistent time dependent vibrational and free electron kinetics for CO_2 dissociation and ionization in cold plasmas. *Plasma Sources Sci. Technol*. 26:055009. doi: 10.1088/1361-6595/aa6427

Čejka, J., Nachtigall, P., and Centi, G. (2018). New catalytic materials for energy and chemistry in transition. *Chem. Soc. Rev*. 47, 8066–8071. doi: 10.1039/C8CS90119H

Centi, G., and Čejka J. (2019). Needs and gaps for catalysis in addressing transitions in chemistry and energy from a sustainability perspective. *ChemSusChem* 12, 621–632. doi: 10.1002/cssc.201802637

Centi, G., Iaquaniello, G., and Perathoner, S. (2019). Chemical engineering role in the use of renewable energy and alternative carbon sources in chemical production. *BMC Chem. Eng*. 1:5. doi: 10.1186/s42480-019-0006-8

Centi, G., and Perathoner, S. (2009). Catalysis: role and challenges for a sustainable energy. *Top. Catal.* 52, 948–961. doi: 10.1007/s11244-009-9245-x

Centi, G., and Perathoner, S. (2010). Towards solar fuels from water and CO_2. *ChemSusChem* 3, 195–208. doi: 10.1002/cssc.200900289

Centi, G., and Perathoner, S. (2020). Chemistry and energy beyond fossil fuels. A perspective view on the role of syngas from waste sources. *Catal. Today*. 342, 4–12. doi: 10.1016/j.cattod.2019.04.003

Chen, G., Britun, N., Godfroid, T., Georgieva, V., Snyders, R., and Delplancke-Ogletree, M.-P. (2017). An overview of CO_2 conversion in a microwave discharge: the role of plasma-catalysis. *J. Phys. D Appl. Phys*. 50:084001. doi: 10.1088/1361-6463/aa5616

Chen, G., Wang, L., Godfroid, T., and Snyders, R. (2018). "Progress in plasma-assisted catalysis for carbon dioxide reduction," in *Plasma Chemistry and Gas Conversion*, ed N. Britun (London: IntechOpen). doi: 10.5772/intechopen.80798

Chen, S., Perathoner, S., Ampelli, C., Wei, H., Abate, S., Zhang, B., et al. (2020). Enhanced performance in the direct electrocatalytic synthesis of ammonia from N_2 and H_2O by an in-situ electrochemical activation of CNT-supported iron oxide nanoparticles. *J. Energy Chem*. 49, 22–32. doi: 10.1016/j.jechem.2020.01.011

Cleiren, E., Heijkers, S., Ramakers, M., and Bogaerts, A. (2017). Dry reforming of methane in a gliding arc plasmatron: towards a better understanding of the plasma chemistry. *ChemSusChem* 10, 4025–4036. doi: 10.1002/cssc.201701274

De Bie, C., van Dijk, J., and Bogaerts, A. (2016). CO_2 hydrogenation in a dielectric barrier discharge plasma revealed. *J. Phys. Chem. C* 120, 25210–25224. doi: 10.1021/acs.jpcc.6b07639

Debek, R., Azzolina-Jury, F., Travert, A., and Mauge, F. (2019). A review on plasma-?catalytic methanation of carbon dioxide - looking for an efficient catalyst. *Renew. Sust. Energy Rev*. 116:109427. doi: 10.1016/j.rser.2019.109427

den Harder, N., van den Bekerom, D. C. M., Al, R. S., Graswinckel, M. F., Palomares, J. M., Peeters, F. J. J., et al. (2017). Homogeneous CO_2 conversion by microwave plasma: wave propagation and diagnostics. *Plasma Processes Polym*. 14:1600120. doi: 10.1002/ppap.201600120

Eliasson, B., Kogelschatz, U., Xue, B., and Zhou, L.-M. (1998). Hydrogenation of carbon dioxide to methanol with a discharge-activated catalyst. *Ind. Eng. Chem. Res*. 37, 3350–3357. doi: 10.1021/ie9709401

Engelmann, Y., Mehta, P., Neyts, E. C., Schneider, W. F., and Bogaerts, A. (2020). Predicted influence of plasma activation on non-oxidative coupling of methane on transition metal catalysts. *ACS Sustain. Chem. Eng.* 8, 6043–6054. doi: 10.1021/acssuschemeng.0c00906

European Commission (2018). *2050 Long-Term Strategy "A Clean Planet for All. A European Strategic Long-Term Vision for a Prosperous, Modern, Competitive and Climate Neutral Economy*.

Fridman, A. (2008). *Plasma Chemistry*. Cambridge: *Cambridge University* Press.

García de Arquer, F. P., Dinh, C.-T., Ozden, A., Wicks, J., Mccallum, C., Kirmani, A. R., et al. (2020). CO_2 electrolysis to multicarbon products at activities greater than 1 A Cm^{-2}. *Science* 367, 661–666. doi: 10.1126/science.aay4217

Gielen, D., Boshell, F., Saygin, D., Bazilian, M. D., Wagner, N., and Gorini, R. (2019). The role of renewable energy in the global energy transformation. *Energy Strat. Rev*. 24, 38–50. doi: 10.1016/j.esr.2019.01.006

Gorbanev, Y., Vervloessem, E., Nikiforov, A., and Bogaerts, A. (2020). Nitrogen fixation with water vapor by nonequilibrium plasma: toward sustainable ammonia production. *ACS Sust. Chem. Eng*. 8, 2996–3004. doi: 10.1021/acssuschemeng.9b07849

Groen, P. W. C., Wolf, A. W., Righart, T. W. H., van de Sanden, M. C. M., Peeters, F. J. J., and Bongers, W. A. (2019). Numerical model for the determination of the reduced electric field in a CO_2 microwave plasma derived by the principle of impedance matching. *Plasma Sources Sci. Technol*. 28:075016. doi: 10.1088/1361-6595/ab1ca1

Grofulović, M., Silva, T., Klarenaar, B. L. M., Morillo-Candas, A. S., Guaitella, O., Engeln, R., et al. (2018). Kinetic study of CO_2 plasmas under nonequilibrium conditions. II. Input of vibrational energy. *Plasma Sources Sci. Technol*. 27:115009. doi: 10.1088/1361-6595/aadb60

Heijkers, S., and Bogaerts, A. (2017). CO_2 conversion in a gliding arc plasmatron: elucidating the chemistry through kinetic modelling. *J. Phys. Chem. C* 121, 22644–22655. doi: 10.1021/acs.jpcc.7b06524

International Renewable Energy Agency - IRENA (2019). *Renewable Energy Statistics 2019.* Abu Dhabi: The IRENA. ISBN: 978-92-9260-137-9

Klarenaar, B. L. M., Engeln, R., van den Bekerom, D. C. M., van de Sanden, M. C. M., Morillo-Candas, A. S., and Guaitella, O. (2017). Time evolution of vibrational temperatures in a CO_2 glow discharge measured with infrared absorption spectroscopy. *Plasma Sources Sci. Technol*. 26:115008. doi: 10.1088/1361-6595/aa902e

Klarenaar, B. L. M., Grofulovi,ć, M., Morillo-Candas, A. S., van den Bekerom, D. C. M., Damen, M. A., van de Sanden, M. C. M., et al. (2018). A rotational raman study under non-thermal conditions in a pulsed CO_2 glow discharge. *Plasma Sources Sci. Technol*. 27:045009. doi: 10.1088/1361-6595/aabab6

Klarenaar, B. L. M., Morillo-Candas, A. S., Grofulovi,ć, M., van de Sanden, M. C. M., Engeln, R., and Guaitella, O. (2019). Excitation and relaxation of the asymmetric stretch mode of CO_2 in a pulsed glow discharge. *Plasma Sources Sci. Technol*. 28:035011. doi: 10.1088/1361-6595/aada5e

Kogelschatz, U. (2003). Dielectric-barrier discharges: their history, discharge physics, and industrial applications. *Plasma Chem. Plasma Process*. 23, 1–46. doi: 10.1023/A:1022470901385

Kotov, V., and Koelman, P. M. J. (2019). Plug flow reactor model of the plasma chemical conversion of CO_2. *Plasma Sources Sci. Technol*. 28:095002. doi: 10.1088/1361-6595/ab3774

Kozák, T., and Bogaerts, A. (2014). Splitting of CO_2 by vibrational excitation in non-equilibrium plasmas: a reaction kinetics model. *Plasma Sources Sci. Technol.* 23:045004. doi: 10.1088/0963-0252/23/4/045004

Kozák, T., and Bogaerts, A. (2015) Evaluation of the energy efficiency of CO_2 conversion in microwave discharges using a reaction kinetics model. *Plasma Sources Sci. Technol.* 24, 015024. doi: 10.1088/0963-0252/24/1/015024

Lanzafame, P., Abate, S., Ampelli, C., Genovese, C. Passalacqua, R., Centi, G., et al. (2017a). Beyond solar fuels: renewable energy-driven chemistry. *ChemSusChem* 10, 4409–4419. doi: 10.1002/cssc.201701507

Lanzafame, P., Perathoner, S., Centi, G., Gross, S., and Hensen, E. J. M. (2017b). Grand challenges for catalysis in the science and technology roadmap on catalysis for Europe: moving ahead for a sustainable future. *Catal. Sci. Technol*. 7, 5182–5194. doi: 10.1039/C7CY01067B

Legasov, V. A., Zhivotov, V. K., Krasheninnikov, E. G., Krotov, M. F., Patrushev, L., Rusanov, V. D., et al. (1978). A nonequilibrium plasma-chemical process of CO_2 dissociation in high-frequency and ultra-high-frequency discharges. *Soviet Phys. Doklady*. 23, 44–46.

Li, K., Liu, J. L., Li, X. S., Zhu, X., and Zhu, A. M. (2016). Warm plasma catalytic reforming of biogas in a heat-insulated reactor: dramatic energy efficiency and catalyst auto-reduction. *Chem. Eng. J*. 288, 671–679. doi: 10.1016/j.cej.2015.12.036

Liu, M., Yi, Y., Wang, L., Guo, H., and Bogaerts, A. (2019). Hydrogenation of carbon dioxide to value-added chemicals by heterogeneous catalysis and plasma catalysis. *Catalysts* 9:275. doi: 10.3390/catal9030275

Liu, P., Liu, X., Shen, J., Yin, Y., Yang, T., Huang, Q., et al. (2019). CO_2 conversion by thermal plasma with carbon as reducing agent: high CO yield and energy efficiency. *Plasma Sci. Technol*. 21:012001. doi: 10.1088/2058-6272/aadf30

Mehta, P., Barboun, P., Go, D. B., Hicks, J. C., and Schneider, W. F. (2019). Catalysis enabled by plasma activation of strong chemical bonds: a review. *ACS Energy Lett*. 4, 1115–1133. doi: 10.1021/acsenergylett.9b00263

Mehta, P., Barboun, P., Herrera, F. A., Kim, J., Rumbach, P., Go, D. B., et al. (2018). Overcoming ammonia synthesis scaling relations with plasma-enabled catalysis. *Nat. Catal.* 1, 269–275. doi: 10.1038/s41929-018-0045-1

Mei, D., Zhu, X., He, Y., Yan, J. D., and Tu, X. (2015). Plasma-assisted conversion of CO_2 in a dielectric barrier discharge reactor: understanding the effect of packing materials. *Plasma Sources Sci. Technol.* 24:015011. doi: 10.1088/0963-0252/24/1/015011

Michielsen, I., Uytdenhouwen, Y., Pype, J., Michielsen, B., Mertens, J., Reniers, F., et al. (2017). CO_2 dissociation in a packed bed DBD reactor: first steps towards a better understanding of plasma catalysis. *Chem. Eng. J.* 326, 477–488. doi: 10.1016/j.cej.2017.05.177

Mori, S., Matsuura, N., Tun, L. L., and Suzuki, M. (2016). Direct synthesis of carbon nanotubes from only CO_2 by a hybrid reactor of dielectric barrier discharge and solid oxide electrolyser cell. *Plasma Chem. Plasma Process.* 36, 231–239. doi: 10.1007/s11090-015-9681-2

Navarrete, A., Centi, G., Bogaerts, A., Martín, Á., York, A., and Stefanidis, G. (2017). Harvesting renewable energy for CO_2 catalysis. *Energy Technol.* 5, 796–811. doi: 10.1002/ente.201600609

Neyts, E. C., Ostrikov, K., Sunkara, M. K., and Bogaerts, A. (2015). Plasma catalysis: synergistic effects at the nanoscale. *Chem. Rev.* 115, 13408–13446. doi: 10.1021/acs.chemrev.5b00362

Nunnally, T., Gutsol, K., Rabinovich, A., Fridman, A., Gutsol, A., and Kemoun, A. (2011). Dissociation of CO_2 in a low current gliding arc plasmatron. *J. Phys. D Appl. Phys.* 44:274009. doi: 10.1088/0022-3727/44/27/274009

Ozkan, A., Dufour, T., Silva, T., Snyders, R., Bogaerts, A., and Reniers, F. (2016). The influence of power and frequency on the filamentary behavior of a flowing DBD – application to the splitting of CO_2. *Plasma Sources Sci. Technol.* 25:025013. doi: 10.1088/0963-0252/25/2/025013

Peeters, F. J. J., Yang, R., and van de Sanden, M. C. M. (2015). The relation between the production efficiency of nitrogen atoms and the electrical characteristics of a dielectric barrier discharge. *Plasma Sources Sci. Technol.* 24:045006. doi: 10.1088/0963-0252/24/4/045006

Perathoner, S., and Centi, G. (2014). CO_2 Recycling: a key strategy to introduce green energy in the chemical production chain. *ChemSusChem* 7, 1274–1282. doi: 10.1002/cssc.201300926

Perathoner, S., and Centi, G. (2019). Catalysis for solar-driven chemistry: the role of electrocatalysis. *Catal. Today* 330, 157–170. doi: 10.1016/j.cattod.2018.03.005

Pietanza, L. D., Colonna, G., and Capitelli, M. (2017b). Nonequilibrium plasma kinetics of reacting CO: an improved state to state approach. *Plasma Sources Sci. Technol.* 26:125007. doi: 10.1088/1361-6595/aa93bd

Pietanza, L. D., Colonna, G., and Capitelli, M. (2018a). Nonequilibrium electron and vibrational distributions under nanosecond repetitively pulsed CO discharges and afterglows: I. Optically thick plasmas. *Plasma Sources Sci. Technol.* 27:095004. doi: 10.1088/1361-6595/aad7ef

Pietanza, L. D., Colonna, G., and Capitelli, M. (2018b). Nonequilibrium electron and vibrational distributions under nanosecond repetitively pulsed CO discharges and afterglows: II. The role of radiative and quenching processes. *Plasma Sources Sci. Technol.* 27:095003. doi: 10.1088/1361-6595/aad7f2

Pietanza, L. D., Colonna, G., and Capitelli, M. (2020). Kinetics versus thermodynamics on CO_2 dissociation in high temperature microwave discharges. *Plasma Sources Sci. Technol.* 29:035022. doi: 10.1088/1361-6595/ab6e5a

Pietanza, L. D., Colonna, G., D'Ammando, G., and Capitelli, M. (2017a). Time-dependent coupling of electron energy distribution function, vibrational kinetics of the asymmetric mode of CO_2 and dissociation, ionization and electronic excitation kinetics under discharge and post-discharge conditions. *Plasma Phys. Control. Fusion* 59:014035. doi: 10.1088/0741-3335/59/1/014035

Pietanza, L. D., Colonna, G., D'Ammando, G., Laricchiuta, A., and Capitelli, M. (2015). Vibrational excitation and dissociation mechanisms of CO_2 under non-equilibrium discharge and post-discharge conditions. *Plasma Sources Sci. Technol.* 24:042002. doi: 10.1088/0963-0252/24/4/042002

Puliyalil, H., Lasic Jurkovic, D., Dasireddy, V. D. B. C., and Likozar, B. (2018). A review of plasma-assisted catalytic conversion of gaseous carbon dioxide and methane into value-added platform chemicals and fuels. *RSC Adv.* 8, 27481–27508. doi: 10.1039/C8RA03146K

Qin, Y., Niu, G., Wang, X., Luo, D., and Duan, Y. (2018). Status of CO_2 conversion using microwave plasma. *J. CO_2 Util.* 28, 283–291. doi: 10.1016/j.jcou.2018.10.003

Ramakers, M., Heijkers, S., Tytgat, T., Lenaerts, S., and Bogaerts, A. (2019). Combining CO_2 conversion and N_2 fixation in a gliding arc plasmatron. *J. CO_2 Util.* 33, 121–130. doi: 10.1016/j.jcou.2019.05.015

Ramakers, M., Trenchev, G., Heijkers, S., Wang, W., and Bogaerts, A. (2017). Gliding arc plasmatron: providing a novel method for CO_2 conversion. *ChemSusChem* 10, 2642–2652. doi: 10.1002/cssc.201700589

Schlögl, R., Abanades, C., Aresta, M., Azapagic, A., Blekkan, E. A., Cantat, T., et al. (2018). *Novel Carbon Capture and Utilisation Technologies: Research And Climate Aspects, SAPEA*, Evidence Review Report No. 2. Berlin: SAPEA. ISBN 978-3-9819415-5-5.

Silva, T., Britun, N., Godfroid, T., and Snyders, R. (2014). Optical characterization of a microwave pulsed discharge used for dissociation of CO_2. *Plasma Sources Sci. Technol.* 23:025009. doi: 10.1088/0963-0252/23/2/025009

Silva, T., Britun, N., Godfroid, T.h., and Snyders, R. (2017). Understanding CO_2 decomposition in microwave plasma by means of optical diagnostics. *Plasma Process Polym.* 14:e1600103. doi: 10.1002/ppap.201600103

Silva, T., Grofulović, M., Klarenaar, B. L. M., Morillo-Candas, A. S., Guaitella, O., Engeln, R., et al. (2018). Kinetic study of low-temperature CO_2 plasmas under non-equilibrium conditions. *I. Relaxation of vibrational energy. Plasma Sources Sci. Technol.* 27:015019. doi: 10.1088/1361-6595/aaa56a

Slaets, J., Ceulemans, S., Van Alphen, S., Aghaei, M., and Bogaerts, A. (2020). CO_2 and CH_4 conversion in "real" gas mixtures in a gliding arc plasmatron: how do N_2 and O_2 affect the performance? *Green Chem.* 22, 1366–1377. doi: 10.1039/C9GC03743H

Snoeckx, R., and Bogaerts, A. (2017). Plasma technology – a novel solution for CO_2 conversion? *Chem. Soc. Rev.* 46, 5805–5863. doi: 10.1039/C6CS00066E

Snoeckx, R., Heijkers, S., Van Wesenbeeck, K., Lenaerts, S., and Bogaerts, A. (2016). CO_2 conversion in a dielectric barrier discharge plasma: N_2 in the mix as helping hand of problematic impurity? *Energy Environm. Sci.* 9, 999–1011. doi: 10.1039/C5EE03304G

Snoeckx, R., Ozkan, A., Reniers, F., and Bogaerts, A. (2017). The quest for value-added products from carbon dioxide and water in a dielectric barrier discharge plasma: a chemical kinetics study. *ChemSusChem* 10, 409–424. doi: 10.1002/cssc.201601234

Song, C., Liu, Q., Ji, N., Deng, S., Zhao, J., Li, Y., et al. (2018). Alternative pathways for efficient CO_2 capture by hybrid processes- a review. *Renew. Sust. Energy Rev.* 82, 215–231. doi: 10.1016/j.rser.2017.09.040

Stewig, C., Schüttler, S., Urbanietz, T., Böke, M., and von Keudell, A. (2020). Excitation and dissociation of CO_2 heavily diluted in noble gas atmospheric pressure plasma. *J. Phys. D Appl. Phys.* 53:125205. doi: 10.1088/1361-6463/ab634f

Sun, S. R., Wang, H. X., Mei, D. H., Tu, X., and Bogaerts, A. (2017). CO_2 conversion in a gliding arc plasma: performance improvement based on chemical reaction modeling. *J. CO_2 Util.* 17, 220–234. doi: 10.1016/j.jcou.2016.12.009

Terraz, L., Silva, T., Morillo-Candas, A., Guaitella, O., Tejero-del-Caz, A., Alves, L. L., et al. (2020). Influence of N_2 on the CO_2 vibrational distribution function and dissociation yield in non-equilibrium plasmas. *J. Phys. D Appl. Phys.* 53:094002. doi: 10.1088/1361-6463/ab55fb

Trenchev, G., and Bogaerts, A. (2020). Dual-vortex plasmatron – a novel plasma source for CO_2 conversion. *J. CO_2 Utiliz.* 39:101152. doi: 10.1016/j.jcou.2020.03.002

Trenchev, G., Kolev, S. T., Wang, W., Ramakers, M., and Bogaerts, A. (2017). CO_2 conversion in a gliding arc plasmatron: multi-dimensional modeling for improved efficiency. *J. Phys. Chem. C* 121, 24470–24479. doi: 10.1021/acs.jpcc.7b08511

Trenchev, G., Nikiforov, A., Wang, W., Kolev, S.t., and Bogaerts, A. (2019). Atmospheric pressure glow discharge for CO_2 conversion: model-based exploration of the optimum reactor configuration. *Chem. Eng. J.* 362, 830–841. doi: 10.1016/j.cej.2019.01.091

Uytdenhouwen, Y., Van Alphen, S., Michielsen, I., Meynen, V., Cool, P., and Bogaerts, A. (2018). A packed-bed DBD micro plasma reactor for CO_2 dissociation: does size matter? *Chem. Eng. J.* 348, 557–568. doi: 10.1016/j.cej.2018.04.210

van ‘t Veer, K., Reniers, F., and Bogaerts, A. (2020). Zero-dimensional modelling of unpacked and packed bed dielectric barrier discharges: the role of vibrational kinetics in ammonia synthesis. *Plasma Sources Sci. Technol.* 29:045020. doi: 10.1088/1361-6595/ab7a8a

van den Bekerom, D. C. M., Palomares Linares, J. M., Verreycken, T., van Veldhuizen, E. M., Nijdam, S., Berden, G., et al. (2019). The importance of thermal dissociation in CO_2 microwave discharges investigated by power pulsing and rotational raman scattering. *Plasma Sources Sci. Technol*. 28:055015. doi: 10.1088/1361-6595/aaf519

van den Bekerom, D. C. M., van de Steeg, A., van de Sanden, M. C. M., and van Rooij, G. J. (2020). Mode resolved heating dynamics in pulsed microwave CO_2 plasma from laser Raman scattering. *J. Phys. D Appl. Phys*. 53:054002. doi: 10.1088/1361-6463/ab5311

Van Laer, K., and Bogaerts, A. (2015). Improving the conversion and energy efficiency of carbon dioxide splitting in a zirconia-packed dielectric barrier discharge reactor. *Energy Technol*. 3, 1038–1044. doi: 10.1002/ente.201500127

Van Laer, K., and Bogaerts, A. (2016). Fluid modeling of a packed bed dielectric barrier discharge plasma reactor. *Plasma Sources Sci. Technol*. 25:015002. doi: 10.1088/0963-0252/25/1/015002

van Rooij, G. J., Van Den Bekerom, D. C. M., Den Harder, N., Minea, T., Berden, G., Bongers, W. A., et al. (2015). Taming microwave plasma to beat thermodynamics in CO_2 dissociation. *Faraday Discuss*. 183, 233–248. doi: 10.1039/C5FD00045A

Vermeiren, V., and Bogaerts, A. (2018). Supersonic microwave plasma: potential and limitations for energy-efficient CO_2 conversion. *J. Phys. Chem. C* 122, 25869–25881. doi: 10.1021/acs.jpcc.8b08498

Vermeiren, V., and Bogaerts, A. (2019). Improving the energy efficiency of CO_2 conversion in nonequilibrium plasmas through pulsing. *J. Phys. Chem. C* 123, 17650–17665. doi: 10.1021/acs.jpcc.9b02362

Wolf, A. (2020). *Thermal aspects of CO_2 conversion in the vortex-stabilized microwave plasma* (Ph.D. dissertation), Eindhoven University of Technology, Eindhoven, Netherlands.

Wolf, A. J., Righart, T. W. H., Peeters, F. J. J., Bongers, W. A., and van de Sanden, M. C. M. (2020). Implications of thermo-chemical instability on the contracted modes in CO_2 microwave plasmas. *Plasma Sources Sci. Technol*. 29:025005. doi: 10.1088/1361-6595/ab5eca

Wolf, A. J., Righart, T. W. H., Peeters, F. J. J., Groen, P. W. C., van de Sanden, M. C. M., and Bongers, W. A. (2019). Characterization of CO_2 microwave plasma based on the phenomenon of skin-depth limited contraction. *Plasma Sources Sci. Technol*. 28:115022. doi: 10.1088/1361-6595/ab4e61

Yang, T., Shen, J., Ran, T., Li, J., Chen, P., and Yin, Y. (2018). Understanding CO_2 decomposition by thermal plasma with supersonic expansion quench. *Plasma Sci. Technol*. 20:065502. doi: 10.1088/2058-6272/aaa969

Zeng, Y., Zhu, X., Mei, D., Ashford, B., and Tu, X. (2015). Plasma-catalytic dry reforming of methane over Al_2O_3 supported metal catalysts. *Catal. Today*. 256, 80–87. doi: 10.1016/j.cattod.2015.02.007

Zheng, T., Jiang, K., Ta, N., Hu, Y., Zeng, J., Liu, J., et al. (2019). Large-scale and highly selective CO_2 electrocatalytic reduction on nickel single-atom catalyst. *Joule* 3, 265–278. doi: 10.1016/j.joule.2018.10.015

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Carbon Recycling Through CO_2-Conversion for Stepping Toward a Cyclic-C Economy. A Perspective

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The conversion of CO_2 into added value chemicals, materials and fuels is a case of transition from the *linear* to the *cyclic-C economy*, a necessary change for stopping the putative negative effect of CO_2 on climate and the environment. Several strategies can be implemented for CO_2 conversion and their potential and timeframe is discussed in this perspective paper. The overall amount of avoided CO_2 is evaluated in the short-, medium-, and long-term. The distinct contribution of Catalysis, Solar Chemistry and integrated Chemocatalysis-Biosystems is discussed.

Keywords: CO_2 conversion, cyclic-C economy, catalysis, biotechnological processes, integrated systems

INTRODUCTION

The continuous immission of anthropogenic-, nonbiogenic-CO_2 in the atmosphere is hold liable of climate-change and extreme events we observe with higher frequency these days. In our opinion, such negative impact must be more correctly ascribed to the general scarce efficiency (Aresta and Dibenedetto, 2020) in the use of the fossil-C chemical energy we do [only an average 32% of the fossil energy is converted into usable energy (electrical-, mechanical-, thermal-energy), the rest ending to heat the atmosphere and our planet]. In fact, direct heating of the atmosphere is causing an increase of water transfer from soil to air (Dai, 2006) with water vapor having a stronger Green House Effect-GHE (at least twice) than CO_2 (Dessler et al., 2008). The continuous increase of CO_2 atmospheric level since the beginning of the industrial-age, is the witness and alarm light of our inefficient use of fossil-C and of our lavishness in the use of any form of energy (electric, thermal, mechanical). Nevertheless, whether the atmospheric level of CO_2 is the protagonist of climate change or has a lower level play-role, whichever is(are) the real responsible for the impact on climate, the reduction of use of fossil-C is a necessity and an opportunity. A necessity for preserving natural resources that are not illimited (**Table 1**), an opportunity for making the best use (direct and indirect) of perennial (solar, wind, hydro, geothermal-SWHG) and renewable energy (biomass) in conjunction with CO_2 use and C-recycling, stepping toward the Circular-C economy.

C-recycling means building a man-made C-cycle that can integrate the natural one and make available at a higher rate, than natural processes, and with a higher selectivity toward a single product, goods that are in our common use and will continue to be used for next generations. The exploitation of such ability will ensure longer usability of the limited natural resources (**Table 1**). The direct use of perennial SWHG energies is possible in a number of cases, but is not so general as fossil-C derivatives are. Fossil-C and their derivatives can be shipped all around the world and used, perennial energies are not (solar-, wind-, hydro, geothermal-power are not exportable) and their key derivative (electricity) has a limited distribution potential. Biomass has limitations to the

TABLE 1 | Estimated worldwide fossil-C availability (Gt_{oe}, t_{oe} = tons oil equivalent).

Region		Europe	Russia	N America	S America	China	India	Middle East	Africa	Australia	Total
Fossil-C reserves, Gt_{oe}	Coal	40	152	170	13	76	62	0	34	60	607
	Oil	2	19	8	15	2	1	101	17	2	167
	Gas	6	52	8	6	2	1	68	14	10	167
	Total	48	223	186	34	80	64	169	65	72	941

TABLE 2 | Energy density of some energy sources/vectors.

Vector	*Diesel*	Gasoline	Carbon-coke	Brown coal	Methanol	Bio-oil (algae)	H_2(l)	CH_4 (g)	H_2(g) 20 MPa
Density *GJ/m*^{3}	*36*	34	30	18	17	13	9	8	2

direct utilization (emissions of particulate and noxious molecules such as N-aromatics and dioxins) and requires upgrading for the best use: anyway alone it cannot solve the problem also because its rate of combustion is much faster (1000–10,000 times) than the rate of formation and this will not solve the problem of CO_2 accumulation in the atmosphere. Fossil-C derivatives (liquid and gaseous fuels) are ideal energy vectors (diesel and gasoline are the most concentrated form of solar energy, see **Table 2**) and, furthermore, are suited for being used in actual infrastructures, without requiring unviable worldwide economic investments.

Do we have the possibility for converting CO_2 on a large scale? Which energy sources we can exploit? Within which time-frame? What kind of products we can target?

This paper will make a survey of opportunities and possibilities, trying to put a timeframe to plausible targets and wrapping an all-inclusive conversion budget of CO_2. Next paragraphs will each make the analysis of specific fields, highlighting barriers to overcome for a transition to a large-scale conversion of CO_2, well beyond actual 220 Mt_{CO2}/y.

Noteworthy, in this Introduction we have used two different terms relevant to CO_2 applications: utilization and conversion. They are not synonyms: conversion infers the chemical transformation of CO_2 into other products such as polymers, materials, fine-chemicals, and fuels; utilization includes the conversion and other applications of CO_2, such as the use of CO_2 as a technical fluid without chemical conversion: additive to beverages, packaging including food conservation, low temperature generation, cleaning of surfaces, fire extinguisher, basic-waters treatment, water-wells regeneration, etc. These aspects will not be treated in this paper, interested readers can eventually look at Chapter 8 in Ref 1.

We recall here, that reactions of CO_2 can be categorized in three main Classes which link the status of the CO_2 molecule to the energetics of reaction, namely: (i) Processes (either exoergonic or moderately endoergonic), in which the entire CO_2 molecule is incorporated into chemicals (carbonates, both organic and inorganic; polycarbonates; carbamates and polyurethanes). The oxidation state of C remains equal to 4; (ii) Average energy processes, with formation of C-C bonds without hydrogen consumption. The oxidation state of C is reduced to 3; (iii) Processes requiring both energy and hydrogen. The oxidation state of C goes down until to reach -4 in CH_4.

In a "energy frame" based on "fossil-C" only the exploitation of Class (i) reactions makes sense, in a "energy frame" that includes substantial contributions from perennial energies, Class (iii) processes are feasible (Aresta et al., 2013a). And this is the great change, which revolutionizes the CO_2 problem. *CO_2 is a resource not a waste* (Aresta and Forti, 1987; Aresta, 2003, 2010). We have been firm supporters of such strategy and already in 1989 we elaborated a strategic approach to CO_2 utilization, based on the use of solar energy (**Figure 1**). The conversion of large volumes of CO_2 had no sense in the past (the perennial and renewable energies contribution to the entire energy budget was very limited), but it is now at the center of the scientific challenge for the future because perennial energies are entering the energy market with growing weight. Using solar energy for coprocessing water and CO_2 allows to convert two very stable molecules into useful products, such as energy-rich hydrocarbons or their derivatives, plus oxygen, that can be separately collected and marketed. This is the future, that is fully mimic of natural processes.

LOW ENERGY PROCESSES FOR CO_2 CONVERSION

The utilization of CO_2 for the synthesis of urea from ammonia (NH_3) and CO_2 (Woehler, 1828), and salicylic acid from phenol (Kolbe, 1860) are the oldest industrial processes known. But the process based on CO_2 utilization with longer life is the plaster lime, made from quicklime and water, used to cover walls. By exposition to the atmosphere, calcium hydroxide [$Ca(OH)_2$] reacts with CO_2 and makes $Ca(HCO_3)_2$, then converted into $CaCO_3$. This technique is very old, used most likely first by Jordans, then by Egyptians, Romans up to our times, passing through the exceptional uses Venetians made of it during Renaissance.

All just mentioned processes maintain the intact CO_2 moiety in the final product, as also do carbamates (RHN-CO_2R') easily formed from amines (aliphatic, primary and secondary), and polymers (polycarbonates and polyurethanes). Such uses have been moderately exploited during last decades, in an energy frame based on fossil-C, as they are characterized by a negative Gibbs free-energy (inorganic carbonates, carbamates

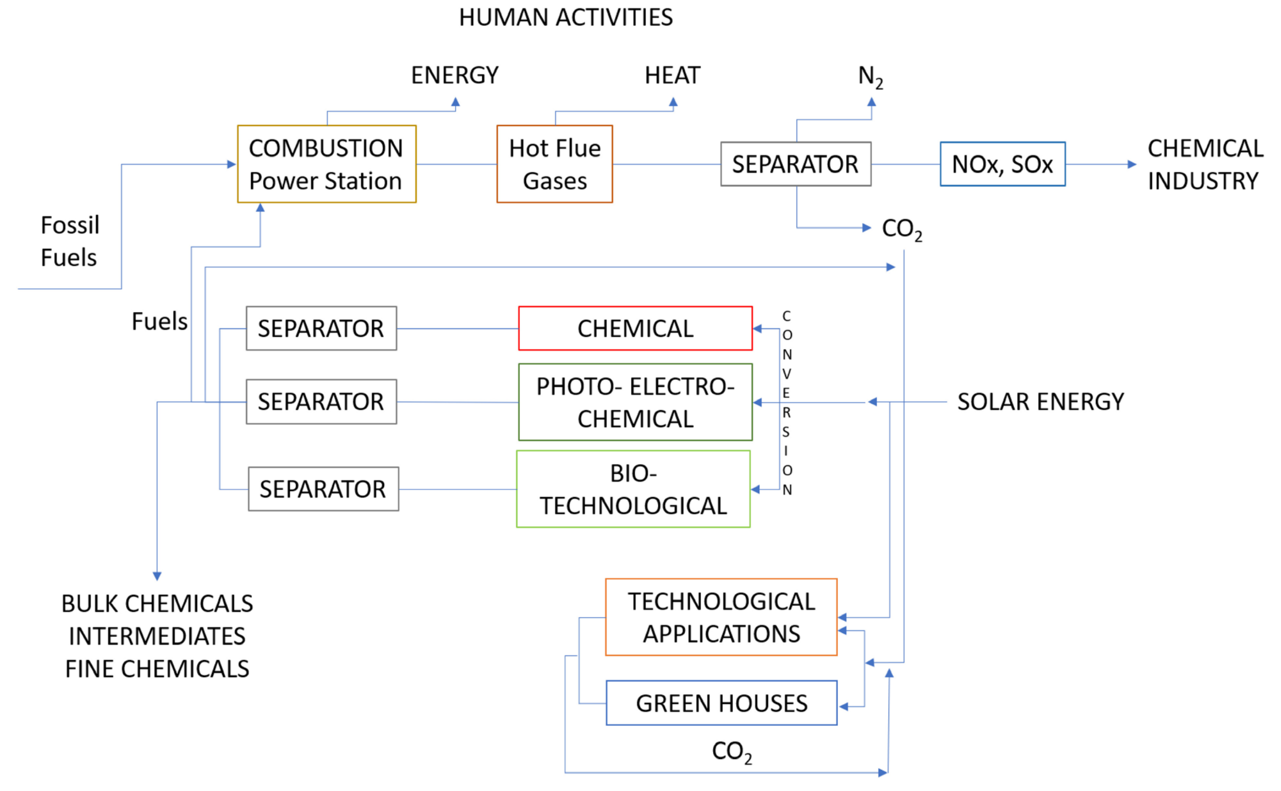

FIGURE 1 | Utilization of CO_2 under solar energy powering of processes (Aresta and Forti, 1987).

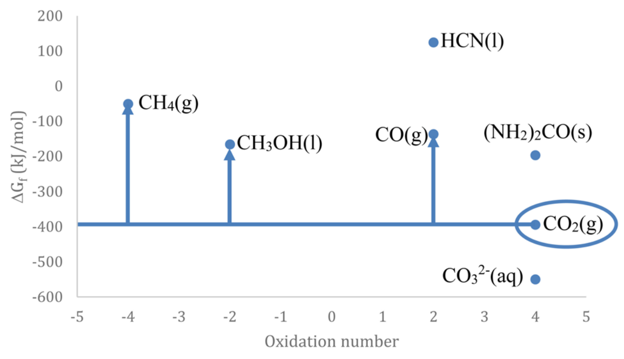

FIGURE 2 | Gibbs free energy for some C1 species.

or polymers), or slightly positive (organic carbonates) in the circle in **Figure 2**.

The total amount of CO_2 used today is around 220 Mt/y, most of it used in the synthesis of urea (over 137 Mt/y), followed by inorganic carbonates and left with CO in the synthesis of methanol. The urea world market has reached 187.8 Mt in 2019 with a foreseen CAGR of 2% until 2025.[1] To such amount, some 20 Mt/y must be added as technical fluid in applications such as: metal cleaning in cuttings and soldering, electronic industry, dry-cleaning, cooling agent, food industry (preservation during transport or stockage and modified packaging atmosphere-MPA), fire extinguisher, water-wells restauration, water treatment, green houses (for rising the atmospheric CO_2 concentration up to 600 ppm) and Enhanced Oil Recovery-EOR. In the latter applications, even if CO_2 is vented at the end of use, there is a large benefit because it substitutes products that would have a much larger Climate Change Power-CCP (for example, ChloroFluoroCarbons-CFCs have a CCP some > 10,000 times higher than CO_2) (Aresta and Dibenedetto, 2020, Ch4). However, some 240 Mt_{CO2}/y are used today, mainly (92%) in the chemical industry. (The Catalyst Group Resources [TGCR], 2012) *Per se* it is a considerable amount, but it represents a drop in the ocean of the emitted CO_2 (35 000+ Mt/y).

In the short term (5–7 years) this amount may grow to 350 Mt_{CO2}/y if CO_2-based synthetic technologies will be promoted. In the long term (2040) the market of CO_2 for chemicals may grow to some 1000 Mt/y, making a difference (Aresta et al., 2018). It is worth to recall, at this point, that what really matters is not the amount of CO_2 converted but the amount of "avoided" CO_2, e.g., of CO_2 "not emitted". In fact, the overall objective is to reduce the CO_2 emission, a target that can be reached by reducing the "Carbon Footprint-CF" of a product or a process. The total reduction is given by the sum of the amount converted plus the amount not emitted because of the process improvement in terms or energy and waste production reduction. This amount

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[1] https://www.expertmarketresearch.com/reports/urea-market

represents the "avoided CO_2" and is calculated by using the Life Cycle Assessment-LCA methodology, (Aresta and Galatola) by comparing a process on stream to an innovative one based on CO_2 utilization. The avoided CO_2 is in the range of 2,3.5, with a good average around 2.8, for a CO_2 based process with respect to a process on stream not based on CO_2. Therefore, if we apply such coefficient to the estimated amount of CO_2 used in the synthesis of chemicals at 2040, considering those chemicals today not made from CO_2 [1000 – (urea+carbonates)] it comes out that to 1000 Mt_{CO2} converted correspond some 2500 Mt_{CO2} avoided, that is 8% of the amount today emitted. This makes sense and suggests that the use of CO_2 may help to considerably reduce its emissions and make more sustainable the chemical industry.

There are some CO_2-based processes which are highly wished at the industrial level because they would substitute either processes which use toxic raw materials ($COCl_2$, used in the synthesis of carbonates and carbamates) or implement direct syntheses, avoiding large waste production (synthesis of acrylates or carboxylates). We shall appraise briefly synthetic methodologies relevant to chemicals with a market over 1 Mt/y, namely: acrylates, carbamates and polyurethanes, carbonates and polycarbonates, and specialty chemicals, highlighting the benefits of using CO_2.

Acrylates

Acrylates ($RCH = CHCO_2R'$; R, R' = H, alkyl moiety) are compounds with a market of some 6 Mt/y; they find utilization in a variety of different fields, from polymers, to varnishes and disposable napkins. Actually, acrylic acid is prepared by stepwise propane oxidation (Eq. 1, left) while could be prepared by a one-step coupling of ethene and CO_2 (Eq 1, right):

$$CH_3 - CH_2 - CH_3 \;>>\; CH_2 = CH - CH_3 \;>>$$

$$CH_2 = CH - CO_2H \;<<\; CO_2 + CH_2 = CH_2 \qquad (1)$$

The use of Pd (Aresta et al., 2007; Limbach et al., 2012; Li et al., 2018) instead of historical Mo (Carmona et al., 1985) or Ni (Hoberg et al., 1987; Papai et al., 2004) has allowed to rise the TON to 10 (Aresta et al., 2007; Limbach et al., 2012)-100 (Li et al., 2018) from 1 (Carmona et al., 1985): a lot there is to do for rising the one-step process to application level that would bring a substantial change in this field with a large atom economy and waste reduction considered that the oxidation process has a large C-footprint due to its low selectivity. This case can be used for highlighting the difference between "used" and "avoided" CO_2. The used CO_2 is one mol per mol of acrylate (Eq. 1 right), while the avoided CO_2 is the sum of such amount plus the non-emitted CO_2 because the CF of the synthetic methodology is neatly improved stepping from the old process (high temperature and low selectivity in oxidation) to the new one (low temperature and CUF = 1).

Carbamates and Polyurethanes

Both title compounds are characterized by bearing the moiety -*NH-CO_2*−. Monomeric carbamates are made by reacting amines with phosgene and alcohols (Eq. 2, left), while could be made by substituting the more reactive and toxic phosgene with CO_2 (Eq. 2, right) (Aresta and Quaranta, 1997, Aresta et al., 2016b).

$$RNH_2 + COCl_2 + R'OH \;>>$$

$$RNH - CO_2R' \;<<\; RNH_2 + CO_2 + R'OH. \qquad (2)$$

Even organic carbonates can be used for making carbamates by reaction with amines (Eq. 3)

$$RNH_2 + \left(R'O\right)_2 C = O \;>>\; RNHCO_2R' + R'OH. \qquad (3)$$

Polyurethanes are made by copolymerization of di-isocyanates, made from dicarbamates, (Eq. 4) with diols (Eq. 5)

$$R'O_2CNH - R - NHCO_2R' \;>>\; OCN - R - NCO \qquad (4)$$

$$nOCN - R - NCO + nHO\,(CH_2)_x\,OH \;>>\; -$$

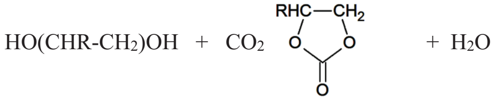
$$[OCN - R - NHC\,(O)\,O\,(CH_2)_x\,O]_n - \qquad (5)$$

All such products can be made by using CO_2. Due to its inertness, reactions based on CO_2 require active and selective catalysts, so to work at the lowest temperature while lowering the waste burden of synthetic processes.

Carbonates and Polycarbonates

These compounds are discussed elsewhere in this SI (Tomishighe et al., this SI). Here we wish to emphasize that the use of CO_2 in the synthesis of both linear (Eq. 6) or cyclic (Eq. 7) is greatly beneficial as reduces the environmental impact on a number of categories (Aresta and Galatola, 1999). Kinetic and thermodynamic issues have to be yet resolved for a practical utilization of Eqs. 6 and 7.

$$2ROH + CO_2 \;>>\; (RO)_2\,CO + H_2O \qquad (6)$$



(7)

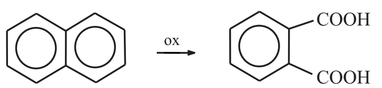
Water is the only co-product in both Eqs. 6 and 7. It may affect the catalyst and shifts the equilibrium to the left. Water elimination has been achieved by using organic [Aresta et al., 2005 and Tomishige et al., 2020, this (SI)] or inorganic water traps (Lercher et al., 2018). The use of cyanides ($RCN >> RC(O)NH_2$) as water trap (Tomishige et al., 2020) requires energy for post-process product separation by distillation; while the use of carbodiimides (RN = C = NR) (Aresta et al., 2005) has the advantage of a spontaneous separation from the reaction medium of the hydrated form urea (RHN-C(O)-NHR). All three processes above demand energy for recovering the water trap for re-use. The use of pervaporation membranes for water separation is a promising technique (Aresta et al., 2012) that has a lower energy demand (Aresta et al., 2017a).

Another approach to cyclic carbonates is the oxidative carboxylation (Aresta et al., 2000; Aresta and Dibenedetto, 2002; Hutchings et al., 2018; Wang et al., 2020) of olefins that has to win the drawback of olefin loss by radical oxidation.

Specialty Chemicals

The direct carboxylation of organic substrates (Aresta et al., 2018) may allow making complex structures shifting from "*several steps-several pots*" to "*one step-one pot*" processes with a lot of simplifications and substantially lowering the Carbon Footprint-CF and waste production of such processes. In general, such reactions imply a C–H activation, a non-simple process to achieve by thermal catalysis but more feasible under photochemical conditions (Aresta et al., 2015, 2017b). Actually, the formation of a carboxylic moiety passes through the oxidation of organic moieties (-CH_3, Eq. 8) or partial oxidative destruction of cyclic structures (naphthalene to dicarboxylic acids, Eq. 9) or even hydrolysis of cyanides (Eq. 10) or use of Grignard reagents (Eq. 11) or carbonylation processes using CO.

$$R - CH_3 >> R - CO_2H \tag{8}$$



(9)

$$R - CN + H_2O\ >>\ RC\,(O)\,NH_2\ >>\ RC\,(O)\,OH \tag{10}$$

$$R - X\ (X = Cl,\ Br,\ I)\ >>$$

$$RMgX\ >>\ RCO_2MgX\ >>\ RCO_2H \tag{11}$$

All such processes are not C-effective and have a high environmental impact. The direct carboxylation of organic substrates would be a winning option (Eq. 12) as a "*one step-one pot*" reaction.

$$RCH_3 + CO_2\ >>\ RCH_2 - CO_2H \tag{12}$$

The direct carboxylation of organic substrates can find application in many fields for the production of large-scale chemicals, such as long-chain carboxylic acids (potential market >10 Mt/y as surfactants and additives to product formulations), and specialty chemicals used in the pharmaceutical industry. Noteworthy, more complex if the structure of a chemical higher is the E-factor associated to its production (the E-factor is the ratio $t_{wasteproduced}/t_{usefulproduct}$ that grows with the complexity of a chemical and the number of steps necessary for its production). Therefore, introducing a carboxylic moiety through a multistep process into a complex organic molecule such as an active principle may cause the generation of large volumes of waste-C. Direct syntheses can be more effective, reduce the amount of waste, lower the CF and the overall environmental impact.

HIGH ENERGY PROCESSES FOR CO_2 CONVERSION

However, it will be the use of CO_2 as source of carbon for making fuels that will produce a big change because the fuels market is 15 times that of chemicals. In an energy frame based on fossil fuels, does not make sense to produce fuels from CO_2 because the production of the necessary hydrogen will emit more CO_2 than is fixed. For making a C_nH_{2n+2} hydrocarbon from CO_2, nCO_2 will be converted using $(n+1)H_2$ that will emit $(n+1)CO_2$ assuming that H_2 is made in a Syngas production frame, according to reaction 13, the known Water Gas Shift Reaction-WGSR:

$$CO + H_2O\ >>\ CO_2 + H_2 \tag{13}$$

To such amount, the CO_2 emitted for producing the necessary thermal energy for driving the synthetic and separation processes must be added, making the whole conversion a non-sense. In the medium-long term a new paradigm will be possible (Aresta et al., 2014a; Aresta et al., 2013a), as H_2 necessary for CO_2 reduction would be generated from water by electrolysis using PV. By 2040, the amount of PV power installed will grow to an estimated 3500-4500 GW, with respect to *ca*. 300 GW today. This will make the difference. The proof of concept is given by the already existing pilot or mini-demo plants[2] that use PV-H_2 for the methanation of CO_2. Today the cost of PV-H_2 is some 2.5,3 times higher than that of H_2 from Methane Reforming-MR. Such difference can be leveled in time by the increased efficiency of future solar cells (from actual 20 to 40^+% efficiency), their lower cost (*ca*. −50%) and longer resistance: the recent history of PV supports such trend. By 2040, PV-H_2 and MR-H_2 might have the same or very close price, allowing the large-scale industrial exploitation of the methanation reaction for which the development of large scale and robust electrolyzers is necessary. Having the correct infrastructure and non-fossil hydrogen at low cost, it will be possible to reach a significant capacity of conversion of solar energy into fuels (StF), with a net conversion of fossil-CO_2. Are we getting closer to a "Man-made C-Cycle"? Sure, we are.

In fact, we can take CO_2 directly from the atmosphere (DAC, Direct Atmosphere Capture, [Wang and Song, 2019]) and convert it into fuels using solar energy: this is mimic of Nature, with the advantage that the Man-Made cycle may be faster than the natural one and even more efficient as light use efficiency toward a single product, even if the efficient use of energy may not be an issue considered the large availability of solar energy. In such approach, it is compulsory that the energy necessary must come from perennial sources: it does not make sense use fossil-C. As for today, it is possible to carry out the conversions categorized below with the specific reported efficiencies:

Solar energy to electricity (StE)	20%
Electricity to H_2 (electrolysis of water) (EtH)	90%
Hydrogen to fuels (CO_2 hydrogenation) (HtF)	70%
or an overall Solar to Fuels (StF)	12.6%

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[2] https://www.caranddriver.com/news/a15370096/audi-opens-first-e-gas-synthetic-fuel-production-facility/

That is much higher than plants (1.8–2.2%) or even microalgae (6–10%), the best solar light utilizers.

Therefore, the Man-Made C-cycle targeting fuels such as methanol and methane is at our hand: it could be exploited in short term even if not yet at costs competitive with fossil-C based technologies, and in the medium term at close to market costs. The conversion of CO_2 into long-chain hydrocarbons is also an important objective that is under deep investigation and may give a strong contribution to C-recycling through CO_2 conversion. Parameters such as selectivity toward target products and chain elongation are still at low TRL (2–3). They need to be improved so to bring the process to a marketable level.

What we have seen so far is based on pure chemo-catalysis and thermal processes, even if combined with PV-hydrogen production. Such approach has a limitation in the fact that it still has some issues for what concerns the storage and use of H_2. Electrolytic hydrogen is already produced today, amounting to a few units per cent of the total amount: most of H_2 comes from MR (85%). The real innovation discussed above is in the use (not yet economically viable, as already specified) of PV in electrolysis. Electrolytic hydrogen is produced at ambient pressure, it needs to be stored (as liquid H_2) and distributed to the utilizers (industrial processes) which need pressurized (3.0-6.0 MPa) H_2. The discontinuity of PV generates a mismatch between the production and utilization phases of H_2 and storage of H_2 is necessary (unless electrolyzers are integrated into the electric grid and use fossil-C generated electricity during dark). We do not consider here the transport of H_2, because in the ideal case production of hydrogen, capture of CO_2, hydrogenation of CO_2 should be clustered on the same site and transport would be internal to the site. The storage of H_2 is not a trivial operation and it requires that high safety standards are met: such safety issues play a fundamental role in moving from a pilot plant to a full-scale plant, and even more when passing to a generalized, disseminated use of the option. The fact that H_2 is produced, rises the comments of some people about: "Why should we lose 30% efficiency in the conversion to C-based fuels? Let us use H_2 directly". This legitim comment finds an answer in the fact that the loss of efficiency is more than compensated by the fact that we can continue to use the same infrastructures, avoiding huge investment costs and reducing risk.

Are there alternative options to H_2-production? Yes: we can avoid producing hydrogen. This specific aspect, that is really innovative, will be discussed in next section.

INTEGRATION OF PHOTO-CATALYSIS AND BIOTECHNOLOGY

Avoiding the production, storage and distribution of hydrogen means to move from the use of solar energy for "*water splitting*" (typical approach of the hydrogen scientific community, so far) to the use of solar energy "*mimicking nature*", i.e., "*co-processing CO_2 and water*" affording directly reduced forms of CO_2, without H_2 production. This shift requires a high ability to implement the "*proton coupled to electron transfer*-PCET" ("$H^+ + e^-$" transfer to CO_2 with parallel O_2 formation) in water utilization as reducing agent of CO_2. The direct use of solar energy in driving chemical processes was foreseen by the Italian Chemist Giacomo Ciamician at the beginning of 1900 (Ciamician, 1912). A new paradigm, that changes the rules of the play and opens the way to a completely different approach to problem solving, leaving apart the old schemes. Nature teaches that for reducing CO_2 it is not necessary to generate hydrogen (Dibenedetto, 2016). However, it is PCET that must operate more than water splitting. The use of engineered semiconductors, coupling *n-p*-type materials for avoiding exciton collapse is the future. Having stable and efficient photocatalysts will allow CO_2 and water co-processing to energy products. Such approach is under investigation since long time, with alternate fortune. In the 1980s the light efficiency was around 0.1 % max (Mackor et al., 1987). Today, the literature shows best cases with > 10% light efficiency, (Hagfeldt and Graetzel, 1995; Esswein and Nocera, 2007; Aresta et al., 2016a) paving the way to a possible application.

A singular approach is the integration of photocatalysis with biotechnology, that means with the use of biosystems, either enzymes or whole microorganisms, for CO_2 reduction in water driven by the injection of electrons generated by using solar energy.Hybrid bioinspired systems have been used for the enzymatic reduction of CO_2 to CH_3OH in water at ambient conditions (Aresta et al., 2014b). The $6e^-$-reduction of CO_2 to CH_3OH is carried out by three NADH-dependent enzymes

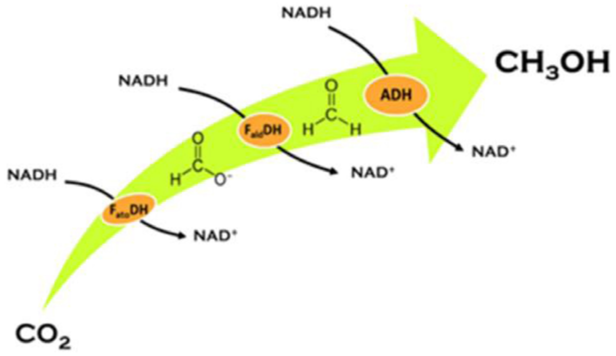

FIGURE 3 | CO_2 reduction to methanol by three dehydrogenase enzymes (Aresta et al., 2014b).

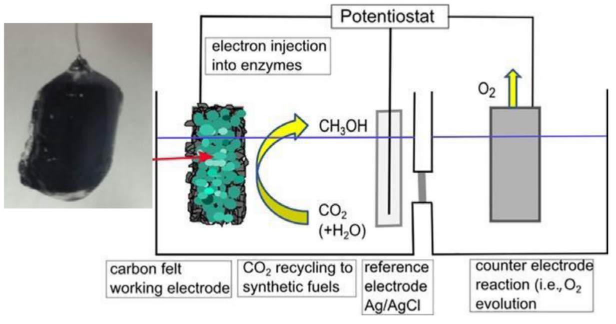

FIGURE 4 | Electrochemical cell for electroenzymatic CO_2 reduction.

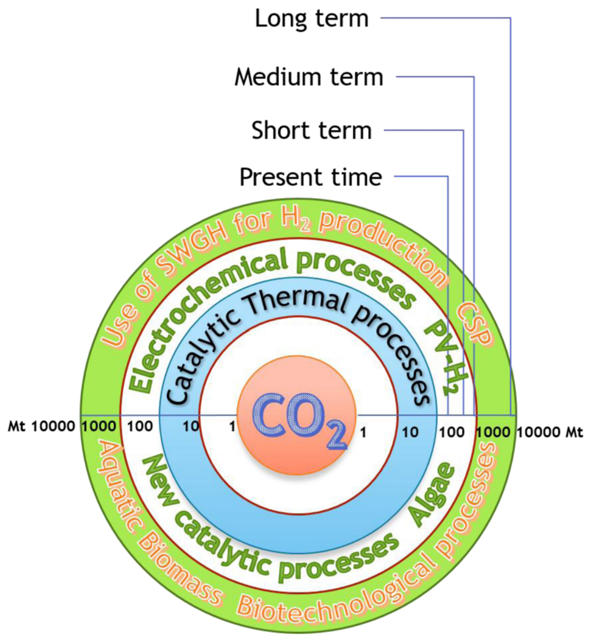

FIGURE 5 | Stepwise implementation of strategic technologies for CO_2 conversion, innovative processes and amount of CO_2 converted into added value products, fuels and materials.

(*Formate dehydrogenase-F$_{ate}$DH, Formaldehyde dehydogenase-F$_{ald}$DH and Alcohol dehydrogenase-ADH*) (**Figure 3**) co-encapsulated into an alginate matrix. As **Figure 3** shows each step uses one NADH as donor of $2e^-$ and protons: in total 3 mol of NADH are used per each mol of CH_3OH. Unless NADH is regenerated, this dream reaction is not economically viable.

An *in situ* photocatalytic reduction of NAD^+ to afford NADH, using semiconductors such as Cu_2O, $InVO_4$, TiO_2 modified either with the organic compound rutin, or with the inorganic complex $[CrF_5(H_2O)]^{2-}$) (Aresta et al., 2013b) and the doped sulfide Fe/ZnS has been carried out. The efficiency of the regeneration process is enhanced by using a Rh^{III}-complex for facilitating the electron and hydride transfer from the H-donor (water or a water-glycerol solution) to NAD^+. In this way one mol of NADH was used for producing over 100 mol of CH_3OH, opening the way to a practical application (Aresta et al., 2016b). The bottleneck in this process is the gap between the rate of consumption and that of regeneration of NADH, an issue still under investigation in our Lab. Following such idea and using catalytic electrodes for heterogeneous electrochemical CO_2 reduction, avoiding the use of NADH, co-encapsulated enzymes and co-factors were immobilized (**Figure 4**) on a carbon felt electrode (Schlager et al., 2017) with direct injection of electrons into them.

CO_2 is reduced to methanol at the working electrode (**Figure 4**) while oxidation reactions take place at the counter electrode. The bottleneck of this approach is the life of enzymes.

Other approaches have been followed by other research groups based on either the use of enzymes for NADH regeneration or on electrochemical NADH regeneration, with alternate fortune (Cazelles et al., 2013; Ullah et al., 2015).

Coupling of electrodes as source of electrons and more robust (than enzymes) whole microorganisms has been attempted in the last decade with the intent of reducing CO_2 to energy products. So, electrodes and hydrogenophilic methanogenic cultures have been used for the direct and indirect extracellular electron transfer for CO_2 reduction to methane (Villano et al., 2010). Such systems are known as BioElectrochemical Systems-BES (see the paper by Pant, this SI) that are rising great expectations as a new and sustainable technology for generation of energy and useful products from waste (Blankenship et al., 2011; Lovley and Nevin, 2013). In such devices, bacteria interact with solid-state electrodes (covered with semiconductor materials so that electricity is generated by shining light on the electrode surface) ad exchange electrons with them, either directly or via redox mediators. Microbial fuel cells (MFCs) and microbial electrolysis cells (MECs) are examples of a BES.

Combining the advantages of solar chemistry and BES could be the way to solve problems related to the use of metal enzymes, trying to make profit of their high conversion rate and selectivity. A "two-step" approach for CO_2 reduction to methane has been recently proposed, that electrochemically converts CO_2 into formate, used as substrate for methanogen *Methanococcus maripaludis* (Huang and Hu, 2018).

BES can be integrated into several processes. For example, biomass is converted into ethanol with less than 50% yield, co-producing liquid and solid waste rich in organics (including lignin) that could be advantageously used. Residual C6 and C5 sugars can be used as substrate in anodic oxidation in BES coupled to other reduction systems, or can be converted to higher energy products.

Even the large-scale production of biodiesel from palm-oil can be integrated with BES. In fact, the production of biodiesel from oils and fats is energy intensive. For example, for 100 kg of biodiesel produced, 5.3 kg of oily waste and 10.7 kg of glycerol are co-produced, while 466 MJ of energy are consumed. BES could be used for the conversion of watery glycerol either into propanediol (used as source of monomers for polymers (Aresta et al., 2013c) or ethanol, (Ito et al., 2005) or even hydrogen (Aresta and Dibenedetto, 2009).

A further step toward hi-tech applications is the building of "*hybrid*" systems integrating chemo- and-enzymatic catalysis (Dumeignil et al., 2018). Such approach aims at extreme simplification of reactive systems by developing one single device that incorporates chemo-catalysts and enzymes for a *single step-single pot* reaction targeting high selectivity and yield. This is not a easy-to-build system, as enzymes often suffer (can be deactivated) the presence of chemicals: in order to have effective systems, high complexity must be win in building both the integrated catalytic system and the reactor.

CONCLUSION

Innovative technologies are pushing the shift from the linear to C-circular economy (Dibenedetto and Nocito, 2020).

Such trend is being more and more integrated with Bio-economy. The "Linear economy" is based on a non-natural attitude: the consumerism (take natural resources-convert into goods-use-throw away), that generates plentiful waste that impacts natural systems and our life. The "Cyclic economy" is close to Nature: like Nature, that does not produce waste, the cyclic-economy recycles used goods, lowering both the extraction of natural resources and the environmental burden of human activities. Process integration will favor this trend.

Processes based on hybrid systems may in the future take the place of pure chemocatalytic-thermal processes, with saving of large amounts of fossil-C and reduction of CO_2 emission. "Cheap and clean" electrons generated by the use of perennial SWHG energies will supplant "dirty" thermal-electrons. CO_2 is renewable carbon, as Nature teaches. The conversion of CO_2 into chemical reactors is faster than both the natural conversion into added value products and the fossilization of C through biomass capture in soil. The integration of chemo-catalysis with bio-systems is happening with increasing intensity. Circular-Economy and Bio-economy are two faces of the same medal, are the strategies that will drive the world economy in future years and both aim at C-recycle through CO_2 conversion. The implementation of all tools we have in our hands, and of the new ones that will be discovered, will allow the conversion of *ca*. 9-10 Gt_{CO2}/y, as depicted in **Figure 5** and this is a great target.

DATA AVAILABILITY STATEMENT

The raw data supporting the conclusions of this article will be made available by the authors, without undue reservation.

AUTHOR CONTRIBUTIONS

MA and AD have contributed on the conceptualization and writing of the manuscript. AD has the responsibility on data collection while MA analyzed the data and provided feedback on the manuscript. All authors contributed to the article and approved the submitted version.

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REFERENCES

Aresta, M., and Dibenedetto, A. (2002). Carbon dioxide as building block for the synthesis of organic carbonates: behavior of homogeneous and heterogeneous catalysts in the oxidative carboxylation of olefins. *J. Mol. Catal. A* 182–183, 399–409. doi: 10.1016/s1381-1169(01)00514-3

Aresta, M., and Dibenedetto, A. (2009). "Energy from organic waste: influence of the process parameters on the production of methane and hydrogen," in *Catalysis for Sustainable Energy Production*, eds P. Barbaro and C. Bianchini (Hoboken, NJ: Wiley).

Aresta, M., and Dibenedetto, A. (2020). *The Carbon Dioxide Revolution*. Berlin: Springer.

Aresta, M., Dibenedetto, A., and Angelini, A. (2013a). The changing paradigm in CO2 utilization. *J. CO2 Util.* 3–4, 65–73. doi: 10.1016/j.jcou.2013.08.001

Aresta, M., Dibenedetto, A., Di Bitonto, L., and Dubois, J. L. (2013b). Synthetic Process of Trimethylene Carbonate From 1,3-Propanediol and Urea by Heterogeneous Catalysts Patent No: EP 13192912.7.

Aresta, M., Dibenedetto, A., Macyk, W., and Baran, T. (2013c). Photocatalysts Working in the Visible Region for the Reduction of NAD+ to NADH within an Hybrid Chemo-enzymatic Process of CO2 Reduction to Methanol Patent No: MI2013A001135.

Aresta, M., Dibenedetto, A., and Angelini, A. (2014a). From CO2 to chemicals and fuels. *Chem. Rev.* 114:1709.

Aresta, M., Dibenedetto, A., Baran, T., Angelini, A., Łabuz, P., et al. (2014b). An integrated photocatalytic-enzymatic system for the reduction of co2 to methanol in bio-glycerol-water *Beilstein. J. Org. Chem.* 10, 2556–2565. doi: 10.3762/bjoc.10.267

Aresta, M., Dibenedetto, A., Angelini, A., and Ethiraj, J. (2012). Synthesis, characterization and use of Nb(V)/Ce(IV)-mixed oxides in the direct carboxylation of ethanol with water removal with pervaporation membranes. *Chem. A Eur. J.* 18, 10324–10334. doi: 10.1002/chem.201201561

Aresta, M., Dibenedetto, A., Baran, T., Wojtyła, S., and Macyk, W. (2015). Solar energy utilization in the direct photocarboxylation of 2,3-dihydrofuran using CO2. *Faraday Discuss.* 183, 413–427. doi: 10.1039/c5fd00040h

Aresta, M., Dibenedetto, A., and Dutta, A. (2017a). Energy issues in the utilization of CO2 in the synthesis of chemicals: the case of the direct carboxylation of alcohols to dialkyl-carbonates. *Catal. Today* 281, 345–351. doi: 10.1016/j.cattod.2016.02.046

Aresta, M., Dibenedetto, A., Zhang, J., Trochowski, M., Angelini, A., et al. (2017b). Photocatalytic carboxylation of CH bonds promoted by popped graphene oxide (PGO) either bare or loaded with CuO. *J. CO2 Util.* 20, 97–104. doi: 10.1016/j.jcou.2017.05.010

Aresta, M., Dibenedetto, A., Fracchiolla, E., Giannoccaro, P., Pastore, C., Papai, I., et al. (2005). Mechanism of formation of organic carbonates from aliphatic alcohols and carbon dioxide under mild conditions promoted by carbodiimides. DFT calculation and experimental study. *J. Org. Chem.* 70, 6177–6186. doi: 10.1021/jo050392y

Aresta, M., Dibenedetto, A., and Macyk, W. (2016a). Photocatalytic carbon dioxide reduction at p-type copper(I) iodide. *ChemSusChem* 9, 2933–2938. doi: 10.1002/cssc.201600289

Aresta, M., Dibenedetto, A., and Quaranta, E. (2016b). *Reaction Mechanisms in Carbon Dioxide Conversion*. Berlin: Springer.

Aresta, M., Dibenedetto, A., and Tommasi, I. (2000). Direct synthesis of organic carbonates by oxidative carboxylation of olefins catalysed by metal oxides: developing green chemistry based on carbon dioxide. *Appl. Organomet. Chem.* 14, 799–802. doi: 10.1002/1099-0739(200012)14:12<799::aid-aoc82>3.0.co;2-8

Aresta, M. (ed.) (2003). *Recovery, and Utilization of Carbon Dioxide*. Dordrecht: Kluwer Acad Publ.

Aresta, M. (ed.) (2010). *Carbon Dioxide as Chemical Feedstock*. Weinheim: Wiley VCH.

Aresta, M., and Forti, G. (eds) (1987). *Carbon Dioxide as Carbon Source, NATO ASI Series C206*. Dordrecht: Reidel Publ.

Aresta, M., and Galatola, M. (1999). Life cycle analysis applied to the assessment of the environmental impact of alternative synthetic processes. The dimethylcarbonate case: part 1. *J. Clean. Product.* 7, 181–190.

Aresta, M., Nocito, F., and Dibenedetto, A. (2018). What catalysis can do for boosting CO2 utilization. *Adv. Catal.* 63, 49–111. doi: 10.1016/bs.acat.2018.08.002

Aresta, M., Pastore, C., Giannoccaro, P., Kovacs, G., Dibenedetto, A., et al. (2007). Evidence for spontaneous release of acrylates from a transition metal complex upon coupling ethene or propene with a carboxylic moiety or CO2. *Chem. A Eur. J.* 13, 9028–9034. doi: 10.1002/chem.200700532

Aresta, M., and Quaranta, E. (1997). Carbon dioxide: a substitute for phosgene. *Chemtech* 27, 32–40.

Blankenship, R. E., Tiede, D. M., Barber, J., Brudvig, G. W., Fleming, G., Ghirardi, M., et al. (2011). Comparing photosynthetic and photovoltaic efficiencies and recognizing the potential for improvement. *Science* 332, 805–809. doi: 10.1126/science.1200165

Carmona, E., Alvarez, R., Cole-Hamilton, D. J., Galindo, A., Gutiérrez-Puebla, E., Monge, A., et al. (1985). Formation of acrylic acid derivatives from the reaction of carbon dioxide with ethylene complexes of molybdenum and tungsten. *J. Am. Chem. Soc.* 107, 5529–5531. doi: 10.1021/ja00305a037

Cazelles, R., Drone, J., Fajula, F., Ersen, O., Moldovan, S., et al. (2013). Reduction of CO2 to methanol by a polyenzymatic system encapsulated in phospholipids-silica nanocapsules. *New J. Chem.* 37, 3721–3730.

Ciamician, G. (1912). "La fotochimica dell'avvenire (The photochemistry of the future)," in *Proceedings of the 8th International Congress on Applied Chemistry*, (New York, NY), 135–150.

Dai, A. (2006). Recent climatology, variability, and trends in global surface humidity. *J. Clim.* 19, 3589–3606. doi: 10.1175/jcli3816.1

Dessler, A. E., Zhang, Z., and Yang, P. (2008). Water-vapor climate feedback inferred from climate fluctuations. *Geophys. Res. Lett.* 35, 2003–2008.

Dibenedetto, A. (2016). Artificial photosynthesis and solar chemistry. *ChemSusChem* 9:3124.

Dibenedetto, A., and Nocito, F. (2020). Atmospheric CO2 mitigation technologies: carbon capture utilization and storage. *Curr. Op. Green Sust. Chem.* 21, 34–43. doi: 10.1016/j.cogsc.2019.10.002

Dumeignil, F., Guehl, M., Gimbernat, A., Capron, M., Ferreira, N. L., Froidevaux, R., et al. (2018). From sequential chemoenzymatic synthesis to integrated hybrid catalysis: taking the best of both worlds to open up the scope of possibilities for a sustainable future. *Catal. Sci. Technol.* 8, 5708–5734. doi: 10.1039/c8cy01190g

Esswein, A. J., and Nocera, D. G. (2007). Hydrogen production by molecular photocatalysis. *Chem. Rev.* 107, 4022–4047. doi: 10.1021/cr050193e

Hagfeldt, A., and Graetzel, M. (1995). Light-induced redox reactions in nanocrystalline systems. *Chem. Rev.* 95, 49–68. doi: 10.1021/cr00033a003

Hoberg, H., Jenni, K., Angermund, K., and Kruger, C. (1987). CC-linkages of ethene with CO2 on an iron (0) complex—synthesis and crystal structure analysis of [(PEt3) 2Fe (C2H4) 2]. *Angew. Chem.* 26, 153–155. doi: 10.1002/anie.198701531

Huang, Y. X., and Hu, Z. (2018). An integrated electrochemical and biochemical system for sequential reduction of CO2 to methane. *Fuel* 220, 8–13. doi: 10.1016/j.fuel.2018.01.141

Hutchings, G. J., Engel, R. V., Alsaiari, R., Nowicka, E., Pattisson, S., Miedziak, P. J., et al. (2018). Oxidative carboxylation of 1-Decene to 1, 2-Decylene carbonate. *Top. Catal.* 61, 509–518. doi: 10.1007/s11244-018-0900-y

Ito, T., Nakashimada, Y., Senba, K., Matsui, T., and Nishio, N. (2005). Hydrogen and ethanol production from glycerol-containing wastes discharged after biodiesel manufacturing process. *J. Biosci. Bioeng.* 100, 260–265. doi: 10.1263/jbb.100.260

Kolbe, H. (1860). Ueber Synthese der Salicylsäure. *Justus Liebigs Ann. Chem.* 113, 125–127. doi: 10.1002/jlac.18601130120

Lercher, J. A., Peng, B., Dou, H., Shi, H., and Ember, E. E. (2018). Overcoming thermodynamic limitations in dimethyl carbonate synthesis from methanol and CO2. *Catal. Lett.* 148, 1914–1919. doi: 10.1007/s10562-018-2402-8

Li, Y., Liu, Z., Cheng, R., and Liu, B. (2018). Mechanistic aspects of acrylic acid formation from CO2–ethylene coupling over palladium-and nickel-based catalysts. *ChemCatChem* 10, 1420–1430. doi: 10.1002/cctc.201701763

Limbach, M., Lejkowski, M. L., Lindner, R., Kageyama, T., Bódizs, G. E., Plessow, P. N., et al. (2012). The first catalytic synthesis of an acrylate from CO2 and an alkene—a rational approach. *Chem. A Eur. J.* 18, 14017–14025. doi: 10.1002/chem.201201757

Lovley, D. R., and Nevin, K. P. (2013). Electrobiocommodities: powering microbial production of fuels and commodity chemicals from carbon dioxide with electricity. *Curr. Opin. Biotechnol.* 24, 385–390. doi: 10.1016/j.copbio.2013.02.012

Mackor, A., Tinnemans, A. H. A., and Koster, T. P. M. (1987). "Reduction of CO2 at titanate powders in sunligth and at electrodes in the light or dark," in *Carbon Dioxide as Carbon Source, NATO ASI Series C206*, eds M. Aresta and G. Forti (Dordrecht: Reidel Publ.), 393.

Papai, I., Schubert, G., Mayer, I., Besennyei, G., and Aresta, M. (2004). Mechanistic details of nickel (0)-assisted oxidative coupling of CO2 with C2H4. *Organomet* 23, 5252–5259. doi: 10.1021/om049496%2B

Schlager, S., Dibenedetto, A., Aresta, M., Apaydin, D. H., Dumitru, L. M., Neugebauer, H., et al. (2017). Biocatalytic and bioelectrocatalytic approaches for the reduction of carbon dioxide using enzymes. *Energy Technol.* 5, 812–821. doi: 10.1002/ente.201600610

The Catalyst Group Resources [TGCR] (2012). *Analysis of Demand for Captured CO2 and Products from CO2 Conversion*. Bethlehem, PA: The Catalyst Group Resources [TGCR].

Tomishige, K., Gu, Y., Nakagawa, Y., and Tamura, M. (2020). Reaction of CO2 with alcohols to linear-, cyclic-, and poly-carbonates using CeO2-based catalysts. *Front. Energy Res.* 8:117. doi: 10.3389/fenrg.2020.00117

Ullah, N., Ali, I., and Omanovic, S. M. (2015). Direct electrocatalytic reduction of coenzyme NAD(+) to enzymatically-active 1,4-NADH employing an iridium/ruthenium-oxide electrode. *Chem. Phys.* 149–150, 413–417. doi: 10.1016/j.matchemphys.2014.10.038

Villano, M., Aulenta, F., Ciucci, C., Ferri, T., Giuliano, A., et al. (2010). Bioelectrochemical reduction of CO2 to CH4 via direct and indirect extracellular electron transfer by a hydrogenophilic methanogenic culture. *Biores. Technol.* 101, 3085–3090. doi: 10.1016/j.biortech.2009.12.077

Wang, L., Que, S., Ding, Z., and Vessally, E. (2020). Oxidative carboxylation of olefins with CO2: environmentally benign access to five-membered cyclic carbonates. *RSC Adv.* 10, 9103–9115. doi: 10.1039/c9ra10755j

Wang, X., and Song, C. (2019). "Capture of CO2 from concentrated sources and the atmosphere," in *An Economy based on Carbon Dioxide and Water*, eds M. Aresta, I. Karimi, and S. Kawi (Cham: Springer).

Woehler, F. (1828). Uber kuenstliche bildung des Harnstoff. *Ann. Phys. Chem.* 88, 253–256. doi: 10.1002/andp.18280880206

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REVIEW
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Toward Enhanced Fixation of CO_2 in Aquatic Biomass: Focus on Microalgae

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The need to reduce the CO_2 footprint of human activities calls for the utilization of new means of production and new sources of products. Microalgae are a very promising source of a large variety of products, from fuels to chemicals for multiple industrial applications (e.g., dyes, pharmaceutical products, cosmetics, food and feed, new materials for high tech manufacture), and for processes such as wastewater treatment. Algae, as photosynthetic organisms, use light to energize the synthesis of organic matter and differently from most terrestrial plants, can be cultured on land that is not used for crop production. We describe the main factors contributing to microalgae productivity in artificial cultivation systems and discuss the research areas that still need investigation in order to pave the way to the generation of photosynthetic cell factories. We shall comment on the main caveats of the possible mode of improving photosynthetic efficiency and to optimize the partitioning of fixed C to products of commercial relevance. We address the problem of the selection of the appropriate strain and of the consequences of their diverse physiology and culture conditions for a successful commercial application. Finally, we shall provide state of the art information on cell factories chassis by means of synthetic biology approaches to produce chemicals of interest.

Keywords: microalgae, photosynthesis, Rubisco, C allocation, lipid metabolism, polycultures, metabolic engineering, cell factory

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INTRODUCTION

Climate changes presently occurring on Earth point toward the need to reduce the CO_2 anthropogenic emissions and call for the utilization of renewable sources of products, especially of fuels. CO_2 accounts for about 76% of total greenhouse gases which are emitted for the most part (72%) by the energy production sector (International Energy Agency, 2019). Global CO_2 emissions in 2019 flattened at around 33 Gt and the reason has been ascribed to clean energy transition happening in the power sector (International Energy Agency, 2020a). Among renewable sources of energy, biomass (that includes agriculture and forest residues, energy crops, and algae) contains stored energy from the sun.

Sunlight is an almost limitless source of energy, with about 100000 TW y^{-1} reaching our Planet. It is a massive amount compared to our current energy consumption of about 15 TW y^{-1}, and to its forecasted increase to about 45 TW y^{-1} by the end of this century (Barber, 2009;

Benedetti et al., 2018). Even though photosynthetic organisms are already able to store about 100 TW y^{-1}, land plants primarily store the energy as lignocellulose, a biopolymer which is not easily exploited as renewable feedstock (Barber, 2009; Aro, 2016). Yet, half of Earth photosynthesis is run by algae in aquatic environments. Conversely to land plants, algal cells do not contain lignin, and the photosynthetically fixed carbon (C) is readily recycled in the ecosystems through the food web (Barber, 2009). Algae display other advantages for industrial applications with respect to land plants. They show higher growth rates, all their biomass is photosynthetically active, and they photosynthesize all year around, leading to about twice as much projected yield per acre with respect to land plants (Chisti, 2007; Clarens et al., 2010, International Energy Agency, 2017). Further, they do not compete for arable land with edible plants, and, in the case of marine species, they avoid the use of drinkable water, highly valuable features considering the forecasted worldwide population increase and future food demand.

Algae as oxygenic phototrophs include, in a broad definition, both prokaryotic and eukaryotic organisms (Raven and Giordano, 2014). In eukaryotic algae two major plastid lineages are observed. The green lineage includes mainly Chlorophyta (green algae) species. The red lineage encloses Rhodophyta (red algae) and several phylogenetic groups originated from secondary endosymbiotic events, like diatoms (Bacillariophyta) (Raven and Giordano, 2014). Microalgae show a wide range of morphologies and cell sizes (1 μm -1 mm) (Giordano and Wang, 2018). They live in marine, freshwater and terrestrial environments, colonizing even habitats characterized by extreme conditions (Raven and Giordano, 2014; de Vargas et al., 2015). They also display a wide range of metabolic diversity, representing a valuable natural source of multiple compounds (Brodie et al., 2017), from biofuels to pharmaceutical products, cosmetics, food and feed, new materials for high tech manufacture (**Table 1**). Carbohydrate-rich microalgal feedstock is also a suitable substrate for fermentative processes to synthesize fine chemicals (such as succinic acid and lactic acid) (Wang et al., 2013; Lee et al., 2017). Further, life cycle analysis and product environmental footprint assessed that microalgae-based products are sustainable, clean and contribute to waste valorization (Dietrich et al., 2017).

Although microalgae have been commercially cultured for over 40 years, their biomass is still quite scant on the market, nowadays ranging around 13600 t y^{-1}, which corresponds to about 27200 t y^{-1} of CO_2 (International Energy Agency, 2017; Morales et al., 2018). Currently, the lacunose understanding of the biological constraints on algal photosynthesis and growth, particularly in large-scale production plants, hampers a cost-effective exploitation of algal biomass as a new mean for CO_2 capture into bioenergy feedstock and as a cheap source of commercial products. Thus, future efforts shall avail a deeper comprehension of physiological and environmental factors controlling microalgal resource allocation to the multiple metabolic pathways. In this way, beside selecting the best natural CO_2 fixers and producers of fine chemicals, we shall also design photosynthetic living factories converting sunlight and inorganic (or recycled) nutrients into valuable biomolecules, at costs which make the biological production system economically viable.

Although technological advances in large scale production plants are also necessary for a sustainable algae-based industry, in this review we will focus on the key biological factors limiting microalgae photosynthetic efficiency and physiological processes associated to their productivity. We will outline how the interplay between algal genotypes and resource availability affects the biomass quality. We shall address open challenges and possible solutions to achieve higher product yields.

MAIN FACTORS AFFECTING MICROALGAE CO_2 FIXATION IN NATURE

Light Capture and Conversion Into Chemical Energy

Photosynthetic organisms currently convert into biomass about 0.1% of the sunlight energy reaching Earth (Barber, 2009; Benedetti et al., 2018). Photosynthetic efficiency increases to 1%, or seldomly to 3%, under controlled growth conditions (Zhu et al., 2008; Melis, 2009; Cotton et al., 2015), while the theoretical maximum of oxygenic photosynthesis energy conversion into biomass is estimated to be about 10-12% (Zhu et al., 2008; Melis, 2009; Blankenship et al., 2011; Peers, 2014).

To convert sunlight into biomass, oxygenic photosynthetic organisms first capture light by means of light harvesting pigments. Energy is then transferred to the photosystem (PS) reaction center (RC), where charge separation occurs. Electrons move along the thylakoid multiprotein complexes PSII, cytb_6f, PSI, to generate reductants and ATP synthase produces ATP. Reducing power and ATP are then used by several metabolic reactions (see **Figure 1** for further details).

Already during the so-called light reactions of photosynthesis several factors contribute to the reduced final yield (**Figure 2**).

(i) Energy loss due to light quality. Some energy losses are intrinsic to the light-harvesting pigments. Each pigment is capable of capturing specific light wavelengths of the visible spectrum, each corresponding to the energy required to promote an electron from the ground state to different excited states. E.g., in chlorophylls, red photons promote electrons to the lowest singlet excited state, while more energetic blue photons span the energy gap to higher excited states. In order to drive photochemistry, pigment molecules first require the internal conversion of such higher excited states to the lowest singlet excited state. The extra energy of high energy photons (e.g., blue photons) is lost as heat before energy transfer and charge separation may occur (Barber, 2009; Johnson, 2016; **Figure 2**). All species performing oxygenic photosynthesis accumulate chlorophyll *a* (Chl *a*) as the main pigment. Primary accessory pigments vary according to the phylogenetic groups and range among Chl *b* (green algae), Chl *c* (e.g., diatoms) or phycobilins (cyanobacteria and red algae). Multiple carotenoids involved both in light harvesting and in photoprotection are also synthesized. Only the

TABLE 1 | Major natural products from microalgae (Gallardo-Rodríguez et al., 2012; Borowitzka, 2013; Enzing et al., 2014; Giordano and Wang, 2018; Kamalanathan and Quigg, 2019 and references there in; Taubert et al., 2019).

Feedstock (algal pools)	Valuable products	Market	Microalgae source
Pigments	ß-Carotene, Astaxanthin, Lutein, Zeaxanthin, Canthaxanthin, Chlorophyll	Nutraceuticals, cosmetics, light protectant, natural dye	*Dunaliella salina, Dunaliella bardawil, Haematococcus pluvialis, Chlorella vulgaris*
	Fucoxanthin		*Phaeodactylum tricornutum*
	Phycocyanin, Phycoerythrin		*Arthrospira, Porphyridium, Rhodella, Galdieria*
	Mycosporine-like amino acids		Cyanobacteria, dinoflagellates
Antioxidants	Catalases, Polyphenols, Superoxide Dismutase, Tocopherols	Nutraceuticals, cosmetics, pharmaceuticals	Many species
Polyhydroxyalkanoates	Poly-3-hydroxybutyrate	Bioplastic	*Nostoc, Arthrospira, Synechocystis*
Lipids	TAG	Biofuels	*Dunaliella, Neochloris oleoabundans, Nannochloropsis, Botryococcus*
Fatty acids (PUFAs)	ARA (C20:4), GLA (C18:3), EPA (C20:5)	Food, feed	*Nannochloropsis, Phaeodactylum tricornutum, Nitzschia*
	DHA (C22:6)		*Schizochrytium, Crypthecodinium cohnii*
Phytosterols	Cholesterol, brassicasterol, sitosterol and stigmasterol	Pharmaceuticals, cosmetics	Many species
Terpenoids	Squalene	Cosmetics	*Aurantiochytrium, Botryococcus*
Carbohydrates	Antifungal, Antimicrobial, Antiviral, Toxins	Pharmaceuticals, cosmetics	*Porphyridium, Rhodella*
	Ethanol and Alcohols	Biofuels	Many species
	Starch	Bioplastics	Chlorophytes
	Fermentable sugars i.e. glucose	Polylactic acid (PLA) polymers	Many species
Proteins, peptides, amino acids		Food, feed	*Arthrospira, Apanizomenon flos-aquae, Chlorella, Pavlova, Phaeodactylum, Chaetoceros, Skeletonema, Thalassiosira, Tetraselmis, Isochrysis, Nannochloropsis*
Vitamins	A, B1, B6, B12, C, E, Biotin, Riboflavin, Nicotinic acid, Pantothenate, Folic acid	Food supplement	*Dunaliella salina, Chlorella vulgaris* and many species
Frustules and Silica shelves	Nanoparticles	Drug delivery, new material	Diatoms
H_2 producing enzymes	H_2	Biofuel	*Chlamydomonas reinhardtii*
Glycolate	Fermentable substrate for methane production	Biofuel	*Chlamydomonas reinhardtii*
Exopolymeric substances	Mostly polysaccharides, proteins but also DNA, RNA, and other macromolecules	Surfactant, lubricant	Many species among chlorophytes, rodophytes, diatoms, cyanobacteria
Biotoxins	Tetrodotoxin, Okadaic acid, Brevetoxin	Bioactive molecules, pharmaceuticals	Dinoflagellates

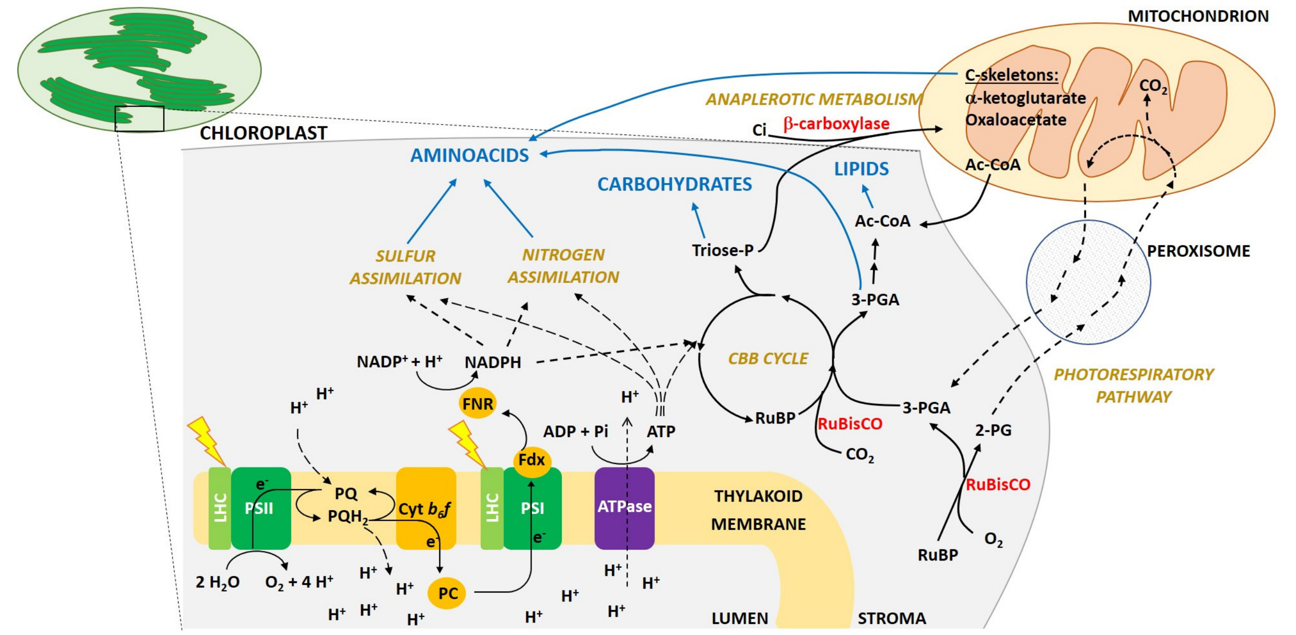
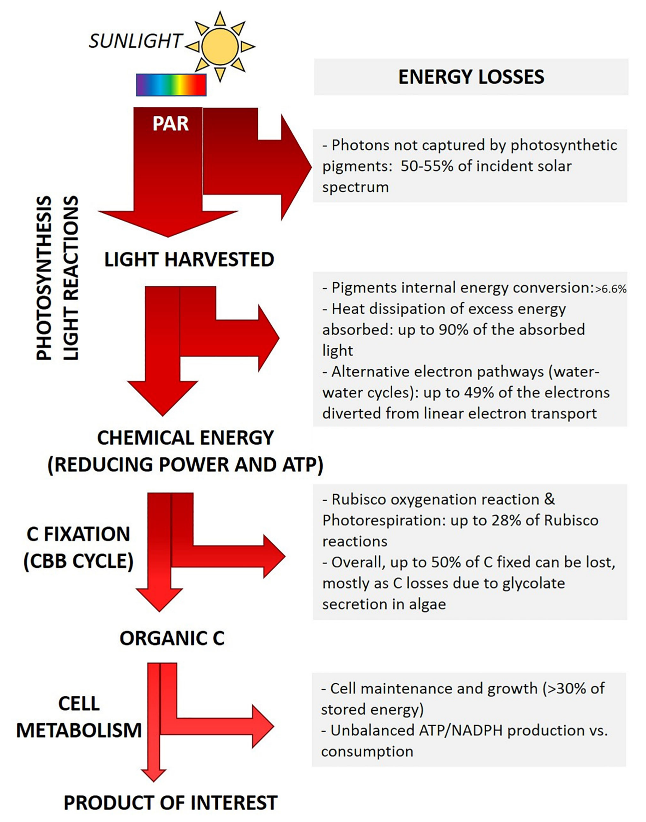


FIGURE 1 | Schematic overview of photosynthesis light reactions, C fixation and allocation into macromolecule pools in eukaryotic algae. The main protein complexes involved in photosynthetic light capture and electron transport are located in the thylakoid membranes inside the chloroplast (PSII, Photosystem II; LHC, Light Harvesting complexes; cytb_6f, cytochrome b_6f; PSI, Photosystem I; ATPase, ATP synthase). The absorption of light energy at PSII and PSI drives the linear electron transport from water to NADPH. Electrons extracted from water at the luminal side of PSII, thanks to the membrane soluble electron carrier plastochinol (PQ/PQH$_2$, plastoquinone/plastoquinol), move to the cytb_6f, which then transfers an electron to plastocyanin (PC), a luminal protein. PC reaches PSI, which then reduces Ferredoxin (Fdx) on its stromal side. Fdx interacts with Ferredoxin NADPH reductase (FNR) to finally reduce NADP$^+$ to NADPH. Regulatory proteins involved in the dissipation as heat of the absorbed exceeding energy (e.g., LHCSR protein), or involved in alternative electron transport routes (e.g., FLV, PGRL1, NDH-1), are not included in the picture. In parallel to electron transport, a proton gradient is generated across the thylakoid membrane, which is used by the ATP synthase to produce ATP. ATP and reducing power generated during electron transport are then used for C fixation in the Calvin-Benson-Bassham (CBB) cycle, as well as for N and S assimilation and other metabolic pathways. Only the main metabolic intermediates and enzymes are shown. Rubisco enzyme catalyzes the carboxylation of Ribulose-1,5-bisphosphate (RuBP), using CO_2 and producing two molecules of 3-phosphoglycerate (3-PGA). 3-PGA is then reduced to triose phosphates sugars (Triose-P; GAP and DHAP). Both 3-PGA and triose-P can be allocated into carbohydrates, lipids and amino acids synthesis, or used to regenerate RuBP in the regeneration phase of the CBB cycle. C-skeletons are also imported from mitochondria, mainly in the form of α-ketoglutarate, oxaloacetate or Acetyl-CoA. Note that even if here we are focusing mainly in photosynthesis and we depict macromolecules synthesis only in the chloroplast stroma, in the cell multiple pathways exist to metabolize sugars, lipids and amino acids also in other cellular compartments. Rubisco, as detailed in the text, also catalyzes an oxygenation reaction, producing from RuBP and molecular oxygen a molecule of 3-PGA, which enters the CBB cycle, and a molecule of 2-phosphoglycolate (2-PG). The latter is first dephosphorylated to glycolate in the chloroplast stroma. The glycolate is then exported from the chloroplast and secreted from the cell or enters a dedicated salvage pathway, the photorespiration, which in eukaryotic cells involves several reactions taking place also in peroxisomes and mitochondria. Part of the C is lost as CO_2 (25%), while the reaming part is converted back to 3-PGA and metabolized as above.

fraction of incident sunlight which can be absorbed by photosynthetic cells is "photosynthetically active" (Photosynthetically Active Radiation - PAR, 400–700 nm), whereas almost half of the solar irradiance spectrum cannot be captured and it is not energizing photosynthesis (Cardona et al., 2018; **Figure 2**). Rarely, Chl *d* or Chl *f* are also synthesized, expanding PAR to the far-red region (till 750 nm) (Cardona et al., 2018; Nürnberg et al., 2018). Introducing pathways to synthesize such far-red absorbing pigments has been suggested as a tool to widen the range of captured light (Cardona et al., 2018). The use of strictly red and far-red light sources would reduce this kind of light energy loss, yet this approach has the drawback to require artificial light sources (Cotton et al., 2015). Recently, new materials able to convert unabsorbed photons with higher energy (e.g., green photons) into red photons have also been developed, possibly contributing to reduce the fraction of unexploited light energy in industrial applications (Ooms et al., 2016).

(ii) Energy loss due to light intensity. In the Nature, the ability to harvest as much sunlight energy as possible, even exceeding cell metabolic demand, is likely to provide a competitive advantage to individuals, as this behavior minimizes the energy harvested by nearby competitors and thus their growth (Melis, 2009). Further, natural light intensity frequently fluctuates from being limiting to in excess. Photosynthetic organisms thus evolved the ability to fine tune the amount of energy spent in photochemistry or dissipated. Energy dissipation is minimal when light irradiance is low and all available energy drives photosynthesis. Conversely, under saturating illumination, the fraction of energy and/or electrons in excess compared to the metabolic demand is safely



- Photons not captured by photosynthetic pigments: 50-55% of incident solar spectrum

- Pigments internal energy conversion:>6.6%
- Heat dissipation of excess energy absorbed: up to 90% of the absorbed light
- Alternative electron pathways (water-water cycles): up to 49% of the electrons diverted from linear electron transport

- Rubisco oxygenation reaction & Photorespiration: up to 28% of Rubisco reactions
- Overall, up to 50% of C fixed can be lost, mostly as C losses due to glycolate secretion in algae

- Cell maintenance and growth (>30% of stored energy)
- Unbalanced ATP/NADPH production vs. consumption

FIGURE 2 | Outline of main energy losses during light energy conversion into biomass. Major biological processes responsible for energy loss are summarized, the corresponding estimated amount of energy dissipated is also outlined (Tabita et al., 2008; Zhu et al., 2008; Blankenship et al., 2011; Wilhelm and Selmar, 2011; Peers, 2014). The actual fraction of energy loss depends on the microalgal genotype and on the specific growth conditions (light intensity and quality, temperature, nutrients concentration and chemical form), as detailed in the text.

dissipated (Peers et al., 2009; Peltier et al., 2010; Wilhelm et al., 2014; Allahverdiyeva et al., 2015; Lepetit et al., 2017). Microalgae display different amplitude and combination of molecular mechanisms to dissipate excess energy, according to their phylogenetic group and habitat (i.e., growth conditions) (Peers et al., 2009; Peltier et al., 2010; Gerotto and Morosinotto, 2013; Meneghesso et al., 2016). Nature-driven evolution of the light harvesting regulation is essential for photosynthetic cells to cope with natural light variations (Wilhelm and Selmar, 2011; Niyogi and Truong, 2013). However, it turns detrimental for the productivity of photosynthetic organisms in commercial application, as it leads to the dissipation of most of the energy harvested, up to 80-90%, in saturating light conditions (Wilhelm and Selmar, 2011; Peers, 2014; **Figure 2**). Noteworthy, in natural environments light saturation of photosynthesis usually occurs at around 10-20% of full sunlight intensity (Melis, 2009; Peers, 2014).

A similar situation occurs in dense microalgal cultures such as those in artificial cultivation systems, where cells of the external layer experience over-saturating illumination and dissipate most of the energy or, in the worst case, suffer of photoinhibition. On the contrary, the inner layer of cells is subjected to light limitation (Melis, 2009; Simionato et al., 2013).

Inorganic Carbon Capture and Conversion

CO_2 in the atmosphere is nowadays above 400 ppm, while future scenarios assume a peak of 750 ppm by the end of this century, according to the Fifth Assessment Report (AR5) of the International Panel of Climate Change [IPCC] (2014). Due to anthropogenic emissions, a net flux of CO_2 from the atmosphere has been reaching the oceans thanks to CO_2 dissolution and biological fixation (Falkowski and Raven, 2007). The former mechanism depends on atmospheric CO_2 pressure, temperature, salinity and pH. At the usual pH of seawater, around 8.0–8.3, the dissolved inorganic carbon (DIC) is mainly in the form of HCO_3^-, so that the equilibrium concentration of CO_2 ranges between 10 and 20 μM in present oceans (Falkowski and Raven, 2007).

Among DIC species, only CO_2 is the chemical form of inorganic carbon (Ci) fixed by Ribulose-1,5-bisphosphate Carboxylase/Oxygenase (Rubisco) enzyme into carbohydrates. Rubisco is the major carboxylase on Earth and, likely, the most common enzyme in the biosphere (Ellis, 1979). Carboxylation of the pentose phosphate sugar ribulose-1,5-bisphosphate (RuBP) by Rubisco produces two 3-phosphoglicerate (3-PGA) molecules (**Figure 1**). Despite being so widespread in oxygenic photosynthetic organisms, Rubisco is a quite inefficient enzyme (Falkowski and Raven, 2007). The reaction has a slow turnover rate (i.e., a low K_{cat}^{c}) and it needs relatively high concentrations of CO_2 (elevated Michaelis-Menten constant, K_m, for CO_2). In addition, O_2 is a competitive inhibitor of the carboxylation reaction. When oxygenation of RuBP occurs, a molecule of phosphoglycolate (2-PG) is produced together with one of 3-PGA (**Figure 1**). The latter enters the Calvin-Benson-Bassham (CBB) cycle, while 2-PG is a toxic compound and not a common metabolic intermediate (Hagemann et al., 2016). The 2-PG phosphate is first recovered by hydrolysis and the glycolate is excreted in variable quantity from the cell (Raven et al., 2000). The glycolate retained inside the cell enters a dedicated salvage pathway, the photorespiration, accomplished in the chloroplast, peroxisome and mitochondrion of eukaryotic algae (see Hagemann et al., 2016 for evolutive details). In this pathway, glycolate is metabolized and up to 75% of the carbon is recovered in the form of 3-PGA, whereas the remaining 25% is lost as CO_2 (**Figure 1**). Rubisco oxygenation side-reaction thus impacts photosynthetic organisms' final productivity in two ways (**Figure 2**). First, due to the high concentration and solubility of O_2, the amount of C lost because of 2-PG formation can be appreciable and decreases photosynthetic efficiency in C fixation. Second, photorespiration increases the energetic cost associated with photosynthesis (Raven et al., 2000).

In the course of evolution, Rubisco CO_2/O_2 selectivity factor ($\tau = V_{maxCO2}\ K_{mO2}/V_{maxO2}\ K_{mCO2}$) showed a tendency to increase as compared to the value in the more primitive cyanobacteria, partially mitigating the impact of oxygenation (**Table 2**; Tabita et al., 2008). Half-saturation constant for CO_2 (K_m for CO_2) also decreased. However, the maximal reaction rate ($K_{cat}{}^{c}$) became lower (**Table 2**). The highest known value of τ is 238 and it is found in red algae (Raven et al., 2000). Diatoms show instead a greater variation in τ and K_{mCO2} values which do not follow the evolutive trend (**Table 2**; Young and Hopkinson, 2017).

No Rubisco with zero oxygenation activity has evolved in Nature, possibly due to intrinsic fragility of the active site. Nevertheless, microalgae achieved a strong reduction in Rubisco oxygenation by evolving the so-called CO_2 concentrating mechanisms (CCMs) to actively pump CO_2 at the Rubisco active site, in an energy-dependent manner (Giordano et al., 2005). Conversely to the so-called "biochemical" CCM, like C4 or CAM metabolism in plants, in algae $HCO_3{}^-$ is not first incorporated into organic intermediates and then released as CO_2 nearby Rubisco (Raven, 1997a, 2010; Giordano et al., 2005). Taking advantage of the different forms of Ci dissolved in water, microalgal "biophysical" CCM uses CO_2 channels and $HCO_3{}^-$ membrane transporters to accumulate Ci, carbonic anhydrases (CAs) to allow the rapid conversion of $HCO_3{}^-$ to CO_2 or *vice versa* following the equilibrium and acidic compartments (primarily the thylakoid lumen) to favor $HCO_3{}^-$ conversion to CO_2 next to the Rubisco. The additional occurrence of Rubisco-containing microcompartments, the carboxysomes in cyanobacteria and the pyrenoids in eukaryotic algae, further facilitates the constitution of high CO_2 concentrations and, at the same time, limits CO_2 leakage through the outward diffusion.

Although widespread in microalgae, CCMs show species-specific features, which result in different energy requirement to effectively concentrate CO_2 nearby Rubisco. More efficient biophysical CCMs have been observed in species where Rubisco selectivity is lower, like cyanobacteria, but also green algae (Giordano et al., 2005) and some diatoms (Hopkinson et al., 2011, 2016; Young et al., 2016). In the latter, CCMs are indeed quite diverse among species and unique, suggesting a co-evolution between Rubisco properties and CO_2 concentrating strategies (Tachibana et al., 2011; Matsuda et al., 2017; Young and Hopkinson, 2017). So far, CCMs with lower energy cost (calculated as mol photons absorbed per mol of Ci converted into one mol C in carbohydrate, assuming no leakage of CO_2 in CCMs) take advantage of $HCO_3{}^-$ entry in the thylakoid lumen driven by the proton gradient generated during photosynthesis (Raven et al., 2014). Luminal CAs, like Cah3 found in the green alga *Chlamydomonas reinhardtii* (Karlsson et al., 1998) and Θ-CA in the diatom *Phaeodactylum tricornutum* (Kroth et al., 2008; Kikutani et al., 2016; Matsuda et al., 2017), then speed up the equilibration of $HCO_3{}^-$ and CO_2, causing the CO_2 diffusion out of the thylakoid into the surrounding pyrenoid, where Rubisco is localized (Raven, 1997b).

In addition to the reaction of oxygenation, the very low value of Rubisco catalytic rate ($K_{cat}{}^{c}$) (2–4 C s^{-1}) is likewise a major barrier to enhance C assimilation, except in cyanobacteria whose $K_{cat}{}^{c}$ is around 12 C s^{-1} (**Table 2**). A higher $K_{cat}{}^{c}$ would reduce the amount of Rubisco required by the cell to sustain a certain growth rate, improving nitrogen (N) use efficiency of Rubisco itself and of the additional proteins involved in its assembly and activation (Raven et al., 2014). In fact, when low temperature slows down enzymatic reactions and also Rubisco's $K_{cat}{}^{c}$ is decreased, algae respond by increasing Rubisco abundance per cell (Young et al., 2015). Since accumulating Rubisco is costly, algae may alternatively adopt the strategy of increasing the abundance of CCM components instead of the Rubisco enzyme at low temperature (Andersson, 2008).

Metabolic Fluxes of C

The 3-PGA produced by Rubisco can be allocated as such to other metabolic pathways like fatty acid synthesis, but it is typically reduced to the triose-phosphate glyceraldehyde-3-phosphate (GAP) in the reduction phase of CBB cycle and, hence, used by the cell (**Figure 1**). Some GAP molecules are further processed in the CBB cycle to regenerate the starting substrate RuBP. Other molecules are the net production of C fixation and are directed to the synthesis of monosaccharides and storage carbohydrates, which are then used in cell growth, respiration and synthesis of the other cell organic compounds (**Figure 1**).

Storage carbohydrates differ among species. Diatoms, under nutrient-replete conditions, store sugars in vacuoles as the β-1,3-glucan polymer (chrysolaminarin) during the day, catabolizing it in the dark (Granum et al., 2002; Caballero et al., 2016). Carbohydrates are also involved in extracellular polymeric substances production (Granum et al., 2002). In green algae (like in plants) carbohydrates accumulate in the form of starch crystalline granules within the plastid, whereas red algal starch is cytosolic and is known as floridean starch (Patron and Keeling, 2005). Cyanobacteria, as most bacteria, accumulate glycogen or poly3-hydroxybutrate (PHB) or other polyhydroxyalkanoates (PHAs) as energy stores (Murphy and Vance, 1999). PHAs are being considered promising candidates for sustainable polymer production as an alternative to conventional plastics (Luengo et al., 2003); PHAs-derived bioplastics would be completely and quickly bio-degraded by a variety of microorganisms into CO_2 and water (**Table 1**).

Cyanobacteria can allocate C also to neutral lipids, which are accumulated as small droplets (30-300 nm) close to the cell or thylakoid membrane (Peramuna and Summers, 2014). Many eukaryotes, instead, form lipid bodies of triacylglycerides (TAGs) that can range from 0.1 to 50 μm in size (Murphy and Vance, 1999; **Figure 3**). The accumulation of large lipid bodies is favored by spatial constraints: lipids accumulate easier than other C reservoirs when space is limiting due to a lower hydration (Palmucci et al., 2011). TAG synthesis starts in plastids from the carboxylation of acetyl-CoA by acetyl-CoA carboxylase (ACCase) to produce malonyl-CoA (Martins et al., 2013; Wichmann et al., 2020). As described in **Figure 3**, acyl chains are synthesized by various enzymes localized in different subcellular compartments. The final steps of acyl elongation, desaturation and insertion in TAGs occur in the endoplasmic reticulum (**Figure 3B**). Microalgae, particularly

TABLE 2 | Forms and catalytic properties of Rubisco in different taxa: functional diversities and specific values are highlighted.

Organism	τ	$K_{cat}{}^{c}$ (s^{-1})	K_{mCO2} (μ M)	References
Cyanobacteria	38–56	2.6–11.4	130–180	Badger and Bek, 2008
Synechococcus sp.	43–52	11.6–13.4	246–340	Savir et al., 2010
Chlorophytes	54–83		12–38	Badger and Bek, 2008
Chlamydomonas reinhardtii	61	5.8	29	Savir et al., 2010
Rodhophytes	129–238	1.2–1.6	3.3–22	Badger et al., 1998
Porphyridium cruentum	128	1.6	22	Raven et al., 2000
Cyanidium	224–238	1.3–1.6	6.6–6.7	Raven et al., 2000
Haptophytes	89–125	2.2–3.3	14.5–24.1	Heureux et al., 2017
Cryptophytes	101	0.83	59	Badger et al., 1998
Heterokontophytes	57–116	2.1–3.7	23–68	Young et al., 2016
Diatoms with CCM	106–114	0.78–5.7	31–36	Badger et al., 1998; Raven, 1984
Embryophytes	77–90	2.5–5.5	10–32	Badger and Bek, 2008; Cummins et al., 2018
C3 plants	82–90	2.9–3.0	10–11	Badger et al., 1998
C4 maize	78	4.2	32	Badger et al., 1998
Dinoflagellates	37			Raven et al., 2000

Colors for τ, $K_{cat}{}^{c}$ and K_m for CO_2 becomes darker when the best performances are observed; for diatoms no color is applied because of their wide range of values. Values of $K_{cat}{}^{O}$ and K_m for O_2 are omitted.

genera as *Schizochrytium*, *Crypthecodium*, *Nannochloropsis* and *Phaeodactylum* (Enzing et al., 2014), are well known to synthesize long and very long chain polyunsaturated fatty acids (LC-PUFA). LC-PUFAs consist of 20-22 C and have a high nutraceutical value as they include, for example, Eicosapentanoic acid (EPA or 20:5n-3) and Docosahexaenoic acid (DHA or 22:6n-3) (**Table 1** and **Figure 3**). In some microalgae, as *Botryococcus braunii*, free fatty acids are substrates for the synthesis of alkanes (Wichmann et al., 2020). Further, in eukaryotic algae, the cytosolic mevalonate (MVA) pathway and the plastidic 2-C-methyl-d-erythritol 4-phosphate (MEP) pathway generate isopentenyl pyrophosphate (IPP) and dimethylallyl pyrophosphate (DMAPP), metabolic precursors of terpenoids (**Figure 3**; Wichmann et al., 2020).

The removal of C-intermediates from the Krebs cycle in the mitochondria, as oxaloacetate and 2-oxoglutarate (**Figure 1**), allows to synthesize various molecules like aspartate and glutamate, which are then substrates for the synthesis of related amino acids and pyrimidines. Anaplerotic reactions replenish the Krebs cycle (**Figure 1**): PEP carboxylase, PYR carboxylase and PEPC carboxykinase β-carboxylate 3 C compounds, either phosphoenolpyruvate (PEP) or pyruvate (PYR), using CO_2 or $HCO_3{}^-$. About 5% of the fixed C in algae is fixed via anaplerotic fixation (Raven and Farquhar, 1990).

NUTRIENT REQUIREMENT AND ALLOCATION INTO MACROMOLECULES

The average macronutrients elemental stoichiometry of microalgae, under resource-replete conditions and optimal environmental parameters (usually adopted during the first phase of biomass production in industrial cultivation plants), is $C_{124}N_{16}S_{1.3}P_1$ (Ho et al., 2003; Quigg et al., 2010; Giordano, 2013). Such stoichiometry is quite conserved among microalgal species, whereas the stoichiometry of micronutrients like Fe, Zn, Mn, Cu, Mo shows higher variability.

The actual elemental stoichiometry depends on both genotype and environmental conditions, like nutrient availability, light, temperature, salinity. E.g., species belonging to the red algae lineage, like diatoms, display a higher S cell quota (and thus a lower C:S ratio) than species from the green lineage (Norici et al., 2005). The assimilation of N in the form of $NO_3{}^-$, due to the N oxidation number of + 5, requires more energy than the assimilation of N as $NH_4{}^+$ (N oxidation number -3); thus, the available chemical source of N constrains C:N ratio and growth when energy is limiting (Norici et al., 2002; Ruan et al., 2017; Ruan and Giordano, 2017).

C, N and S are all assimilated through energy-demanding reductive pathways into macromolecular pools. C, the most abundant element in algal cells (36–65% of dry matter), is allocated into proteins, carbohydrates and lipids. Proteins are also the primary functional reservoir of cellular N (**Figure 1**). Remarkably, 15-25% of total cellular N is allocated to proteins involved in the light reactions of photosynthesis and 5-10% to the Rubisco protein, depending on the growth light (Li et al., 2015). Essential amino acids (cysteine and methionine) and glutathione are sinks of cellular S (Giordano and Raven, 2014). Phospholipids and nucleic acids are the major functional reservoirs of cellular P. In some algae, polyphosphates are additional P stores resulting from luxury uptake, a process which may divert the elemental composition from the cell essential requirement when energy and resources are available in excess (Giordano and Ratti, 2013).

Under replete nutrient supply, microalgae contain the following macromolecular composition (expressed as percentage of dry weight): from 27 to 43% proteins, from 12 to 21% lipids, from 12 to 23% carbohydrates, 8–27% ash, 5–6% nucleic acids, about 1% chl *a* (Finkel et al., 2016). Carotenoid content ranges between 0.1–0.2% of dry weight; however, β-carotene can increase up to 14% of dry weight in *Dunaliella* (Spolaore et al., 2006; Becker, 2007). Vitamins B1, B2, B3, B6, B12, E, K, and D are also present in traces (Becker, 2007; Kamalanathan and Quigg, 2019; Bacchetti et al., 2020).

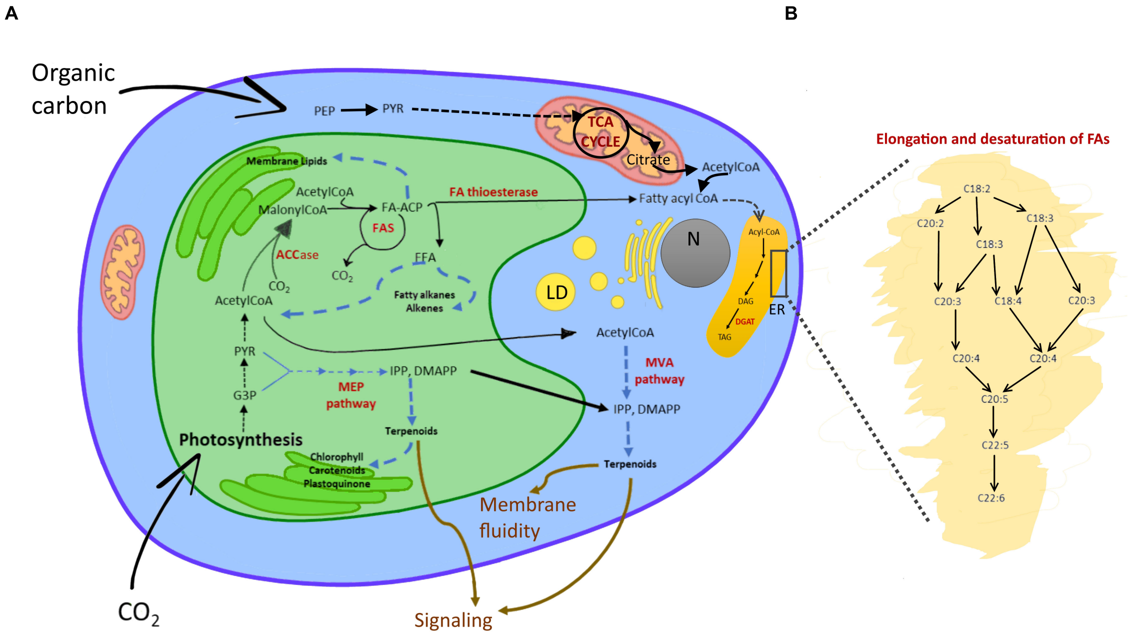


FIGURE 3 | Lipid metabolism in eukaryotic algae. **(A)** Schematic view of fatty acid and isoprenoid biosynthesis. In the chloroplast, Acetyl-CoA from the triose phosphates pool, or imported as acetate from cytosol and mitochondria to the plastid, is carboxylated by ACCase to malonyl-CoA (Martins et al., 2013; Wichmann et al., 2020). The malonyl group is transferred to an ACP. Malonyl-ACP undergoes a series of condensation reactions with acetyl-CoA, catalyzed by a β-ketoacyl-ACP synthase (KAS). Thanks to the FAS multi-subunit complex, saturated C16:0- and C18:0-ACP are synthetized. The acyl groups are then either retained in the plastids to be incorporated into membrane lipids or they are hydrolyzed from ACP by specific fatty acyl-ACP thioesterases that release FFAs. C16:0- and C18:0-ACPs can be desaturated into C18:1 before being hydrolyzed. FFA are exported to the cytosol and esterified to CoA by a long-chain acyl-CoA synthase located in the outer envelope of the plastid to form acyl-CoAs (Martins et al., 2013). By analogy with higher plants, it is predicted that these extraplastidic acyl-CoA esters are then transferred to the endoplasmic reticulum or acylated onto a phospholipid backbone before further participation in the synthesis of membrane lipids or storage TAGs (see Sayanova et al., 2017 for details). Enzymatic reactions are indicated by solid arrows, series of reactions by dashed arrows, pathway names in bold black, intermediates in black, main enzymes in red, functions of products in brown. Abbreviations: LD, lipid droplet; N, nucleus; ER, endoplasmic reticulum; MEP, 2-C-methyl-D-erythriol 4-phosphate; MAV, mevalonate, ACCase, acetyl-CoA carboxylase; ACP, acyl carrier protein; FAS, fatty acid synthase; DGAT, diacylglycerol acyltransferase; DAG, diacylglycerol; FFA, free fatty acid; G3P, glyceraldehyde-3-phosphate; PYR, pyruvate; TAG, triacylglycerol. **(B)** Enlarged ER segment detailing elongation and desaturation of algal fatty acids.

Similarly to elemental stoichiometry, also macromolecular composition varies according to phylogenetic groups (Finkel et al., 2016; **Figure 4A**) and environment. It reflects fundamental cellular properties in terms of structural and functional organization, like primary storage pools (some species are well-recognized as oleaginous for their strategy to accumulate lipids instead of carbohydrates), light harvesting apparatus, cell wall. Notably, each macromolecular pool is characterized by a different cost in terms of chemical energy (ATP equivalents). Allocating C to lipids has a major cost compared to the one of carbohydrate synthesis (Montechiaro and Giordano, 2010; Palmucci et al., 2011). Protein pool is costly as it requires the assimilation of different elements, C, N and S, into amino acids (Giordano and Raven, 2014). Energy investment in the three macromolecular pools has been calculated in **Figure 4B** according to their abundance. The "cheapest" biomass appears to be that of diatoms. Compared to the other groups, diatoms are characterized by a higher ash content and a lower amount of proteins and carbohydrates (**Figure 4A**; Finkel et al., 2016). Consistently, unlike other algae (e.g., green algae), diatoms do not possess cellulosic cell wall, but they harbor a silica shell named frustule which makes Si a macronutrient for this algal group. Further, they display a different C allocation and regulation of the C metabolism, resulting in enriched lipid fraction (Wagner et al., 2017).

High lipid content is a desirable trait for industrial purposes as neutral lipids (TAGs) can be transesterified to fatty acid methyl esters to obtain biodiesel. In oleaginous species, the lipid content can increase up to 77% of dry weight by altering the available C:N ratio in growth media (Chisti, 2007; Li et al., 2008; Sun et al., 2019); in fact, C is largely allocated into lipid stores when N is depleted and protein synthesis is stopped. However, during severe elemental imbalance and lipid accumulation, cell growth is hampered, representing a major issue in developing economically viable biofuel producers.

An ideal biofuel producer would thus allocate a major C quota to lipids already during exponential growth phase, without nutritional stress, and show remarkable rates of biomass production. As proposed in **Figure 4**, an ideal biofuel producer would harbor protein and carbohydrate contents as low as in the diatom example, but a lipid content as high as 50% of dry weight. The energy cost associated to the intended composition is 1.3-1.6 times higher than what required for the average composition of existing algae (**Figure 4**). In line with a higher biomass cost, many

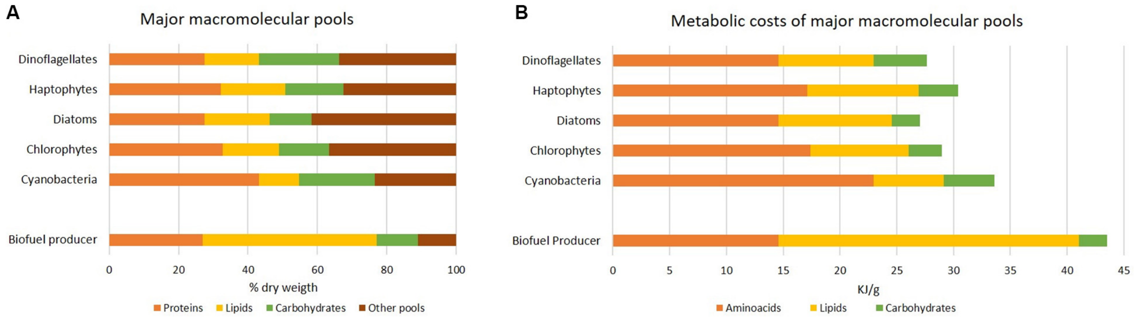


FIGURE 4 | Metabolic cost of macromolecular pools in different group of microalgae. **(A)** Average macromolecular composition in different algal phyla, as percentage of dry weight under nutrient-sufficient exponential growth; all data except for the "biofuel producer" are according to Finkel et al. (2016). The biofuel producer is suggested as a cell containing the lowest protein and carbohydrate percentage and a lipid percentage suitable for biofuel production in exponentially growing algae. **(B)** Estimate of the energy investment (kJ g^{-1}) by algal phyla according to data reported in **(A)**. The hydrolysis of 1 ATP was assumed to yield 55 kJ mol^{-1} and the transfer of $2e^-$ was assumed to correspond to 4 ATP equivalents (Giordano and Raven, 2014). Budgets of ATP equivalents per mole are 11, 15, 41 and 33 corresponding to the assimilation of CO_2 into carbohydrates, CO_2 into lipids, nitrate into glutamate and sulfate into cysteine (the latter two as proxy for proteins), respectively (Palmucci et al., 2011; Giordano and Raven, 2014); molecular weight of macromolecules used in calculations are according to Geider and La Roche (2002) and Sterner and Elser (2002). Note that we are presenting only the costs of amino acids, lipids and carbohydrates pools.

known oleaginous species, like *B. braunii*, are characterized by a poor growth rate; when a major energy quota is allocated to lipid storage, energy is likely diverted from the cellular quota reserved for growth (Giordano and Wang, 2018).

Energetic constraints to biomass composition become relevant when energy availability limits growth (Wagner et al., 2006; Jakob et al., 2007; Nogueira et al., 2015; Ruan and Giordano, 2017; Ruan et al., 2017; Alboresi et al., 2016). This is often the case in dense commercial cultures, where light is limiting. A domesticated biofuel producer strain shall therefore present an improved energy utilization through genetic modifications.

OPEN CHALLENGES TOWARD ENHANCED CO_2 FIXATION IN MICROALGAE: BUILDING LIVING FACTORIES

The impact of above described biological constraints on microalgal composition and growth has been weighed in **Table 3**, which focuses on biofuel production. Input data are representative of species, cultivation systems and climatic conditions showing different lipid content and biomass productivity, then used to calculate the biodiesel productivity. The most productive species/plant still requires roughly half of the Italian area (corresponding to the entire Italian arable land) to fulfill 9% of the energy demand by 2030 in the transport sector, the estimated goal for biofuel quota according to the Sustainable Development Scenario (International Energy Agency, 2020b). If vast areas are required, climatic parameters also come into play when assessing the potential final yield, as exemplified by *T. suecica* cultivation plants in Tuscany or Tunisia, showing almost 40% less biomass yield in the former than in the latter (**Table 3**).

It follows that current assessment will not allow a fast transition to clean sustainable energy. Yet, theoretical estimates of maximum light conversion into biomass production (10-12%) (Zhu et al., 2008; Barber, 2009; Melis, 2009; Blankenship et al., 2011; Peers, 2014) are still quite distant from the actual values (**Table 3**).

A major goal for the scientific community is thus to significantly increase the efficiency of light energy conversion into biomass, allowing the use of photosynthetic cells as cost-effective factories. Multiple challenges need to be overcome: (i) deepening our knowledge of the physiological constraints cells experience as cultivation systems get larger; (ii) combining production of exploitable biomass with waste valorization, which results in important cost reduction; (iii) improving the light use efficiency and rewiring cell metabolism to the desired product.

Screening of natural variants, optimization of culturing conditions and new *ad hoc* solutions by means of synthetic biology approaches are pivotal to overcome these issues and to reach significant impacts in terms of renewable biomass feedstock for energy conversion and captured CO_2 emissions.

Strain Selection, Microbial Consortia and Optimization of Nutrient Resources

To date, research in the applied field of algal research has more often focused on a limited number of so-called model species, as *Synechocystis* and *Synechococcous* for cyanobacteria, *C. reinhardtii* for green algae, *P. tricornutum* for diatoms, since their genomes are sequenced and several molecular tools are available or rapidly developing. At the same time, algae-based industry has focused on a few robust algal strains, like *Arthrospira platensis* and *Dunaliella salina*, primarily selected for "health-foods" and antioxidants production (see **Table 1**). Further, their ability to thrive at extreme pH (*A. platensis*) and salinity (*D. salina*) avoids easy contamination by wild algal strains, grazers, and pathogens even if cultured in open ponds. It has been estimated that 10 to 30% of annual production in open ponds is lost due to pond contamination (Richardson et al., 2014). Closed cultivation systems as PBRs, on the other hand,

TABLE 3 | Lipid content, areal biomass and lipid productivity, projected biodiesel productivity (assuming 96% recovery of lipids through direct transesterification; Lepage and Roy, 1984) for microalgae cultured in different climatic conditions, cultivation systems, laboratory or pilot or industrial scale.

	Lipid content (% DW)	Areal productivity of biomass (t $ha^{-1}y^{-1}$)	% light energy conversion into biomass	Areal productivity of lipids (t $ha^{-1}y^{-1}$)	Areal productivity of biodiesel (t $ha^{-1}y^{-1}$)	Mha needed for biofuel global demand by 2030	How many times Italy?	CO_2 consumption into dry biomass (t $ha^{-1}y^{-1}$)
Chlorella vulgaris[1] - lab scale	46	15.7	0.6	7.2	7	50.5	1.7	28
Tetraselmis suecica[2] – pilot plant in Italy *vs.* Tunisia	20	36 *vs.*54	1.3 *vs.*1.9	7.2 *vs.*10.8	7 *vs.*10	50.5 *vs.*33.6	1.7 *vs.*1.1	65 *vs.*97
ORP[3]	20	28	1	5.6	5	64.9	2.2	54
PBR[3]	40	56	2	22.4	22	16.2	0.5	101
Range for microalgae cultivation[4] - industrial plant	12–20	37–110	1.3–3.9	7.3–21.9	7–21	49.8–16.6	1.7–0.6	66–197
Algae consortium dominated by diatoms[5] – WWT plant	22	128	4.5	28.1	27	13	0.4	230

Areal biomass productivity is used to calculate the percentage of light energy conversion into biomass considering 281 t $ha^{-1}y^{-1}$ as the productivity corresponding to 10% of light use efficiency (Barber, 2009; Benedetti et al., 2018). Areal biodiesel productivity is used to calculate the cultivation area needed to fulfil biofuel global demand by 2030 [estimated as 300 Mtoe in the Sustainable Development Scenario (International Energy Agency, 2020b), equal to 9% of transport fuel demand]; since Italy has a national area of 30 Mha, cultivation area required to produce such 300 Mtoe biofuels has been converted in Italian areas; CO_2 consumption into dry biomass is calculated considering 1.8 kg of CO_2 is fixed to produce 1 Kg biomass (Hossain et al., 2019). [1]Stephenson et al., 2010; [2]Tredici et al., 2016; [3]Hossain et al., 2019; [4]International Energy Agency, 2017; [5]Marella et al., 2019. WWT, wastewater treatment.

TABLE 4 | Features of open and closed cultivation system.

	Open pond	Photobioreactor
Biomass loss due to contamination	high	low
Sterility	none	achievable
Process control	easy	difficult
Mixing	low	high
Growth	batch; semicontinous	batch; semicontinous
Area required	high	moderate
Cell density	low	high
Investment cost	low	high
Operation costs	low	moderate
Mantainance	easy	difficult
Light use efficiency	low	high
Evaporation of growth medium	high	low
CO_2 sparging efficiency	low	high
O_2 inhibition	low	high
Scale-up	difficult	difficult
Biomass quality	variable	reproducible

guarantee greater crop protection and allow a better control of the growth environment (**Table 4**); it is therefore easier to reach higher biomass yield and to direct algal C allocation to target compounds with respect to cultivation in open ponds (**Tables 3**, **4**). However, PBRs pose other challenges (**Table 4**). They require higher energy input. Photosynthetic build-up of O_2 is another disadvantage of PBRs. If no O_2 degassing system is present, dissolved O_2 can reach 250% of saturation, much higher than expected at air equilibrium. This leads to inhibition of Rubisco, to ROS formation, and it hinders microalgae growth (Raso et al., 2012; Bilanovic et al., 2016).

Suitable microalgae for industrial production should thus own high growth rates, natural ability to tolerate extreme conditions required by scale-up or specific industrial application, high productivity for native or heterologous products (Picardo et al., 2013; Giordano et al., 2015b).

Besides monospecific cultures, more and more evidences are pointing toward the advantages of using consortia of algal species or of algae and bacteria (Newby et al., 2016 and references there in). Polycultures enclosing both photosynthetic and heterotrophic species provide a more stable crop, protected from grazing and infection losses (Corcoran and Boeing, 2012), and a greater potential for overyielding and C fixation (Shurin et al., 2014; Newby et al., 2016). It is noteworthy that, in **Table 3**, the diatom-dominated consortium reached the highest areal biomass productivity as compared to the other monoculture systems. This most likely relies on the functional complementary of species, as for nutrient and light utilization. Biomass quality may also improve in the polyculture relative to the one of most productive monocultures: e.g., higher lipid production of highly diverse algal communities compared to that of the respective monocultures under similar growth conditions (Stockenreiter et al., 2012).

One of the basic principles of microbial ecology is that species diversity promotes ecosystem productivity and stability (Cardinale et al., 2011). This principle applies also to traditional wastewater treatment plants, which are robust and large open systems that rely on many species of different microorganisms naturally assembled to remove nutrients from wastewaters (Brenner et al., 2008). When selecting species for polyculture, thus, functional richness is the primary goal (Newby et al., 2016). For example, in N limited growth media, N_2 can be biologically fixed by diazotrophic cyanobacteria, allowing N to become available to symbiotic algae (Stockenreiter and Litchman, 2019). The described strategy based on functional complementarity of the mixed strains reduces nutrient demand and associated costs in a large-scale cultivation plant (Stockenreiter and Litchman, 2019). Alternatively, the chief commercial method to produce N fertilizers by fixing atmospheric nitrogen into ammonia, is the highly energy demanding Haber–Bosch process (Travis, 1993). Non-photosynthetic bacteria may contribute to functional consortia also providing vitamins, phytohormones like indole-3-acetic acid, siderophores involved in Fe solubility (for detailed literature see in Newby et al., 2016).

The valorization of wastewaters as sustainable source of nutrients (P, N, trace metals) for algal cultivation, while achieving water treatment demand, is a promising path since it can strongly reduce biomass production cost and environmental impact; the entire production chain can meet sustainable and circular bioeconomy criteria. Growth on wastewaters imposes mixotrophy and heterotrophy nutrition for algae. Beside autotrophic nutrition in the presence of inorganic C sources and light, microalgae can act as heterotrophs and use either soluble organic carbon (such as glucose, acetate, and glycerol; osmotrophy) or particulate organic carbon (phagotrophy) (Selosse et al., 2017) as energy and carbon source in the dark, possibly resulting in high biomass density. Mixotrophic cultivation of microalgae is a combination of photoautotrophy and heterotrophy to use both inorganic and organic carbon substrates in the presence of light. Mixotrophic nutritional regime cannot be applied indistinctively to all microalgae. Mixotrophy is more frequent in eukaryotic algae which originated themselves from events of phagotrophy, as secondary and tertiary endosymbiotic events (Beardall and Raven, 2016); similarly, it has been shown that the presence of specific membrane transporters and enzymes of carbohydrate metabolism are usually involved in the ability to grow in soluble organic matter rich media (Barbier et al., 2005). Thus, mixotrophy enhances the biomass productivity only in specific genotypes. For example, glycerol as C source and NH_4^+ as N source enhanced growth of *P. tricornutum* and increased the productivity of highly valuable omega-3 LC-PUFAs, such as EPA, by a factor of 10 when compared with photoautotrophic control conditions (Ceron et al., 2000; Villanova et al., 2017). In *Galdiera* sp., higher biomass and PUFA production, despite a lower concentration of lipids, were observed under mixotrophic and heterotrophic conditions with respect to autotrophic conditions; also, the lipid profile was affected by nutritional regime (López et al., 2019).

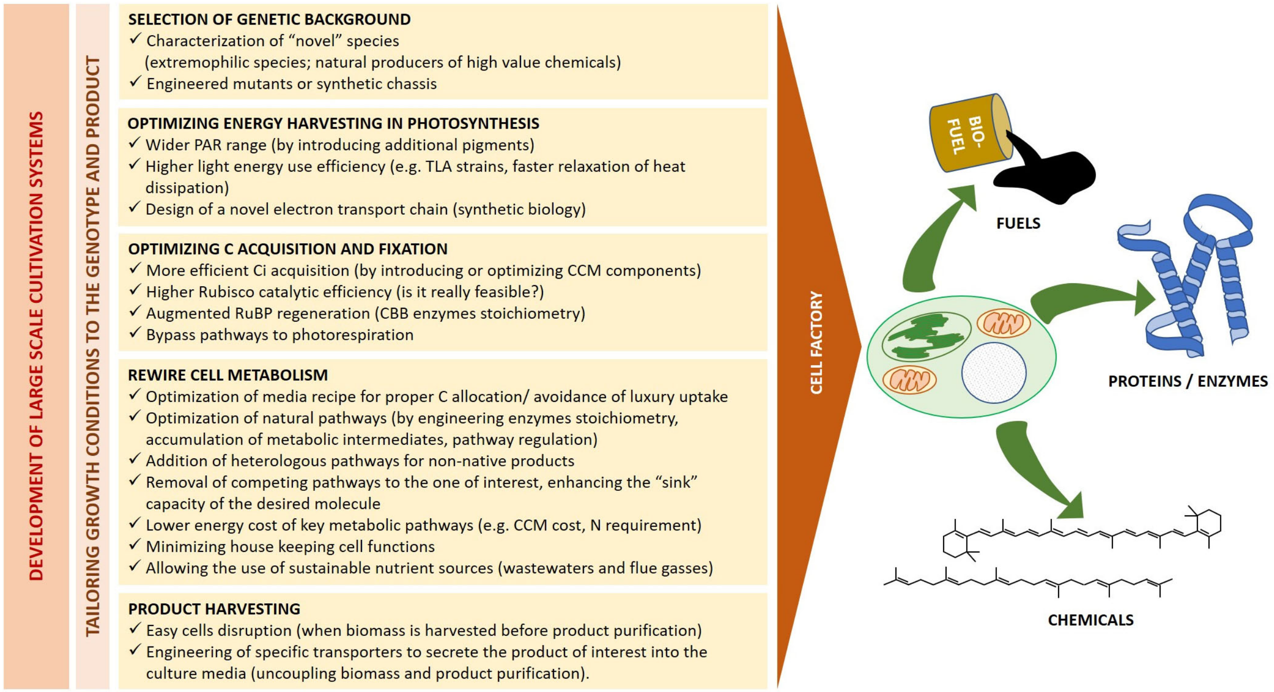
In parallel with the use of wastewaters for algal cultivation, the use of flue gases has been studied to mitigate greenhouse gas emission and temporarily sequester CO_2 into biomass. Flue gases may contain pCO_2 values from 3 to 25% of its volume (Packer, 2009); when directly bubbled in algal cultures, flue gases cause growth medium acidification, which can be reduced by adding a pH buffer. Not all algae are suited for CO_2 bioremediation since they cannot equally tolerate high CO_2 concentrations: for example, *D. salina* is CO_2-sensitive and inhibited at 10% CO_2 while *Chlorococcum littorale* is extremely CO_2-tolerant and grows rapidly at CO_2 concentrations up to 60% (Kodama et al., 1993; Sergeenko et al., 2000; Muradyan et al., 2004). High CO_2 tolerance requires the ability to maintain intracellular pH homeostasis by down regulating CAs and the CCMs (Borowitzka, 2016). It is worth mentioning acidophilic and acidotolerant microalgae which lack CCMs (Diaz and Maberly, 2009) have also been tested for cultivation in plants fed on flue gases (Eibl et al., 2014; Nagappan et al., 2020; De Farias-Neves et al., 2019).

Noteworthy, the ability to cope with up to 20% or more CO_2 may not imply a higher growth rate. Since a higher growth rate is consequent to an increased nutrient use efficiency, bubbling cultures with CO_2 stimulates growth if C is the limiting nutrient, as it might be the case in CCM lacking species (Beardall and Giordano, 2002; Raven et al., 2011, 2012; Venuleo et al., 2018), or if a decreased cost for CCM allows a higher energy investment into making new cells (Raven et al., 2014; Li et al., 2015). Moreover, when CO_2 is bubbled into the culture, it may elicit a nutritional (C/N) imbalance leading to a change in biomass quality (Beardall and Giordano, 2002; Giordano and Ratti, 2013; Palmucci et al., 2011; Raven et al., 2011, 2012).

Designing *Ad hoc* Bio-Factories for Fuels and High-Value Chemicals

The above described strain selection and optimization of culturing condition are pivotal to make the best possible use of available energy and resources according to target products. However, as suggested by the biofuel yields exemplified in **Table 3**, it is unlikely that such approach alone will achieve significant stocks and allow a major breakthrough in most applications. Genetic manipulation shall thus provide additional *ad hoc* solutions to optimize energy harvesting and utilization, and to rewire cell metabolism toward specific products (**Figure 5**).

Synthetic biology is a recent discipline which deals with the application of engineering principles to biology. It aims both at simplifying complex systems and at constructing novel ones by combining individual parts from multiple biological sources, introducing functions not previously held by the host (Kliebenstein, 2014; Liu and Steward, 2015; Shih, 2018; Luan and Lu, 2018). One of the most powerful application of plant synthetic biology is thus to design “domesticated” photosynthetic cells for a continuous production of biofuels and high-value compounds, starting from sunlight and inorganic or recycled nutrients. To this goal, microalgae metabolic engineering shall be applied at multiple levels, from enhancing the catalytic efficiency of native enzymes to introducing novel functions, like product secretion, which will ease the harvesting of commercial product (**Figure 5**).



SELECTION OF GENETIC BACKGROUND
- ✓ Characterization of "novel" species (extremophilic species; natural producers of high value chemicals)
- ✓ Engineered mutants or synthetic chassis

OPTIMIZING ENERGY HARVESTING IN PHOTOSYNTHESIS
- ✓ Wider PAR range (by introducing additional pigments)
- ✓ Higher light energy use efficiency (e.g. TLA strains, faster relaxation of heat dissipation)
- ✓ Design of a novel electron transport chain (synthetic biology)

OPTIMIZING C ACQUISITION AND FIXATION
- ✓ More efficient Ci acquisition (by introducing or optimizing CCM components)
- ✓ Higher Rubisco catalytic efficiency (is it really feasible?)
- ✓ Augmented RuBP regeneration (CBB enzymes stoichiometry)
- ✓ Bypass pathways to photorespiration

REWIRE CELL METABOLISM
- ✓ Optimization of media recipe for proper C allocation/ avoidance of luxury uptake
- ✓ Optimization of natural pathways (by engineering enzymes stoichiometry, accumulation of metabolic intermediates, pathway regulation)
- ✓ Addition of heterologous pathways for non-native products
- ✓ Removal of competing pathways to the one of interest, enhancing the "sink" capacity of the desired molecule
- ✓ Lower energy cost of key metabolic pathways (e.g. CCM cost, N requirement)
- ✓ Minimizing house keeping cell functions
- ✓ Allowing the use of sustainable nutrient sources (wastewaters and flue gasses)

PRODUCT HARVESTING
- ✓ Easy cells disruption (when biomass is harvested before product purification)
- ✓ Engineering of specific transporters to secrete the product of interest into the culture media (uncoupling biomass and product purification).

FIGURE 5 | Microalgae as cell factories. Heading to a sustainable industrial production, the bioreactor design and growth conditions must be tailored to the selected genetic background and final product of interest. The major biological traits which require simultaneous optimization for fuel and high-value chemicals production from living factories are outlined.

However, in order to extensively apply this approach to photosynthetic organisms, several tools still need to be fully developed to manipulate microalgal cells in a predictable way.

Molecular Biology Tools: State-of-the-Art and Open Challenges

Both prokaryotic and eukaryotic microalgae are suitable candidates as producing platforms: their different features are critical for accumulation of different kinds of product. Cyanobacteria naturally accumulate bioplastic precursors (**Table 1**; Luengo et al., 2003) and are good hosts for small molecules not requiring eukaryotic post-translational modifications. Conversely, eukaryotic algae are valuable when such modifications (e.g., glycosylation) are essential, or when product compartmentalization is necessary. Eukaryotic algae are also a precious source of several secondary metabolites (Wijffels et al., 2013), and include some well-known oleaginous species, as *P. tricornutum* or *N. gaditana*.

The ability to change, remove or introduce gene(s) of interest in a programmable way, and to achieve a stable phenotype of the engineered strains over time, is pivotal to industrial application of photosynthetic bio-factories (Patel et al., 2019; Pérez et al., 2019). Molecular tools are better established for cyanobacteria than for eukaryotic algae, but nuclease-based genome editing tools like Clustered Regulatory Interspaced Short Palindromic Repeats (CRISPR)/Cas9 and Transcription Activator-Like Effector Nucleases (TALEN) are rapidly developing and applied to algal species of different phylogeny and commercial value (Doron et al., 2016; Nymark et al., 2016; Shin et al., 2016; Kroth et al., 2018; Verruto et al., 2018; Ortega-Escalante et al., 2019; Pérez et al., 2019; Ng et al., 2020). Yet, genetic manipulation of microalgae, particularly eukaryotic ones, still encounters several challenges. They are mostly related to the low efficiency of the transformation protocols and to the low and unstable expression levels of transgenes. Such weaknesses have been mainly ascribed to positional effects of gene integration and/or gene silencing. Secondary off-target mutations in edited strains, even when targeted genome editing has been performed with nucleases (Patel et al., 2019), are an undesirable aspect of algae transformation. To minimize issues due to off-target mutations, ribonucleoproteins (RNP-) based methods for CRISPR/Cas gene editing have been developed in substitution to vector-mediated protocols (Patel et al., 2019).

The selection of genetic backgrounds which minimizes gene silencing is a tool to achieve a stable expression of transgenes. Mutants of the model green alga *C. reinhardtii* that showed increased nuclear transgene expression, called UVM4 and UVM11, have been obtained with random UV mutagenesis (Neupert et al., 2009). Knowledge on molecular mechanisms underlying gene expression regulation shall be deepened to fully overcome drawbacks due to low heterologous gene expression, avoiding at the same time labor intensive screening of random mutants. The optimization of *cis* regulatory elements like promoters, ribosome binding sites (RBS), UTR sequences, and the optimization of heterologous sequence codon usage according to the selected cell chassis, have also been recognized as a key feature for successful transgene expression (Rasala et al., 2011; Jinkerson and Jonikas, 2015; Till et al., 2020); specifically in eukaryotic cells, mimicking a native nuclear gene sequence as accurately as possible, by interrupting the transgene coding sequence with introns, shall also contribute to a stable transgene expression (Baier et al., 2018). Finally, efforts have been made to identify and characterize the best genomic environment where to introduce transgenes, the so-called neutral sites, *loci* in which gene integration is not compromising other cell functions (Ng et al., 2015; Pinto et al., 2015; Kroth et al., 2018).

Once productive genome edited microalgae are obtained and ready to be exploited in large scale industrial plants, the biosafety issue must be timely addressed by specific agencies (Spicer and Molnar, 2018): both potential harm to human and animal health and potential risk for the environment (i.e., vertical or horizontal gene transfer, strain competition with wild-type strain) are to be assessed (Henley et al., 2013). Although genetically modified algae are predicted not to have fitness advantages in nature, safety measures to avoid the spill over of modified strains must be regulated and applied especially in outdoor cultivation systems (Wijffels et al., 2013; Henley et al., 2013; Spicer and Molnar, 2018).

Cellular Targets to Enhance Bio-Factories Productivity

All biological processes described in section 2, from light harvesting to metabolic energy consumption, are characterized by substantial energy losses (**Figure 2** and **Table 5**) and are potential targets for improving energy use efficiency.

Adjusting the efficiency of photosynthetic light reactions will rise the amount of energy available for cell metabolism. A key strategy to improve light conversion into chemical energy deals with modulation of light harvesting and photoprotection. They are both very dynamic processes which readily respond to changes in light intensity, and account for substantial energy dissipation when light irradiation exceeds the photosynthesis saturation point (**Figure 2** and **Table 5**; Peltier et al., 2010; Wilhelm and Selmar, 2011; Peers, 2014).

The reduction of light harvesting capacity is a valuable strategy, which has already been tested in strains with genetically Truncated Light harvesting Antennae (TLA). TLA approach reduces the light harvesting cross-section in photosynthetic cells and potentially triplicates the productivity of plants and algae (Melis, 2009; Kirst et al., 2017). In a dense microalgal culture, TLA phenotype diminishes the energy harvested by the external layer of cells which are directly exposed to intense illumination. Therefore, their need for energy dissipation and risk of photoinhibition are reduced, while their photosynthetic efficiency enhanced. TLA phenotype also favor the diffusion and homogeneity of light into the culture. This increases light availability for the inner layer of cells that instead, in the case of WT cultures, suffer light limitation and reduced growth. TLA benefits were demonstrated in different species, where TLA cultures showed up to 1.5 times the growth and productivity of WT (Nakajima et al., 2001; Polle et al., 2003; Mussgnug et al., 2007; Perrine et al., 2012; Kirst et al., 2014; Shin et al., 2017). However, TLA advantages have been proved under specific growth conditions (i.e., high light) which accentuate TLA positive traits. Conversely, when limiting light was supplied, TLA growth was reduced compared to the WT one (Nakajima et al., 2001; Perrine et al., 2012; Shin et al., 2017). In addition, some TLA mutants showed null advantages in their productivity, irrespective of the condition tested (Page et al., 2012; Nymark et al., 2019). Diverging phenotypes among TLA mutants have been ascribed to undesirable side effects of the mutation or to an unbalanced photoprotection caused by the altered antenna system (de Mooij et al., 2015; Nymark et al., 2019). In TLA *Synechocystis* cells, the reduced size of phycobilisomes was also shown to have a wide impact on cell proteome (Liberton et al., 2017). Remarkably, despite TLA approach still faces challenges to be solved in future studies, TLA approach has a further central advantage on resource use efficiency: as it reduces cellular N quota invested in light harvesting proteins, more energy can be allocated to other metabolic pathways (**Figures 4**, **5**).

A further approach to optimize light harvesting capacity deals with modulation of photoprotection. Photoprotection results from an intricate network of processes regulating photosynthetic electron transport. It is essential to cope with variable and excess light: the light reactions promptly respond to any burst of higher illumination, increasing the amount of energy captured by the antenna system and electron transport. Conversely, the metabolic reactions are not equally fast to respond to increased energy availability. This creates a dangerous imbalance between production and utilization of ATP and reductants, leading to over-reduction of electron transport chain and photoinhibition. Photoprotection mechanisms thus provide the cell safe valves to dissipate these bursts of excess energy. If fully abolished, the cells will be prone to reactive oxygen species (ROS) formation, photoinhibition, and eventually cell damage when light is absorbed in excess (Wilhelm and Selmar, 2011; Niyogi and Truong, 2013; Gerotto et al., 2016). Thus, a valuable option to optimize photoprotection processes targets their relaxation kinetics. It is estimated that the sustained energy quenching upon a switch from high to low light accounts for about 20% reduction in crop yield (Taylor and Long, 2017): their activation/deactivation kinetic in response to light intensity fluctuations is a possible target of improvement. Validation of this hypothesis has been obtained in tobacco, where the simultaneous over-expression of three key proteins regulating heat dissipation of absorbed excess energy (i.e., PSBS; VDE; ZE) resulted in 9% increased C fixation rates and an average of 15% increase plant dry weight with respect to WT. This was due to a faster deactivation of the heat dissipation mechanisms when plants were moved from strong to limiting light (Kromdijk et al., 2016). A similar approach can be transferred to algae expecting analogous potential benefits. For example, in PBRs, culture mixing leads microalgae to experience a fluctuating light regime: cells are alternatively exposed to strong illumination in the external layer or to limiting light in the internal layer. Thus, the activation/deactivation timescale of photoprotection mechanisms shall fit with the PBR mixing kinetic, in order to protect cells from bursts of high light when cells are in the external layer, while relaxing fast when cells are back to the inner section of the PBR (Sforza et al., 2012; Simionato et al., 2013).

TABLE 5 | Examples of efficiency of solar energy conversion into biomass, in the absence or presence of different sources of energy dissipation.

	Energy dissipation in light reactions (% of energy harvested)	Energy dissipation due to photorespiration	Solar energy to biomass conversion (%)	Solar energy to biomass conversion (%), including cost for cell maintenance
"Basal" dissipation	–	–	10.2	
Light energy loss	80	–	2.0	1.4
Metabolic energy loss	–	25% RBC oxygenase activity	4.1	2.8
Light and metabolic energy loss	80	25% RBC oxygenase activity	0.8	0.6
Reduced light and metabolic energy loss	10	10% RBC oxygenase activity	8.6	6.0

*Estimated costs (KJ of solar irradiations) and final yield (calorific value in KJ) of proteins, lipids and carbohydrates of the putative "Biofuel producer" (**Figure 4**) have been used in the calculations. "Basal" dissipation only includes the minimum or unavoidable energy loss from solar energy to biomass formation (coefficients according to Williams and Laurens, 2010, are used). Energy losses due to the regulation of photosynthesis light reactions (dissipating 80% or 10% of the harvested energy) or photorespiration are then applied. When oxygenation accounts for 25% of Rubisco (RBC) reactions, metabolic cost per mol of fixed C is 60% higher; 10% of oxygenation by Rubisco instead increases the cost of fixed C by 6%. A minimum cell maintenance cost of 30% of the energy requirement has been also considered in the last column.*

Conversely to light harvesting system and photoprotection processes, photosystem RCs are highly conserved among oxygenic photosynthetic organisms and they are already extremely efficient machines (0.8 and 1 electron/photon for PSII and PSI, respectively) (Caffarri et al., 2014; Raven et al., 2014; Romero et al., 2017). Thus, instead of modifying PSI and PSII, synthetic biology shall design novel architectures of the electron transport chain, in which protein complexes from multiple natural sources are merged together to improve photosynthetic performance (Ort et al., 2015; Pérez et al., 2019). For example, the introduction of bacterial type reaction centers holding bacteriochlorophyll pigments will allow PAR to be expanded up to 1100 nm. It requires a complete redesign of the electron transport chain, thus relying on extensive application of synthetic biology. The modified oxygenic photosynthesis is suggested to potentially double the efficiency of its electron transport (Ort et al., 2015).

Once light energy is temporary stored as chemical energy, ATP and NADPH are used to fix C. Rubisco enzyme causes a considerable loss in energy conversion due to its competitive oxygenase activity: when 25% of the reactions catalyzed by Rubisco use molecular oxygen as substrates rather than CO_2, the energy requirement for mol of C fixed increases by 60% compared to the sole carboxylation activity (**Table 5**). So far attempts to engineer the enzymatic properties of Rubisco by enhancing carboxylation kinetic while limiting oxygenation reactions have failed, despite a massive number of studies focused on the characterization of Rubisco crystal structures in different cyanobacterial, algal and plant species and a detailed knowledge on the catalytic reaction mechanisms both for carboxylation and oxygenation (Taylor et al., 2001; Andersson, 2008; Tcherkez, 2013, 2016). Thus, if Rubisco has already been "optimized" by the Nature during photosynthetic life evolution (Tcherkez et al., 2006; Savir et al., 2010; Kerfeld, 2015), it will possibly remain a major source of energy loss. What can research still pursue? Following a synthetic biology approach, the "best" available natural option of Rubisco (i.e., showing the highest $K_{cat}{}^{c}$, as in cyanobacteria, or the best τ, as in red algae, **Table 2**) may be combined with the most energy-saving and efficient CCM set up (as in some green algae and diatoms) in the cell chassis. Another suggested solution to improve Rubisco catalytic efficiency, particularly under fluctuating irradiation, deals with engineering Rubisco activase, a Rubisco regulatory protein which facilitates the release of inhibitors from Rubisco active site in an ATP-dependent manner (Carmo-Silva et al., 2015). Moreover, being Rubisco a relatively big and highly expressed enzyme (Ellis, 1979), the removal of high-N content amino acids such as arginine from its sequence may represent a way to increase N and energy use efficiency (**Figure 4**).

RuBP regeneration is also recognized as a main bottleneck reducing CBB cycle efficiency (Falkowski and Raven, 2007). A path to improve C fixation thus relies on optimization of CBB enzymes' stoichiometry to ease the regeneration of RuBP. Mutants harboring modified amounts of Rubisco, sedoheptulose-1,7-bisphosphatase, fructose-1,6-bisphosphatase (the latter two as a bifunctional enzyme in cyanobacteria), fructose 1,6-bisphosphate aldolase or transketolase, have been obtained both in eukaryotic algae and cyanobacteria (Fang et al., 2012; Ogawa et al., 2015; Liang and Lindblad, 2016; Yang et al., 2017; De Porcellinis et al., 2018). As described above for TLA mutants, manipulated abundance of CBB enzymes led to variable results, according to the species and to the specific enzyme under investigation. Yet, these mutants often displayed increased photosynthesis and growth. For example, overexpression of sedoheptulose-1,7-bisphosphatase or sedoheptusole-1,7/fructose-1,6-bisphosphatase increased glycerol accumulation in *Dunaliella bardawil* and wax esters in *Euglena gracilis* (Fang et al., 2012; Ogawa et al., 2015). In *Synechococcus*, the overexpression of the bifunctional enzyme led to a large adjustment of C metabolism, enhancing photosynthetic C fixation while decreasing respiration (De Porcellinis et al., 2018). These findings prove that modifying the expression of specific CBB enzymes shall contribute to an improved C fixation and cell productivity.

Another attracting option to enhance C fixation efficiency relies on engineering or replacing the photorespiratory pathway, in order to metabolize glycolate produced by Rubisco with lower energy cost and resource consumption. A first functional synthetic metabolic bypass to photorespiration has been successfully introduced in *Synechococcus elongatus* PCC7942. Six heterologous genes of the C fixing 3-hydroxypropionate pathway from *Chloroflexus aurantiacus*, a thermophilic anoxygenic phototroph, were expressed in *S. elongatus* (Shih et al., 2014). Next steps on the same path rely on further engineering of cell metabolism to allocate the metabolic intermediates generated by the bypass pathway to the production of industrially relevant molecules (Shih et al., 2014).

More ambitious routes would be to import oxygen-insensitive pathways for the key reaction of C fixation to bypass Rubisco altogether. The possibility to introduce (at least in addition to carboxylation) CO_2 reductive pathways into photosynthetic cells has also been considered. Verifying the actual feasibility and potential of these synthetic pathways *in vivo* is a major task for the future (Bar-Even et al., 2010; Bar-Even, 2018; Cotton et al., 2018).

For some specific purposes, a fully opposite option can be envisioned, which takes advantage of Rubisco oxygenation side reaction instead of trying to limit it. Under specific growth conditions, glycolate is a main sink of fixed C and a very high amount of glycolate is produced and secreted by *C. reinhardtii* cells. Glycolate can be recovered from the culture media and used as a substrate for other biotechnological applications, as methane production (Taubert et al., 2019; **Table 1**).

In parallel with maximizing biomass productivity, several research groups worldwide are constructing genetically modified strains with the goal of improving the yield of natural products or introducing the ability to synthesize non-native molecules (examples in **Table 6**; Case and Atsumi, 2016; Sun et al., 2019; Wichmann et al., 2020). Multiple strategies are under investigation to enhance the accumulation of biofuel feedstocks like alcohols or TAG. They range from overexpression of native or heterologous enzymes of the fatty acid biosynthetic pathway, like diacylglycerol acyltransferase (DGAT) enzyme; increased accumulation of metabolic intermediates used for lipids synthesis, like boosting acetyl-CoA supply; disruption of competing pathways; up to modulation of transcription factors accumulation (Sun et al., 2019; **Figure 3** and **Table 6**).

Terpenoids, also known as terpenes or isoprenoids, are another valuable class of hydrocarbon-derived molecules for industrial purposes. They are naturally produced by photosynthetic cells in the form of pigments, plant hormones and species-specific secondary metabolites with defensive role or mediating interactions with the environment (**Figure 3**; Pichersky and Raguso, 2018). They include thousands of chemicals with a wide range of human applications, from fuels, to pharmaceuticals (e.g., artemisinin has anti-malarial properties), to food and cosmetic additives, as menthol, limonene and squalene (Davies et al., 2015; Vavitsas et al., 2018; Wichmann et al., 2020). However, terpenoids are usually accumulated in low amount, harnessing an economically viable extraction from their natural producer. Currently, some terpenoids are produced in heterotrophic hosts like *E. coli* and *S. cerevisiae*, which require multiple genetic modification to establish the biosynthetic pathway. Conversely, microalgae already hold core terpenoid biosynthetic pathways for production of primary molecules like pigments, being a valuable host for heterologous production of non-native plant terpenes (Vavitsas et al., 2018; Wichmann et al., 2020; **Table 6** lists some examples).

In addition to hydrocarbons, microalgae, particularly green algae, have been used as valuable hosts for heterologous protein productions. Proteins expressed in *C. reinhardtii*, but also *Dunaliella salina*, *D. tertiolecta* and *Chlorella ellipsoidea* include antibodies, immonotoxins, enzymes and subunits of vaccines (for a review see Rasala and Mayfield, 2015), further demonstrating the potential of microalgae as an important source of fuels, food, feed and pharmaceutical products.

Working on a Whole Cell Physiology Level: Source/Sink Balance, -Omic Sciences and Computational Simulations

The above-mentioned examples and findings on the genetic engineering of single processes in photosynthetic cells show a few folds impact on algal productivity. According to the estimations on the energy conversion efficiency and CO_2 sequestration reported in **Tables 3**, **5**, this increase is still not enough to reach a major productivity breakthrough in multiple applications. Further, many studies highlight important side effects on other cell functions. This can be due to secondary effects of the mutations, but also to unpredicted interactions among physiological processes, leading e.g., to C allocation into different ready-to-use or storage macromolecular pools, luxury uptake of nutrients, functional and compositional homeostasis (see review Giordano, 2013 for details on homeostasis; Giordano et al., 2015a; Finkel et al., 2016; Ruan et al., 2018; Giordano and Wang, 2018). Our lacunose knowledge on cell strategies regarding homeostasis, acclimation and adaptation responses, even in the case of extensively studied species (e.g., diatoms), is still a major issue in the manipulation of photosynthetic cells (Wagner et al., 2017).

It is thus clear that any attempt to improve CO_2 fixation and biomass quality should be based on the holistic view of cell physiology, by simultaneously adapting (i.e., balancing) the activity and the regulation of multiple cellular functions.

First, chemical energy (ATP) and reductants produced by photosynthesis light reaction must be carefully tied with the energy cost of C fixation and other metabolic pathways (**Figures 1**, **4**) (Cotton et al., 2015; Giordano and Wang, 2018). Remarkably, the source/sink balance is not the only way in which photosynthetic light reactions and cell metabolism are interdependent. The redox poise in chloroplast stroma generated by the electron transport, in the form of reduced ferredoxin or NADPH, is also a crucial regulatory signal for several metabolic pathways through redox regulation of multiple enzymes by the thioredoxin system (Kikutani et al., 2012; Morisse et al., 2014; Nikkanen and Rintamäki, 2014).

Further, any change driven by metabolic engineering design must also be carefully customized to the selected genetic background and the specific growth environment cells will experience in large scale production, to avoid downstream issues during the scale up of the process, which is currently among the biggest obstacles to economically viable bio-factories (Borowitzka, 2016; Newby et al., 2016).

Even though some common features of bio-factory strains can be outlined, like the ability to thrive in extreme environment to limit contaminations, a fast growth rate, a high cell density, a high biomass productivity, it is conceivable that multiple *ad hoc* cell chassis should be designed according to each specific purpose, to minimize all the bottlenecks of each specific production system.

TABLE 6 | Examples of metabolic engineering for bio-fuel precursors and high-value molecules production.

Product	**Examples**			
	Specific product	**Species**	**Gene(s) targeted or introduced**	**References**
Alcohols (Fuels)	Ethanol	*Synechocystis* sp. *PCC6803*	OE of 3 genes: one CBB cycle enzyme among: Rubisco, fructose-1,6/sedoheptulose-1,7-bisphosphatase (FBP/SBPase), transketolase (TK), aldolase (FBA); pyruvate decarboxylase (PDC) (ethanol synthesis); alcohol dehydrogenase (ADH) (Ethanol synthesis)	Liang et al., 2018
	Ethanol	*Synechocystis* sp. *PCC6803*	OE G6P dehydrogenase (zwf gene)	Choi and Park, 2016
	Isobutanol	*Synechocystis* sp. *PCC6803*	*Lactococcus lactis* α-ketoisovalerate decarboxylase (*kivd*); alcohol dehydrogenases (ADH) yqhD or yjgB, from *E. coli*, or slr0942 or slr1192 from *Synechocystis*	Miao et al., 2017
	Isopropanol	*S. elongatus PCC 7942*	*E. coli pta* gene (phosphate acetyltransferase),	Hirokawa et al., 2017
Fatty acids (Fuels)	TAGs	*Nannochloropsis salina*	Pyruvate dehydrogenase kinase knockdown	Ma et al., 2017
	TAGs	*Nannochloropsis salina*	OE *bZIP* transcription factor	Kwon et al., 2018
	Lipids	*Nannochloropsis gaditana*	Transcription factor *Zn(II)*$_2$*Cys6* deleted	Ajjawi et al., 2017
	TAGs	*Phaeodactylum tricornutum*	*Haematococcus* oil globule protein	Shemesh et al., 2016
	Alkanes, alkenes	*Synechocystis* sp. *PCC6803*	aas (acyl ACP synthase) depleted; genes introduced: *E. coli* TesA (thioesterase TesA), *Pseudomonas mendocina* UndB, *Chlorella variabilis* fatty acid photodecarboxylase (FAP)	Yunus et al., 2018
		Chlamydomonas reinhardtii	*E. coli* TesA, *Jeotgalicoccus* sp. terminal olefin-forming fatty acid decarboxylase (OleT), *Rhodococcus* sp. P450 reductase (RhFRED), OE native FAP	
Fatty acids (LC-PUFA, nutraceuticals)	alpha-linolenic acid (omega-3)	*Synechococcus elongatus PCC 7942*	*fabF* OE; *fadD* deleted; *Synechococcus* sp. PCC 7002 *desA* and *desB* desaturases OE	Santos-Merino et al., 2018
	omega-3 PUFA docosahexaenoic acid (DHA) (as TAGs)	*Phaeodactylum tricornutum*	Δ6-desaturase and Δ5-elongase from *Otreococcus tauri*	Hamilton et al., 2014
Terpenoids (Fuels, nutraceuticals, pharmaceuticals)	β-phellandrene (PHL, monoterpene)	*Synechocystis* sp. *PCC6803*	*Picea abies* geranyl diphosphate synthase (GPPS); *Lavandula angustifolia* β-phellandrene synthase (PHLS)	Betterle and Melis, 2019
	Squalene (triterpenoid)	*Synechocystis* sp. *PCC6803*	*Synechocystis Shc* (squalene hopene cyclase) inactivated; *Botryococcus braunii* squalene synthase introduced; heterologous MEP pathway: *Coleus forskholii* deoxyxylulose-5-phosphate synthase (CfDXS); *E. coli* isopentenyl diphosphate isomerase (EcIDI); *E. coli* farnesyl diphosphate synthase (EcIspA)	Pattanaik et al., 2020
	Limonene and α-bisabolene	*Synechococcus* sp. *PCC 7002*	*Mentha spicata* L-limonene synthase or *Abies grandis* (E)-α-bisabolene synthase	Davies et al., 2014
	(E)-α-bisabolene (sesquiterpene, biodiesel precursor)	*Chlamydomonas reinhardtii*	*Abies grandis* bisabolene synthase OE; amiRNA-based repression of competing pathways.	Wichmann et al., 2018
	Geraniol (intermediate in the synthesis of the monoterpenoid indole alkaloids (MIAs)	*Phaeodactylum tricornutum*	*Catharanthus roseus* geraniol synthase (CrGES)	Fabris et al., 2020

Recent examples of genetic modifications to enhance the accumulation of lipids and of non-native terpenoids in different prokaryotic and eukaryotic microalgal species are listed in the table. OE, over expression. For other examples, please refer to the review papers Davies et al., 2015; Gao et al., 2016; Vavitsas et al., 2018; Sun et al., 2019; Wichmann et al., 2020 *and refs therein.*

Rapidly developing -omic sciences, i.e., transcriptomic, proteomic and metabolomic, shall support a comprehensive understanding of cell physiology and of the consequences of each targeted mutation on cell functions. Such a holistic view of cell functioning shall then drive the selection of additional processes which require metabolic energy optimization or which can be minimized to save metabolic energy (**Figure 5**). Performing direct validation of the productivity and the drawbacks of different metabolic variants with experimental studies on living cells is a labor-intensive and time-consuming procedure. Mathematical models which mimic the consequences of a mutation *in silico* are thus extremely relevant to develop a successful, wide-ranging, metabolic engineering approach to design photosynthetic cells as a function of the selected species and growth environments.

Biochemical simulations for photosynthetic C assimilation started in the 80s (Farquhar et al., 1980, 2001), then being constantly improved and expanded. Available models now include reactions from multiple pathways, like CBB cycle, photorespiration, starch and sucrose synthesis, as a function of nutrient availability (Zhu et al., 2007, 2013). Given the high metabolic cost of N assimilation into amino acids (**Figure 4**), a further advantage of computational modeling is, for example, that a constant N quota can be allocated to the whole set of enzymes considered. This will avoid additional energy investment of the cell in N acquisition, while optimizing enzymes relative stoichiometry (Zhu et al., 2007). Similar computational predictions are recently under development also for economically relevant algal species. They simulate the complex network of photosynthetic light reactions and their regulation, as well as algal metabolic reactions in different environmental conditions, like illumination regime, nutrient and CO_2 availability (Chang et al., 2011; Du et al., 2018; Perin et al., 2019; Fachet et al., 2020; Toyoshima et al., 2020). Remarkably, robust mathematical models rely on a deep understanding of the cell physiology, to include as many parameters as possible in the simulation. This multidisciplinary approach shall allow to design living factory where all the house-keeping functions are present but minimized and most of the energy is directed to the commercial products (**Table 5** and **Figure 5**).

CONCLUSION AND PERSPECTIVES

Photosynthetic organisms that are able to fix more CO_2 with less resources will be of paramount relevance to face major global challenges regarding climate change, sustainable management of natural resources, food and energy demand. Among photosynthetic organisms, microalgae have gained the highest attention due to several unique capabilities, that make them outcompete higher plants when considering their exploitation in the bio-based industry.

The microalgae evolutive history results in a variety of genotypes, wide functional diversity and metabolic flexibility, which play a crucial role in determining resource demand and use efficiency. At the same time, metabolic flexibility and homeostasis in response to external perturbations are also responsible for the fact that cultures may easily diverge from the intended biomass quality. These factors are often underestimated when selecting candidates and setting up production plants. The only chance to reach stable quality and meaningful amount of the products is to consider such physiological complexity. Further, in order to reach a clean transition toward renewable energy and circular economy, cell factories should approach the maximal theoretical value for light energy conversion into biomass. Valuable strategies leading to an economically sustainable algal cultivation are currently under research and enclose: selection of robust strains and consortia as natural producers of high-value molecules along with the implementation of nutrient recycling from wastewaters or flue gases; characterization of cell physiological responses in different environments; optimization of molecular tools for predictable genetic manipulation, metabolic design, computational modeling; selection of functional "building blocks" from different biological sources to be reassembled in optimized synthetic cell factories. Future efforts shall eventually combine a careful selection of the most appropriate genetic background, culturing conditions and *ad hoc* genetic engineering, to significantly improve photosynthetic cells bio-commodities productivity.

AUTHOR CONTRIBUTIONS

MG conceived the outline of the manuscript. CG and AN wrote the manuscript and generated the figures. All authors contributed to the article and approved the submitted version.

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REFERENCES

Ajjawi, I., Verruto, J., Aqui, M., Soriaga, L. B., Coppersmith, J., Kwok, K., et al. (2017). Lipid production in *Nannochloropsis gaditana* is doubled by decreasing expression of a single transcriptional regulator. *Nat. Biotechnol.* 35, 647–652. doi: 10.1038/nbt.3865

Alboresi, A., Perin, G., Vitulo, N., Diretto, G., Block, M., Jouhet, J., et al. (2016). Light remodels lipid biosynthesis in *Nannochloropsis gaditana* by modulating carbon partitioning between organelles. *Plant Physiol.* 171, 2468–2482. doi: 10.1104/pp.16.00599

Allahverdiyeva, Y., Suorsa, M., Tikkanen, M., and Aro, E.-M. (2015). Photoprotection of photosystems in fluctuating light intensities. *J. Exp. Bot.* 66, 2427–2436. doi: 10.1093/jxb/eru463

Andersson, I. (2008). Catalysis and regulation in Rubisco. *J. Exp. Bot.* 59, 1555–1568. doi: 10.1093/jxb/ern091

Aro, E.-M. (2016). From first generation biofuels to advanced solar biofuels. *Ambio* 45, S24–S31. doi: 10.1007/s13280-015-0730-0

Bacchetti, T., Annibaldi, A., Comitini, F., Ciani, M., Damiani, E., Norici, A., et al. (2020). "Alternative ingredients for feed and food," in *The First Outstanding*

50 Years of "Università Politecnica delle Marche", eds S. Longhi, et al. (Cham: Springer). doi: 10.1007/978-3-030-33832-9_34

Badger, M. R., Andrews, T. J., Whitney, S. M., Ludwig, M., Yellowlees, D. C., Leggat, W., et al. (1998). The diversity and coevolution of Rubisco, plastids, pyrenoids, and chloroplast-based CO2-concentrating mechanisms. *Can. J. Bot.* 76, 1052–1071. doi: 10.1139/b98-074

Badger, M. R., and Bek, E. J. (2008). Multiple Rubisco forms in *Proteobacteria*: their functional significance in relation to CO2 acquisition by CBB cycle. *J. Exp. Bot.* 59, 1525–1541. doi: 10.1093/jxb/erm297

Baier, T., Wichmann, J., Kruse, O., and Lauersen, K. J. (2018). Intron-containing algal transgenes mediate efficient recombinant gene expression in the green microalga *Chlamydomonas reinhardtii*. *Nucleic Acids Res.* 46, 6909–6919. doi: 10.1093/nar/gky532

Barber, J. (2009). Photosynthetic energy conversion: natural and artificial. *Chem. Soc. Rev.* 38, 185–196. doi: 10.1039/b802262n

Barbier, G., Oesterhelt, C., Larson, M. D., Halgren, R. G., Wilkerson, C., Garavito, R. M., et al. (2005). Comparative genomics of two closely related unicellular thermo-acidophilic red algae, *Galdieria sulphuraria* and *Cyanidioschyzon merolae*, reveals the molecular basis of the metabolic flexibility of *Galdieria sulphuraria* and significant differences in carbohydrate metabolism of both algae. *Plant Physiol.* 137, 460–474. doi: 10.1104/pp.104.051169

Bar-Even, A. (2018). Daring metabolic designs for enhanced plant carbon fixation. *Plant Sci.* 273, 71–83.

Bar-Even, A., Noor, E., Lewis, N. E., and Milo, R. (2010). Design and analysis of synthetic carbon fixation pathways. *Proc. Natl. Acad. Sci. U.S.A.* 107, 8889–8894. doi: 10.1073/pnas.0907176107

Beardall, J., and Giordano, M. (2002). Ecological implications of microalgal and cyanobacterial CO2 concentrating mechanisms, and their regulation. *Funct. Plant Biol.* 29, 335–347. doi: 10.1071/PP01195

Beardall, J., and Raven, J. A. (2016). "Carbon acquisition by microalgae," in *The physiology of microalgae. Developments in Applied Phycology 6*, eds M. A. Borowitzka, J. Beardall, and J. A. Raven (Cham: Springer), 89–99. doi: 10.1007/978-3-319-24945-2_4

Becker, E. W. (2007). Micro-algae as a source of protein. *Biotechnol. Adv.* 25, 207–210. doi: 10.1016/j.biotechadv.2006.11.002

Benedetti, M., Vecchi, V., Barera, S., and Dall'Osto, L. (2018). Biomass from microalgae: the potential of domestication towards sustainable biofactories. *Microb. Cell Fact.* 17:173.

Betterle, N., and Melis, A. (2019). Photosynthetic generation of heterologous terpenoids in cyanobacteria. *Biotechnol. Bioeng.* 116, 2041–2051. doi: 10.1002/bit.26988

Bilanovic, D., Holland, M., Starosvetsky, J., and Armon, R. (2016). Co-cultivation of microalgae and nitrifiers for higher biomass production and better carbon capture. *Bioresour. Technol.* 220, 282–288. doi: 10.1016/j.biortech.2016.08.083

Blankenship, R. E., Tiede, D. M., Barber, J., Brudvig, G. W., Fleming, G., Ghirardi, M., et al. (2011). Comparing Photosynthetic and the Potential for Improvement. *Science* 332, 805–810. doi: 10.1126/science.1200165

Borowitzka, M. A. (2013). High-value products from microalgae—Their development and commercialisation. *J. Appl. Phycol.* 25, 743–756. doi: 10.1007/s10811-013-9983-9

Borowitzka, M. A. (2016). "Algal physiology and large-scale outdoor cultures of microalgae," in *The Physiology of Microalgae. Developments in Applied Phycology* 6, eds M. A. Borowitzka, J. Beardall, and J. A. Raven (Cham: Springer), 600–652. doi: 10.1007/978-3-319-24945-2_23

Brenner, K., You, L., and Arnold, F. H. (2008). Engineering microbial consortia: a new frontier in synthetic biology. *Trends Biotechnol.* 26, 483–489. doi: 10.1016/j.tibtech.2008.05.004

Brodie, J., Chan, C. X., De Clerck, O., Cock, J. M., Coelho, S. M., Gachon, C., et al. (2017). The algal revolution. *Trends Plant Sci.* 22, 726–738. doi: 10.1016/j.tplants.2017.05.005

Caballero, M. A., Jallet, D., Shi, L., Rithner, C., Zhang, Y., and Peers, G. (2016). Quantification of chrysolaminarin from the model diatom *Phaeodactylum tricornutum*. *Algal Res.* 20, 180–188. doi: 10.1016/j.algal.2016.10.008

Caffarri, S., Tibiletti, T., Jennings, R. C., and Santabarbara, S. (2014). A comparison between plant photosystem I and photosystem II architecture and functioning. *Curr. Protein Pept. Sci.* 15, 296–331. doi: 10.2174/1389203715666140327102218

Cardinale, B. J., Matulich, K. L., Hooper, D. U., Byrnes, J. E., Duffy, E., Gamfeldt, L., et al. (2011). The functional role of producer diversity in ecosystems. *Am. J. Bot.* 98, 572–592. doi: 10.3732/ajb.1000364

Cardona, T., Shao, S., and Nixon, P. J. (2018). Enhancing photosynthesis in plants: the light reactions. *Essays Biochem.* 62, 85–94. doi: 10.1042/EBC20170015

Carmo-Silva, E., Scales, J. C., Madgwick, P. J., and Parry, M. A. J. (2015). Optimizing Rubisco and its regulation for greater resource use efficiency. *Plant Cell Environ.* 38, 1817–1832. doi: 10.1111/pce.12425

Case, A. E., and Atsumi, S. (2016). Cyanobacterial chemical production. *J. Biotechnol.* 231, 106–114. doi: 10.1016/j.jbiotec.2016.05.023

Ceron, G. M. C., Fernandez, S. J. M., Molina, G. E., and Garcia, C. F. (2000). Mixotrophic growth of *Phaeodactylum tricornutum* on glycerol: growth rate and fatty acid profile. *J. Appl. Phycol.* 12, 239–248. doi: 10.1023/A:1008123000002

Chang, R. L., Ghamsari, L., Manichaikul, A., Hom, E. F. Y., Balaji, S., Fu, W., et al. (2011). Metabolic network reconstruction of *Chlamydomonas* offers insight into light-driven algal metabolism. *Mol. Syst. Biol.* 7:518. doi: 10.1038/msb.2011.52

Chisti, Y. (2007). Biodiesel from microalgae. *Biotechnol. Adv.* 25, 294–306. doi: 10.1016/j.biotechadv.2007.02.001

Choi, Y.-N., and Park, J. M. (2016). Enhancing biomass and ethanol production by increasing NADPH production in *Synechocystis* sp. PCC 6803. *Bioresource Technol.* 213, 54–57. doi: 10.1016/j.biortech.2016.02.056

Clarens, A. F., Resurreccion, E. P., White, M. A., and Colosi, L. M. (2010). Environmental life cycle comparison of algae to other bioenergy feedstocks. *Environ. Sci. Technol.* 44, 1813–1819. doi: 10.1021/es902838n

Corcoran, A. A., and Boeing, W. J. (2012). Biodiversity increases the productivity and stability of phytoplankton communities. *PLoS One* 7:e49397. doi: 10.1371/journal.pone.0049397

Cotton, C. A., Edlich-Muth, C., and Bar-Even, A. (2018). Reinforcing carbon fixation: CO2 reduction replacing and supporting carboxylation. *Curr. Opin. Biotechnol.* 49, 49–56. doi: 10.1016/j.copbio.2017.07.014

Cotton, C. A. R., Douglass, J. S., De Causmaecker, S., Brinkert, K., Cardona, T., Fantuzzi, A., et al. (2015). Photosynthetic constraints on fuel from microbes. *Front. Bioeng. Biotechnol.* 3:36. doi: 10.3389/fbioe.2015.00036

Cummins, P. L., Kannappan, B., and Gready, J. E. (2018). Directions for optimization of photosynthetic carbon fixation: RuBisCO's efficiency may not be so constrained after all. *Front. Plant Sci.* 9:183. doi: 10.3389/fpls.2018.00183

Davies, F. K., Jinkerson, R. E., and Posewitz, M. C. (2015). Toward a photosynthetic microbial platform for terpenoid engineering. *Photosynth. Res.* 123, 265–284. doi: 10.1007/s11120-014-9979-6

Davies, F. K., Work, V. H., Beliaev, A. S., and Posewitz, M. C. (2014). Engineering limonene and bisabolene production in wild type and a glycogen-deficient mutant of *Synechococcus* sp. PCC 7002. *Front. Bioeng. Biotechnol.* 2:21. doi: 10.3389/fbioe.2014.00021

De Farias-Neves, F., Hoinaski, L., Rubi-Rörig, L., Bianchini-Derner, R., and de Melo-Lisboa, H. (2019). Carbon biofixation and lipid composition of an acidophilic microalga cultivated on treated wastewater supplied with different CO2 levels. *Environ. Technol.* 40, 3308–3317. doi: 10.1080/09593330.2018.1471103

de Mooij, T., Janssen, M., and Cerezo-Chinarro, O. (2015). Antenna size reduction as a strategy to increase biomass productivity: a great potential not yet realized. *J. Appl. Phycol.* 27, 1063–1077. doi: 10.1007/s10811-014-0427-y

De Porcellinis, A. J., Nørgaard, H., Furelos Brey, L. M., Erstad, S. M., Jones, P. R., Heazlewood, J. L., et al. (2018). Overexpression of bifunctional fructose-1,6-bisphosphatase/sedoheptulose-1,7-bisphosphatase leads to enhanced photosynthesis and global reprogramming of carbon metabolism in *Synechococcus* sp. PCC 7002. *Metab. Eng.* 47, 170–183. doi: 10.1016/j.ymben.2018.03.001

de Vargas, C., Audic, S., Henry, N., Decelle, J., Mahe, F., Logares, R., et al. (2015). Eukaryotic plankton diversity in the sunlit ocean. *Science* 348:1261605. doi: 10.1126/science.1261605

Diaz, M. M., and Maberly, S. C. (2009). Carbon-concentrating mechanisms in acidophilic algae. *Phycologia* 48, 77–85. doi: 10.2216/08-08.1

Dietrich, K., Dumont, M. J., Del Rio, L. F., and Orsat, V. (2017). Producing PHAs in the bioeconomy – Towards a sustainable bioplastic. *Sustain. Prod. Consum.* 9, 58–70. doi: 10.1016/j.spc.2016.09.001

Doron, L., Segal, N., and Shapira, M. (2016). Transgene expression in microalgae—From tools to applications. *Front. Plant Sci.* 7:505. doi: 10.3389/fpls.2016.00505

Du, W., Jongbloets, J. A., van Boxtel, C., Pineda Hernández, H., Lips, D., Oliver, B. G., et al. (2018). Alignment of microbial fitness with engineered product formation: obligatory coupling between acetate production and photoautotrophic growth. *Biotechnol. Biofuels* 11:38.

Eibl, J. K., Corcoran, J. D., Senhorinho, G. A., Zhang, K., Hosseini, N. S., Marsden, J., et al. (2014). Bioprospecting for acidophilic lipid-rich green microalgae isolated from abandoned mine site water bodies. *AMB Expr.* 4:7. doi: 10.1186/2191-0855-4-7

Ellis, R. J. (1979). The most abundant protein in the world. *Trends Biochem. Sci.* 4, 241–244.

Enzing, C., Ploeg, M., Barbosa, M., and Sijtsma, L. (2014). *Microalgae-Based Products for the Food and Feed Sector: An Outlook for Europe. JRC Scientific and Policy Reports. Report No. EUR 26255 EN*. Brussels: European Union. doi: 10.2791/3339

Fabris, M., George, J., Kuzhiumparambil, U., Lawson, C. A., Jaramillo-Madrid, A. C., Abbriano, R. M., et al. (2020). Extrachromosomal genetic engineering of the marine diatom *Phaeodactylum tricornutum* enables the heterologous production of monoterpenoids. *ACS Synth. Biol.* 9, 598–612. doi: 10.1021/acssynbio.9b00455

Fachet, M., Witte, C., Flassig, R. J., Rihko-struckmann, L. K., Mckie-krisberg, Z., Polle, J. E. W., et al. (2020). Reconstruction and analysis of a carbon-core metabolic network for *Dunaliella salina*. *BMC Bioinformatics* 21:1. doi: 10.1186/s12859-019-3325-0

Falkowski, P., and Raven, J. A. (2007). *Aquatic Photosynthesis 488*, 2nd Edn. Princeton, NJ: Princeton University Press.

Fang, L., Lin, H. X., Low, C. S., Wu, M. H., Chow, Y., et al. (2012). Expression of the *Chlamydomonas reinhardtii* Sedoheptulose-1, 7-bisphosphatase in *Dunaliella bardawil* leads to enhanced photosynthesis and increased glycerol production. *Plant Biotechnol. J.* 10, 1129–1135. doi: 10.1111/pbi.12000

Farquhar, G. D., von Caemmerer, S., and Berry, J. A. (1980). A biochemical model of photosynthetic CO2 assimilation in leaves of C3 species. *Planta* 149, 78–90. doi: 10.1007/BF00386231

Farquhar, G. D., von Caemmerer, S., and Berry, J. A. (2001). Models of photosynthesis. *Plant Physiol.* 125, 42–45. doi: 10.1104/pp.125.1.42

Finkel, Z. V., Follows, M. J., Liefer, J. D., Brown, C. M., Benner, I., and Irwin, A. J. (2016). Phylogenetic diversity in the macromolecular composition of microalgae. *PLoS One* 11:e0155977. doi: 10.1371/journal.pone.0155977

Gallardo-Rodríguez, J., Sanchez-Mirón, A., García-Camacho, F., López-Rosales, L., Chisti, Y., and Molina-Grima, E. (2012). Bioactives from microalgal dinoflagellates. *Biotechnol. Adv.* 30, 1673–1684. doi: 10.1016/j.biotechadv.2012.07.005

Gao, X., Sun, T., Pei, G., Chen, L., and Zhang, W. (2016). Cyanobacterial chassis engineering for enhancing production of biofuels and chemicals. *Appl. Microbiol. Biotechnol.* 100, 3401–3413. doi: 10.1007/s00253-016-7374-2

Geider, R., and La Roche, J. (2002). Redfield revisited: variability of C:N:P in marine microalgae and its biochemical basis. *Eur. J. Phycol.* 37, 1–17. doi: 10.1017/S0967026201003456

Gerotto, C., Alboresi, A., Meneghesso, A., Jokel, M., Suorsa, M., Aro, E.-M., et al. (2016). Flavodiiron proteins act as safety valve for electrons in *Physcomitrella patens*. *Proc. Natl. Acad. Sci. U.S.A.* 113, 12322–12327. doi: 10.1073/pnas.1606685113

Gerotto, C., and Morosinotto, T. (2013). Evolution of photoprotection mechanisms upon land colonization: evidence of PSBS-dependent NPQ in late Streptophyte algae. *Physiol. Plant.* 149, 583–598. doi: 10.1111/ppl.12070

Giordano, M. (2013). Homeostasis: an underestimated focal point of ecology and evolution. *Plant Sci.* 211, 92–101. doi: 10.1016/j.plantsci.2013.07.008

Giordano, M., Beardall, J., and Raven, J. A. (2005). CO2 concentrating mechanisms in algae: mechanisms, environmental modulation, and evolution. *Annu. Rev. Plant Biol.* 56, 99–131. doi: 10.1146/annurev.arplant.56.032604.144052

Giordano, M., Norici, A., and Beardall, J. (2015a). Impact of inhibitors of amino acid, protein, and RNA synthesis on C allocation in the diatom *Chaetoceros muellerii*: a FTIR approach. *Algae* 32, 161–170. doi: 10.4490/algae.2017.32.6.6

Giordano, M., Palmucci, M., and Norici, A. (2015b). Taxonomy and growth conditions concur to determine the energetic suitability of algal fatty acid complements. *J. Appl. Phycol.* 27, 1401–1413. doi: 10.1007/s10811-014-0457-5

Giordano, M., and Ratti, S. (2013). The biomass quality of algae used for CO2 sequestration is highly species-specific and may vary over time. *J. Appl. Phycol.* 25, 1431–1434. doi: 10.1007/s10811-012-9966-2

Giordano, M., and Raven, J. A. (2014). Nitrogen and sulfur assimilation in plants and algae. *Aquat. Bot.* 118, 45–61. doi: 10.1016/j.aquabot.2014.06.012

Giordano, M., and Wang, Q. (2018). "Microalgae for industrial purposes," in *Biomass and Green Chemistry: Building a renewable Pathway*, ed. S. Vaz Jr. (Cham: Springer). doi: 10.1007/978-3-319-66736-2_6

Granum, E., Kirkvold, S., and Myklestad, S. M. (2002). Cellular and extracellular production of carbohydrates and amino acids by the marine diatom *Skeletonema costatum*: diel variations and effects of N depletion. *Mar. Ecol. Prog. Ser.* 242, 82–93. doi: 10.3354/meps242083

Hagemann, M., Kern, R., Maurino, V. G., Hanson, D. T., Weber, A. P. M., Sage, R. F., et al. (2016). Evolution of photorespiration from cyanobacteria to land plants, considering protein phylogenies and acquisition of carbon concentrating mechanisms. *J. Exp. Bot.* 67, 2963–2976. doi: 10.1093/jxb/erw063

Hamilton, M., Haslam, R., Napier, J., and Sayanova, O. (2014). Metabolic engineering of microalgae for enhanced production of omega-3 long chain polyunsaturated fatty acids. *Metab. Eng.* 22, 3–9. doi: 10.1016/j.ymben.2013.12.003

Henley, W. J., Litaker, R. W., Novoveská, L., Duke, C. S., Quemada, H. D., and Sayre, R. T. (2013). Initial risk assessment of genetically modified (GM) microalgae for commodity-scale biofuel cultivation. *Algal Res.* 2, 66–77. doi: 10.1016/j.algal.2012.11.001

Heureux, A. M. C., Young, J. N., Whitney, S. M., Eason-Hubbard, M. R., Lee, R. B. Y., Sharwood, R. E., et al. (2017). The role of Rubisco kinetics and pyrenoid morphology in shaping the CCM of haptophyte microalgae. *J. Exp. Bot.* 68, 3959–3969. doi: 10.1093/jxb/erx179

Hirokawa, Y., Dempo, Y., Fukusaki, E., and Hanai, T. (2017). Metabolic engineering for isopropanol production by an engineered cyanobacterium, *Synechococcus elongatus* PCC 7942, under photosynthetic conditions. *J. Biosci. Bioeng.* 12, 39–45. doi: 10.1016/j.jbiosc.2016.07.005

Ho, T.-Y., Quigg, A., Finkel, Z. V., Allen, J. M., Wyman, K., Falkowski, P. G., et al. (2003). Elemental composition of some marine phytoplankton. *J. Phycol.* 39, 1145–1159. doi: 10.1111/j.0022-3646.2003.03-090.x

Hopkinson, B. M., Dupont, C. L., Allen, A. E., and Morel, F. M. M. (2011). Efficiency of the CO2-concentrating mechanism of diatoms. *Proc. Natl. Acad. Sci. U.S.A.* 108, 3830–3837. doi: 10.1073/pnas.1018062108

Hopkinson, B. M., Dupont, C. L., and Matsuda, Y. (2016). The physiology and genetics of CO2 concentrating mechanisms in model diatoms. *Curr. Opin. Plant Biol.* 31, 51–57. doi: 10.1016/j.pbi.2016.03.013

Hossain, N., Zaini, J., and Indra Mahlia, T. M. (2019). Life cycle assessment, energy balance and sensitivity analysis of bioethanol production from microalgae in a tropical country. *Renew. Sustain. Energy Rev.* 115:109371. doi: 10.1016/j.rser.2019.109371

International Energy Agency (2017). *State of Technology Review on Algae Bioenergy*. Available online at: https://www.ieabioenergy.com/wp-content/uploads/2016/01/Laurens-Algae-Bioenergy-Report-IEA-webinar-170124-final-rev1.pdf (accessed March 10, 2020).

International Energy Agency (2019). *World Energy Outlook 2019*. Paris: IEA.

International Energy Agency (2020a). *Global CO2 Emissions in 2019*. Available online at: https://www.iea.org/articles/global-co2-emissions-in-2019 (accessed March 10, 2020).

International Energy Agency (2020b). *Transport Biofuels -Analyses*. Available online at: https://www.iea.org/reports/transport-biofuels (accessed June 24, 2020).

International Panel of Climate Change [IPCC] (2014). *Synthesis Report. Contribution of Working Groups I, II and III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Core Writing Team*, eds R. K. Pachauri and L. A. Meyer (Geneva: IPCC).

Jakob, T., Wagner, H., Stehfest, K., and Wilhelm, C. (2007). A complete energy balance from photons to new biomass reveals a light- and nutrient-dependent variability in the metabolic costs of carbon assimilation. *J. Exp. Bot.* 58, 2101–2112. doi: 10.1093/jxb/erm084

Jinkerson, R. E., and Jonikas, M. C. (2015). Molecular techniques to interrogate and edit the *Chlamydomonas* nuclear genome. *Plant J.* 82, 393–412. doi: 10.1111/tpj.12801

Johnson, M. P. (2016). Photosynthesis. *Essays Biochem.* 60, 255–273. doi: 10.1042/EBC20160016

Kamalanathan, M., and Quigg, A. (2019). *Physiological Limitations and Solutions to Various Applications of Microalgae," in Microalgae*. Available online at: https://www.intechopen.com/books/microalgae-from-physiology-to-application/physiological-limitations-and-solutions-to-various-applications-of-microalgae (accessed January 29, 2020).

Karlsson, L., Clarke, A. K., Chen, Z.-Y., Hugghins, S. Y., and Park, Y. I. (1998). A novel α-type carbonic anhydrase associated with the thylakoid membrane in *Chlamydomonas reinhardtii* is required for growth at ambient CO2. *EMBO J.* 17, 1208–1216. doi: 10.1093/emboj/17.5.1208

Kerfeld, C. A. (2015). Plug-and-play for improving primary productivity. *Am. J. Bot.* 102, 1949–1950. doi: 10.3732/ajb.1500409

Kikutani, S., Nakajima, K., Nagasato, C., Tsuji, Y., Miyatake, A., and Matsuda, Y. (2016). Thylakoid luminal u-carbonic anhydrase critical for growth and photosynthesis in the marine diatom *Phaeodactylum tricornutum*. *Proc. Natl Acad. Sci. U.S.A.* 113, 9828–9833. doi: 10.1073/pnas.1603112113

Kikutani, S., Tanaka, R., Yamazaki, Y., Hara, S., Hisabori, T., Kroth, P. G., et al. (2012). Redox regulation of carbonic anhydrases via thioredoxin in chloroplast of the marine diatom *Phaeodactylum tricornutum*. *J. Biol. Chem.* 287, 20689–20700. doi: 10.1074/jbc.M111.322743

Kirst, H., Formighieri, C., and Melis, A. (2014). Maximizing photosynthetic efficiency and culture productivity in cyanobacteria upon minimizing the phycobilisome light-harvesting antenna size. *Biochim. Biophys. Acta Bioenerg.* 1837, 1653–1664. doi: 10.1016/j.bbabio.2014.07.009

Kirst, H., Gabilly, S. T., Niyogi, K. K., Lemaux, P. G., and Melis, A. (2017). Photosynthetic antenna engineering to improve crop yields. *Planta* 245, 1009–1020. doi: 10.1007/s00425-017-2659-y

Kliebenstein, D. J. (2014). Synthetic biology of metabolism: using natural variation to reverse engineer systems. *Curr. Opin. Plant Biol.* 19, 20–26. doi: 10.1016/j.pbi.2014.03.008

Kodama, M., Ikemoto, H., and Miyachi, S. (1993). A new species of highly CO2-tolerant fast-growing marine microalga for high-density cultivation. *J. Mar. Biotechnol.* 1, 21–25.

Kromdijk, J., Glowacka, K., Leonelli, L., Gabilly, S. T., Iwai, M., Niyogi, K. K., et al. (2016). Improving photosynthesis and crop productivity by accelerating recovery from photoprotection. *Science* 354, 857–861. doi: 10.1126/science.aai8878

Kroth, P. G., Bones, A. M., Daboussi, F., Ferrante, M. I., Jaubert, M., Kolot, M., et al. (2018). Genome editing in diatoms: achievements and goals. *Plant Cell Rep.* 37, 1401–1408.

Kroth, P. G., Chiovitti, A., Gruber, A., Martin-Jezequel, V., Mock, T., Parker, M. S., et al. (2008). A model for carbohydrate metabolism in the diatom *Phaeodactylum tricornutum* deduced from comparative whole genome analysis. *PLoS One* 3:e1426. doi: 10.1371/journal.pone.0001426

Kwon, S., Kang, N. K., Koh, H. G., Shin, S.-E., Lee, B., Jeong, B., et al. (2018). Enhancement of biomass and lipid productivity by overexpression of a bZIP transcription factor in *Nannochloropsis salina*. *Biotechnol. Bioeng.* 115, 331–340. doi: 10.1002/bit.26465

Lee, T., Tseng, Y., Cheng, C., Chen, Y., Lin, C., Su, H., et al. (2017). Characterization of a heat-tolerant *Chlorella* sp. GD mutant with enhanced photosynthetic CO2 fixation efficiency and its implication as lactic acid fermentation feedstock. *Biotechnol. Biofuels* 10:214. doi: 10.1186/s13068-017-0905-y

Lepage, G., and Roy, C. C. (1984). Improved recovery of fatty acid through direct transesterification without prior extraction or purification. *J. Lipid Res.* 25, 1391–1396.

Lepetit, B., Gélin, G., Lepetit, M., Sturm, S., Vugrinec, S., Rogato, A., et al. (2017). The diatom *Phaeodactylum tricornutum* adjusts nonphotochemical fluorescence quenching capacity in response to dynamic light via fine-tuned Lhcx and xanthophyll cycle pigment synthesis. *New Phytol.* 214, 205–218. doi: 10.1111/nph.14337

Li, G., Brown, C. M., Jeans, J. A., Donaher, N. A., McCarthy, A., and Campbell, D. A. (2015). The nitrogen costs of photosynthesis in a diatom under current and future pCO2. *New Phytol.* 205, 533–543. doi: 10.1111/nph.13037

Li, Y., Horsman, M., Wang, B., Wu, N., and Lan, C. Q. (2008). Effects of nitrogen sources on cell growth and lipid accumulation of green alga *Neochloris oleoabundans*. *Appl. Microbiol. Biotechnol.* 81, 629–636. doi: 10.1007/s00253-008-1681-1

Liang, F., Englund, E., Lindberg, P., and Lindblad, P. (2018). Engineered cyanobacteria with enhanced growth show increased ethanol production and higher biofuel to biomass ratio. *Metab. Eng.* 46, 51–59. doi: 10.1016/j.ymben.2018.02.006

Liang, F., and Lindblad, P. (2016). Effects of overexpressing photosynthetic carbon flux control enzymes in the cyanobacterium *Synechocystis* PCC 6803. *Metab. Eng.* 38, 56–64. doi: 10.1016/j.ymben.2016.06.005

Liberton, M., Chrisler, W. B., Nicora, C. D., Moore, R. J., Smith, R. D., Koppenaal, D. W., et al. (2017). Phycobilisome truncation causes widespread proteome changes in *Synechocystis* sp. PCC 6803. *PLoS One* 12:e0173251. doi: 10.1371/journal.pone.0173251

Liu, W., and Steward, C. N. J. (2015). Plant synthetic biology. *Trends Plant Sci.* 20, 309–317. doi: 10.1016/j.tplants.2015.02.004

López, G., Yate, C., Ramos, F. A., Cala, M. P., Restrepo, S., and Baena, S. (2019). Production of polyunsaturated fatty acids and lipids from autotrophic, mixotrophic and heterotrophic cultivation of *Galdieria* sp. strain USBA-GBX-832. *Sci. Rep.* 9:10791. doi: 10.1038/s41598-019-46645-3

Luan, G., and Lu, X. (2018). Tailoring cyanobacterial cell factory for improved industrial properties. *Biotechnol. Adv.* 36, 430–442. doi: 10.1016/j.biotechadv.2018.01.005

Luengo, J. M., García, B., Sandoval, A., Naharro, G., and Olivera, E. A. R. (2003). Bioplastics from microorganisms. *Curr. Opin. Microbiol.* 6, 251–260. doi: 10.1016/S1369-5274(03)00040-7

Ma, X., Yao, L., Yang, B., Lee, Y. K., Chen, F., and Liu, J. (2017). RNAi-mediated silencing of a pyruvate dehydrogenase kinase enhances triacylglycerol biosynthesis in the oleaginous marine alga *Nannochloropsis salina*. *Sci. Rep.* 7:11485. doi: 10.1038/s41598-017-11932-4

Marella, T. K., Datta, A., Patil, M. D., Dixit, S., and Tiwari, A. (2019). Biodiesel production through algal cultivation in urban wastewater using algal floway. *Bioresour. Technol.* 280, 222–228.

Martins, D. A., Custódio, L., Barreira, L., Pereira, H., Ben-Hamadou, R., Varela, J., et al. (2013). Alternative sources of n-3 long-chain polyunsaturated fatty acids in marine microalgae. *Mar. Drugs* 11, 2259–2281. doi: 10.3390/md1107 2259

Matsuda, Y., Hopkinson, B. M., Nakajima, K., Dupont, C. L., and Tsuji, Y. (2017). Mechanisms of carbon dioxide acquisition and CO2 sensing in marine diatoms: a gateway to carbon metabolism. *Philos. Trans. R. Soc. B* 372:20160403. doi: 10.1098/rstb.2016.0403

Melis, A. (2009). Solar energy conversion efficiencies in photosynthesis: minimizing the chlorophyll antennae to maximize efficiency. *Plant Sci.* 177, 272–280. doi: 10.1016/j.plantsci.2009.06.005

Meneghesso, A., Simionato, D., Gerotto, C., La Rocca, N., Finazzi, G., and Morosinotto, T. (2016). Photoacclimation of photosynthesis in the Eustigmatophycean Nannochloropsis gaditana. *Photosynth. Res.* 129, 291–305. doi: 10.1007/s11120-016-0297-z

Miao, R., Liu, X., Englund, E., Lindberg, P., and Lindblad, P. (2017). Isobutanol production in *Synechocystis* PCC 6803 using heterologous and endogenous alcohol dehydrogenases. *Metab. Eng. Commun.* 5, 45–53. doi: 10.1016/j.meteno.2017.07.003

Montechiaro, F., and Giordano, M. (2010). Compositional homeostasis of the dinoflagellate *Protoceratium reticulatum* grown at three different pCO2. *J. Plant Physiol.* 167, 110–113. doi: 10.1016/j.jplph.2009.07.013

Morales, M., Sanchez, L., and Revah, S. (2018). The impact of environmental factors on carbon dioxide fixation by microalgae. *FEMS Microbiol. Lett.* 365:fnx262. doi: 10.1093/femsle/fnx262

Morisse, S., Michelet, L., Bedhomme, M., Marchand, C. H., Calvaresi, M., Trost, P., et al. (2014). Thioredoxin-dependent redox regulation of chloroplastic phosphoglycerate kinase from *Chlamydomonas reinhardtii*. *J. Biol. Chem.* 289, 30012–30024. doi: 10.1074/jbc.M114.597997

Muradyan, E. A., Klyachko-Gurvich, G. L., Tsoglin, L. N., Sergeyenko, T. V., and Pronina, N. A. (2004). Changes in lipid metabolism during adaptation of the *Dunaliella salina* photosynthetic apparatus to high CO2 concentration. *Russ. J. Plant Physiol.* 51, 53–62. doi: 10.1023/B:RUPP.0000011303.11957.48

Murphy, D. J., and Vance, J. (1999). Mechanisms of lipid-body formation. *Trends Biochem. Sci.* 24, 109–115. doi: 10.1016/S0968-0004(98)01349-8

Mussgnug, J. H., Thomas-Hall, S., Rupprecht, J., Foo, A., Klassen, V., McDowall, A., et al. (2007). Engineering photosynthetic light capture: impacts on improved solar energy to biomass conversion. *Plant Biotechnol. J.* 5, 802–814. doi: 10.1111/j.1467-7652.2007.00285.x

Nagappan, S., Tsai, P., Devendran, S., Alagarsamy, V., and Ponnusamy, V. K. (2020). Enhancement of biofuel production by microalgae using cement flue gas as substrate. *Environ. Sci. Pollut. Res.* 27, 17571–17586. doi: 10.1007/s11356-019-06425-y

Nakajima, Y., Tsuzuki, M., and Ueda, R. (2001). Improved productivity by reduction of the content of light-harvesting pigment in *Chlamydomonas perigranulata*. *J. Appl. Phycol.* 13, 95–101.

Neupert, J., Karcher, D., and Bock, R. (2009). Generation of *Chlamydomonas* strains that efficiently express nuclear transgenes. *Plant J.* 57, 1140–1150. doi: 10.1111/j.1365-313X.2008.03746.x

Newby, D. T., Mathews, T. J., Pate, R. C., Huesemann, M. H., Lane, T. W., Wahlen, B. D., et al. (2016). Assessing the potential of polyculture to accelerate algal biofuel production. *Algal Res.* 19, 264–277. doi: 10.1016/j.algal.2016.09.004

Ng, A. H., Berla, B. M., and Pakrasi, H. B. (2015). Fine-Tuning of photoautotrophic protein production by combining promoters and neutral sites in the cyanobacterium *Synechocystis* sp. *Appl. Environ. Microbiol.* 81, 6857–6863.

Ng, I., Keskin, B. B., and Tan, S. (2020). A critical review of genome editing and synthetic biology applications in metabolic engineering of microalgae and cyanobacteria. *Biotechnol. J.* 15:1900228. doi: 10.1002/biot.201900228

Nikkanen, L., and Rintamäki, E. (2014). Thioredoxin-dependent regulatory networks in chloroplasts under fluctuating light conditions. *Philos. Trans. R. Soc. Lond. B. Biol. Sci.* 369:20130224. doi: 10.1098/rstb.2013.0224

Niyogi, K. K., and Truong, T. B. (2013). Evolution of flexible non-photochemical quenching mechanisms that regulate light harvesting in oxygenic photosynthesis. *Curr. Opin. Plant Biol.* 16, 307–314. doi: 10.1016/j.pbi.2013.03.011

Nogueira, D. P. K., Silva, A. F., Araújo, O. Q. F., and Chaloub, R. M. (2015). Impact of temperature and light intensity on triacylglycerol accumulation in marine microalgae. *Biomass Bioenerg.* 72, 280–287. doi: 10.1016/j.biombioe.2014.10.017

Norici, A., Dalsass, A., and Giordano, M. (2002). Role of phosphoenolpyruvate carboxylase in anaplerosis in the green microalga *Dunaliella salina* cultured under different nitrogen regimes. *Physiol. Plant.* 116, 186–191. doi: 10.1034/j.1399-3054.2002.1160207.x

Norici, A., Hell, R., and Giordano, M. (2005). Sulfur and primary production in aquatic environments: an ecological perspective. *Photosynth. Res.* 86, 409–417. doi: 10.1007/s11120-005-3250-0

Nürnberg, D. J., Morton, J., Santabarbara, S., Telfer, A., Joliot, P., Antonaru, L. A., et al. (2018). Photochemistry beyond the red limit in chlorophyll f–containing photosystems. *Science* 360, 1210–1213. doi: 10.1126/science.aar8313

Nymark, M., Sharma, A. K., Sparstad, T., Bones, A. M., and Winge, P. (2016). A CRISPR / Cas9 system adapted for gene editing in marine algae. *Sci. Rep.* 6:24951. doi: 10.1038/srep24951

Nymark, M., Volpe, C., Hafskjold Grønbech, C. M., Kirst, H., Serif, M., Vadstein, O., et al. (2019). Loss of ALBINO3b insertase results in truncated light-harvesting antenna in diatoms. *Plant Physiol.* 181, 1257–1276. doi: 10.1104/pp.19.00868

Ogawa, T., Tamoi, M., Kimura, A., Mine, A., Sakuyama, H., Yoshida, E., et al. (2015). Enhancement of photosynthetic capacity in *Euglena gracilis* by expression of cyanobacterial fructose-1,6-/sedoheptulose-1,7-bisphosphatase leads to increases in biomass and wax ester production. *Biotechnol. Biofuels* 8:80.

Ooms, M. D., Dinh, C. T., Sargent, E. H., and Sinton, D. (2016). Photon management for augmented photosynthesis. *Nat. Commun.* 7:12699. doi: 10.1038/ncomms12699

Ort, D. R., Merchant, S. S., Alric, J., Barkan, A., Blankenship, R. E., and Bock, R. (2015). Redesigning photosynthesis to sustainably meet global food and bioenergy demand. *Proc. Natl. Acad. Sci. U.S.A.* 112, 8529–8536. doi: 10.1073/pnas.1424031112

Ortega-Escalante, J. A., Jasper, R., and Miller, S. M. (2019). CRISPR / Cas9 mutagenesis in *Volvox carteri*. *Plant J.* 97, 661–672. doi: 10.1111/tpj.14149

Packer, M. (2009). Algal capture of carbon dioxide; biomass generation as a tool for greenhouse gas mitigation with reference to New Zealand energy strategy and policy. *Energy Policy* 37, 3428–3437. doi: 10.1016/j.enpol.2008.12.025

Page, L. E., Liberton, M., and Pakrasi, H. B. (2012). Phycobilisome antenna truncation reduces photoautotrophic productivity in *Synechocystis* sp. PCC 6803, a cyanobacterium. *Appl. Environ. Microbiol.* 165, 705–714.

Palmucci, M., Ratti, S., and Giordano, M. (2011). Ecological and evolutionary implications of carbon allocation in marine phytoplankton as a function of nitrogen availability: a Fourier transform infrared spectroscopy approach. *J. Phycol.* 47, 313–323. doi: 10.1111/j.1529-8817.2011.00963.x

Patel, V. K., Soni, N., Prasad, V., Saper, A., Dasgupta, S., and Bhadra, B. (2019). CRISPR – Cas9 System for genome engineering of photosynthetic microalgae. *Mol. Biotechnol.* 61, 541–561.

Patron, N. J., and Keeling, P. J. (2005). Common evolutionary origin of starch biosynthetic enzymes in green and red algae. *J. Phycol.* 41, 1131–1141. doi: 10.1111/j.1529-8817.2005.00135.x

Pattanaik, B., Englund, E., Nolte, N., and Lindberg, P. (2020). Introduction of a green algal squalene synthase enhances squalene accumulation in a strain of *Synechocystis* sp. PCC 6803. *Metab. Eng. Commun.* 10:e00125. doi: 10.1016/j.mec.2020.e00125

Peers, G. (2014). Increasing algal photosynthetic productivity by integrating ecophysiology with systems biology. *Trends Biotechnol.* 32, 551–555. doi: 10.1016/j.tibtech.2014.09.007

Peers, G., Truong, T. B., Ostendorf, E., Busch, A., Elrad, D., Grossman, A. R., et al. (2009). An ancient light-harvesting protein is critical for the regulation of algal photosynthesis. *Nature* 462, 518–521. doi: 10.1038/nature08587

Peltier, G., Tolleter, D., Billon, E., and Cournac, L. (2010). Auxiliary electron transport pathways in chloroplasts of microalgae. *Photosynth. Res.* 106, 19–31.

Peramuna, A., and Summers, M. L. (2014). Composition and occurrence of lipid droplets in the cyanobacterium *Nostoc punctiforme*. *Arch. Microbiol.* 196, 881–890. doi: 10.1007/s00203-014-1027-6

Pérez, A. A., Chen, Q., Pineda Hernandez, H., Branco, dos Santos, F., and Hellingwerf, K. J. (2019). On the use of oxygenic photosynthesis for the sustainable production of commodity chemicals. *Physiol. Plant.* 166, 413–427. doi: 10.1111/ppl.12946

Perin, G., Bellan, A., Bernardi, A., Bezzo, F., and Morosinotto, T. (2019). The potential of quantitative models to improve microalgae photosynthetic efficiency. *Physiol. Plant.* 166, 380–391. doi: 10.1111/ppl.12915

Perrine, Z., Negi, S., and Sayre, R. T. (2012). Optimization of photosynthetic light energy utilization by microalgae. *Algal Res.* 1, 134–142. doi: 10.1016/j.algal.2012.07.002

Picardo, M. C., de Medeiros, J. L., Monteiro, J. G. M., Chaloub, R. M., Giordano, M., de Queiroz, O., et al. (2013). A methodology for screening of microalgae as a decision making tool for energy and green chemical process applications. *Clean Technol. Environ. Policy* 15, 275–291. doi: 10.1007/s10098-012-0508-z

Pichersky, E., and Raguso, R. A. (2018). Why do plants produce so many terpenoid compounds? *New Phytol.* 220, 692–702. doi: 10.1111/nph.14178

Pinto, F., Pacheco, C. C., Oliveira, P., Montagud, A., Landels, A., Couto, N., et al. (2015). Improving a *Synechocystis* -based photoautotrophic chassis through systematic genome mapping and validation of neutral sites. *DNA Res.* 22, 425–437. doi: 10.1093/dnares/dsv024

Polle, J. E. W., Kanakagiri, S., and Melis, A. (2003). tla1, a DNA insertional transformant of the green alga *Chlamydomonas reinhardtii* with a truncated light-harvesting chlorophyll antenna size. *Planta* 217, 49–59.

Quigg, A., Irwin, A. J., and Finkel, Z. V. (2010). Evolutionary inheritance of elemental stoichiometry in phytoplankton. *Proc. R. Soc. B* 278, 526–534. doi: 10.1098/rspb.2010.1356

Rasala, B. A., and Mayfield, S. P. (2015). Photosynthetic biomanufacturing in green algae; production of recombinant proteins for industrial, nutritional, and medical uses. *Photosynth. Res.* 123, 227–239. doi: 10.1007/s11120-014-9994-7

Rasala, B. A., Muto, M., Sullivan, J., and Mayfield, S. P. (2011). Improved heterologous protein expression in the chloroplast of *Chlamydomonas reinhardtii* through promoter and 5' untranslated region optimization. *Plant Biotechnol. J.* 9, 674–683. doi: 10.1111/j.1467-7652.2011.00620.x

Raso, S., Genugten, B., Vermuë, M., and Wijffels, R. (2012). Effect of oxygen concentration on the growth of *Nannochloropsis* sp. at low light intensity. *J. Appl. Phycol.* 24, 863–871. doi: 10.1007/s10811-011-9706-z

Raven, J. A. (1984). *Energetics and Transport in Aquatic Plants*. New York, NY: A.R. Liss.

Raven, J. A. (1997a). Inorganic carbon acquisition by marine autotrophs. *Adv. Bot. Res.* 27, 85–209. doi: 10.1016/S0065-2296(08)60281-5

Raven, J. A. (1997b). CO2 concentrating mechanisms: a direct role for thylakoid lumen acidification? *Plant Cell Environ.* 20, 147–154. doi: 10.1046/j.1365-3040.1997.d01-67.x

Raven, J. A. (2010). Inorganic carbon acquisition by eukaryotic algae: four current questions. *Photosynth. Res.* 106, 123–134. doi: 10.1007/s11120-010-9563-7

Raven, J. A., Beardall, J., and Giordano, M. (2014). Energy costs of carbon dioxide concentrating mechanisms in aquatic organisms. *Photosynth. Res.* 121, 111–124.

Raven, J. A., and Farquhar, G. D. (1990). The influence of N metabolism and organic acid synthesis on the natural abundance of C isotopes in plants. *New Phytol.* 116, 505–529. doi: 10.1111/j.1469-8137.1990.tb00536.x

Raven, J. A., and Giordano, M. (2014). Algae. *Curr. Biol.* 24, R590–R595. doi: 10.1016/j.cub.2014.05.039

Raven, J. A., Giordano, M., Beardall, J., and Maberly, S. C. (2011). Algal and aquatic plant carbon concentrating mechanisms in relation to environmental change. *Photosynth. Res.* 109, 281–296. doi: 10.1007/s11120-011-9632-6

Raven, J. A., Giordano, M., Beardall, J., and Maberly, S. C. (2012). Algal evolution in relation to atmospheric CO2: carboxylases, carbon-concentrating mechanisms and carbon oxidation cycles. *Philos. Trans. R Soc. B* 367, 493–507. doi: 10.1098/rstb.2011.0212

Raven, J. A., Kübler, J. E., and Beardall, J. (2000). Put out the light and then put out the light. *J. Mar. Biol. Assoc. U.K.* 80, 1–25. doi: 10.1017/S0025315499001526

Richardson, J. W., Johnson, M. D., Zhang, X., Zemke, P., Chen, W., and Hu, Q. (2014). A financial assessment of two alternative cultivation systems and their contributions to algae biofuel economic viability. *Algal Res.* 4, 96–104.

Romero, E., Novoderezhkin, V. I., and Van Grondelle, R. (2017). Quantum design of photosynthesis for bio-inspired solar-energy conversion. *Nature* 543, 355–365. doi: 10.1038/nature22012

Ruan, Z., and Giordano, M. (2017). The use of NH4+ rather than NO3- affects cell stoichiometry, C allocation, photosynthesis and growth in the cyanobacterium *Synechococcus* sp. UTEX LB 2380, only when energy is limiting. *Plant Cell Environ.* 40, 227–236. doi: 10.1111/pce.12858

Ruan, Z., Prášil, O., and Giordano, M. (2018). The phycobilisomes of *Synechococcus* sp. are constructed to minimize nitrogen use in nitrogen-limited cells and to maximize energy capture in energy-limited cells. *Environ. Exp. Bot.* 150, 152–160. doi: 10.1016/j.envexpbot.2018.01.015

Ruan, Z., Raven, J. A., and Giordano, M. (2017). In *Synechococcus* sp. competition for energy between assimilation and acquisition of C and those of N only occurs when growth is light limited. *J. Exp. Bot.* 68, 3829–3839. doi: 10.1093/jxb/erx074

Santos-Merino, M., Garcillán-Barcia, M. P., and de la Cruz, F. (2018). Engineering the fatty acid synthesis pathway in *Synechococcus elongatus* PCC 7942 improves omega-3 fatty acid production. *Biotechnol. Biofuels* 11:239. doi: 10.1186/s13068-018-1243-4

Savir, Y., Noor, E., Milo, R., and Tlusty, T. (2010). Cross-species analysis traces adaptation of Rubisco toward optimality in a low-dimensional landscape. *Proc. Natl. Acad. Sci. U.S.A.* 107, 3475–3480. doi: 10.1073/pnas.0911663107

Sayanova, O., Mimouni, V., Ulmann, L., Morant-Manceau, A., Pasquet, V., Schoefs, B., et al. (2017). Modulation of lipid biosynthesis by stress in diatoms. *Philos. Trans. R. Soc. B* 372:20160407. doi: 10.1098/rstb.2016.0407

Selosse, M. A., Charpin, M., and Not, F. (2017). Mixotrophy everywhere on land and in water: the grand écart hypothesis. *Ecol. Lett.* 20, 246–263. doi: 10.1111/ele.12714

Sergeenko, T. V., Muradyan, E. A., Pronina, N. A., Klyachko-Gurich, G. L., Mishina, I. M., and Tsoglin, L. N. (2000). The effect of extremely high CO2 concentration on the growth and biochemical composition of microalgae. *Russ. J. Plant Physiol.* 47, 632–638.

Sforza, E., Simionato, D., Giacometti, G. M., Bertucco, A., and Morosinotto, T. (2012). Adjusted light and dark cycles can optimize photosynthetic efficiency in algae growing in photobioreactors. *PLoS One* 7:e38975. doi: 10.1371/journal.pone.0038975

Shemesh, Z., Leu, S., Khozin-Goldberg, I., Didi-Cohen, S., Zarka, A., and Boussiba, S. (2016). Inducible expression of *Haematococcus* oil globule protein in the diatom *Phaeodactylum tricornutum*: association with lipid droplets and enhancement of TAG accumulation under nitrogen starvation. *Algal Res.* 18, 321–331. doi: 10.1016/j.algal.2016.07.002

Shih, P. M. (2018). Towards a sustainable bio-based economy: redirecting primary metabolism to new products with plant synthetic biology. *Plant Sci.* 273, 84–91. doi: 10.1016/j.plantsci.2018.03.012

Shih, P. M., Zarzycki, J., Niyogi, K. K., and Kerfeld, C. A. (2014). Introduction of a synthetic CO2-fixing photorespiratory bypass into a cyanobacterium. *J. Biol. Chem.* 289, 9493–9500. doi: 10.1074/jbc.C113.543132

Shin, S., Lim, J., Koh, H. G., Kim, E. K., Kang, N. K., Jeon, S., et al. (2016). CRISPR / Cas9-induced knockout and knock-in mutations in *Chlamydomonas reinhardtii*. *Sci. Rep.* 6:27810. doi: 10.1038/srep27810

Shin, W., Lee, B., Kang, N. K., Kim, Y., and Jeong, W. (2017). Complementation of a mutation in RP43 causing partial truncation of light-harvesting chlorophyll antenna in *Chlorella vulgaris*. *Sci. Rep.* 7:1929.

Shurin, J. B., Mandal, S., and Abbott, R. L. (2014). Trait diversity enhances yield in algal biofuel assemblages. *J. Appl. Ecol.* 51, 603–611. doi: 10.1111/1365-2664.12242

Simionato, D., Basso, S., Giacometti, G. M., and Morosinotto, T. (2013). Optimization of light use efficiency for biofuel production in algae. *Biophys. Chem.* 182, 71–78. doi: 10.1016/j.bpc.2013.06.017

Spicer, A., and Molnar, A. (2018). Gene editing of microalgae: scientific progress and regulatory challenges in Europe. *Biology* 7:21. doi: 10.3390/biology7010021

Spolaore, P., Joannis-Cassan, C., Duran, E., and Isambert, A. (2006). Commercial applications of microalgae. *J. Biosci. Bioeng.* 101, 87–96. doi: 10.1263/jbb.101.87

Stephenson, A. I., Dennis, J. S., Howe, C. J., Scott, S. A., and Smith, A. G. (2010). Influence of nitrogen-limitation regime on the production by Chlorella vulgaris of lipids for biodiesel feedstocks. *Biofuels* 1, 47–58.

Sterner, R. W., and Elser, J. J. (2002). *Ecological Stoichiometry: The Biology of Elements from Molecules to the Biosphere*. Princeton, NJ: Princeton University.

Stockenreiter, M., Graber, A., Haupt, F., and Stibor, H. (2012). The effect of species diversity on lipid production by micro-algal communities. *J. Appl. Phycol.* 24, 45–54. doi: 10.1007/s10811-010-9644-1

Stockenreiter, M., and Litchman, E. (2019). Nitrogen-fixer enhances lipid yields in algal polycultures. *Algal Res.* 44:101676. doi: 10.1016/j.algal.2019.101676

Sun, X.-M., Ren, L.-J., Zhao, Q.-Y., Ji, X.-J., and Huang, H. (2019). Enhancement of lipid accumulation in microalgae by metabolic engineering. *Biochim. Biophys. Acta* 1864, 552–566. doi: 10.1016/j.bbalip.2018.10.004

Tabita, F. R., Hanson, T. E., Satagopan, S., Witte, B. H., and Kreel, N. E. (2008). Phylogenetic and evolutionary relationships of Rubisco and the Rubisco-like proteins and the functional lessons provided by diverse molecular forms. *Philos. Trans. R Soc. Lond. B Biol. Sci.* 363, 2629–2640. doi: 10.1098/rstb.2008.0023

Tachibana, M., Allen, A. E., Kikutani, S., Endo, Y., Bowler, C., and Matsuda, Y. (2011). Localization of putative carbonic anhydrases in two marine diatoms, *Phaeodactylum tricornutum* and *Thalassiosira pseudonana*. *Photosynth. Res.* 109, 205–221. doi: 10.1007/s11120-011-9634-4

Taubert, A., Jakob, T., and Wilhelm, C. (2019). Glycolate from microalgae: an efficient carbon source for biotechnological applications. *Plant Biotechnol. J.* 1, 1538–1546. doi: 10.1111/pbi.13078

Taylor, S. H., and Long, S. P. (2017). Slow induction of photosynthesis on shade to sun transitions in wheat may cost at least 21% of productivity. *Philos. Trans. R. Soc. B Biol. Sci.* 372:20160543. doi: 10.1098/rstb.2016.0543

Taylor, T. C., Backlund, A., Bjorhall, K., Spreitzer, R. J., and Andersson, I. (2001). First crystal structure of Rubisco from a green alga, *Chlamydomonas reinhardtii*. *J. Biol. Chem.* 276, 48159–48164. doi: 10.1074/jbc.M107765200

Tcherkez, G. (2013). Modelling the reaction mechanism of ribulose-1, 5-bisphosphate carboxylase / oxygenase and consequences for kinetics parameters. *Plant Cell Environ.* 36, 1586–1596. doi: 10.1111/pce.12066

Tcherkez, G. (2016). The mechanism of Rubisco-catalysed oxygenation. *Plant Cell Environ.* 39, 983–997. doi: 10.1111/pce.12629

Tcherkez, G. G. B., Farquhar, G. D., and Andrews, T. J. (2006). Despite slow catalysis and confused substrate specificity, all ribulose bisphosphate carboxylases may be nearly perfectly optimized. *Proc. Natl. Acad. Sci. U.S.A.* 103, 7246–7251. doi: 10.1073/pnas.0600605103

Till, P., Toepel, J., Buhler, B., Mach, R. L., and Mach-Aigner, A. R. (2020). Regulatory systems for gene expression control in cyanobacteria. *Appl. Microbiol. Biotechnol.* 104, 1977–1991. doi: 10.1007/s00253-019-10344-w

Toyoshima, M., Toya, Y., and Shimizu, H. (2020). Flux balance analysis of cyanobacteria reveals selective use of photosynthetic electron transport components under different spectral light conditions. *Photosynth. Res.* 143, 31–43. doi: 10.1007/s11120-019-00678-x

Travis, T. (1993). The Haber-Bosch process—exemplar of 20th-century chemical industry. *Chem. Ind.* 15, 581–585.

Tredici, M. R., Rodolfi, L., Biondi, N., Bassi, N., and Sampietro, G. (2016). Techno-economic analysis of microalgal biomass production in a 1-ha Green Wall Panel (GWP®) plant. *Algal Res.* 19, 253–263.

Vavitsas, K., Fabris, M., and Vickers, C. E. (2018). Terpenoid metabolic engineering in photosynthetic microorganisms. *Genes* 9:520. doi: 10.3390/genes9110520

Venuleo, M., Prásil, O., and Giordano, M. (2018). Life at elevated CO2 modifies the cell composition of *Chromera velia* (Chromerida). *Eur. J. Phycol.* 53, 58–66. doi: 10.1080/09670262.2017.1376255

Verruto, J., Francis, K., Wang, Y., Low, M. C., Greiner, J., Tacke, S., et al. (2018). Unrestrained markerless trait stacking in *Nannochloropsis gaditana* through combined genome editing and marker recycling technologies. *Proc. Natl. Acad. Sci. U.S.A.* 115, 7015–7022. doi: 10.1073/pnas.1718193115

Villanova, V., Fortunato, A. E., Singh, D., Dal, Bo, D., Conte, M., et al. (2017). Investigating mixotrophic metabolism in the model diatom *Phaeodactylum tricornutum*. *Philos. Trans. R. Soc. B* 372:20160404. doi: 10.1098/rstb.2016.0404

Wagner, H., Jakob, T., Fanesi, A., and Wilhelm, C. (2017). Towards an understanding of the molecular regulation of carbon allocation in diatoms: the interaction of energy and carbon allocation. *Philos. Trans. R. Soc. Lond. B. Biol. Sci.* 372:20160410. doi: 10.1098/rstb.2016.0410

Wagner, H., Jakob, T., and Wilhelm, C. (2006). Balancing the energy flow from captured light to biomass under fluctuating light conditions. *New Phytol.* 169, 95–108. doi: 10.1111/j.1469-8137.2005.01550.x

Wang, C., Thygesen, A., Liu, Y., Li, Q., Yang, M., Dang, D., et al. (2013). Bio-oil based biorefinery strategy for the production of succinic acid. *Biotechnol. Biofuels* 6:74. doi: 10.1186/1754-6834-6-74

Wichmann, J., Baier, T., Wentnagel, E., Lauersen, K. J., and Kruse, O. (2018). Tailored carbon partitioning for phototrophic production of (E)-α-bisabolene from the green microalga *Chlamydomonas reinhardtii*. *Metab. Eng.* 45, 211–222. doi: 10.1016/j.ymben.2017.12.010

Wichmann, J., Lauersen, K. J., and Kruse, O. (2020). Green algal hydrocarbon metabolism is an exceptional source of sustainable chemicals. *Curr. Opin. Biotechnol.* 61, 28–37. doi: 10.1016/j.copbio.2019.09.019

Wijffels, R. H., Kruse, O., and Hellingwerf, K. J. (2013). Potential of industrial biotechnology with cyanobacteria and eukaryotic microalgae. *Curr. Opin. Biotechnol.* 24, 405–413. doi: 10.1016/j.copbio.2013.04.004

Wilhelm, C., Jungandreas, A., Jakob, T., and Goss, R. (2014). Light acclimation in diatoms: from phenomenology to mechanisms. *Mar. Genomics* 16, 5–15. doi: 10.1016/j.margen.2013.12.003

Wilhelm, C., and Selmar, D. (2011). Energy dissipation is an essential mechanism to sustain the viability of plants: the physiological limits of improved photosynthesis. *J. Plant Physiol.* 168, 79–87. doi: 10.1016/j.jplph.2010.07.012

Williams, P. J. B., and Laurens, L. M. L. (2010). Microalgae as biodiesel and biomass feedstocks: review and analyses of the biochemistry, energetics and economics. *Energy Environ. Sci.* 3, 554–590.

Yang, B., Liu, J., Ma, X., Guo, B., Liu, B., Wu, T., et al. (2017). Genetic engineering of the Calvin cycle toward enhanced photosynthetic – CO2 fixation in microalgae. *Biotechnol. Biofuels* 10:229.

Young, J. N., Goldman, J. A., Kranz, S. A., Tortell, P. D., and Morel, F. M. (2015). Slow carboxylation of Rubisco constrains the rate of carbon fixation during Antarctic phytoplankton blooms. *New Phytol.* 205, 172–181. doi: 10.1111/nph.13021

Young, J. N., Heureux, A. M., Sharwood, R. E., Rickaby, R. E., Morel, F. M., and Whitney, S. M. (2016). Large variation in the Rubisco kinetics of diatoms reveals diversity among their carbon-concentrating mechanisms. *J. Exp. Bot.* 67, 3445–3456. doi: 10.1093/jxb/erw163

Young, J. N., and Hopkinson, B. M. (2017). The potential for co-evolution of CO2-concentrating mechanisms and Rubisco in diatoms. *J. Exp. Bot.* 68, 3751–3762. doi: 10.1093/jxb/erx130

Yunus, I. S., Wichmann, J., Wordenweber, R., Lauersen, K. J., Kruse, O., and Jones, P. R. (2018). Synthetic metabolic pathways for photobiological conversion of CO2 into hydrocarbon fuel. *Metabolic Eng.* 49, 201–211. doi: 10.1016/j.ymben.2018.08.008

Zhu, X., Long, S. P., and Ort, D. R. (2008). What is the maximum efficiency with which photosynthesis can convert solar energy into biomass? *Curr. Opin. Biotechnol.* 19, 153–159. doi: 10.1016/j.copbio.2008.02.004

Zhu, X., Wang, Y. U., Ort, D. R., and Long, S. P. (2013). *e*-photosynthesis: a comprehensive dynamic mechanistic model of C3 photosynthesis: from light capture to. *Plant Cell Environ.* 36, 1711–1727. doi: 10.1111/pce.12025

Zhu, X.-G., de Sturler, E., and Long, S. P. (2007). Optimizing the distribution of resources between enzymes of carbon metabolism can dramatically increase photosynthetic rate: a numerical simulation using an evolutionary algorithm. *Plant Physiol.* 145, 513–526. doi: 10.1104/pp.107.103713

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REVIEW
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Economics of CO_2 Utilization: A Critical Analysis

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The economics of CO_2 utilization are discussed from a critical perspective, with a concise analysis of the state-of-the-art of economics in power-to-X (methanol, methane). The main elements of the analysis of the economics are commented to provide guidelines on how to interpret the techno-economic results in the area of CO_2 utilization. It remarks the need of a careful analysis of the specific context, and of the limits of the evaluation, in order to go beyond the just use of the results without a proper analysis of how the data support the conclusions, their limits and applicability. Case examples discussed in a more detail regard the CO_2 to methanol or methane conversion, from the perspective of highlighting possible issues or limits rather than to indicate which results are more valuable, which is out of the scope of this contribution.

Keywords: CO_2 economics, methanol, power-to-X, techno-economic analysis, CO_2 impact, CO_2 utilization

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INTRODUCTION

The techno-economic feasibility of CO_2 utilization routes is a crucial element for their industrial implementation, together with other relevant aspects, such as the impact on the reduction of CO_2 emissions (Centi et al., 2019a; Centi et al., 2019b). This impact must be considered in terms of services provided using CO_2 to substitute fossil resources rather than in terms of 1) amount of CO_2 stored and 2) storage time (Schlögl et al., 2018). CO_2 large-scale reduction is when its use is as medium to increase renewable energy utilization. This is the way to account the impact of CCU (CO_2 utilization) routes (Lanzafame et al., 2017a).

Many reviews and papers have discussed the costs and techno-economic feasibility of CO_2 utilization routes, a selection (not exhaustive) of which is the following: Centi and Perathoner (2010), Quadrelli et al. (2011), Aresta et al. (2013), Centi et al. (2013), Barbato et al. (2014), Centi and Perathoner (2014), Perathoner and Centi (2014), Laumb et al. (2013), Ampelli et al. (2015), Dimitriou et al. (2015), Pérez-Fortes et al. (2016), Naims (2016), Navarrete et al. (2017), Ordomsky et al. (2017), Senftle and Carter, (2017), Zheng et al. (2017), Iaquaniello et al. (2018), Koytsoumpa et al. (2018), González-Garay et al. (2019a), Hepburn et al. (2019), Jens et al. (2019), Zhang et al. (2019), Grim et al. (2020), Meunier et al. (2020), Mustafa et al. (2020), Zhang et al. (2020), and Zimmermann et al. (2020). Although the conclusions are often contradictory, it is commonly suggested that there still exist large barriers for the implementation and deployment of CCU.

There is, on the other hand, a fast-evolving scenario for CO_2 utilization paths, in terms of both costs and technical feasibility. A number of industrial pilot plants or demo size units have been developed to demonstrate techno-economic feasibility. Examples include CO_2 methanation (Schiebahn et al., 2015; Bailera et al., 2017; Chwola et al., 2020) or conversion to methanol (Son et al., 2018). Haldor Topsoe is building an around 50 t/yr methanol plant to demonstrate their eSMR

Methanol™ technology for cost-competitive production of sustainable methanol from biogas by using an electrified reactor. Carbon Recycling International (CRI) and other members of the MefCO_2 research consortium are building in Germany an about 300 t/yr CO_2-to-methanol demo unit.

Carbon Recycling International was the first to construct a demo/semi-commercial plant for methanol production from CO_2 in Iceland. In this case, CO_2 and electricity derive from geothermal sources and thus it is not an easily replicable model. Carbon2Chem pilot plant at the Thyssenkrupp steel mill in Duisburg (Germany) is also designed to produce about 50 t/yr of methanol. Audi e-Gas pilot plant produces 1,000 tons/yr of methane from CO_2. STORE and GO demo plant in Germany produces 1,400 cubic meters of synthetic methane from CO_2 per day. These are few of the many examples of pilot and demo plants around the so-called power-to-liquid and power-to-gas technologies. Pilot/demo plants are present also for other CO_2 utilization paths.

There is thus an apparent discrepancy between the many industrial initiatives in the area of CO_2 utilization and the debate on CO_2 economics, going from sceptical to optimistic, but often with an intrinsic difficulty to identify which is the more appropriate conclusion. Together with the discussion on CO_2 economics, the environmental impact is often also made, typically through the use of Life Cycle Assessment (LCA) or derived methodologies. For environmental and greenhouse gas (GHG) impact, there is also often a spread of indications (Aresta et al., 2002; von der Assen et al., 2013, von der Assen et al., 2014; Garcia-Herrero et al., 2016; Thonemann, 2020). It may be thus questioned why different conclusions can be obtained for the same problem.

Both analyses of the process economics and environmental impact follow complex methodologies, and the final result depends on several parameters and the boundary limits applied on the analysis. It is thus not surprising that even with the same base of data, different conclusions can be present. Thus, particularly attention is necessary in using the results out of the proper context.

For this reason, it is good to provide some guidelines and general comments about CO_2 economics. The aim is to give a background of knowledge allowing a better analysis of literature data, and of their eventual limits. This contribution aims to discuss these aspects, although avoiding to indicate which results should be considered valid or not. This could be made, in fact, only for specific contexts and situations, which may change with time. The aim here is instead to provide the bases for this analysis evidencing also the key factors determining economics. Although some example will be also discussed in a more detail, this contribution is not intended to be neither a review of the state-of-the-art on CO_2 economics, neither a didactic presentation of the methodologies for this analysis.

The aim is to remark the need of a critical approach in evaluating CO_2 economics, providing also the main background technical aspects necessary, in particular, for not-experts. A concise state-of-the-art, limited to CO_2 economics in power-to-X (methanol, methane) solutions, is also presented, to provide the reader elements for a better understanding.

The Context and Approach for the Analysis of CO_2 Utilization Routes

As a general statement, it may be indicated that CO_2 utilization paths are already feasible routes to consider and thus to analyze in a more detail with reference to 1) the specific case of applications, 2) the synergies possible, and 3) the benefits and barriers. Scale-up is also a relevant aspect, and this is also the reason of the many pilot/demo projects. However, most of these studies are focused mainly at increasing the technology readiness level (TRL) up to a 6–7 value (TRL 7 is system prototype demonstration in operational environment), rather than to create the right value chain in relation to energy transition. Being present a full transition in energy, rather than the implementation of single novel technologies, the feasibility of CO_2 utilization routes, which include economic assessment, must be analyzed in the context of the value chain. However, current approaches are lacking from this perspective. This is a crucial issue to solve also for CO_2 economics and thus for the proper analysis of the feasibility of CO_2 utilization routes.

It should be also remarked that rather than by economic only aspects, the industrial exploitability is often technology-limited today. In other words, the new generation technologies, which can enable a larger use of CO_2 utilization paths, are still at a too early stage while those available and implemented at pilot/demo scale, still suffer of many limitations. There is thus an innovation gap for a wider spread of CO_2 utilization solutions. Typically only the technological gap between fundamental research (up to TRL of three corresponding to the proof of the concept) and a TRL of 6–7 (technology demonstrated in industrially relevant) is considered as the key element.

The innovation gap is that existing when a proper pipeline between current and next generation technologies is missing. It is the innovation rather than the technological gap the crucial aspects to solve in a system change as that related to energy transition. This aspect will be further commented later.

Energy and chemistry systems are strongly linked even if their nexus is changing (Abate et al., 2015a). They define together the set of production, transformation, transport and distribution processes of raw materials and products. Thus, a proper analysis of CO_2 economics cannot be made without properly considering this evolving nexus. Some elements on this aspect will be commented later.

Part of the innovation gap is a consequence also that a correct evaluation of the process economics is often difficult and complex, being these new generation technologies still at a not-sufficient level of development. This is also the problem for LCA and analogous methodologies, not well suited, or having a too high uncertainty, when applied to technologies at a too early stage of development. This is always valid in changing the technologies. However, this becomes a critical issue when this occurs simultaneously to a system change, as that on-going due to energy transition. This will be concisely discussed in the following section.

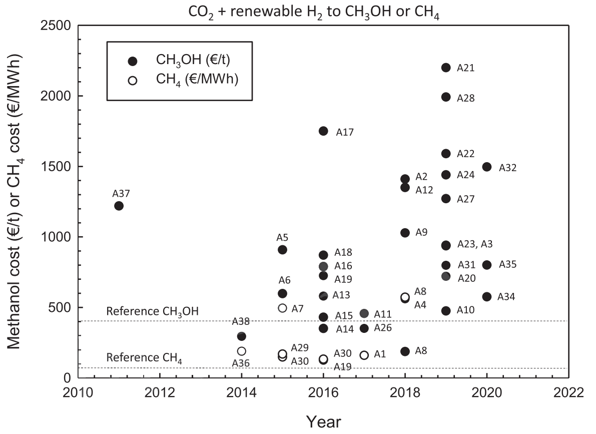

FIGURE 1 | An overview of the results in terms of costs of methanol production (€/t) and of methane production (€/MWh) in CO_2 conversion using H_2 produced from renewable energy sources. References: A1, Parra et al., 2017; A2, Asif et al., 2018; A3, Nieminen et al., 2019; A4, Moellenbruck et al., 2018; A5, Hannula, 2015; A6, Roh et al., 2015; A7, De Saint Jean et al., 2015; A8, Hoppe et al., 2018; A9, Hank et al., 2018; A10, Zhang et al., 2019b; A11, Rivarloo et al., 2017; A12, Michailos et al., 2018; A13–A15, Kourkoumpas et al., 2016; A16–A17, Rivera-Tinoco et al., 2016; A18, Atsonios et al., 2016; A19, Räuchle et al., 2016; A20–A22, Nguyen Zondervan, 2019; A23, Alsayegh et al., 2019; A24, Nami et al., 2019; A25, Pérez-Fortes et al., 2016; A26, Gonzàlez-Aparicio et al., 2017; A27–A28, Gonzàlez-Garay et al., 2019b; A29, Schiebahn et al., 2015; A30, Gutièrrez-Martin and Rodriguez-Anton, 2016; A31, Do and Kim, 2019; A32, Khunathorncharoenwong et al., 2020; A33, Tremel et al., 2015; A34, Zhang and Desideri, 2020; A35, Bos et al., 2020; A36, Hofstetter et al., 2014; A37, Kim et al., 2011; A38, Barbato et al., 2014. Original Figure.

To remark that notwithstanding the large R&D effort the range of novel concepts and solutions explored is limited (Ampelli et al., 2015). In addition, often constrains in terms of industrial applicability and of the impact related to a system change are not properly considered, as commented later. There is a need of a broader-view approach, exploring new solutions, synergies and possibilities (Centi and Čejka, 2019a), but at the same time also strongly guided from an industrial vision on targets, issues, integration, solutions.

In addition, the synergies created from the system change, for example from the integration between solar- and bio-refineries (Abate et al., 2015b), offer new perspectives. However, these emerge only from a system analysis rather than from a classical techno-economic assessment (Centi et al., 2019b).

A CONCISE STATE-OF-THE-ART ON POWER-TO-X (METHANOL, METHANE) ECONOMICS

As indicated in the introduction, this contribution is not a review on CO_2 economics or on the methodologies for this analysis, but rather aims to provide elements for a critical analysis and how to put current results on CO_2 economics in the right perspective. At the same time, the scope is also to remark the needs of a different approach, based on considering the elements remarked above (value chain, energy-chemistry nexus, innovation gap, system change). However, for a proper analysis, it is useful to provide concise background indications on the state-of-the-art in the area. This is limited to Power-to-X (methanol, methane) economics for conciseness.

Many studies have been reported in literature about the techno-economic assessment of Power-to-X (PtX) technologies. A not-exhaustive list is the following: Kim et al. (2011), Barbato et al. (2014), Hofstetter et al. (2014), De Saint Jean et al. (2015), Hannula (2015), Roh et al. (2015), Schiebahn et al. (2015), Tremel et al. (2015), Atsonios et al. (2016), Gutièrrez-Martin and Rodriguez-Anton (2016), Kourkoumpas et al. (2016), Pérez-Fortes et al. (2016), Räuchle et al. (2016), Rivera-Tinoco et al. (2016), Rivarolo et al. (2017), Gonzàlez-Aparicio et al. (2017), Parra et al. (2017), Asif et al. (2018), Hank et al. (2018), Hoppe et al. (2018), Michailos et al. (2018), Moellenbruck et al. (2018), Alsayegh et al. (2019), Do and Kim (2019), Gonzàlez-Garay et al. (2019a), Nami et al. (2019), Nguyen and Zondervan (2019), Nieminen et al. (2019), Zhang et al. (2019b), Bos et al. (2020), Khunathorncharoenwong et al. (2020), and Zhang and Desideri (2020).

In few cases, and limited essentially to methanol case, these technologies were evaluated out of the specific context of storage of local excess of renewable energy. Few studies have considered the impact on energy transition and sustainability of the transport of remote renewable energy sources by PtX technologies, and very few the impact on aspects such as value chain, energy-chemistry nexus, innovation gap, and system change. The impact on saving CO_2 emissions, and in general on lowering impact on the environment, is often considered, but a broader view, able to predict the effective impact related to system change, is not typically present.

Figure 1 summarizes the results in terms of cost of production of methanol (€/h) or of methane (€/MWh) from CO_2 by using renewable energy sources. The year indicated in **Figure 1** is the year of publication of the related paper. When data were in US$ a conversion factor of 1.18 was used. Refence values for methanol and methane are also indicated. The results were not homogeneous in terms of database for costs of raw materials, technologies, approach, and boundary limits, and it is out of the scope to analyze here these specific aspects. However, this **Figure 1** clearly remarks how the results are very spread, with estimated costs varying up to one order of magnitude, which is largely beyond the usual ±30‰ variation in costs assumed in preliminary techno-economic evaluations. There is thus an intrinsic basic issue in these estimations, and a clear trend, for example with year of publication, cannot also be evidenced.

Figure 1 also remarks that the use of one or few of these results, is misleading, when used to assess techno-economic feasibility, but also to evaluate the impact. In fact, the impact of CCU technologies is clearly related to economics. For example, all estimations (about one third of those in **Figure 1**) for a methanol production cost above about 800 €/t, i.e., about twice the current average methanol value, indicate the not feasibility of this solution, and thus a close to zero impact. The area of estimations below this threshold, and up to reference methanol value, may be discussed in relation to incentives in CO_2 reduction, carbon taxes and other opportunities. Thus, the impact may greatly depend on these aspects. The estimations below the reference methanol value (about 12‰ of the total) indicate instead that this technology may be ready to be applied commercially and potentially on large scale.

Although we discuss here only CO_2 economics, it is evident from above considerations, the strong nexus also with impact on GHG reduction targets and transition on energy and chemical production.

ECONOMICS OF CO_2 UTILIZATION IN THE BROADER CONTEXT OF ENERGY TRANSITION

While current state-of-the-art CO_2 utilization technologies are an important element to foster the transformation, the real opportunities and positive economics in CO_2 utilization technologies will likely derive from the second generation processes. This term indicates those which both introduce new technological solutions, (for example, a more efficient direct use of renewable energy sources) and which are designed to effectively integrate within the new value chain deriving from energy transition. A consequence is the need of novel assessment approaches, which include new models for evaluation of CO_2 economics (Centi et al., 2019b).

Applying conventional assessments and analysis methodologies to a system in transition leads to misleading analyses, In fact, the latter is characterized from high non-linearity between the components, while conventional assessment is based largely on linear relations between the elements (although often not explicitly stated). This was proved historically in the past transition occurring in chemical production around 70 years ago (Centi et al., 2009). This is a general aspect to consider in evaluating the economics of CO_2 utilization. It is also emerging from the analysis of the past transitions, that companies not able to understand these aspects, and thus not well prepared to the transition, largely lost their core business. Thus, novel conceptual approaches to analyze business strategies in transition periods including advanced economical methodologies are a crucial industrial aspect. A proper analysis of the economics of CO_2 utilization processes is thus a relevant element for an effective industrial strategy.

Cost of renewable energy is a determining factor in CO_2 economics, often accounting more of 70% of the total costs (Centi and Perathoner, 2020). Power-to-X routes (Chehade et al., 2019; Rego de Vasconcelos and Lavoie, 2019) are largely based on the production of H_2 by electrolysis, which is then used for the catalytic conversion of CO_2. The cost of producing renewable electrical energy has been dramatically decreased in recent years. Part of the large spread in results (**Figure 1**) derives from the difference in renewable energy costs. On these bases, results are too spread to make reliable conclusions and predict a future trend. There are problems of accounting methodology, but especially on how to properly consider the evolution trend, which is not linear in transition economy.

Another related issue is the availability of renewable energy sources to account for the transition and to convert CO_2. Often who is negative about the use of CO_2 utilization technologies objects that there is not a sufficient excess renewable electrical energy for large-scale application. While in the past Power-to-X technologies were developed originally to store the excess available of renewable energy, there is no reason today to use this limited view. Dedicated production is feasible and preferable, but still not solving the issue of fluctuation and a constant supply of energy. If energy comes from the grid to bypass the discontinuity issue, it is on the average over 70‰ deriving from non-renewable sources even in the coming decade. The use of green certificates claiming that only energy from renewable sources is used, is a clear unproper sustainable approach.

However, the main point is that the products of CO_2 conversion (methanol, methane) are chemical energy vectors, and particularly methanol can be easy transported and stored. Thus, this reaction can be used to store/transport renewable energy which can be produced in remote areas at low cost. These chemical energy vectors will thus allow to create a trading system of renewable energy substituting the current one based on fossil fuels (or derivates). This full renewable-energy economy will be at the basis of the system change related to energy transition, and it is thus important to analyze the enabling technologies, among which catalysis plays certainly a relevant role (Centi and Perathoner, 2009; Lanzafame et al., 2017b; Čejka et al., 2018). Strictly related to these aspects is also the concept of solar fuels and chemicals (Perathoner and Centi, 2014; Ampelli et al., 2015; Perathoner and Centi, 2019). Without including the evaluation of Power-to-X technologies in this broader context and sustainable future, all the economics fail to produce the relevant estimations. This is the question remarked before. A transition period requires to use new conceptual assessment models, while the application of the current one often fails in making reliable indications. The very spread estimations summarized in **Figure 1**, are a good indication of the basic problem which exists. As a side comment, it evidences also why just a review of the results has a scarce meaning, and thus why this contribution has a different approach.

In order to assess properly the impact and economics of CO_2 utilization, it is thus necessary to put them in the general context of on-going system change, and its future implications. The analysis of the costs should take into account these aspects. CO_2 economics cannot be thus disjointed from a proper contextualization in terms of energy transition.

IMPACT AND ECONOMICS OF CO_2 UTILIZATION

Relations and Misleading Concepts

Another general issue in the discussion of economics of CO_2 utilization is the often assumption that the production of chemicals will lead to marginal impacts in terms of contribution to the reduction of GHG emissions. Different is the case of the production of fuels, but in this case the low impact is related to being not economically competitive. A recent Nature paper cites in the abstract that “Pathways that involve chemicals, fuels and microalgae might reduce emissions of carbon dioxide but have limited potential for its removal” (Hepburn et al., 2019). To analyze this conclusion, and in general the relation between scale and economics of CO_2 utilization, it is necessary to enter in the details of this analysis. The technologies considered able to contribute significantly to GHG emission reduction (in the Gt scale), do not include typically CCU (or Power-to-X), but only land- or marine-based sequestration techniques. See, for example, Intergovernmental Panel on Climate Change (IPCC) reports (IPCC, 2014). We should comment that this conclusion is due to a too limited vision of how accounting the impact. An example will be given in the section on economics of CO_2 to methanol to enable a worldwide economy based on renewable energy.

Hepburn et al. (2019) considers ten pathways: 1) CO_2-based production of chemicals (urea, methanol, polyols and polymers); 2) CO_2-based fuels (methanol, methane, dimethyl ether, and Fischer–Tropsch fuels); 3) microalgae fuels and other microalgae products; 4) concrete building materials; 5) CO_2 enhanced oil recovery (CO_2-EOR—Enhanced Oil Recovery); 6) bio-energy with carbon capture and storage (BECCS); 7) enhanced weathering; 8) forestry techniques, including afforestation/reforestation, forest management and wood products; 9) land management via soil carbon sequestration techniques; and 10) biochar. Among the parameters accounted, the time of storage and likelihood of release are considered as key elements. We remark, however, that this is not a correct way to evaluate the impact. It is not the amount of captured CO_2 and for how long time it remains stored, but the amount of fossil fuels used that can be avoided (Schlögl et al., 2018). Thus, a short cycle such as for fuels could be beneficial rather than negative, because implies the possibility to substitute a larger amount of fossil fuels with renewable resources over a given period.

To clarity better this aspect, it should be remarked that it is the same concept of changing from a linear to a circular economy. In a linear economy resources are taken from the environment, and wastes are introduced in the environment. In a carbon circular economy, the use of carbon should be circular i.e. the waste reused to avoid, or minimize, both the use of resources and the production of waste. The storage of emitted CO_2 will still maintain this linear model. It could reduce GHG, but remains a wrong approach. In some cases, differently from what considered by Hepburn et al. (2019), technologies like Enhanced Oil recovery (EOR) are even negative instead that positive, because lead to the higher exploitation of fossil resources.

In a circular model, a longer time of storage/sequestration is eventually a negative element, because reduces the circularity. In a carbon circular model, the GHG impact should be calculated as the reduction induced by substituting with renewable sources the current use of fossil fuels. Accounting CO_2 utilization potential as the volume of product multiplied by the amount of CO_2 required to make an equivalent amount of the product (Hepburn et al., 2019), is not correct and leads to underestimation (in the case of power-to-X) or overestimation (in the case of EOR). Note also that EOR impact is overestimated due to the many effective constrains in use. Hepburn et al. (2019) also not properly accounted the impact of urea production. CO_2 derives from the process itself, i.e. from the fossil fuels (typically methane) used to produce the H_2 necessary for ammonia synthesis. Thus, current urea production is not a way to capture CO_2 in chemicals, if green or solar ammonia is not used. The difference between green and solar is in the separate production of green H_2 and its use in the nearly conventional catalytic synthesis of ammonia, or instead the direct production of NH_3 from N_2, H_2O and sunlight. This is, however, a technology still not commercial.

In the specific estimation of CO_2 economics, the costs indicated by Hepburn et al. (2019) are based on an uncritical analysis of literature. It is not the aim here to criticize this paper, but to use as an example to remark how often in terms of economics of CO_2 utilization there are not correct conclusions based on a not enough critical analysis of the problems. **Figure 1** well remarks this issue, and how could influence the estimation of the potential impact. On the other hand, it is evident that the input given to the debate on the methodologies to reduce GHG by this and other papers may lead to misleading conclusions. In general, it thus contributes to the existing confusion regarding the effective potential and economics of CCU.

The SAPEA report “Novel carbon capture and utilization technologies: research and climate aspects” (Schlögl. et al., 2018) attempted this analysis to provide an independent scientific opinion. However, a further effort is necessary, because there are still too strong lobby interests in all the area of GHG emissions, being energy so pervasive for our life and thus being at its core also in terms of economical consequences. Thus, changing from a fossil fuel centric to a renewable energy-based vision has macro-economic and geo-political consequences affecting strong lobbies. Often, in addition, there is the tendency to advertise solutions to preserve these lobby interest as in favor of the environment (greenwashing).

Concepts and Elements of the Analysis

Using Hepburn et al. (2019) as a working example, some relevant concepts and elements of the analysis may be commented. Discussion is limited to economics for methanol and methane from CO_2. For methanol, the paper indicates a cost of production of 510 $/t with respect to a market value they indicated in 400 $/t (quite large fluctuations were observed in this average methanol commercial price, reaching even a minimum of 160 $/t in May 2020 at Rotterdam). It should be also remarked that market value of a fuel/chemical is different from the cost of production, which is generally lower, but a series of clarifications are needed to explain the meaning of the term “generally.”

The cost of production is determined from the combination of CAPEX (Capital Expenses) and OPEX (Operative Expenses). There are many aspects which determine the cost of production, some discussed later. Note also that especially for new technologies, estimation of CAPEX is difficult and complex and thus requires significant specific professional experience, and estimations by just using simulation software (for example, Aspen or ChemCad, as commented later) may give not correct indications. Even for engineering societies, it is a common practice to include contingencies of 15–40‰ to consider the difficulties in the estimations.

One aspect to remark here is that the costs are determined assuming often a full capacity of production (100‰, excluding typical interruptions for maintenance and causalities), but typical operations are at lower capacity. This is due to several aspects, among the highly fluctuating market demand is relevant. Typically, to operate economically, chemical plants should operate at a minimum 90–95‰ of the full capacity, but in the actual highly volatile situation, operations below this threshold are common. Thus, a plant which is designed to operate for a given cost may effectively operates at a higher production cost and higher than market value. This in addition to the many other factors determining the costs.

The situation is also different if the product is for the market (for which often high competition is present) with respect to an internal use by the company itself. In addition, in CO_2 utilization technologies, there are a series of additional relevant factors, for example all the incentives for the production of biofuels, to avoid CO_2 emissions, or on the contrary taxation on CO_2 emissions. Sustainability, in addition, is becoming an increasing driving factor to determine industrial strategies in this area (Basile et al., 2019).

Note furthermore that also market value depends on many factors and may change largely. Contract price are different from spot prices, and there are large differences on regional bases and by quarterly. In methanol, for example, these variations influence typically ±20 the average market value, in some cases even more. In 2019, EU methanol spot vs. contract price, had negative peaks up to −140 €/t, thus up to 30–35‰ of the average contract price. In addition, contract prices may depend on many factors, and can be different for internal use and when, for example, the target is a mandatory reduction of the CO_2 emissions. Thus, what could be supposed to be not economic based on average values, could be instead quite different for specific situations. When there are large differences, it may be expected that may be difficult to overcome them. However, it is prudential not make this assumption when estimated costs are within the ±50 range, for which contextualization of the analysis is necessary (e.g., referred to a specific business case). This is often the actual case for various CO_2 utilization cases, particularly for the Power-to-X area. This is also the motivation why many demo/pilot units are under evaluation.

Turning back to the discussion of the cost for methanol from CO_2, this cost depends on several aspects, among which the two critical are the cost of electrical energy (if green H_2 is produced using electrolyzers) and CAPEX amortization time. Amortization time defines the time needed to decrease, or account for, the investment cost. CAPEX is the capital expenditure, i.e. the fixed cost for construction of the plant. The amortization time, in the definition used here for Power-to-X technologies, considers that the fixed costs have to account also for how many hours per year the plant will operate, and not only for how many years the plant will be in operations. In using renewable energy, if only few hours per day of available electrical energy could be used (besides to all other problems related to start up/shut down operations) the CAPEX amortization will largely increase the costs of production. Costs can be significantly lower when full time operations are considered. Note also that in addition to amortization for CAPEX, the interest rate on the capital, usually in the form of weighted average cost of capital (WACC), must be considered. This could change significantly based on the economic period and may vary from about 3 to 8‰.

At the same time, the years of amortization of the plant can largely vary, depending on various considerations, going typically from 7 years for environmental technologies to 20 years or longer for mature technologies. Environmental technologies are supposed to be substituted with more efficient ones after short times. Considering that in CO_2 utilization technologies, CAPEX account for up to 70‰ of the production cost, it is evident that the CO_2 estimations can produce positive or negative indications without a proper analysis.

Note also that CAPEX in chemical processes has a much lower impact on the production costs, typically <40–50‰. On the other hand, an analysis of the specific CAPEX costs for CO_2 to methanol, reveals that over 50‰ of these costs are related to the electrolyzer. Although in terms of efficiency this technology cannot be largely improved, the costs are instead largely related to the possibility of a larger-scale industrialization, besides that on the nominal power. Note finally that H_2 production from electrolyzers is the commonly considered solution, because H_2 (from solar splitting of water) is still at an initial stage of development. However, green H_2 (e.g., not based on fossil fuels), can be produced in other ways, for example, from waste or from biomethane (i.e., methane in biogas). In the latter case, H_2 derives from its catalytic decomposition to H_2 and carbon. These alternative solutions are often not considered but could be part of a platform of technologies to guarantee continuous production of green H_2 on a regional basis through pipeline distribution.

Dimensioning Cost to Scale of Production

Figure 2 reports an example of the specific investment costs (thus CAPEX normalized per kW of electrical energy) for producing H_2 by three type of electrolyzers (PEMEC: Proton Exchange Membrane Electrolyzer; AEC: Alkaline Electrolyzer; SOEC: Solid Oxide). These costs are reported as a function of the scaling effects (size of the electrolyzer) and technological learning (e.g., expected progresses from year 2020 to 2050). This technology learning is often difficult to estimate. Often progresses in the reduction of costs can be even larger than optimistic expectations, as teaches well the case of decrease of costs of photovoltaic electrical energy production.

These costs may be discussed, but this is not relevant here. The point evidenced from **Figure 2** is that the costs (for example, for PEMEC electrolyzers) can change from less than 250 €/kW$_{el}$ to over 1,000 €/kW$_{el}$ (Zauner et al., 2019) which thus reflect in large differences in the production cost. Depending on which cost is chosen, the overall cost for the product of CO_2 utilization can largely change. These aspects add to the other factors indicated before.

The scale factor in economic cost estimations is usually determined using the following relation:

$$c_b = c_a\left(\frac{S_b}{S_a}\right)^f \qquad (1)$$

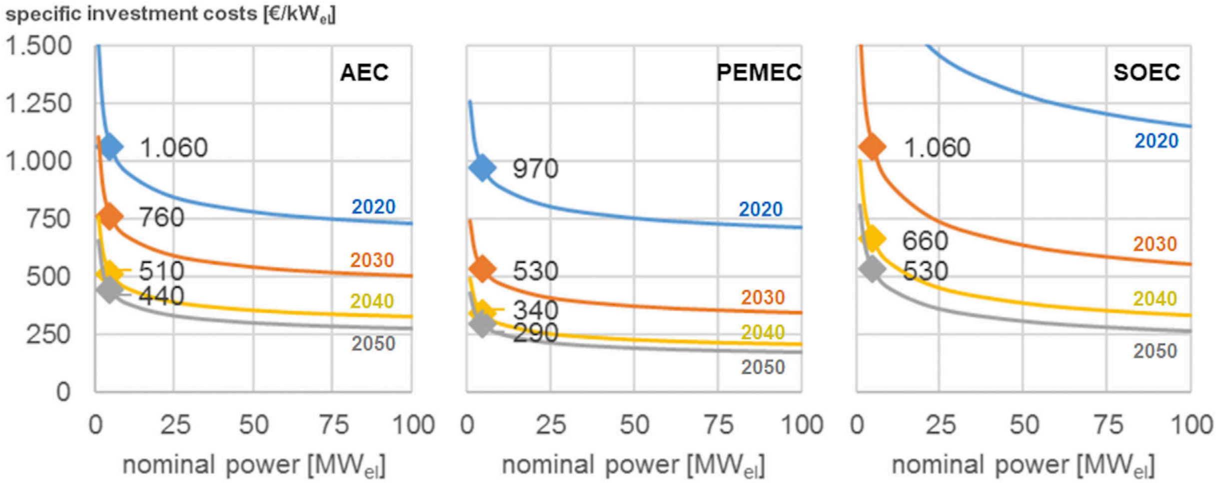

FIGURE 2 | Cost development of H_2 electrolyzers for three type of electrolyzers (PEMEC, Proton Exchange Membrane Electrolyzer; AEC, Alkaline Electrolyzer; SOEC, Solid Oxide) as function of the nominal power of the electrolyzers and estimated decrease in costs of production for different years in the 2020–2050 range. Elaborated from Zauner et al. (2019). No copyright.

The cost (c_b) is related to a standard cost (c_a) multiplied the ratio of the respective size (S) powered to a factor *f*, which typically is less than one and in the 0.6–0.9 typical range. This equation is used for single equipment, but it is practice the use also for plants, although may be not easy to find an appropriate reference, eg a plant with analogous characteristics. More correctly, although with a margin of error typically of ±30%, the process cost and thus CAPEX, is determined usually from the proper identification of the quantified process flowsheet and of the main equipment necessary and their size (Palo et al., 2019). Then, the cost for the various single equipment can be estimated as in **Eq. 1**.

Today, most of the engineering software for simulation already contain methods to calculate these costs (this is what typically made in many publications). The difference between estimations made by engineering companies experienced in the area is that they have an internal database of the effective costs typically not available for those at academic level using these software. Reliability of the results is thus largely different. From the cost of the equipment, the overall cost is estimated by adding typical percentages for all the other necessary elements (Palo et al., 2019). Again, there are large differences possible between estimations and their reliability based on this method, which can largely depend on the experience. Simulation software produce good results for relatively standard and established processes, but reliability in addressing new technologies in limited. Therefore, quantification of CAPEX costs can produce large differences. In CO_2 utilization technologies, where CAPEX and its amortization procedure are crucial components for the final production cost, a proper analysis, not limited to the final number, is essential.

This should include a proper estimation of the degree of cost reduction by technological and industrial development, the first related to improvement in the technology efficiency, while the second, and often the more relevant, is the cost reduction related to larger-scale industrial manufacture. This could decrease by a factor up to 5–10, and thus a relevant aspect to consider, but difficult to predict.

Putting in the right context of the energy transition is another important element. It was introduced before the concept that if the time of utilization of electrolyzers is limited to the few hours of when surplus of renewable energy is available, cost can be high, being amortization charged on too few hours. On the other hand, if high full-load hours operations are considered (typically >5.000–6.000 h/h), a gray electricity mix should be used (today, on the average and in an optimistic view, 70‰ from fossil fuels and 30‰ from renewable sources). This will largely decrease the cost of production, depending on the type of renewable energy source.

Case Analysis

Zauner et al. (2019) estimated for year 2020 that methane cost (produced from CO_2) is on the average 43 € cents/kWh$_{LHV}$ for electricity deriving from PV cells, around 27 € cents/kWh$_{LHV}$ for electricity produced from wind (which allow more extended times of operations, when low-cost electricity is available) and around 13 € cents/kWh$_{LHV}$ for electricity derived from the grid and 6,000 h/y operations. This time of operations is 68‰ of the full time theoretically possible and thus is a low prudential value. The usual time of operation for chemical processes is in the 86–90‰ of full time, depending on process reliability. Thus, further reduction of the cost is even possible. There is thus a factor four between the costs, depending on the time of operations.

Clearly, today a technology which uses CO_2 and electricity deriving from fossil fuels has no meaning, but in the future, with a progressive increase of renewable energy in the energy mix, the use of electricity from the grid could be realistic. For this reason, Zauner et al. (2019) indicated that the costs of methane from CO_2 could be in the 3–6 range (for year 2050) by combining technology development and cost reduction associated to this change in the energy mix. Thus, up to one order of magnitude less than the maximum estimated costs today. As a reference, the average cost of production of CH_4 from CO_2 given in the Nature paper of Hepburn et al. (2019) is 1739 $/t which translated to a unit as that indicated above is about 12 € cents/kWh_{LHV}. The usual way to indicate costs for a gas fuel like methane is by volume, i.e. €/Nm^3, a value currently around 0.2 (methane lower calorific power–PCI–i.e., the amount of energy released during the stoichiometric combustion of a fuel, is about 8,600 kcal/Nm^3).

A correct reference to compare these values should be not fossil methane, which cost is largely associated to geo-political motivations, but rather biomethane. International Energy Agency (IEA) in a recent report (IEA, 2020) indicates biomethane production costs ranging from 3 to over 20 USD/MBtu (Btu is the British thermal unit) in 2018 depending on the sources (crops, manure, municipal solid waste or wastewater) and potential global biogas demand. Currently (year 2020) natural gas has a value around 2 USD/MBtu in US, 5–7 in Europe and 10 in Japan). The costs of biomethane tendentially decrease over time, narrowing the cost gap with projected natural gas prices. By considering as reference 19 USD/MBtu, this translate to about 50 € cents/kWh_{LHV}. However, a fraction of potential biomethane (up to 30 Mtoe) has a cost of around 10–15 cents/kWh_{LHV}, which is in the range of competition with the domestic price of natural gas.

IEA report indicates that the biomethane actual production (35 Mtoe) is only a fraction of the potential (730 Mtoe) and is expected to increase to 200 and 330 Mtoe for years 2030 and 2040, respectively, in a sustainable development scenario. Thus, these data well evidence that producing methane from biogenic CO_2 sources (which can be also the fraction of CO_2 present in the biogas) and green H_2 is a route economically in line with biomethane (e.g., the methane fraction in biogas). It is a well reasonable approach to reduce carbon footprint of biogas production by utilization of the CO_2 component of biogas and its methanation, thus integrating biogas with renewable energy sources (Abate et al., 2015b). Thus, putting in the right perspective of energy transition, economics of CO_2 methanation indicates a potential large impact, in contradiction to the cited Nature paper of Hepburn et al. (2019).

The same remark could be applied to the case of CO_2 to methanol. Here the difference with respect to methane is that methanol is a liquid and can be thus easily transported and stored, by ship for example. Methanol can be thus used to establish a world trading of renewable energy stored in a liquid (Barbato et al., 2014), e.g., the equivalent of current fossil-centric energy system, largely associated to the possibility of easy transport of oil. Methane could be liquefied, but this is an energy-intense operation. It can be transported via pipeline, but where the network exists, and also storage can be possible underground, but in specific geological situations. Thus, flexibility of use is strongly reduced.

With the concept of using methanol as chemical energy storage (CES) vector, it is possible to bypass the limit of the use of excess renewable energy sources, using instead sources around the world where can be produced at economic costs. There is still large potential, but untapped, for hydropower sources which cannot be exploited, being in geographical areas where the produced electrical energy cannot be exploited. This concept will be further discussed later, but it is worth to comment here that the main advantage of hydropower as renewable electrical source is that it allows a continuous production of energy, without the fluctuations present in other cases (PV, wind). This is, as commented before, a crucial factor for economics.

There are many areas, deserts for example, where a combined availability of PV and wind production exists, which together with available technologies for short-term storage of electrical energy, could guarantee a constant production. In terms of impact on the land use and on the population, these areas do not have specific issues, and instead their utilization can have a positive impact on precipitations (around doubled) and the land fraction of vegetation covered (Li et al., 2018). This is a combination of reduced albedo, creation of microclima, effect on wind, etc. Deserts make up to one third of the land's surface area. Just 1/18 of Saharan Desert is enough to fuel (with PV at the current efficiency level) the world energy need. These are just indicative numbers, but remarking that there is not a potential limitation in terms of land use and potential impact on population. The current limit is the transport of renewable electrical energy, but CES technology could solve it. Thus, the potential impact is large, in Gton scale (as commented later), differently from what indicated in the cited Nature paper of Hepburn et al. (2019). In terms of economics, as discussed later, this is a potentially attractive solution, although it is not important here to demonstrate this point.

The relevant point here is that without putting well in the context of energy transition and future scenario, the economics of CO_2 and the impact of CO_2 utilization technologies cannot give the right indications. It is necessary not just use numbers but enter in detail and analyze how estimations have been made, which limits they have, which assumptions have been made, how these are valid out of the specific context. In terms of assessment, there is the need to also have a broader model of analysis, as commented later. Techno-economic estimation are and remain a very valuable instrument, but that should be used in the proper way. It is necessary to have well in mind the advantages and the limits. This is even more relevant when a system change is present, with thus also major changes in the full value chain, supply-demand, and technology requirements.

EXTENDING THE METHOD TO ASSESS THE TECHNO-ECONOMIC IMPACT

Zimmermann et al. (2020) recently discussed that there are no generally accepted techno-economic assessment (TEA) methods and often "apples vs. oranges" are compared with thus low transparency and readability, as remarked also in the introduction. They thus developed guideline for TEA and LCA technologies for the case of CO_2 utilization technologies. These guidelines will be shortly summarized here for the main relevant aspects for the discussion. An initial recommendation they made is that TEA should start from the identification of the context, the intended use and the limitations, concepts which are well coincident with what discussed above.

Zimmermann et al. (2020) indicated that TEA should follow the concepts of LCA in terms of structuring the approach and different phases of the analysis: goal and scope, inventory, calculation of indicators, interpretation, and reporting. TEA should state clearly and unambiguously 1) the study context (location, time horizon, scale and partners, etc.), 2) the intended application and motivations (like decision support for R&D funding allocation, investment decisions or policy, etc.), and 3) the target audience (e.g.,, R&D experts, funding agencies, investors, etc.). In addition, being TEA studies functional for decision making having also long-term implications, scenario analysis should be adequately described. System boundaries should be clearly defined and be consistent with the TEA goal and perspective. Up- and down-stream units (for example, CO_2 capture, separation and transport processes, hydrogen or electricity production, etc.) should be clearly defined if included or not, but consistently with parallel LCA studies. A proper benchmarking is necessary.

Criteria and assessment indicators should be also correctly defined. After the goal and scope phase, the inventory phase should follow. Data quality, what are the collected data, how a CO_2 price is derived, how data for other inputs (hydrogen, electricity, and other materials) are obtained, what are the documents of the inventory data are among main elements proving the input for calculations. The latter should include best practices and economic indicators (including, but not limited, to CAPEX/OPEX). Finally, interpretation is the final phase, which should include uncertainty and sensitivity analysis, interpretation of indicators and multicriteria decision analysis. Reporting concludes the assessment.

This procedure formalizes the mechanism, such as the ISO 14044 norms formalize the LCA methodology. Thus, it guarantees a better transparency of the data, and their usability, but do not addresses the key of the remarks discussed before. They require a step-change in the procedure, and how to integrate in the strategy of development and in general in a novel engineering approach to assess processes based on the use of renewable energy and alternative carbon sources (Centi at al., 2019b). Suitable novel indicators for both economics and LCA have also to be developed.

We early remarked that the traditional economic models and concepts, such as scale-economy, does not well account for the analysis of emerging CO_2 utilization technologies. New assessment tools are required. They need to include relevant elements, which are not currently present (or present in a too limited amount) in TEA methodologies, such as "the capability to analyze socio-economical macro-trends, market evolution, competitiveness related to entire ecosystems, sustainability and integration into territory (rather than globalization), non-linear dynamic of changes and costs evolution, extended life-cycle cost and social analysis" (Centi at al., 2019b).

Note, that also a trend in LCA is to expand the scope and a series of new LCA methodologies have been developed, for example Life Cycle Cost analysis (LCC), Social or Environmental LCA (S-LCA, E-LCA) which can then all be integrated in Life Cycle Sustainability Analysis (LCSA) (Heijungs et al., 2013). The application of these novel methods to CO_2 utilization cases, however, is still limited (von der Assen et al., 2014). Although LCSA accounts better of climate change issues and biodiversity and offers a more holistic perspective, as all the LCA methods, they are implemented largely through the use of database, rather than on actual data and effective specific, process-linked, analyses. They could be thus not a substitution of TEA, but allow to integrate the specific process in its and its input/output life cycles, i.e. from "cradle-to-grave."

A CASE EXAMPLE: ECONOMICS OF CO_2 TO METHANOL

Producing Methanol to Import Renewable Energy From Remote Areas

To complete the discussion of the economics of CO_2 utilization, a specific example will be discussed in this section: the conversion of CO_2 to methanol which is used to transport renewable energy from remote areas (the specific example, refers to hydropower produced in Chile, where a large potential production is present, but which cannot be exploited locally) (Barbato et al., 2014). CO_2 is transported by ship, while methanol transported back in the same ship, a technology current feasible. This is thus an example of using untapped remote renewable energy sources. Hydropower allows to have a continuous production, here considering a capacity factor of 320 days per year.

What is the potential impact of this technology? This was estimated by considering the potential power available worldwide as untapped renewable energy, either of hydropower and of PV + wind sources in remote areas, such as deserts. Prudential estimation is of an amount of 10 PWh per year of additional renewable energy that could be exploited by enabling an effective route for the conversion of electrical to chemical energy to store and transport renewable energy. 10 PWh correspond to 7 Gt of CO_2 equivalent emissions saved. There are some energy losses in the process, but the message is that the potential is in the Gt range, thus well equivalent or even superior than many alternatives.

Often it is questioned that the storage in fuels is not relevant, because CO_2 is re-emitted. As commented before, the point is that the fuel provides a service (energy, heating etc.) than otherwise should be produced by using fossil fuels. Thus, the GHG impact is in terms of avoidance of use of fossil fuels at equivalent service, rather than in terms of sequestration of CO_2. Nevertheless, the rational approach is to re-capture CO_2. This is possible, for example by using methanol in turbines to generate electrical energy and heat, with integrated recapture of CO_2 (an available technology, by using pressurized turbines and CO_2 separation membranes, technologies already available). Thus, a closed-cycle could be realized, with an efficiency in storing renewable energy of the order of 50–60‰ (Barbato et al., 2014), which is well aligned to current large energy-storage technologies, for example, pumped hydroelectric energy storage (PHES). Note that for efficiencies >50‰ in a close-loop approach, the technology will act as a negative CO_2 emission technology.

From the technology side, as indicated, there are already various pilot units that have developed the conversion of CO_2 to methanol with green H_2, generally produced using

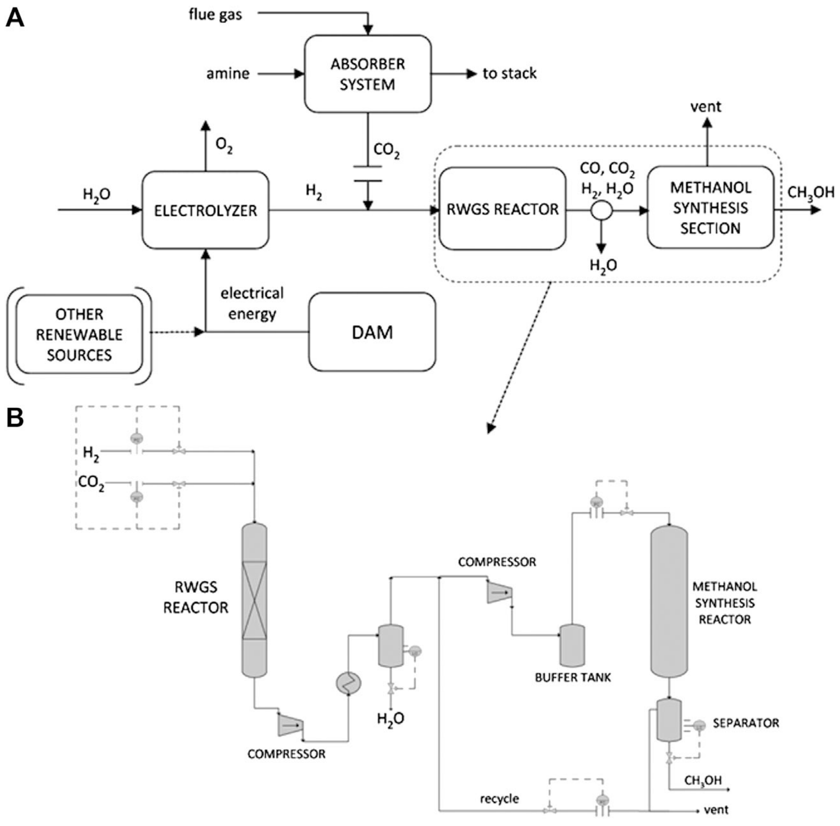

FIGURE 3 | A) Simplified block diagram of different material flows participating in the process of methanol synthesis from CO_2 and renewable H_2. (**B**) Simplified flowsheet for the section of the RWGS reactor and methanol synthesis system. Reproduced with permission from Barbato et al. (2014).

electrolyzers. Still some degrees of improvement are possible but may be considered that the technology is currently nearly mature for exploitation, also for remote and small-scale productions, requiring efficient and compact units. Electrolyzers are also commercially available. Improvements in terms of stability and pressure of operation could improve further the performances and operability, and the integration with the catalytic step, (for example, operations without the need to compress H_2, a costly element). Even if simplified as analysis, it may be concluded that there are not significant current technical limitations to implement the technology, just a "normal" further technological progress as necessary in exploiting new technologies.

The question is thus the cost of producing methanol. The cited paper by Barbato et al. (2014) reports all the details. **Figure 3** reports the simplified process flowsheet used to estimate, by process simulation, the production cost of methanol from CO_2 using green H_2 from electrolysis with electrical energy produced by hydropower. There are five major process blocks:

(1) Production of renewable electricity using a dedicated hydropower unit, which costs are integrated in the calculations;
(2) Production of green H_2 using AEC electrolyzers (operating a 15 bar, as the current state of the art of commercial units);
(3) Capture of CO_2 (from concentrated and rather pure sources, as some stream in refinery or in biogas units, after methane separation), and transport to a 1,500 km distance by ship after drying and compression at 75 bar (using Carbotube 75 technology proprietary of the Maire Tecnimont Group; transport costs are based on their commercial experience);
(4) Preparation of the feed mixture for the methanol step, by compressing and mixing CO_2/H_2 and then converting part of the CO_2 in a RWGS reaction (using commercial copper-based catalysts) to produce a $CO/CO_2/H_2$ mixture suitable for the methanol synthesis; water, which is produced in RWGS step, is removed by a conventional drying technology;
(5) Catalytic synthesis of methanol (using commercial copper-zinc-oxide based catalysts), followed by purification and storage; methanol is then transported back using the same ships used to transport CO_2.

Note that CO_2 may be converted also directly to methanol, without a first RWGS reactor (the catalysts active for methanol synthesis are also active for RWGS). Separation in two stages, with intermediate water elimination, adds costs (although not very large), but avoid the inhibition by water on the reaction rate

TABLE 1 | Key economic parameters used to estimate the methanol production costs. Reproduced with permission from Barbato et al. (2014).

Item	Value
CO_2 cost at site (€ per ton of methanol)	35
Removal from flue gas (€ per ton of CO_2)	25
Transport at site (1,500 km) (€ per ton of CO_2)	20
Benefit of avoided emissions (€ per ton of CO_2)	–20
TOT COST (€ per ton of CO_2)	25
TOT COST per ton of methanol (€ per ton of methanol)	35
Electricity consumption for H_2 production (kWh Nm^3 H_2)[a]	4.24
Renewable H_2 production cost (€ Nm^3 H_2)[a]	0.140
Methanol plant capacity (tons per day)	2,400
Capacity factor (days per year)	320
CAPEX	
A: dam and ancillary items (million €)	900
B: electrolysis section, CO_2 storage and methanol production section (million €)	944
Depreciation value	
A: (€ M per year)	75.4
B: (€ M per year)	96.1
Maintenance materials and labor	
Power section costs (% of CAPEX per year)	1
Chemical section (% of CI per year)	2
WACC (%)	8
Production cost of methanol (€ per ton)	294

[a] *The volumetric unit is defined at "normal conditions" (0°C and 1.01325 bar).*

of methanol production. Developing hydrophobic methanol synthesis catalysts, thus less sensitive to inhibition by water allows thus to make more effective the direct CO_2 to methanol conversion, thus saving on CAPEX costs.

Reliability of Estimations

The H_2 production by hydropower is assumed €0.140 per Nm^3 H_2, which is the current cost of electrolysis for large-scale H_2 production with an H_2 efficiency in the range of 62–65‰, a currently feasible efficiency. This would correspond to 4.5–4.8 kWh per Nm^3 of H_2 produced. The cost of CO_2 capture was estimated by considering a conventional CO_2 absorption amine process, which is a robust and available technology. It uses an aqueous solution with 30‰ by weight monoethanolamine (MEA). Cost for CO_2 capture are based on actual costs for this technology used in other processes, and thus are quite reliable values. There is a growing research on alternative and less expensive capture technologies, which can reduce the cost of CO_2 capture by over 20‰. Margins to reduce further the costs are thus present.

Note that in general in all CO_2 utilization technologies, the cost of capture/purification of CO_2 can be significant, up to half of the overall cost (Schlögl et al., 2018). Thus, decreasing these costs are a crucial element for future developments. Note that, although not valid for this specific case but for other relevant cases as the direct conversion of CO_2 by artificial-like photosynthetic devices, elimination of the step of a separated CO_2 capture unit may be possible. For example, by including membrane-like systems able to capture CO_2 directly and transfer to the machinery for its photoelectrocatalytic conversion (as occurs in leaves). In other cases, CO_2 nearly pure (as in biogas after separation of methane, or in fermentation processes, but also in some refinery cases), could be available. Thus, cost of separation/purification of CO_2 could strongly depend on the specific case analyzed. The main key economic parameters used to estimate the methanol production costs are summarized in **Table 1** (Barbato et al., 2014).

CO_2 is captured in the examined case at refinery sources, where it is available with good concentration and purity. The recovered CO_2 is first dehydrated (to prevent wet carbonate corrosion) and then compressed up to 75 bars before shipping. Shipping is made with CO_2 cargos at a distance of 1,500 km. CO_2 is stored in the ship in tanks filled with a carbon-based support (Carbolite). This is a commercially available solution, which allows to use the ships to transport back methanol. Shipping costs has a low impact on the overall costs, thus changing the distance has not a relevant impact.

While on-step direct CO_2 conversion is possible, in this example it was preferred to have a first stage of reverse water gas shift–RWGS (to form thus CO from CO_2) followed by catalytic CO_2-rich syngas conversion. Water removal is realized with conventional techniques between these two stages. There are degrees of improvement in terms of 1) better (more productive) and more stable catalysts (less sensitive to higher water content and CO_2 concentration in the feed with respect to commercial methanol catalysts), 2) use of microreactors to intensify the process and more efficient control of the reaction temperature profile (it is an exothermic reversible reaction), 3) optimized integration with the electrolyzer, and 4) efficient heat integration. There is thus also here the possibility to decrease further the costs by about 15–20‰. However, it is a prudential approach to evaluate, as base case, a reliable state-of-the-art technology.

The costs, although estimated with a simplified method based on the quantified flow sheet and cost for main equipment, with then estimation of final CAPEX by fixed percentages for other components, are reliable within the indicated ±30 range. Due to in-house available experience on analogous equipment and plants in building commercial units, the estimation results robust and reliable. OPEX are estimated by considering operating and maintenance (O&M) and variable operating costs (VOC). CAPEX is the predominant factor influencing the overall cost of production (about 75‰). CAPEX has been split in two main components. The first is related to produce the electrical energy by hydropower. This investment cost for hydropower unit construction was estimated in 1,000 € kW^{-1}, a current realistic cost indicated by hydropower plant producers. For this part of the investment, the depreciation rate was calculated using a 40-year period. For the second part of the investment, related to the costs of the electrolysis and methanol synthesis units, the depreciation value was calculated using a 20-year period. It was then assumed to calculate the depreciation rate for a WACC of 8‰. Currently (year 2020), this value is significantly lower, i.e., < 4–5‰. This lowers the depreciation costs.

Cost of CO_2 at site (thus including capture and delivery) was considered 35 € per ton of methanol, considering that one-ton CO_2 produces 0.77 tons methanol. Cost is low but includes 20 € per ton CO_2 of benefit for avoided emissions. This is a reasonable assumption, although may be different case to case. Costs were calculated for a methanol plant capacity of 2,400 tons per day. Note that as indicated before, the costs are calculated including those related to produce the hydropower unit. Often instead costs are estimated by using commercial values for renewable electrical energy and not including the CAPEX for dedicated renewable electrical energy production.

Thus, all the elements of the calculation are valid and reliable. Based on these indications, the cost of production of methanol was about 300 € per ton. The cost is largely lower than that reported in the cited Nature paper of Hepburn et al. (2019) and in many of other TEA studies (**Figure 1**). This cost makes competitive to use this technology to import untapped renewable energy sources. Contract price for methanol, as a general indication, may be considered around 300 €/t.

Impact and Market

Beginning year 2020 the methanol average market price was about 270 €/t, with European spot prices averaging around €205/t during the fourth quarter of 2019, but this year prices and forecasts are largely affected from coronavirus outbreak. New methanol productions started in Iran, Trinidad and the US, and MTO-based olefin production (MTO–methanol to olefin; a major process consuming methanol) is running near-peak levels, while conventional (from oil) olefin and olefin-derivative capacity in Asia-Pacific was growing.

Thus, short term forecasts for methanol are not positive, but the possibility to use methanol as biofuel (when produced from waste or biogenic CO_2) in substitution of bioethanol, suffering of increasing costs and social concerns, opens new prospects and markets. These brief notes just to evidence the difficulty in predicting market value trends for chemicals and thus in making reliable conclusions about the use of new technologies.

A Comparison with Literature

How compare indications above with other literature results? Here the aim is not to provide an analysis with all published data. In the cited Nature paper of Hepburn et al. (2019) they reported to have analyzed 24 papers in total on methanol production case, arriving to the conclusion of a cost of methanol production of 510 $/t, i.e., about 465 €/t, about 40‰ higher with respect to that indicated in **Table 1**. This could make a significant difference between possibility of application of the technology, as indicated by Barbato et al. (2014) and consideration instead of a marginal possible impact, as indicated by Hepburn et al. (2019). It results thus interesting to analyze as exercise some other estimations on CO_2 economics for methanol production.

Pérez-Fortes et al. (2016) reported a techno-economic and environmental assessment of the process of methanol synthesis using captured CO_2. The two main conclusions were that 1) "production costs results too high for a financially attractive project", and 2) "there is a net potential for CO_2 emissions reduction of 2.71 $MtCO_2$/yr in Europe." Thus, quite in contrast with those discussed above, and it is thus interesting to analyze more in-depth the reasons of the different conclusions.

The conceptual design of the process of capture CO_2 and catalytic conversion to methanol is made by Pérez-Fortes et al. (2016) using ChemCad commercial software, which is used for academic exercises, but typically not in engineering societies. Aspen is another simulation software often used in TEA studies, but not in engineering societies which use for estimation of the purchased equipment costs mainly in-house direct values on analogous systems. H_2 generation and transport is not included within the boundary limits of calculations, but it is supposed will arrive to CO_2 conversion plant through a pipeline. The price of H_2 is 3,090 €/t. This is one of the critical estimations, because influences the conclusions of a negative gross margin for the methanol plant, because "the H_2 cost surpasses the revenues obtained by selling the methanol" and determines that "the total cost of production is almost 1.7 times the expected revenue" (Pérez-Fortes et al., 2016).

Just as a reference, one ton of methanol requires 0.189 tons H_2, thus for a CH_3OH market value of 400 €/t, the cost of H_2 results thus higher (580€ for a hydrogen price of 3,090 €/t). It is certain that with this H_2 cost CO_2 economics to methanol result negative. The problem is thus to analyze whether a lower H_2 production cost is possible. Therefore, an integrated production of low-cost green H_2 which guarantee continuous operations has to be considered, as made in the Barbato et al. (2014) paper. They include CAPEX for construction of a dedicated hydropower plant, but the result is a largely lower H_2 production cost.

CO_2 capture and transport, and further purification steps of the CO_2 stream are also out of the boundary limits considered by Pérez-Fortes et al. (2016). Sensitivity with respect to this and H_2 cost were calculated by these authors for their estimations. For base case price (€/t) of a methanol cost of 400 €/t, they reported that CO_2 and H_2 cost should be 0 and 3,090 €/t, respectively. This would correspond to a net present value NPV of −1,036.2 M€ for a project of 20 years. NPV represents the present value of a cash flow, thus a negative value indicates that the entrance due to selling the products are lower with respect to costs. To obtain a NPV of zero, they estimated that the CO_2 cost should be negative (−222 €/t) and H_2 cost also nearly half (1,453 €/t), with a market value for methanol of 724 €/t. From here the conclusion, that the process is not economic, having considered 400 €/t the commercial product value for methanol. As commented before, Barbato et al. (2014) estimated instead a cost of production of methanol of nearly 300 €/t (thus lower than the market value) by using an on-site (integrated) production of H_2 by electrolysis using the electrical energy of a dedicated hydropower unit.

A closer look at the results of Pérez-Fortes et al. (2016) with respect to those in the Barbato et al. (2014) paper reveals also that CAPEX and OPEX costs are highly different, even if the process scheme is not so different to justify the difference. CAPEX indicated by Pérez-Fortes et al. (2016) is 496.5 €/(t_{CH3OH}/y) for a methanol production is 1,320 t/day. CAPEX for Barbato et al. (2014) is 61 €/(t_{CH3OH}/y) for a 2,400 t/day, excluding CAPEX for producing the electrical energy, in order to have comparable data. OPEX (assuming the same capacity factor) are 58% of the total costs for Pérez-Fortes et al. (2016), while 25% of the total costs for Barbato et al. (2014). It is thus evident that there are very different ways to estimate the costs, which produce these large differences and thus reflect also in the final costs and derived conclusion on competitiveness and impact of the technology.

It is not the scope here to comment which of these two estimations is the more reliable. The aim is to remark only that without entering in the details of the calculations and estimation, the final conclusions itself have limited value. The same analysis could be applied to other estimations of TEA for methanol productions or other CO_2 economic estimations. The examples discussed represent thus only practical cases rather than be model for correct or not procedures. As a final comment, the focus here on only economics aspects, rather than also on technological one, does not intend to minimize the crucial role of technology development, including for example creating and mastering nano-objects to develop next-generation of catalytic materials (Centi and Perathoner, 2011). All these technological aspects have a decisive role in the progress and practical use of the CO_2 utilization route. Limiting discussion to economics is just to focus the analysis.

CONCLUSIONS

The economic assessment of new processes for CO_2 utilization is a crucial element to establish the impact and contribution of CCU to GHG reduction and climate mitigation. Discussion was focused on Power-to-X (methanol, methane), being that studied in a more detail from an economic perspective among CCU technologies. There are many areas of growing interest for CO_2 utilization, for example that of electrocatalytic processes (Genovese et al., 2013; Perathoner and Centi, 2019), but they are at a much lower level of industrial development. Only the area of CO_2 utilization for production of CO_2-containing polymers can be considered at an equal level of development. However, in these cases, the interest is as low-cost carbon source, rather than as effective technologies to mitigate climate changes.

It is necessary to stress again that this is not a review of economics of CO_2 utilization, neither a didactic presentation of how to estimate these economics. It is rather a conceptual perspective contribution around a key question: how reliable literature data on CO_2 economics are, and related estimation of the impact on GHG emissions and climate change mitigation (Centi et al., 2013; Centi and Perathoner, 2014). The starting point is **Figure 1**, based on state-of-the-art analysis of literature indications on economics of Power-to-X technologies. Data show the very large spread of results in estimating the cost of production of methanol and methane from CO_2 by using renewable energy source. This Figure clearly evidences that without a guide to analyze these results, it is not possible to use some or few of these results to make conclusions, whether or not these are technologies suitable to contribute significantly to GHG emission reduction.

In order to provide this guide for interpretation of literature results on CO_2 economics, we have analyzed here some of the questions, and methods related to CO_2 economics as a procedure to assess the feasibility of the CO_2 utilization processes, and thus also their potential impact. Although with a focus on Power-to-X technologies for CO_2 conversion to methanol and methane (Centi and Perathoner, 2020), the discussion has a more general relevance for all the area of the so-called CO_2 utilization technologies. In fact, here the attention was to comment on the methodologies to analyze CO_2 economics and their limit and validity, using some examples to clarify these aspects. Note also that the objective was not to indicate what is the effective costs, but to provide the basic elements to understand the values reported in literature and the limits related to the analysis.

The need of a proper contextualization of the results was remarked, particularly in relation to the impact which is strongly associated not only to economics, but also to a proper identification of the future value chain. A correct prospects analysis requires to go beyond the current often too limited approaches (as considering CO_2 utilization as a storage option) and have a broader view in relation to the system change related to energy (and chemistry) transition.

Note as final remark that we have utilized here the term CCU only as utilization, and not as the full definition of CCU (carbon capture and utilization) or CCSU (carbon capture, storage and utilization). These acronyms indicate the categorial need to have a carbon capture step, and indirectly also that utilization is just a complementary option to storage of CO_2. We have commented in the text that both indications are not correct, neither lead to a correct evaluation of the economics and impact. From a semantic definition, note also that the definition "perennial energy sources" is more correct with respect to that of "renewable energy sources", although the latter is more extensively used and thus utilized also here.

In conclusion, we hope that this critical perspective provides some useful elements for a better analysis of the economics of chemical processes in the area of CO_2 utilization and providing also some guidelines on how to account for techno-economic results and their impact on GHG reduction.

AUTHOR CONTRIBUTIONS

All authors contributed equally to the discussion and analysis, while CG wrote the text that was revised and approved by co-authors.

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REFERENCES

Abate, S., Centi, G., Lanzafame, P., and Perathoner, S. (2015a). The energy-chemistry nexus: a vision of the future from sustainability perspective. *J. Energy Chem.* 24, 535–547. doi:10.1016/j.jechem.2015.08.005

Abate, S., Lanzafame, P., Perathoner, S., and Centi, G. (2015b). New sustainable model of biorefineries: biofactories and challenges of integrating bio- and solar refineries, *Chem. Sus. Chem.* 8, 2854–2866. doi:10.1002/cssc.201500277

Alsayegh, S., Johnson, J. R., Ohs, B., and Wessling, M. (2019). Methanol production via direct carbon dioxide hydrogenation using hydrogen from photocatalytic water splitting: process development and techno-economic analysis. *J. Clean. Prod.* 208, 1446–1458. doi:10.1016/j.jclepro.2018.10.132

Ampelli, C., Perathoner, S., and Centi, G. (2015). CO_2 utilization: an enabling element to move to a resource- and energy-efficient chemical and fuel production. *Phil. Trans. R. Soc. A* 373, 1–35. doi:10.1098/rsta.2014.0177

Aresta, M., Caroppo, A., Dibenedetto, A., and Narracci, M. (2002). "Life cycle assessment (LCA) applied to the synthesis of methanol. Comparison of the use of syngas with the use of CO_2 and dihydrogen produced from renewables," in *Environmental challenges and greenhouse gas control for fossil fuel utilization in the 21st century*. Editors M. M. Maroto-Valer, C. Song, and Y. Soong (New York, NY: Springer US), 329–347.

Aresta, M., Dibenedetto, A., and Angelini, A. (2013). The changing paradigm in CO_2 utilization. *J. CO_2 Util.* 3–4, 65–73. doi:10.1016/j.jcou.2013.08.001

Asif, M., Gao, X., Lv, H., Xi, X., and Dong, P. (2018). Catalytic hydrogenation of CO^+ from 600 MW supercritical coal power plant to produce methanol: a techno-economic analysis. *Int. J. H_2 Energy* 43, 2726–2741. doi:10.1016/j.ijhydene.2017.12.086

Atsonios, K., Panopoulos, K. D., and Kakaras, E. (2016). Investigation of technical and economic aspects for methanol production through CO_2 hydrogenation. *Int. J. H_2 Energy* 41, 2202–2214. doi:10.1016/j.ijhydene.2015.12.074

Bailera, M., Lisbona, P., Romeo, L. M., and Espatolero, S. (2017). Power to gas projects review: lab, pilot and demo plants for storing renewable energy and CO_2. *Renew. Sustain. Energy Rev.* 69, 292–312. doi:10.1016/j.rser.2016.11.130

Barbato, L., Centi, G., Iaquaniello, G., Mangiapane, A., and Perathoner, S. (2014). Trading renewable energy by using CO_2: an effective option to mitigate climate change and increase the use of renewable energy sources. *Energy Technol.* 2, 453–461. doi:10.1002/ente.201300182

A. Basile, G. Centi, M. De Falco, and G. Iaquaniello (Editors) (2019). "The vision of future sustainable energy, catalyst, and chemistry: opportunities for innovation and business," in *Catalysis, green chemistry and sustainable energy. Studies in surface science and catalysis.* Amsterdam, Netherlands: Elsevier B.V., Vol. 79, 7–20.

Bos, M. J., Kersten, S. R. A., and Brilman, W. F. D. (2020). Wind power to methanol: renewable methanol production using electricity, electrolysis of water and CO_2 air capture. *Appl. Energy* 264, 114672. doi:10.1016/j.apenergy.2020.114672

Čejka, J., Nachtigall, P., and Centi, G. (2018). New catalytic materials for energy and chemistry in transition. *Chem. Soc. Rev.* 47, 8066–8071. doi:10.1039/C8CS90119H

Centi, G., and Čejka, J. (2019a). Needs and gaps for catalysis in addressing transitions in chemistry and energy from a sustainability perspective. *ChemSusChem* 12, 621–632. doi:10.1002/cssc.201802637

Centi, G., Iaquaniello, G., and Perathoner, S. (2019b). Chemical engineering role in the use of renewable energy and alternative carbon sources in chemical production. *BMC Chem. Eng.* 1, 5. doi:10.1186/s42480-019-0006-8

Centi, G., and Perathoner, S. (2009). Catalysis: role and challenges for a sustainable energy. *Top. Catal.* 52, 948–961. doi:10.1007/s11244-009-9245-x

Centi, G., and Perathoner, S. (2020). Chemistry and energy beyond fossil fuels. A perspective view on the role of syngas from waste sources. *Catal. Today* 342, 4. doi:10.1016/j.cattod.2019.04.003

Centi, G., and Perathoner, S. (2011). Creating and mastering nano-objects to design advanced catalytic materials. *Coord. Chem. Rev.* 255, 1480–1498. doi:10.1016/j.ccr.2011.01.021

Centi, G., and Perathoner, S. (2014). *Green carbon dioxide: advances in CO_2 utilization*. Hoboken, NJ: Wiley Publisher. ISBN-10: 9781118590881

Centi, G., Perathoner, S., and Rak, Z. S. (2003). Reduction of greenhouse gas emissions by catalytic processes. *Appl. Catal. B Environ.* 41, 143–155. doi:10.1016/s0926-3373(02)00207-2

Centi, G., and Perathoner, S. (2010). Towards solar fuels from water and CO_2. *Chem. Sus. Chem.* 3, 195–208. doi:10.1002/cssc.200900289

Centi, G., Quadrelli, E. A., and Perathoner, S. (2013). Catalysis for CO_2 conversion: a key technology for rapid introduction of renewable energy in the value chain of chemical industries. *Energy Environ. Sci.* 6, 1711–1731. doi:10.1039/c3ee00056g

Centi, G., Trifiró, F., Perathoner, S., and Cavani, F. (2009). *Sustainable industrial processes*. Weinheim, Germany: Wiley VCH Publishers. ISBN 978-3-527-31552-9

Chehade, Z., Mansilla, C., Lucchese, P., Hilliard, S., and Proost, J. (2019). Review and analysis of demonstration projects on power-to-X pathways in the world. *Int. J. Hydrogen Energy* 44, 27637–27655. doi:10.1016/j.ijhydene.2019.08.260

Chwola, T., Spietz, T., Wieclaw-Solny, L., Tatarczuk, A., Krotki, A., Dobras, S., et al. (2020). Pilot plant initial results for the methanation process using CO_2 from amine scrubbing at the Laziska power plant in Poland. *Fuel* 263, 116804. doi:10.1016/j.fuel.2019.116804

De Saint Jean, M., Baurens, P., Bouallou, C., and Couturier, K., (2015). Economic assessment of a power-to-substitute-natural-gas process including high-temperature steam electrolysis. *Int. J. Hydrogen Energy* 40, 6487–6500. doi:10.1016/j.ijhydene.2015.03.066

Dimitriou, I., García-Gutiérrez, P., Elder, R. H., Cuéllar-Franca, R. M., Azapagic, A., and Allen, R. W. K. (2015). Carbon dioxide utilisation for production of transport fuels: process and economic analysis. *Energy Environ. Sci.* 8, 1775–1789. doi:10.1039/c4ee04117h

Do, T. N., and Kim, J. (2019). Process development and techno-economic evaluation of methanol production by direct CO_2 hydrogenation using solar-thermal energy. *J. CO_2 Util.* 33, 461–472. doi:10.1016/j.jcou.2019.07.003

IPCC Climate Change (2014). *IPCC Climate Change 2014: mitigation of climate change*. Editors O. Edenhofer (Cambridge: Cambridge University Press).

Garcia-Herrero, I., Cuéllar-Franca, R. M., Enríquez-Gutiérrez, V. M., Alvarez-Guerra, M., Irabien, A., and Azapagic, A. (2016). Environmental assessment of dimethyl carbonate production: comparison of a novel electrosynthesis route utilizing CO_2 with a commercial oxidative carbonylation process. *ACS Sustain. Chem. Eng.* 4, 2088–2097. doi:10.1021/acssuschemeng.5b01515

Genovese, C., Ampelli, C., Perathoner, S., and Centi, G. (2013). Electrocatalytic conversion of CO_2 on carbon nanotube-based electrodes for producing solar fuels. *J. Catal.* 308, 237–249. doi:10.1016/j.jcat.2013.08.026

González-Aparicio, I., Pérez-Fortes, M., Zucker, A., and Tzimas, E. (2017). Opportunities of integrating CO2 utilization with RES-E: a power-to-methanol business model with wind power generation. *Energy Proc.* 114, 6905–6918. doi:10.1016/j.egypro.2017.03.1833

González-Garay, A., Frei, M. S., Al-Qahtani, A., Mondelli, C., Guillén-Gosálbez, G., and Pérez-Ramírez, J. (2019). Plant-to-planet analysis of CO_2-based methanol processes. *Energy Environ. Sci.* 12, 3425–3436. doi:10.1039/c9ee01673b

Grim, R. G., Huang, Z., Guarnieri, M. T., Ferrell, J. R., III, Tao, L., and Schaidle, J. A. (2020). Transforming the carbon economy: challenges and opportunities in the convergence of low-cost electricity and reductive CO_2 utilization. *Energy Environ. Sci.* 13, 472–494. doi:10.1039/c9ee02410g

Gutiérrez-Martín, F., and Rodríguez-Antón, L. M. (2016). Power-to-SNG technology for energy storage at large scales. *Int. J. Hydrogen Energy* 41, 19290–19303. doi:10.1016/j.ijhydene.2016.07.097

Hank, C., Gelpke, S., Schnabl, A., White, R. J., Full, J., Wiebe, N., et al. (2018). Economics and carbon dioxide avoidance cost of methanol production based on renewable hydrogen and recycled carbon dioxide: power-to-methanol. *Sust. Energy Fuels* 2, 1244–1261. doi:10.1039/c8se00032h

Hannula, I. (2015). Co-production of synthetic fuels and district heat from biomass residues, carbon dioxide and electricity: performance and cost analysis. *Biomass Bioenergy* 74, 26–46. doi:10.1016/j.biombioe.2015.01.006

Heijungs, R., Settanni, E., and Guinée, J. (2013). Towards a computational structure for life cycle sustainability analysis: unifying LCA and LCC. *Int. J. Life Cycle Assess.* 18, 1722–1733. doi:10.1007/s11367-012-0461-4

Hepburn, C., Adlen, E., Beddington, J., Carter, E. A., Fuss, S., Mac Dowell, N., et al. (2019). The technological and economic prospects for CO_2 utilization and removal. *Nature* 575, 87–97. doi:10.1038/s41586-019-1681-6

Hofstetter, D., Battke, B., Cox, B., and Hughes, J. (2014). *Power-to-Gas in Switzerland - demand, regulation, economics, technical potential.* Zurich: Swiss Federal Institute of Technology.

Hoppe, W., Bringezu, S., and Wachter, N. (2018). Economic assessment of CO_2-based methane, methanol and polyoxymethylene production. *J. CO_2 Util.* 27, 170–178. doi:10.1016/j.jcou.2018.06.019

Iaquaniello, G., Setini, S., Salladini, A., and De Falco, M. (2018). CO_2 vaporization through direct methanation of flue gas and renewable hydrogen: a technical and economic assessment. *Int. J. Hydrogen Energy* 43, 17069–17081. doi:10.1016/j.ijhydene.2018.07.099

International Energy Agency (IEA) (2020). Outlook for biogas and biomethane: prospects for organic growth. Paris: IEA Publishers. . Available at: https://webstore.iea.org/download/direct/2970?fileName=Outlook_for_biogas_and_biomethane.pdf (Accessed May 27, 2020).

Jens, C. M., Mueller, L., Leonhard, K., and Bardow, A. (2019). To integrate or not to integrate-techno-economic and life cycle assessment of CO_2 capture and conversion to methyl formate using methanol, *ACS Sustain. Chem. Eng.* 7, 12270–12280

Khunathorncharoenwong, N., Charoensuppanimit, P., Assabumrungrat, S., and Kim-Lohsoontorn, P. (2020). Techno-economic analysis of alternative processes for alcohol-assisted methanol synthesis from carbon dioxide and hydrogen, *Int. J. Hydrogen Energy* in press. doi:10.1016/j.ijhydene.2020.01.230

Kim, J., Henao, C. A., Johnson, T. A., Dedrick, D. E., Miller, J. E., Stechel, E. B., et al. (2011). Methanol production from CO_2 using solar-thermal energy: process development and techno-economic analysis. *Energy Environ. Sci.* 4, 3122e3132. doi:10.1039/c1ee01311d

Kourkoumpas, D. S., Papadimou, E., Atsonios, K., Karellas, S., Grammelis, P., and Kakaras, E. (2016). Implementation of the power to methanol concept by using CO_2 from lignite power plants: techno-economic investigation. *Int. J. Hydrogen Energy* 41, 16674–16687. doi:10.1016/j.ijhydene.2016.07.100

Koytsoumpa, E. I., Bergins, C., and Kakaras, E. (2018). The CO_2 economy: review of CO_2 capture and reuse technologies. *J. Supercrit. Fluids* 132, 3–16. doi:10.1016/j.supflu.2017.07.029

Lanzafame, P., Abate, S., Ampelli, C., Genovese, C., Passalacqua, R., Centi, G., et al. (2017a). Beyond solar fuels: renewable energy-driven chemistry. *Chem. Sus. Chem.* 10, 4409–4419.

Lanzafame, P., Perathoner, S., Centi, G., Gross, S., and Hensen, E. J. M. (2017b). Grand challenges for catalysis in the Science and Technology Roadmap on Catalysis for Europe: moving ahead for a sustainable future. *Catal. Sci. Technol.* 7, 5182–5194. doi:10.1039/c7cy01067b

Laumb, J. D., Kay, J. P., Holmes, M. J., Cowan, R. M., Azenkeng, A., Heebink, L. V., et al. (2013). Economic and market analysis of CO_2 utilization technologies: focus on CO_2 derived from north Dakota lignite. *Energy Proc.* 37, 6987–6998. doi:10.1016/j.egypro.2013.06.632

Li, Y., Kalnay, E., Motesharrei, S., Rivas, J., Kucharski, F., Kirk-Davidoff, D., et al. (2018). Climate model shows large-scale wind and solar farms in the Sahara increase rain and vegetation. *Science* 361, 1019–1022. doi:10.1126/science.aar5629

Meunier, N., Chauvy, R., Mouhoubi, S., Thomas, D., and De Weireld, G. (2020). Alternative production of methanol from industrial CO_2. *Renew. Energy* 146, 1192–1203. doi:10.1016/j.renene.2019.07.010

Michailos, S., Sanderson, P., Villa Zaragoza, A., McCord, S., Armstrong, K., Styring, P., et al. (2018). Methanol worked examples for the TEA and LCA guidelines for CO_2 utilization. Available at: https://deepblue.lib.umich.edu/handle/2027.42/145723 (Accessed July 10, 2020).

Moellenbruck, F., Kempken, T., Dierks, M., Oeljeklaus, G., and Goerner, K. (2018). Cogeneration of power and methanol based on a conventional power plant in Germany. *J. Energy Storage* 19, 393–401. doi:10.1016/j.est.2018.08.018

Mustafa, A., Lougou, B. G., Shuai, Y., Wang, Z., and Tan, H. (2020). Current technology development for CO_2 utilization into solar fuels and chemicals: a review. *J. Energy Chem.* 49, 96–123. doi:10.1016/j.jechem.2020.01.023

Naims, H. (2016). Economics of carbon dioxide capture and utilization-a supply and demand perspective. *Environ. Sci. Pollut. Res.* 23, 22226–22241. doi:10.1007/s11356-016-6810-2

Nami, H., Ranjbar, F., and Yari, M. (2019). Methanol synthesis from renewable H_2 and captured CO_2 from S-Graz cycle: energy, exergy, exergoeconomic and exergoenvironmental (4E) analysis. *Int. J. Hydrogen Energy* 44, 26128–26147. doi:10.1016/j.ijhydene.2019.08.079

Navarrete, A., Centi, G., Bogaerts, A., Martín, Á., York, A., and Stefanidis, G. D. (2017). Harvesting renewable energy for carbon dioxide catalysis. *Energy Technol.* 5, 796–811. doi:10.1002/ente.201600609

Nguyen, T. B. H., and Zondervan, E. (2019). Methanol production from captured CO_2 using hydrogenation and reforming technologies environmental and economic evaluation. *J. CO_2 Util.* 34, 1–11. doi:10.1016/j.jcou.2019.05.033

Nieminen, H., Laari, A., and Koiranen, T. (2019). CO_2 hydrogenation to methanol by a liquid-phase process with alcoholic solvents: a techno-economic analysis. *Processes* 7, 405. doi:10.3390/pr7070405

Ordomsky, V. V., Dros, A.-B., Schwiedernoch, R., and Khodakov, A. Y. (2017). "Challenges and role of catalysis in CO_2 conversion to chemicals and fuels," in *Nanotechnology in catalysis*. Editors B. Sels and M. Van de Voorde (Hoboken, NJ: Wiley) Vol. 3, 803–850.

Pérez-Fortes, M., Schöneberger, J. C., Boulamanti, A., and Tzimas, E. (2016). Methanol synthesis using captured CO_2 as raw material: techno-economic and environmental assessment. *Appl. Energy* 161, 718–732. doi:10.1016/j.apenergy.2015.07.067

Palo, E., Iaquaniello, G., and Mosca, L. (2019). "Calculate the production costs of your own process," in *Catalysis, green chemistry and sustainable energy*. Editors A. Basile, G. Centi, M. De Falco, and G. Iaquaniello, *Studies in surface science and catalysis* (Amsterdam, Netherlands: Elsevier B.V.), Vol. 179, 141–157.

Parra, D., Zhang, X., Bauer, C., and Patel, M. K. (2017). An integrated techno-economic and life cycle environmental assessment of power-to-gas systems. *Appl. Energy* 193, 440–454.doi:10.1016/j.apenergy.2017.02.063

Perathoner, S., and Centi, G. (2014). CO_2 Recycling: a key strategy to introduce green energy in the chemical production chain. *Chem. Sus. Chem.* 7, 1274–1282. doi:10.1002/cssc.201300926

Perathoner, S., and Centi, G. (2019). Catalysis for solar-driven chemistry: the role of electrocatalysis. *Catal. Today* 330, 157–170. doi:10.1016/j.cattod.2018.03.005

Quadrelli, E. A., Centi, G., Duplan, J. L., and Perathoner, S. (2011). Carbon dioxide recycling: emerging large-scale technologies with industrial potential. *Chem. Sus. Chem* 4, 1194–1215. doi:10.1002/cssc.201100473

Räuchle, K., Plass, L., Wernicke, H. J., and Bertau, M. (2016). Methanol for renewable energy storage and utilization. *Energy techn*. 4, 193–200. doidoi:10.1002/ente.201500322

Rego de Vasconcelos, B., and Lavoie, J. M. (2019). Recent advances in power-to-X technology for the production of fuels and chemicals. *Front. Chem* 7, 392. doi:10.3389/fchem.2019.00392

Rivarolo, M., Bellotti, D., Magistri, L., and Massardo, A. F. (2017). Feasibility study of methanol production from different renewable sources and thermo-economic analysis. *J. CO_2 Util.* 21, 132–138.

Rivera-Tinoco, R., Farran, M., Bouallou, C., Auprêtre, F., Valentin, S., Millet, P., et al. (2016). Investigation of power-to-methanol processes coupling electrolytic hydrogen production and catalytic CO_2 reduction. *Int. J. Hydrogen Energy* 41, 4546–4559. doi:10.1016/j.ijhydene.2016.01.059

Roh, K., Nguyen, T. B. H., Suriyapraphadilok, U., Lee, J. H., and Gani, R. (2015). "Development of sustainable CO_2 conversion processes for the methanol production," in 12th international symposium on process systems engineering. Editors V. Gernaey, J.K. Huusom, and R. Gani (Amsterdam: Elsevier Publishing), 1145–1150.

Schiebahn, S., Grube, T., Robinius, M., Tietze, V., Kumar, B., and Stolten, D. (2015). Power to gas: technological overview, systems analysis and economic assessment for a case study in Germany, *Int. J. Hydrogen Energy* 40, 4285–4294. doi:10.1016/j.ijhydene.2015.01.123

Schlögl, R., Abanades, C., Aresta, M., Azapagic, A., Blekkan, E. A., Cantat, T., et al. (2018). "Novel carbon capture and utilisation technologies: research and climate aspects, SAPEA (Novel carbon capture and utilisation technologies: research and climate aspects)," in *Evidence review report No. 2* (Berlin, Germany:SAPEA Publishers). ISBN 978-3-9819415-5-5

Senftle, T. P., and Carter, E. A. (2017). The holy grail: chemistry enabling an economically viable CO_2 capture, utilization, and storage strategy. *Acc. Chem. Res.* 50, 472–475. doi:10.1021/acs.accounts.6b00479

Son, M., Park, M.-J., Kwak, G., Park, H. G., and Jun, K. W. (2018). Maximum production of methanol in a pilot-scale process, *Kor. J. Chem. Eng.*, 35, 355–363. doi:10.1007/s11814-017-0295-7

Thonemann, N. (2020). Environmental impacts of CO_2-based chemical production: a systematic literature review and meta-analysis. *Appl. Energy* 263, 114599. doi:10.1016/j.apenergy.2020.114599

Tremel, A., Wasserscheid, P., Baldauf, M., and Hammer, T. (2015). Techno-economic analysis for the synthesis of liquid and gaseous fuels based on hydrogen production via electrolysis. *Int. J. Hydrogen Energy* 40, 11457–11464. doi:10.1016/j.ijhydene.2015.01.097

von der Assen, N., Jung, J., and Bardow, A. (2013). Life-cycle assessment of carbon dioxide capture and utilization: avoiding the pitfalls. *Energy Environ. Sci.* 6, 2721–2734. doi:10.1039/c3ee41151f

von der Assen, N., Voll, P., Peters, M., and Bardow, A. (2014). Life cycle assessment of CO2capture and utilization: a tutorial review. *Chem. Soc. Rev.* 43, 7982–7994. doi:10.1039/c3cs60373c

Zauner, A., Böhm, H., Rosenfeld, D. C., and Tichler, R. (2019). Analysis on future technology options and on techno-economic optimization (D7.7 of STORE&GO EU project no. 691797). Available at: https://www.storeandgo.info/fileadmin/downloads/deliverables_2019/20190801-STOREandGO-D7.7-EIL-Analysis_on_future_technology_options_and_on_techno-economic_optimization.pdf (Accessed May 26, 2020).

Zhang, C., Gao, R., Jun, K. W., Kim, S. K., Hwang, S. M., Park, H. G., et al. (2019). Direct conversion of carbon dioxide to liquid fuels and synthetic natural gas using renewable power: techno-economic analysis. *J. CO_2 Util.* 34, 293–302. doi:10.1016/j.jcou.2019.07.005

Zhang, H., and Desideri, U. (2020). Techno-economic optimization of power-to-methanol with co-electrolysis of CO_2 and H_2O in solid-oxide electrolyzers. *Energy*, 199, 117498. doi:10.1016/j.energy.2020.117498

Zhang, H., Wang, L., Van herle, J., Maréchal, F., and Desideri, U. (2019). Techno-economic optimization of CO_2-to-methanol with solid-oxide electrolyzer. *Energies* 12, 3742. doi:10.3390/en12193742

Zhang, S., Zhuang, Y., Liu, L., Zhang, L., and Du, J. (2020). Optimization-based approach for CO_2 utilization in carbon capture, utilization and storage supply chain. *Comput. Chem. Eng.* 139, 106885. doi:10.1016/j.compchemeng.2020.106885

Zheng, Y., Zhang, W., Li, Y., Chen, J., Yu, B., Wang, J., et al. (2017). Energy related CO_2 conversion and utilization: advanced materials/nanomaterials, reaction mechanisms and technologies. *Nanomater. Energy* 40, 512–539. doi:10.1016/j.nanoen.2017.08.049

Zimmermann, A. W., Wunderlich, J., Müller, L., Buchner, G. A., Marxen, A., Michailos, S., et al. (2020). Techno-economic assessment guidelines for CO_2 utilization. *Front. Energy Res.* 8. doi:10.3389/fenrg.2020.00005

GLOSSARY

AEC, Alkaline Electrolyzer BECCS Bio-Energy with Carbon Capture and Storage; CAPEX, CAPital EXpenditure; CES, Chemical Energy Storage; CCSU, Carbon Capture, Storage and Utilization; CCU, Carbon Capture and Utilization; E-LCA, Environmental LCA; EOR, Enhanced Oil Recovery; GHG, GreenHouse Gas; IPCC, Intergovernmental Panel on Climate Change; LCA, Life Cycle Assessment; LCC, Life Cycle Cost; LCSA, Life Cycle Sustainability Analysis; LHV, Lower Heating Value; MEA, Mono Ethanol Amine; MTO, Methanol to Olefin; Mtoe, Million tons of oil equivalent; NPV, Net Present Value; O&M, Operating and Maintenance; OPEX, OPerative EXpenses; PEMEC, Proton Exchange Membrane Electrolyzer; PtX, Power-to-X, including Power-to-Gas (PtG or P2G) and Power-to-Liquid (PtL or P2L); PHES, Pumped Hydroelectric Energy Storage; PV, PhotoVoltaic; RWGS, Reverse Water Gas Shift; S-LCA, Social LCA; SOEC, Solid Oxide Electrolyzer; TEA, Techno-Economic Assessment; TRL, Technology Readiness Level; VOC, Variable Operating Costs; WACC, Weighted Average Cost of Capital.

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REVIEW
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Carbon Capture From Flue Gas and the Atmosphere: A Perspective

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Climate change has become a worldwide concern with the rapid rise of the atmospheric CO_2 concentration. To mitigate CO_2 emissions, the research and development efforts in CO_2 capture and separation both from the stationary sources with high CO_2 concentrations (e.g., coal-fired power plant flue gas) and directly from the atmosphere have grown significantly. Much progress has been achieved, especially within the last twenty years. In this perspective, we first briefly review the current status of carbon capture technologies including absorption, adsorption, membrane, biological capture, and cryogenic separation, and compare their advantages and disadvantages. Then, we focus mainly on the recent advances in the absorption, adsorption, and membrane technologies. Even though numerous optimizations in materials and processes have been pursued, implementing a single separation process is still quite energy-intensive or costly. To address the challenges, we provide our perspectives on future directions of CO_2 capture research and development, that is, the combination of flue gas recycling and hybrid capture system, and one-step integrated CO_2 capture and conversion system, as they have the potential to overcome the technical bottlenecks of single capture technologies, offering significant improvement in energy efficiency and cost-effectiveness.

Keywords: carbon dioxide capture, flue gas, air capture, hybrid system, carbon capture and conversion

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INTRODUCTION

Today's primary energy supply is heavily relying on carbonaceous fuels, mainly the three typical fossil energies, that is, coal, petroleum, and conventional and unconventional natural gas. The control of pollutants emitted from combustion of these fuels in various stationaries including power plants, mobile energy systems, and industrial factories is a major challenge to the environment and human health and safety. It is initially related to the emissions of SO_x, NO_x, mercury, and particulate matters. Now, it also involves the emissions of carbon dioxide (CO_2) and methane (CH_4), two major greenhouse gases which have been regarded as the main reason for the climate change worldwide. With increasing concerns on global climate change (Melillo et al., 1993; Houghton et al., 2001; IPCC, 2015), reducing greenhouse gases emissions, particularly CO_2 emissions, has been significantly heightened in both academia and industry in recent years (Maroto-Valer et al., 2002; Brovkin et al., 2004; Song, 2006), in part because the increased CO_2 emissions are believed to contributing to ocean acidification and sea level rise in addition to global warming and climate change.

Since the industrial revolution, CO_2 emissions have increased continuously due mainly to the anthropogenic activities. **Figure 1** shows the CO_2 concentration in the atmosphere within the last six decades from 1958 to 2019. As of December 2019, CO_2 concentration in the atmosphere has reached

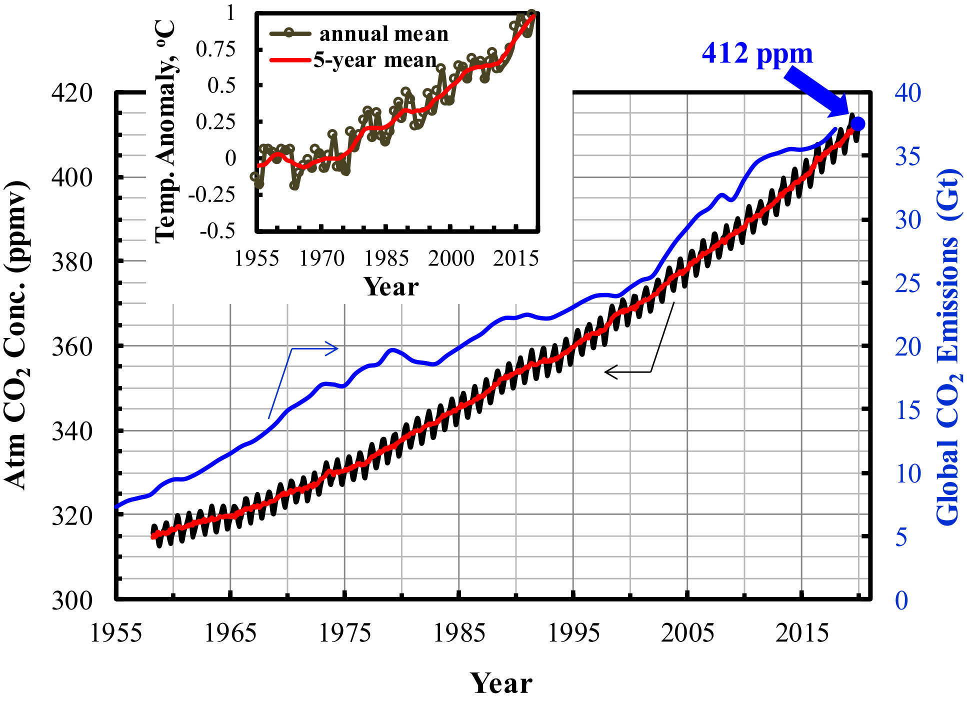

FIGURE 1 | Atmospheric CO_2 concentration during 1950–2019 (data sources: http://climate.nasa.gov/vital-signs/carbon-dioxide/).

412 ppm, accounting for about 31% increase of that in 1958 (~5.1‰ per year). In contrast, it took about a hundred years for the atmospheric CO_2 concentration to reach 315 ppm by 1958 (IPCC, 2015; Seneviratne et al., 2016), an increase of ~12.5% (~1.25‰ per year). Such a change clearly shows that the atmospheric CO_2 concentration has increased significantly, and the rising rate becomes faster and faster. The CO_2 concentration in air would surpass 550 ppm by 2050 if no action were taken to curb CO_2 emissions while keeping fossil fuels utilization as is (Smith and Myers, 2018), possibly reaching to 900–1,100 ppm by the end of this century (Kiehl, 2011). If so, it could cause catastrophic impact on global climate and human nutrition and societies.

In 2015, a global agreement was reached at the United Nations Climate Change Conference, known as the Paris Agreement. It sets a target of keeping the global temperature rise at 2°C or less by the end of the 21st century (United Nations Climate Change, 2015), accentuating well on the urgency in reducing CO_2 emissions (Seneviratne et al., 2016). However, with fast growth of global economies and world population which demands more and more energy supply globally, fossil fuels will continue playing a major role. Although the supply of alternative energies such as biomass, solar, and wind is increasing, they are still in the developing stage, yet far from ready to replace the fossil energy completely. Thus, developing strategies to significantly reduce CO_2 emissions both from the stationary sources with high CO_2 concentrations (e.g., coal-fired power plants, and manufacturing industries) and directly from air have attracted increasing attention worldwide (Lackner, 2003; Song, 2006; Keith, 2009; Lackner et al., 2012; IPCC, 2015; Sanz-Pérez et al., 2016; National Academies of Sciences, Engineering, and Medicine, 2019).

There are several pathways to mitigate CO_2 emissions: reducing energy use, improving energy efficiency, shifting to low-carbon or even non-carbon energy, and implementing carbon capture and sequestration (CCS) (Pacala and Socolow, 2004). Reducing energy use is not realistic on a global scale, while improving energy efficiency is a highly challenging task to meet the climate change mitigation goals. The use of low-carbon energy such as natural gas can slow but not be able to solve the problem. Renewable energy such as biomass, wind, and solar is still at its early stage and not able to replace the current fossil fuel-based energy in near future, while the future of nuclear energy is under much debating with big uncertainty. In contrast, carbon capture, utilization, and sequestration (CCUS), which refers to a process that captures CO_2 from sources like power plants or ambient air followed by recycling it for utilization or sequestrating it underground permanently, is now widely regarded as a viable option to quickly alleviate CO_2 emissions within a midterm. Especially, when the captured CO_2 is utilized as a valuable (and renewable) feedstock and cheap carbon source for industrial chemicals and fuels production, it offers a cost-competitive way to solve the contradict between the ever-increasing energy demand and CO_2 emissions reduction (Markewitz et al., 2012).

Today, the global energy-related CO_2 emissions are at the level of 35–37 gigatonnes per year (Gt/yr), with over 80% coming from fossil fuel combustion--> (National Academies of Sciences, Engineering, and Medicine, 2019; IEA, 2010; OECD, 2012). In the United States, the energy-related CO_2 emissions are about 5.1–5.3 Gt/yr in recent years (U.S. Energy Information Administration, 2020). Among them, the CO_2 emissions from power plants, industrial sector, and the transportation sector account for 30, 21, and 26% of total carbon emissions, respectively (United States Environmental Protection Agency, 2016). Capturing CO_2 from these sources is thus critical to maintain or slow down the increase of the atmospheric CO_2 level (Sanz-Pérez et al., 2016). About 1.3 Gt-CO_2 is emitted annually from the transportation sector in the United States, which is expected to increase significantly by 2050 due to the increasing demand for vehicles and aviation (OECD, 2012). Unfortunately, till today, onboard CO_2 capture from the mobile system is still not available. To address the challenge, negative emission strategies have recently been proposed. One method is directly removing CO_2 from air, the so-called direct air carbon capture (DACC) (Keith, 2009; Lackner et al., 2012; Sanz-Pérez et al., 2016; National Academies of Sciences, Engineering, and Medicine, 2019). According to the Intergovernmental Panel on Climate Change (IPCC), the current global CO_2 emissions are more than those envisaged with the most pessimistic model (Stocker et al., 2013). Thus, combining CO_2 capture both from the high and low CO_2 concentration sources could be essential to achieve the Paris Agreement goal of limiting anthropogenic global temperature increase below 2°C.

Aqueous amine scrubbing is the benchmark carbon capture technology currently commercially available in industry (Rochelle, 2009; Rochelle, 2016; Tontiwachwuthikul and Idem, 2013; Darunte et al., 2016). This process, however, is very energy intensive. It is predicted that the required parasitic loads or the so-called energy penalty for CO_2 removal is around 0.2–0.5 MWh/ton-CO_2, which is equivalent to 20–30% of power plant output (Rochelle, 2009). Particularly, the absorbent regeneration and CO_2 recovery step consumes about 50% of the overall energy in the form of low-pressure steam for the stripper reboiler due largely to the high heating capacity of water. The high energy penalty induces both high capital cost and operating cost. The use of basic amine solution can cause corrosion to the equipment. Furthermore, the amine loss due to the degradation and evaporation in the process generates pollutants to the environment. It is estimated that the application of the technology could result in the increase in the cost of electricity by 25–40% (Rubin et al., 2015), thus limiting its widespread use (Haszeldine, 2009). Therefore, developing new technologies to minimize energy penalty and improve cost-effectiveness for carbon capture is highly desired yet quite challenging (Song, 2006; Chu, 2009; Keith, 2009). In this article, we first convey a short review on the R&D status of carbon capture technologies including absorption, adsorption, membrane, biological capture, and cryogenic separation; compare their advantages and disadvantages; and elaborate mainly on absorption, adsorption, and membrane technologies more in detail. Then, we provide our perspective on future directions in CO_2 capture research and development.

CURRENT STATUS OF CARBON CAPTURE TECHNOLOGIES

Currently, several technological pathways are pursued for CO_2 separation and capture including carbon capture from post-combustion, pre-combustion, oxy-combustion, chemical looping combustion (CLC), and ambient air as well, which is illustrated in **Figure 2**. **Table 1** lists the advantages and disadvantages of those pathways (Figueroa et al., 2008; Rackley, 2017).

- Post-combustion capture involves CO_2 separation from flue gases after combustion, which has a low CO_2 partial pressure (0.03–0.2 bar) and/or a low CO_2 concentration (3–20%) (Figueroa et al., 2008; Feron and Hendriks, 2005). The carbon capture from some industrial sources such as cement manufacturing, stainless steel factory can also be categorized into post-combustion capture, although the CO_2 concentration from those industrial processes is higher than that of a typical flue gas from post-combustion power plants. **Table 2** lists the typical CO_2 concentration of a flue gas stream from various sources (Metz et al., 2005; Husebye et al., 2012; Liguori and Wilcox, 2018). The commercially available post-combustion capture process is the chemical absorption-based aqueous amine solution, such as 30% monoethanolamine (MEA) solution. Post-combustion capture is considered as a more viable option for existing coal-fired power plants (Wang Y. et al., 2017).
- In a pre-combustion process, which is based on the scaled industrial processes for the production of hydrogen and chemical commodities (Jansen et al., 2015), fuel feedstocks (i.e., coal and natural gas) are converted into syngas (H_2 and CO) *via* gasification, steam reforming, auto thermal reforming, or partial oxidation (Steinberg and Cheng, 1989), and then CO is transferred into CO_2 by water, with more hydrogen produced (the so-called water–gas shift reaction, WGS), followed by carbon capture system to remove CO_2. After CO_2 is captured, the hydrogen-rich fuel gas is utilized for power and heat generation such as boilers, gas turbines, and fuel cells (Metz et al., 2005). After WGS, the CO_2 concentration in the flue gas is relatively high, which is in the range of 15–60% (dry basis) at a total pressure of 2–7 MPa (Gazzani et al., 2013a; Gazzani et al., 2013b), thus physical solvents such as Selexol and Rectisol rather than chemical solvents are commonly used for pre-combustion capture.
- Oxy-combustion is a relatively new technology (Jurado et al., 2015) and involves the combustion of fuel feedstocks in a nearly pure oxygen (95–99%) or O_2–CO_2–rich environment (Miller, 2017), resulting in a flue gas with very high CO_2 concentration, where the capture of CO_2 is thus normally not needed and CO_2 is basically ready for sequestration (Miller, 2017; Li et al., 2018; Wu et al., 2019). However, in order to obtain nearly pure oxygen (>95%) (Kather et al., 2008), usually a cryogenic air separation unit is required for oxygen separation from air, which makes the whole process costly.

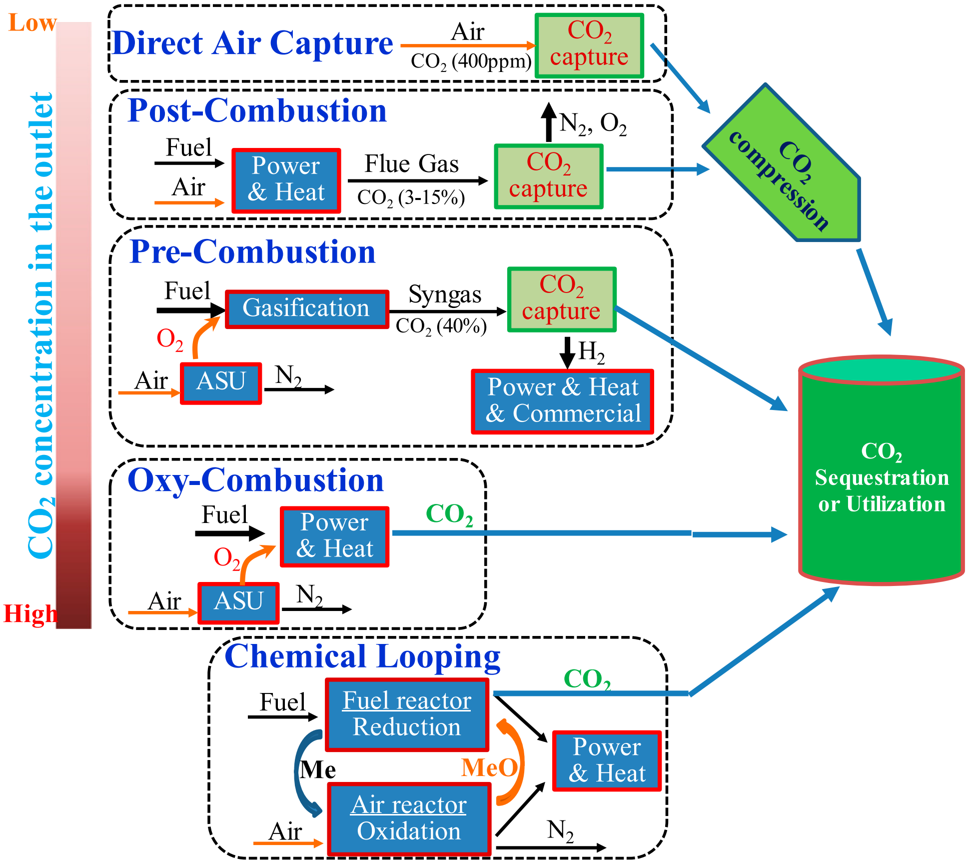

FIGURE 2 | Schematic diagram of the existing CO_2 capture pathways.

- CLC is an emerging combustion process similar to oxy-combustion producing the CO_2-concentrated flue gas (Abanades et al., 2015; Miller, 2017), so that the separation of CO_2 from fuel gas (e.g., pre-combustion) or flue gas (e.g., post-combustion) is not needed. In a typical chemical looping process, an oxygen carrier such as Fe, Mn, Cu, Ni, and Co metals is oxidized in air in one reactor (called the air-reactor), which is then reduced with a hydrocarbon fuel in another reactor (called the fuel-reactor) to regenerate the metal and release CO_2 and water (Abanades et al., 2015). The metal is then sent back to start another cycle in the air- and fuel-reactors. The exothermic air-reactor provides higher temperature heat and power, while the fuel-reactor can also generate some heat and power as well. CLC was introduced first by Lewis et al. (Lewis et al., 1951) and later applied for CO_2 mitigation by Ishida et al. (Ishida et al., 1987; Ishida and Jin, 1994). Since then over 900 materials have been tested (Lyngfelt and Mattisson, 2011) and a number of reviews have been published (Fan, 2010; Adanez et al., 2012; Lyngfelt, 2014; Abanades et al., 2015). Compared to oxy-combustion, CLC eliminates the costly air separation unit, thus is more cost-effective, but the process is relatively more complicated, requiring more studies. To be more cost competitive, a suitable metal/metal–oxide pair as the oxygen carrier plays a critical role in the chemical looping process. More recently, the machine learning algorithms and artificial neural networks have been utilized to estimate the performance of hetero- and multi-component materials as oxygen carriers for CLC (Yan et al., 2020).
- DACC represents a process for CO_2 extraction or removal directly from the atmosphere, which was first introduced for the mitigation of climate change by Lackner in 1999 (Lackner et al., 1999). DACC could play a crucial role for CO_2 capture from decentralized and mobile emission sources such as vehicles, ships, or air planes (Sanz-Pérez et al., 2016; Bhown et al., 2020; Jones, 2011; Goeppert et al., 2012), thus gaining increasing attention. In 2012, Kulkarni and Sholl (Kulkarni and Sholl, 2012) developed a steam-based process using aminosilica sorbents, which can recover CO_2 at 1–3 ton/unit/year. Currently, multiple companies including Carbon Engineering (Carbon Engineering, 2020), Climeworks (Climeworks, 2020), and Global Thermostat (Global Thermostat, 2020) are developing DACC systems at a commercial scale. However, it is quite challenging due to the exceptionally low CO_2 concentration (~400 ppm in air). It requires moving very large volume of air through the capture unit and high adsorption heat to execute the CO_2

TABLE 1 | Pros and cons of current CO_2 capture technological approaches.

Capture pathway	Pros	Cons
Post-combustion	√Mature technology (e.g., aqueous monoethanolamine (MEA)), commercially deployed in some industries √Good for most existing power plants √Possible for retrofit to existing plants	• High parasitic power requirement • Low capture efficiency due to low CO_2 partial pressure
Pre-combustion	√High CO_2 concentration √High partial pressure √Mature physical absorption technology (e.g., Selexol and Recticol), commercially deployed in some industries,	• High capital and operating costs • Applicable mainly to new IGCC plants • H_2-rich gas-induced temperature and efficiency issues
Oxyfuel combustion	√Developed air separation technologies available √Very high CO_2 concentration √Possible for retrofit and repowering to existing plants	• Costly and energy intensive air separation step • Retrofit unattractive due to Significant plant changes
Chemical looping combustion	√Very high CO_2 concentration √Low cost oxygen carrier materials	• Immature, currently under development
Air capture	√Truly and directly reduce the atmospheric CO_2 concentration √Viable alternative for CO_2 capture from mobile and decentralized sources	• Immature, currently under development • Costly and energy intensive due to extremely low CO_2 concentration (~400 ppm) in air

extraction, making this pathway more energy intensive and costly than removing CO_2 from the concentrated sources. There is a debate on whether DACC is an enabling factor (Realmonte et al., 2019; Azarabadi and Lackner, 2020) or just a costly distraction for effective climate change mitigation (Chatterjee and Huang, 2020).

Other industrial processes such as hydrogen production, ammonia synthesis, and methanol manufacture release the tail gases with a high concentration of CO_2, which could be captured and directly used or transported for storage after some purification. Similar to the oxy-combustion and CLC processes, an individual CO_2 capture unit is normally not needed for those processes.

As shown in **Figure 2**, only post-combustion capture, pre-combustion capture and air capture require a CO_2 capture system. So far, many technological approaches are available for a carbon capture system; however, the choice of a specific capture technology differs widely depending on the sources and CO_2-generating processes, resulting in different energy penalties. **Figure 3** illustrates various CO_2 capture technologies including absorption, adsorption, membrane, biological capture, and cryogenic capture under investigation in both academia and industry for the past few decades, while **Table 3** briefly compares the advantages and limitations of these carbon capture technologies (Singh and Dhar, 2019). Among them, absorption, adsorption, and membrane methods are more intensively studied, thus are further discussed in the following section.

Absorption

Among the abovementioned CO_2 capture options, the technology based on liquid absorption is most mature and commercially available, especially in the petroleum and chemical industries. Based on the nature of the interaction between the absorbent and CO_2, it separates as chemical absorption (mainly applied for CO_2 capture from post-combustion flue gas) and physical absorption (mainly used for CO_2 capture from pre-combustion flue gas). Aqueous amine solutions (e.g., 20–30 wt% MEA, and diethanolamine (DEA)) and liquid ammonia are typical solvents for chemical absorption. MEA solution has become the benchmark amine for CO_2 capture from power plants because it has good CO_2 transfer rates, relatively low cost, and biodegradable. However, it suffers from toxicity and solvent loss due to evaporation and degradation (Bui et al., 2018). In addition, at higher concentrations, MEA solution is highly corrosive to the equipment.

Developing new CO_2 absorbents to replace MEA has thus aroused much interests and is still ongoing. Normally, thermal swing absorption–regeneration is used for chemical absorption; thus, selecting an absorbent with optimized thermal and physical properties is crucial to the development of energy-efficient and cost-effective carbon capture absorption technology. So far, a large number of solvents, including single amines, amine blends, and amino acids, have been evaluated individually for their performance in CO_2 capture (Bui et al., 2018; Sreedhar et al., 2017). **Figure 4** shows the CO_2 absorption capacities in mol-CO_2

TABLE 2 | Typical CO_2 concentration of a flue gas from various sources (Metz et al., 2005; Husebye et al., 2012; Liguori and Wilcox, 2018).

Flue gas source	CO_2 conc. (%)	P (atm)	CO_2 partial pressure (atm)
Gas turbine	3–4	1	0.03–0.04
Fired boiler of oil refinery and petrochemical plant	~8	1	0.08
Natural gas fired boilers	7–10	1	0.07–0.10
Oil-fired boilers	11–13	1	0.11–0.13
Coal-fired boilers	12–14	1	0.12–0.14
IGCC[a] after combustion	12–14	1	0.12–0.14
Hydrogen production	15–20	22–27	3–5
Steel production (blast furnace)	20–27	1–3	0.2–06
Aluminum production	1–2	1	0.01–0.02
Cement process	14–33	1	0.14–0.33

[a] *IGCC, integrated gasification combined cycle. Data extracted from the literature (Figueroa et al., 2008; Chu, 2009).*

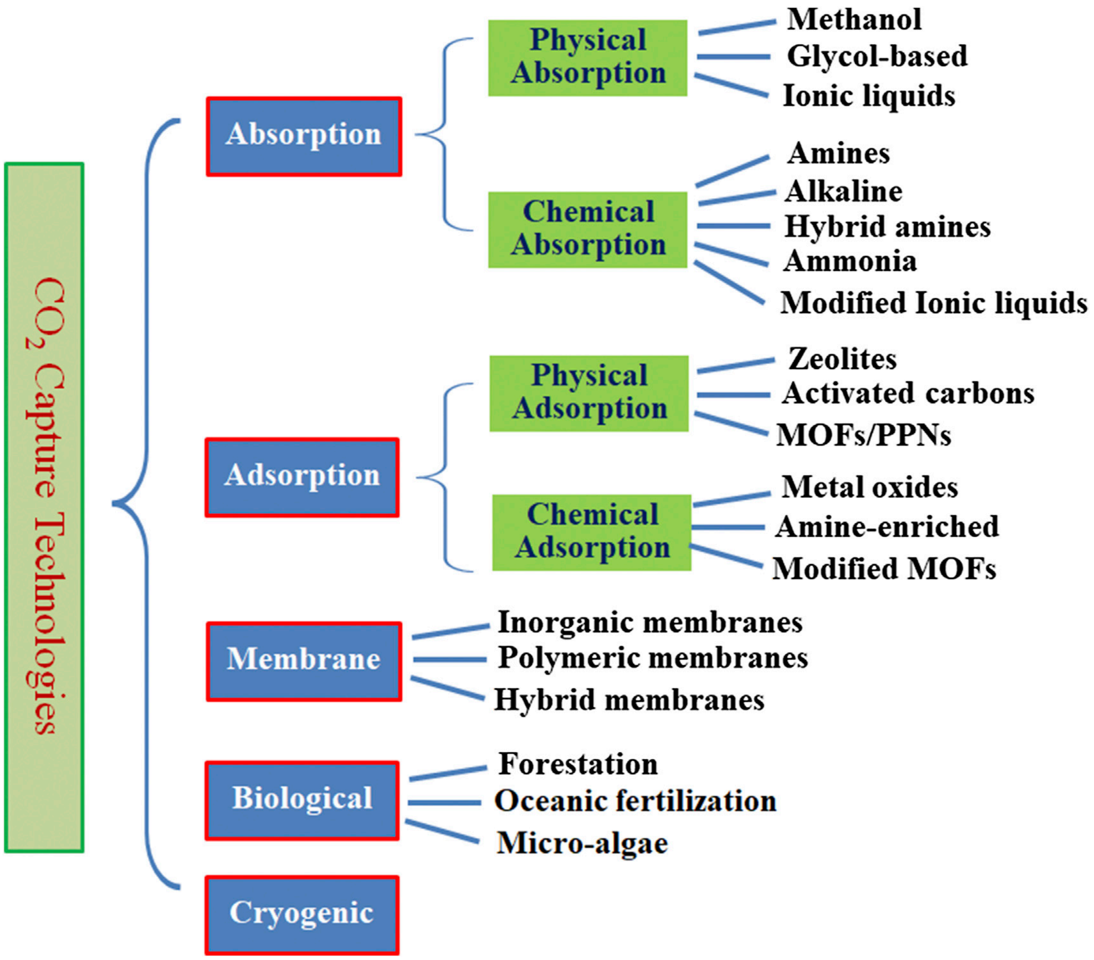

FIGURE 3 | Illustration of various CO_2 capture technologies along with typical materials currently under investigation.

per mol-amine obtained at 40°C and CO_2 partial pressure of 15 kPa using different amines with different structures at different amine concentrations (Shen and Li, 1992; Jou et al., 1995; Park et al., 2002; Benamor and Aroua, 2005; Derks et al., 2005; Maneeintr et al., 2009; Puxty et al., 2009; Chen and Rochelle, 2011; Rebolledo-Morales et al., 2011; Schäffer et al., 2012; Tong et al., 2012; Chang et al., 2013; Monteiro et al., 2013; Yamada et al., 2013; Arshad et al., 2014; Bougie and Iliuta, 2014; Li et al., 2014; Li and Rochelle, 2014; Nouacer et al., 2014; Chen S. et al., 2015; Conway et al., 2015; Mondal et al., 2015; El Hadri

TABLE 3 | Comparison of typical CO_2 capture technologies.

Technology		Mechanisms	Pros	Cons
Absorption	Chemical absorption (e.g., MEA and NaOH)	chemical reaction between a solvent and CO_2	✓High capacity at low CO_2 pressure ✓Mature technology	• Energy-intensive regeneration • Low absorption–desorption rate • Corrosion • Absorbent degradation • High operating cost
	Physical absorption (e.g.,methanol, Selexol, and Rectisol)	The solubility of CO_2 in a solvent	✓High capacity at low temperature and high pressure ✓Cheaper solvent ✓Mature technology	• Low selectivity • High energy consumption • Low capacity at high temperature and low pressure • Absorbent loss
Adsorption	Physical adsorbents (e.g., AC, zeolites, and MOF)	Molecular sieve confinement effect of solid materials, normally with micropores	✓High capacity at low temperature and high pressure ✓Low waste generation	• Low CO_2 selectivity • Capacity decreases with temperature • Normally require high pressure • Moisture degrades the adsorbent performance
	Chemical adsorbents (e.g., CaO and Na_2SiO_3)	Through the formation of carbonates or bicarbonates	✓Work at high temperature ✓High capacity	• Require high temperature for CO_2 sorption and adsorbent regeneration
	—	—	✓Low waste generation	• High energy consumption • Performance loss with cycles
	Solid amine sorbents (e.g., PEI/SiO_2)	Chemical reaction between amine groups and CO_2	✓High capacity at low CO_2 pressure ✓High selectivity ✓Fast kinetics ✓Mild conditions ✓Positive effect of moisture ✓Lower energy consumption ✓Less corrosion ✓Low waste generation	• Thermal and oxidative degradation • Degradation due to contaminants (e.g., SO_x and NO_x)
Membrane		Different gas permeability	✓Relatively low operation cost ✓Easy handling and Operation	• High manufacturing cost • Relatively low separation selectivity • Permeability still low • Negative effect of moisture
Biological absorption/utilization		Captured and utilized through photosynthesis in plants	✓No hazards of chemicals ✓Coproduction of food, biofuels, and value-added products	• Long time requirement • Large area requirement • May affect biological diversity • Sensitive to other flue gas contaminants (e.g., SO_x and NO_x) and culture conditions (pH, temperature, and salinity)
Cryogenic separation		Different condensation temperature	✓High capture efficiency (up to 99.9%)	• High energy requirement • Low efficiency • Moisture pre-removal is required • Solidified CO_2 may be accumulated on the surface of heat exchanger

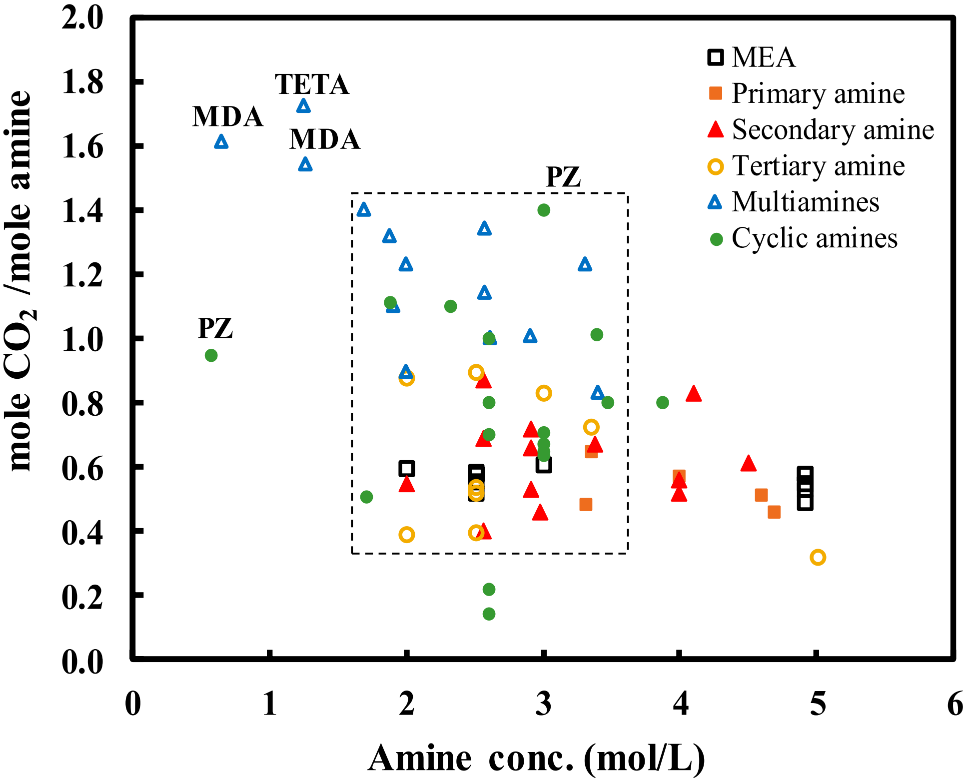

FIGURE 4 | CO_2 uptakes obtained at 40°C and CO_2 partial pressure of 15 kPa using different liquid amines with different structures at different amine concentrations. Data from the literature (Shen and Li, 1992; Jou et al., 1995; Park et al., 2002; Benamor and Aroua, 2005; Derks et al., 2005; Maneeintr et al., 2009; Puxty et al., 2009; Chen and Rochelle, 2011; Rebolledo-Morales et al., 2011; Schäffer et al., 2012; Tong et al., 2012; Chang et al., 2013; Monteiro et al., 2013; Yamada et al., 2013; Arshad et al., 2014; Bougie and Iliuta, 2014; Li et al., 2014; Li and Rochelle, 2014; Nouacer et al., 2014; Chen S. et al., 2015; Conway et al., 2015; Mondal et al., 2015; El Hadri et al., 2017).

et al., 2017). The majority were examined at the amine concentration between 2 and 3.5 mol/L. The CO_2 absorption capacity is ranged from 0.4 to 1.4 mol-CO_2/mol-amine. More specifically, for the primary, secondary, and tertiary mines in straight chains, multi-amines, and amines in cyclic chains, their capacities are in the range of 0.5–0.7, 0.4–0.8, 0.4–0.9, 0.8–1.4, and 0.5–1.1 mol-CO_2/mol-amine, respectively. The CO_2 absorption capacity decreases generally following the amine structure as cyclic amines ≈ multi-amines > tertiary-amines > secondary-amines > primary-amines. Among them, piperazine (PZ) absorbent has been suggested as a good alternative to conventional chemical solvents. Compared to MEA, it shows fast kinetics in reaction with CO_2, better chemical stability, and requires lower energy input for regeneration (Rochelle, 2009; Dugas and Rochelle, 2011). It also exhibits better resistance to oxidative and thermal degradation (Freeman et al., 2010a). Other amine blends such as PZ/AMP (Seo and Hong, 2000; Khan et al., 2016) and K_2CO_3/PZ (Tim Cullinane et al., 2005; Cullinane and Rochelle, 2006) have also been studied, and it has been found that the blending can improve the absorption kinetics, thermodynamic efficiency, and resistance to degradation. The main drawback of PZ is that it could form precipitation and nitrosamine during CO_2 capture process (Freeman et al., 2010b; Cousins et al., 2015).

There is another class of amine-based solvents which is called phase-change solvents including amine–alcohol system and amine–water system. Upon CO_2 absorption or increasing the temperature after CO_2 absorption, the solvent divides into two phases: CO_2-rich and CO_2-lean phases (Zhuang et al., 2016; Papadopoulos et al., 2019). In contrast to traditional solvents, only the CO_2-rich phase is sent for regeneration; therefore, the energy demand and the size of the regenerator can be dramatically reduced in comparison to non–phase-change solvents. Gomez et al. compared the performance of phase-change solvent process to the conventional MEA process, showing the CO_2 capture cost could be saved by 15.4% for the power plant, and as much as 51.7% for the cement plant (Gomez et al., 2014). Although the phase-change absorbent systems exhibit some potential merits and economic incentives for scaling up, they may be volatile and corrosive due to the use of amine solution in nature. The formation of precipitation and salts is another important issue for the implementation of the phase-change solvent-based absorption process.

Besides the chemisorption using amine solutions, another type of absorption technology is using physical solvents to absorb CO_2, which is based on their CO_2 solubility (Chakma, 1999). Physical absorption is generally preferred at higher pressures. Selexol, Rectisol, Purisol, and Fluor are the well-established commercial physical absorption technologies, and also energy-intensive processes due to their heat transfer requirements (Figueroa et al., 2008). Since the physical absorption is depended on physical interaction rather than chemical reaction, it normally requires higher partial pressure of CO_2 and is preferred at low temperatures in order to achieve high CO_2 capture capacity, which thus reduces its efficiency and increases its operation cost.

Recently, ionic liquids (ILs), which consist of ions and act as liquid at room temperature (Hallett and Welton, 2011), are considered as suitable alternatives to the traditional physical absorbents, because ILs have unique properties such as low volatility, low vapor pressure, and good thermal stability (Bates et al., 2002; Corvo et al., 2015; Zeng et al., 2017). In addition, after CO_2 absorption, its energy requirement for regeneration is also relatively low. **Figure 5** presents the CO_2 absorption capacities of some typical ILs (Zhang et al., 2008; Pérez-Salado Kamps et al., 2003; Shiflett and Yokozeki, 2005; Shin et al., 2008; Carvalho et al., 2010; Kilaru and Scovazzo, 2008; Anderson et al., 2007; Aki et al., 2004; Blanchard et al., 2001). As seen, the CO_2 absorption capacity varies with the type of ionic liquid. The highest value of 0.88 mol-CO_2/mol-IL (moles of CO_2 per mole of IL) was obtained with [THTDP][NTf2] ionic liquid, while the [hmpy][Tf2N] ionic liquid gave the lowest value of 0.20 mol-CO_2/mol-IL (Anderson et al., 2007). The max CO_2 solubility in ILs reported in the literature is largely within the range of 0.4–0.8 mol-CO_2/mol-IL, which is comparable to those of most aqueous amine solutions as shown in **Figure 4**. However, their high viscosities and relatively low working capacity are the two main obstacles for their application in CO_2 capture. To attain higher CO_2 capacity, a series of the so-called task-specific ILs have been designed by incorporation of various functionalities, such as carboxylate anions, amine and amino acid groups, or azolates for chemisorption of CO_2, thereby significantly boosting the absorption capacity up to about 0.5–2.0 mol-CO_2/mol-IL under atmospheric pressure (Bates et al., 2002; Giernoth, 2010; Wappel et al., 2010; Petkovic et al., 2011; Shannon and Bara, 2012; Cui et al., 2016). Several groups have also studied the physical and chemical properties of CO_2–IL systems using thermodynamic modeling (Zhang et al., 2008; de Riva et al., 2017), kinetics (Wang C. et al., 2011; Moya et al., 2014; de Riva et al., 2017) and CO_2 sorption mechanisms (Carvalho et al., 2009; Shiflett et al., 2010). Although higher capacity can be obtained, the functionalized ILs show higher viscosities than unfunctionalized ILs. Therefore, how to greatly reduce the viscosity while maintaining its high capacity is the largest technical challenge for the successful use of ILs in CCS. High cost and difficulty in scale-up are other two significant barriers to the wide spread of ILs for CCS (Singh and Dhar, 2019).

Adsorption

Adsorption is widely deemed as a promising technology for CO_2 capture as it can be retrofitted to any power plants, operated at various conditions with relatively high capacity, high CO_2 selectivity, and low energy requirement for regeneration. It can be applied for both pre- and post-combustion pathways (Bui et al., 2018). If waste materials are utilized for preparation of adsorbents, the adsorption process could be potentially more sustainable. It should also be highlighted that adsorption method is well suited for CO_2 capture directly from air.

Currently, most efforts in developing advanced adsorbents have been focused on improving CO_2 adsorption capacity, CO_2 selectivity, and impurity tolerance. So far, a large number of solid adsorbents have been investigated, including carbons and carbon nanotubes (Aaron and Tsouris, 2005; Huang et al., 2007; Plaza et al., 2007; Razavi et al., 2011), clays and oxides (Ding and Alpay, 2000; Yong et al., 2001; Gray et al., 2005; Hiyoshi et al., 2005), microporous zeolites and mesoporous molecular sieves (Takamura et al., 2001; Siriwardane et al., 2003; Son et al., 2008; Zelenak et al., 2008a), and microporous metal–organic framework materials (MOFs) (Torrisi et al., 2010; Zhang Z. et al., 2013; Gonzalez-Zamora and Ibrra, 2017).

Zeolites are widely used in refinery and gas separation industry, and have shown high CO_2 uptake such as zeolite 13X and Ca-A, reaching about 3 and 3.72 mmol/g, respectively (Bae et al., 2013). CO_2 adsorption over zeolites is derived from the interaction between the electric field of zeolite and the large quadrupole moment of CO_2. Thus, both the structure and composition of zeolite framework, and the composition and location of cations govern its CO_2 adsorption performance (Grajciar et al., 2012; Kim et al., 2012). Lin et al. screened over hundreds of thousands of zeolites and zeolitic imidazolate frameworks (ZIFs) *via* a computational approach and identified potential materials for CO_2 capture (Lin et al., 2012). The main weakness of zeolites is their sensitivity to moisture, which results in a significant reduction of CO_2 uptake (Bui et al., 2018).

MOFs are a relatively new class of crystalline porous materials constructed *via* self-assemblage of metal "nodes" and organic linkers (Long and Yaghi, 2009; Zhou et al., 2012; Lu et al., 2014). MOFs possess very high surface areas and pore volumes. Theoretically, by varying the metal and the linker, infinite different MOFs can be synthesized, and their physicochemical properties are consequently tuned in terms of CO_2 capacity, selectivity, and heat of adsorption, which makes them highly attractive for CO_2 capture (Singh et al., 2020). For example, MOF-74(Mg) showed a high CO_2 adsorption capacity of 5.5 mmol/g at 0.15 bar CO_2 and 40°C (Caskey et al., 2008; Bae et al., 2013), while UiO-66 and SIFSIX-6_Zn exhibited good resistance to other flue gas components such as water, SO_x, and NO_x (Nugent et al., 2013; Burtch et al., 2014; Wang C. et al., 2016). In a recent article, Ding et al. conducted a comprehensive review on MOFs for CO_2 capture and conversion, where they summarized and compared the reported MOFs for CO_2 capture in terms of their CO_2 capacities (Ding et al., 2019).

Carbon materials including activated carbons, carbon nanotubes, and graphene have also been studied for CO_2 capture due to their low cost and wide availability (Wang Q. et al., 2011; Montagnaro et al., 2015; Taheri Najafabadi, 2015; Mohamedali et al., 2016). The capability of carbon materials for CO_2 adsorption mainly relies on its porosity; thus, the higher the pore volume, particularly the micropores, the higher the CO_2 capacity (Estevez et al., 2018). Carbons work better at high pressure. While at low pressure, their CO_2 capacities are typically lower than those of zeolites. Compared to zeolites, carbons possess much better stability in the presence of water (Xu et al., 2013).

Another type of solid adsorbents is oxides including CaO, MgO, and FeO (Feng et al., 2007; Florin and Harris, 2009; Mutch

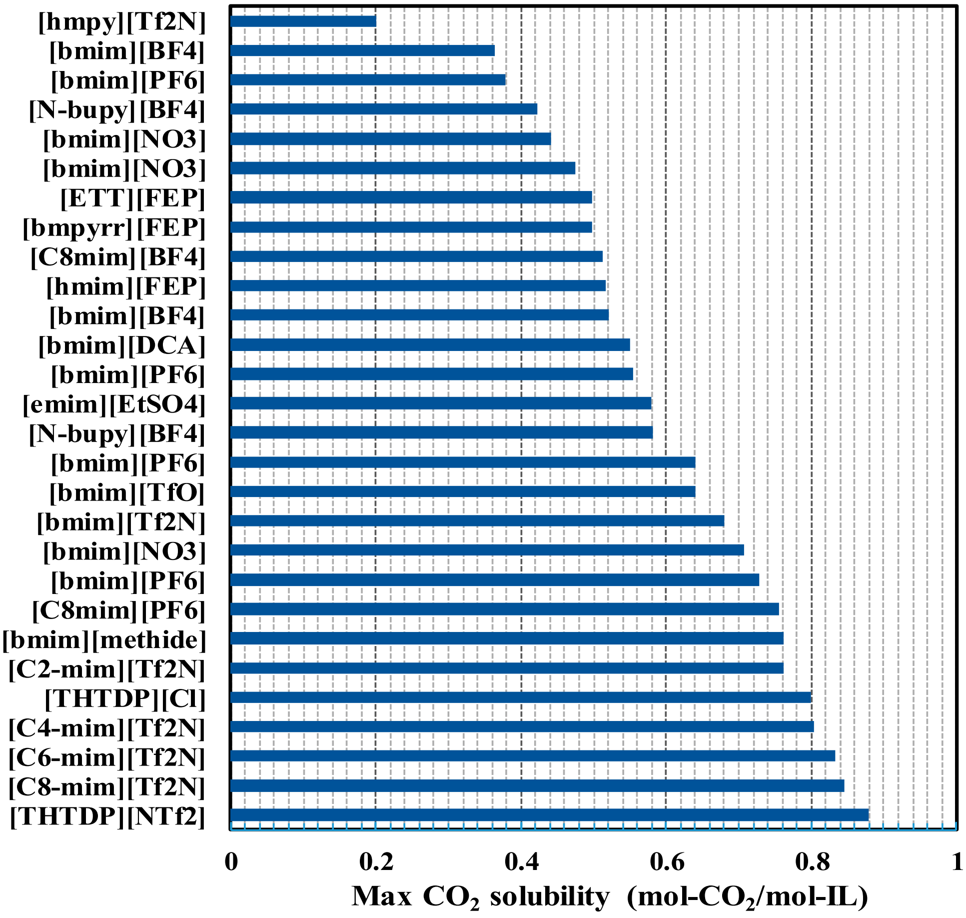

FIGURE 5 | The reported maximum CO_2 absorption capacity of some typical ionic liquids for CO_2 capture at 40°C with CO_2 partial pressure of 15 kPa, data from the literature (Zhang et al., 2008; Pérez-Salado Kamps et al., 2003; Shiflett and Yokozeki, 2005; Shin et al., 2008; Carvalho et al., 2010; Kilaru and Scovazzo, 2008; Anderson et al., 2007; Aki et al., 2004; Blanchard et al., 2001).

et al., 2018; Mora Mendoza et al., 2019); layered double hydroxides (LDHs) (Ram Reddy et al., 2006; Ram Reddy et al., 2008); and alkali metal–containing ceramics such as Li_2ZrO_3 (Nakagawa, 1998), Li_4SiO_4 (Gauer and Heschel, 2006), and Na_2SiO_3 (Rodríguez and Pfeiffer, 2008). Those adsorbents are normally handled at high temperatures within the cyclic carbonation/calcination reactors. High temperature (>500°C) causes the sintering of oxides, which results in the dramatic reduction of their CO_2 capture performance (Erans et al., 2016).

Compared to abovementioned adsorbents, amine-based solid sorbents are the center of investigation in adsorption. Since the first report on polyethylenimine (PEI)-based sorbents showing good performance for CO_2 separation, the so-called molecular basket sorbents (**Figure 6**) (Xu et al., 2002), in the past twenty years, solid sorbents containing amines, have aroused significant interests for CO_2 capture and later for CO_2 removal directly from air (Yu et al., 2012). The use of amine-functionalized sorbents can greatly reduce the need in the parasitic energy input (mainly because solid has lower heat capacity than water), and offer high CO_2 capacity and selectivity, fast kinetics, multicycle stability, and tolerance to water with no or less corrosion to the equipment (Ma et al., 2009; Choi et al., 2009; Wang et al., 2009; Bollini et al., 2011; Wang and Song, 2019). By far, three popular approaches are proceeding in preparation of those amine-based sorbents, which are outlined in **Figure 6**, including 1) immobilizing amine compounds (e.g., PEI, TEPA, DEA, and dendrimers (Wang et al., 2005; Yue et al., 2006; Liang et al., 2008; Qi et al., 2011)) onto a nanoporous support (Xu et al., 2002; Xu et al., 2003; Xu et al., 2005; Ma et al., 2009; Chen et al., 2010; Liu et al., 2010; Tanthana and Chuang, 2010; Wang D. et al., 2011; Zhang et al., 2012; Yang et al., 2013) and/or microporous zeolites (Kim et al., 2016) and MOFs (Demessence et al., 2009; Lee et al., 2014; McDonald et al., 2015) by a conventional wet impregnation method; 2) growing reactive amine monomers inside the porous material *via in situ* polymerization method or incorporating amine compounds with silica precursor during mesoporous material preparation *via* co-condensation method (Tsuda et al., 1992; Tsuda and Fujiwara, 1992; Rosenholm et al., 2006; Rosenholm and Linden, 2007; Hicks et al., 2008); and 3) covalently grafting amine compounds (e.g., (3-aminopropyl) trimethoxysilane and (3-aminopropyl)triethoxysilane) on a

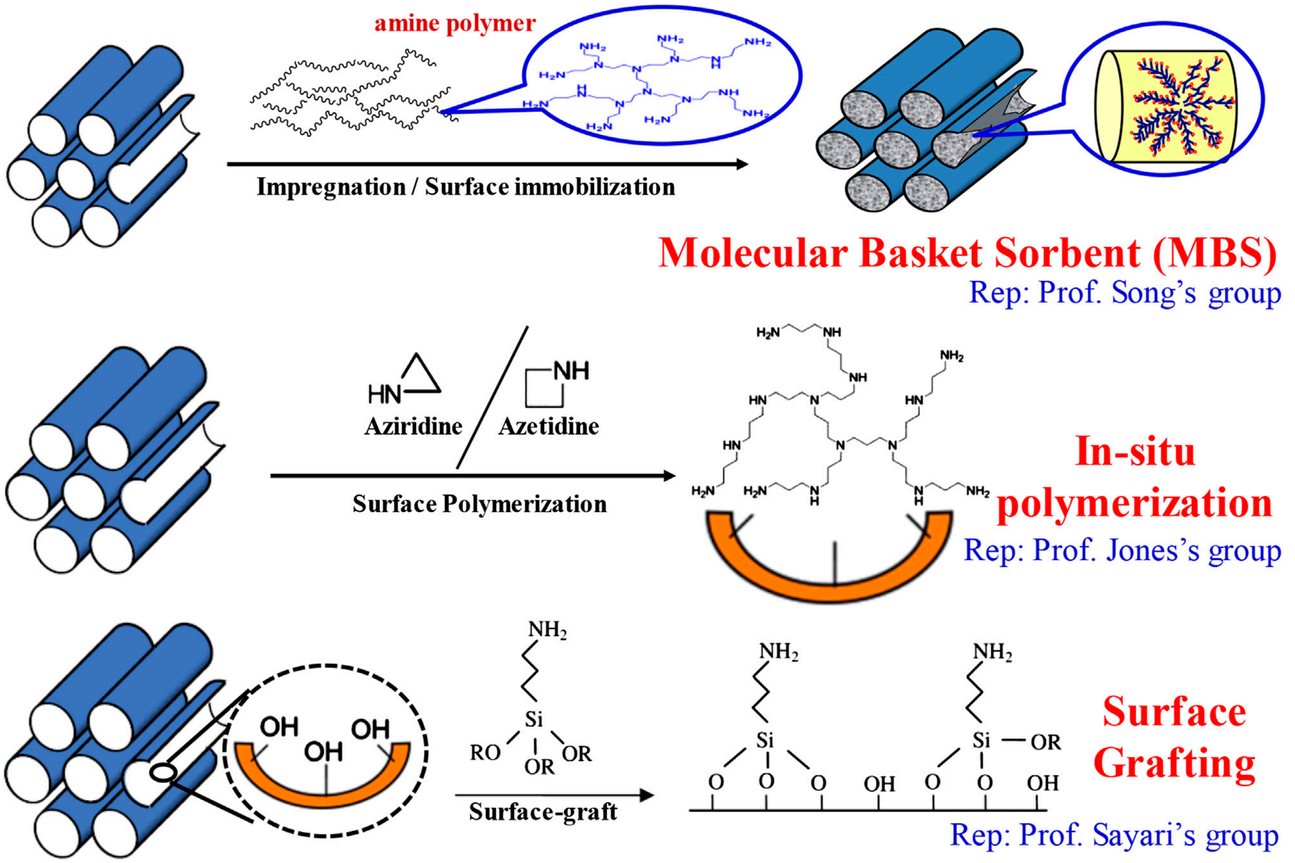

FIGURE 6 | Schematic illustration of the widely used three approaches in preparation of the amine-based sorbents.

support surface *via* post-synthesis method (Huang et al., 2003; Hiyoshi et al., 2004; Hiyoshi et al., 2005; Zelenak et al., 2008b; Belmabkhout and Sayari, 2009; Kumar and Guliants, 2010).

Polymer PEI contains repeating -CH_2CH_2-NH-units. Because it has high nitrogen content in mass and relatively good thermal stability (Yue et al., 2008; Goeppert et al., 2011), PEI is often selected for amine-based sorbents, becoming a promising candidate suitable not only for CO_2 capture from flue gases with relatively high CO_2 concentration, but also good for direct air capture. Other amines such as tetraethylenepentamine (TEPA), pentaethylenehexamine (PEHA), MEA, DEA, and diisopropanolamine are more prone to leaching issue due to their relatively low molecular weight and boiling points, which could cause CO_2 capacity loss and pollute the downstream equipment of the sorption system (Goeppert et al., 2014). Many reviews on solid-sorbent–based CO_2 capture have been published (Song, 2006; Sanz-Pérez et al., 2016; Darunte et al., 2016; Choi et al., 2009; D'Alessandro et al., 2010; Lin et al., 2016; Didas et al., 2015; Dutcher et al., 2015; Chen C. et al., 2014; Gargiulo et al., 2014; Olajire, 2017). In a recent book chapter (Wang and Song, 2019), we summarized the recent advances of solid PEI-based sorbents for CO_2 capture focusing on the development of sorbent materials, the mechanism and kinetics in CO_2 sorption, the regeneration and deactivation, and the current and future CO_2 capture approaches.

To have a better overall picture, the CO_2 capacities reported in the literature with different support at different PEI loading and sorption temperature for CO_2 capture from pure CO_2 and the simulated air containing ~400 ppm CO_2 are plotted in **Figure 7**. For CO_2 capture from pure CO_2 (**Figure 7A**), the higher the PEI loading, the higher the CO_2 uptake. Increasing temperature also benefits CO_2 sorption. Generally, high CO_2 capture capacity of around 150–200 mg/g is mostly reported, which is favored at 50–70 wt.% PEI loading at 70–90°C. The amine efficiency (termed as A.E.), which is defined as moles of CO_2 captured per mole of N groups in the sorbent, is presented as an inset in **Figure 7A**. It shows the major value of about 0.30 (the black dot line in the inset of **Figure 7A**). It is widely accepted that under dry condition, two N sites are needed for one CO_2 molecule through the formation of zwitterions. Although tertiary amine does not directly react with CO_2, it could accept the proton from zwitterions generated by the reactions between CO_2 and primary/secondary amines, contributing to CO_2 sorption. Thus, it is projected that the theoretic value for the maximum amine efficiency would be 0.5 (the blue dot line in the inset of **Figure 7A**). Clearly, most PEI-based sorbents are still not able to achieve this theoretic value, although there are a few reports showing their amine efficiency close to 0.5. Only one article reported the amine efficiency over 0.5, which was attributed to the contribution of

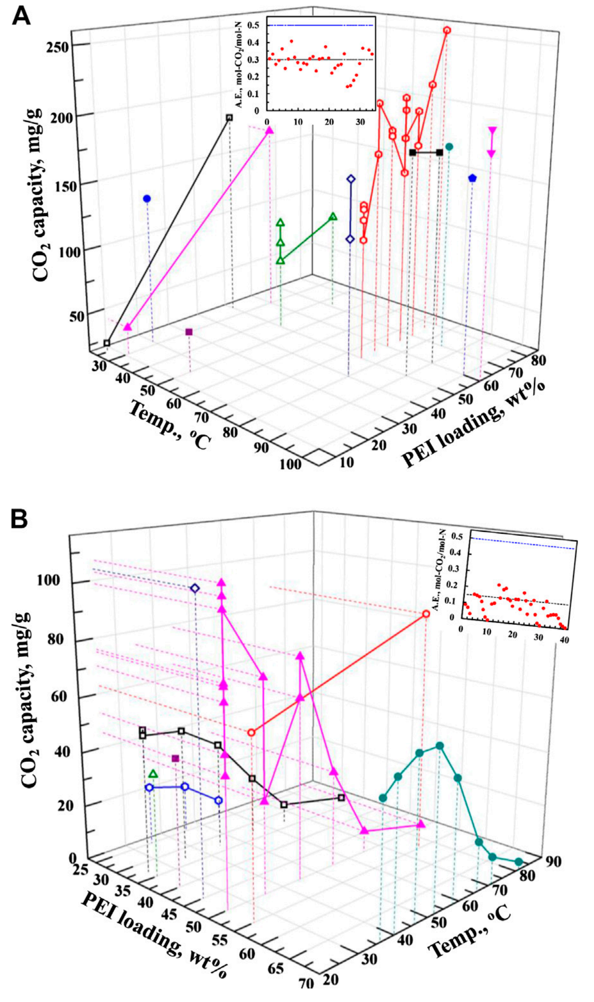

FIGURE 7 | CO_2 capacity reported in the literature with different support at different PEI loading and temperature for CO_2 capture from **(A)** pure CO_2 and **(B)** from simulated air with about 400 ppm CO_2 along with the insets showing the amine efficiency (A.E., mol-CO_2/mol-N). All data are from the reported values (Wang and Song, 2019).

CO_2 physisorption on the porous support (Gaikwad et al., 2019). As for the air capture (**Figure 7B**), most work was studied over the sorbents with PEI loading of 50 wt.% at room temperature. Unlike CO_2 capture from pure CO_2, increasing temperature results in the decrease of CO_2 uptake, making it suitable for air capture operation. Compared to those amine efficiency for pure CO_2, the amine efficiency for air capture is much lower, in between 0.05 and 0.15. It reflects that CO_2 capture directly from the air is more challenging than that from the concentrated CO_2 sources.

Figure 7 displays an indication of the current development status of the PEI-based solid sorbents. Considering the low amine efficiency compared to the theoretic value, especially for the air capture, we believe there is still a possibility to further enhance CO_2 capture from both the concentrated sources and the air. Thus, further investigations are required to determine at what level of PEI dispersion could be best for maximizing the amine efficiency with high capacity, or whether there is a limit in the amine efficiency in order to maintain the best CO_2 sorption capacity and kinetics.

With the aid of modern and advanced characterization techniques, the CO_2 sorption/deactivation mechanism over PEI-based sorbents has been fundamentally better understood. Zhang et al. studied CO_2 sorption behavior with small angle neutron scattering (SANS) technique and identified that the swelling of PEI with CO_2 sorption and temperature increase played an important role in CO_2 sorption process (Zhang et al., 2019). Using solid-state nuclear magnetic resonance (SSNMR), Mafra et al. (Mafra et al., 2017) found three chemisorbed CO_2 species involving hydrogen bonds with either surface silanols or amines. Chen et al. (2018) confirmed the formation of bicarbonate in the presence of water. During CO_2 sorption, both carbamate and carbamic acid are formed (Foo et al., 2017; Shimon et al., 2018), but only carbamic acid desorbs while carbamate persists (Shimon et al., 2018). The formation of C=O and −CH = N- species is a main reason for the air degradation of amine sorbents (Ahmadalinezhad and Sayari, 2014). To improve the regeneration and long-term stability of PEI-based sorbents, a two-step synthesis strategy involving support modification followed by PEI loading has been proposed and studied (Choi et al., 2016; Jeon et al., 2018; Min et al., 2018a; Min et al., 2018b; Xu et al., 2018; Kim et al., 2019; Wang et al., 2020), which have been summarized and elaborated in our recent book chapter (Wang and Song, 2019).

Additionally, there has been important progress in the development of adsorption processes for CO_2 capture. A large number of different cyclic regeneration processes using temperature, pressure, vacuum, steam or moisture, or combinations thereof have been studied. Recently, Inventys Inc. (now is Svante Inc.) reported the VeloxoTherm™ process using a rotary unit packed with structured honeycomb adsorbent for both CO_2 adsorption and desorption, which can complete a full cycle in about 60 s (Greeson, 2016). The comprehensively review of the development of these processes can be found in the literature (Grande and Rodrigues, 2008; Webley, 2014).

It should be pointed out that with the advance of the technologies, some novel structured CO_2 adsorbents have emerged, such as thin film nanocomposites (Shah and Imae, 2016; Yong, 2016; Niranjana et al., 2019) and adsorbent-coated monoliths made of zeolites, MOFs, or carbons (Öhrman et al., 2004; Ramos-Fernandez et al., 2011; Akhtar et al., 2014; Lee et al., 2015). Monolithic contactors have substantial advantages like uniform flow, high gas throughput, low pressure drop, and less attrition in comparison with conventional packed-bed reactors (Rezaei and Webley, 2009; Rezaei and Webley, 2010). Both the diameter of the parallel channels and the density per cross-sectional area of monoliths are controllable. Most recently, three-dimensional (3D) printing or additive manufacturing technique has gained worldwide attention and has been applied for fabrication of 3D-printed monoliths including zeolites (e.g., 5A and 13X) and MOFs (MOF-74-Ni and UTSA-16-Co (Thakkar et al., 2016; Thakkar et al., 2017a; Thakkar et al., 2017b; Thakkar et al., 2018; Nguyen et al., 2019; Regufe et al., 2019; Thompson et al., 2019). Compared to those prepared by conventional method, the 3D-printed adsorbent materials exhibited comparable CO_2 capacity, fast adsorption rate, and relative stability and regenerability. Although 3D-printing shows flexibility in material design and requires less steps and resources, extensive study on fabricating the adsorbent materials at large scale for carbon capture is needed.

Membrane

Compared to other separation methods, membrane separation is generally more energy efficient and environmentally benign, thus has been much studied for CO_2 removal from flue gases (Merkel et al., 2010; Japip et al., 2014). In membrane separation, the driving force is the pressure and/or concentration difference. The higher the pressure difference, the better the membrane separation. Therefore, it is more applicable to pre-combustion capture processes, while it is quite challenging for post-combustion capture due mainly to the low CO_2 partial pressure and/or concentration in the post-combustion flue gases. Furthermore, unlike other methods, membrane separation involves multistage operation and streams recycling, which makes this method more complicated and complex.

Based on the properties of the fabrication materials, there are three types of membranes in general (Powell and Qiao, 2006; Low et al., 2013): inorganic (or ceramic), organic (or polymeric), and hybrid membranes. Those made up of zeolites, oxides (e.g., Al_2O_3, TiO_2, and ZrO_2), ceramics, carbons, and MOFs are typical inorganic membranes (Al-Mamoori et al., 2017). Inorganic membranes are capable of high temperature operation with good mechanical stability, but high fabrication cost limits their scale-up (Al-Mamoori et al., 2017). Compared to inorganic membranes, polymeric membranes have several advantages including ease of synthesis, low production cost, good mechanical stability, and excellent separation performance (Songolzadeh et al., 2014). Thus, more and more polymeric membranes are practically replacing inorganic membranes in large-scale industrial gas separation processes (Bernardo et al., 2009), and gradually dominating most commercial membranes (Siagian et al., 2019). However, their thermal stability is relatively low, which curbs their application in post-combustion CO_2 capture. Flue gases normally have to be cooled down first for membrane process (Du et al., 2011; Favre, 2011). The separation performance of polymeric membrane materials can be further improved by incorporating or blending organic or inorganic compounds (Du et al., 2011; Dai et al., 2019).

Recently, new types of polymeric membranes have been developed, for example, thermally rearranged (TR) and intrinsic microporosity polymeric (PIM) membranes. TR membranes exhibit improved thermal stability through structural rearrangement and molecular transformation during the heat treatment, which can generate interconnected microcavities with narrow size distribution, decreasing the mechanical strength of TR membranes (Jo et al., 2015; Liu Q. et al., 2016; Scholes, 2016). PIM membranes are promising for CO_2 capture as they exhibit high CO_2 permeability and selectivity, surpassing the Robeson's upper bond due largely to their pore structure, thus receiving much attention (Alaslai et al., 2016; Yong et al., 2016; Gemeda et al., 2017). Siagian et al. compared various polymeric membranes in terms of CO_2/N_2 selectivity vs. the permeability (Siagian et al., 2019). The conventional polymers are not able to reach the desired performance for CO_2 separation. The performance of TR membranes is close to the Robeson's upper bond, while some of PIM membranes show the performance above the Robeson's upper value, suggesting PIM membranes are more promising than TR membranes for CO_2 removal. However, more tests are needed for these new membranes to be practical for CO_2 capture in industries.

Hybrid membrane, or mixed matrix membrane (MMM), which normally consists of an inorganic component such as zeolites, carbon nanotubes, silicates, alumina, or MOFs incorporated into the polymer matrix in the nanoparticles form (Vinoba et al., 2017; Ahmad et al., 2018; Sarfraz and Ba-Shammakh, 2018; Dilshad et al., 2019; Julian et al., 2019), is becoming a new trend to improve polymeric membranes' properties, as it could possess both advantages of inorganic and organic materials. Incorporating inorganic particles improves both the mechanical and thermal properties, making the polymeric membranes more stable. Thus, it provides a solution to go beyond the restraint of polymeric membranes and the inherent drawbacks of inorganic membranes in cost and production (Ramasubramanian et al., 2012; Tanh Jeazet et al., 2012; Bae and Long, 2013). MMM membranes show the potential to exceed the Robeson's upper value and are comparable to the PIM membranes. The main drawback for MMM membranes is that inorganic particles could be poorly dispersed, even aggregated within the polymer matrix, leading to membrane defects, deteriorating its overall performance (Zhang Y. et al., 2013; Siagian et al., 2019). In addition, they are under early development along with costly and complex fabrication processes (Ramasubramanian and Ho, 2011).

A new type of MMM membranes called facilitated transport hybrid membranes (FTHMs) or fixed carrier membranes (FCMs) has been proposed and studied (Wu et al., 2014). By incorporating the polymeric matrix with functional groups, it exhibits fairly high CO_2 permeability, CO_2 selectivity, and material stability (Wang S. et al., 2016), thus is promising as next-generation membrane for CO_2 separation. For example, at 107°C and 15 bar, the CO_2 permeability and the CO_2/N_2 selectivity of the FCM containing amino-functionalized multi-wall carbon nanotubes was 975 Barrer and 384, respectively (Ansaloni et al., 2015). The CO_2 permeance of 5693 GPU and CO_2/N_2 selectivity of 268 were reported over the FCM incorporated with nanosized hydrotalcite in PEI–epichlorohydrin copolymer (PEIE) at around 25°C and 1.1 bar (Liao et al., 2014). Similar to other MMM membranes, one of the biggest challenges for industrial application of FCMs is to prepare the membranes without defects and the use of nanosized carriers without agglomeration.

Besides the membrane materials, the configuration of membrane modules is also crucial. There are four main types of modular configurations mostly adopted: tubular, plate-and-frame (Martín, 2016; Berk, 2018), spiral wound (Qi and Henson, 1998; Chen X. et al., 2015; Liu C. et al., 2016), and hollow fiber (Yoshimune and Haraya, 2013; Chen X. et al., 2015; Esposito et al., 2015; Liu C. et al., 2016). Compared to other types of modules, hollow-fiber membranes exhibit better popularity and more compact because of its optimum geometry and high surface-to-volume ratio (Koros, 2004; Al-Mamoori et al., 2017; Wang Y. et al., 2017). Furthermore, highly porous polymeric substructures supporting a thin selective layer of hollow fiber membranes show the potential in advancing the development of membranes (Chen H. et al., 2014).

FUTURE CONSIDERATION OF CARBON CAPTURE TECHNOLOGIES

Combination of Flue Gas Recycling and Hybrid Capture

The current development of CO_2 capture processes has largely centered on a single separation technology. Although numerous optimizations in materials and processes have been pursued, implementing a single separation process (e.g., aqueous amine-based chemical absorption) is either energy intensive or costly. Only few studies have looked at integrating two or more technologies (i.e., absorption, adsorption, membrane, and cryogenic) into a hybrid process for CO_2 capture (Freeman et al., 2014). The integration of different separation technologies could avoid their individual disadvantages, thus may be superior to the standalone process (Scholz et al., 2013).

Recently, Song et al. reviewed the hybrid CO_2 capture technologies and explored possible combinations (Song et al., 2018), including absorption-, adsorption-, membrane-, and cryogenic-based hybrid processes with different options. Nakhjiri and Heydarinasab compared the performance of the hybrid membrane absorption process using ethylenediamine (EDA), 2-(1-piperazinyl)-ethylamine (PZEA), and potassium sarcosinate (PS) absorbents (Nakhjiri and Heydarinasab, 2019). They found that the CO_2 separation efficiency decreases as PZEA > PS > EDA. Atlaskin et al. (Atlaskin et al., 2020) studied a hybrid membrane-assisted gas absorption (MAGA) process for CO_2 and H_2S removal. The efficiency for CO_2/H_2S separation was significantly increased by mixing imidazolium ionic liquid (ca. 5 v %) into the methyldiethanolamine (MDEA) solution. Over the hybrid membrane absorption system using 2-methylpiperazine (2MPZ)-promoted potassium carbonate for CO_2 separation, increasing 2MPZ concentration, absorbent flow rate, porosity to tortuosity ratio, and membrane fibers can enhance the CO_2 removal percentage up to over 98% (Izaddoust and Keshavarz, 2017; Mesbah et al., 2019). Scholes et al. recently reported the pilot plant trials with hollow fiber membrane-MEA (MEA, 30 wt %) contactor for post-combustion CO_2 capture, showing the energy duty less than 4.2 GJ/ton of CO_2 captured (Scholes et al., 2020). Through the comparison to the standalone methods, they found that the hybrid processes are superior in terms of CO_2 recovery, energy penalty, and installation investment, thus are promising as future carbon capture technology (Song et al., 2018).

As above-pointed out, the high energy penalty for CO_2 capture process is mainly caused by the low concentration or partial pressure of CO_2 in a flue gas, which results in high cost for CCS, as the capture step accounts for about 70–80% of the overall CCS cost (Figueroa et al., 2008). As shown in **Table 2**, the typical CO_2 concentration in flue gases is about 3–14%. The current prevail economic analysis estimates a cost of \$70–100/tonne-CO_2 for carbon capture from flue gas (Vitillo et al., 2017). With only 400 ppm CO_2 in air, a DACC process requires a cost between \$300 and \$1,500 per tonne of CO_2 captured (National Academies of Sciences, Engineering, and Medicine, 2019). One viable strategy is to increase the partial pressure or concentration of CO_2 in flue gas. For example, through exhaust gas recycling, in which flue gas from natural gas boiler (containing ~4% CO_2) is recycled and used in place of air for the fuel combustion, CO_2 concentration in the flue gas can be enriched up to ~8%, making CO_2 capture less thermodynamically challenging (Vaccarelli et al., 2014). However, considering the significant capital investment in exhaust gas recycling with respect to the combustion unit, the balance between exhaust gas recycling and carbon capture energy penalty has to be carefully and thoroughly examined and optimized (Vaccarelli et al., 2014).

Membranes can also be utilized to concentrate CO_2 from flue gas for recycling. Merkel et al. obtained up to 20% increase in CO_2 concentration and up to 40% reduction in the minimum energy required for CO_2 capture (Merkel et al., 2013). A set of membranes in series or parallel may be used for selective CO_2 recycling, offering increased driving force for CO_2 separation. It could be more efficient if coupled with other capture technologies (e.g., absorption, adsorption, and cryogenics), especially with those hybrid systems.

Although it could increase capital and maintenance costs, recycling flue gas or pre-concentrating CO_2 with membranes can simplify the CO_2 capture process. By combining the advantages of hybrid CO_2 capture systems, we believe that the benefits in the subsequent CO_2 capture step could be substantial, which may ultimately make this approach more energy efficient and cost effective. Although currently the experimental data are not enough, the primary results have convinced us that the proposed concept would be plausible as future CCS direction, especially to overcome the technical bottlenecks encountered when using single carbon capture technology.

One-Step Integrated CO_2 Capture and Conversion

Another encouraging strategy is integrating the CO_2 capture and conversion in one stage. In nature, organisms or organelles indeed systematically utilize and store CO_2 directly. However, compared to chemical-based approaches, they are much limited by the long time and large contact area requirements (**Table 3**). When CO_2 capture is integrated directly with subsequent *in situ* CO_2 utilization/conversion to value-added products in one step, the concept of which is depicted in **Figure 8**, the process could eliminate the needs of the steps for CO_2 desorption, compression, transportation, and storage, eradicating the energy penalty associated with these steps. It is particularly useful to the

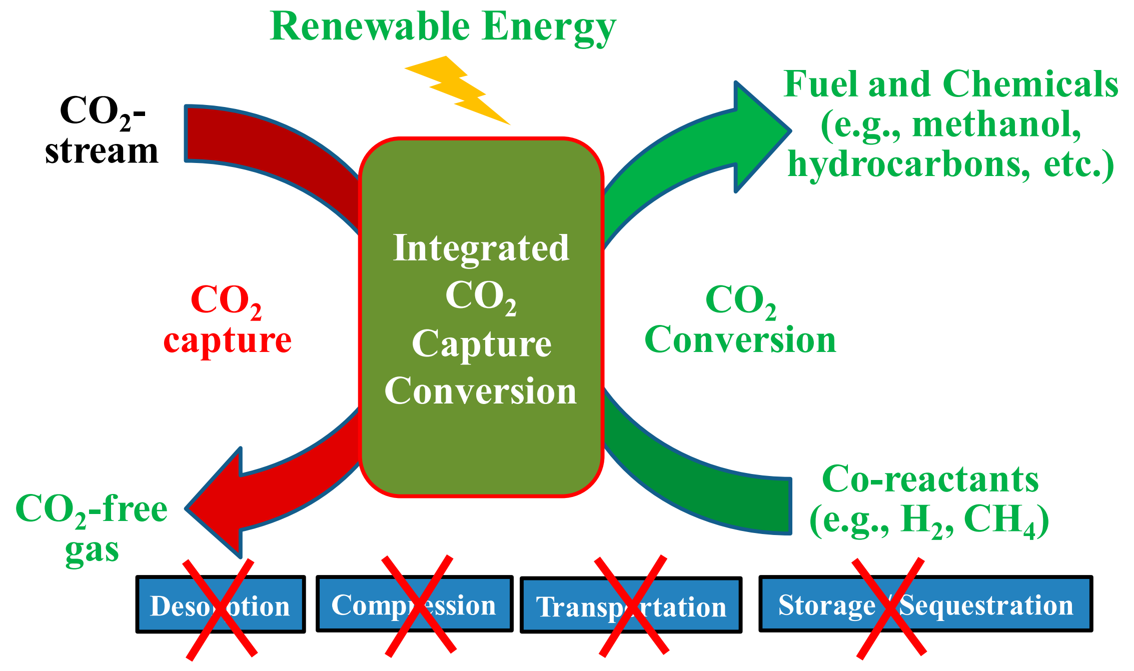

FIGURE 8 | Concept of one step direct integration of CO_2 capture and *in situ* CO_2 conversion.

chemical absorption-based CO_2 capture technologies, where the significant energy penalty occurs at the desorption step. Furthermore, the production of value-added chemicals and fuels could generate revenues to compensate the cost for carbon capture, which helps reducing the economic barrier for the commercial deployment of the CO_2 capture technologies. This is also a pathway to functionalizing metal–organic frameworks, electrocatalysts, photocatalysts, and more—for their potential applications in CO_2 capture and conversion.

Recent years, more reports about the one-step integration of CO_2 capture and conversion are coming out. Gassner and Leitner first reported the attempt to integrate catalytic CO_2 conversion to capture *via* CO_2 hydrogenation to formate in the presence of aqueous amine solutions (Gassner and Leitner, 1993). He et al. explored a combined system containing a superbase, a poly (ethylene glycol) (PEG), ionic liquid and amino acid for *in situ* CO_2 capture-conversion to carbonates, urea, and formate salts (Yang et al., 2011a; Yang et al., 2011b; Liu et al., 2012). Kim et al. experimentally demonstrated a process directly integrating CO_2 utilization into CO_2 capture, allowing for the full conversion of the CO_2 captured into syngas in a single reactor using limestone for CO_2 capture and a non-precious metal catalyst for CO_2 conversion with CH_4 (Kim et al., 2018). Liu et al. developed a novel hybrid MgAl(LDO)/TiO_2 adsorbent/photocatalyst for the integrated CO_2 capture plus photocatalytic conversion directly to C1 products at 100–200°C (Liu et al., 2015). The regeneration of the developed material can be easily achieved with low-grade waste heat and/or solar energy (Liu et al., 2015). Kar et al. systematically reviewed the current progress in the integrated capture-conversion process using aqueous amine and hydroxide solutions for CO_2 capture followed by *in situ* hydrogenation using coexisted homogeneous metal complex catalysts to formate salts and methanol (Kar et al., 2019). The whole process is regenerable for multiple cycles. Consequently, they suggested that the amine-assisted CO_2 capture and conversion to methanol process is very encouraging. Stuardi et al. also suggested the integration of CO_2 capture and utilization as a priority research direction (Marocco Stuardi et al., 2019).

Besides the liquid amine processes, the solid adsorbent catalyst-based CO_2 capture-conversion processes using dual function materials (DFMs) consisting of the methanation catalyst (e.g., Ru and Ni) and CO_2 adsorbent (e.g., CaO, Na_2O, and MgO) on a support have also been studied at mild conditions (200–350°C and 1 atm) (Duyar et al., 2015; Duyar et al., 2016; Miguel et al., 2017; Wang S. et al., 2017; Wang et al., 2018; Arellano-Treviño et al., 2019; Zhou et al., 2020).Those DFMs exhibit stable performance in CO_2 capture and conversion to synthetic CH_4 for over 50 cycles. No loss in CO_2 capture capacity and Ru dispersion was observed (Wang et al., 2018). Over the 2D-layered Ni–MgO–Al_2O_3 nanosheets, continuous and nearly 100% capture of CO_2 during prolonged cycling tests was achieved at temperatures below 250°C (Zhou et al., 2020). Its hydrogen efficiency reached 60% for CO_2 conversion to CH_4, making the process attractive for large CO_2 emission sources.

Patterson et al. proposed an approach to recycle atmospheric CO_2 into liquid fuels on a large-scale marine-based artificial island, using renewable energy (solar or wind) to power the production of hydrogen and CO_2 extraction from seawater, followed by catalytic conversion to liquid methanol fuel (Patterson et al., 2019). The major advantage of the proposed approach is the utilization of sea as the CO_2 absorber, in which it is always in equilibrium with the atmosphere, along with the usage of renewable energy, generating negative CO_2 emission through the process.

These efforts in the integration of CO_2 capture and conversion in one step have demonstrated their promise, although mainly C1 products are generated. Through the research entailing experimental results coupled with theory to improve fundamental understanding, and the design of innovative polyfunctional and multi-structured materials for the one-step integrated CO_2 capture and conversion, the production of liquid hydrocarbon fuels, chemicals, polymers, carbon materials (e.g., nanotubes and nanofibers) directly from flue gas or atmospheric CO_2 can be envisaged in future. It will also lead to developing carbon capture technologies with smaller size, greener process, and better energy efficiency. If implemented, it could significantly change the way in CO_2 capture, compress, transport, conversion, and/or storage, thus increasing opportunities for CO_2 valorization, and offer a feasible solution to the current global environmental problems associated with energy use.

CONCLUDING REMARKS

Through the past few decades of research and development, there have been significant progresses in CO_2 capture technologies, but still far from economically attractive commercialization. It requires a comprehensive investigation on the characteristics and relationships of the materials and process performance, which is crucial to the development of next-generation carbon capture technologies with improved energy efficiency and cost-effectiveness. In this perspective, we believe the two plausible approaches, that is, the combination of flue gas recycling and hybrid capture system, and one-step integration of CO_2 capture and conversion, are promising for future research, as they could offer significant improvement in energy efficiency and cost-effectiveness, by simplifying the capture process in the former and eliminating the desorption, compression, transportation, and storage steps in the latter, respectively. However, more research and development such as materials development, synergistic assessment, process design, process optimization, and scale-up are required. Their environmental impacts and the life-cycle analysis should also be considered. Nonetheless, the proposed and emerging approaches appear to be promising with better commercial potential in the future, and offer a viable solution to the technical bottlenecks of current carbon capture technologies, and to the global dilemma in meeting more energy demand while reducing environmental impact.

AUTHOR CONTRIBUTIONS

All authors listed have made a substantial, direct, and intellectual contribution to the work and approved it for publication.

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REFERENCES

Aaron, D. and Tsouris, C. (2005). Separation of CO_2 from flue gas: a review. *Sep. Sci. Technol.* 40, 321–348. doi:10.1081/SS-200042244

Abanades, J. C., Arias, B., Lyngfelt, A., Mattisson, T., Wiley, D. E., Li, H., et al. (2015). Emerging CO_2 capture systems. *Int. J. Greenh. Gas Control.* 40, 126–166. doi:10.1016/j.ijggc.2015.04.018

Adanez, J., Abad, A., Garcia-Labiano, F., Gayan, P., and de Diego, L. F. (2012). Progress in chemical-looping combustion and reforming technologies. *Prog. Energy Combust. Sci.* 38, 215–282. doi:10.1016/j.pecs.2011.09.001

Ahmad, M. Z, Navarro, M., Lhotka, M., Zornoza, B., Téllez, C., de Vos, W. M., et al. (2018). Enhanced gas separation performance of 6FDA-DAM based mixed matrix membranes by incorporating MOF UiO-66 and its derivatives. *J. Membr. Sci.* 558, 64–77. doi:10.1016/j.memsci.2018.04.040

Ahmadalinezhad, A. and Sayari, A. (2014). Oxidative degradation of silica-supported polyethylenimine for CO_2 adsorption: insights into the nature of deactivated species. *Phys. Chem. Chem. Phys.* 16, 1529–1535. doi:10.1039/c3cp53928h

Akhtar, F., Keshavarzi, N., Shakarova, D., Cheung, O., Hedin, N., and Bergström, L. (2014). Aluminophosphate monoliths with high CO_2-over-N_2 selectivity and CO_2 capture capacity. *RSC Adv.* 4, 55877–55883. doi:10.1039/C4RA05009F

Aki, S. N. V. K., Mellein, B. R., Saurer, E. M., and Brennecke, J. F. (2004). High-pressure phase behavior of carbon dioxide with imidazolium-based ionic liquids. *J. Phys. Chem. B* 108, 20355–20365. doi:10.1021/jp046895

Alaslai, N., Ghanem, B., Alghunaimi, F., and Pinnau, I. (2016). High-performance intrinsically microporous dihydroxyl-functionalized triptycene-based polyimide for natural gas separation. *Polymer* 91, 128–135. doi:10.1016/j.polymer.2016.03.063

Al-Mamoori, A., Krishnamurthy, A., Rownaghi, A. A., and Rezaei, F. (2017). Carbon capture and utilization update. *Energy Technol.* 5, 834–849. doi:10.1002/ente.201600747

Anderson, J. L., Dixon, J. K., and Brennecke, J. F. (2007). Solubility of CO_2, CH_4, C_2H_6, C_2H_4, O_2, and N_2 in 1-hexyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide: comparison to other ionic liquids. *Accounts Chem. Res.* 40, 1208–1216. doi:10.1021/ar7001649

Ansaloni, L., Zhao, Y., Jung, B. T., Ramasubramanian, K., Baschetti, M. G., and Ho, W. S. W. (2015). Facilitated transport membranes containing amino-functionalized multi-walled carbon nanotubes for high-pressure CO_2 separations. *J. Membr. Sci.* 490, 18–28. doi:10.1016/j.memsci.2015.03.097

Arellano-Treviño, M. A., He, Z., Libby, M. C., and Farrauto, R. J. (2019). Catalysts and adsorbents for CO_2 capture and conversion with dual function materials: limitations of Ni-containing DFMs for flue gas applications. *J. CO_2 Util.* 31, 143–151. doi:10.1016/j.jcou.2019.03.009

Arshad, M. W., Svendsen, H. F., Fosbøl, P. L., Von Solms, N., and Thomsen, K. (2014). Equilibrium total pressure and CO_2 solubility in binary and ternary aqueous solutions of 2-(Diethylamino)ethanol (DEEA) and 3-(Methylamino) propylamine (MAPA). *J. Chem. Eng. Data* 59, 764–774. doi:10.1021/je400886w

Atlaskin, A. A., Kryuchkov, S. S., Yanbikov, N. R., Smorodin, K. A., Petukhov, A. N., Trubyanov, M. M., et al. (2020). Comprehensive experimental study of acid gases removal process by membrane-assisted gas absorption using imidazolium ionic liquids solutions absorbent. *Sep. Purif. Technol.* 239, 116578. doi:10.1016/j.seppur.2020.116578

Azarabadi, H. and Lackner, K. S. (2020). Postcombustion capture or direct air capture in decarbonizing US natural gas power? *Environ. Sci. Technol.* 54, 5102–5111. doi:10.1021/acs.est.0c00161

Bae, T.-H. and Long, J. R. (2013). CO_2/N_2 separations with mixed-matrix membranes containing Mg2(dobdc) nanocrystals. *Energy Environ. Sci.* 6, 3565–3569. doi:10.1039/c3ee42394h

Bae, T.-H., Hudson, M. R., Mason, J. A., Queen, W. L., Dutton, J. J., Sumida, K., et al. (2013). Evaluation of cation-exchanged zeolite adsorbents for post-combustion carbon dioxide capture. *Energy Environ. Sci.* 6, 128–138. doi:10.1039/C2EE23337A

Bates, E. D., Mayton, R. D., Ntai, I., and Davis, J. H. (2002). CO_2 capture by a task-specific ionic liquid. *J. Am. Chem. Soc.* 124, 926–927. doi:10.1021/ja017593d

Belmabkhout, Y. and Sayari, A. (2009). Effect of pore expansion and amine functionalization of mesoporous silica on CO_2 adsorption over a wide range of conditions. *Adsorpt.-J. Int. Adsorpt. Soc.* 15, 318–328. doi:10.1007/s10450-009-9185-6

Benamor, A. and Aroua, M. K. (2005). Modeling of CO_2 solubility and carbamate concentration in DEA, MDEA and their mixtures using the Deshmukh-Mather model. *Fluid Phase Equil.* 231, 150–162. doi:10.1016/j.fluid.2005.02.005

Berk, Z. (2018). "Membrane processes," in *Food process engineering and technology*. 3rd Edn, Editors Z. Berk (Cambridge, MA: Academic Press), Chap. 10, 261–287

Bernardo, P., Drioli, E., and Golemme, G. (2009). Membrane gas separation: a review/state of the art. *Ind. Eng. Chem. Res.* 48, 4638–4663. doi:10.1021/ie8019032

Bhown, A. S., Bromhal, G., and Barki, G. (2020). "CO_2 capture and sequestration," in *Fossil energy*. Editors R. Malhotra (New York, NY: Springer), 503–517

Blanchard, L. A., Gu, Z., and Brennecke, J. F. (2001). High-pressure phase behavior of ionic liquid/CO_2 systems. *J. Phys. Chem. B* 105, 2437–2444. doi:10.1021/jp003309d

Bollini, P., Didas, S. A., and Jones, C. W. (2011). Amine-oxide hybrid materials for acid gas separations. *J. Mater. Chem.* 21, 15100–15120. doi:10.1039/C1JM12522B

Bougie, F. and Iliuta, M. C. (2014). Solubility of CO_2 in and density, viscosity, and surface tension of aqueous 2-amino-1,3-propanediol (serinol) solutions. *J.Chem. Eng. Data* 59, 355–361. doi:10.1021/je4008298

Brovkin, V., Sitch, S., Von Bloh, W., Claussen, M., Bauer, E., and Cramer, W. (2004). Role of land cover changes for atmospheric CO_2 increase and climate change during the last 150 years. *Global Change Biol.* 10, 1253–1266. doi:10.1111/j.1365-2486.2004.00812.x

Bui, M., Adjiman, C. S., Bardow, A., Anthony, E. J., Boston, A., Brown, S., et al. (2018). Carbon capture and storage (CCS): the way forward *Energy Environ. Sci.* 11, 1062–1176. doi:10.1039/c7ee02342a

Burtch, N. C., Jasuja, H., and Walton, K. S. (2014). Water stability and adsorption in metal–organic frameworks. *Chem. Rev.* 114, 10575–10612. doi:10.1021/cr5002589

Carbon Engineering (2020). Carbon engineering website. Available at: https://carbonengineering.com/ (Accessed July 15, 2020).

Carvalho, P. J., Álvarez, V. H., Schröder, B., Gil, A. M., Marrucho, I. M., Aznar, M., et al. (2009). Specific solvation interactions of CO_2 on acetate and trifluoroacetate imidazolium based ionic liquids at high pressures. *J. Phys. Chem. B* 113, 6803–6812. doi:10.1021/jp901275b

Carvalho, P. J., Álvarez, V. H., Marrucho, I. M., Aznar, M., and Coutinho, J. A. P. (2010). High carbon dioxide solubilities in trihexyltetradecylphosphonium-based ionic liquids. *J. Supercrit. Fluids* 52, 258–265. doi:10.1016/j.supflu.2010.02.002Get

Caskey, S. R., Wong-Foy, A. G., and Matzger, A. J. (2008). Dramatic tuning of carbon dioxide uptake via metal substitution in a coordination polymer with cylindrical pores. *J. Am. Chem. Soc.* 130, 10870–10871. doi:10.1021/ja8036096

Chakma, A. (1999). Formulated solvents: new opportunities for energy efficient separation of acid gases. *Energy Sources* 21, 51–62. doi:10.1080/00908319950014957

Chang, Y. C., Leron, R. B., and Li, M. H. (2013). Equilibrium solubility of carbon dioxide in aqueous solutions of (diethylenetriamine + piperazine). *J. Chem. Thermodyn.* 64, 106–113. doi:10.1016/j.jct.2013.05.005

Chatterjee, S. and Huang, K.-W. (2020). Unrealistic energy and materials requirement for direct air capture in deep mitigation pathways. *Nat. Commun.* 11, 3287. doi:10.1038/s41467-020-17203-7

Chen, X. and Rochelle, G. T. (2011). Aqueous piperazine derivatives for CO_2 capture: accurate screening by a wetted wall column. *Chem. Eng. Res. Des.* 89, 1693–1710. doi:10.1016/j.cherd.2011.04.002

Chen, C., Son, W. J., You, K. S., Ahn, J. W., and Ahn, W. S. (2010). Carbon dioxide capture using amine-impregnated HMS having textural mesoporosity. *Chem. Eng. J.* 161, 46–52. doi:10.1016/j.cej.2010.04.019

Chen, C., Kim, J., and Ahn, W. S. (2014). CO_2 capture by amine-functionalized nanoporous materials: a review. *Korean J. Chem. Eng.* 31, 1919–1934. doi:10.1007/s11814-014-0257-2

Chen, H. Z., Thong, Z., Li, P., and Chung, T.-S. (2014). High performance composite hollow fiber membranes for CO_2/H_2 and CO_2/N_2 separation. *Int. J. Hydrog. Energy* 39, 5043–5053. doi:10.1016/j.ijhydene.2014.01.047

Chen, S., Chen, S., Fei, X., Zhang, Y., and Qin, L. (2015). Solubility and characterization of CO_2 in 40 mass % N -ethylmonoethanolamine solutions: explorations for an efficient nonaqueous solution. *Ind. Eng. Chem.* 54, 7212–7218. doi:10.1021/acs.iecr.5b01654

Chen, X. Y., Vinh-Thang, H., Ramirez, A. A., Rodrigue, D., and Kaliaguine, S. (2015). Membrane gas separation technologies for biogas upgrading. *RSC Adv.* 5, 24399–24448. doi:10.1039/C5RA00666J

Chen, C.-H., Shimon, D., Lee, J. J., Mentink-Vigier, F., Hung, I., Sievers, C., et al. (2018). The "missing" bicarbonate in CO_2 chemisorption reactions on solid amine sorbents. *J. Am. Chem. Soc.* 140, 8648–8651. doi:10.1021/jacs.8b04520

Choi, S., Drese, J. H., and Jones, C. W. (2009). Adsorbent materials for carbon dioxide capture from large anthropogenic point sources. *ChemSusChem* 2, 796–854. doi:10.1002/cssc.200900036

Choi, W., Min, K., Kim, C., Ko, Y. S., Jeon, J. W., Seo, H., et al. (2016). Epoxide-functionalization of polyethyleneimine for synthesis of stable carbon dioxide adsorbent in temperature swing adsorption. *Nat. Commun.* 7, 12640. doi:10.1038/ncomms12640

Chu, S. (2009). Carbon capture and sequestration. *Science* 325, 1599. doi:10.1126/science.1181637

Climeworks (2020). *Climeworks website*. Available at: http://www.climeworks.com (Accessed July 15, 2020).

Conway, W., Bruggink, S., Beyad, Y., Luo, W., Melián-Cabrera, I., Puxty, G., et al. (2015). CO_2 absorption into aqueous amine blended solutions containing monoethanolamine (MEA), N,N-dimethylethanolamine (DMEA), N,N-diethylethanolamine (DEEA) and 2-amino-2-methyl-1-propanol (AMP) for post-combustion capture processes. *Chem. Eng. Sci.* 126, 446–454. doi:10.1016/j.ces.2014.12.053

Corvo, M. C., Sardinha, J., Casimiro, T., Marin, G., Seferin, M., Einloft, S., et al., (2015). A rational approach to CO_2 capture by imidazolium ionic liquids: tuning CO_2 solubility by cation alkyl branching, *ChemSusChem*, 8 1935–1946.doi:10.1002/cssc.201500104

Cousins, A., Nielsen, P. T., Huang, S., Rowland, R., Edwards, B., Cottrell, A., et al. (2015). Pilot-scale evaluation of concentrated piperazine for CO_2 capture at an Australian coal-fired power station: nitrosamine measurements. *Int. J. Greenh. Gas Control* 37, 256–263. doi:10.1016/j.ijggc.2015.03.007

Cui, G., Wang, J., and Zhang, S. (2016). Active chemisorption sites in functionalized ionic liquids for carbon capture. *Chem. Soc. Rev.* 45, 4307–4339. doi:10.1039/c5cs00462d

Cullinane, J. T. and Rochelle, G. T. (2006). Kinetics of carbon dioxide absorption into aqueous potassium carbonate and piperazine. *Ind. Eng. Chem. Res.* 45, 2531–2545. doi:10.1021/ie050230s

Dai, Z., Deng, J., Aboukeila, H., Yan, J., Ansaloni, L., Mineart, K. P., et al. (2019). Highly CO_2-permeable membranes derived from a midblock-sulfonated multiblock polymer after submersion in water. *NPG Asia Mater.* 11, 53. doi:10.1038/s41427-019-0155-5

D'Alessandro, D. M., Smit, B., and Long, J. R. (2010). Carbon dioxide capture: prospects for new materials. *Angew. Chem. Int. Ed.* 49, 6058–6082. doi:10.1002/anie.201000431

Darunte, L. A., Walton, K. S., Sholl, D. S., and Jones, C. W., (2016). CO_2 capture via adsorption in amine-functionalized sorbents. *Curr. Opin. Chem. Eng.* 12, 82–90. doi:10.1016/j.coche.2016.03.002

de Riva, J., Suarez-Reyes, J., Moreno, D., Díaz, I., Ferro, V., and Palomar, J. (2017). Ionic liquids for post-combustion CO_2 capture by physical absorption: thermodynamic, kinetic and process analysis. *Int. J. Greenh. Gas Control* 61, 61–70. doi:10.1016/j.ijggc.2017.03.019

Demessence, A., D'Alessandro, D. M., Foo, M. L., and Long, J. R. (2009). Strong CO_2 binding in a water-stable, triazolate-bridged Metal−Organic framework functionalized with ethylenediamine. *J. Am. Chem. Soc.* 131, 8784–8786. doi:10.1021/ja903411w

Derks, P. W. J., Dijkstra, H. B. S., Hogendoorn, J. A., and Versteeg, G. F. (2005). Solubility of carbon dioxide in aqueous piperazine solutions. *AIChE J.* 51, 2311–2327. doi:10.1002/aic.10442

Didas, S. A., Choi, S., Chaikittisilp, W., and Jones, C. W. (2015). Amine-oxide hybrid materials for CO_2 capture from ambient air. *Accounts Chem. Res.* 48, 2680–2687. doi:10.1021/acs.accounts.5b00284

Dilshad, M. R., Islam, A., Hamidullah, U., Jamshaid, F., Ahmad, A., Butt, M. T. Z., et al. (2019). Effect of alumina on the performance and characterization of cross-linked PVA/PEG 600 blended membranes for CO_2/N_2 separation. *Sep. Purif. Technol.* 210, 627–635. doi:10.1016/j.seppur.2018.08.026

Ding, Y. and Alpay, E. (2000). Equilibria and kinetics of CO_2 adsorption on hydrotalcite adsorbent. *Chem. Eng. Sci.* 55, 3461–3474. doi:10.1016/S0009-2509(99)00596-5

Ding, M., Flaig, R. W., Jiang, H.-L., and Yaghi, O. M. (2019). Carbon capture and conversion using metal–organic frameworks and MOF-based materials. *Chem. Soc. Rev.* 48, 2783–2828. doi:10.1039/c8cs00829a

Du, N., Park, H. B., Robertson, G. P., Dal-Cin, M. M., Visser, T., Scoles, L., et al. (2011). Polymer nanosieve membranes for CO_2-capture applications. *Nature Mater.* 10, 372–375. doi:10.1038/nmat2989

Dugas, R. E. and Rochelle, G. T. (2011). CO_2 absorption rate into concentrated aqueous monoethanolamine and piperazine. *J. Chem. Eng. Data* 56, 2187–2195. doi:10.1021/je101234t

Dutcher, B., Fan, M. H., and Russell, A. G. (2015). Amine-based CO_2 capture technology development from the beginning of 2013-A review. *ACS Appl. Mater. Interfaces* 7, 2137–2148. doi:10.1021/am507465f

Duyar, M. S., Treviño, M. A. A., and Farrauto, R. J. (2015). Dual function materials for CO_2 capture and conversion using renewable H_2. *Appl. Catal. B* 168-169, 370–376. doi:10.1016/j.apcatb.2014.12.025

Duyar, M. S., Wang, S., Arellano-Treviño, M. A., and Farrauto, R. J. (2016). CO_2 utilization with a novel dual function material (DFM) for capture and catalytic conversion to synthetic natural gas: an update. *J. CO_2 Util.* 15, 65–71. doi:10.1016/j.jcou.2016.05.003

El Hadri, N., Quang, D. V., Goetheer, E. L. V., and Abu Zahra, M. R. M. (2017). Aqueous amine solution characterization for post-combustion CO_2 capture process. *Appl. Energy* 185, 1433–1449. doi:10.1016/j.apenergy.2016.03.043

Erans, M., Manovic, V., and Anthony, E. J. (2016). Calcium looping sorbents for CO_2 capture. *Appl. Energy* 180, 722–742. doi:10.1016/j.apenergy.2016.07.074

Esposito, E., Clarizia, G., Bernardo, P., Jansen, J. C., Sedláková, Z., Izák, P., et al. (2015). Pebax®/PAN hollow fiber membranes for CO_2/CH_4 separation. *Chem. Eng. Process.* 94, 53–61. doi:10.1016/j.cep.2015.03.016

Estevez, L., Barpaga, D., Zheng, J., Sabale, S., Patel, R. L., Zhang, J.-G., et al. (2018). Hierarchically porous carbon materials for CO_2 capture: the role of pore structure. *Ind. Eng. Chem. Res.* 57, 1262–1268. doi:10.1021/acs.iecr.7b03879

Pérez-Salado Kamps, Á., Tuma, D., Xia, J., and Maurer, G. (2003). Solubility of CO_2 in the ionic liquid [bmim][PF6]. *J Chem. Eng. Data* 48, 746–749. doi:10.1021/je034023f

Fan, L. S. (2010). *Chemical looping systems for fossil energy conversions*. Hoboken, NJ: John Wiley & Sons

Favre, E. (2011). Membrane processes and postcombustion carbon dioxide capture: challenges and prospects. *Chem. Eng. J.* 171, 782–793. doi:10.1016/j.cej.2011.01.010

Feng, B., An, H., and Tan, E. (2007). Screening of CO_2 adsorbing materials for zero emission power generation systems. *Energy Fuels* 21, 426–434. doi:10.1021/ef0604036

Feron, P. H. M. and Hendriks, C. A. (2005). CO_2 capture process principles and costs. *Oil & Gas Sci. Tech. - Rev. IFP* 60, 451–459. doi:10.2516/ogst:2005027

Figueroa, J. D., Fout, T., Plasynski, S., McIlvried, H., and Srivastava, R. D. (2008). Advances in CO_2 capture technology—the U.S. Department of energy's carbon sequestration program. *Int. J. Greenh. Gas Control* 2, 9–20. doi:10.1016/S1750-5836(07)00094-1

Florin, N. H. and Harris, A. T. (2009). Reactivity of CaO derived from nano-sized $CaCO_3$ particles through multiple CO_2 capture-and-release cycles. *Chem. Eng. Sci.* 64, 187–191. doi:10.1016/j.ces.2008.10.021

Foo, G. S., Lee, J. J., Chen, C.-H., Hayes, S. E., Sievers, C., and Jones, C. W. (2017). Elucidation of surface species through in Situ FTIR spectroscopy of carbon dioxide adsorption on amine-grafted SBA-15. *ChemSusChem* 10, 266–276. doi:10.1002/cssc.201600809

Freeman, S. A., Davis, J., and Rochelle, G. T. (2010a). Degradation of aqueous piperazine in carbon dioxide capture. *Int. J. Greenh. Gas Control* 4, 756–761. doi:10.1016/j.ijggc.2010.03.009

Freeman, S. A., Dugas, R., Van Wagener, D. H., Nguyen, T., and Rochelle, G. T. (2010b). Carbon dioxide capture with concentrated, aqueous piperazine. *Int. J. Greenh. Gas Control* 4, 119–124. doi:10.1016/j.ijggc.2009.10.008

Freeman, B., Hao, P., Baker, R., Kniep, J., Chen, E., Ding, J., et al. (2014). Hybrid membrane-absorption CO_2 capture process. *Energy Procedia* 63, 605–613. doi:10.1016/j.egypro.2014.11.065

Gaikwad, S., Kim, S.-J., and Han, S. (2019). CO_2 capture using amine-functionalized bimetallic MIL-101 MOFs and their stability on exposure to humid air and acid gases. *Micropor. Mesopor. Mat.* 277, 253–260. doi:10.1016/j.micromeso.2018.11.001

Gargiulo, N., Pepe, F., and Caputo, D. (2014). CO_2 adsorption by functionalized nanoporous materials: a review. *J. Nanosci. Nanotechnol.* 14, 1811–1822. doi:10.1166/jnn.2014.8893

Gassner, F. and Leitner, W. (1993). Hydrogenation of carbon dioxide to formic acid using water-soluble rhodium catalyststs. *J. Chem. Soc., Chem. Commun.* 1465–1466. doi:10.1039/C39930001465

Gauer, C. and Heschel, W. (2006). Doped lithium orthosilicate for absorption of carbon dioxide. *J. Mater. Sci.* 41, 2405–2409. doi:10.1007/s10853-006-7070-1

Gazzani, M., Macchi, E., and Manzolini, G. (2013a). CO_2 capture in integrated gasification combined cycle with SEWGS – Part A: thermodynamic performances. *Fuel* 105, 206–219. doi:10.1016/j.fuel.2012.07.048

Gazzani, M., Macchi, E., and Manzolini, G. (2013b). CO_2 capture in natural gas combined cycle with SEWGS. Part A: thermodynamic performances. *Int. J. Greenh. Gas Control* 12, 493–501. doi:10.1016/j.ijggc.2012.06.010

Gemeda, A. E., De Angelis, M. G., Du, N., Li, N., Guiver, M. D., and Sarti, G. C. (2017). Mixed gas sorption in glassy polymeric membranes. III. CO_2/CH_4 mixtures in a polymer of intrinsic microporosity (PIM-1): effect of temperature. *J. Membr. Sci.* 524, 746–757. doi:10.1016/j.memsci.2016.11.053

Giernoth, R. (2010). Task-specific ionic liquids. *Angew. Chem. Int. Ed.* 49, 2834–2839. doi:10.1002/anie.200905981

Global Thermostat (2020). Global Thermostat website. Available at: https://globalthermostat.com/ (Accessed July 15, 2020).

Goeppert, A., Czaun, M., May, R. B., Prakash, G. K. S., Olah, G. A., and Narayanan, S. R. (2011). Carbon dioxide capture from the air using a polyamine based regenerable solid adsorbent. *J. Am. Chem. Soc.* 133, 20164–20167. doi:10.1021/ja2100005

Goeppert, A., Czaun, M., Surya Prakash, G. K., and Olah, G. A. (2012). Air as the renewable carbon source of the future: an overview of CO_2 capture from the atmosphere. *Energy Environ. Sci.* 5, 7833–7853. doi:/10.1039/C2EE21586A

Goeppert, A., Zhang, H., Czaun, M., May, R. B., Prakash, G. K. S., Olah, G. A., et al. (2014). Easily regenerable solid adsorbents based on polyamines for carbon dioxide capture from the air. *ChemSusChem* 7, 1386–1397. doi:10.1002/cssc.201301114

Gomez, A., Briot, P., Raynal, L., Broutin, P., Gimenez, M., Soazic, M., et al. (2014). ACACIA project – development of a post-combustion CO_2 capture process. Case of the DMXTM Process. *Oil Gas Sci. Technol. – Rev. IFP Energies nouvelles* 69, 1121–1129. doi:10.2516/ogst/2014035

Gonzalez-Zamora, E. and Ibrra, I. A. (2017). CO_2 capture under humid conditions in metal–organic frameworks. *Mater. Chem. Front.* 1, 1471–1484. doi:10.1039/C6QM00301J

Grajciar, L., Čejka, J., Zukal, A., Otero Areán, C., Turnes Palomino, G., and Nachtigall, P. (2012). Controlling the adsorption enthalpy of CO_2 in zeolites by framework topology and composition. *ChemSusChem* 5, 2011–2022. doi:10.1002/cssc.201200270

Grande, C. A. and Rodrigues, A. E. (2008). Electric Swing Adsorption for CO_2 removal from flue gases. *Int. J. Greenh Gas Control* 2, 194–202. doi:10.1016/S1750-5836(07)00116-8

Gray, M. L., Soong, Y., Champagne, K. J., Pennline, H., Baltrus, J. P., Stevens, R. W., et al. (2005). Improved immobilized carbon dioxide capture sorbents, *Fuel Process. Technol.* 86, 1449–1455. doi:10.1016/j.fuproc.2005.01.005

Greeson, D. (2016). NRG CO_2NCEPT - confirmation of novel cost-effective emerging post-combustion technology. DE-FE0026581 Final Technical Report. Report NO. 81.089. https://www.netl.doe.gov/sites/default/files/2017-12/fe0026581-final-report.pdf.

Hallett, J. P. and Welton, T. (2011). Room-temperature ionic liquids: solvents for synthesis and catalysis. 2. *Chem. Rev.* 111. 3508–3576. doi:10.1021/cr1003248

Haszeldine, R. S. (2009). Carbon capture and storage: how green can black Be? *Science* 325, 1647–1652. doi:10.1126/science.1172246

Hicks, J. C., Drese, J. H., Fauth, D. J., Gray, M. L., Qi, G. G., and Jones, C. W. (2008). Designing adsorbents for CO_2 capture from flue gas-hyperbranched aminosilicas capable of capturing CO_2 reversibly. *J. Am. Chem. Soc.* 130, 2902–2903. doi:10.1021/ja077795v

Hiyoshi, N., Yogo, K., and Yashima, T. (2004). Adsorption of carbon dioxide on amine modified SBA15 in the presence of water vapor. *Chem. Lett.* 33, 510–511. doi:10.1246/cl.2004.510

Hiyoshi, N., Yogo, K., and Yashima, T. (2005). Adsorption characteristics of carbon dioxide on organically functionalized SBA-15. *Micropor. Mesopor. Mat* 84, 357–365. doi:10.1016/j.micromeso.2005.06.010

Houghton, J. T., Ding, Y., Griggs, D. J., Noguer, M., Linden, P. J. v. d., Dai, X., et al. (2001). *Climate change 2001: the scientific basis*. Cambridge, UK: Cambridge University Press

Huang, H. Y., Yang, R. T., Chinn, D., and Munson, C. L. (2003). Amine-grafted MCM-48 and silica xerogel as superior sorbents for acidic gas removal from natural gas. *Ind. Eng. Chem. Res.* 42, 2427–2433. doi:10.1021/ie020440u

Huang, L. L., Zhang, L. Z., Shao, Q., Lu, L. H., Lu, X. H., Jiang, S. Y., et al. (2007). Simulations of binary mixture adsorption of carbon dioxide and methane in carbon nanotubes: temperature, pressure, and pore size effects. *J. Phys. Chem. C* 111, 11912–11920. doi:10.1021/jp067226u

Husebye, J., Brunsvold, A. L., Roussanaly, S., and Zhang, X. (2012). Techno economic evaluation of amine based CO_2 capture: impact of CO_2 concentration and steam supply. *Energy Procedia* 23, 381–390. doi:10.1016/j.egypro.2012.06.053

IEA (2010). *Energy Technology Perspectives (2010): Scenarios and strategies to 2050*. Paris: OECD

IPCC (2015). Climate change 2014 synthesis report summary for Policymakers. Available at: https://www.ipcc.ch/pdf/assessment-report/ar5/syr/AR5_SYR_FINAL_SPM.pdf

Ishida, M. and Jin, H. (1994). A novel combustor based on chemical-looping reactions and its reaction kinetics. *J. Chem. Eng. JPN.* 27, 296–301. doi:10.1252/jcej.27.296

Ishida, M., Zheng, D., and Akehata, T. (1987). Evaluation of a chemical-looping-combustion power-generation system by graphic exergy analysis. *Energy* 12, 147–154. doi:10.1016/0360-5442(87)90119-8

Izaddoust, A. and Keshavarz, P. (2017). Experimental and theoretical study of CO_2 absorption with piperazine-promoted potassium carbonate solution in hollow fiber membrane contactors. *Energy Fuels* 31, 9790–9799. doi:10.1021/acs.energyfuels.7b01554

Jansen, D., Gazzani, M., Manzolini, G., Dijk, E. v., and Carbo, M. (2015). Pre-combustion CO_2 capture. *Int. J. Greenh. Gas Control* 40, 167–187. doi:10.1016/j.ijggc.2015.05.028

Japip, S., Wang, H., Xiao, Y., and Shung Chung, T. (2014). Highly permeable zeolitic imidazolate framework (ZIF)-71 nano-particles enhanced polyimide membranes for gas separation. *J. Membr. Sci.* 467, 162–174. doi:10.1016/j.memsci.2014.05.025

Jeon, S., Jung, H., Kim, S. H., and Lee, K. B. (2018). Double-layer structured CO_2 adsorbent functionalized with modified polyethyleneimine for high physical and chemical stability. *ACS Appl. Mater. Interfaces* 10, 21213–21223. doi:10.1021/acsami.8b01749

Jo, H. J., Soo, C. Y., Dong, G., Do, Y. S., Wang, H. H., Lee, M. J., et al. (2015). Thermally rearranged poly(benzoxazole-co-imide) membranes with superior mechanical strength for gas separation obtained by tuning chain rigidity. *Macromolecules* 48, 2194–2202. doi:10.1021/acs.macromol.5b00413

Jones, C. W. (2011). CO_2 capture from dilute gases as a component of modern global carbon management. *Annu. Rev. Chem.* 2, 31–52. doi:10.1146/annurev-chembioeng-061010-114252

Jou, F. Y., Mather, A. E., and Otto, F. D. (1995). The solubility of CO_2 in a 30 mass percent monoethanolamine solution. *Can. J. Chem. Eng.* 73, 140–147. doi:10.1002/cjce.5450730116

Julian, H., Sutrisna, P. D., Hakim, A. N., Harsono, H. O., Hugo, Y. A., and Wenten, I. G. (2019). Nano-silica/polysulfone asymmetric mixed-matrix membranes (MMMs) with high CO_2 permeance in the application of CO_2/N_2 separation. *Polym.-Plast. Technol.* 58, 678–689. doi:10.1080/03602559.2018.1520253

Jurado, N., Darabkhani, H. G., Anthony, E. J., and Oakey, J. E. (2015). "Oxy-fuel combustion for carbon capture and sequestration (CCS) from a coal/biomass power plant: experimental and simulation studies," in *Progress in clean energy, volume 2: novel systems and applications*. Editors I. Dincer, C.O. Colpan, O. Kizilkan, and M.A. Ezan (Cham, Switzerland: Springer International Publishing), Vol. 2, 177–192

Kar, S., Goeppert, A., and Prakash, G. K. S. (2019). Integrated CO_2 capture and conversion to formate and methanol: connecting two threads. *Accounts Chem. Res.* 52, 2892–2903. doi:10.1021/acs.accounts.9b00324

Kather, A., Rafailidis, S., Hermsdorf, C., Klostermann, M., Maschmann, A., Mieske, K., et al. (2008). *Research and development needs for clean coal deployment*. London, UK: International Energy Association Clean Coal Centre

Keith, D. W. (2009). Why capture CO_2 from the atmosphere? *Science* 325, 1654–1655. doi:10.1126/science.1175680

Khan, A. A., Halder, G. N., and Saha, A. K. (2016). Experimental investigation of sorption characteristics of capturing carbon dioxide into piperazine activated aqueous 2-amino-2-methyl-1-propanol solution in a packed column. *Int. J. Greenh. Gas Control* 44, 217–226. doi:10.1016/j.ijggc.2015.11.020

Kiehl, J. (2011). Lessons from earth's past. *Science* 331, 158–159. doi:10.1126/science.1199380

Kilaru, P. K. and Scovazzo, P. (2008). Correlations of low-pressure carbon dioxide and hydrocarbon solubilities in imidazolium-, phosphonium-, and ammonium-based room-temperature ionic liquids. Part 2. Using activation energy of viscosity. *Ind. Eng. Chem.* 47, 910–919. doi:10.1021/ie070836b

Kim, J., Lin, L.-C., Swisher, J. A., Haranczyk, M., and Smit, B. (2012). Predicting large CO_2 adsorption in aluminosilicate zeolites for postcombustion carbon dioxide capture. *J. Am. Chem. Soc.* 134, 18940–18943. doi:10.1021/ja309818u

Kim, C., Cho, H. S., Chang, S., Cho, S. J., and Choi, M. (2016). An ethylenediamine-grafted Y zeolite: a highly regenerable carbon dioxide adsorbent via temperature swing adsorption without urea formation. *Energy Environ. Sci.* 9, 1803–1811. doi:10.1039/C6EE00601A

Kim, S. M., Abdala, P. M., Broda, M., Hosseini, D., Copéret, C., and Müller, C. (2018). Integrated CO_2 capture and conversion as an efficient process for fuels from greenhouse gases. *ACS Catalysis* 8, 2815–2823. doi:10.1021/acscatal.7b03063

Kim, C., Choi, W., and Choi, M. (2019). SO_2-Resistant amine-containing CO_2 adsorbent with a surface protection layer. *ACS Appl. Mater. Interfaces* 11, 16586–16593. doi:10.1021/acsami.9b02831

Koros, W. J. (2004). Evolving beyond the thermal age of separation processes: membranes can lead the way. *AIChE J.* 50, 2326–2334. doi:10.1002/aic.10330

Kulkarni, A. R. and Sholl, D. S. (2012). Analysis of equilibrium-based TSA processes for direct capture of CO_2 from air. *Ind. Eng. Chem. Res.* 51, 8631–8645. doi:10.1021/ie300691c

Kumar, P. and Guliants, V. V. (2010). Periodic mesoporous organic-inorganic hybrid materials: applications in membrane separations and adsorption. *Micropor. Mesopor. Mat.* 132, 1–14. doi:10.1016/j.micromeso.2010.02.007

Lackner, K., Ziock, H.-J., and Grimes, P. (1999). "Carbon dioxide extraction from air: is it an option?," in 24th annual technical conference on coal utilization and fuel systems, Clearwater, FL, March 8, 1999–March 11, 1999

Lackner, K. S., Brennan, S., Matter, J. M., Park, A.-H. A., Wright, A., and van der Zwaan, B. (2012). The urgency of the development of CO_2 capture from ambient air. *Proc. Natl. Acad. Sci. Unit. States Am.* 109, 13156–13162. doi:10.1073/pnas.1108765109

Lackner, K. S. (2003). A guide to CO_2 sequestration *Science* 300, 1677–1678. doi:10.1126/science.1079033

Lee, W. R., Hwang, S. Y., Ryu, D. W., Lim, K. S., Han, S. S., Moon, D., et al. (2014). Diamine-functionalized metal–organic framework: exceptionally high CO_2 capacities from ambient air and flue gas, ultrafast CO_2 uptake rate, and adsorption mechanism. *Energy Environ. Sci.* 7, 744–751. doi:10.1039/C3EE42328J

Lee, T. S., Cho, J. H., and Chi, S. H. (2015). Carbon dioxide removal using carbon monolith as electric swing adsorption to improve indoor air quality. *Build. Environ.* 92, 209–221. doi:10.1016/j.buildenv.2015.04.028

Lewis, W. K., Gilliland, E. R., and Sweeney, M. P. (1951). Gasification of carbon: metal oxides in a fluidized powder bed. *Chem. Eng. Prog.* 47, 251–256

Li, L. and Rochelle, G. (2014). CO_2 mass transfer and solubility in aqueous primary and secondary amine. *Energy Procedia* 63, 1487–1496. doi:10.1016/j.egypro.2014.11.158

Li, J., Lin, X., Ning, P. G., Cao, H. B., and Zhang, Y. (2014). Measurement and modelling of the solubility of carbon dioxide in aqueous 1,8-p-menthane-diamine solution. *J. Chem. Thermodyn.* 71, 64–70. doi:10.1016/j.jct.2013.11.018

Li, X., Zhang, L., Luo, C., Zhang, Z., Xu, Y., and Zheng, C. (2018). Experimental investigation and process simulation of oxy-fuel flue gas denitrification in CO_2 compression process. *Energy Fuels* 32, 11666–11673. doi:10.1021/acs.energyfuels.8b02660

Liang, Z., Fadhel, B., Schneider, C. J., and Chaffee, A. L. (2008). Stepwise growth of melamine-based dendrimers into mesopores and their CO_2 adsorption properties. *Micro. Meso. Mat.* 111, 536–543. doi:10.1016/j.micromeso.2007.08.030

Liao, J., Wang, Z., Gao, C., Li, S., Qiao, Z., Wang, M., et al. (2014). Fabrication of high-performance facilitated transport membranes for CO_2 separation. *Chemical Science* 5, 2843–2849. doi:10.1039/C3SC53334D

Liguori, S. and Wilcox, J. (2018). "Design considerations for postcombustion CO_2 capture with membranes," in *Current trends and future developments on (bio-) membranes*. Editors A. Basile and E.P. Favvas (Amsterdam, Netherlands: Elsevier), 385–413

Lin, L.-C., Berger, A. H., Martin, R. L., Kim, J., Swisher, J. A., Jariwala, K., et al. (2012). In silico screening of carbon-capture materials. *Nature Materials* 11, 633–641. doi:10.1038/nmat3336

Lin, Y. C., Kong, C. L., and Chen, L. (2016). Amine-functionalized metal-organic frameworks: structure, synthesis and applications. *RSC Adv.* 6, 32598–32614. doi:10.1039/C6RA01536K

Liu, Y. M., Shi, J. J., Chen, J., Ye, Q., Pan, H., Shao, Z. H., et al. (2010). Dynamic performance of CO_2 adsorption with tetraethylenepentamine-loaded KIT-6. *Micro. Meso. Mat.* 134, 16–21. doi:10.1016/j.micromeso.2010.05.002

Liu, A.-H., Ma, R., Song, C., Yang, Z.-Z., Yu, A., Cai, Y., et al. (2012). Equimolar CO_2 capture by N-substituted amino acid salts and subsequent conversion, *Angew. Chem. Int. Ed.* 51, 11306–11310. doi:10.1002/anie.201205362

Liu, L., Zhao, C., Xu, J., and Li, Y. (2015). Integrated CO_2 capture and photocatalytic conversion by a hybrid adsorbent/photocatalyst material. *Appl. Catal. B* 179, 489–499. doi:10.1016/j.apcatb.2015.06.006

Liu, C., Greer, D. W., and O'Leary, B. W. (2016). "Advanced materials and membranes for gas separations: the UOP approach," in *Nanotechnology: delivering on the promise*. Washington, D.C.: American Chemical Society, Vol. 2, 119–135

Liu, Q., Paul, D. R., and Freeman, B. D. (2016). Gas permeation and mechanical properties of thermally rearranged (TR) copolyimides. *Polymer* 82, 378–391. doi:10.1016/j.polymer.2015.11.051

Long, J. R. and Yaghi, O. M. (2009). The pervasive chemistry of metal–organic frameworks. *Chem. Soc. Rev.* 38, 1213–1214. doi:10.1039/B903811F

Low, B. T., Zhao, L., Merkel, T. C., Weber, M., and Stolten, D. (2013). A parametric study of the impact of membrane materials and process operating conditions on carbon capture from humidified flue gas. *J. Membr. Sci.* 431, 139–155. doi:10.1016/j.memsci.2012.12.014

Lu, W., Wei, Z., Gu, Z.-Y., Liu, T.-F., Park, J., Park, J., et al. (2014). Tuning the structure and function of metal–organic frameworks via linker design. *Chem. Soc. Rev.* 43, 5561–5593. doi:10.1039/C4CS00003J

Lyngfelt, A. and Mattisson, T. (2011). "Materials for chemical-looping combustion," in *Efficient carbon capture for coal power plants*. D. Stolten and V. Scherer (Weinheim, Germany: WILEY-VCH Verlag GmbH & Co. KGaA)

Lyngfelt, A. (2014). Chemical-looping combustion of solid fuels – status of development. *Appl. Energy* 113, 1869–1873. doi:10.1016/j.apenergy.2013.05.043

Ma, X. L., Wang, X. X., and Song, C. S. (2009). "Molecular basket" sorbents for separation of CO_2 and H_2S from various gas streams. *J. Am. Chem. Soc.* 131, 5777–5783. doi:10.1021/ja8074105

Mafra, L., Čendak, T., Schneider, S., Wiper, P. V., Pires, J., Gomes, J. R. B., et al. (2017). Structure of chemisorbed CO_2 species in amine-functionalized mesoporous silicas studied by solid-state NMR and computer modeling. *J. Am. Chem. Soc.* 139, 389–408. doi:10.1021/jacs.6b11081

Maneeintr, K., Idem, R. O., Tontiwachwuthikul, P., and Wee, A. G. H. (2009). Synthesis, solubilities, and cyclic capacities of amino alcohols for CO_2 capture from flue gas streams. *Energy Procedia* 1, 1327–1334. doi:10.1016/j.egypro.2009.01.174

Markewitz, P., Kuckshinrichs, W., Leitner, W., Linssen, J., Zapp, P., Bongartz, R., et al. (2012). Worldwide innovations in the development of carbon capture technologies and the utilization of CO_2. *Energy Environ. Sci.* 5, 7281–7305. doi:10.1039/C2EE03403D

Marocco Stuardi, F., MacPherson, F., and Leclaire, J. (2019). Integrated CO_2 capture and utilization: a priority research direction. *Curr. Opin. Green Sustain. Chem.* 16, 71–76. doi:10.1016/j.cogsc.2019.02.003

Maroto-Valer, M. M., Song, C. S., and Soong, Y. (2002). *Envrionmental challenges and greenhouse gas control for fossil fuel utilization in the 21st century*. New York, NY: Kluwer Academic/Plenum Publishers

Martín, M. M. (2016). "Water," in *Industrial chemical process analysis and design*. Editors M.M. Martín (Boston, MA: Elsevier), Chap. 4, 125–197

McDonald, T. M., Mason, J. A., Kong, X., Bloch, E. D., Gygi, D., Dani, A., et al. (2015). Cooperative insertion of CO_2 in diamine-appended metal-organic frameworks. *Nature* 519, 303–308. doi:10.1038/nature14327

Melillo, J. M., McGuire, A. D., Kicklighter, D. W., Moore, B., Vorosmarty, C. J., and Schloss, A. L. (1993). Global climate-change and terrestrial net primary production. *Nature* 363, 234–240. doi:10.1038/363234a0

Merkel, T. C., Lin, H., Wei, X., and Baker, R. (2010). Power plant post-combustion carbon dioxide capture: an opportunity for membranes. *J. Membr. Sci.* 359, 126–139. doi:10.1016/j.memsci.2009.10.041

Merkel, T. C., Wei, X., He, Z., White, L. S., Wijmans, J. G., and Baker, R. W. (2013). Selective exhaust gas recycle with membranes for CO_2 capture from natural gas combined cycle power plants. *Ind. Eng. Chem. Res.* 52, 1150–1159. doi:10.1021/ie302110z

Mesbah, M., Momeni, M., Soroush, E., Shahsavari, S., and Galledari, S. A. (2019). Theoretical study of CO_2 separation from CO_2/CH_4 gaseous mixture using 2-methylpiperazine -promoted potassium carbonate through hollow fiber membrane contactor. *J. Environ. Chem. Eng.* 7, 102781

Metz, B., Davidson, O., Coninck, H. d., Loos, M., and Meyer, L. (2005). *IPCC special report on carbon dioxide capture and storage*. Cambridge, UK: Cambridge University Press

Miguel, C. V., Soria, M. A., Mendes, A., and Madeira, L. M. (2017). A sorptive reactor for CO_2 capture and conversion to renewable methane. *Chem. Eng. J.* 322, 590–602. doi:10.1016/j.cej.2017.04.024

Miller, B. G.,(2017). "Carbon dioxide emissions reduction and storage," in *Clean coal engineering technology*. 2nd Edn. Editors B.G. Miller (Oxford, UK: Butterworth-Heinemann), Chap. 13, 609–668

Min, K., Choi, W., Kim, C., and Choi, M. (2018a). Oxidation-stable amine-containing adsorbents for carbon dioxide capture. *Nat. Commun.* 9, 726. doi:10.1038/s41467-018-03123-0

Min, K., Choi, W., Kim, C., and Choi, M. (2018b). Rational design of the polymeric amines in solid adsorbents for postcombustion carbon dioxide capture. *ACS Appl. Mater. Interfaces* 10, 23825–23833. doi:10.1021/acsami.8b05988

Mohamedali, M., Nath, D., Ibrahim, H., and Henni, A. (2016). *Review of recent developments in CO_2 capture using solid materials: metal organic frameworks (MOFs)*. London, UK: IntechOpen

Mondal, B. K., Bandyopadhyay, S. S., and Samanta, A. N. (2015). Vapor-liquid equilibrium measurement and ENRTL modeling of CO_2 absorption in aqueous hexamethylenediamine. *Fluid Phase Equil.* 402, 102–112. doi:10.1016/j.fluid.2015.05.033

Montagnaro, F., Silvestre-Albero, A., Silvestre-Albero, J., Rodríguez-Reinoso, F., Erto, A., Lancia, A., et al. (2015). Post-combustion CO_2 adsorption on activated carbons with different textural properties. *Micropor. Mesopor. Mat.* 209, 157–164. doi:10.1016/j.micromeso.2014.09.037

Monteiro, J. G. M. S., Pinto, D. D. D., Zaidy, S. A. H., Hartono, A., and Svendsen, H. F. (2013). VLE data and modelling of aqueous N,N-diethylethanolamine (DEEA) solutions. *Int. J. Greenh. Gas Control* 19, 432–440. doi:10.1016/j.ijggc.2013.10.001

Mora Mendoza, E. Y., Sarmiento Santos, A., Vera López, E., Drozd, V., Durygin, A., Chen, J., et al. (2019). Iron oxides as efficient sorbents for CO_2 capture. *J. Mater. Res.* 8, 2944–2956. doi:10.1016/j.jmrt.2019.05.002

Moya, C., Palomar, J., Gonzalez-Miquel, M., Bedia, J., and Rodriguez, F. (2014). Diffusion coefficients of CO_2 in ionic liquids estimated by gravimetry. *Ind. Eng. Chem. Res.* 53, 13782–13789. doi:10.1021/ie501925d

Mutch, G. A., Shulda, S., McCue, A. J., Menart, M. J., Ciobanu, C. V., Ngo, C., et al. (2018). Carbon capture by metal oxides: unleashing the potential of the (111) facet. *J. Am. Chem. Soc.* 140, 4736–4742. doi:10.1021/jacs.8b01845

Nakagawa, K. (1998). A novel method of CO_2 capture from high temperature gases. *J. Electro.Society* 145, 1344

Nakhjiri, A. T. and Heydarinasab, A. (2019). Computational simulation and theoretical modeling of CO_2 separation using EDA, PZEA and PS absorbents inside the hollow fiber membrane contactor. *J. Ind. Eng. Chem.* 78, 106–115. doi:10.1016/j.jiec.2019.06.031

National Academies of Sciences, Engineering, and Medicine (2019). *Negative emissions technologies and reliable sequestration: a research agenda*. Washington, DC: The National Academies Press

Nguyen, D., Murialdo, M., Hornbostel, K., Pang, S., Ye, C., Smith, W., et al. (2019). 3D printed polymer composites for CO_2 capture. *Ind. Eng. Chem. Res.* 58, 22015–22020. doi:10.1021/acs.iecr.9b04375

Niranjana, K., Jerald Maria Antony, G., and Raja, S. (2019). A study on adsorption of gases in the thin film nanocomposites. *Mater. Today: Proceed.* 8, 79–84. doi:10.1016/j.matpr.2019.02.083

Nouacer, A., Belaribi, F. B., Mokbel, I., and Jose, J. (2014). Solubility of carbon dioxide gas in some 2.5 M tertiary amine aqueous solutions. *J. Mol. Liq.* 190, 68–73. doi:10.1016/j.molliq.2013.10.026

Nugent, P., Belmabkhout, Y., Burd, S. D., Cairns, A. J., Luebke, R., Forrest, K., et al. (2013). Porous materials with optimal adsorption thermodynamics and kinetics for CO_2 separation. *Nature* 495, 80–84. doi:10.1038/nature11893

OECD (2012). *OECD environmental Outlook to 2050*. Paris, France: OECD publishing

Öhrman, O., Hedlund, J., and Sterte, J. (2004). Synthesis and evaluation of ZSM-5 films on cordierite monoliths. *Appl. Catal. A: Gen.* 270, 193–199. doi:10.1016/j.apcata.2004.05.004

Olajire, A. A. (2017). Synthesis of bare and functionalized porous adsorbent materials for CO_2 capture. *Greenh. Gases* 7, 399–459. doi:10.1002/ghg.1657

Pacala, S. and Socolow, R. (2004). Stabilization wedges: solving the climate problem for the next 50 Years with current technologies. *Science* 305, 968. doi:10.1126/science.1100103

Papadopoulos, A. I., Tzirakis, F., Tsivintzelis, I., and Seferlis, P. (2019). Phase-change solvents and processes for postcombustion CO_2 capture: a detailed review. *Ind. Eng. Chem. Res.* 58, 5088–5111. doi:10.1021/acs.iecr.8b06279

Park, J. Y., Yoon, S. J., Lee, H., Yoon, J. H., Shim, J. G., Lee, J. K., et al. (2002). Solubility of carbon dioxide in aqueous solutions of 2-amino-2-ethyl-1,3-propanediol. *Fluid Phase Equil.* 202, 359–366. doi:10.1016/S0378-3812(02)00142-5

Patterson, B. D., Mo, F., Borgschulte, A., Hillestad, M., Joos, F., Kristiansen, T., et al. (2019). Renewable CO_2 recycling and synthetic fuel production in a marine environment. *Proc. Natl. Acad. Sci. Unit. States Am.* 116, 12212–12219. doi:10.1073/pnas.1902335116

Petkovic, M., Seddon, K. R., Rebelo, L. P. N., and Silva Pereira, C. (2011). Ionic liquids: a pathway to environmental acceptability. *Chem. Soc. Rev.* 40, 1383–1403. doi:10.1039/C004968A

Plaza, M. G., Pevida, C., Arenillas, A., Rubiera, F., and Pis, J. J. (2007). CO_2 capture by adsorption with nitrogen enriched carbons. *Fuel* 86, 2204–2212. doi:10.1016/j.fuel.2007.06.001

Powell, C. E. and Qiao, G. G. (2006). Polymeric CO_2/N_2 gas separation membranes for the capture of carbon dioxide from power plant flue gases. *J. Membr. Sci.* 279, 1–49. doi:10.1016/j.memsci.2005.12.062

Puxty, G., Rowland, R., Allport, A., Yang, Q., Bown, M., Burns, R., et al. (2009). Carbon dioxide postcombustion capture: a novel screening study of the carbon dioxide absorption performance of 76 amines. *Environ. Sci. Technol.* 43, 6427–6433. doi:10.1021/es901376a

Qi, R. and Henson, M. A. (1998). Optimization-based design of spiral-wound membrane systems for CO_2/CH_4 separations. *Sep. Purif. Technol.* 13, 209–225. doi:10.1016/S1383-5866(98)00044-6

Qi, G., Wang, Y., Estevez, L., Duan, X., Anako, N., Park, A.-H. A., et al. (2011). High efficiency nanocomposite sorbents for CO_2 capture based on amine-functionalized mesoporous capsules. *Energy Environ. Sci.* 4, 444–452. doi:10.1039/C0EE00213E

Rackley, S. A. (2017). "Carbon capture from power generation," in *Carbon capture and storage*. 2nd Edn. Editors S.A. Rackley (Boston, MA: Butterworth-Heinemann), Chap. 4, 75–101

Ram Reddy, M. K., Xu, Z. P., Lu, G. Q., and Diniz da Costa, J. C. (2006). Layered double hydroxides for CO_2 capture: structure evolution and regeneration. *Ind. Eng. Chem. Res.* 45, 7504–7509. doi:10.1021/ie060757k

Ram Reddy, M. K., Xu, Z. P., and Diniz da Costa, J. C. (2008). Influence of water on high-temperature CO_2 capture using layered double hydroxide derivatives. *Ind. Eng. Chem. Res.* 47, 2630–2635. doi:10.1021/ie0716060

Ramasubramanian, K. and Ho, W. S. W. (2011). Recent developments on membranes for post-combustion carbon capture. *Curr. Opin. Chem. Eng.* 1, 47–54. doi:10.1016/j.coche.2011.08.002

Ramasubramanian, K., Verweij, H., and Winston Ho, W. S. (2012). Membrane processes for carbon capture from coal-fired power plant flue gas: a modeling and cost study. *J. Membr. Sci.* 421-422, 299–310. doi:10.1016/j.memsci.2012.07.029

Ramos-Fernandez, E. V., Garcia-Domingos, M., Juan-Alcañiz, J., Gascon, J., and Kapteijn, F. (2011). MOFs meet monoliths: hierarchical structuring metal organic framework catalysts. *Appl. Cataly. A: General* 391, 261–267. doi:10.1016/j.apcata.2010.05.019

Razavi, S. S., Hashemianzadeh, S. M., and Karimi, H. (2011). Modeling the adsorptive selectivity of carbon nanotubes for effective separation of CO_2/N_2 mixtures. *J. Mol. Model.* 17, 1163–1172. doi:10.1007/s00894-010-0810-9

Realmonte, G., Drouet, L., Gambhir, A., Glynn, J., Hawkes, A., Köberle, A. C., et al. (2019). An inter-model assessment of the role of direct air capture in deep mitigation pathways. *Nat. Commun.* 10, 3277. doi:10.1038/s41467-019-10842-5

Rebolledo-Morales, M. A., Rebolledo-Libreros, M. E., and Trejo, A. (2011). Equilibrium solubility of CO_2 in aqueous solutions of 1-amino-2-propanol as function of concentration, temperature, and pressure. *J. Chem. Thermodyn.* 43, 690–695. doi:10.1016/j.jct.2010.12.008

Regufe, M. J., Ferreira, A. F. P., Loureiro, J. M., Rodrigues, A., and Ribeiro, A.- M. (2019). Electrical conductive 3D-printed monolith adsorbent for CO_2 capture. *Micropor. Mesopor. Mater.* 278, 403–413. doi:10.1016/j.micromeso.2019.01.009

Rezaei, F. and Webley, P. (2009). Optimum structured adsorbents for gas separation processes. *Chem. Eng. Sci.* 64, 5182–5191. doi:10.1016/j.ces.2009.08.029

Rezaei, F. and Webley, P. (2010). Structured adsorbents in gas separation processes. *Sep. Purif. Technol.* 70, 243–256. doi:10.1016/j.seppur.2009.10.004

Rochelle, G. T. (2009). Amine scrubbing for CO_2 capture. *Science* 325, 1652–1654. doi:10.1126/science.1176731

Rochelle, G. T. (2016). "Conventional amine scrubbing for CO_2 capture," in *Absorption-based post-combustion capture of carbon dioxide*. Editors P.H.M. Feron (Cambridge, UK: Woodhead Publishing), Chap. 3, 35–67

Rodríguez, M. T. and Pfeiffer, H. (2008). Sodium metasilicate (Na_2SiO_3): a thermo-kinetic analysis of its CO_2 chemical sorption. *Thermochimica Acta* 473, 92–95. doi:10.1016/j.tca.2008.04.022

Rosenholm, J. M. and Linden, M. (2007). Wet-chemical analysis of surface concentration of accessible groups on different amino-functionalized mesoporous SBA-15 silicas. *Chem. Mat.* 19, 5023–5034. doi:10.1021/cm071289n

Rosenholm, J. M., Penninkangas, A., and Linden, M. (2006). Amino-functionalization of large-pore mesoscopically ordered silica by a one-step hyperbranching polymerization of a surface-grown polyethyleneimine. *Chem. Commun.* 37, 3909–3911. doi:10.1039/B607886A

Rubin, E. S., Davison, J. E., and Herzog, H. J. (2015). The cost of CO_2 capture and storage. *Int. J. Greenh. Gas Control.* 40, 378–400. doi:10.1016/j.ijggc.2015.05.018

Sanz-Pérez, E. S., Murdock, C. R., Didas, S. A., and Jones, C. W. (2016). Direct capture of CO_2 from ambient air. *Chem. Rev.* 116, 11840–11876. doi:10.1021/acs.chemrev.6b00173

Sarfraz, M. and Ba-Shammakh, M. (2018). ZIF-based water-stable mixed-matrix membranes for effective CO_2 separation from humid flue gas. *Can. J. Chem. Eng.* 96, 2475–2483. doi:10.1002/cjce.23170

Schäffer, A., Brechtel, K., and Scheffknecht, G. (2012). Comparative study on differently concentrated aqueous solutions of MEA and TETA for CO_2 capture from flue gases. *Fuel* 101, 148–153. doi:10.1016/j.fuel.2011.06.037

Scholes, C. A., Kentish, S. E., and Qader, A. (2020). Membrane gas-solvent contactor pilot plant trials for post-combustion CO_2 capture. *Sep. Purif. Technol.* 237, 116470. doi:10.1016/j.seppur.2019.116470

Scholes, C. A. (2016). Thermally rearranged poly(benzoxazole) copolymer membranes for improved gas separation: a review. *Aust. J. Chem.* 69, 601–611. doi:10.1071/CH15523

Scholz, M., Frank, B., Stockmeier, F., Falß, S., and Wessling, M. (2013). Techno-economic analysis of hybrid processes for biogas upgrading. *Ind. Eng. Chem. Res.* 52, 16929–16938. doi:10.1021/ie402660s

Seneviratne, S. I., Donat, M. G., Pitman, A. J., Knutti, R., and Wilby, R. L. (2016). Allowable CO_2 emissions based on regional and impact-related climate targets. *Nature* 529, 477. doi:10.1038/nature16542

Seo, D. J. and Hong, W. H. (2000). Effect of piperazine on the kinetics of carbon dioxide with aqueous solutions of 2-Amino-2-methyl-1-propanol. *Ind. Eng. Chem. Res.* 39, 2062–2067. doi:10.1021/ie990846f

Shah, K. J. and Imae, T. (2016). Selective gas capture ability of gas-adsorbent-incorporated cellulose nanofiber films. *Biomacromolecules* 17, 1653–1661. doi:10.1021/acs.biomac.6b00065

Shannon, M. S. and Bara, J. E. (2012). Reactive and reversible ionic liquids for CO_2 capture and acid gas removal. *Sep. Sci. Technol.* 47, 178–188. doi:10.1080/01496395.2011.630055

Shen, K. P. and Li, M. H. (1992). Solubility of carbon dioxide in aqueous mixtures of monoethanolamine with methyldiethanolamine. *J. Chem. Eng. Data* 37, 96–100. doi:10.1021/je00005a025

Shiflett, M. B. and Yokozeki, A. (2005). Solubilities and diffusivities of carbon dioxide in ionic liquids: [bmim][PF6] and [bmim][BF4]. *Ind. Eng. Chem.* 44, 4453–4464. doi:10.1021/ie058003d

Shiflett, M. B., Drew, D. W., Cantini, R. A., and Yokozeki, A. (2010). Carbon dioxide capture using ionic liquid 1-Butyl-3-methylimidazolium acetate. *Energy Fuels* 24, 5781–5789. doi:10.1021/ef100868a

Shimon, D., Chen, C.-H., Lee, J. J., Didas, S. A., Sievers, C., Jones, C. W., et al. (2018). ^{15}N solid state NMR spectroscopic study of surface amine groups for carbon capture: 3-aminopropylsilyl grafted to SBA-15 mesoporous silica. *Environ Sci Technol* 52, 1488–1495. doi:10.1021/acs.est.7b04555

Shin, E. K., Lee, B. C., and Lim, J. S. (2008). High-pressure solubilities of carbon dioxide in ionic liquids: 1-Alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide. *J. Supercrit. Fluids* 45, 282–292. doi:10.1016/j.supflu.2008.01.020

Siagian, U. W. R., Raksajati, A., Himma, N. F., Khoiruddin, K., and Wenten, I. G. (2019). Membrane-based carbon capture technologies: membrane gas separation vs. membrane contactor. *J Nat Gas Sci Eng.* 67, 172–195. doi:10.1016/j.jngse.2019.04.008

Singh, J. and Dhar, D. W. (2019). Overview of carbon capture technology: microalgal biorefinery concept and state-of-the-art. *Front. Mar. Sci.* 6, 1–9. doi:10.3389/fmars.2019.00029

Singh, G., Lee, J., Karakoti, A., Bahadur, R., Yi, J., Zhao, D., et al. (2020). Emerging trends in porous materials for CO_2 capture and conversion. *Chem. Soc. Rev.* 49, 4360–4404. doi:10.1039/D0CS00075B

Siriwardane, R. V., Shen, M. S., and Fisher, E. P. (2003). Adsorption of CO_2, N_2, and O_2 on natural zeolites. *Energy Fuels* 17, 571–576. doi:10.1021/ef020135l

Smith, M. R. and Myers, S. S. (2018). Impact of anthropogenic CO_2 emissions on global human nutrition. *Nat. Clim. Change* 8, 834–839. doi:10.1038/s41558-018-0253-3

Son, W. J., Choi, J. S., and Ahn, W. S. (2008). Adsorptive removal of carbon dioxide using polyethyleneimine-loaded mesoporous silica materials. *Micropor. Mesopor. Mater.* 113, 31–40. doi:10.1016/j.micromeso.2007.10.049

Song, C., Liu, Q., Ji, N., Deng, S., Zhao, J., Li, Y., et al. (2018). Alternative pathways for efficient CO_2 capture by hybrid processes—a review. *Renew. Sustain. Energy Rev.* 82, 215–231. doi:10.1016/j.rser.2017.09.040

Song, C. S. (2006). Global challenges and strategies for control, conversion and utilization of CO_2 for sustainable development involving energy, catalysis, adsorption and chemical processing. *Catal. Today* 115, 2–32. doi:10.1016/j.cattod.2006.02.029

Songolzadeh, M., Soleimani, M., Ravanchi, M. T., and Songolzadeh, R. (2014). Carbon dioxide separation from flue gases: a technological review emphasizing reduction in greenhouse gas emissions. *Sci. World J.* 2014, 828131. doi:10.1155/2014/828131

Sreedhar, I., Nahar, T., Venugopal, A., and Srinivas, B. (2017). Carbon capture by absorption – path covered and ahead. *Renew. Sustain. Energy Rev.* 76, 1080–1107. doi:10.1016/j.rser.2017.03.109

Steinberg, M. and Cheng, H. C. (1989). Modern and prospective technologies for hydrogen production from fossil fuels. *Int. J. Hydrog.* 14, 797–820. doi:10.1016/0360-3199(89)90018-9

Stocker, T. F., Qin, D., Plattner, G.-K., Tignor, M., Allen, S. K., Boschung, J., et al. (2013). *Climate change 2013: the physical science basis. Contribution of working group I to the fifth assessment report of the intergovernmental Panel on climate change*. Cambridge, UK and New York, NY: Cambridge University Press, 1585

Taheri Najafabadi, A. (2015). Emerging applications of graphene and its derivatives in carbon capture and conversion: current status and future prospects. *Renew. Sustain. Energy Rev.* 41, 1515–1545. doi:10.1016/j.rser.2014.09.022

Takamura, Y., Narita, S., Aoki, J., Hironaka, S., and Uchida, S. (2001). Evaluation of dual-bed pressure swing adsorption for CO_2 recovery from boiler exhaust gas. *Sep. Purif. Technol.* 24, 519–528. doi:10.1016/S1383-5866(01)00151-4

Tanh Jeazet, H. B., Staudt, C., and Janiak, C. (2012). Metal–organic frameworks in mixed-matrix membranes for gas separation. *Dalton Trans.* 41, 14003–14027. doi:10.1039/C2DT31550E

Tanthana, J. and Chuang, S. S. C. (2010). In Situ infrared study of the role of PEG in stabilizing silica-supported amines for CO_2 capture. *Chemsuschem* 3, 957–964. doi:10.1002/cssc.201000090

Thakkar, H., Eastman, S., Hajari, A., Rownaghi, A. A., Knox, J. C., and Rezaei, F. (2016). 3D-Printed zeolite monoliths for CO_2 removal from enclosed environments. *ACS Appl. Mater. Interfaces* 8, 27753–27761. doi:10.1021/acsami.6b09647

Thakkar, H., Eastman, S, Al-Mamoori, A., Hajari, A., Rownaghi, A. A., and Rezaei, F. (2017a). Formulation of aminosilica adsorbents into 3D-printed monoliths and evaluation of their CO_2 capture performance. *ACS Appl. Mater. Interfaces* 9, 7489–7498. doi:10.1021/acsami.6b16732

Thakkar, H., Eastman, S., Al-Naddaf, Q., Rownaghi, A. A., and Rezaei, F. (2017b). 3D-Printed metal–organic framework monoliths for gas adsorption processes. *ACS Appl. Mater. Interfaces* 9, 35908–35916. doi:10.1021/acsami.7b11626

Thakkar, H., Lawson, S., Rownaghi, A. A., and Rezaei, F. (2018). Development of 3D-printed polymer-zeolite composite monoliths for gas separation. *Chem. Eng. J.* 348, 109–116. doi:10.1016/j.cej.2018.04.178

Thompson, J. F., Bellerjeau, C., Marinick, G., Osio-Norgaard, J., Evans, A., Carry, P., et al. (2019). Intrinsic thermal desorption in a 3D printed multifunctional composite CO_2 sorbent with embedded heating capability. *ACS Appl. Mater. Interfaces* 11, 43337–43343. doi:10.1021/acsami.9b14111

Tim Cullinane, J., Oyenekan, B. A., Lu, J., and Rochelle, G. T. (2005). "Aqueous piperazine/potassium carbonate for enhanced CO_2 capture," in *Greenhouse gas control technologies 7*. Editors E.S. Rubin, D.W. Keith, C.F. Gilboy, M. Wilson, T. Morris, J. Gale, et al. (Oxford, UK: Elsevier Science Ltd)

Tong, D., Trusler, J. P. M., Maitland, G. C., Gibbins, J., and Fennell, P. S. (2012). Solubility of carbon dioxide in aqueous solution of monoethanolamine or 2-amino-2-methyl-1-propanol: experimental measurements and modelling. *Int. J. Greenh. Gas Control* 6, 37–47. doi:10.1016/j.ijggc.2011.11.005

Tontiwachwuthikul, P. and Idem, R. (2013). "Recent progress and new developments in post-combustion carbon-capture technology with reactive solvents," in *Recent progress and new developments in post-combustion carbon-capture technology with reactive solvents*, Editors P. Tontiwachwuthikul and R. Idem, Future Science Book Series, pp. 2–8.

Torrisi, A., Bell, R. G., and Mellot-Draznieks, C. (2010). Functionalized MOFs for enhanced CO_2 capture. *Cryst. Growth Des.* 10, 2839–2841. doi:10.1021/cg100646e

Tsuda, T. and Fujiwara, T. (1992). Polyethyleneimine and macrocyclic polyamine silica gels acting as carbon dioxide absorbents. *J. Chem. Soc.-Chem. Commun.* 1659–1661. doi:10.1039/C39920001659

Tsuda, T., Fujiwara, T., Taketani, Y., and Saegusa, T. (1992). Amino silica gels acting as a carbon dioxide absorbent. *Chem. Lett.* 21, 2161–2164. doi:10.1246/cl.1992.2161

United Nations Climate Change (2015). The Paris agreement. Available at: https://unfccc.int/process-and-meetings/the-paris-agreement/the-paris-agreement. (Accessed October 15, 2019).

United States Environmental Protection Agency (2016). Inventory of U.S. Greenhouse gas emissions and sinks: 1990-2014. Washington DC: US EPA, 558. Available at: https://www.epa.gov/sites/production/files/2017-04/documents/us-ghg-inventory-2016-main-text.pdf (Accessed April 15, 2016).

U.S. Energy Information Administration (2020). DOE/EIA-0035(2020/6). Monthly energy review, June 2020. Available at: https://www.eia.gov/totalenergy/data/monthly/archive/00352006.pdf

Vaccarelli, M., Carapellucci, R., and Giordano, L. (2014). Energy and economic analysis of the CO_2 capture from flue gas of combined cycle power plants. *Energy Procedia* 45, 1165–1174. doi:10.1016/j.egypro.2014.01.122

Vinoba, M., Bhagiyalakshmi, M., Alqaheem, Y., Alomair, A. A., Pérez, A., and Rana, M. S. (2017). Recent progress of fillers in mixed matrix membranes for CO_2 separation: a review. *Sep. Purif. Technol.* 188, 431–450. doi:10.1016/j.seppur.2017.07.051

Vitillo, J. G., Smit, B., and Gagliardi, L. (2017). Introduction: carbon capture and separation. *Chem. Rev.* 117, 9521–9523. doi:10.1021/acs.chemrev.7b00403

Wang, X. and Song, C. (2019). "Capture of CO_2 from concentrated sources and the atmosphere," in *An economy based on carbon dioxide and water: potential of large scale carbon dioxide utilization*. Editors M. Aresta, I. Karimi, and S. Kawi (Switzerland, Cham: Springer International Publishing), 35–72

Wang, Y. M., Wu, Z. Y., Shi, L. Y., and Zhu, J. H. (2005). Rapid functionalization of mesoporous materials: directly dispersing metal oxides into as-prepared SBA-15 occluded with template. *Adv. Mater.* 17, 323–327. doi:10.1002/adma.200400860

Wang, X. X., Schwartz, V., Clark, J. C., Ma, X. L., Overbury, S. H., Xu, X. C., et al. (2009). Infrared study of CO_2 sorption over "molecular basket" sorbent consisting of polyethylenimine-modified mesoporous molecular sieve. *J. Phys. Chem. C* 113, 7260–7268. doi:10.1021/jp809946y

Wang, C., Luo, X., Luo, H., Jiang, D.-e., Li, H., and Dai, S. (2011). Tuning the basicity of ionic liquids for equimolar CO_2 capture. *Angew. Chem. Int. Ed. Engl.* 50, 4918–4922. doi:10.1002/anie.201008151

Wang, D. X., Sentorun-Shalaby, C., Ma, X. L., and Song, C. S. (2011). High-capacity and low-cost carbon-based "molecular basket" sorbent for CO_2 capture from flue gas. *Energy Fuels* 25, 456–458. doi:10.1021/ef101364c

Wang, Q., Luo, J., Zhong, Z., and Borgna, A. (2011). CO_2 capture by solid adsorbents and their applications: current status and new trends. *Energy Environ. Sci.* 4, 42–55. doi:10.1039/C0EE00064G

Wang, C., Liu, X., Keser Demir, N., Chen, J. P., and Li, K. (2016). Applications of water stable metal–organic frameworks. *Chem. Soc. Rev.* 45, 5107–5134. doi:10.1039/C6CS00362A

Wang, S., Li, X., Wu, H., Tian, Z., Xin, Q., He, G., et al. (2016). Advances in high permeability polymer-based membrane materials for CO_2 separations. *Energy Environ. Sci.* 9, 1863–1890. doi:10.1039/C6EE00811A

Wang, S., Schrunk, E. T., Mahajan, H., and Farrauto, A. R. J. (2017). The role of ruthenium in CO_2 capture and catalytic conversion to fuel by dual function materials (DFM). *Catalysts* 7, 88

Wang, Y., Zhao, L., Otto, A., Robinius, M., and Stolten, D. (2017). A review of post-combustion CO_2 capture technologies from coal-fired power plants. *Energy Procedia* 114, 650–665. doi:10.1016/j.egypro.2017.03.1209

Wang, S., Farrauto, R. J., Karp, S., Jeon, J. H., and Schrunk, E. T. (2018). Parametric, cyclic aging and characterization studies for CO_2 capture from flue gas and catalytic conversion to synthetic natural gas using a dual functional material (DFM). *J. CO2 Util.* 27, 390–397. doi:10.1016/j.jcou.2018.08.012

Wang, X., Fujii, M., Wang, X., and Song, C. (2020). New approach to enhance CO_2 capture of "molecular basket" sorbent by using 3-aminopropyltriethoxysilane to reshape fumed silica support. *Ind. Eng. Chem. Res.* 59, 7267–7273. doi:10.1021/acs.iecr.9b06459

Wappel, D., Gronald, G., Kalb, R., and Draxler, J. (2010). Ionic liquids for post-combustion CO_2 absorption. *Int. J. Greenh. Gas Control* 4, 486–494. doi:10.1016/j.ijggc.2009.11.012

Webley, P. A. (2014). Adsorption technology for CO_2 separation and capture: a perspective. *Adsorption* 20, 225–231. doi:10.1007/s10450-014-9603-2

Wu, H., Li, X., Li, Y., Wang, S., Guo, R., Jiang, Z., et al. (2014). Facilitated transport mixed matrix membranes incorporated with amine functionalized MCM-41 for enhanced gas separation properties. *J. Membr. Sci.* 465, 78–90. doi:10.1016/j.memsci.2014.04.023

Wu, H., Chen, W., Wu, J., Zheng, Z., and Duan, L. (2019). Synergistic removal of SOx and NOx in CO_2 compression and purification in oxy-fuel combustion power plant. *Energy Fuels* 33, 12621–12627. doi:10.1021/acs.energyfuels.9b03284

Xu, X. C., Song, C. S., Andresen, J. M., Miller, B. G., and Scaroni, A. W. (2002). Novel polyethylenimine-modified mesoporous molecular sieve of MCM-41 type as high-capacity adsorbent for CO_2 capture. *Energy Fuels* 16, 1463–1469. doi:10.1021/ef020058u

Xu, X. C., Song, C. S., Andresen, J. M., Miller, B. G., and Scaroni, A. W. (2003). Preparation and characterization of novel CO_2 "molecular basket" adsorbents based on polymer-modified mesoporous molecular sieve MCM-41. *Micropor. Mesopor. Mater.* 62, 29–45. doi:10.1016/S1387-1811(03)00388-3

Xu, X. C., Song, C. S., Miller, B. G., and Scaroni, A. W. (2005). Influence of moisture on CO_2 separation from gas mixture by a nanoporous adsorbent based on polyethylenimine-modified molecular sieve MCM-41. *Ind. Eng. Chem. Res.* 44, 8113–8119. doi:10.1021/ie050382n

Xu, D., Xiao, P., Zhang, J., Li, G., Xiao, G., Webley, P. A., et al. (2013). Effects of water vapour on CO_2 capture with vacuum swing adsorption using activated carbon. *Chem. Eng. J.* 230, 64–72. doi:10.1016/j.cej.2013.06.080

Xu, X., Pejcic, B., Heath, C., and Wood, C. D. (2018). Carbon capture with polyethylenimine hydrogel beads (PEI HBs). *J. Mater. Chem. A* 6, 21468–21474. doi:10.1039/C8TA07760F

Yamada, H., Chowdhury, F. A., Goto, K., and Higashii, T. (2013). CO_2 solubility and species distribution in aqueous solutions of 2-(isopropylamino)ethanol and its structural isomers. *Int. J. Greenh. Gas Control.* 17, 99–105. doi:10.1016/j.ijggc.2013.03.027

Yan, Y., Mattisson, T., Moldenhauer, P., Anthony, E. J., and Clough, P. T. (2020). Applying machine learning algorithms in estimating the performance of heterogeneous, multi-component materials as oxygen carriers for chemical-looping processes. *Chem. Eng. Trans.* 387, 124072. doi:10.1016/j.cej.2020.124072

Yang, Z.-Z., He, L.-N., Zhao, Y.-N., Li, B., and Yu, B. (2011a). CO_2 capture and activation by superbase/polyethylene glycol and its subsequent conversion. *Energy Environ. Sci.* 4, 3971–3975. doi:10.1039/C1EE02156G

Yang, Z.-Z., Zhao, Y.-N., and He, L.-N. (2011b). CO_2 chemistry: task-specific ionic liquids for CO_2 capture/activation and subsequent conversion. *RSC Adv.* 1, 545–567. doi:10.1039/C1RA00307K

Yang, S. B., Zhan, L., Xu, X. Y., Wang, Y. L., Ling, L. C., and Feng, X. L. (2013). Graphene-based porous silica sheets impregnated with polyethyleneimine for superior CO_2 capture. *Adv. Mater.* 25, 2130–2134. doi:10.1002/adma.201204427

Yong, Z., Mata, V., and Rodriguez, A. E. (2001). Adsorption of carbon dioxide onto hydrotalcite-like compounds (HTlcs) at high temperatures. *Ind. Eng. Chem. Res.* 40, 204–209. doi:10.1021/ie000238w

Yong, W. F., Lee, Z. K., Chung, T.-S., Weber, M., Staudt, C., and Maletzko, C. (2016). Blends of a polymer of intrinsic microporosity and partially sulfonated polyphenylenesulfone for gas separation. *ChemSusChem* 9, 1953–1962. doi:10.1002/cssc.201600354

Yong, J. K. J. (2016). The development of thin films for efficient carbon capture and storage. PhD thesis. (Melbourne, Australia: The University of Melbourne)

Yoshimune, M. and Haraya, K. (2013). CO_2/CH_4 mixed gas separation using carbon hollow fiber membranes. *Energy Procedia* 37, 1109–1116. doi:10.1016/j.egypro.2013.05.208

Yu, C. H., Huang, C. H., and Tan, C. S. (2012). A review of CO_2 capture by absorption and adsorption. *Aerosol Air Qual. Res.* 12, 745–769. doi:10.4209/aaqr.2012.05.0132

Yue, M. B., Chun, Y., Cao, Y., Dong, X., and Zhu, J. H. (2006). CO_2 capture by As-prepared SBA-15 with an occluded organic template. *Adv. Funct. Mater.* 16, 1717–1722. doi:10.1002/adfm.200600427

Yue, M. B., Sun, L. B., Cao, Y., Wang, Y., Wang, Z. J., and Zhu, J. H. (2008). Efficient CO_2 capturer derived from as-synthesized MCM-41 modified with amine. *Chem. – A Eur. J.* 14, 3442–3451. doi:10.1002/chem.200701467

Zelenak, V., Badanicova, M., Halamova, D., Cejka, J., Zukal, A., Murafa, N., et al. (2008a). Amine-modified ordered mesoporous silica: effect of pore size on carbon dioxide capture. *Chem. Eng. J.* 144, 336–342. doi:10.1016/j.cej.2008.07.025

Zelenak, V., Halamova, D., Gaberova, L., Bloch, E., and Llewellyn, P. (2008b). Amine-modified SBA-12 mesoporous silica for carbon dioxide capture: effect of amine basicity on sorption properties. *Micropor. Mesopor. Mater.* 116, 358–364. doi:10.1016/j.micromeso.2008.04.023

Zeng, S., Zhang, X., Bai, L., Zhang, X., Wang, H., Wang, J., et al. (2017). Ionic-liquid-based CO_2 capture systems: structure, interaction and process. *Chem. Rev.* 117, 9625–9673. doi:10.1021/acs.chemrev.7b00072

Zhang, X., Liu, Z., and Wang, W. (2008). Screening of ionic liquids to capture CO_2 by COSMO-RS and experiments. *AIChE J.* 54, 2717–2728. doi:10.1002/aic.11573

Zhang, Z. H., Ma, X. L., Wang, D. X., Song, C. S., and Wang, Y. G. (2012). Development of silica-gel-supported polyethylenimine sorbents for CO_2 capture from flue gas. *Aiche J.* 58, 2495–2502. doi:10.1002/aic.12771

Zhang, Y., Sunarso, J., Liu, S., and Wang, R. (2013). Current status and development of membranes for CO_2/CH_4 separation: a review. *Int. J. Greenh. Gas Control* 12, 84–107. doi:10.1016/j.ijggc.2012.10.009

Zhang, Z. J., Zhao, Y. G., Gong, Q. H., Li, Z., and Li, J. (2013). ChemInform Abstract:MOFs for CO_2 capture and separation from flue gas mixtures: the effect of multifunctional sites on their adsorption capacity and selectivity. *Chem. Commun.* 49, 653–661. doi:10.1039/c2cc35561b

Zhang, R., Wang, X., Liu, S., He, L., Song, C., Jiang, X., et al. (2019). Discovering inherent characteristics of polyethylenimine-functionalized porous materials for CO_2 capture. *ACS Appl. Mater. Interfaces* 11, 36515–36524. doi:10.1021/acsami.9b08496

Zhou, H.-C., Long, J. R., and Yaghi, O. M. (2012). Introduction to metal–organic frameworks. *Chem. Rev.* 112, 673–674. doi:10.1021/cr300014x

Zhou, Z., Sun, N., Wang, B., Han, Z., Cao, S., Hu, D., et al. (2020). 2D-Layered Ni–MgO–Al_2O_3 nano-sheets for integrated capture and methanation of CO_2. *ChemSusChem* 13, 360–368. doi:10.1002/cssc.201902828

Zhuang, Q., Clements, B., Dai, J., and Carrigan, L. (2016). Ten years of research on phase separation absorbents for carbon capture: achievements and next steps. *Int. J. Greenh. Gas Control* 52, 449–460. doi:10.1016/j.ijggc.2016.04.022

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REVIEW
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Catalytic Conversion of Carbon Dioxide to Methanol: Current Status and Future Perspective

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With the increasing environmental problems caused by carbon dioxide (CO_2) emission and the ultimate carbon resources needed for the development of human society, CO_2 hydrogenation to methanol with H_2 produced with renewable energy represents a promising path forward. Comprehensive analysis shows that the production of methanol by thermal catalytic CO_2 hydrogenation is the most promising technology for large-scale industrialization. This review highlights current developments and future perspectives in the production of methanol from CO_2, as well as the main existing problems based on a thorough techno-economic analysis. Moreover, the utilization status and future role of methanol as a platform molecule in the energy system is analyzed. Finally, in this review attention is paid to the development of new catalysts, new routes and new technologies for CO_2 conversion aiming to clarify the future direction.

Keywords: CO_2 conversion, methanol synthesis, new catalysts, new routes, new technologies

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INTRODUCTION

While absorbing solar radiation, the earth is also losing energy to the space, so that the energy in and out of the earth system is basically the same (**Figure 1A**). However, human activities are breaking the balance, and the situation is becoming more and more serious. In May 2019, CO_2 concentration in the atmosphere exceeded 415 ppm, about 48% higher than that before the industrial revolution. The magnitude and rate of this increase, at least in the earth's nearly 800,000 years of history, is unprecedented (**Figure 1B**). The greenhouse effect caused by carbon emission has led to a series of extreme weather and is threatening the future of our living planet (Iizumi et al., 2018). Researchers speculate that the increase of extremely severe cyclonic storms over the Arabian Sea caused by ocean warming may be the ringleader of this unprecedented locust disaster in 2020 (Murakami et al., 2017). Moreover, global warming will continue to increase the risk of a deadly flood outbreak due to the collapse of an ice lake in the Himalayas (Veh et al., 2020). Related researches also pointed out that global warming is making some originally quiet volcanoes restless due to the increase of extremely heavy rainfall (Zhang et al., 2018; Farquharson and Amelung, 2020). Presently, slow GDP growth and rising energy prices have not stopped the rise of energy consumption, and carbon emission exceeded ~34,000 million tons both in 2018 and 2019, higher than the emission in recent years (**Figure 2**) (Dudley, 2019).

CO_2 utilization has been defined as the process of using it as a raw material for products or services with a potential market value. The utilization includes direct approach (International Energy Agency, 2019; Ra et al., 2020), where CO_2 is not chemically altered (non-conversion), and the chemical and biological conversion of CO_2 to useful products (**Figure 3**). Most existing commercial applications

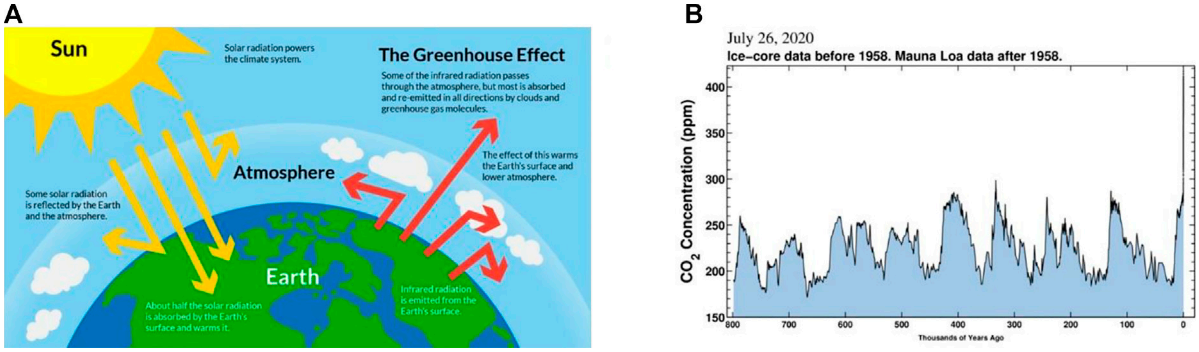

FIGURE 1 | (A) Schematic diagram of the energy budget of the earth: the yellow arrows are the short wave radiation reflected and absorbed by the earth; the red arrows are the long wave radiation absorbed by greenhouse gases and released from the earth. Figure from: https://science-u.org/experiments/solar-oven-smores.html. **(B)** Changes of atmospheric CO_2 concentration in the past 800,000 years. Figure from: Scripps Institute of Oceanography, https://sioweb.ucsd.edu/programs/keelingcurve/.

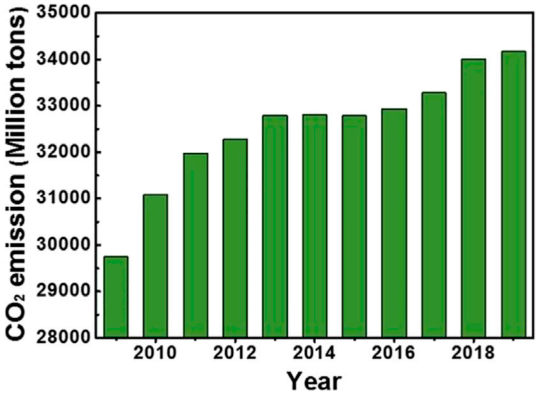

FIGURE 2 | Global CO_2 emission from the activities related to the combustion of oil, coal and natural gas (Dudley, 2019).

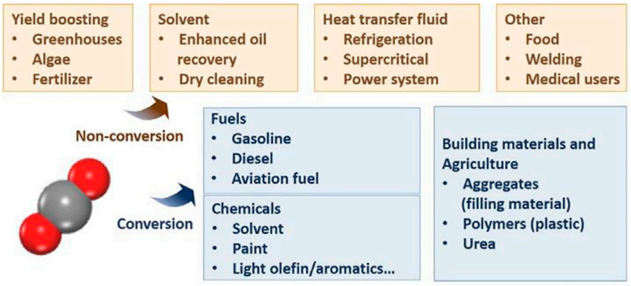

FIGURE 3 | Simple classification of CO_2 utilization pathways.

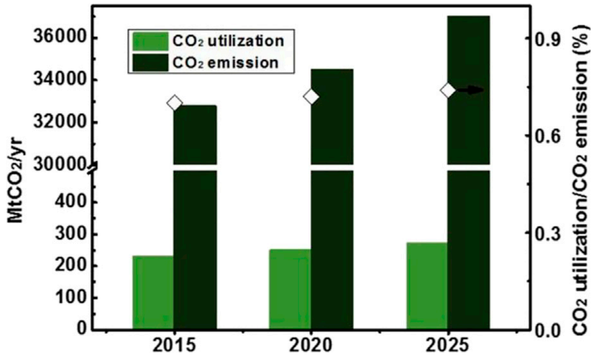

FIGURE 4 | Growth in global utilization and emission of CO_2. Note: Projections for future global CO_2 demand are based on an average year-on-year growth rate of 1.7% (International Energy Agency, 2019). Projections for future global CO_2 emission are based on an average year-on-year growth rate of 1.4% (based on the annual average growth rate of 2009–2019) (Dudley, 2019).

involve direct utilization, including the production of food and beverages, metals fabrication, dry cleaning, healthcare, fire suppression, and the petroleum industry. Although still under development, the chemical and biological utilization has drawn much attention in recent years, including developing CO_2-derived fuels (Satthawong et al., 2013), chemicals and building materials (Jiang et al., 2015; Li et al., 2018; Liu et al., 2018a; Wang et al., 2020a; Zhu et al., 2020). Today, around 230 million tons (Mt) of CO_2 are used each year (IEA, 2019a). However, the CO_2 utilization is less than 1% of the CO_2 released (**Figure 4**). The largest consumer is agriculture, where around 130 Mt of CO_2 per year is used in urea manufacturing, followed by the oil industry, with a consumption of 70 to 80 Mt of CO_2 for enhanced oil recovery (IEA, 2019b). More than two-thirds of current global demand for CO_2 come from North America (33%), China (21%) and Europe (16%), and the demand for existing uses is expected to grow steadily year-on-year (IEA, 2019a). Until now, the process of CO_2 conversion to chemicals is limited by the market scale. Therefore, the development of target product methanol, which can be used as fuels and chemicals (Sakakura et al., 2007; Yu et al., 2010; Cokoja et al., 2011; Peters et al., 2011), is of great significance for achieving a large-scale application.

Methanol can be integrated into the current energy system and used as 1) a convenient energy-storage material, 2) a fuel, and 3) a feedstock to synthesize hydrocarbons, and an all-around substitute for petroleum (Olah, 2005; He et al., 2013; Araya et al., 2020). Indian government has been promoting clean transportation and the application of fuel-cell vehicles (Reddy et al., 2018). Dor Group began pilot testing in 2012 after the government of Israel determined one of the most favorable way to reduce the reliance on conventional fuels which is the use of methanol as the gasoline replacement, or gasoline-blending component, in internal combustion engines (Dor Group, 2019). China is also speeding up the layout of methanol fuel market. Eight departments including the Ministry of Industry and Information technology of China jointly issued the Guidance on the Application of Methanol Vehicles in Some Regions (2019). Shanxi, Shaanxi, Guizhou, Gansu and other regions are accelerating the application of M100 methanol vehicle and realizing the diversification of vehicle fuel to ensure energy safety, for they have good resource endowment conditions and methanol vehicle operation experience (Ministry of Industry and Information Technology of the People's Republic of China, 2019). Compared with the top-down development mode of natural gas, ethanol and other clean energy (policy in front, promotion and application in the back), that of methanol is bottom-up, and after long-term exploration, practice and verification, the above policy documents are in place.

Comprehensive reviews were presented about the recent significant advances in CO_2 hydrogenation to methanol, focusing on development of catalysts including metals, metal oxides, and bimetallic catalysts, as well as the structure-activity relationship, *in situ* characterizations on identifying key descriptors and understanding reaction mechanisms (Jiang et al., 2020; Zhong et al., 2020). Researchers also provided an in-depth assessment of core-shell materials for the catalytic conversion of CO_2 into chemicals and fuels (Das et al., 2020). ZrO_2-containing catalysts are also systematically reviewed to offer insights into the modification of surface properties and bulk structure of catalysts driven by the supports and the resulting effects on the performance for CO_2 hydrogenation to methanol (Li and Chen, 2019). Based on the summary of the research status of the catalytic materials in published reviews, this review is organized toward the future development prospects, with an emphasis on the role of methanol in the energy system in the future and technical feasibility. By analyzing the current status of thermocatalytic conversion of CO_2 into methanol, the review highlights the development of catalysts regarding precise preparation, large-scale production, high efficiency and low cost.

ANALYSIS OF THE WHOLE PROCESS OF THERMAL CATALYSIS OF CO_2 TO METHANOL

CO_2 life cycle assessment is helpful to pick out the main problems existing in the process of CO_2 conversion. Researchers have introduced a mathematical formulation to select the promising CO_2 capture and utilization (CCU) paths. The results indicate that the optimal solution is greatly influenced by the market demand, scale of CO_2 emission source, and H_2 availability (Roh et al., 2019). Therefore, target products that can be used as fuels and chemicals are of great significance for the large-scale emission reduction. Moreover, small-molecule products have irreplaceable advantages compared with large-molecule products, due to the high selectivity, simple process, low energy consumption, etc. As a fuel and an important chemical feedstock, methanol is used on a large scale, and has been used as a feedstock for the synthesis of chemicals and fuels (Olsbye et al., 2012). The hydrogenation of CO_2 to methanol has attracted much attention as a promising way (Behrens et al., 2012; Kattel et al., 2017a; Wang et al., 2017; Lam et al., 2018; Dang et al., 2019b; Wang et al., 2019b; Li and Chen 2019). Next, we will discuss the role of methanol in the future energy system, technical feasibility and techno-economic analysis for methanol synthesis from CO_2. By analyzing the research status and development potential of CO_2 hydrogenation to methanol, we aim to find out the existing problems and point out the direction for future research.

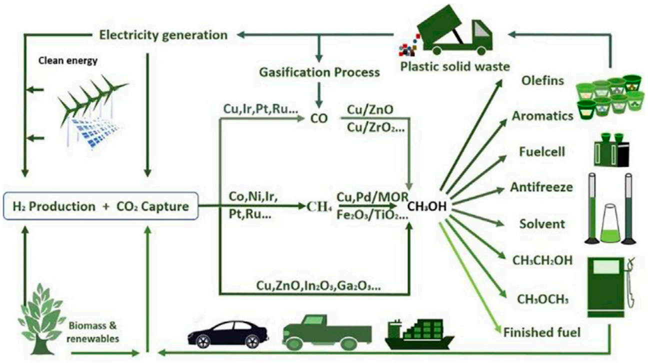

FIGURE 5 | The simplified carbon cycle with methanol as platform molecule in the future.

The Importance of Methanol in the Field of Energy

In the future we will phase out fossil fuels and switch to sustainable energy, especially hydroelectricity, wind and photovoltaic energy. However, due to the variable nature of the latter sources which depend on time of day, and season of the year, we need to store such energy at peak production times for use in times of low production. Converting such energy into chemical energy and storing it in methanol molecules is regarded as one of the promising methods. Methanol is considered as one of the potential platform molecules because of its available applications in the fields of fuels and chemicals in the future (**Figure 5**) (Su et al., 2013). At present, methanol-based technologies include methanol synthesis, methanol to olefins, chemicals (formaldehyde, acetic acid, methylamines, glycol, etc.), gasoline, biodiesel, direct combustion and so on (**Figure 6**). The methanol economy through chemical recycling of CO_2 will eventually free human from dependence on fossil fuels (Tountas et al., 2019). In recent years, China has developed a

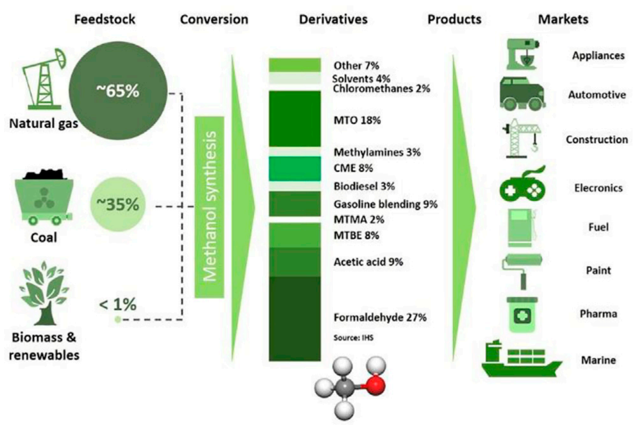

FIGURE 6 | Fuels and chemicals based on methanol. Source: Methanol Institute, www.methanol.org.

series of clean coal technologies to transform black-dirty coal into clean fuels and chemicals. Clean coal technologies based on methanol platform will play an important role in Chinese energy system in the future (Xu et al., 2017). Shenhua, the largest coal company in China is leading the commercialization of modern clean-coal technologies for value-added chemicals and transportation fuels.

As a potential clean energy carrier, methanol has been widely used in the transportation fields such as methanol vehicles, ships, heavy trucks, industrial boilers, stoves and other industrial and civil fields. The use of methanol as transport power has begun to take shape. There are more than 6,000 well-running methanol vehicles and 20 methanol filling stations in Xi'an, China (China Energy News, 2019). The pilot projects around methanol fuel are also increasing. Methanol gasoline has the characteristics of high-octane value, clean and low energy consumption. Compared with gasoline and diesel, methanol can burn fully, and its application as fuels can effectively reduce the emission of harmful gases. The emission of PM2.5 can be reduced by 80–85%, NO_x by 60–80%, and CO by 75–90% (Olah, 2005). According to the economic analysis of methanol vehicles in Xi'an pilot project, the methanol consumption per 100 kilometers is about RMB 35 yuan, and the gasoline consumption is about RMB 70 yuan. The price comparison of conventional oil products is summarized in **Table 1**.

Dor Group's pilot tests in Israel suggest that methanol can at least provide a partial alternative to conventional or reformulated gasoline, particularly in regions with abundant but seemingly stranded supplies of natural gas, such as the United States. Based upon methanol-gasoline price ratios as of early January 2015, a reduction of ~20% in unit energy costs could be achieved depending on the fluctuating cost of crude oil, as well as other market factors (Netzer et al., 2015). Based on the current methanol-gasoline price ratio, at least in China, it is economically feasible to replace conventional gasoline with methanol. Methanol is also used as internal combustion engine fuel for large ships. Diesel methanol dual-fuel ships have entered the marine transportation trade. The first methanol smart industrial park is located at Jiangxi, China. The intelligent industrial park of new energy will be the first specialized industrial cluster in China with "methanol smart industrial chain" as the main body, and the annual output value is expected to reach 10 billion after it is put into operation. ZHONGSHANG GUOXIN is planning to build six distribution centers in China, striving to gradually cover more than 10,000 retail terminals in 3–5 years. As the world's largest methanol producer and consumer, Chinese methanol production capacity accounts for more than 50% of the world's total. As of 2016, the annual production capacity has reached 80 million tons, and the production capacity of methanol is still increasing (China Energy News, 2019). Several locations in North America are also considering to convert petroleum coke into methanol. Methanol is becoming an important part of the future energy system.

TABLE 1 | Comparison of oil prices.

Products	Methanol	ethanol	Gasoline
Price ($/kg)[a]	0.30	0.75	1.00
($/km)[b]	0.05		0.1
Endurance mileage (km/kg)	6		10

[a] *Data from Wanhua Chemical's Petrochemical Information, 20190911;*
[b] *Data from: (China Energy News, 2019).*

Technical Feasibility

Thermocatalytic methanol synthesis from CO_2 has a solid theoretical basis. Catalysts with different metals like Cu, Zn, Ag, Cr, and Pd have been employed for CO_2 hydrogenation to methanol (Kattel et al., 2017a; Dang et al., 2019b; Din et al., 2019). Nevertheless, Cu-based catalysts exhibit high activity and selectivity. Different promoters (ZnO, ZrO_2, and LaO_x, etc.) have been used to improve the activity of Cu-based catalysts (Ham et al., 2018; Hu et al., 2018; Chen et al., 2019a; Mureddu et al., 2019; Noh et al., 2019). In addition, the reaction conditions (temperature, pressure, and feed gas ratio, etc.) have also been investigated systematically (Arena et al., 2013; Kobl et al., 2016; Din et al., 2019). Due to exothermic nature of the reaction, the process is thermodynamically favorable at low temperature. According to Le Chatelier's principle, higher pressure will promote the formation of methanol. Therefore, reactors must be able to work at high pressure and moderate temperature. Most importantly, there must be 1) an efficient method to remove the heat released from the reactor, and 2) a recycle facility to send unreacted feedstocks back to the reactor after separating methanol and H_2O. The exotherm from the reactor will be used elsewhere, for instance, in preheat of the feedstocks, or distillation of the methanol (Bowker, 2019).

Thermal catalytic methanol production from CO_2 has a mature industrial application background (Luu et al., 2015). As early as 1923, methanol was produced at the industrial scale from syngas derived from coal, thanks to the work of Alwin Mittasch and Mathias Pier at BASF (Aresta et al., 2015). Today, more than 90 plants are in operation worldwide, nearly 200,000 tons of methanol is used as a chemical feedstock or a transportation fuel every day

(Methanol Institute, 2020). George Olah's methanol economy is exemplified in a renewable methanol production plant in Reykjavik, Iceland. This industrial facility commissioned in 2007 annually produces 4,000 metric tons of methanol from CO_2 and H_2 (Tountas et al., 2019). There is another demonstrator plant for methanol synthesis, namely the pan-European MefCO_2 project (MefCO2, 2020). It has been constructed very recently at Niederaussem near Cologne, at the RWE coal-fired power station with an annual output of 500 tons of methanol.

Techno-Economic Analysis for Methanol Synthesis From CO_2

Techno-economic assessment for CO_2 hydrogenation to methanol is helpful to guide decision-making regarding R&D investment and construction of large-scale CCU plants in the future. Therefore, researchers have investigated a solar-based system for methanol synthesis from CO_2 and H_2O. The entire system (thermochemical reactor, water gas shift reaction system, methanol synthesis reaction system, amine-based CO_2 separation system and methanol purification system) is based on mature industrial processes, except for the thermochemical reactor currently under development. Thermochemical reactor is a solar chemical heat engine that allows for the thermochemical splitting of CO_2, which is an ultra-high temperature two-step FeO/Fe_3O_4 cycle process. Detailed sensitivity analysis shows that a breakeven price of methanol produced using this process would be 1.22 \$/kg; which is higher than current market price of 0.24 \$/kg. Importantly, the analysis here identifies that more than 90% of the capital investment comes from the solar concentrator/reactor system (Kim et al., 2011). Life cycle analysis shows that methanol synthesis from CO_2 emitted by coal plant exhaust is predicted to be 1.3–2.6 times higher than that of its fossil-based analogue, which can be estimated to decrease significantly with a drop in electricity cost for H_2 production (González-Garay et al., 2019). China will levy carbon tax after 2020 for enterprises whose comprehensive energy consumption is less than 5,000 tons of standard coal (China Energy News, 2019). The implementation of carbon tax policy will further improve the market competitiveness of methanol by reducing the cost of CO_2 capture. In addition, significant advances can be achieved by improving separation, combing splitting of H_2O and CO_2, and process integration and distribution in the future.

Based on a comprehensive economic analysis, the best-case scenario, where electricity price is 0.06 \$/kWh with 30 years plant lifetime, 0.02 \$/kg CO_2 cost and solar-to-hydrogen (STH) efficiency of 10%, has a break-even value of 0.96 \$/kg for methanol (Alsayegh et al., 2019). The current price of H_2 from natural gas and coal plants varies between 1–3 \$/kg, among which the price of H_2 by steam methane reforming is about 1.59 \$/kg (Roy et al., 2018; Esposito, 2017). The price of H_2 from renewable energy sources varies between 4.00–10.00 \$/kg (Roy et al., 2018). If the cost of H_2 from renewable energy sources can be reduced to 2.75 \$/kg, CO_2-based fuel becomes cost competitive with gasoline (Smejkal et al., 2014). Fortunately, the cost of H_2 varied from 1.60–10.40 \$/kg for the photoelectrochemical water splitting by the analysis of all operating costs, capital expenditures for the auxiliaries (compressors, control systems, etc.) and reactors with the particle bed systems (Pinaud et al., 2013), indicating that commercial-scale water splitting could be cost-competitive with fossil-based fuels. CO_2 capture incurs costs from capital investment, energy for operating the process, cost of CO_2 release, sorbent losses, maintenance of equipment, CO_2 compression and transportation. The estimated cost for flue gas capture is between 0.028–0.104 \$/kg of CO_2 depending on the emission source (Rubin et al., 2015), while estimates for direct air capture costs are still under debate, with reports ranging from 0.030 to 1.000 \$/kg of CO_2 (Sanz-Pérez et al., 2016). Moreover, the implementation of carbon tax policy will further reduce the cost of CO_2 capture. The single pass yield of CO_2 hydrogenation to methanol is about 15% (Ham et al., 2018; Chen et al., 2019a; Mureddu et al., 2019; Wang et al., 2019b). Several examples of overall water splitting processes using semiconductor photocatalysts have been reported. The maximum STH efficiency is more than 1%, but still lower than the benchmark STH value of 10% (Chen et al., 2018b). Analysis of the above parameters shows that there is still a big gap between the current technical level and the requirements based on the techno-economic analysis, and detailed parameters are shown in **Table 2**. However, the efficiency can be improved by adjusting the process route. For example, H_2 can be produced by electrolysis of H_2O by using clean energy to generate electricity, and the STH value is expected to exceed 20% (silicon-perovskite solar cells: 25.2% efficiency (Service, 2016); Faradaic efficiency of H_2 production from electrolytic water: 99% (Dotan et al., 2019). Recently, perovskite/Si dual-absorber cells have been used for the stand-alone solar water splitting. 17.6% STH efficiency was achieved when a Si photocathode was paired in tandem with a perovskite cell (Karuturi et al., 2020). Of course, we must consider its impact on methanol production costs while pursuing energy efficiency. In order to improve the yield of methanol, the production of methanol should be carried out under the conditions of low temperature and high pressure, but

TABLE 2 | Optimization parameters of techno-economic analysis and current data.

	Electricity price	Cost of H_2 produced	Cost of CO_2 captured	STH efficiency	Methanol yield	Methanol price
Data analysis parameters Alsayegh et al. (2019)	0.06 \$/kWh	0.65 \$/kg	0.02 \$/kg	10%	92%	0.96 \$/kg
Current data	0.14 \$/kWh[a]	1.6 \$/kg Pinaud et al. (2013)	0.035 \$/kg Rubin et al. (2015)	1% Chen et al. (2018b)	14.5% Wang et al. (2019b)	0.24 \$/kg[b]

[a] *Electricity price of china.*

[b] *Data from Wanhua Chemistry (20200702).*

the high pressure will inevitably increase the operating cost. Therefore, the development of high efficiency catalysts working at low temperature and pressure for CO_2 hydrogenation to methanol is an important research direction in the future. It is essential to combine *in situ* spectroscopy and theoretical calculation to better understand the mechanism of CO_2 conversion, and then develop new catalysts and new reaction paths to improve methanol production efficiency. With the innovation of catalyst preparation technology, new technologies and methods are adopted to achieve precise construction and modification of the active sites, thereby to achieve efficient production of methanol.

RESEARCH DIRECTION OF CATALYSIS

A wide variety of heterogeneous catalysts have been evaluated in CO_2 hydrogenation to methanol (**Figure 7**) (Jiang et al., 2015; Dang et al., 2019b; Nie et al., 2019; Das et al., 2020; Jiang et al., 2020; Zhong et al., 2020). The development of high-activity catalysts is conducive to reducing operating pressure and production costs. Simultaneously, the development of multifunctional catalysts to produce value-added products can also pull the equilibrium of the reaction by consuming the methanol intermediate according to the Le Chatelier's principle, and it can realize the coupling of multiple units such as the capture unit and the different conversion units. The new preparation technology is also a key link in catalyst research and development, which aims to achieve one-step synthesis of catalysts from precursors to industrial shaped catalysts. Therefore, the following four aspects will be discussed: 1) the research progress on active sites for methanol synthesis; 2) development of new catalysts; 3) exploration on new routes, mainly including CO_2 capture-transformation and metal oxide-zeolite catalysts; 4) exploration on new technology for catalysts preparation (3D-printing, plasma and atomic layer deposition technologies), emphasizing surface chemistry and engineering, so as to find the direction of future research.

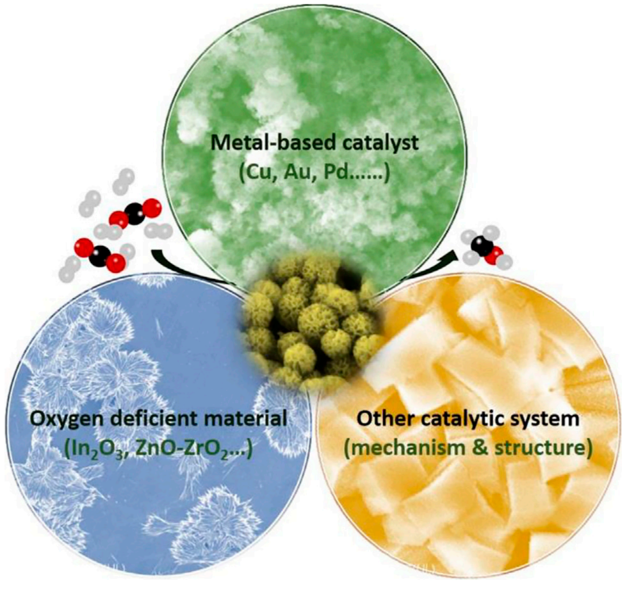

FIGURE 7 | Heterogeneous catalysts for methanol synthesis from CO_2 hydrogenation.

Understanding the Active Sites

One of the main obstacles in developing rational strategies for heterogeneous catalysis is that the complexity of catalysts hinders efforts to characterize their active sites. Deeper insights aid in the design of next-generation catalysts in an optimal manner, which will provide the opportunity to tune the catalytic performance by optimizing the functions of the components. In recent years, surface composition and structure of commercial Cu-ZnO-Al_2O_3 for methanol synthesis have attracted wide attention from both industry and academia. Active sites such as Zn-Cu bimetallic sites (Li et al., 2016), ZnO-Cu interfacial sites (Kattel et al., 2017b) and Cu steps decorated with Zn atoms have been reported (**Figures 8A,B**) (Behrens et al., 2012; Kuld et al., 2016). Experimental and theoretical investigation show that ZnCu alloy undergoes surface oxidation under the reaction conditions, which converts surface Zn into ZnO and allows ZnCu to reach the activity of ZnO/Cu with the same Zn coverage (Kattel et al., 2017b). Moreover, researchers found the formation of metastable "graphite-like" ZnO layers during the reductive activation of Cu/ZnO/Al_2O_3 (**Figure 8C**). Understanding this metastable layer might help to understand the synergistic effect between the components of Cu/ZnO/Al_2O_3 (Lunkenbein et al., 2015).

Supported Cu-based catalysts for methanol synthesis display strong support effects. Researchers attribute the difference between oxides to variation in the initial activation of CO_2 (Reichenbach et al., 2018). Through DFT (density functional theory) calculations and spectroscopic characterizations, researchers found that the ZrO_2-Cu interface is crucial for the conversion of formate to methanol (Larmier et al., 2017). It was also pointed that the beneficial role of the Zn ensemble in the Cu-vacant site of the stepped Cu (211) surface can enhance the reactivity and durability of catalysts for methanol production. The increased activity in the Zn-associated stepped sites is related to the enhancement of the surface affinity toward the adsorbate with the oxygen moiety (especially, HCOO) (Jo et al., 2019). The pre-assembled $Zr_6(\mu3\text{-}O)_4(\mu3\text{-}OH)_4$ and bpy sites in UiO-bpy metal-organic frameworks were used to anchor ultrasmall Cu/ZnO_x nanoparticles, thus preventing the agglomeration of Cu nanoparticles and phase separation of Cu/ZnO_x nanoparticles (**Figure 9A**). The Cu/ZnO_x@MOF shows high activity with a space-time yield of up to 2.59 $g_{MeOH}\ kg_{Cu}{}^{-1}h^{-1}$, 100% methanol selectivity and high stability over 100 hours (An et al., 2017). A $CuZnCeO_x$ catalyst with excellent activity, selectivity and stability was prepared by a parallel flow coprecipitation method. Characterization results show that a significant synergistic effect between Cu and metal oxides was observed at the composite catalysts (Hu et al., 2018). CuZnZr catalysts were treated by vapor-phase-treatment (VPT) method. This VPT method with TPABr promotes the formation of the rod-like structure, Zr and Zn enrichments on surface and the presence of more oxygen vacancies. The CuZnZr-TPABr-3 days shows a methanol selectivity above 90% and no significant deactivation within 100 h (Chen et al., 2019b). In short, the conversion of CO_2 can also be achieved at the interfacial sites by taking advantage of the synergy between the metals (Au, Cu, Ag, Pt, Pd, etc.) and oxides.

The study on metal-oxide interface provides a better understanding of the complex reaction network to identify the key descriptors of the activity and tune reaction performance (Kattel et al., 2017a). Surface organometallic chemistry has been used to tailor active components and oxide supports to understand the structure-activity relationship of catalysts. Cu/Al_2O_3 catalysts prepared by surface organometallic chemistry display higher activity toward CO_2 hydrogenation compared to Cu/SiO_2. Researchers found that methanol formation involves formate intermediates and that the increase of rate originates from the metal-oxide interface (Lam et al., 2019). Moreover, Cu nanoparticles supported on isolated Zr(IV) sites modified SiO_2 exhibit high methanol selectivity and activity compared to those loaded on SiO_2 (Lam et al., 2018). SiO_2 decorated with isolated Ti(IV) sites also show significantly improved methanol selectivity and CO_2 hydrogenation activity. These isolated Ti(IV) sites stabilize intermediates at the interface between the support and Cu nanoparticles (Noh et al., 2019). However, researchers found that the surface organometallic chemistry approach does not affect the rate of CO formation. Here, further exploration is needed to understand the differences of active sites and reaction paths for methanol and CO formation.

In the study on the support effect of Cu-based catalysts, we need to understand the difference between oxide supports with and without oxygen vacancies. Moreover, the exact structure and composition of the active sites need to be further identified under the reaction conditions, especially for the $Cu\text{-}ZnO\text{-}Al_2O_3$ catalysts. This also requires us to rethink the role of supports in industrial Cu-based catalysts, which is an active component and participating in the construction of interfacial active sites for CO_2 and H_2 activation or is mainly used to disperse active metals.

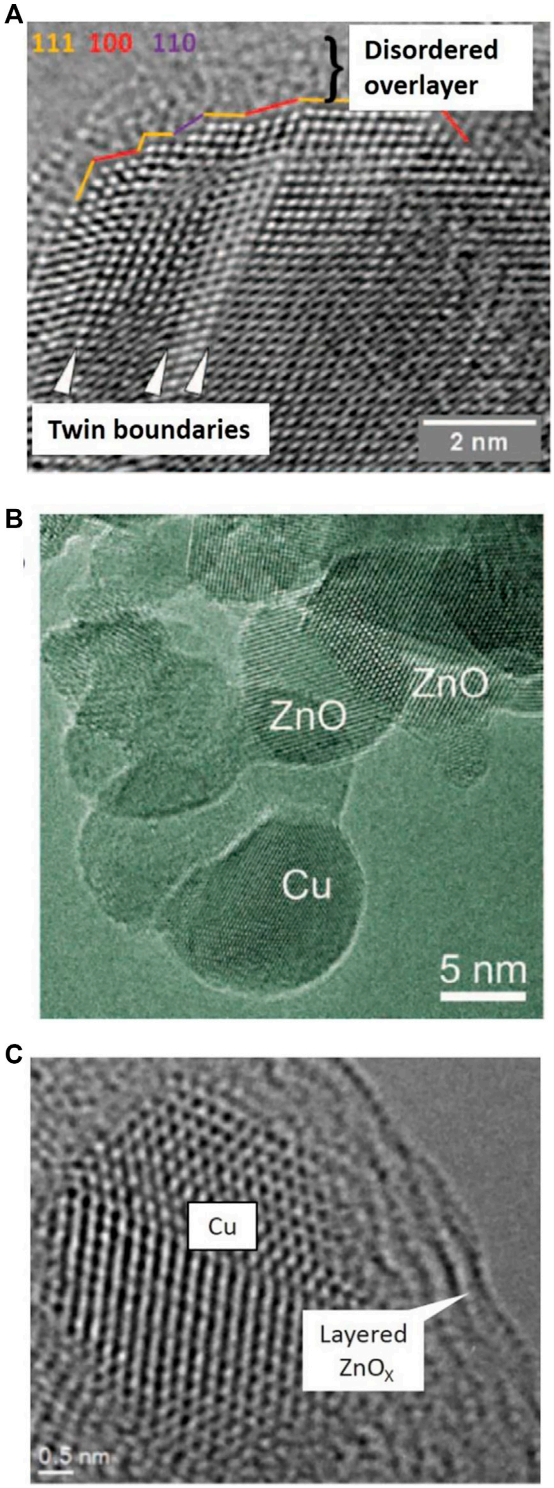

FIGURE 8 | (A) Aberration-corrected HRTEM images of Cu particles in the conventionally prepared, most-active $Cu/ZnO/Al_2O_3$ catalyst (Behrens et al., 2012). **(B)** Promoting effect of ZnO on Cu catalysts for methanol synthesis (Kuld et al., 2016). **(C)** Formation of a ZnO overlayer in industrial $Cu/ZnO/Al_2O_3$ catalysts induced by strong metal-support interactions (Lunkenbein et al., 2015).

New Catalyst Development

Metal oxide (indium-, zinc-based oxide, etc.) catalysts have drawn increasing attention, due to their excellent catalytic performance in the CO_2 hydrogenation reaction (Wang et al., 2020a). High activity and stability for 1,000 h on stream of In_2O_3/ZrO_2 has been achieved. Characterization points that the oxygen vacancies are active sites for methanol synthesis (Martin et al., 2016). Pd is applied to enhance the performance of indium-based catalysts. Pd atoms replacing indium atoms in the active In_3O_5 attract additional Pd atoms to form low-nuclearity clusters, which promotes H_2 activation (Frei et al., 2019). Methanol synthesis on the defective $In_2O_3(110)$ surface was investigated by DFT calculations. The calculation results indicate that the hydrogenation of H_2CO^* to H_3CO^* is the rate-limiting step for methanol formation (Ye et al., 2013). A binary metal oxide, $ZnO\text{-}ZrO_2$ solid solution catalyst, can achieve high methanol selectivity, high CO_2 single-pass conversion and high stability for at least 500 hours. Moreover, no deactivation was observed in the presence of SO_2 or H_2S in the reactants (Wang

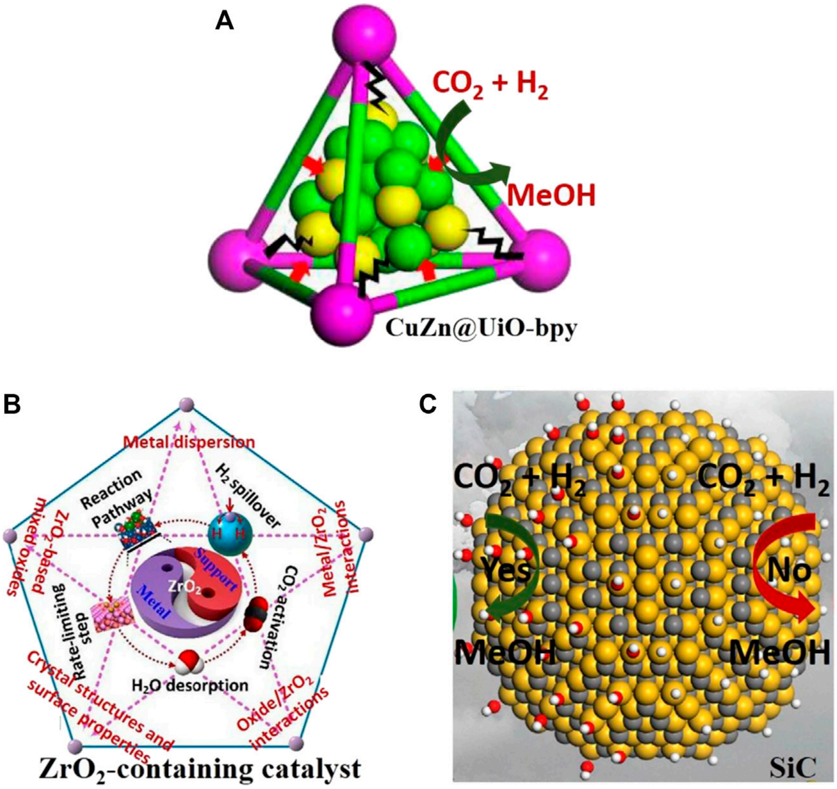

FIGURE 9 | (A) CuZn@UiO-bpy for selective methanol synthesis from CO_2 hydrogenation (An et al., 2017). **(B)** CO_2 hydrogenation to methanol over ZrO_2-containing catalysts (Li and Chen, 2019). **(C)** Hydroxyl groups of SiC surface boosting catalytic activity in CO_2 hydrogenation into methanol (Peng et al., 2018).

et al., 2017). ZrO_2 support always plays important roles such as dispersants of active components, promoter and even active component. The interaction between ZrO_2 and metals (or oxides) affects the adsorption and activation of CO_2 and H_2, and changes the reaction pathways and/or the binding of key intermediates (**Figure 9B**) (Li and Chen, 2019).

Exploring how surface properties regulate catalytic activity is also very important to deepen the mechanistic understanding. A molybdenum phosphide catalyst for methanol synthesis can improve the activity and stability of the catalyst in a wide range of $CO/CO_2/H_2$ feeds through weakening the interaction with formate (Duyar et al., 2018). Manganese-cobalt catalysts are also promising for methanol synthesis. A significant improvement in methanol selectivity was observed due to a synergistic effect between cobalt and manganese as well as an increase in surface basicity (Stangeland et al., 2019). Hydrophilic SiC quantum dots (QDs) exhibited higher activity than commercial SiC for CO_2 hydrogenation to methanol (**Figure 9C**). Mechanistic studies show that the surface hydroxyl species directly participate in CO_2 hydrogenation through the addition of H atoms in hydroxyl groups into CO_2 to form HCOO* intermediate (Peng et al., 2018). Understanding the interactions among different components (active metals, oxide supports and doped ions) and surface properties should help elucidate the governing principles for designing high-performance catalysts with multiple active components.

Researchers reported that supported Pt nanoparticles on MoO_x/TiO_2 promote selective hydrogenation of CO_2 to methanol under mild conditions (Toyao et al., 2019). Another kind of catalyst (Ni_aIn_bAl/SiO_2) for methanol synthesis at ambient pressure was prepared by a phyllosilicate precursor, which can form well-dispersed metallic particles. The performances of Ni_aIn_bAl/SiO_2 is better than that of conventional $Cu/ZnO/Al_2O_3$ catalyst at ambient pressure (Richard and Fan, 2017). A Ni-Ga catalyst can reduce CO_2 to methanol at ambient pressure. Ni_5Ga_3 is particularly active and selective among a series of tested catalysts (Studt et al., 2014). Moreover, SiO_2, acting as a ligand and support, can also modify cobalt species via Co-O-Si linkages, which favors the reactivity of $^*CH_3O$ intermediates and hydrogenation to methanol rather than the C-O dissociation to produce methane (Wang et al., 2020b).

At present, the harsh operation conditions of industrial process restrict the development of the methanol industry, and also bring large energy consumption. In the future, the research and development of new catalysts should proceed toward mild operating conditions, with the purpose of reducing energy consumption. Simultaneously, if H_2 production is decentralized, small-scale CO_2 reduction devices that can be operated at low pressures and low temperature are required. Moreover, the development of catalysts with high activity at low temperature is also conducive to coupling the active components of CO_2 capture, and realizing the integrated operation of CO_2

capture and conversion. Transition metals (Ni, Co, etc.) often have high hydrogenation activity. How to realize the synthesis of methanol with high selectivity by transition metal catalysts is a fascinating research direction in the future.

New Route Exploration

Integrative CO_2 Capture and Conversion

The integration of CO_2 capture and conversion can simplify the CO_2 cycle process and reduce energy consumption. An air-stable and well-defined Mn-PNP pincer complex catalyzed one-pot homogeneous CO_2 hydrogenation to methanol is demonstrated. The hydrogenation consists of two steps, N-formylation of an amine utilizing CO_2 and H_2, and subsequent formamide reduction to methanol, regenerating the amine. Methanol yields up to 71% and 84% (w.r.t amine) were obtained, when morpholine and benzylamine were used, respectively; and a TON (turn over number) of 36 was observed (Kar et al., 2017). CO_2 can also be captured in amine aqueous solution and then hydrogenated to methanol (>90% yield) in a biphasic 2-Methyltetrahydrofuran/water system, which allows for easy separation and recycling of the amine. CO_2 from air can also be converted to methanol using this route (Kar et al., 2018). Amines were also immobilized onto silica support and employed for tandem CO_2 capture and methanol synthesis. Covalently attached amine functionalities on solid supports displayed high recycling potential with almost no leaching under the reaction conditions (Kar et al., 2019). CZA-HT catalyst was prepared by physically mixing copper-based catalyst for methanol synthesis with hydrotalcite for high temperature CO_2 adsorption. The catalytic performance of the CZA-HT catalyst was clearly promoted by CO_2 adsorption on hydrotalcite. The sample containing 40 wt% hydrotalcite and 60 wt% CZA shows the highest methanol selectivity of 73.4% (Fang et al., 2019).

In the current demonstration project, CO_2 capture and conversion are two independent operation units, which may also involve CO_2 transportation, storage and different downstream conversion processes. We postulate that tandem CO_2 capture and hydrogenation to methanol system presented here could be an important step toward the implementation of the carbon neutral and methanol economy concept, which can reduce the energy consumption and simplify the production process. However, matching the working conditions of CO_2 conversion and capture is a key issue that must be solved, and the adsorbent also faces the problems of decomposition and poisoning of nitrogen oxides and sulfur oxides. Although this process is still in the embryonic stage of research and facing many problems, it has an attractive prospect.

Metal Oxide-zeolite Catalysts

To improve the efficiency of CO_2 conversion, researchers are trying to transform the methanol and other intermediates into fuels and chemicals *in situ* (Wang et al., 2018a; Ye et al., 2019). Therefore, metal oxide-zeolite bifunctional catalysts have been developed, which can catalyze CO_2 to gasoline. Metal oxide is responsible for CO_2 hydrogenation to oxygenates, and zeolite accounts for the subsequent C-C coupling reaction (**Figure 10A**). A bifunctional catalyst composed of reducible In_2O_3 and ZSM-5 has shown high selectivity to gasoline (78.6%) with a very low methane selectivity (1%) (Gao et al., 2017). Moreover, the catalysts exhibit a better performance during an industry-relevant test, which indicates promising prospects of its industrial application.

Metal oxide-zeolite bifunctional catalysts can also catalyze CO_2 to lower olefins with high selectivity. For example, a series of bifunctional catalysts containing In_2O_3-based or ZnO-based oxides and various SAPO (Silicoaluminophosphate) zeolites with different crystal sizes, pore structures and amount of acid sites were developed for the production of lower olefins by CO_2 hydrogenation (Dang et al., 2019a; Tan et al., 2019). It can remarkably realize highly selective synthesis of lower olefins and inhibit the formation of methane. In-Zr oxide and SAPO-34 bifunctional catalyst exhibits an excellent $C_2^=$-$C_4^=$ selectivity of up to 80% at more than 35% CO_2 conversion, and no significant deactivation was observed within 150 h (Gao et al., 2017). ZnZrO/SAPO tandem catalyst fabricated with ZnO-ZrO_2 solid solution and Zn-modified SAPO-34 zeolite can also achieve a selectivity for $C_2^=$-$C_4^=$ as high as 80–90% among hydrocarbons through CO_2 hydrogenation (Li et al., 2017). Similarly, a $ZnGa_2O_4$ and SAPO-34 bifunctional catalyst can also catalyze the direct conversion of CO_2 to $C_2^=$-$C_4^=$ with a selectivity of 86% (Liu et al., 2018b).

Researchers have also developed metal oxide-zeolite bifunctional catalysts to convert CO_2 to aromatics in a single path with methanol and other oxygenates as the intermediates. A composite catalyst of $ZnAlO_x$ and H-ZSM-5 has high aromatics selectivity (73.9%) with low CH_4 selectivity (0.4%) among hydrocarbons. Furthermore, The selectivity of p-xylene in xylenes is 58.1% on the composite catalyst containing Si-H-ZSM-5 (Ni et al., 2018). Cr_2O_3/H-ZSM-5 bifunctional catalyst can also realize the one-step conversion of CO_2 to aromatics. Due to the synergistic effect between the two components, aromatics selectivity of ~76% was achieved, and there was no deactivation after 100 h on stream (Wang et al., 2019). ZnO/ZrO_2-ZSM-5 tandem catalyst was prepared for direct CO_2 conversion to aromatics with a selectivity of 70%, and the selectivity of CH_4 is greatly suppressed to lower than 1% (**Figure 10B**) (Zhang et al., 2019). Similarly, CO_2 is converted into aromatics with selectivity up to 73% over ZnZrO/ZSM-5 tandem catalyst (**Figure 10C**). The presence of H_2O and CO_2 suppresses the formation of polycyclic aromatics and enhances the stability of the catalyst (Li et al., 2019). Moreover, the conversion of CO_2 into para-xylene was also reported, in one-pass by combining Zn-ZSM-5@SiO_2 and Cr_2O_3. Through regulation of the acidity of Zn-ZSM-5@SiO_2, high p-xylene selectivity (38.7% in the total products) at a CO_2 conversion of 22.1% was achieved (Wang et al., 2019a).

In brief, the direct transformation of CO_2 into high value-added hydrocarbons (i.e., olefins and aromatics) has obtained important fruits (Ye et al., 2019). The development of multifunctional catalysts can often achieve high-value and complex chemicals synthesis. Moreover, the multifunctional catalyst has become a research direction favored by the industry due to its simple operation and low energy consumption. However, there is a lack of in-depth understanding of its reaction paths, intermediate species, and

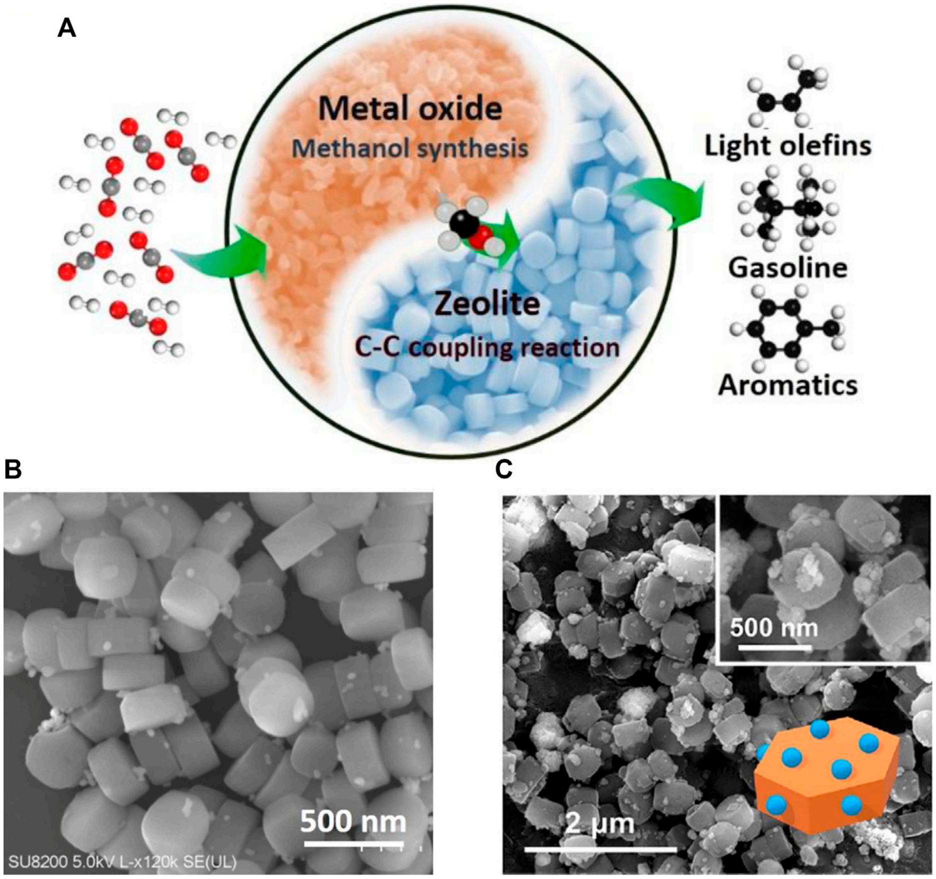

FIGURE 10 | (A) Schematic for CO_2 conversion on metal oxide-zeolite bifunctional catalysts. **(B)** ZnO/ZrO_2-ZSM-5 bifunctional catalyst was designed for the direct conversion of CO_2 to aromatics. **(C)** Highly selective conversion of CO_2 to aromatics over ZnZrO/ZSM-5 (Li et al., 2019).

the synergistic effect among multiple components. The bifunctional catalyst has shown obvious advantages in terms of anti-carbon deposition deactivation compared with the single methanol conversion process. The permanent deactivation of the acid sites of the zeolite, due to the migration of metal oxides during the reaction, restricts the regeneration and utilization of the catalyst. At present, we still lack powerful tools to control the distance between two components to prevent the acidic sites from being covered by metal oxides. The development of multi-functional catalysts also requires more efficient technology for precise control of the distance between different components. Although the current understanding is limited, its excellent performance attracts the unremitting efforts of researchers.

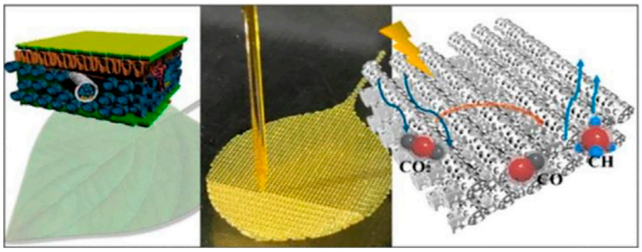

FIGURE 11 | 3D printing of artificial leaf with tunable hierarchical porosity for CO_2 photoreduction (Chen et al., 2018a).

New Technology Exploration

3D-Printing Technology

3D-printing technology has been considered for numerous research fields, ranging from medicine, mechanical engineering, and materials science to chemistry. For example, 3D-printing technologies pave the way for the design and manufacture of higher performing and cheaper electrochemical devices (Ambrosi and Pumera, 2016). It is believed that some concepts of supramolecular chemistry can be directly transferred to the bio-ink developments in future. A 3D printing method has been developed for rapid, programmable, and scalable manufacturing of artificial micro-leaves with 3D architectures ranging from nanometer to centimeter. Thus, a TiO_2-based ink was developed to construct hierarchical 3D architectures with high surface area (~259 m^2 g^{-1}) (**Figure 11**) (Chen et al., 2018a). 3D printing has unique advantages on the modification of catalytic surfaces and the fabrication of catalysts (Jungst et al., 2016). It provides a convenient and economical way to prepare

3D architectures with well-designed patterns. With the reduction of operation cost in the future, 3D printing will be more widely used in the preparation of catalysts with controllable structure and highly dispersed active components (Zhou and Liu, 2017), as well as integration of the whole process from the design of active sites to the shaping of industrial catalysts.

Plasma Technology

Plasma technology is increasingly attracting interest in the preparation of catalysts. Nucleation and crystal growth of materials under the influence of plasma is different from those in the conventional thermal method. Plasma is also an effective tool for oxidation, reduction, etching, doping, coating and surface treatment. It can operate at room temperature and allows the catalyst preparation on temperature-sensitive supporting materials. A method using plasma to remove template has been established for zeolites synthesis (Liu et al., 2015). In addition, transition-metal catalysts prepared by plasma technology show enhanced activity at low-temperature (Yan et al., 2015; Wang et al., 2018b). Moreover, plasma-assisted CO_2 conversion is attracting more and more attention (Zhang et al., 2010; Shirazi et al., 2017). However, the process is highly complex due to the interaction between plasma and catalysts, and little is known about the factors leading to the observed synergy. Catalytic mechanisms relevant to the specific application should be extensively studied (Neyts et al., 2015). Plasma has been introduced as a promising technology for modification of carbon materials, and modification of surface can often provide sites that can anchor active components. Hydrophobic/hydrophilic properties can also be tuned via plasma technology (Zhang et al., 2017). The water produced in the process of CO_2 hydrogenation can accelerate the sintering of metal catalysts and occupy the active sites through competitive adsorption. The stability of catalysts used for the hydrogenation of CO_2 to methanol can be enhanced by replacing oxide supports (i.e., Al_2O_3, SiO_2, TiO_2, etc.) with hydrophobic carbon supports (Furimsky, 2020). Therefore, plasma technology can further optimize the performance of catalysts by adjusting the hydrophobic/hydrophilic properties. Cold plasma is also used to improve the dispersion of active components and enhance metal-support interaction. Plasma reduction under room temperature was developed for the reduction of metal oxides, where no hazardous reducing agent or H_2 were needed. This provides many opportunities for the preparation of supported catalysts with heat sensitive supports (high surface area carbon, metal organic frameworks (MOFs), covalent organic framework (COFs), peptide, proteins and others) (Liu et al., 2016). As an example, β-Mo_2C nanorods were coupled with non-thermal plasma to catalyze CO_2 reduction to CO by H_2. In the absence of additional thermal input, the turnover frequency was an order of magnitude higher than that obtained during thermal catalysis (Zhang et al., 2020). The combination of the plasma with Pt/γ-Al_2O_3 or Cu/γ-Al_2O_3 enhanced the methanol yield compared to the plasma hydrogenation of CO_2 without catalyst. The methanol selectivity of 53.7% and methanol yield of 11.3% were achieved over Cu/γ-Al_2O_3 with a CO_2 conversion of 21.2% in the plasma process (Wang et al., 2018). Chemicals (e.g., acetic acid, methanol, ethanol, and formaldehyde) were synthesized in a one-step process from CO_2 and CH_4 at 30 °C and atmospheric pressure by using a plasma reactor with a water electrode. The total selectivity to oxygenates was approximately 50–60%, with acetic acid being the major component at 40.2% selectivity (Wang et al., 2017). The use of plasma with the catalytic bed enhanced the CO_2 conversion (~20 times) relative with thermal catalysis, whereas CH_4 selectivity increased around 5 times by introducing nickel catalyst into plasma discharge compared to plasma only at 150 °C (Ahmad et al., 2020). In the future, plasma technology will play an important role in the preparation of catalysts and subsequent CO_2 conversion.

Atomic Layer Deposition Technology

Atomic layer deposition (ALD) technology is expanding into new areas and discovering other applications that benefit from its precise control capability (George, 2010). The design of catalysts for CO_2 conversion requires high selectivity, activity and stability. ALD is a promising technology to address the main problems of CO_2 reduction, since it can construct catalysts with atomic precision in a highly controllable manner. Researchers have been focusing on the designs of nanomaterials via ALD technology and its applications in CO_2 capture and conversion (Chen et al., 2019c). The preparation of CaO-based sorbents assisted via ALD technology has shown high and cyclically stable CO_2 uptake (Armutlulu et al., 2017). Arrays of parallel CuO nanowires were surface decorated with dense ZnO islands via a few pulsed cycles of ALD. A mechanism of CO_2 reduction and H_2O oxidation occurred simultaneously in the active region between CuO nanowires and ZnO islands is proposed to elaborate the photocatalysis of CO_2 into CO (Wang et al., 2015). Pore mouth of 5 Å zeolite was decorated by depositing an ultrathin TiO_2 layer on its external surface. The composite sorbents show an ideal CO_2/N_2 adsorption selectivity, which is 4-fold higher than uncoated zeolite sorbents, while maintaining a fast CO_2 adsorption rate and a high capacity (Song et al., 2018). Porous TiO_2 from a metal-organic framework MIL-125 was surface engineered using ALD method to deposit an ultrathin MgO layer. The CO_2 photoreduction activity increased more than 4 times compared with that of the commercial P25 (Feng et al., 2018). Surface atomic-layer modification technology has provided an effective strategy to control the performance of nanomaterials. In the future, development of low-temperature precursor presents unique opportunities, because it is easy to perform ALD at low temperatures and it can avoid the aggregation of particles at high temperature (Adhikari et al., 2018).

SUMMARY AND FUTURE PERSPECTIVE

Capturing CO_2 from flue gas and the atmosphere and its catalytic conversion to fuel and chemicals using H_2 from renewable energy can lead to a sustainable future for humankind. Methanol can be used as fuel-substitute and raw material for hydrocarbon and chemicals with many industrial applications. The hydrogenation of CO_2 to methanol not only effectively alleviates the greenhouse

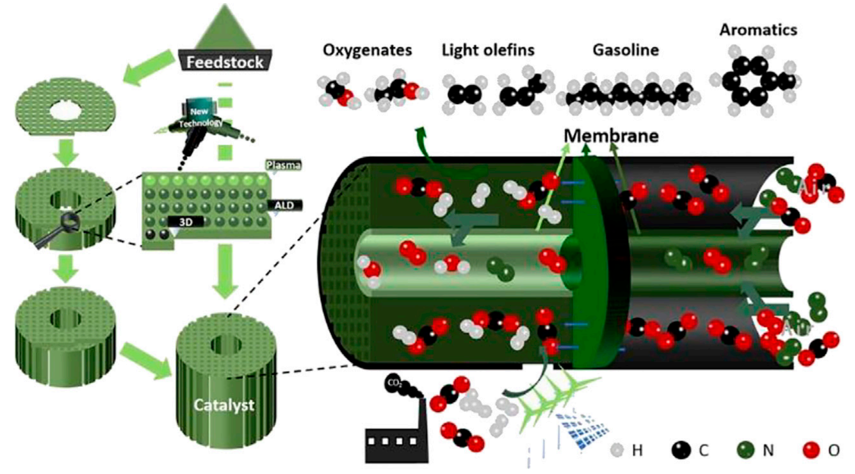

FIGURE 12 | Schematic diagram of CO_2 capture and conversion process and industrialization process of catalysts assisted by new technologies.

effect, but also produces fuel and value-added chemicals. Carbon capture and storage efforts are expected to reduce CO_2 emissions by about 8 Gt in the IEA 2010 Energy technology perspectives by year 2050 (Styring et al., 2015). At present, the production capacity of methanol in the world is about 0.20 Gt (China Energy News, 2019). If methanol is produced entirely from CO_2, it will consume 0.27 Gt of CO_2. Therefore, the energy system with methanol as the platform molecule requires further expansion of methanol production scale. One of the main obstacles in developing rational strategies for methanol synthesis is the complexity of the catalysts, which hinders characterization of the active sites. Therefore, an in-depth understanding of active sites and reaction mechanism is significant for the rational design of high-performance catalysts. Furthermore, *operando* characterization of catalysts under working conditions is highly recommended to correlate the structure-activity relationship. *In situ* techniques with high sensitivity of surface species (e.g., *in situ* IR, *in situ* XPS) and active sites (e.g., *in situ* TEM, *in situ* X-ray absorption techniques) should be widely employed.

Various strategies have been explored for thermocatalytic CO_2 hydrogenation into methanol via heterogeneous catalysis, spanning from new catalyst development (transition metals/metal oxides to main group metal/metal oxides) to new route exploration (metal oxide-zeolite catalysts and integrative CO_2 capture and hydrogenation). The development of new catalysts is toward the direction of lower energy consumption (e.g., low-pressure hydrogenation process) and higher methanol yield (e.g., low temperature methanol synthesis). Here, we need to take into account the problem that highly active catalysts are more likely to be poisoned by impurities. On the other hand, the design of membrane reactor is of great practical significance for delaying water-induced catalyst deactivation and for the shift of thermodynamic equilibrium after the *in situ* removal of the water byproduct. Highly efficient *in situ* by-product H_2O removal through water-conduction membrane has led to a drastic increase in ethanol yield in CO_2 hydrogenation to `methanol (Li et al., 2020). Moreover, nano-reactor with hydrophilic/hydrophobic surfaces will act as powerful supports for metal nanoparticles, and the molecular-fence concept should open a promising route to more-efficient catalysts for methanol synthesis (Jin et al., 2020). The construction of multifunctional catalysts to realize the further conversion of product methanol to high value-added chemicals can also drive the shift of thermodynamic equilibrium. What we must explore is how to achieve controllable coupling between different components while avoiding cross-contamination issues. Moreover, more sensitive spectroscopy techniques should be used to characterize key intermediate species, and combined with kinetic simulation to explore the influence of reaction atmosphere and intermediates concentration on the yield of the target products. It is expected to guide the development of high-performance composite catalysts based on a deep understanding of the reaction paths.

The research and development of catalysts will also go hand in hand in high-throughput screening mode and precision construction mode. Because the function of heterogeneous catalysts is defined by a mixture of molecular and mesoscopic components, atomistic simulations cannot fully capture this multi-length-scale complexity in present, and the design of such catalyst from first principles is still rare (Woodley and Catlow, 2008). At present, the integration of machine learning and high-throughput technology have been emerging to improve the development of new materials and performance of catalysts (Cole et al., 2017; Damith et al., 2018; Hartrampf et al., 2020). High-throughput synthesis and evaluation devices are speeding up the development of new catalysts. Moreover, robots will become one of researchers in the future laboratory, and the heavy and repetitive work will be completed by robots (Burger et al., 2020; Epps et al., 2020). High-throughput technology will also be the mainstream means of catalyst research and development in the months and years to come. With the development of new technology (3D, Plasmas and ALD), efforts are also being made to engineer catalytic materials with desired structure in nanoscale or even at the atomic level. New technologies are applied to design of catalysts toward precise construction of active sites and environmental protection in the preparation process. Moreover, the preparation of the catalyst and the molding technology are no longer independent, but the synthesis of catalyst from the precursor to the industrial catalyst is realized in one step to eliminate the current amplification effect of the catalyst in industrial applications. In the future, the reactor integrates the functions of CO_2 capture from air, methanol synthesis, *in situ* by-product H_2O removal and further conversion of methanol (**Figure 12**). With the development of distributed wind and solar energy, energy generation will gradually decentralize. Fragmented forms of energy utilization also require development of CO_2 capture units, separation units and conversion units toward the direction of assembly and modularization. Promoting the development of CO_2 conversion process toward high integration, green and efficient process.

AUTHOR CONTRIBUTIONS

XZ summarized the literature and wrote the paper. GZ made the manuscript design, writing-reviewing and funding acquisition. CS made the writing-reviewing, editing and supervision. XG made the writing-reviewing, editing, supervision and funding acquisition. All authors contributed to the article and approved the submitted version.

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REFERENCES

Adhikari, S., Selvaraj, S., and Kim, D.-H. (2018). Progress in powder coating technology using atomic layer deposition. *Adv. Mater. Interfaces* 5, 1800581. doi:10.1002/admi.201800581

Ahmad, F., Lovell, E. C., Masood, H., Cullen, P. J., Ostrikov, K. K., Scott, J. A., et al. (2020). Low-temperature CO_2 methanation: synergistic effects in plasma-Ni hybrid catalytic system. *ACS Sustain. Chem. Eng.* 8, 1888–1898. doi:10.1021/acssuschemeng.9b06180

Alsayegh, S., Johnson, J. R., Ohs, B., and Wessling, M. (2019). Methanol production via direct carbon dioxide hydrogenation using hydrogen from photocatalytic water splitting: process development and techno-economic analysis. *J. Clean. Prod.* 208, 1446–1458. doi:10.1016/j.jclepro.2018.10.132

Ambrosi, A., and Martin, P. (2016). 3D-printing technologies for electrochemical applications. *Chem. Soc. Rev.* 45, 2740–2755. doi:10.1039/C5CS00714C

An, B., Zhang, J., Cheng, K., Ji, P., Wan, C., Lin, W., et al. (2017). Confinement of ultrasmall Cu/ZnO. *J. Am. Chem. Soc.* 139, 3834–3840. doi:10.1021/jacs.7b00058

Araya, S. S., Liso, V., Cui, X.-T., Li, N., Zhu, J.-M., Sahlin, S. L., et al. (2020). A review of the methanol economy: the fuel cell route. *Energies* 13, 596. doi:10.3390/en13030596

Arena, F., Mezzatesta, G., Zafarana, G., Trunfio, G., Frusteri, F., Spadaro, L., et al. (2013). Effects of oxide carriers on surface functionality and process performance of the Cu-ZnO system in the synthesis of methanol via CO_2 hydrogenation. *J. Catal.* 300, 141–151. doi:10.1016/j.jcat.2012.12.019

Aresta, M., Karimi, I., and Kawi, S. (2015). *Methanol: the basic chemical and energy feedstock of the future*, Geneva, Switzerland: Springer Nature Switzerland AG.

Armutlulu, A., Naeem, M. A., Liu, H.-J., Kim, S. M., Kierzkowska, A., Fedorov, A., et al. (2017). Multishelled CaO microspheres stabilized by atomic layer deposition of Al_2O_3 for enhanced CO_2 capture performance. *Adv. Mater.* 29, 1702896. doi:10.1002/adma.201702896

Behrens, M., Studt, F., Kasatkin, I., Kühl, S., Hävecker, M., Abild-Pedersen, F., et al. (2012). The active site of methanol synthesis over $Cu/ZnO/Al_2O_3$ industrial catalysts. *Science* 336, 893–897. doi:10.1126/science.1219831

Bowker, M. (2019). Methanol synthesis from CO_2 hydrogenation. *ChemCatChem* 11, 4238–4246. doi:10.1002/cctc.201900401

Burger, B., Maffettone, P. M., Gusev, V. V., Aitchison, C. M., Bai, Y., Wang, X.-Y., et al. (2020). A mobile robotic chemist. *Nature* 583, 237–241. doi:10.1038/s41586-020-2442-2

Chen, K., Fang, H.-H., Wu, S., Liu, X., Zheng, J.-W., Zhou, S., et al. (2019a). CO_2 hydrogenation to methanol over Cu catalysts supported on La-modified SBA-15: the crucial role of Cu-LaO_x interfaces. *Appl. Catal. B Environ.* 251, 119–129. doi:10.1016/j.apcatb.2019.03.059

Chen, L., Tang, X.-W., Xie, P.-W., Xu, J., Chen, Z.-H., Cai, Z.-C., et al. (2018a). 3D printing of artificial leaf with tunable hierarchical porosity for CO_2 photoreduction. *Chem. Mater.* 30, 799–806. doi:10.1021/acs.chemmater.7b04313

Chen, S.-S., Qi, Y., Li, C., Domen, K., and Zhang, F.-X. (2018b). Surface strategies for particulate photocatalysts toward artificial photosynthesis. *Joule* 2, 2260–2288. doi:10.1016/j.joule.2018.07.030

Chen, S.-Y., Zhang, J.-F., Wang, P., Wang, X.-X., Song, F.-E., Bai, Y.-X., et al. (2019b). Effect of vapor-phase-treatment to CuZnZr catalyst on the reaction behaviors in CO_2 hydrogenation into methanol. *ChemCatChem.* 11, 1448–1457. doi:10.1002/cctc.201801988

Chen, Z.-S., Zhang, G.-X., Prakash, J., Zheng, Y., and Sun, S.-H. (2019c). Rational design of novel catalysts with atomic layer deposition for the reduction of carbon dioxide. *Adv. Energy Mater. 1900889* 9 (37), 1900889. doi:10.1002/aenm.201900889

China Energy News (2019). *E. coli*. Availble at: http://www.cnenergynews.cn/ (Accessed May 6, 2020).

Cokoja, M., Bruckmeier, C., Rieger, B., Herrmann, W. A., and Kühn, F. E. (2011). Transformation of carbon dioxide with homogeneous transition-metal catalysts: a molecular solution to a global challenge? *Angew. Chem. Int. Ed.* 50, 8510–8537. doi:10.1002/anie.201102010

Cole, K. P., Groh, M., Johnson, M. D., Burcham, C. L., Campbell, B. M., et al. (2017). Kilogram-scale prexasertib monolactate monohydrate synthesis under continuous-flow CGMP conditions. *Science* 356, 1144–1150. doi:10.1126/science.aan0745

Damith, P., Tucker, J. W., Brahmbhatt, S., Helal, C. J., Chong, A., Farrell, W., et al. (2018). A platform for automated nanomolescale reaction screening and micromole-scale synthesis in flow. *Science* 359, 429–434. doi:10.1126/science.aap9112

Dang, S.-S., Li, S.-G., Yang, C.-G., Chen, X.-Q., Li, X.-P., Zhong, L.-S., et al. (2019a). Selective transformation of CO_2 and H_2 into lower olefins over In_2O_3-$ZnZrO_x$/SAPO-34 bifunctional catalysts. *ChemSusChem* 12, 3582–3591. doi:10.1002/cssc.201900958

Dang, S.-S., Yang, H.-Y., Gao, P., Wang, H., Li, X.-P., Wei, W., et al. (2019b). A review of research progress on heterogeneous catalysts for methanol synthesis from carbon dioxide hydrogenation. *Catal. Today* 330, 61–75. doi:10.1016/j.cattod.2018.04.021

Das, S., Pe´rez-Ramı´rez, J., Gong, J.-L., Dewangan, N., Hidajat, K., Gates, B. C., et al. (2020). Core-shell structured catalysts for thermocatalytic, photocatalytic, and electrocatalytic conversion of CO_2. *Chem. Soc. Rev.* 49, 2937–3004. doi:10.1039/C9CS00713J

Din, I. U., Shaharun, M. S., Alotaibi, M. A., Alharthi, A. I., and Naeem, A. (2019). Recent developments on heterogeneous catalytic CO_2 reduction to methanol. *J. CO_2 Util.* 34, 20–33. doi:10.1016/j.jcou.2019.05.036

Dor Group (2019). *E. coli*. Available at: http://www.dorchemicals.com/eng/family/Methanol?catid=Dor-Chem_Methanol. (Accessed March 19, 2020).

Dotan, H., Landman, A., Sheehan, S. W., Malviya, K. D., Shter, G. E., Grave, D. A., et al. (2019). Decoupled hydrogen and oxygen evolution by a two-step electrochemical-chemical cycle for efficient overall water splitting. *Nat. Energy* 4, 786–795. doi:10.1038/s41560-019-0462-7

Dudley, B. (2019). *BP statistical review of world energy*. London, United Kingdom; BP Statistical Review.

Duyar, M. S., Tsai, C., Snider, J. L., Singh, J. A., Gallo, A., Yoo, J. S., et al. (2018). A highly active molybdenum phosphide catalyst for methanol synthesis from CO and CO_2. *Angew. Chem. Int. Ed.* 57, 15045–15050. doi:10.1002/anie.201806583

Epps, R. W., Bowen, M. S., Volk, A. A., Abdel-Latif, K., Han, S., Reyes, K. G., et al. (2020). Artificial chemist: an autonomous quantum dot synthesis bot. *Adv. Mater.* 32, 2001626. doi:10.1002/adma.202001626

Esposito, D. V. (2017). Membraneless electrolyzers for low-cost hydrogen production in a renewable energy future. *Joule* 1, 651–658. doi:10.1016/j.joule.2017.07.003

Fang, X., Men, Y.-H., Wu, F., Zhao, Q.-H., Singh, R., Xiao, P., et al. (2019). Promoting CO_2 hydrogenation to methanol by incorporating adsorbents into catalysts: effects of hydrotalcite. *Chem. Eng. J.* 378, 122052. doi:10.1016/j.cej.2019.122052

Farquharson, J. I., and Amelung, F. (2020). Extreme rainfall triggered the 2018 rift eruption at Kilauea Volcano. *Nature* 580, 491–495. doi:10.1038/s41586-020-2172-5

Feng, X.-H., Pan, F.-P., Zhao, H.-L., Deng, W., Zhang, P., Zhou, H.-C., et al. (2018). Atomic layer deposition enabled MgO surface coating on porous TiO_2 for improved CO_2 photoreduction. *Appl. Catal. B Environ.* 238, 274–283. doi:10.1016/j.apcatb.2018.07.027

Frei, M. S., Mondelli, C., García-Muelas, R., Kley, K. S., Puertolas, B., López, N., et al. (2019). Atomic-scale engineering of indium oxide promotion by palladium for methanol production via CO_2 hydrogenation. *Nat. Commun.* 10, 3377. doi:10.1038/s41467-019-11349-9

Furimsky, E. (2020). CO_2 hydrogenation to methanol and methane over carbon-supported catalysts. *Ind. Eng. Chem. Res.* 59, 15393–15423. doi:10.1021/acs.iecr.0c02250

Gao, P., Dang, S.-S., Li, S.-G., Bu, X.-N., Liu, Z.-Y., Qiu, M.-H., et al. (2017). Direct production of lower olefins from CO_2 conversion via bifunctional catalysis. *ACS Catal.* 8, 571–578. doi:10.1021/acscatal.7b02649

Gao, P., Li, S.-G., Bu, X.-N., Dang, S.-S., Liu, Z.-Y., Wang, H., et al. (2017). Direct conversion of CO_2 into liquid fuels with high selectivity over a bifunctional catalyst. *Nat. Chem.* 9, 1019–1024. doi:10.1038/nchem.2794

George, S. M. (2010). Atomic layer deposition: an overview. *Chem. Rev.* 110, 111–131. doi:10.1021/cr900056b

González-Garay, A., Frei, M. S., Al-Qahtani, A., Mondelli, C., Guillén-Gosálbez, G., Pérez-Ramírez, J., et al. (2019). Plant-to-planet analysis of CO_2-based methanol processes. *Energy Environ. Sci.* 12, 3425–3436. doi:10.1039/c9ee01673b

Ham, H., Baek, S. W., Shin, C.-H., and Bae, J. W. (2018). Roles of structural promoters for direct CO_2 hydrogenation to dimethyl ether over ordered mesoporous bifunctional Cu/M-Al_2O_3 (M = Ga or Zn). *ACS Catal.* 9, 679–690. doi:10.1021/acscatal.8b04060

Hartrampf, N., Saebi, A., Poskus, M., Gates, Z. P., Callahan, A. J., Cowfer, A. E., et al. (2020). Synthesis of proteins by automated flow chemistry. *Science* 368, 980–987. doi:10.1126/science.abb2491

He, M.-Y., Sun, Y.-H., and Han, B.-X. (2013). Green carbon science: scientific basis for integrating carbon resource processing, utilization, and recycling. *Angew. Chem. Int. Ed.* 52, 9620–9633. doi:10.1002/anie.201209384

Hu, X.-S., Qin, W., Guan, Q.-X., and Li, W. (2018). The synergistic effect of $CuZnCeO_x$ in controlling the formation of methanol and CO from CO_2 hydrogenation. *ChemCatChem* 10, 4438–4449. doi:10.1002/cctc.201800668

Iizumi, T., Shiogama, H., Imada, Y., Hanasaki, N., Takikawa, H., and Nishimori, M. (2018). Crop production losses associated with anthropogenic climate change for 1981-2010 compared with preindustrial levels. *Int. J. Climatol.* 38, 5405–5417. doi:10.1002/joc.5818

International Energy Agency (2019b). *Exploring clean energy pathways: the role of CO2 storage, IEA*, Paris, France; IEA.

International Energy Agency (2019a). *Putting CO_2 to use*, Paris, France; IEA.

Jiang, X., Koizumi, N., Guo, X.-W., and Song, C.-S. (2015). Bimetallic Pd-Cu catalysts for selective CO_2 hydrogenation to methanol. *Appl. Catal. B Environ.* 170, 173–185. doi:10.1016/j.apcatb.2015.01.010

Jiang, X., Nie, X.-W., Guo, X.-W., Song, C.-S., and Chen, J.-G. G. (2020). Recent advances in carbon dioxide hydrogenation to methanol via heterogeneous catalysis. *Chem. Rev.* 120, 7984–8034. doi:10.1021/acs.chemrev.9b00723

Jin, Z., Wang, L., Zuidema, E., Mondal, K., Zhang, M., and Zhang, J. (2020). Hydrophobic zeolite modification for *in situ* peroxide formation in methane oxidation to methanol. *Science* 367, 193–197. doi:10.1126/science.aaw1108

Jo, D. Y., Lee, M. W., Ham, H. C., and Lee, K.-Y. (2019). Role of the Zn atomic arrangements in enhancing the activity and stability of the kinked Cu(2 1 1) site in CH_3OH production by CO_2 hydrogenation and dissociation: first-principles microkinetic modeling study. *J. Catal.* 373, 336–350. doi:10.1016/j.jcat.2019.04.00

Jungst, T., Smolan, W., Schacht, K., Scheibel, T., and Groll, J. (2016). Strategies and molecular design criteria for 3D printable hydrogels. *Chem. Rev.* 116, 1496–1539. doi:10.1021/acs.chemrev.5b00303

Kar, S., Goeppert, A., Kothandaraman, J., and Prakash, G. K. S. (2017). Manganese-catalyzed sequential hydrogenation of CO_2 to methanol via formamide. *ACS Catal.* 7, 6347–6351. doi:10.1021/acscatal.7b02066

Kar, S., Goeppert, A., and Prakash, G. K. S. (2019). Combined CO_2 capture and hydrogenation to methanol: amine immobilization enables easy recycling of active elements. *ChemSusChem.* 12, 3172–3177. doi:10.1002/cssc.201900324

Kar, S., Sen, R., Goeppert, A., and Prakash, G. K. S. (2018). Integrative CO_2 capture and hydrogenation to methanol with reusable catalyst and amine: toward a carbon neutral methanol economy. *J. Am. Chem. Soc.* 140, 1580–1583. doi:10.1021/jacs.7b12183

Karuturi, S. K., Shen, H.-P., Sharma, A., Beck, F. J., Varadhan, P., Duong, T., et al. (2020). Over 17% efficiency stand-alone solar water splitting enabled by perovskite-silicon tandem absorbers. *Adv. Energy Mater.* 10, 2000772. doi:10.1002/aenm.202000772

Kattel, S., Liu, P., and Chen, J.-G. G. (2017a). Tuning selectivity of CO_2 hydrogenation reactions at the metal/oxide interface. *J. Am. Chem. Soc.* 139, 9739–9754. doi:10.1021/jacs.7b05362

Kattel, S., Ramírez, P. J., Chen, J.-G., Rodriguez, J. A., and Liu, P. (2017b). Active sites for CO_2 hydrogenation to methanol on Cu/ZnO catalysts. *Science* 355, 1296–1299. doi:10.1126/science.aal3573

Kim, J., Henao, C. A., Johnson, T. A., Dedrick, D. E., Miller, J. E., and Stecheld, E. B. (2011). Methanol production from CO_2 using solar-thermal energy: process development and techno-economic analysis. *Energy Environ. Sci.* 4, 3122–3132. doi:10.1039/c1ee01311d

Kobl, K., Thomas, S., Zimmermann, Y., Parkhomenko, K., and Roger, A.-C. (2016). Power-law kinetics of methanol synthesis from carbon dioxide and hydrogen on copper-zinc oxide catalysts with alumina or zirconia supports. *Catal. Today* 270, 31–42. doi:10.1016/j.cattod.2015.11.020

Kuld, S., Thorhauge, M., Falsig, H., Elkjær, C. F., Helveg, S., Chorkendorff, I., et al. (2016). Quantifying the promotion of Cu catalysts by ZnO for methanol synthesis. *Science* 352, 969–974. doi:10.1126/science.aaf0718

Lam, E., Corral-Pérez, J. J., Larmier, K., Noh, G., Wolf, P., Comas-Vives, A., et al. (2019). CO2 hydrogenation on Cu/Al2O3: role of metal/support interface in driving activity and selectivity of a bifunctional catalyst. *Angew. Chem. Int. Ed.* 58, 13989–13996. doi:10.1002/anie.201908060

Lam, E., Larmier, K., Wolf, P., Tada, S., Safonova, O. V., and Copéret, C. (2018). Isolated Zr surface sites on silica promote hydrogenation of CO_2 to CH_3OH in supported Cu catalysts. *J. Am. Chem. Soc.* 140, 10530–10535. doi:10.1021/jacs.8b05595

Larmier, K., Liao, W.-C., Tada, S., Lam, E., Verel, R., Bansode, A., et al. (2017). CO_2-to-methanol hydrogenation on Zirconia-supported copper nanoparticles: reaction intermediates and the role of the metal-support interface. *Angew. Chem. Int. Ed.* 56, 2318–2323. doi:10.1002/anie.201610166

Li, H.-Z., Qiu, C.-L., Ren, S.-J., Dong, Q.-B., Zhang, S.-X., Zhou, F.-L., et al. (2020). Na^+-gated water-conducting nanochannels for boosting CO_2 conversion to liquid fuels. *Science* 367, 667–671. doi:10.1126/science.aaz6053

Li, K.-Z., and Chen, J.-G. G. (2019). CO_2 hydrogenation to methanol over ZrO_2-containing catalysts: insights into ZrO_2 induced synergy. *ACS Catal.* 9, 7840–7861. doi:10.1021/acscatal.9b01943

Li, M. M.-J., Zeng, Z.-Y., Liao, F.-L., Hong, X.-L., and Tsang, S. C. E. (2016). Enhanced CO_2 hydrogenation to methanol over CuZn nanoalloy in Ga modified Cu/ZnO catalysts. *J. Catal.* 343, 157–167. doi:10.1016/j.jcat.2016.03.020

Li, W.-H., Nie, X.-W., Jiang, X., Zhang, A.-F., Ding, F.-S., Liu, M., et al. (2018). ZrO_2 support imparts superior activity and stability of Co catalysts for CO_2 methanation. *Appl. Catal. B Environ.* 220, 397–408. doi:10.1016/j.apcatb.2017.08.048

Li, Z.-L., Qu, Y.-Z., Wang, J.-J., Liu, H.-L., Li, M.-R., Miao, S., et al. (2019). Highly selective conversion of carbon dioxide to aromatics over tandem catalysts. *Joule* 3, 570–583. doi:10.1016/j.joule.2018.10.027

Li, Z.-L., Wang, J.-J., Qu, Y.-Z., Liu, H.-L., Tang, C.-Z., Miao, S., et al. (2017). Highly selective conversion of carbon dioxide to lower olefins. *ACS Catal.* 7, 8544–8548. doi:10.1021/acscatal.7b03251

Liu, C.-J., Li, M.-Y., Wang, J.-Q., Zhou, X.-T., Guo, Q.-T., Yan, J.-M., et al. (2016). Plasma methods for preparing green catalysts: current status and perspective. *Chin. J. Catal.* 37, 340–348. doi:10.1016/S1872-2067(15)61020-8

Liu, J.-H., Zhang, A.-F., Jiang, X., Liu, M., Sun, Y.-W., Song, C.-S., et al. (2018a). Selective CO_2 hydrogenation to hydrocarbons on Cu-promoted Fe-based catalysts: dependence on Cu-Fe interaction. *ACS Sustain. Chem. Eng.* 6, 10182–10190. doi:10.1021/acssuschemeng.8b01491

Liu, X.-L., Wang, M.-H., Zhou, C., Wei, Z., Cheng, K., Kang, J.-C., et al. (2018b). Selective transformation of carbon dioxide into lower olefins with a bifunctional catalyst composed of $ZnGa_2O_4$ and SAPO-34. *Chem.Commun.* 54, 140–143. doi:10.1039/C7CC08642C

Liu, Y., Wang, Z., and Liu, C.-J. (2015). Mechanism of template removal for the synthesis of molecular sieves using dielectric barrier discharge. *Catal. Today* 256, 137–141. doi:10.1016/j.cattod.2015.03.009

Lunkenbein, T., Schumann, J., Behrens, M., Schlogl, R., and Willinger, M. G. (2015). Formation of a ZnO overlayer in industrial $Cu/ZnO/Al_2O_3$ catalysts induced by strong metal-support interactions. *Angew. Chem. Int. Ed.* 54, 4544–4548. doi:10.1002/anie.201411581

Luu, M.-T., Milani, D., Bahadori, A., and Abbas, A. (2015). A comparative study of CO_2 utilization in methanol synthesis with various syngas production technologies. *J. CO_2 Util.* 12, 62–76. doi:10.1016/j.jcou.2015.07.001

Martin, O., Martín, A. J., Mondelli, C., Mitchell, S., Segawa, T. F., Hauert, R., et al. (2016). Indium oxide as a superior catalyst for methanol synthesis by CO_2 hydrogenation. *Angew. Chem. Int. Ed.* 55, 6261–6265. doi:10.1002/anie.201600943

MefCO_2 (Methanol fuel from CO_2) (2020). *E. coli*. Available at: https://www.spire2030.eu/mefco2 (Accessed October 21, 2020).

Methanol Institute (2020). *E. coli*. Available at: https://www.methanol.org/the-methanol-industry/ (Accessed October 21, 2020).

Ministry of Industry and Information Technology of the People's Republic of China (2019). *E. coli*. Available at: http://www.miit.gov.cn/index.html (Accessed March 19, 2020).

Murakami, H., Vecchi, G. A., and Underwood, S. (2017). Increasing frequency of extremely severe cyclonic storms over the Arabian Sea. *Nat. Clim. Change* 7, 885–889. doi:10.1038/s41558-017-0008-6

Mureddu, M., Ferrara, F., and Pettinau, A. (2019). Highly efficient CuO/ZnO/ZrO_2@SBA-15 nanocatalysts for methanol synthesis from the catalytic hydrogenation of CO_2. *Appl. Catal. B Environ.* 258, 117941. doi:10.1016/j.apcatb.2019.117941

Netzer, D., Antverg, J., and Goldwine, G. (2015). Methanol proves low-cost, sustainable option for gasoline blending. *Oil Gas J.* 113, 82–87.

Neyts, E. C., Ostrikov, K. K., Sunkara, M. K., and Bogaerts, A. (2015). Synergistic effects at the nanoscale. *Chem. Rev.* 115, 13408–13446. doi:10.1021/acs.chemrev.5b00362

Ni, Y.-M., Chen, Z.-Y., Fu, Y., Liu, Y., Zhu, W.-L., and Liu, Z.-M. (2018). Selective conversion of CO_2 and H_2 into aromatics. *Nat. Commun.* 9, 3457. doi:10.1038/s41467-018-05880-4

Nie, X.-W., Li, W.-H., Jiang, X., Guo, X.-W., and Song, C.-S. (2019). Recent advances in catalytic CO_2 hydrogenation to alcohols and hydrocarbons. *Adv. Catal.* 65, 121–233. doi:10.1016/bs.acat.2019.10.002

Noh, G., Lam, E., Alfke, J. L., Larmier, K., Searles, K., Wolf, P., et al. (2019). Selective hydrogenation of CO_2 to CH_3OH on supported Cu nanoparticles promoted by isolated Ti (IV) surface sites on SiO_2. *ChemSusChem* 12, 968–972. doi:10.1002/cssc.201900134

Olah, G. A. (2005). Beyond oil and gas: the methanol economy. *Angew. Chem. Int. Ed.* 44, 2636–2639. doi:10.1002/anie.200462121

Olsbye, U., Svelle, S., Bjørgen, M., Beato, P., Janssens, T. V. W., Joensen, F., et al. (2012). Conversion of methanol to hydrocarbons: how zeolite cavity and pore size controls product selectivity. *Angew. Chem. Int. Ed.* 51, 5810–5831. doi:10.1002/anie.201103657

Peng, Y.-H., Wang, L.-B., Luo, Q.-Q., Cao, Y., Dai, Y.-Z., Li, Z.-L., et al. (2018). Molecular-level insight into how hydroxyl groups boost catalytic activity in CO_2 hydrogenation into methanol. *Chem.* 4, 613–625. doi:10.1016/j.chempr.2018.01.019

Peters, M., Köhler, B., Kuckshinrichs, W., Leitner, W., Markewitz, P., and Müller, T. E. (2011). Chemical technologies for exploiting and recycling carbon dioxide into the value chain. *ChemSusChem*. 4, 1216–1240. doi:10.1002/cssc.201000447

Pinaud, B. A., Benck, J. D., Seitz, L. C., Forman, A. J., Chen, Z.-B., Deutsch, T. G., et al. (2013). Technical and economic feasibility of centralized facilities for solar hydrogen production via photocatalysis and photoelectrochemistry. *Energy Environ. Sci.* 6, 1983–2002. doi:10.1039/c3ee40831k

Ra, E. C., Kim, K. Y., Kim, E. H., Lee, H., An, K., and Lee, J. S. (2020). Recycling carbon dioxide through catalytic hydrogenation: recent key developments and perspectives. *ACS Catal.* 10, 11318–11345. doi:10.1021/acscatal.0c02930

Reddy, B. M., Samuel, P., and Reddy, N. S. M. (2018). Government policies help promote clean transportation in India: proton-exchange membrane fuel cells for vehicles. *IEEE Electrification Magazine* 6, 26–36. doi:10.1109/mele.2017.2784633

Reichenbach, T., Mondal, K., Jäger, M., Vent-Schmidt, T., Himmel, D., Dybbert, V., et al. (2018). Ab initio study of CO_2 hydrogenation mechanisms on inverse ZnO/Cu catalysts. *J. Catal.* 360, 168–174. doi:10.1016/j.jcat.2018.01.035

Richard, A. R., and Fan, M. (2017). Low-pressure hydrogenation of CO_2 to CH_3OH using Ni-In-Al/SiO_2 catalyst synthesized via a phyllosilicate precursor. *ACS Catal.* 7, 5679–5692. doi:10.1021/acscatal.7b00848

Roh, K., Al-Hunaidy, A. S., Imran, H., and Lee, J.-H. (2019). Optimization-based identification of CO_2 capture and utilization processing paths for life cycle greenhouse gas reduction and economic benefits. *AIChE J.* 65, e16580. doi:10.1002/aic.16580

Roy, S., Cherevotan, A., and Peter, S. C. (2018). Thermochemical CO_2 hydrogenation to single carbon products: scientific and technological challenges. *ACS Energy Lett.* 3, 1938–1966. doi:10.1021/acsenergylett.8b00740

Rubin, E. S., Davison, J. E., and Herzog, H. J. (2015). The cost of CO_2 capture and storage. *Int. J. Greenh. Gas. Con.* 40, 378–400. doi:10.1016/j.ijggc.2015.05.018

Sakakura, T., Choi, J.-C., and Yasuda, H. (2007). Transformation of carbon dioxide. *Chem. Rev.* 107, 2365–2387. doi:10.1021/cr068357u

Sanz-Pérez, E. S., Murdock, C. R., Didas, S. A., and Jones, C. W. (2016). Direct capture of CO2 from ambient air. *Chem. Rev.* 116, 11840–11876. doi:10.1021/acs.chemrev.6b00173

Satthawong, R., Koizumi, N., Song, C.-S., and Prasassarakich, P. (2013). Bimetallic Fe-Co catalysts for CO_2 hydrogenation to higher hydrocarbons. *J. CO_2 Util.* 3-4, 102–106. doi:10.1016/j.jcou.2013.10.002

Service, R. F. (2016). Perovskite solar cells gear up to go commercial. *Science* 354, 1214–1215. doi:10.1126/science.354.6317.1214

Shirazi, M., Neyts, E. C., and Bogaerts, A. (2017). DFT study of Ni-catalyzed plasma dry reforming of methane. *Appl. Catal. B Environ.* 205, 605–614. doi:10.1016/j.apcatb.2017.01.004

Smejkal, Q., Rodemerck, U., Wagner, E., and Baerns, M. (2014). Economic assessment of the hydrogenation of CO_2 to liquid fuels and petrochemical feedstock. *Chem. Ing. Tech.* 86, 679–686. doi:10.1002/cite.201300180

Song, Z.-N., Dong, Q.-B., Xu, W.-W. L., Zhou, F.-L., Liang, X.-H., and Yu, M. (2018). Molecular layer seposition-modified 5A zeolite for highly efficient CO_2 capture. *ACS Appl. Mater. Interfaces* 10, 769–775. doi:10.1021/acsami.7b16574

Stangeland, K., Kalai, D. Y., Ding, Y., and Yu, Z.-X. (2019). Mesoporous manganese-cobalt oxide spinel catalysts for CO_2 hydrogenation to methanol. *J. CO_2 Util.* 32, 146–154. doi:10.1016/j.jcou.2019.04.018

Studt, F., Sharafutdinov, I., Abild-Pedersen, F., Elkjaer, C. F., Hummelshøj, J. S., Dahl, S., et al. (2014). Discovery of a Ni-Ga catalyst for carbon dioxide reduction to methanol. *Nat. Chem.* 6, 320–324. doi:10.1038/nchem.1873

Styring, P., Quadrelli, E. A., and Armstrong, K. (2015). *Carbon dioxide utilisation: closing the carbon cycle*, Holand, Europe; Elsevier: Academic Press.

Su, L.-W., Li, X.-R., and Sun, Z.-Y. (2013). The consumption, production and transportation of methanol in China: a review. *Energy Pol.* 63, 130–138. doi:10.1016/j.enpol.2013.08.031

Tan, L., Zhang, P.-P., Cui, Y., Suzuki, Y., Li, H.-J., Guo, L.-S., et al. (2019). Direct CO_2 hydrogenation to light olefins by suppressing CO by-product formation. *Fuel Process.Technol.* 196, 106174, doi:10.1016/j.fuproc.2019.106174

Tountas, A. A., Peng, X.-Y., Tavasoli, A. V., Duchesne, P. N., Dingle, T. L., Dong, Y.-C., et al. (2019). Towards solar methanol: past, present, and future. *Adv. Sci.* 6, 1801903. doi:10.1002/advs.201801903

Toyao, T., Kayamori, S., Maeno, Z., Siddiki, S. M. A. H., and Shimizu, K.-I. (2019). Heterogeneous Pt and MoO_x Co-loaded TiO_2 catalysts for low-temperature CO_2 hydrogenation to form CH_3OH. *ACS Catal.* 9, 8187–8196. doi:10.1021/acscatal.9b01225

Veh, G., Korup, O., and Walz, A. (2020). Hazard from Himalayan glacier lake outburst floods. *PNA* 117, 907–912. doi:10.1073/pnas.1914898117

Wang, J.-J., Li, G.-N., Li, Z.-L., Tang, C.-Z., Feng, Z.-C., An, H.-Y., et al. (2017). A highly selective and stable ZnO-ZrO_2 solid solution catalyst for CO_2 hydrogenation to methanol. *Sci. Adv.* 3, e1701290. doi:10.1126/sciadv.1701290

Wang, J.-Y., Liu, C.-Y., Senftle, T. P., Zhu, J., Zhang, G.-H., Guo, X.-W., et al. (2020a). Variation in In_2O_3 crystal phase alters catalytic performance toward the reverse water gas shift reaction. *ACS Catal.* 10, 3264–3273. doi:10.1021/acscatal.9b04239

Wang, J.-Y., Zhang, A.-F., Jiang, X., Song, C.-S., and Guo, X.-W. (2018a). Highly selective conversion of CO_2 to lower hydrocarbons (C_2-C_4) over bifunctional catalysts composed of In_2O_3-ZrO_2 and zeolite. *J. CO_2 Util.* 27, 81–88. doi:10.1016/j.jcou.2018.07.006

Wang, L.-X., Guan, E.-J., Wang, Y.-Q., Wang, L., Gong, Z.-M., Cui, Y., et al. (2020b). Silica accelerates the selective hydrogenation of CO_2 to methanol on cobalt catalysts. *Nat. Commun.* 11, 1033. doi:10.1038/s41467-020-14817-9

Wang, L., Yi, Y.-H., Guo, H.-C., and Tu, X. (2018). Atmospheric pressure and room temperature synthesis of methanol through plasma-catalytic hydrogenation of CO_2. *ACS Catal.* 8, 90–100. doi:10.1021/acscatal.7b02733

Wang, L., Yi, Y.-H., Wu, C.-F., Guo, H.-C., and Tu, X. (2017). One-step reforming of CO_2 and CH_4 into high-value liquid chemicals and fuels at room temperature by plasma-driven catalysis. *Angew. Chem. Int. Ed.* 56, 13679–13683. doi:10.1002/anie.201707131

Wang, W.-N., Wu, F., Myung, Y., Niedzwiedzki, D. M., Im, H. S., Park, J., et al. (2015). Surface engineered CuO nanowires with ZnO islands for CO_2 photoreduction. *ACS Appl. Mater. Interfaces* 7, 5685–5692. doi:10.1021/am508590j

Wang, Y.-H., Kattel, S., Gao, W.-G., Li, K.-Z., Liu, P., Chen, J.-G. G., et al. (2019b). Exploring the ternary interactions in Cu-ZnO-ZrO_2 catalysts for efficient CO_2 hydrogenation to methanol. *Nat. Commun.* 10, 1166. doi:10.1038/s41467-019-09072-6

Wang, Y., Gao, W.-Z., Kazumi, S., Li, H.-J., Yang, G.-H., and Tsubaki, N. (2019a). Direct and oriented conversion of CO_2 into value-added aromatics. *Chem. Eur J.* 25, 5149–5153. doi:10.1002/chem.201806165

Wang, Y., Tan, L., Tan, M.-H., Zhang, P.-P., Fang, Y., Yoneyama, Y., et al. (2019). Rationally designing bifunctional catalysts as an efficient strategy to boost CO_2 hydrogenation producing value-added aromatics. *ACS Catal.* 9, 895–901. doi:10.1021/acscatal.8b01344

Wang, Z., Zhang, Y., Neyts, E. C., Cao, X.-X., Zhang, X.-S., Jang, B. W.-L., et al. (2018b). Catalyst preparation with plasmas: how does it work?. *ACS Catal.* 8, 2093–2110. doi:10.1021/acscatal.7b03723

Woodley, S. M., and Catlow, R. (2008). Crystal structure prediction from first principles. *Nat. Mater.* 7, 937–946. doi:10.1038/nmat2321

Xu, X.-Y., Liu, Y., Zhang, F., Di, W., and Zhang, Y.-L. (2017). Clean coal technologies in China based on methanol platform. *Catal. Today* 298, 61–68. doi:10.1016/j.cattod.2017.05.070

Yan, X.-L., Zhao, B.-R., Liu, Y.-L., and Li, Y.-N. (2015). Dielectric barrier discharge plasma for preparation of Ni-based catalysts with enhanced coke resistance: current status and perspective. *Catal. Today* 256, 29–40. doi:10.1016/j.cattod.2015.04.045

Ye, J.-Y., Liu, C.-J., Mei, D.-H., and Ge, Q.-F. (2013). Active oxygen vacancy site for methanol synthesis from CO_2 hydrogenation on In_2O_3(110): a DFT study. *ACS Catal.* 3, 1296–1306. doi:10.1021/cs400132a

Ye, R.-P., Ding, J., Gong, W.-B., Argyle, M. D., Zhong, Q., Wang, Y.-J., et al. (2019). CO_2 hydrogenation to high-value products via heterogeneous catalysis. *Nat. Commun.* 10, 5698. doi:10.1038/s41467-019-13638-9

Yu, T., Cristiano, R., and Weiss, R. G. (2010). From simple, neutral triatomic molecules to complex chemistry. *Chem. Soc. Rev.* 39, 1435–1447. doi:10.1039/b821320h

Zhang, A.-J., Zhu, A.-M., Guo, J., Xu, Y., and Shi, C. (2010). Conversion of greenhouse gases into syngas via combined effects of discharge activation and catalysis. *Chem. Eng. J.* 156, 601–606. doi:10.1016/j.cej.2009.04.069

Zhang, L.-F., Sadanandam, G., Liu, X.-Y., and Scurrell, M. S. (2017). Carbon surface modifications by plasma for catalyst support and electrode materials applications. *Top. Catal.* 60, 823–830. doi:10.1007/s11244-017-0747-7

Zhang, W.-X., Zhou, T.-J., Zou, L.-W., Zhang, L.-X., and Chen, X.-L. (2018). Reduced exposure to extreme precipitation from 0.5 °C less warming in global land monsoon regions. *Nat. Commun.* 9, 3153. doi:10.1038/s41467-018-05633-3

Zhang, X.-B., Zhang, A.-F., Jiang, X., Zhu, J., Liu, J.-H., Li, J.-J., et al. (2019). Utilization of CO_2 for aromatics production over ZnO/ZrO_2-ZSM-5 tandem catalyst. *J. CO_2 Util.* 29, 140–145. doi:10.1016/j.jcou.2018.12.002

Zhang, X., Liu, Y., Zhang, M.-T., Yu, T., Chen, B.-B., Xu, Y., et al. (2020). Synergy between β-Mo_2C nanorods and non-thermal plasma for selective CO_2 reduction to CO. *Chem.* 6, 3312–3328. doi:10.1016/j.chempr.2020.09.016

Zhong, J.-W., Yang, X.-F., Wu, Z.-L., Liang, B.-L., Huang, Y.-Q., and Zhang, T. (2020). State of the art and perspectives in heterogeneous catalysis of CO_2 hydrogenation to methanol. *Chem. Soc. Rev.* 49, 1385–1413. doi:10.1039/C9CS00614A

Zhou, X.-T., and Liu, C.-J. (2017). Three-dimensional printing for catalytic applications: current status and perspectives. *Adv. Funct. Mater.* 27, 1701134. doi:10.1002/adfm.201701134

Zhu, J., Zhang, G.-H., Li, W.-H., Zhang, X.-B., Ding, F.-S., Song, C.-S., et al. (2020). Deconvolution of the particle size effect on CO_2 hydrogenation over iron-based catalysts. *ACS Catal.* 10, 7424–7433. doi:10.1021/acscatal.0c01526

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CO_2 Utilization and Long-Term Storage in Useful Mineral Products by Carbonation of Alkaline Feedstocks

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Accelerated carbonation is a carbon utilization option which allows the manufacturing of useful products, employing CO_2-concentrated or -diluted emission sources and waste streams such as industrial or other processing solid residues, in a circular economy perspective. If properly implemented, it may reduce the exploitation of virgin raw materials and their associated environmental footprint and permanently store CO_2 in the form of Ca and/or Mg carbonates, thus effectively contributing to climate change mitigation. In this perspective article, we first report an overview of the main mineral carbonation pathways that have been developed up to now, focusing on those which were specifically designed to obtain useful products, starting from different alkaline feedstocks. Based on the current state of the art, we then discuss the main critical issues that still need to be addressed in order to improve the overall feasibility of mineral carbonation as a CCUS option, as well as research needs and opportunities.

Keywords: mineral carbonation, aggregates, compacts, precipitated calcium carbonate, curing, CO_2 utilization, CO_2 storage

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INTRODUCTION

Achieving the UN target of 1.5–2.0°C maximum temperature increase by 2100, set by the COP 21 Paris Climate Conference, requires the implementation of different actions aimed at mitigating climate change (IPCC et al., 2018; Woodall et al., 2019). A shift to low carbon energy technologies will be required to achieve such stringent targets, but this implies a nontrivial transformation of the status quo, where fossil fuels account for more than 80% of the global primary energy supply (Vinca et al., 2018). This suggests that any pathway aimed at reducing carbon emissions shall include a transition phase, during which fossil fuels will still need to be used but their related emissions should be captured and not released into the atmosphere. Besides, as probably we will need in the future to reduce the CO_2 concentration in the atmosphere, carbon capture and storage (CCS) should be applied also to emissions from biomass to energy plants (BECCS) or even directly to air (DACCS), leading effectively to negative carbon emissions (Realmonte et al., 2019). CCS according to some scenarios might represent from 30 to 40% of the primary energy use (Vinca et al., 2018); however, geological storage, already applied at scales of around 1 Mt CO_2/y, is still facing concerns about storage sites, public acceptance, costs, and large-scale feasibility (Vinca et al., 2018). In this context, CO_2 utilization has been proposed as an alternative or integration to geological storage since it allows conversion of CO_2 into a wide variety of end products, including chemicals and fuels (MacDowell et al., 2017). According to the National Academies of Sciences, Engineering, and Medicine (NASEM - National Academies of Sciences, Engineering, and Medicine, 2019), CO_2 utilization technologies have a role to play in future carbon management and the circular carbon economy; among these, mineral or accelerated carbonation (MC) is considered the closest option to commercial scale implementation due to its thermodynamic favorability and market size (Woodall et al., 2019). In MC, which is considered a process that can allow the bridging of CO_2 storage and CO_2 utilization, CO_2 reacts with alkaline earth metal oxide-bearing phases, such as Ca/Mg (hydr)-oxides and silicates, forming stable solid carbonates. This process may be tailored to manufacture products for construction applications and high purity Ca- and Mg-based carbonates for different uses (Librandi et al., 2019). Potential alkalinity sources for mineralization include geologically derived feedstock materials such as olivine and serpentine or alkaline industrial residues (Hills et al., 2020). These residues are typically available in the proximity of CO_2 source emissions, present a high reactivity even at mild operating conditions, and, differently from natural ores, may also present suitable grain size without pretreatment (Librandi et al., 2019). Despite MC achieving permanent sequestration of CO_2 in solid form similarly to other CCS options, the primary driver of MC as a CCU option should be feedstock substitution and the production of materials at a lower cost and with an associated lower fossil carbon footprint rather than locking up CO_2 (MacDowell et al., 2017). We share this vision, and this perspective article is focused on the application of MC to manufacture useful products, as we believe that this will allow acceleration of MC deployment at large scale.

Fundamentals of Accelerated Carbonation

Mineral carbonation is a naturally occurring weathering reaction which involves the interaction of carbon dioxide with minerals typically found in mafic and ultramafic rocks (i.e., mainly Mg- and Ca-based silicates), leading to the formation of thermodynamically stable mineral carbonates (such as magnesite, calcite, and dolomite). This reaction is exothermic and contributes to the chemical weathering of continental surfaces, which has been suggested to be enhanced by the current modifications in climate and atmospheric composition and, although presents slow reaction kinetics, could play a role in the evolution of the global carbon cycle over the next centuries (Beaulieu et al., 2012). Weathering of silicates is a multiphase reaction since CO_2 dissolves and ionizes in water leading to the formation of carbonic acid (H_2CO_3) that in turn can partly dissolve the rocks, releasing the CaO/MgO phases that react with HCO_3^-/CO_3^{2-}, yielding the final carbonate product.

The exploitation of MC as a CO_2 storage option has been investigated through both *in situ* and *ex situ* process routes, as reviewed extensively in Sanna et al. (2014) and Kelemen et al. (2019). *In situ* MC processes basically consist in enhancing mineral trapping of CO_2 by weathering through the injection of CO_2-rich fluids in reactive geological formations, such as mantle peridotites (Kelemen and Matter, 2008) and basalt deposits (Gislason et al., 2010). In particular, most of the CO_2 injected into subsurface pore space in basaltic lavas in Iceland was reported to have mineralized in less than two years (Matter et al., 2016). This approach is at a lower stage of technological readiness compared to geological storage; however, it has been estimated that globally *in situ* MC has the potential of sequestering up to 60,000,000 $GtCO_2$ if the resource is economically accessible and fully carbonated (Kelemen et al., 2019). As for *ex situ* MC, several processes have been developed to speed up the reactivity of alkaline feedstocks such as minerals and industrial residues, thus allowing to achieve relevant CO_2 storage yields (several $GtCO_2$/y) in industrially feasible time frames (i.e., up to a few hours) (Sanna et al., 2014; NASEM - National Academies of Sciences, Engineering, and Medicine, 2019). Kelemen et al. (2019) actually report a third MC pathway—surficial MC—by which dilute or concentrated CO_2 is reacted on-site with the alkaline feedstock, such as mafic and ultramafic mine tailings. This MC option represents an interesting application for offsetting mining CO_2 emissions on-site (Wilson et al., 2009; Mervine et al., 2018) and was estimated that may provide in the next decades an increasing capture capacity from hundreds of Mton CO_2/y to over 1 Gton CO_2/y, depending on the socioeconomic scenario considered (Renforth, 2019). In addition, *in situ* carbonation of artificial soils (i.e., soils containing calcium-rich materials such as demolition waste or steel slag) was indicated as an option that could allow to sequester globally 290 Mt C/y in construction/development sites (Renforth et al., 2009).

With regard to *ex situ* MC pathways, which may be applicable also for CO_2 utilization besides storage, many different alkalinity feedstocks, process routes, and sets of operating conditions have been tested. The most investigated minerals include worldwide abundant Mg-based silicates such as serpentine and olivine and Ca silicates such as wollastonite, which is much more limited—with global reserves estimated at only 100 Mt (U.S. Geological Survey, 2021)—but presents a greater reactivity with CO_2 due to the higher precipitation rate of $CaCO_3$ compared to $MgCO_3$. As for residues, several types of alkaline waste materials, including coal fly ash, cement kiln dust (CKD), concrete waste, paper mill waste, municipal solid waste incineration residues such as bottom ash and air pollution control (APC) residues, steel-making by-products, asbestos, and Ni tailings and red mud (Al extraction waste) have been tested (see e.g., Pan et al., 2012; Sanna et al., 2014). Overall, the amounts of industrial residues suitable for MC treatment, which currently are mostly landfilled or employed only for low-end applications, have been estimated to exceed 2 Gt/y (Hills et al., 2020).

As previously mentioned, at ambient conditions, carbonation proceeds via gas–liquid–solid pathways. Most of the research on accelerated carbonation has focused on the aqueous route, generally mixing the alkaline feedstock with water applying liquid to solid (L/S) ratios above 2 L/kg (slurry-phase) (Baciocchi et al., 2014). This route may be applied directly, that is, alkaline oxide dissolution and carbonate precipitation can be performed in the same reactor in a one-stage process, or indirectly, separating the dissolution and precipitation steps. In this latter process, carbonation can be completed under milder conditions because of the independent optimization of each step, leading to an enhancement of the overall carbonate conversion rate and to a product with a higher purity (Mission Innovation, 2017), as discussed in Paragraph 2.1. With regard to indirect treatment routes, many different types of reagents have been tested for promoting Mg extraction from the feedstock, including, in particular, ammonium salts (e.g., Wang and Maroto-Valer 2011; Zevenhoven et al., 2017). The direct route is best suited to treating concentrated CO_2 streams, whereas the indirect approach can be applied also to diluted CO_2 streams, including untreated flue gases (Mission Innovation, 2017). Several pretreatments have been applied to enhance the reaction kinetics of minerals, and in particular of serpentine to remove hydroxyl groups including mechanical, chemical, and thermal activation (Sanna et al., 2014). It should be noted, however, that thermal activation may lead to the formation of undesirable side reactions (i.e., the reformation of crystalline serpentine and precipitation of amorphous magnesium silicate hydroxide phases on the surface of reacting particles), resulting in a significant decrease in reaction efficiency (Benhelal et al., 2019). Besides, biochemical enhancement employing the enzyme carbonic anhydrase to catalyze the hydration of aqueous CO_2 has been also tested (e.g., Patel et al., 2013; Power et al., 2016). High carbonate conversion yields (above 80%) have been achieved by applying the NETL-Albany direct slurry-phase process to olivine employing a pCO_2 of 150 atm, temperatures greater than 90°C, and a 1 M NaCl and 0.64 M $NaHCO_3$ solution (Gerdemann et al., 2007). The reactivity of Ca-bearing minerals, such as labradorite and Ca, and/or Mg-bearing rocks, such as anorthosite and basalt, at reaction conditions similar to those reported above is one to two orders of magnitude lower than that of olivine (Gadikota et al., 2020). The reactivity of residues, which is different from minerals, is mostly related to Ca-based phases and depends upon the abundance and the type of mineral phases. Specifically, free oxide and hydroxide phases, such as lime and portlandite, are typically found in significant amounts only in APC residues, CKD, and paper mill waste, and basic oxygen furnace (BOF) steel slag is highly reactive even at mild operating conditions. As for silicate phases, the most reactive are reported to be tricalcium (alite, Ca_3SiO_5) and dicalcium (belite, Ca_2SiO_4) silicates, which are generally retrieved in materials such as concrete demolition waste or steel manufacturing slag (Baciocchi et al., 2014). For residues characterized by the abovementioned types of phases, the aqueous direct route may be run also using very low L/S ratios (typically below 1 L/kg) and in this case is often referred to as the wet or thin film route. This route has been particularly investigated for manufacturing construction materials from industrial residues and for cement curing, as discussed in Paragraphs 2.2–2.3. Alternatively, direct gas–solid pathways have been also tested; residues from thermal treatment processes can be directly contacted with CO_2 diluted streams at atmospheric pressure, exploiting the high temperature of the residues and/or of the flue gas, but the reaction involves only calcium oxides or hydroxides phases (Prigiobbe et al., 2009; Santos et al., 2012).

CARBONATION ROUTES FOR USEFUL PRODUCTS

The application of direct and indirect MC processes to minerals and industrial alkaline materials offers the opportunity to produce a range of products and by-products that may find several uses. Applications include construction materials (e.g., cements, concrete, and mortars), aggregates or compacts (e.g., for road-base, erosion, sea, and flood protection barriers), and calcium- and magnesium-based carbonates (specialty products) that may be used for different applications (e.g., as additives for protective coatings such as paints and polymers). Specialty products resulting from carbonation of alkaline materials also include hydrated Mg carbonates that may be employed for thermal energy storage or as CO_2 transport medium and other products that may be obtained by selective dissolution of the reacting feedstock, such as silica and metals or metalloids (Mission Innovation, 2017).

As shown in **Figure 1**, some of the MC products, such as aggregates, may be employed in concrete manufacturing, contributing to further decrease the carbon footprint of this material compared to CO_2 curing, which consists already in an improvement versus the traditional steam curing method, as discussed below.

Specialty Products

The main focus of this section is on high purity carbonates which represent the specialty product with the most relevant market potential. The market of high purity carbonates is constituted mainly by precipitated calcium carbonate (PCC), which is used as filler or coating material in various types of applications, comprising paper, paint, plastics, and adhesives, among many others (Jimoh et al., 2018; Zevenhoven et al., 2019). As of 2014, the market for mineral fillers and pigments is about 14 Mt/y with a high value of 375–550 USD/t (Woodall et al., 2019). PCC is made of either fine or very fine nanoparticles that are synthesized either by a lime soda process, a calcium chloride process, or a process based on the carbonation of calcium hydroxide produced after calcination and hydration of a carbonate rock (Teir et al., 2005; Jimoh et al., 2018). The need to manufacture precipitated calcium carbonate with a definite morphology, structure, and particle size is necessary due to its wide application in various industries (Jimoh et al., 2018). The most important crystalline forms of PCC are the rhombohedral calcite type, scalenohedral calcite type, and orthorhombic acicular aragonite type. The scalenohedral form is favoured in most applications. There are several various types of PCC grades, but the purity of PCC is usually over 99% with a density of 2700 kg/m^3 (Teir et al., 2005).

Teir et al. (2005) first introduced and modeled different processes for producing PCC from calcium silicate as alkalinity source instead of calcium carbonate. From this work, the so-called Slag2PCC process was developed, in which the alkalinity source is provided by steel slags, in particular BOF slags (Said et al., 2013; Mattila et al., 2014; Zevenhoven et al., 2019). As reported in **Figure 2**, calcium is first extracted using an ammonia salt (typically chloride), and the obtained Ca-rich slurry is fed to a carbonation section, where PCC is obtained after reaction with CO_2, even from a diluted source without the need for a separate CO_2 capture step (Zevenhoven, 2020).

Despite the process being developed up to pilot scale (Said et al., 2013), achieving product purity above 99.5% using a 1 M

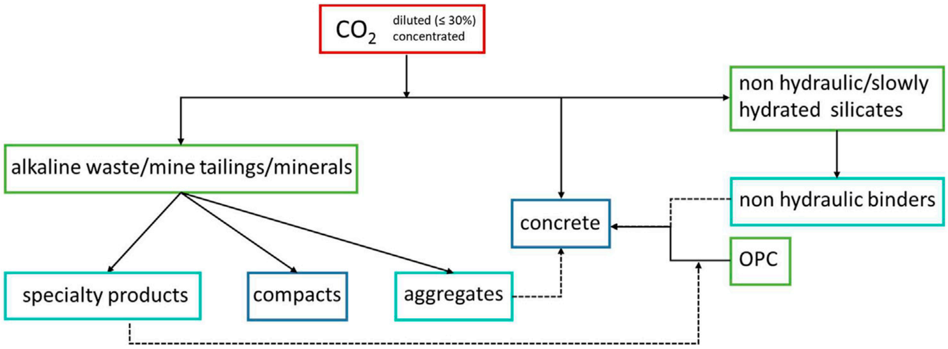

FIGURE 1 | Scheme of current CO_2 utilization pathways for producing carbonated materials to use in construction or other applications. Solid reagents are reported in green boxes, whereas final products in blue. Turquois boxes highlight MC products that can be used as reagents to manufacture other products.

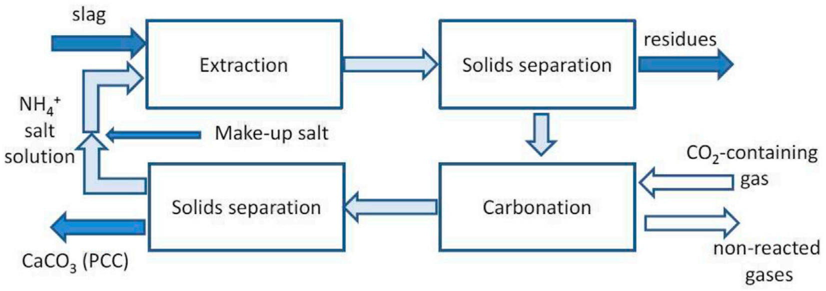

FIGURE 2 | Flow diagram of the Slag2PCC concept for PCC production from steel-making slags. Reproduced with permission from Zevenhoven et al. (2019).

ammonium chloride solution for Ca extraction, the scale-up to an industrial size process, for example, ~25 t/h BOF slag, faces several challenges/drawbacks. These include: the significant amount of water needed to wash the PCC product (to recover the solvent salt), the separation of the solids (slag residue and PCC product) from the aqueous streams, and the low calcium amount extracted from the slag, with a significant amount of residual solids resulting from the process (Zevenhoven et al., 2019). The cradle-to-gate LCA of the process showed that operating at the experimentally tested ammonia concentration in the extraction solution (0.65 M) and at a 0.1 kg/L slag to solution ratio, the Slag2PCC approach suffers from the large amount of process steam required for recycling the washing water, which increases the environmental impact of the process, even compared to traditional PCC manufacturing (Mattila et al., 2014). Operating at a much lower ammonia concentration, that is, 0.01 M, the Slag2PCC process results into negative CO_2 emissions, that is, CO_2 stored into the PCC product, although in this case, the calcium extraction step must be repeated several times with the same slag to obtain the same total conversion as with an over-stoichiometric solvent concentration (Mattila et al., 2014). Besides PCC, also other specialty products have been recently investigated, namely, Erlund and Zevenhoven. (2019) studied the heat effects and storage capacity for thermal energy storage applications of a composite materialmade by magnesium carbonate hydrate (Nesquehonite) and silica gel, where the former one is produced by carbonation of alkalinematerials with Mg-bearing phases. Carbonation for production of metastable carbonates such as nesquehonite was also recently proposed and tested as carbon growth media for microalgae, for cases in which pure or even diluted CO_2 sources may not be available nearby algae production plants (Ye et al., 2019).

Aggregates and Compacts

Synthetic aggregates may be produced by treating different types of alkaline residues by carbonation through the carbo-granulation pathway (see **Figure 3A**). This process consists in combining wet-route MC with a cold-bonding granulation process, during manufacturing and/or product curing (Gunning et al., 2011). Alkaline residues may, in fact, present a fine particle size as-produced, for example, fly ash or APC residues, or after grinding for ferrous/nonferrous metals removal, for example, bottom ash or steel slag. Carbo-granulation applied to ground BOF slag allowed to achieve a significant increase in particle size and a CO_2 uptake of around 10% by weight (Morone et al., 2014). However, alkaline activation, consisting in the use of a sodium silicate/sodium hydroxide solution instead of water as binder, proved necessary to attain granules with a mechanical strength close to the one typically exhibited by gravel (Morone et al., 2017). Carbon8 Systems have achieved commercial operation of plants that make use of alkaline waste materials, APC residues in particular, concentrated CO_2 streams, and other

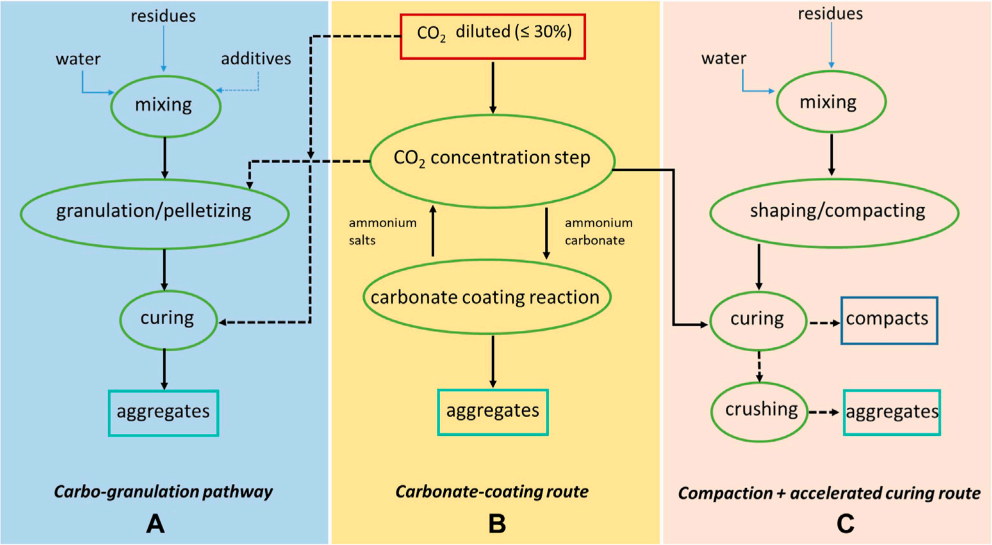

FIGURE 3 | Mineral carbonation pathways to produce aggregates or compacts. **(A)** Carbo-granulaion pathway. **(B)** Carbonate-coating route. **(C)** Compacting + accelerated curing route.

binders and fillers to produce lightweight aggregates for use mainly in concrete. A recent innovation of this process is the development of a mobile plant with a capacity of 12,000 t/y of manufactured aggregates that can directly use flue gas and be located in the proximity of point-source emitters of CO_2 and residues, thus avoiding the need for transport and CO_2 capture (Hills et al., 2020). Co-location of an aggregate manufacturing plant with CO_2 emission sources such as power plants and industries generating solid reactants is also part of the concept of the Blue Planet process that employs alkaline residues such as concrete waste and produces lightweight carbonate-coated aggregates (Blue Planet, 2021). Specifically, as shown in **Figure 3B**, CO_2 from diluted sources is absorbed in an ammonium salt solution; the ammonium carbonated water is then contacted with the residues and synthetic $CaCO_3$ layers are formed over a substrate. A field trial was performed in 2016 in which lightweight carbon-coated aggregates were used as partial replacement of coarse aggregates in the concrete mix employed for building a pedestrian atrium deck at San Francisco airport (Blue Planet, 2021). Another process based on MC to produce aggregates from alkaline residues was reported by Ghouleh et al. (2017); in this process, hydrated BOF slag was first compacted in cylindrical specimens that were cured under 100% CO_2; the compacts were then crushed to angular shape in order to achieve a particle size distribution typical of fine aggregates (**Figure 3C**). Concrete slabs prepared from this waste material displayed comparable strengths to granite-based slabs and better strength than slabs prepared from commercial lightweight aggregates (Ghouleh et al., 2017).

Aggregates, including sand, gravel, and crushed stone, represent a low-value commodity with a global market of over 50 Gt/y and a relatively low associated carbon intensity (7.85 $kgCO_2$ eq/t aggregates) (Woodall et al., 2019). This makes it difficult for MC-produced aggregates to be competitive with the traditionally employed ones, unless the former ones present superior properties and/or allow storage of large amounts of CO_2. An additional asset, if not the main driver currently for employing industrial residues in aggregate manufacturing, is the payment of gate fees for the treatment of waste such as APC residues, a hazardous waste that presents a high landfilling cost. Another aspect that should also be considered besides the technical properties of the product is its environmental properties since alkaline residues may release significant amounts of metals, metalloids, and salts, and carbonation has shown to be able to improve the chemical stability only of some constituents (see e.g., Costa et al., 2007; Morone et al., 2014). Specific end-of-waste criteria are established at a country or even provincial or regional level and may require the compliance with leaching guidelines also for artificial aggregates employed in bound applications.

Another interesting application of MC, also depicted in **Figure 3C**, is a patented process that allows manufacturing of blocks or compacts called Carbstone using finely milled steel slags that, by curing with concentrated CO_2 streams at elevated temperature and pressure, achieve high mechanical performance without the use of cementitious binders (Quaghebeur et al., 2015). Two MC processes have been developed up to industrial scale: a low-pressure process for the production of common building blocks (compressive strength up to 50 MPa) using 50% dried fine-grained stainless steel slags and 50% fine sand and a high-pressure process for the production of high-strength materials (compressive strength>50 MPa) (Di Maria et al., 2020). LCA of the low-pressure process that includes different capture options for the CO_2 to use in the curing step indicates that this technology can be considered carbon-negative since the amount of CO_2 stored during the process (around 9% by weight) is higher than the amount of CO_2 emitted, considering the whole life cycle of the block. Nonetheless, electricity and heat requirements represent the main environmental burden of this technology in terms of CO_2 emissions (Di Maria et al., 2020).

Concrete Curing and Binders

Steam-cured conventional concrete market use amounts currently to over 27 Gt/y and presents an associated carbon intensity around 0.14 tCO_2/t concrete (Woodall et al., 2019). It has been estimated that the application of MC to concrete, for example, through early-stage CO_2 curing, has a global CO_2 avoidance potential of more than 1.5 $GtCO_2$/year (Woodall et al., 2019). CO_2 curing has been proposed to manufacture concrete blocks using different binders alternative to Portland cement (OPC) such as binary mixtures of wollastonite–Portland cement (WPC), MgO–Portland cement (MPC), limestone–Portland cement (LPC), and slag–Portland cement (SPC) (Huang et al., 2019). If Portland cement is used as a binder, carbonation curing may lead to a lower pH than in steam-cured concrete, which may limit its use to nonreinforced applications (Zhang et al., 2017). Using nonhydraulic binders may allow avoiding this limitation, but care must be taken in ensuring homogeneous and in-depth carbonation of the block, as the material's strength relies solely on the carbonation reaction rather than on hydration reactions (Zhang et al., 2017). Cements made with nonhydraulic binders, such as wollastonite and rankinite ($Ca_3Si_2O_7$), are marketed by Solidia, which claims a reduction of CO_2 emissions associated with cement production of up to 30% with respect to traditional cement and a further permanent sequestration of CO_2 of up to 300 kg per tonne of cement incorporated in the concrete formulation after CO_2 curing (Solidia Cement^{TM}, 2013). Carbon dioxide treatment of concrete upstream from product mold is also currently marketed by Carboncure in the United States (Niven et al., 2012) with a claimed number of more than 562,000 trucks of CO_2-cured concrete delivered (indicatively a fully loaded truckload holds 10 cubic yards, i.e., 7.5 m^3 of concrete) and a net CO_2 reduction of 40,000 t achieved in the last year (period March 2020–March 2021) (Carbon Cure, 2021).

Another MC product that may find application in concrete is amorphous silica that can be obtained through indirect routes. In particular, acid-treated silica-enriched residues from serpentine dissolution were found to display pozzolanic activity and hence were suggested as high-quality reactive cement additives (e.g., Sanna et al., 2012; Benhelal et al., 2018).

In 2008, the United Kingdom–based company Novacem, in collaboration with Lafrange, developed a process to manufacture cement, termed as green or carbon-negative, from magnesium silicate rocks (e.g., olivine or serpentine). In this process, these rocks are carbonated with CO_2 at 200°C and 180 bar to produce magnesium carbonate, which is then decarbonated at 700°C to produce magnesium oxide. The final Novacem cement composition is a mix of magnesium oxide, hydrated magnesium carbonates, and pozzolans (Naqi and Jang, 2019).

IMPACT OF CARBONATION ON LONG-TERM CARBON STORAGE

The distinctive feature of carbonation as a CCUS option relies in the long-term carbon storage that can be achieved in most of the manufactured products, the potential of which has been discussed in several studies. Even not considering the development of a tailored mining activity aimed at the extraction of silicate minerals, which could, in principle, lead to a carbonation potential of the same scale of CO_2 yearly emissions, the production of ultramafic (and mafic) tailings alone is estimated to be about 200–400 Mt year, thus leading to a carbonation potential approximately between 100 and 200 $MtCO_2$/y, assuming serpentine as the main mineral phase and magnesite as carbonation product (Woodall et al., 2019). The remaining alkaline materials, which include a wide range of industrial waste, may also contribute around 0.97 $GtCO_2$/y (Woodall et al., 2019). Renforth (2019) recently estimated the future trend of the global CO_2 carbonation potential of alkaline materials, with figures (excluding carbon absorption by cement) between 0.8 and 1.3 $GtCO_2$ yr^{-1} in 2050 and 1.4 and 2.7 $GtCO_2$ yr^{-1} by 2100, depending on the socioeconomic global pathway considered. According to Renforth (2019), these figures represent a theoretical maximum potential, which, in practice, would be difficult to realize. In fact, they are limited by the effective conversion of Ca or Mg mineral phases to carbonates and by the availability of a market for the carbonation products (see again Woodall et al., 2019, for further discussion).

CONCLUSIONS AND PERSPECTIVES

Mineral carbonation has been extensively investigated during the last 25 years. Nevertheless, full-scale applications are still limited in number and in market coverage. A wider diffusion of MC has been hindered so far, mainly by the limited CO_2 and alkalinity sources suitable to make the process feasible in terms of energy requirements and by the limited interest of the market for MC products. It should be noted that the direct use of CO_2-diluted sources such as flue gas, biogas, or syngas, which allows avoiding a preliminary CO_2 capture step, can significantly reduce the energy requirements of the process. However, the direct use of off-gas should not affect the quality and purity of the products; therefore, depending on the characteristics of gas flow and of the targeted product, the use of specific pretreatments for impurity removal should be considered.

Besides, a still insufficient understanding of the fundamental mechanisms and reaction pathways underlying mineral carbonation probably did not allow the development of the most efficient carbonation routes. So far, the applications which have achieved pilot or full-scale stage are based on the more reactive alkalinity sources, that is, alkaline industrial residues (specifically APC residues and steel slag), cement, or even minerals containing Ca-bearing phases rather than Mg-bearing ones.

The reactivity of alkalinity sources must be increased by improving the extraction efficiency of alkaline metals as well as by investigating process integration and industrial symbiosis opportunities to reduce energy requirements.

Besides, we need more effort at a fundamental scale to not only improve the knowledge on the mechanisms underlying the carbonation process but also to increase the extent and quality of experimental data in order to make mass/energy requirement assessment more precise. This will allow to assess in a more comprehensive way the actual contribution of mineral carbonation by detailed and more consistent life cycle assessment (LCA) approaches that should be applied with the same level of detail to evaluate all MC pathways.

Carbonation processes should be developed with the aim of manufacturing improved or new products, which may have a wider market than the current ones. Currently, MC product use in construction is limited to precast building materials and nonreinforced applications. An important step ahead would be if the technology could be adapted to replace the cement binder in ready-mix concrete and in reinforced (concrete) building applications; however, to reach this goal, further improvements in the mechanical behavior and environmental quality of the carbonated products would be necessary (Mission Innovation, 2017).

New ideas include, for instance, the integration of the recovery of rare earth elements during the mineral carbonation treatment to maximize the exploitation and valorization of steel slags, while contributing to the reduction of CO_2 emissions and the sustainable utilization of energy.

Besides, new feedstocks need to be explored since aggregates, compacts, and binder manufacturing by MC are constrained by the availability of alkaline residues and not by the market demand for these products. Supplementary feedstocks may include brines from desalination, as first proposed in Ferrini et al. (2009) and Mignardi et al. (2011), or oil and gas extraction fluids that present high concentrations of dissolved Ca and Mg, but require alkali additives to balance the solution acidity that results from CO_2 injection, besides the removal of Cl buildup in solution. A recent study reports the development of a closed-loop cyclical process to remove chloride anions from brines by ion exchange with hydrotalcites that release hydroxyl anions, sufficiently raising the pH to enable the precipitation of calcium carbonates (Zhang et al., 2020).

Another opportunity that could be further exploited may be represented by mineral or waste materials bearing Mg-phases, which are widely available worldwide. Nevertheless, in order to make their application feasible, new market opportunities for Mg carbonate products should be investigated, besides novel sustainable pathways to enhance the reactivity of Mg-phases that, as highlighted previously, is lower than that of Ca-bearing materials.

Finally, as for many other circular economy processes, in order to favor the deployment of MC products in place of virgin raw materials, governments should provide ways of addressing financial and nonfinancial barriers. For example, due to concerns related to the release of elements of potential environmental concern from alkaline waste materials, such as metals or metalloids, products obtained from these materials have been typically employed only in limited applications under restricted conditions. In this regard, the Green Deal program of the Netherlands, that has established that waste-derived secondary construction materials can only be employed in unrestricted applications, implies on the one hand that more stringent environmental quality parameters should be met, for example, by applying pretreatments, but also that waste-derived materials presenting suitable properties are substantially equivalent to primary raw material. The issuing of end-of-waste criteria, present currently only in some European countries and only for specific waste-derived materials and uses, will certainly help to promote the recycling of secondary construction materials, presenting adequate technical and environmental properties, by clarifying administrative procedures, thus allowing companies to make more resilient business plans. In addition, to promote the use of these materials in private but also public tenders by green public procurement, environmental product declarations deriving from product-based LCAs, that could allow highlighting of the positive implications deriving from the permanent uptake of CO_2 in the product as well as the partial substitution of virgin raw materials, should be achieved.

DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/Supplementary Material; further inquiries can be directed to the corresponding author.

AUTHOR CONTRIBUTIONS

RB: conceptualization, writing, review, and editing. GC: conceptualization, writing, review, and editing.

REFERENCES

Baciocchi, R., Costa, G., and Zingaretti, D. (2014). “Accelerated Carbonation Processes for Carbon Dioxide Capture, Storage and Utilisation,” in *Transformation and Utilization of Carbon Dioxide*. Editors B. M. Bhanage and M. Arai (Springer), 263–299. doi:10.1007/978-3-642-44988-8_11

Beaulieu, E., Goddéris, Y., Donnadieu, Y., Labat, D., and Roelandt, C. (2012). High Sensitivity of the Continental-Weathering Carbon Dioxide Sink to Future Climate Change. *Nat. Clim Change* 2, 346–349. doi:10.1038/nclimate1419

Benhelal, E., Rashid, M. I., Holt, C., Rayson, M. S., Brent, G., Hook, J. M., et al. (2018). The Utilisation of Feed and Byproducts of Mineral Carbonation Processes as Pozzolanic Cement Replacements. *J. Clean. Prod.* 186, 499–513. doi:10.1016/j.jclepro.2018.03.076

Benhelal, E., Rashid, M. I., Rayson, M. S., Brent, G. F., Oliver, T., Stockenhuber, M., et al. (2019). Direct Aqueous Carbonation of Heat Activated Serpentine: Discovery of Undesirable Side Reactions Reducing Process Efficiency. *Appl. Energ.* 242, 1369–1382. doi:10.1016/j.apenergy.2019.03.170

Blue Planet (2021). Available at: www.blueplanet-ltd.com (Accessed May 3, 2021).

Carbon Cure (2021). Available at: www.carboncure.com (Accessed March 27, 2021).

Costa, G., Baciocchi, R., Polettini, A., Pomi, R., Hills, C. D., and Carey, P. J. (2007). Current Status and Perspectives of Accelerated Carbonation Processes on Municipal Waste Combustion Residues. *Environ. Monit. Assess.* 135, 55–75. doi:10.1007/s10661-007-9704-4

Di Maria, A., Snellings, R., Alaerts, L., Quaghebeur, M., and Van Acker, K. (2020). Environmental Assessment of CO2 Mineralisation for Sustainable Construction Materials. *Int. J. Greenhouse Gas Control.* 93, 102882. doi:10.1016/j.ijggc.2019.102882

Erlund, R., and Zevenhoven, R. (2019). Thermal Energy Storage (TES) Capacity of a Lab Scale Magnesium Hydro Carbonates/silica Gel System. *J. Energ. Storage* 25, 100907. doi:10.1016/j.est.2019.100907

Ferrini, V., De Vito, C., and Mignardi, S. (2009). Synthesis of Nesquehonite by Reaction of Gaseous CO2 with Mg Chloride Solution: Its Potential Role in the Sequestration of Carbon Dioxide. *J. Hazard. Mater.* 168, 832–837. doi:10.1016/j.jhazmat.2009.02.103

Gadikota, G., Matter, J., Kelemen, P., Brady, P. V., and Park, A.-H. A. (2020). Elucidating the Differences in the Carbon Mineralization Behaviors of Calcium and Magnesium Bearing Alumino-Silicates and Magnesium Slicates for CO_2 Storage. *Fuel*, 277–117900. doi:10.1016/j.fuel.2020.117900

Gerdemann, S. J., O'Connor, W. K., Dahlin, D. C., Penner, L. R., and Rush, H. (2007). *Ex situ* Aqueous Mineral Carbonation. *Environ. Sci. Technol.* 41, 2587–2593. doi:10.1021/es0619253

Ghouleh, Z., Guthrie, R. I. L., and Shao, Y. (2017). Production of Carbonate Aggregates Using Steel Slag and Carbon Dioxide for Carbon-Negative Concrete. *J. CO2 Utilization* 18, 125–138. doi:10.1016/j.jcou.2017.01.009

Gislason, S. R., Wolff-Boenisch, D., Stefansson, A., Oelkers, E. H., Gunnlaugsson, E., Sigurdardottir, H., et al. (2010). Mineral Sequestration of Carbon Dioxide in Basalt: A Pre-injection Overview of the CarbFix Project. *Int. J. Greenhouse Gas Control.* 4, 537–545. doi:10.1016/j.ijggc.2009.11.013

Gunning, P. J., Hills, C. D., and Carey, P. J. (2011). Production of Lightweight Aggregate from Industrial Waste and Carbon Dioxide. *Waste Manag.* 29, 2722–2728. doi:10.1016/j.wasman.2009.05.021

Hills, C., Tripathi, N., and Carey, P. J. (2020). Mineralization Technology for Carbon Capture, Utilization, and Storage. *Front. Energ. Res.* 8, 142. doi:10.3389/fenrg.2020.00142

Huang, H., Wang, T., Kolosz, B., Andresen, J., Garcia, S., Fang, M., et al. (2019). Life-cycle Assessment of Emerging CO2 Mineral Carbonation-Cured Concrete Blocks: Comparative Analysis of CO2 Reduction Potential and Optimization of Environmental Impacts. *J. Clean. Prod.* 241, 118359. doi:10.1016/j.jclepro.2019.118359

Jimoh, O. A., Ariffin, K. S., Hussin, H. B., and Temitope, A. E. (2018). Synthesis of Precipitated Calcium Carbonate: a Review. *Carbonates Evaporites* 33, 331–346. doi:10.1007/s13146-017-0341-x

Kelemen, P., Benson, S. M., Pilorgé, H., Psarras, P., and Wilcox, J. (2019). An Overview of the Status and Challenges of CO2 in Minerals and Geological Formations. *Front. Clim.* 1, 9. doi:10.3389/fclim.2019.00009

Kelemen, P. B., and Matter, J. (2008). *In situ* carbonation of Peridotite for CO2 Storage. *Proc. Natl. Acad. Sci.* 105, 17295–17300. doi:10.1073/pnas.0805794105

Librandi, P., Nielsen, P., Costa, G., Snellings, R., Quaghebeur, M., and Baciocchi, R. (2019). Mechanical and Environmental Properties of Carbonated Steel Slag Compacts as a Function of Mineralogy and CO2 Uptake. *J. CO2 Utilization* 33, 201–214. doi:10.1016/j.jcou.2019.05.028

Mac Dowell, N., Fennell, P. S., Shah, N., and Maitland, G. C. (2017). The Role of CO2 Capture and Utilization in Mitigating Climate Change. *Nat. Clim Change* 7, 243–249. doi:10.1038/nclimate3231

Matter, J. M., Stute, M., Snæbjörnsdottir, S. Ó., Oelkers, E. H., Gislason, S. R., Aradottir, E. S., et al. (2016). Rapid Carbon Mineralization for Permanent Disposal of Anthropogenic Carbon Dioxide Emissions. *Science* 352, 312–1314. doi:10.1126/science.aad8132

Mattila, H.-P., Hudd, H., and Zevenhoven, R. (2014). Cradle-to-gate Life Cycle Assessment of Precipitated Calcium Carbonate Production from Steel Converter Slag. *J. Clean. Prod.* 84, 611–618. doi:10.1016/j.jclepro.2014.05.064

Mervine, E. M., Wilson, S. A., Power, I. M., Dipple, G. M., Turvey, C. C., Hamilton, J. L., et al. (2018). Potential for Offsetting Diamond Mine Carbon Emissions through Mineral Carbonation of Processed Kimberlite: an Assessment of De Beers Mine Sites in South Africa and Canada. *Miner. Petrol.* 112, 755–765. doi:10.1007/s00710-018-0589-4

Mignardi, S., De Vito, C., Ferrini, V., and Martin, R. F. (2011). The Efficiency of CO_2 Sequestration via Carbonate Mineralization with Simulated Wastewaters of High Salinity. *J. Hazard. Mater.* 191, 49–55.

Mission Innovation (2017). Accelerating the Clean Energy Revolution. Carbon Capture Innovation Challenge. *Report of the Carbon Capture, Utilization and Storage Experts' Workshop*. Houston (USA). Available at: https://www.energy.gov/fe/downloads/accelerating-breakthrough-innovation-carboncapture-utilization-and-storage (Accessed September 26–28, 2017).

Morone, M., Costa, G., Georgakopoulos, E., Manovic, V., Stendardo, S., and Baciocchi, R. (2017). Granulation-Carbonation Treatment of Alkali Activated Steel Slag for Secondary Aggregates Production. *Waste Biomass Valor.* 8 (5), 1381–1391. doi:10.1007/s12649-016-9781-0

Morone, M., Costa, G., Polettini, A., Pomi, R., and Baciocchi, R. (2014). Valorization of Steel Slag by a Combined Carbonation and Granulation Treatment. *Minerals Eng.* 59, 82–90. doi:10.1016/j.mineng.2013.08.009

Naqi, A., and Jang, J. (2019). Recent Progress in Green Cement Technology Utilizing Low-Carbon Emission Fuels and Raw Materials: A Review. *Sustainability* 11, 537. doi:10.3390/su11020537

NASEM - National Academies of Sciences Engineering and Medicine (2019). *Gaseous Carbon Waste Streams Utilization: Status and Research Needs*. Washington, DC: The National Academies Press.

Niven, R., Monkman, G. S., and Forgeron, D. (2012). *Carbon Dioxide Treatment of Concrete Upstream from Product Mold*. US Patent 8845940B2. Halifax, CA: Applicant: Carbon Cure Tecnologies Inc..

Pan, S.-Y., Chang, E. E., and Chiang, P.-C. (2012). CO2 Capture by Accelerated Carbonation of Alkaline Wastes: A Review on its Principles and Applications. *Aerosol Air Qual. Res.* 12, 770–791. doi:10.4209/aaqr.2012.06.0149

Patel, T. N., Park, A.-H. A., and Banta, S. (2013). Periplasmic Expression of Carbonic Anhydrase inEscherichia Coli: A New Biocatalyst for CO2hydration. *Biotechnol. Bioeng.* 110, 1865–1873. doi:10.1002/bit.24863

Power, I. M., Harrison, A. L., and Dipple, G. M. (2016). Accelerating Mineral Carbonation Using Carbonic Anhydrase. *Environ. Sci. Technol.* 50, 2610–2618. doi:10.1021/acs.est.5b04779

Prigiobbe, V., Polettini, A., and Baciocchi, R. (2009). Gas-solid Carbonation Kinetics of Air Pollution Control Residues for CO2 Storage. *Chem. Eng. J.* 148, 270–278. doi:10.1016/j.cej.2008.08.031

Quaghebeur, M., Nielsen, P., Horckmans, L., and Van Mechelen, D. (2015). Accelerated Carbonation of Steel Slag Compacts: Development of High-Strength Construction Materials. *Front. Energy Res.* 3, 52. doi:10.3389/fenrg.2015.00052

Realmonte, G., Drouet, L., Gambhir, A., Glynn, J., Hawkes, A., Koberle, A. C., et al. (2019). An Inter-model Assessment of the Role of Direct Air Capture in Deep Mitigation Pathways-. *Nat. Commun.* 10, 3277. doi:10.1038/s41467-019-10842-5

Renforth, P. (2019). The Negative Emission Potential of Alkaline Materials. *Nat. Commun.* 10. doi:10.1038/s41467-019-09475-5

Renforth, P., Manning, D. A. C., and Lopez-Capel, E. (2009). Carbonate Precipitation in Artificial Soils as a Sink for Atmospheric Carbon Dioxide. *Appl. Geochem.* 24, 1757–1764. doi:10.1016/j.apgeochem.2009.05.005

Said, A., Mattila, H. P., Jarvinen, M., and Zevenhoven, R. (2013). Pilot-scale Experimental Work on Carbon Dioxide Sequestration Using Steelmaking Slag. *Appl. Energ.* 177, 602–611.

Sanna, A., Dri, M., Wang, X. L., Hall, M. R., and Maroto-Valer, M. (2012). Micro-Silica for High-End Application from Carbon Capture and Storage by Mineralisation. *Kem* 517, 737–744. doi:10.4028/www.scientific.net/kem.517.737

Sanna, A., Uibu, M., Caramanna, G., Kuusik, R., and Maroto-Valer, M. M. (2014). A Review of Mineral Carbonation Technologies to Sequester CO2. *Chem. Soc. Rev.* 43, 8049–8080. doi:10.1039/c4cs00035h

Santos, R. M., Ling, D., Sarvaramini, A., Guo, M., Elsen, J., Larachi, F., et al. (2012). Stabilization of Basic Oxygen Furnace Slag by Hot-Stage Carbonation Treatment. *Chem. Eng. J.* 203, 239–250.

Solidia Cement^{TM} (2013). Part One of a Two-Part Series Exploring the Chemical Properties and Performance Results of Sustainable Solidia Cement™ and Solidia Concrete™. Available at: www.solidiatech.com (Accessed August 3, 2020).

Teir, S., Eloneva, S., and Zevenhoven, R. (2005). Production of Precipitated Calcium Carbonate from Calcium Silicates and Carbon Dioxide. *Energ. Convers. Manage.* 46, 2954–2979.

U.S. Geological Survey (2021). Mineral Commodity Summaries. Available at: https://pubs.usgs.gov/periodicals/mcs2021/mcs2021-wollastonite.pdf (Accessed April 21, 2021).

Vinca, A., Rottoli, M., Marangoni, G., and Tavoni, M. (2018). The Role of Carbon Capture and Storage Electricity in Attaining 1.5 and 2 °C. *Int. J. Greenhouse Gas Control.* 78, 148–159. doi:10.1016/j.ijggc.2018.07.020

IPCC (2018). Global Warming of 1.5 ˚C.an IPCC Special Report on the Impacts of Global Warming of 1.5˚C above Pre-industrial Levels and Related Global Greenhouse Gas Emission Pathways, in *The Context of Strengthening the Global Response to the Threat of Climate Change, Sustainable Development, and Efforts to Eradicate Poverty [Masson-Delmotte*, V. P. Zhai, H.-O. Pörtner, D. Roberts, J. Skea, P. R. Shukla, et al. (eds.)]. © 2019 Intergovernmental Panel on Climate Change

Wang, X., and Maroto-Valer, M. M. (2011). Dissolution of Serpentine Using Recyclable Ammonium Salts for CO2 Mineral Carbonation. *Fuel* 90, 1229–1237. doi:10.1016/j.fuel.2010.10.040

Wilson, S. A., Dipple, G. M., Power, I. M., Thom, J. M., Anderson, R. G., Raudsepp, M., et al. (2009). Carbon Dioxide Fixation within Mine Wastes of Ultramafic-Hosted Ore Deposits: Examples from the Clinton Creek and Cassiar Chrysotile Deposits, Canada. *Econ. Geology* 104, 95–112. doi:10.2113/gsecongeo.104.1.95

Woodall, C. M., McQueen, N., Pilorgé, H., and Wilcox, J. (2019). Utilization of Mineral Carbonation Products: Current State and Potential. *Greenhouse Gas Sc.i Technol.* 9, 1096–1113. doi:10.1002/ghg.1940

Ye, Z., Abraham, J., Christodoulatos, C., and Prigiobbe, V. (2019). Mineral Carbonation for Carbon Utilization in Microalgae Culture. *Energy Fuels* 33, 9, 8843–8851. doi:10.1021/acs.energyfuels.9b01232

Zevenhoven, R., Legendre, D., Said, A., and Järvinen, M. (2019). Carbon Dioxide Dissolution and Ammonia Losses in Bubble Columns for Precipitated Calcium Carbonate (PCC) Production. *Energy* 175, 1121–1129. doi:10.1016/j.energy.2019.03.112

Zevenhoven, R. (2020). Metals Production, CO2 Mineralization and LCA. *Metals* 10, 342. doi:10.3390/met10030342

Zevenhoven, R., Slotte, M., Koivisto, E., and Erlund, R. (2017). Serpentinite Carbonation Process Routes Using Ammonium Sulfate and Integration in Industry. *Energy Technol.* 5, 945–954. doi:10.1002/ente.201600702

Zhang, D., Ghouleh, Z., and Shao, Y. (2017). Review on Carbonation Curing of Cement-Based Materials. *J. CO2 Utilization* 21, 119–131. doi:10.1016/j.jcou.2017.07.003

Zhang, N., Santos, R. M., and Šiller, L. (2020). CO2 Mineralisation of Brines with Regenerative Hydrotalcites in a Cyclical Process. *Chem. Eng. J.* 404. 126450. doi:10.1016/j.cej.2020.126450

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REVIEW
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Lignocellulosic Biomass Pretreatment for Enhanced Bioenergy Recovery: Effect of Lignocelluloses Recalcitrance and Enhancement Strategies

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Bioenergy recovery from lignocellulosic (LC) biomass is the beneficial and sustainable approach due to its abundant availability. On the Otherhand, its recalcitrant nature makes the biomass to resist biological hydrolysis and it limits the conversion potential of organics to biomethane. Thus, it is essential to evaluate the association among the recalcitrant nature of LC biomass and its biomethane conversion efficiency. Consequently, this review critically recaps the recalcitrance of LC biomass and its effects on bioenergy recovery, its composition and characteristics. In addition, various enhancement approaches (pretreatments) were conferred as main aspect which plays main role in biomass disintegration and biomethane increment. Based on up -to -date information, elevated energy input and cost necessities of the pretreatments are the main factors that mediates the economic feasibility of the process. The present review apart from spotlighting the pretreatment efficiency, it also focusses on the challenges and limitations of enhancement strategies, energy and technoeconomic feasibility of the various pretreatments of LC biomass.

Keywords: lignocellulose biomass, pretreatment, anaerobic digestion, lignin, cellulose

INTRODUCTION

Rapid economic progress at global level have currently increased the demand for alternate energy sources chiefly owing to the destructive impacts of utilizing fossil fuels which includes global warming, green-house gases emission. Therefore, replacement of fossil fuels with renewable energy resource affords prospect to overcome these challenges (Scaramuzzino et al., 2019). Lignocellulosic (LC) biomass is considered as the chiefly available renewable energy sources (Patinvoh et al., 2017). LC biomass is a cheap and adequately available substrate for anaerobic digestion (AD) and biomethane production (Grosser, 2017).

Hypothetically, it has been reported that AD can degrade the biodegradable portion of any substrate (Kavitha et al., 2014a; Xu et al., 2019). On the otherhand, biomethane generation differs highly based on various kinds of lignocellulosic substrates. For instance, a greater methane production of 450 ml/g volatile solids can be obtained by using terrestrial crops, whereas

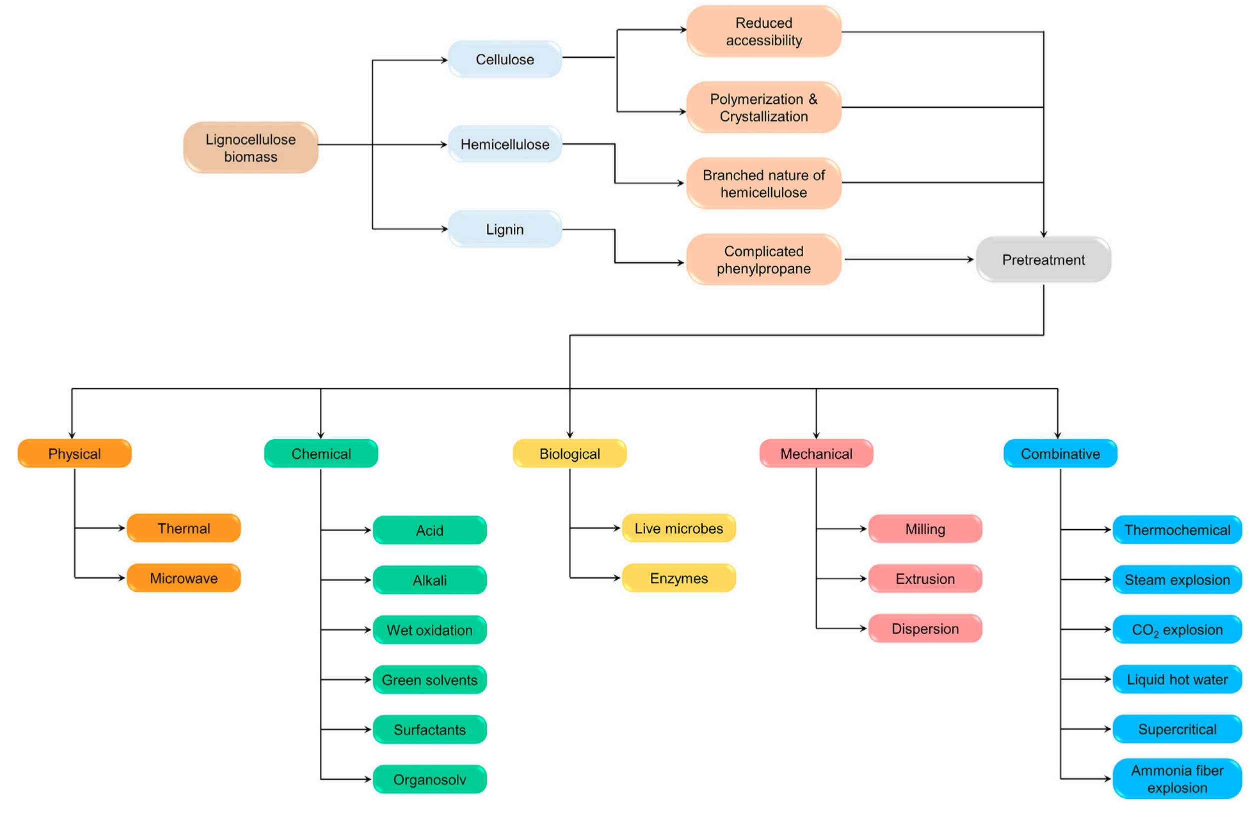

FIGURE 1 | Overall concept diagram of the present review.

methane production of 0.272 gCOD/gCOD and 330 ml CH_4/g volatile solids can be obtained from other lignocellulosic biomass (*Marsilea sps* and *Miscanthus. giganteus*) (Wahid et al., 2015; Banu et al., 2018a). The complex nature of LC biomass is considered as the main limitation of which greatly resist AD and eventually reduces the production of methane (Sawatdeenarunat et al., 2016).

To surpass this limitation, lignocellulosic biomass structure should be disintegrated and as a result various pretreatment methods have been reported so far in literature (chemical, physical, mechanical and biological). These various pretreatments brings about greater effects on lignocellulosic biomass structure such as increment in surface area, removal of lignin, decrement in crystalline nature of cellulose and these effects have been described in many reports. Yet, a complete evaluation and analysis about lignocellulosic recalcitrant effects on anaerobic biodegradability and production of methane is still required and essential for more biomethanation research and progress. Henceforth, the main aim of this review article is to afford more insights into LC biomass recalcitrance and its virtual impacts on AD and methane yield. Besides, the strategies for enhancement of bioenergy recovery from LC biomass, energy, techno economic feasibility aspects of pretreatments and future outlook were also conferred. **Figure 1** represents the overall concept diagram of the present review.

COMPONENTS AND CHARACTERISTICS OF LIGNOCELLULOSIC BIOMASS

LC biomass consist of cellulose, hemicellulose and lignin in their structure and its composition differs according to the structure of the biomass; based on the region in which the biomass develops and the climatic state of the soil. The cellulose is found to be the homogeneous substance which forms a backbone to the lignin-carbohydrate complex. In the case of hemicellulose, it is intracellular in nature forming covalent bonds to increase the cell wall layer (Somerville et al., 2004). Yuan et al. (2013) reported that while considering the lignin, it acts as glue among the cellulose and the hemicellulose and improves the cell wall integrity. The compositional analysis of various LC biomass is tabulated in **Table 1**.

Cellulose

The cellulose is a fibrous, insoluble, crystalline, polysaccharide molecule present in the range of about 40–50% in the LC biomass. Since the cellulose is readily available in large amount, it is considered as a renewable source of energy to obtain bio-based energy products (Kavitha et al., 2020a). The degree of the cellulose polymerization refers to the molecular weight of the cellulose chain. The molecular weight of the cellulose chain was found to be 100,000 and it is a major factor disturbing the enzymatic hydrolysis process of the cellulose. The composition

TABLE 1 | Compositional Analysis of various lignocellulosic biomass.

S.No	Type of lignocellulosic biomass	Lignin (%)	Cellulose (%)	Hemicellulose (%)	Ash (%)	References
1	Wheat Straw	15.6	35	22.3	7.49	Bolado-Rodríguez et al. (2016)
2	Sugarcane bagasse	22.67	46.21	20.86	1.19	Bolado-Rodríguez et al. (2016)
3	Corn Straw	10.8	45.4	22.6	-	Fu et al. (2015)
4	Sweet sorghum	20.7	44.6	27.1	0.4	Kim and Day (2011)
5	Barley Straw	13.3	34.3	23.0		Saha and Cotta (2010)
6	Corn cobs	15	45	35	-	Prasad et al. (2007)
7	Switch grass	5–20	30–50	10–40	4–5	Prasad et al. (2007)
8	Miscanthus	24.1	38.2	24.3	2	De Vrije et al. (2002)
9	Grasses	10–30	25–40	25–50	2–5	Malherbe and Cloete (2002)
10	Rice Straw	19.17	31.57	22.38	11.2	Thelin (1950)

of the cellulose structure consists of D-glucopyronase units connected by β-1, 4 linkages.

Hemicellulose

The hemicellulose is considered as the second important polymer and it is found to be in the range of 20–35% in the lignocellulosic biomass. The hemicellulose containing pentose, hexoses and organic acid are the heterogonously bonded biopolymer and it is built up by the sugar monomers (Kannah et al., 2021a). Hemicellulose has a lower molecular weight of about less than 30,000 and hence it can be hydrolyzed easily. The easy degradation is due to its amorphous nature and the absence of crystallinity. The polymeric chains are connected by the acetyl groups.

Lignin

The space between the cellulose and hemicellulose are filled by gluelike substance called lignin. The lignin is an aromatic polymer found in the range of about 10–25% in the lignocellulosic biomass with phenyl propane units. These units consist of syringyl, guaicyl and *p*-hydroxylphenol matrix which are linked together by set of linkages to make it complicated (Banu et al., 2019a).

CHARACTERIZATION OF LIGNOCELLULOSIC BIOMASS AND ITS IMPACT ON PRETREATMENT

LC biomass in nature resist degradation and this forms a factual hindrance to its valorization at industrial scale to obtain bioenergy and value-added products. For optimization of biomass disintegration and deconstruction it is essential to recognize and overwhelm the physical and chemical characteristics that confers resistance nature to lignocellulosic biomass.

Physical Characteristics

The physical characteristics of LC biomass are particle size, grindability, accessible surface area, accessible volume and thermal properties.

Particle Size

The particle size of LC biomass is an important parameter that impact the mixing, fluidization, contact area for mass and heat transfer and the flowability during pretreatment. Therefore, LC biomass with varying particle size could possess various conversion ability and consumption of energy. The LC biomass are normally pre-treated prior to thermal conversion processes (Vidal et al., 2011). In the selection of thermochemical conversion processes, the particle size plays a major role. During enzymatic hydrolysis, the enhancement of surface area contact between cellulosic fibers and enzymes, deconstruction of compact LC biomass structure, increment of hydrolysis rate can be achieved due to particle size reduction through milling, grinding, and extrusion (Silva et al., 2012; Pang et al., 2019; Yu et al., 2019). Many reports have proved that disintegration of LC biomass such as woody chips (Jiang et al., 2017), corn stover (Yu et al., 2019), miscanthus and wheat straw (Kim et al., 2018) via mechanical pretreatment reduces the particle size and this facilitates the subsequent enzymatic hydrolysis (Kavitha et al., 2017a; Banu et al., 2018b) On the otherhand, few literature have reported that depending on the LC biomass, there is a threshold limit for particle size. Chang and Holtzapple. (2000) have reported that reduction in particle size less than 400 μm does not impacts rate of hydrolysis in poplar biomass. Silva et al. (2012) reported particle size threshold limit for wheat straw was 270 μm.

Grindability

Grindability is another physical property that impacts the LC biomass pretreatment which involves particle size reduction. The measurement of the resistance of any substance to grind is called as grindability. The components of LC biomass which are fibrous and hard to grind are cellulose and lignin. Presently, no typical grindability analysis tests for LC biomass there is available. Various literature have reported that Hardgrove Grindability Index (HGI) test has been used for analysis of coal in LC biomass (Capareda, 2013). The HGI analysis is insufficient for grindability characterization of LC biomass as it encompasses pregrinding to get biomass of particle size ranging from 0.6 to 12 mm before HGI analysis. In HGI analysis, the energy spent for grinding is not taken into account. Therefore, another alternate analysis such as Bond Work Index (BWI) was suggested for grindability analysis of LC biomass (Williams et al., 2015). In a ball milling pretreatment, in order to grind a substance, more energy is needed.

Accessible Surface Area

Another important factor that critically affect the pretreatment of LC biomass is the Accessible surface area. Accessible surface area is linked to structural characteristics which includes specific surface area and pore volume (Liu et al., 2015). Particle size reduction and pore volume increment can cause increase in accessible surface area. Reduction in the particle size or increase in pore volumecan leads to increment in accessible surface area. Torr et al. (2016) have suggested that accessible surface area can be increased in enzymatic hydrolysis of disintegrated pine wood. In addition, another researcher, Goshadrou et al. (2013) have suggested that disintegration of aspen wood increases the accessible surface area which in turn increases the accessibility of fibers to subsequent to enzymatic hydrolysis. On the otherhand, analysis of accessible surface is very hard. In that case, specific surface area is SSA is employed to estimate the actual availability of surface to enzymatic hydrolysis (Octavia et al., 2017). Reducing the particle size will increase the specific surface area (Octavia et al., 2017). It has been reported in literature that hydrothermal pretreatment of corn stover leads to two fold increase in specific surface area and resulted in 138% improvement in subsequent enzymatic hydrolysis Zhang et al. (2018). Lu et al. (2019) reported that pretreatment of LC biomass with ball milling pretreatment causes increase in specific surface are of cellulosic component because of particle size reduction. This causes increment in accessibility of cellulose and enhanced yield of glucose.

Accessible Volume

In LC biomass, accessible volume of cellulose is regarded as an essential parameter impacting physical, chemical and enzymatic pretreatments. Based on the particle sizes and shapes, pore volume accessibility was estimated. It has been reported in literature that pore size and the product yield potential of enzymatic conversion for dilute acid pretreated poplar biomass and cellulosic substrates have close association (Meng et al., 2013; Peciulyte et al., 2015). Herbaut et al. (2018) reported that the ranges of porosity are definite to LC biomass and they reliant on pre-treatment. For instance, yield of hydrolysis linked sturdily to porosity range of 15–30 nm for wheat straw, while it linked to porosity range of 10–15 nm for poplar plants. Herbaut et al. (2018) reported that porosity range limited to 10 nm linked with pretreatment for miscanthus biomass. The authors added that no specific porosity range for improvement of enzymatic hydrolysis was reported so far and proved that enzyme diffusion within the cellwalls of plants is specific to LC biomass. In contrast, few reports suggested that no specific relation among porosity range and yield of hydrolysis was observed in case of disintegrated pine (Kruyeniski et al., 2019) and delignified and dilute acid disintegrated sugarcane (Santos et al., 2018). Besides, few reports suggested that in case of biomass with lignin content below 15%, increment in pore volume has no impact on enzymatic hydrolysis of disintegrated pine (Stoffel et al., 2014; Vaidya et al., 2016).

Thermal Properties

The thermal chemical conversion efficiency of LC biomass is strongly influenced by its thermal characteristics. The significant thermal characteristics of LC biomass are thermal conductivity and specific heat.

Thermal Conductivity

During thermochemical conversion, the LC biomass are subjected to conduction of heat laterally and transversely which in line impacts its thermochemical conversion characteristics (Yu et al., 2014). Mason et al. (2016) established a test for estimating the biomass thermal conductivity with the aid of custom-built test equipment. With this apparatus, the authors stated that for LC biomass such as miscanthus, wood pellets and willows, the thermal conductivity ranges between 0.1–0.12 w/m/K while thermal conductivity of wheat and rape straws was very low 0.05 w $m^{-1} K^{-1}$. The thermal conductivity of LC biomass relies on direction of heat, porous nature, temperature and compactness (Dahlquist, 2013).

Specific Heat

Another vital thermal characteristic of LC biomass is specific heat which is essential for thermodynamic analysis. It is a sign of the heating potential of a substance (Dupont et al., 2014). The moisture content of LC biomass and the medium temperature related mainly with specific heat.

Chemical Factors That Impact Pretreatment

Polymers Interaction

In addition to physical characteristics, chemical factors such as interaction between polymers also plays a major role in recalcitrant nature of the cell walls to pretreatment. Du et al. (2014) reported that interactions among microfibers of celluloses and hemicelluloses and lignin carbohydrate complex association imparts an important part in woody biomass structure and considerably impacts the biological pretreatment thereby minimizing the accessibility of cellulose for enzymes. Literature reports on LCC biomass is a debated theme so far owing to the complications in the LC biomass properties and due to lignin carbohydrate complex. Therefore, it is essential to invent effective techniques to investigate lignin carbohydrate complexes which includes chemical or enzymatic pretreatment to analyze lignin carbohydrate complex qualitatively (Giummarella et al., 2019).

RECALCITRANCE OF LIGNOCELLULOSIC BIOMASS AND ITS EFFECT ON ANAEROBIC BIODEGRADABILITY

Steps Involved in Anaerobic Digestion

The preliminary steps involved in anaerobic digestion involve four successive phases such as hydrolysis, acidogenesis, acetogenesis and methanogenesis. During hydrolysis, complex macromolecules are broken down into simpler compounds like monosaccharides, aminoacids, glycerol, etc. Because of the presence of lignin in the lignocellulosic substrates, which develops a rigid three-dimensional complex molecule with cellulose and hemicellulose units, hydrolysis is considered to be a rate-limiting step (Piven et al., 2012).

In the second phase (acidogenesis), the hydrolyzed products are further subjected to fermentation by strict and facultative anaerobic bacteria. In this phase volatile fatty acids, carbon dioxide, alcohols and hydrogen are produced.

In the third phase, acetate is formed by the oxidation of fatty acids, hydrogen and carbondioxide. Moreover, the products formed during acidogenesis are utilized by hydrogen producing acetogens. Removal of hydrogen through this process favors the growth of methanogens.

In general, establishing a synchronised state between the different steps is critical throughout the process, and any fluctuation or decrease in the activity of one or more microbial groups can have a significant impact on process performance and efficiency, and even result in process failure.

In the final step (methanogenesis), the acetate formed earlier is converted into methane and carbondioxide by methanogenic bacteria.

Recalcitant Nature of Lignocellulosic

The recalcitrant nature of the LC biomass explains the anti-degradation effect of native lignocellulose, which acts as a protective layer for the cell wall from the pathogen's attack, microorganisms and enzymes. This is possible with the complex structure and the cell wall composition. The chief composition of lignocellulosic biomass was cellulose, hemicellulose, lignin, and the other constituents like the cell wall proteins, lipids, pectin, mineral present in the lignocellulose is involved in the biomass recalcitrance. To block the deconstruction of microbes and enzymes, the lignocellulose building blocks were provoked and known as the biomass recalcitrance. The combined structure of transparent cellulose within the microfibrils, polysaccharides, lignin and other components make the LC biomass recalcitrant. During hydrolysis of AD, the recalcitrant nature of LC biomass shields the biomass structure from bacterial and enzymatic decomposition and this could reduce the bioconversion of complex molecules and restricts the methane production potential. As already mentioned, the recalcitrant extent differs based on the LC biomass composition (that related to genotype, ecological circumstances, human activities etc). The factors that induce recalcitrance effect on LC biomass are described in following subsection.

Reduced Accessibility of Cellulose

During AD process, accessibility of substrate (cellulose) to microbial enzyme (cellulase) can be limited due to reduced accessibility of surface area between the biomass and the microbes. This would restrict the biodegradation of lignocelluloses and will ends in inadequate fermentable sugars for succeeding biological process. Surface area accessibility can be influenced through various parameters such as layer of epidermis, particle size of feedstock, physiochemical composition of the LC biomass cell wall. Surface area accessibility are of two types such as inner surface area that is associated with porosity of raw material and the external surface area that is associated with size of particles (Xu et al., 2019). Normally, LC biomass possess tiny inner surfaces particularly when it is in dry form. It has been reported in literature that accessibility of cellulose to enzymatic microbial attack is chiefly via the inner pores of the LC biomass instead of exterior surface signifying that the outer surface does not contribute much to hydrolysis process (Arantes and Saddler, 2011). The hydrolytic microbes hydrolyze the LC biomass to discharge the monosaccharides for AD process. These microbes will attach to surface layer of LC biomass via physical mode of attachment and initiate the secretion of exoenymes to hydrolyze the biomass. Normally, the pore dia of inner surface extended from 0.2–2 μm and this is alike of the size of microbes. In AD process, the surface area contact will show increment with increase in fractional exclusion of cell wall compounds and this result in greater surface area accessibility. But the hydrolysis process mediated by enzymes is generally rapid at the initial phase and stumpy at the final phases (Vivekanand et al., 2014), representing that accessible surface are is not only the important regulating parameter in fermentative process. During start phase, the increased surface area permits adequate relationship among enzymes and biodegradable amorphous cellulose and will results in rapid fermentation. However, during the final phase of AD, although the surface area is sufficiently accessible the greater existence of residual crystal cellulose and its complicated nature are the critical parameters that ultimately restrict the hydrolytic potential.

Polymeric and Crystalline Nature of Cellulose

The polymerization extent of celluloses which is associated with mol wt of cellulose linkages is regarded as an essential parameter influencing the hydrolytic potential of cellulose by enzymes. Depolymerization of cellulose is defined as the hydrolysis of cellulose by cellulase enzyme. Usually, hydrogen linkages in longer cellulosic chains will hamper the bioconversion of cellulose than shorter cellulosic chains (Xu et al., 2019). Huang et al. (2015) have reported that steam explosion pretreatment reduces the extent of cellulose polymerization and results in 5–6 times increment in enzyme mediated saccharification. The crystalline portion of cellulose contributes 30–80 percent and this region is responsible for crystallinity of cellulose. The two forces or bonds responsible for crystallinity of cellulose are hydrogen bonds and vander waals interactions. When cellulase enzyme comes in contact with cellulose, initially it may show greater endo-glucanase action with amorphous region of cellulose and in such cases, crystallinity of cellulose imparts obvious role in impacting primary hydrolysis of cellulose. The yield of reducing sugars are reported to decrease with increase in cellulose crystallinity designating that amorphous phase of cellulose are hydrolysed initially prior to the hydrolysis of crystalline phase of cellulose (Ling et al., 2017). It has been reported by Mirahmadi et al. (2010) that pretreatment of birch and spruce with sodium hydroxide shows considerable drop in crystallinity of cellulose and this in turn enhances the enzyme mediated hydrolysis with 83 and 74 percent enhancement in biomethane yield.

Branched Nature of Hemicelluloses and Lignin

Hemicellulose is a cleft saccharide complex comprising of different units of sugar molecules. Xylan is considered as the major copious compound of hemicellulose. The structure of hemicellulose is complex in nature and considerably impacted via cross linkers. for example ferulate; composition of saccharides and existence of branching chains. Usually, it has been supposed that hemicellulose could enhance the physical integrity of LC biomass and restricts the increase in surface area ensuing in decrease of hydrolytic potential. The availability of cellulose to microbial or enzymatic attack can be achieved via pretreatments which can efficiently solubilize or remove lignin and hemicellulose. During AD, with cautious regulation of biomass retention time, yield of methane can be increased from hemicellulose wholly, whereas cellulose and lignin are remained as residuals. In anaerobic biodegradation of LC biomass, hemicellulose can be normally disintegrated priorly which could reduce the hindrances extent of enzyme mediated hydrolysis. Due to the complex nature of hemicellulose and existence of cross linkages among cell wall compounds of LC biomass, further investigation is yet required to cautiously infer the hemicellulose characteristics and its impact on biomethane yield.

Lignin is the polymer of complicated structure with units of phenylpropane which are arranged in 3-dimensionalmesh like structure within the cell wall of LC biomass. Lignin is usually regarded as the major parameter restricting the biodegradation of LC biomass. It has been reported in literature that lignin content in excess of 1 g/L will reduce the methane yield of LC biomass (Kavitha et al., 2020a). Lignin hampers the hydrolysis of polysaccharides of LC biomass mediated by lytic enzymes thus hindering the anaerobic conversion of lignocelluloses (Banu et al., 2018a). The major mechanism of lignin which imparts predominant role in LC biomass recalcitrance is the covalent cross linking of lignin with other cell wall compounds. This results in reduced surface area contact and hinders the enzyme mediated hydrolysis of sugars. The structural characteristics of lignin in addition may have impact on LC biomass biodegradation potential. The ratio of monolignols and interlinking phenols could impact enzymatic biodegradation although after alkali and acidic disintegration of LC biomass.

ENHANCEMENT APPROACHES-ROLE OF PRETREATMENTS

The role of the pretreatment is to disintegrate the polymeric substances of the LC biomass. The pretreatment helps in breaking down the complex organic molecules to simple monomeric sugars (Kavitha et al., 2013) and is necessary for reducing the crystalline nature of the cellulose seen in the LC biomass (Kavitha et al., 2017b). There are some pretreatments that help remove lignin, which helps increase the binding capacity of the LC biomass with the enzyme. The pretreatment is important to access the LC biomass for hydrolysis process effectively. There are various pretreatment techniques for the LC biomass and the output from each pretreatment technique varies for the same biomass. The pretreatment is selected based on LC biomass type and the crystalline structure of the cellulose, hemicellulose, and lignin. Overall, the pretreatment is mainly useful for the lignin removal, cell cleavage, hemicellulose disintegration, and alteration in the cellulose crystalline nature which could further enhance AD and biomethane production. **Figure 2** represent the impact of pretreatment on biogas yield of lignocellulosic biomass.

LIGNOCELLULOSIC BIOMASS PRETREATMENTS

The LC biomass consists of the biodegradable part and the recalcitrant part. The recalcitrant part consists of the cellulose, the hemicellulose, and the lignin (Viola et al., 2008). For the efficient hydrolysis of the recalcitrant part and for efficient methane generation by the anaerobic digestion process, the pretreatment is necessary. There are various pretreatments involved in treating the LC biomass. The pretreatment techniques are classified into physical, chemical, mechanical and biological pretreatments. The thermal and microwave are physical pretreatments (Kannah et al., 2017a; Banu et al., 2018c; Kavitha et al., 2018). The chemical pretreatment consists of acid, alkaline, wet oxidation, Green solvents, Surfactants, and organosolv (Kannah et al., 2017b; Banu et al., 2020a; Kavitha et al., 2020b). The mechanical pretreatment involves the milling, ultrasonication, extrusion, and rotor stator homogenization (Disperser) (Kavitha et al., 2014b; Banu et al., 2018b; Kannah et al., 2020). The Biological pretreatment involves the live microbes (bacterial/Fungi), Immobilized microbes, and Enzymes (Kavitha et al., 2019).

Physical Pretreatments

Thermal

The thermal pretreatment process increases the solubilization of the LC biomass. Increasing the temperature decreases the viscosity, and the heat treatment also causes the solubilization and the release of the organic matter from the biomass (Banu et al., 2020b). The hydrogen links in the molecule are broken down by the thermal process (Carrère et al., 2010). The thermal process promotes the methanogenic enzyme in the anaerobic biodegradation process. For the thermal treatment, the temperature varies from 50°C to 160°C. increasing the temperature increases the biomass's solubilization. In a study conducted by Chandra et al. the rice straw was hydrothermally pretreated prior to anaerobic digestion and the increase in methane production in pretreated sample (132.7 L/kg VS) was two times higher than the untreated substrate (59.8 L/kg VS). In another study by Rodriguez, grass (*Eleusine indica*) was pretreated thermally in a oil bath at 80°C for 3 days to increase the biogas production. There was 46% increase in the

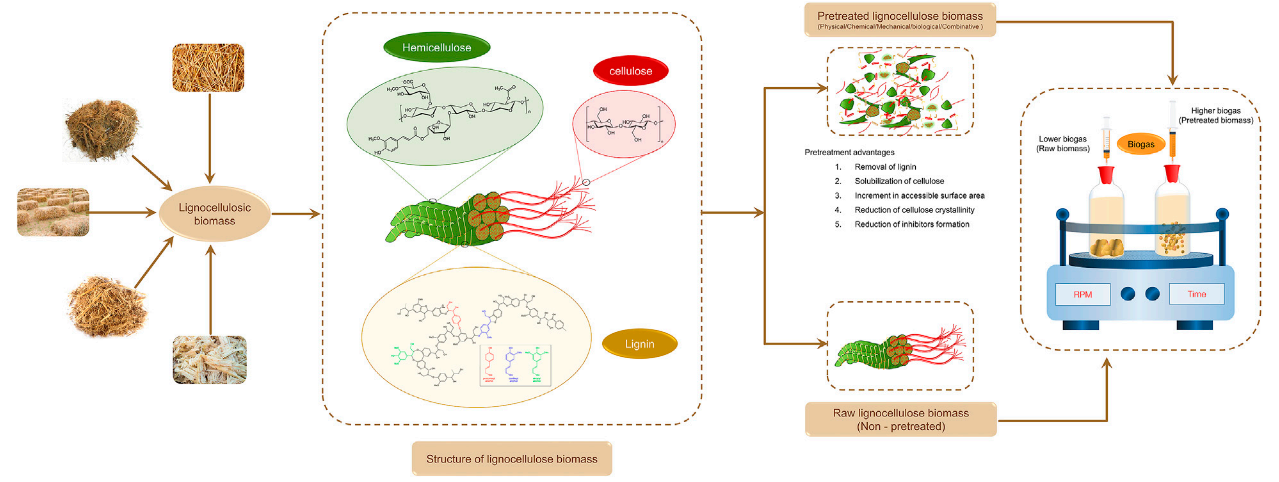

FIGURE 2 | Impact of LC biomass pretreatment on biomethane yield.

methane yield. When Two-phase olive mill solid waste or alperujo was pretreated thermally when exposed to steam at 200°C for 5 min at a pressure of 1.57 MPa, there was 61% increase in methane yield (Rincón et al., 2016). Many such studies revealed that the thermal process from 70 to 90°C enhances the soluble organic release, which favors the rate of biodegradability (Jard et al., 2013). Apart from the high energy requirements and high-pressure operation, the main disadvantage of these procedures is the potential creation of inhibitors, such as furfural and soluble phenolic compounds, which impede methane synthesis (Hendriks and Zeeman, 2009). To avoid the generation of these inhibitory compounds, pH should be maintained in the range of 4-7.

Microwave

The microwave treatment process is a powerful technique, it has become more trending because of its reduction in the treatment time (Eskicioglu et al., 2007). The microwave fields disrupt the molecule's links, and it was regularized by an electric field, which causes cleavage of hydrogen bond and changes in the liquid phase. The main parameters of microwave irradiation that disturbs the dielectric system are the temperature, intensity, and reaction period (Park et al., 2010). The thermal and non-thermal effect are the major mode of action of this treatment (Banu et al., 2019b). The thermal process is initiated with the bipolar components containing the electric field. The rotating motion obtained by the dipoles causes the heating effect (Doğan and Sanin, 2009). The study of Passos et al. (2014) explains the non-thermal effect that changes the dipole direction in the biomass cell wall layer containing side chains, leading to the breakage of the bonds causes protein deconformation. This leads to the increase in the biogas yield. In a research conducted by Siddique et al., microwave pre-treatments on waste sludge resulted in further biomethane enhancements of 53%. When microwave radiation of frequency 2.45 GHz, power 680 W, time 24 min was applied to the lignocellulosic biomass prior to anaerobic digestion (Liu et al., 2012), the biogas generation speed was increased rather than the enhancement.

Chemical Pretreatments

Acid

In the acid pretreatment, both, dilute acid or concentrated acid are usually used. The nature of concentrated sulfuric acid and then concentrated hydrochloric acid are toxic, corrosive, and hazardous, and so it is not preferred (Singh et al., 2014). While pretreating with dilute acid, high sugar yield can be obtained from hemicellulose at higher temperature. If the temperature is high, the yield can be obtained at a short interval of time, and for the lower temperature, it involves a longer time period. While treating wheat straw with sulfuric acid, the saccharification yield of 74% is obtained at 121°C for 1 h (Rezania et al., 2017). When the cashew apple bagasse was processed with dilute sulfuric acid, 0.47 g/g glucose of ethanol yield was obtained at 121°C for 15 min. Similiarly when rice straw was pretreated with propionic and acetic acid, there was 36% increase in methane when compared with the untreated rice straw (Zhao et al., 2010).

But due to the usage of concentrated acids which may be corrosive and toxic, they may incur cost for maintenance. Furthermore, they cause cellulose degradation that results in the formation of inhibitory chemicals such as furfurals, 5-hydroxymethyl furfural, acidic phenolic compounds, and aldehydes. The effect of these inhibitors has to be neutralized further using chemical (peroxide and ozone) and biological (enzymes or live microbes) detoxication methods by converting them into inert substances.

Alkaline

The alkaline treatment is considered as the supporting step for the anaerobic digestion process (Hendriks and Zeeman, 2009). The alkaline pretreatment is mainly preferred for the LC biomass as it highly disintegrated the phenolic nature and lignin content. The alkaline pretreatment efficiently enhances the methane generation (Cheng et al., 2010). Sodium hydroxide is the mainly used alkali for many years in lignocellulosic biomass since it interrupts the lignin structure (Brodeur et al., 2011). The corn Stover, switch grass, bagasse, wheat, rice straw are the reported biomass pretreated with alkali (Zhu et al., 2010). The methane yield of NaOH-pretreated corn straw was found to be approximately 220 ml/gVS, which was 73.4 percent greater than that of untreated corn straw, according to the study by Zheng et al. (Zheng et al., 2009). When calcium hydroxide was used to pretreat municipal solid waste, the methane yield was increased by 172% which was considered as the highest increase of biogas production (López Torres and Espinosa Lloréns del, 2008). Also, the alkaline pretreatment helps the enzymes to reach the cellulose and hemicellulose easily. The lime is also one of the cheaper alkali used for pretreatment process (Ibrahim et al., 2011).

Wet Oxidation

Oxygen and water take part in wet oxidation process. The oxygen is used as an oxidizing agent. The hydrolyte reaction takes place at low temperatures and the oxidative reaction happens at elevated temperatures in the wet oxidation procedure (Martín et al., 2007). The samples are well dried and milled into small crumps of 2 mm in length. The biomass and water are taken as 6 g/L, respectively. The sodium carbonate is used in the wet oxidation method to minimize the byproducts formed in the process. The air is pumped at a particular temperature above 120°C (Pedersen and Meyer, 2009). The wet oxidation process splits out the LC biomass by disintegrating hemicellulose and eliminates the lignin (Martín et al., 2007; Chaturvedi and Verma, 2013).

Green Solvents

Green solvents are ionic liquids (IL) used for the pretreatment and it do not produce any toxic products during disintegration of LC biomass and 1 L is recoverable. The ionic liquids with very low vapor pressure consist of the small amount of anion and a large amount of organic cation (Fort et al., 2007). These liquids dissolve various types of LC biomass, and it involves the hydrolysis of lignin and hemicellulose. The adverse effect found in this pretreatment involves high solvent cost, and the solvent recovery and the recycling are also needed. However, a main issue linked to ionic liquid usage at pilot scale extent is its extreme expensiveness when compared to conventional solvents. But this cost can be counterbalanced to somewhat when the ionic liquids are recycled. Thus, effective separation and recovery of ionic liquids are important on the aspect of environmental applications. In recent years, more attention have been focused on recovery and recycling methods of ionic liquids such as distillation, extraction, adsorption, crystallization and aqueous dual phase separation etc (Zhou et al., 2018).

Surfactants

Surfactant plays a very important role in disrupting the secondary layer of the LC biomass. It also helps in removing the inorganic material from the biomass. Surfactant is amphiphilic molecule which has both hydrophilic and lipophilic group. The surfactant is classified into ionic and non-ionic surfactant. The ionic surfactants are cationic and anionic surfactants. The non-ionic surfactants are more effective than the ionic surfactant (Agrawal et al., 2017). The surface tension between two liquids or the surface tension between the solid and the liquid is reduced by the surfactant addition (Banks et al., 2014). The surfactant is mainly used in the LC biomass case since it helps to inhibit the binding of cellulase with lignin due to the hydrophobic interactions (Okino et al., 2013). Adding surfactant also helps to prevent aggregation of the biomass (Kumar et al., 2018). The surfactant acts as the barrier and does not allow the lignin to bind with the methanogenic enzyme, and hence the methane generation is also enhanced by the addition of the surfactant.

Organosolv

Pretreatment of lignocellulosic biomasses with organic solvents (eg: methanol, ethanol, acetone, etc.) weakens the internal bond between lignin and hemicelluloses and thereby lysing it, resulting in a reasonably pure cellulose residue. The temperature of about 200°C is used for the process, and it is lowered in some processes based on biomass nature and the addition of catalyst. The mainly used catalysts are the organic and inorganic acids (HCl or H_2SO_4). Solvents used in the process need to be evacuated from the reactor, evaporated, condensed and recycled. The solvent shows a negative effect in the hydrolysis process, and hence the solvent must be removed before the fermentation process. The solvent recovery helps in the reduction of cost and has the environmental safety (Sun and Cheng, 2002). However, cost effective recycling of solvents is needed for large-scale application.

Mechanical Pretreatments

Milling

The size of the particle plays a significant task in the methane generation. If the size of the particles is small, it is easier for the microbes to degrade, so smaller size particle provide greater solubilization. The smaller sized particle has the greater hydrolysis rate breaking the long chains into the smaller chains and increases the hydrolysis rate, which promotes easy biodegradation. To reduce the particle size, milling or grinding is required, but it is not suitable for the hardwoods, so chipping is done to reduce the particle size. The study of Sharma et al. (1988) explains about agricultural residue treated in five different particle sizes. It is found out that the smaller particle size provides greater biogas production due to the reason of more comfortable handling and the increased surface area. In the case of the mechanical pretreatment, the parameters like the capital cost, operational cost, scale-up possibilities, and reduction of the equipment are also considered. However, in this process, there is absence of generation of toxic compounds or inhibitors and thus this treatment is preferred widely.

Ultrasonication

Ultrasonication is one of the effectual mechanical pretreatment for the LC biomass. The use of the high-intensity ultrasound changes the biomass structure and thus, it favors the methane generation. Compared with the untreated sample, the ultrasound treated sample gave more significant methane generation. The study of Kim et al. (2003), Wang et al. (1999), and Dewil et al.

(2006) revealed that the ultrasonic pretreatment increases the biogas production and decreases the volatile solids. In a study by Zeynali et al. (2017), it was reported that the biogas yield increased from 139 to 396 ml biogas g^{-1} VS_{in} when exposed to ultrasonication for 18 min. The drawback of this pretreatment on LC biomass is not noticed in these studies.

Extrusion

Extrusion is the process of combining different operations in one unit. It is the mechanical process in which the biomass is taken into the extruder in one end and travels along the length (Haghighi et al., 2013). The barrel is placed along the length, and the screw drives it. The barrel is shaped in a way with a compression zone at the center and the expanded part at the end. The pressure release taking place at the end breaks down the cell wall of LC biomass. The cellulose, hemicellulose, and lignin are depolymerized. The main operating factors are the time, pressure, and dry matter of the biomass (Zheng et al., 2014). The study of Hjorth et al. (2011) revealed that the extrusion process improves the biogas production of LC biomass. It reduces the particle size, surface area increment, promotes the hydrolysis rate, and improves the anaerobic digestion process. The research conducted by Novarino and Zanetti. (2012) reported that when the organic fraction of the municipal solid waste is treated by extrusion, it resulted in a biogas yield of 800 L/kg VS, containing about 60% of methane content.

Rotor Stator Homogenization (Disperser)

The disperser or homogenizer is the advanced mechanical pretreatment process that replaces all the other mechanical treatment since it overcomes the other process by reducing the treatment time. Mainly all the type of the biomass is treated by this process (Tamilarasan et al., 2017). The disperser consists of the rotor and the stator, which breakdown the complex matter into a simpler one. The rpm plays a vital role in the disperser (Kumar et al., 2018).

Biological Pretreatment

The biological pretreatment of the lignocellulosic biomass is categorized into fungal pretreatment (oxidative ligninolytic system and hydrolytic system), microbial consortium pretreatment, and the enzymatic pretreatment. The oxidative ligninolytic and hydrolytic system present in the fungus distract the lignin phenyl bond and disintegrates cellulose and hemicellulose (Kudanga and Le Roes-Hill, 2014). The microbes are involved in the microbial consortium pretreatment. The enzymes are employed in the enzymatic pretreatment process to degrade the lignocelluloses. The pretreatment is mainly done to increase the methane generation. The main role of the biological treatment (using delignifying and cellulose degrading enzymes) is to reduce carbohydrate use and maximize the removal of lignin for the lignocellulosic biomass.

Live Microbes (Bacterial/Fungal)

The fungal pretreatment consists of two systems the oxidative ligninolytic system and the hydrolytic system. The oxidative ligninolytic system present in the fungus distracts the phenyl bond in the lignin. The hydrolytic system in the fungus degrades the cellulose and hemicellulose in the lignocellulosic biomass (Ma et al., 2017). The rotten LC biomass is used as a substrate for the live bacteria. Compared to the fungal treatment process, the bacterial consortium process degrades the cellulose and hemicellulose effectively. Though these biological methods involve low energy and low chemical demand, it involves longer treatment time which limits its potential towards commercial purposes. Another limitation of the bacterial consortium process is the requirement of carbon sources, which reduces the methane generation (Zhang et al., 2014).

Enzymes

The commercial enzymes are employed in the enzymatic pretreatment process to degrade the lignocelluloses. The mainly used enzymes are lactases and manganese peroxidase, commonly known as degrading enzymes for cellulose, hemicellulose, and lignin. The enzyme lactase and the enzyme manganese peroxidase help remove the fermentable sugars in the LC biomass, which improves the methane generation. When the paper and pulp sludge is pretreated with the enzyme endoglucanase laccase, there was an increase in 34% of the methane yield (Yunqin et al., 2010). The drawback of the enzymatic pretreatment is that enzymes are available at a high cost (Amin et al., 2017).

Combined Pretreatments

To get the efficient methane yield, the pretreatments like the physical, chemical, thermal, ultra-sonication are combined (Kavitha et al., 2015). The combined pretreatments are employed to obtain the full-fledged pretreatment effect (Kannah et al., 2019).

Thermochemical Pretreatment

In the thermochemical pretreatment, both the thermal, and the chemical treatment, including the acid or the alkali, are used. For the thermochemical pretreatment, the temperature is maintained in the water bath to adjust the temperature, and the acid or the alkali is added to adjust the pH. The addition of the chemical to adjust the pH disrupts the nature of the lignin, which is a recalcitrant in the LC biomass (Koyama et al., 2015).

The thermochemical treatment of LC biomass was performed to improve methane generation (Patel et al., 1993). In this study, thermochemical pretreatment of water hyacinth was done to improve the anaerobic biodegradation and methane generation. From the result, it is clear that the solubilization is increased by the pretreatment and improves the methane production. The efficient methane generation was obtained at pH 11 and 121°C. Above this optimized condition, the methane generation was decreased due to the toxic compounds produced due to harsh disintegration of LC biomass.

In another study by Monlau et al. (2013), when the sunflower oil cake is treated at 170°C along with the addition of 1% (weight) concentrated sulphuric acid, the biogas yield was 302 ml CH_4/g VS which is 50% greater than the untreated waste.

Steam Explosion

In steam explosion pretreatment, both the physical and the chemical methods are involved to disrupt the structure of the LC biomass. This process is mostly applied because of its low chemical usage and minimal energy consumption. It is the hydrothermal method of treatment in which the high pressure and temperature are given for a short period and when it suddenly depressurizes, it collapses the fibril structure. This action helps the cellulose to be easily accessible for the enzymes reported by Duff and Murray (1996). While injecting the steam the temperature was increased from 160 to 260°C and at the same time pressure was suddenly decreased and the biomass undergoes disintegration. The particle size, residence time and the temperature have a major role in the effectiveness of the treatment (Ballesteros et al., 2002). Viola et al. (2008) explains that the addition of the some chemicals such as the acid or the alkali improve the outcome of the steam explosion treatment. Furthermore, harsh conditions favours the generation of inhibitors such as aromatic compounds and furan derivatives which greatly impacts the subsequent hydrolysis process which is considered as the major drawback of this process (Verardi et al., 2018); (Ballestero et al., 2006).

Ammonia Fiber Explosion

In the AFEX process, both the physical and the chemical methods are involved. In this the biomass is treated with the liquid ammonia at high pressure and temperature for a certain time period and the pressure is reduced suddenly (Lansing, 2005). Taherzadeh and Karimi (2008) explain that the AFEX process carried out at temperature 90°C- 120°C for a time period of 30 min. This method is suitable for the biomass with less lignin. The AFEX pretreatment cost includes the cost of ammonia and the ammonia recovery cost. Due to the volatile nature of the ammonia, it can be easily recovered and it must be recovered to manage the cost and to prevent the environmental hazard. The main advantage of this pretreatment is that only trace amount of inhibitor compounds are formed.

Liquid Hot Water

In this method, water is used at high temperature and pressure for disintegrating LC biomass. It is the hydrothermal process in which the water under high pressure penetrates the biomass and disrupts the layer of the lignin and degrades the hemicellulose. The major benefit of this process is the devoid of chemicals usage for treating the biomass in liquid hot water process (Taherzadeh and Karimi, 2008). The liquid hot water is a type of thermal pretreatment here in the place of the steam the liquid hot water is used. The main aim of this treatment is to degrade the hemicellulose and make the cellulose easily accessible for the AD process. The pH is maintained in the range of 4-7 to avoid the formation of the inhibitors (Hendriks and Zeeman, 2009).

CO_2 Explosion

CO_2 explosion system is used for disintegrating LC biomass similar to the steam explosion system and ammonia fiber explosion system. In this method, the CO_2 is injected with high pressure and it forms the carbonic acid and increases the hydrolysis rate. The outcome obtained from this pretreatment is found to be lower than the steam explosion or the ammonia explosion pretreatment (Sun and Cheng, 2002). The benefits of this pretreatment is that it can obtain acid catalyst by the action of the carbonic acid without the addition of the sulphuric acid. The pH of the carbonic acid is noted by determining the partial pressure of the CO_2 in water. The water dissolved carbon dioxide induces the dissolution of LC biomass and results in carbonic acid production. During carbonic acid production, an increment in hydronium ion content is noted owing to the solubilization of unstable acid. The dissolution of unstable acid causes a decrement in pH which is adequate to enhance solubilization and hemicellulose degradation into sugars. In addition, the acidic condition of the medium would not lead to ecological issue as the depressurization removes carbon dioxide leading to increment in pH of the medium. Under supercritical conditions, carbondioxide acts as a catalyst in the presence of liquid hot water leading to greater diffusion and biomass swelling.

The study of Zheng et al. (1998) explains about the pretreatment of recycled paper mix and the sugarcane bagasse with CO_2 explosion, ammonia explosion and steam explosion and it found out that CO_2 explosion is found to be more cost effective than the ammonia explosion and the CO_2 explosion does not produce any inhibitory compounds as formed by the steam explosion.

Supercritical Fluid

The supercritical fluid is an element which can be a liquid or a gas which is used in the condition above the critical pressure and the critical temperature where the supercritical fluid can coexist. Though it is a type of the liquid or the gas it has some unique properties like liquid density and the transport properties like the gas viscosity. This is the reason and the benefit of the supercritical fluid pretreatment. This fluid can easily penetrate into the LC biomass structure where other pretreatments fails in this case (Brodeur et al., 2011). Brand et al. investigated the conversion of red pinewood at temperatures ranging from 280 to 400°C, nitrogen pressures ranging from 0.4 to 7.5 MPa, residence times of up to 240 min, and ethanol as the solvent. The highest biofuel yield and biomass conversion rates were 59.9% and 98.1 percent, respectively (Brand et al., 2013).

Comparison of Various Pretreatment

In LC biomass-based bioenergy generation, pretreatment is still a challenging issue for achieving profitable and viable technology for conversion of LC biomass into soluble organics with less recalcitrant nature. It has been reported in literature, that the potential of pretreatment depends on the substrate and its characteristics. Determination of suitable pretreatment for LC biomass is a complicated problem. Irrespective of the pretreatment technique to be applied for LC biomass, reduction of particle size is the prime disintegration technique. Although, pretreatment of LC by mechanical means is essentially linked to enhanced biogas production, it has few limitations such as its incapability to delignify, an essential hindrance related to bioaccessibility of cellulose for anaerobic digestion. It has been reported in literature that LC biomass should be subjected to particle size reduction of 1–2 mm to avoid disadvantages happened at hydrolysis step (Neumann et al., 2016). On the other hand, reduction of particle size is a costly treatment as it requires nearly 33 percent of the total electrical energy needed for the entire treatment method. In the view of greater energy need of mechanical disintegration and increase of energy price, it is considered as an expensive process. So, minimizing the demand of energy and enhancing the efficacy of homogenization and milling of LC biomass can aid to increase the economy of the entire treatment method. In chemical pretreatment process, cost associated with chemicals and treatments, additional neutralization phase and the need of reactors with rust resistance were the recognized problems (Paudel et al., 2017). In addition, recalcitrant materials formation is regarded as an important step as in hinder or considerably minimize the process efficiency of LC biomass to biomethane. Therefore, obtaining greater conversion potential and minimizing the recalcitrant compound synthesis by coupling chemical pretreatment with other disintegration process could help in cost minimization.

Pretreatment of LC biomass with alkalis effectively liquefies the lignin and the existence of minor quantity of residual chemical in the pretreated biomass helps in pH neutralization at acidogenic step of anaerobic digestion. Thus, pretreatment of LC biomass with alkali is promisingly well suited with consequent anaerobic digestion than acid pretreatment (Taherdanak and Zilouei, 2014). Pretreatment of LC biomass with organic solvents is considered as a most promising disintegration process. The organic solvents let the removal of components of LC biomass such as lignin, cellulose and hemicellulose etc. This improves the capital cost thus making the process more beneficial on the basis of biorefinery approach. Pretreatment of LC biomass with ionic liquid have wide application, but, the extreme cost and the requirement of recycling is the major problem. Despite the benefits, pretreatments of biomass by biological means have several limitations which includes Definite conditions for growth (pH, temperature, etc), extended pretreatment period and carbohydrates exhaustion (Paudel et al., 2017). During this pretreatment, the formation of recalcitrant compounds is very less in comparison to chemical and physiochemical pretreatments.

According to the literatures reviewed, several physical, chemical, biological, thermal, and combination pretreatment approaches have recently been developed to address the issues of bio-digestion of lignocellulose feedstocks. The various process like the mechanical, steam explosion, ammonia fiber explosion, CO_2 explosion, ozonolysis, acid hydrolysis, alkaline hydrolysis, organosolv, pyrolysis, and biological methods are used for treating the LC biomass. Every process has their own benefits and drawbacks over the other (Kumar et al., 2009). Though mechanical pretreatment has reduced the cellulose crystallinity, it has a disadvantage of more significant power usage. In the case of the steam explosion, it is cost-effective and degrades the hemicellulose effectively it has the limitation of forming inhibitory products where ammonia fiber explosion does not produce any inhibitory products, but it is not suited for LC biomass with high lignin content (Haghighi et al., 2013).

The CO_2 explosion process is found to increase the surface area in a cost-efficient manner and does not form any inhibitory products, but it has a limitation that it does not modify the lignin or the hemicellulose structure. The ozonolysis process needs a large amount of ozone for the treatment process, but it reduces the biomass lignin content and does not create any toxic compound. Though the lignin and the hemicellulose are well hydrolyzed in the organosolv process, it is a high-cost treatment process (Arato et al., 2005). The biological pretreatment has a significant benefit of very low energy requirement, it also promotes lignin degradation, and it fails to support the hydrolysis process (Wagner et al., 2018). **Table 2** represents the effect of various pretreatments on the lignocellulosic biomass. However, due to their restricted bioavailability, the structure of lignocellulosic wastes still presents technological hurdles, and pretreatment of these resistant substrates is critical to improving the performance of anaerobic digesting technology. The downstream bioprocess of generating biogas or other value-added products is hindered by energy costs, operational costs, and the development of inhibitory chemicals. Though a combination of different pretreatments may offer a solution, it must be suited to the substrates and downstream bioprocesses in order to produce bioenergy and other products. It can be deduced that each of these pretreatment procedures has advantages and disadvantages, and that the goal of pretreatment can only be attained when the feedstock composition and pretreatment technique are properly matched. In addition, for the selected pretreatment method, several technological variables such as energy balancing, solvent recycling, and corrosion, as well as environmental factors, should be carefully examined.

TECHNO ECONOMIC FEASIBILITY OF PRETREATMENT PROCESS

Techno-economic analysis is regarded as the essential factor to evaluate the commercial feasibility of pretreatments and bioenergy generation form LC biomass (Carlsson et al., 2012; Kannah et al., 2021b). It has been estimated that LC biomass pretreatment cost embodies about 19–22% in a bioenergy recovery process (Baral and Shah, 2017). Various researchers have performed techno economic assessment of many pretreatments to explain the cost-effective conditions for energy efficient bioenergy recovery. Alkaline lignocellulosic biomass preparation results in an elevated sugar production, with low inhibitor development. Since there is no equipment cost found in this pretreatment, it is found to be successful at the pilot scale. The key benefit of the procedure is that lignin is removed, and hemicellulose improves the surface area and the disadvantage is the extended treatment time.

The steam explosion pretreatment has a high sugar yield and a high inhibitor formation. Though the equipment cost is high, it is found to be successful at pilot scale with the removal of the hemicellulose effectively and the lignin structure's alteration, but this pretreatment does not destruct the lignin matrix completely.

TABLE 2 | Effect of various pretreatments on the lignocellulosic biomass.

S.No	Type of lignocellulosic biomass	Pretreatment methods	Pretreatment condition	Lignin removal efficiency	Inhibitors formed	Methane production (%)	References
1	Rice straw	Fungal pretreatment	37 ± 1°C for 45 days	33.4	Yes	42.2	Mustafa et al. (2016)
2	Corn straw	Thermophilic pretreatment	55°C	-	No	-	Fu et al. (2015)
3	Potamogeton maackianus	Thermochemical pretreatment	0.20 g g-TSsubstrate^{-1}, 80°C, 3.0 h	59.7	No	50.6	Koyama et al. (2015)
4	Egeria densa	Thermochemical pretreatment	0.20 g g-TSsubstrate^{-1}, 80°C, 3.0 h	43.1	No	63.2	Koyama et al. (2015)
5	Wheat straw	Enzymatic pretreatment	Laccase, versatile peroxidase pretreatment	6	Yes	19.92	Schroyen et al. (2015)
6	Grass	Extrusion	-	-	No	47	Hjorth et al. (2011)

The ozonolysis pretreatment has a high sugar yield with low inhibitor capacity, and high byproduct generation. Since the ozonolysis pretreatment has high equipment cost, this pretreatment is not successful at the pilot scale. The drawback is that a great deal of ozone is required, but the lignin can be removed without inhibitors formation.

The organosolv pretreatment has a high sugar yield, low inhibitor production, and high byproduct generation. The chemicals used in the organosolv pretreatment can be reused. Though the equipment cost is high, it has the advantage of hydrolyzing the lignin and the hemicellulose, and it is found to be success at pilot scale (Anwar et al., 2014).

The mineral acid pretreatment has a high sugar yield, high inhibitor formation, and high byproduct generation. The mineral acid pretreatment effectively hydrolyzes the cellulose and hemicellulose and alters the lignin structure. The drawback of the mineral acid pretreatment is that it is hazardous, toxic and corrosive but it was quite successful at pilot scale.

The mechanical pretreatment has a low sugar yield, and there is no inhibitor formation or the byproduct generation. There is no need for chemicals for this pretreatment, and this type of pretreatment is applicable for all types of feedstock. The main benefit found in the mechanical pretreatment is it reduces the cellulose crystallinity with a drawback of high power consumption than inherent biomass energy. The equipment cost is high, but it was successful at the pilot-scale (Menon and Rao, 2012). Vasco-Correa and Shah. (2019)have done and evaluated the techno economic feasibility of large scale pretreatment of four LC biomass—perennial grasses, corn stover, agricultural residues and hardwood with fungal pretreatment. The authors reported that sugar recovery costs of these feedstocks were estimated to be 1.7, 1.6, 2.0, and 2.8 USD/kg, respectively. Baral and Shah. (2017) have reported the sugar production potential of corn stover, switch grass and poplar wood with chemical pretreatment (IL) to evaluate its feasibility at commercial scale. The sugar recovery cost for IL pretreatment of corn stover, switch grass and poplar wood were calculated to be 2.7, 3.2, and 3.0 USD/kg of biomass, respectively. Economic analysis of mechanical pretreatment of softwood biomass into fermentable sugars was studied by Brand et al. (2013) with the help of three phase milling. The cost of sugar production was calculated to be 0.496 USD/kg. On the otherhand, the environmental and profitability of the disintegration process was not studied. Safarian and Unnthorsson. (2018) suggested that steam explosion pretreatment is the proficient and profitable technique on the basis of energetic, economic and ecological point of view. Dilute acid pretreatment is the another effective pretreatment of LC biomass but it is not desirable owing to greater production cost and elevated green house gases release. It has been reported in literature that Soam et al. (2018) suggested that treatment of LC biomass with alkali at lower dose prior to biological pretreatment minimize the dosage of enzyme to 23–39% but the authors reported that they observed a negative ecological effect. Thus, it has been suggested that more investigations are required to choose suitable coupling of disintegration methods and operational circumstances required to be designed to minimize the ecological effects reduce environmental impacts and the costs associated with pretreatments. Thus, the costs incurred for the pretreatment methods were met by the production of excess amount of bioenergy which will in turn lead to net gain. However, the overall annual expenses include only the fixed capital investment and variable costs. The bioenergy productivity should be evaluated for all the pretreatments when the production process is dealing with a fixed amount of lignocellulosic feedstock to appropriately evaluate the process profitability.

CONCLUSION

LC biomass is considered as the potent and cost effective feedstock for bioenergy recovery. Owing to intrinsic complex biomass structure and recalcitrant nature of LC biomass cell wall, the biomass could not be effectively used for AD process. Usually, the surface area contact is the main parameter influencing the biomass hydrolysis due to the existence of chemical groups and it acts as a mesh like barrier. It acts as a barrier limiting the enzyme mediated hydrolysis by restricting substrate availability to enzymes. Besides, the structural based factors of cellulose such as (crystalline and polymeric nature of cellulose) imparts significant role in the inhibition of substrate biodegradation. Though much information is relevant with LC biomass cell wall and its recalcitrant nature, yet there exist some basic queries which require further studies particularly for biodegradation process. In the regard of recent information, various enhancement strategies are employed to improve bioenergy recovery from LC biomass. Thus, pretreatment is the essential technique to surpass this challenge and chosen of appropriate pretreatment is critical for bioenergy recovery at large scale. On the otherhand elevated energy and cost input are the main limitations in case of some pretreatments. Profitable methane generation from LC biomass relies on considerable enhancement in biomass recalcitrance reduction and bioconversion potential. Moreover, agriculture waste residues like fruits wastes (eg: banana), wheat straw etc., which are rich in lignocelluloses are not completely digested anaerobically even if pretreated. The residues can be used to recover cellulosic fibers when pretreated physically and biologically. These fibers can be then converted into Cellulose Nanofibrils which are of great economic value. In food industries, these nanocellulose materials are utilised to make bio-components, packaging materials, polymer matrix, and antimicrobial barrier or coatings. Cellulose nano fibrils are also used in pharmaceutical industries, textile industries and also in recent 3D-structural technologies. Therefore, further investigation must focus on studying the association of biomass recalcitrant nature and prime parameters influencing the AD process and this would be employed to discover novel approaches to increase methane generation.

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All authors listed have made a substantial, direct, and intellectual contribution to the work and approved it for publication.

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REFERENCES

Agrawal, R., Satlewal, A., Kapoor, M., Mondal, S., and Basu, B. (2017). Investigating the Enzyme-Lignin Binding with Surfactants for Improved Saccharification of Pilot Scale Pretreated Wheat Straw. *Bioresour. Techn.* 224, 411–418. doi:10.1016/j.biortech.2016.11.026

Amin, F. R., Khalid, H., Zhang, H., Rahman, S. u., Zhang, R., Liu, G., et al. (2017). Pretreatment Methods of Lignocellulosic Biomass for Anaerobic Digestion. *AMB Expr.* 7, 72. doi:10.1186/s13568-017-0375-4

Anwar, Z., Gulfraz, M., and Irshad, M. (2014). Agro-industrial Lignocellulosic Biomass a Key to Unlock the Future Bio-Energy: A Brief Review. *JRRAS* 7, 163–173. doi:10.1016/j.jrras.2014.02.003

Arantes, V., and Saddler, J. N. (2011). Cellulose Accessibility Limits the Effectiveness of Minimum Cellulase Loading on the Efficient Hydrolysis of Pretreated Lignocellulosic Substrates. *Biotechnol. Biofuels* 4, 3. doi:10.1186/1754-6834-4-3

Arato, C., Pye, E. K., and Gjennestad, G. (2005). The Lignol Approach to Biorefining of Woody Biomass to Produce Ethanol and Chemicals. *Appl. Biochem. Biotechnol.* 121-124, 871–882. doi:10.1385/abab:123:1-3:0871

Ballesteros, I., Negro, M. J., Oliva, J. M., Cabanas, A., Manzanares, P., and Ballesteros, M. (2006). Ethanol Production from Steam-Explosion Pretreated Wheat Straw. *Abab* 130, 496–508. doi:10.1385/abab:130:1:496

Ballesteros, I., Oliva, J. M., Negro, M. J., Manzanares, P., and Ballesteros, M. (2002). Enzymic Hydrolysis of Steam Exploded Herbaceous Agricultural Waste (Brassica Carinata) at Different Particule Sizes. *Process Biochem.* 38, 187–192. doi:10.1016/s0032-9592(02)00070-5

Banks, S. W., Nowakowski, D. J., and Bridgwater, A. V. (2014). Fast Pyrolysis Processing of Surfactant Washed Miscanthus. *Fuel Process. Techn.* 128, 94–103. doi:10.1016/j.fuproc.2014.07.005

Banu, J. R., Sugitha, S., Kannah, R. Y., Kavitha, S., and Yeom, I. T. (2018a). Marsilea spp.-A Novel Source of Lignocellulosic Biomass: Effect of Solubilized Lignin on Anaerobic Biodegradability and Cost of Energy Products. *Bioresour. Techn.* 255, 220–228. doi:10.1016/j.biortech.2018.01.103

Banu, J. R., Kannah, R. Y., Kavitha, S., Gunasekaran, M., Yeom, I. T., and Kumar, G. (2018b). Disperser-induced Bacterial Disintegration of Partially Digested Anaerobic Sludge for Efficient Biomethane Recovery. *Chem. Eng. J.* 347, 165–172. doi:10.1016/j.cej.2018.04.096

Banu, J. R., Kannah, R. Y., Kavitha, S., Gunasekaran, M., and Kumar, G. (2018c). Novel Insights into Scalability of Biosurfactant Combined Microwave Disintegration of Sludge at Alkali pH for Achieving Profitable Bioenergy Recovery and Net Profit. *Bioresour. Techn.* 267, 281–290. doi:10.1016/j.biortech.2018.07.046

Banu, J. R., Kavitha, S., Yukesh Kannah, R., Poornima Devi, T., Gunasekaran, M., Kim, S.-H., et al. (2019a). A Review on Biopolymer Production via Lignin Valorization. *Bioresour. Techn.* 290, 121790. doi:10.1016/j.biortech.2019.121790

Banu, J. R., Parvathy Eswari, A., Kavitha, S., Yukesh Kannah, R., Kumar, G., Jamal, M. T., et al. (2019b). Energetically Efficient Microwave Disintegration of Waste Activated Sludge for Biofuel Production by Zeolite: Quantification of Energy and Biodegradability Modelling. *Int. J. Hydrogen Energ.* 44, 2274–2288. doi:10.1016/j.ijhydene.2018.06.040

Banu, J. R., Yukesh Kannah, R., Kavitha, S., Ashikvivek, A., Bhosale, R. R., and Kumar, G. (2020a). Cost Effective Biomethanation via Surfactant Coupled Ultrasonic Liquefaction of Mixed Microalgal Biomass Harvested from Open Raceway Pond. *Bioresour. Techn.* 304, 123021. doi:10.1016/j.biortech.2020.123021

Banu, J. R., Kavitha, S., Kannah, R. Y., Usman, T. M. M., and Kumar, G. (2020b). Application of Chemo thermal Coupled Sonic Homogenization of marine Macroalgal Biomass for Energy Efficient Volatile Fatty Acid Recovery. *Bioresour. Techn.* 303, 122951. doi:10.1016/j.biortech.2020.122951

Baral, N. R., and Shah, A. (2017). Comparative Techno-Economic Analysis of Steam Explosion, Dilute Sulfuric Acid, Ammonia Fiber Explosion and Biological Pretreatments of Corn stover. *Bioresour. Techn.* 232, 331–343. doi:10.1016/j.biortech.2017.02.068

Bolado-Rodríguez, S., Toquero, C., Martín-Juárez, J., Travaini, R., and García-Encina, P. A. (2016). Effect of thermal, Acid, Alkaline and Alkaline-Peroxide Pretreatments on the Biochemical Methane Potential and Kinetics of the Anaerobic Digestion of Wheat Straw and Sugarcane Bagasse. *Bioresour. Techn.* 201, 182–190. doi:10.1016/j.biortech.2015.11.047

Brand, S., Susanti, R. F., Kim, S. K., Lee, H.-s., Kim, J., and Sang, B.-I. (2013). Supercritical Ethanol as an Enhanced Medium for Lignocellulosic Biomass

Liquefaction: Influence of Physical Process Parameters. *Energy* 59, 173–182. doi:10.1016/j.energy.2013.06.049

Brodeur, G., Yau, E., Badal, K., Collier, J., Ramachandran, K. B., and Ramakrishnan, S. (2011). Chemical and Physicochemical Pretreatment of Lignocellulosic Biomass: A Review. *Enzyme Res.* 2011, 787532. doi:10.4061/2011/787532

Capareda, S. (2013). *Introduction to Biomass Energy Conversions*. United States: CRC Press.

Carlsson, M., Lagerkvist, A., and Morgan-Sagastume, F. (2012). The Effects of Substrate Pre-treatment on Anaerobic Digestion Systems: A Review. *Waste Manage.* 32, 1634–1650. doi:10.1016/j.wasman.2012.04.016

Carrère, H., Dumas, C., Battimelli, A., Batstone, D. J., Delgenès, J. P., Steyer, J. P., et al. (2010). Pretreatment Methods to Improve Sludge Anaerobic Degradability: A Review. *J. Hazard. Mater.* 183, 1–15. doi:10.1016/j.jhazmat.2010.06.129

Chang, V. S., and Holtzapple, M. T. (2000). Fundamental Factors Affecting Biomass Enzymatic Reactivity. *Appl. Biochem. Biotechnol.* 84, 5–37. doi:10.1007/978-1-4612-1392-5_1

Chaturvedi, V., and Verma, P. (2013). An Overview of Key Pretreatment Processes Employed for Bioconversion of Lignocellulosic Biomass into Biofuels and Value Added Products. *3 Biotech.* 3, 415–431. doi:10.1007/s13205-013-0167-8

Cheng, Y.-S., Zheng, Y., Yu, C. W., Dooley, T. M., Jenkins, B. M., and Vandergheynst, J. S. (2010). Evaluation of High Solids Alkaline Pretreatment of rice Straw. *Appl. Biochem. Biotechnol.* 162, 1768–1784. doi:10.1007/s12010-010-8958-4

Dahlquist, E. (2013). *Technologies for Converting Biomass to Useful Energy: Combustion, Gasification, Pyrolysis, Torrefaction and Fermentation*. United States: CRC Press.

Devrije, T., De Haas, G., Tan, G. B., Keijsers, E. R. P., and Claassen, P. A. M. (2002). Pretreatment of Miscanthus for Hydrogen Production by Thermotoga Elfii. *Int. J. Hydrogen Energ.* 27, 1381–1390. doi:10.1016/s0360-3199(02)00124-6

Dewil, R., Baeyens, J., and Goutvrind, R. (2006). Ultrasonic Treatment of Waste Activated Sludge. *Environ. Prog.* 25, 121–128. doi:10.1002/ep.10130

Doğan, I., and Sanin, F. D. (2009). Alkaline Solubilization and Microwave Irradiation as a Combined Sludge Disintegration and Minimization Method. *Water Res.* 43, 2139–2148. doi:10.1016/j.watres.2009.02.023

Du, X., Pérez-Boada, M., Fernández, C., Rencoret, J., del Río, J. C., and Jiménez-Barbero, J. (2014). Analysis of Lignin Carbohydrate and Lignin Lignin Linkages after Hydrolase Treatment of Xylan Lignin, Glucomannan Lignin and Glucan Lignin Complexes from spruce wood. *Planta* 239, 1079–1090. doi:10.1007/s00425-014-2037-y

Duff, S. J. B., and Murray, W. D. (1996). Bioconversion of forest Products Industry Waste Cellulosics to Fuel Ethanol: A Review. *Bioresour. Techn.* 55, 1–33. doi:10.1016/0960-8524(95)00122-0

Dupont, C., Chiriac, R., Gauthier, G., and Toche, F. (2014). Heat Capacity Measurements of Various Biomass Types and Pyrolysis Residues. *Fuel* 115, 644–651. doi:10.1016/j.fuel.2013.07.086

Eskicioglu, C., Terzian, N., Kennedy, K., Droste, R., and Hamoda, M. (2007). Athermal Microwave Effects for Enhancing Digestibility of Waste Activated Sludge. *Water Res.* 41, 2457–2466. doi:10.1016/j.watres.2007.03.008

Fort, D. A., Remsing, R. C., Swatloski, R. P., Moyna, P., Moyna, G., and Rogers, R. D. (2007). Can Ionic Liquids Dissolve wood? Processing and Analysis of Lignocellulosic Materials with 1-N-Butyl-3-Methylimidazolium Chloride. *Green. Chem.* 9, 63–69. doi:10.1039/b607614a

Fu, S.-F., Wang, F., Yuan, X.-Z., Yang, Z.-M., Luo, S.-J., Wang, C.-S., et al. (2015). The Thermophilic (55°C) Microaerobic Pretreatment of Corn Straw for Anaerobic Digestion. *Bioresour. Techn.* 175, 203–208. doi:10.1016/j.biortech.2014.10.072

Giummarella, N., Pu, Y., Ragauskas, A. J., and Lawoko, M. (2019). A Critical Review on the Analysis of Lignin Carbohydrate Bonds. *Green. Chem.* 21, 1573–1595. doi:10.1039/c8gc03606c

Goshadrou, A., Karimi, K., and Lefsrud, M. (2013). Characterization of Ionic Liquid Pretreated aspen wood Using Semi-quantitative Methods for Ethanol Production. *Carbohydr. Polym.* 96, 440–449. doi:10.1016/j.carbpol.2013.04.017

Grosser, A. (2017). The Influence of Decreased Hydraulic Retention Time on the Performance and Stability of Co-digestion of Sewage Sludge with Grease Trap Sludge and Organic Fraction of Municipal Waste. *J. Environ. Manage.* 203, 1143–1157. doi:10.1016/j.jenvman.2017.04.085

Haghighi Mood, S., Hossein Golfeshan, A., Tabatabaei, M., Salehi Jouzani, G., Najafi, G. H., Gholami, M., et al. (2013). Lignocellulosic Biomass to Bioethanol, a Comprehensive Review with a Focus on Pretreatment. *Renew. Sustain. Energ. Rev.* 27, 77–93. doi:10.1016/j.rser.2013.06.033

Hendriks, A. T. W. M., and Zeeman, G. (2009). Pretreatments to Enhance the Digestibility of Lignocellulosic Biomass. *Bioresour. Techn.* 100, 10–18. doi:10.1016/j.biortech.2008.05.027

Herbaut, M., Zoghlami, A., Habrant, A., Falourd, X., Foucat, L., Chabbert, B., et al. (2018). Multimodal Analysis of Pretreated Biomass Species Highlights Generic Markers of Lignocellulose Recalcitrance. *Biotechnol. Biofuels* 11, 52. doi:10.1186/s13068-018-1053-8

Hjorth, M., Gränitz, K., Adamsen, A. P. S., and Møller, H. B. (2011). Extrusion as a Pretreatment to Increase Biogas Production. *Bioresour. Techn.* 102, 4989–4994. doi:10.1016/j.biortech.2010.11.128

Huang, Y., Wei, X., Zhou, S., Liu, M., Tu, Y., Li, A., et al. (2015). Steam Explosion Distinctively Enhances Biomass Enzymatic Saccharification of Cotton Stalks by Largely Reducing Cellulose Polymerization Degree in G. barbadense and G. Hirsutum. *Bioresour. Techn.* 181, 224–230. doi:10.1016/j.biortech.2015.01.020

Ibrahim, M. M., El-Zawawy, W. K., Abdel-Fattah, Y. R., Soliman, N. A., and Agblevor, F. A. (2011). Comparison of Alkaline Pulping with Steam Explosion for Glucose Production from rice Straw. *Carbohydr. Polym.* 83, 720–726. doi:10.1016/j.carbpol.2010.08.046

Jard, G., Dumas, C., Delgenes, J. P., Marfaing, H., Sialve, B., Steyer, J. P., et al. (2013). Effect of Thermochemical Pretreatment on the Solubilization and Anaerobic Biodegradability of the Red Macroalga Palmaria Palmata. *Biochem. Eng. J.* 79, 253–258. doi:10.1016/j.bej.2013.08.011

Jiang, J., Wang, J., Zhang, X., and Wolcott, M. (2017). Assessing Multi-Scale Deconstruction of wood Cell wall Subjected to Mechanical Milling for Enhancing Enzymatic Hydrolysis. *Ind. Crops Prod.* 109, 498–508. doi:10.1016/j.indcrop.2017.09.009

Kannah, R. Y., Kavitha, S., Rajesh Banu, J., Yeom, I. T., and Johnson, M. (2017a). Synergetic Effect of Combined Pretreatment for Energy Efficient Biogas Generation. *Bioresour. Techn.* 232, 235–246. doi:10.1016/j.biortech.2017.02.042

Kannah, R. Y., Kavitha, S., Rajesh Banu, J., Parthiba Karthikeyan, O., and Sivashanmugham, P. (2017b). Dispersion Induced Ozone Pretreatment of Waste Activated Biosolids: Arriving Biomethanation Modelling Parameters, Energetic and Cost Assessment. *Bioresour. Techn.* 244, 679–687. doi:10.1016/j.biortech.2017.08.001

Kannah, R. Y., Kavitha, S., Sivashanmugham, P., Kumar, G., Nguyen, D. D., Chang, S. W., et al. (2019). Biohydrogen Production from rice Straw: Effect of Combinative Pretreatment, Modelling Assessment and Energy Balance Consideration. *Int. J. Hydrogen Energ.* 44, 2203–2215. doi:10.1016/j.ijhydene.2018.07.201

Kannah, R. Y., Kavitha, S., Gunasekaran, M., Kumar, G., Banu, J. R., and Zhen, G. (2020). Biohydrogen Production from Seagrass via Novel Energetically Efficient Ozone Coupled Rotor Stator Homogenization. *Int. J. Hydrogen Energ.* 45, 5881–5889. doi:10.1016/j.ijhydene.2019.04.151

Kannah R., Y., S., K., P., S., Kumar, G., and Banu J., R. (2021a). Ultrasonic Induced Mechanoacoustic Effect on Delignification of rice Straw for Cost Effective Biopretreatment and Biomethane Recovery. *Sustain. Energ. Fuels* 5, 1832–1844. doi:10.1039/d0se01814g

Kannah, R. Y., Kavitha, S., Preethi, Karthikeyan, O. P., Dai-Viet, N. V., Kumar, G., et al. (2021b). Techno-economic Assessment of Various Hydrogen Production Methods - A Review. *Bioresour. Techn.* 319, 124175. doi:10.1016/j.biortech.2020.124175

Kavitha, S., Adish Kumar, S., Yogalakshmi, K. N., Kaliappan, S., and Rajesh Banu, J. (2013). Effect of Enzyme Secreting Bacterial Pretreatment on Enhancement of Aerobic Digestion Potential of Waste Activated Sludge Interceded through EDTA. *Bioresour. Techn.* 150, 210–219. doi:10.1016/j.biortech.2013.10.021

Kavitha, S., Jayashree, C., Adish Kumar, S., Yeom, I. T., and Rajesh Banu, J. (2014a). The Enhancement of Anaerobic Biodegradability of Waste Activated Sludge by Surfactant Mediated Biological Pretreatment. *Bioresour. Techn.* 168, 159–166. doi:10.1016/j.biortech.2014.01.118

Kavitha, S., Jayashree, C., Adish Kumar, S., Kaliappan, S., and Rajesh Banu, J. (2014b). Enhancing the Functional and Economical Efficiency of a Novel Combined Thermo Chemical Disperser Disintegration of Waste Activated

Sludge for Biogas Production. *Bioresour. Techn.* 173, 32–41. doi:10.1016/j.biortech.2014.09.078

Kavitha, S., Yukesh Kannah, R., Yeom, I. T., Do, K.-U., and Banu, J. R. (2015). Combined Thermo-Chemo-Sonic Disintegration of Waste Activated Sludge for Biogas Production. *Bioresour. Techn.* 197, 383–392. doi:10.1016/j.biortech.2015.08.131

Kavitha, S., Yukesh Kannah, R., Rajesh Banu, J., Kaliappan, S., and Johnson, M. (2017a). Biological Disintegration of Microalgae for Biomethane Recovery-Prediction of Biodegradability and Computation of Energy Balance. *Bioresour. Techn.* 244, 1367–1375. doi:10.1016/j.biortech.2017.05.007

Kavitha, S., Banu, J. R., Priya, A. A., Uan, D. K., and Yeom, I. T. (2017b). Liquefaction of Food Waste and its Impacts on Anaerobic Biodegradability, Energy Ratio and Economic Feasibility. *Appl. Energ.* 208, 228–238. doi:10.1016/j.apenergy.2017.10.049

Kavitha, S., Rajesh Banu, J., Kumar, G., Kaliappan, S., and Yeom, I. T. (2018). Profitable Ultrasonic Assisted Microwave Disintegration of Sludge Biomass: Modelling of Biomethanation and Energy Parameter Analysis. *Bioresour. Techn.* 254, 203–213. doi:10.1016/j.biortech.2018.01.072

Kavitha, S., Schikaran, M., Yukesh Kannah, R., Gunasekaran, M., Kumar, G., and Rajesh Banu, J. (2019). Nanoparticle Induced Biological Disintegration: A New Phase Separated Pretreatment Strategy on Microalgal Biomass for Profitable Biomethane Recovery. *Bioresour. Techn.* 289, 121624. doi:10.1016/j.biortech.2019.121624

Kavitha, S., Yukesh Kannah, R., Kasthuri, S., Gunasekaran, M., Pugazhendi, A., Rene, E. R., et al. (2020a). Profitable Biomethane Production from Delignified rice Straw Biomass: the Effect of Lignin, Energy and Economic Analysis. *Green. Chem.* 22, 8024–8035. doi:10.1039/d0gc02738c

Kavitha, S., Kannah, R. Y., Gunasekaran, M., Banu, J. R., and Kumar, G. (2020b). Rhamnolipid Induced Deagglomeration of Anaerobic Granular Biosolids for Energetically Feasible Ultrasonic Homogenization and Profitable Biohydrogen. *Int. J. Hydrogen Energ.* 45, 5890–5899. doi:10.1016/j.ijhydene.2019.04.063

Kim, M., and Day, D. F. (2011). Composition of Sugar Cane, Energy Cane, and Sweet Sorghum Suitable for Ethanol Production at Louisiana Sugar Mills. *J. Ind. Microbiol. Biotechnol.* 38, 803–807. doi:10.1007/s10295-010-0812-8

Kim, J., Park, C., Kim, T.-H., Lee, M., Kim, S., Kim, S.-W., et al. (2003). Effects of Various Pretreatments for Enhanced Anaerobic Digestion with Waste Activated Sludge. *J. Biosci. Bioeng.* 95, 271–275. doi:10.1016/s1389-1723(03)80028-2

Kim, S., Um, B., Im, D., Lee, J., and Oh, K. (2018). Combined Ball Milling and Ethanol Organosolv Pretreatment to Improve the Enzymatic Digestibility of Three Types of Herbaceous Biomass. *Energies* 11, 2457. doi:10.3390/en11092457

Koyama, M., Yamamoto, S., Ishikawa, K., Ban, S., and Toda, T. (2015). Enhancing Anaerobic Digestibility of Lignin-Rich Submerged Macrophyte Using Thermochemical Pre-treatment. *Biochem. Eng. J.* 99, 124–130. doi:10.1016/j.bej.2015.03.013

Kruyeniski, J., Ferreira, P. J. T., Videira Sousa Carvalho, M. d. G., Vallejos, M. E., Felissia, F. E., and Area, M. C. (2019). Physical and Chemical Characteristics of Pretreated Slash pine Sawdust Influence its Enzymatic Hydrolysis. *Ind. Crops Prod.* 130, 528–536. doi:10.1016/j.indcrop.2018.12.075

Kudanga, T., and Le Roes-Hill, M. (2014). Laccase Applications in Biofuels Production: Current Status and Future Prospects. *Appl. Microbiol. Biotechnol.* 98, 6525–6542. doi:10.1007/s00253-014-5810-8

Kumar, P., Barrett, D. M., Delwiche, M. J., and Stroeve, P. (2009). Methods for Pretreatment of Lignocellulosic Biomass for Efficient Hydrolysis and Biofuel Production. *Ind. Eng. Chem. Res.* 48, 3713–3729. doi:10.1021/ie801542g

Kumar, M. D., Tamilarasan, K., Kaliappan, S., Banu, J. R., Rajkumar, M., and Kim, S. H. (2018). Surfactant Assisted Disperser Pretreatment on the Liquefaction of Ulva Reticulata and Evaluation of Biodegradability for Energy Efficient Biofuel Production through Nonlinear Regression Modelling. *Bioresour. Techn.* 255, 116–122. doi:10.1016/j.biortech.2018.01.116

Lansing, E. (2005). Pretreatment of Switchgrass by Ammonia Fiber Explosion (AFEX). *Appl. Biochem. Biotechnol.* 124, 1133–1141. doi:10.1385/abab:124:1-3:1133

Ling, Z., Chen, S., Zhang, X., and Xu, F. (2017). Exploring Crystalline-Structural Variations of Cellulose during Alkaline Pretreatment for Enhanced Enzymatic Hydrolysis. *Bioresour. Techn.* 224, 611–617. doi:10.1016/j.biortech.2016.10.064

Liu, W., Ma, H., Cao, C., Yang, Z., Zhao, M., and Kong, X. (2012). Effects of Pretreatments with Steam-Explosion Using Solar Energy and Microwave Irradiation on Biogas Production of Corn Stalk. *Nongye Gongcheng Xuebao/Transactions Chin. Soc. Agric. Eng.* 28, 227–234.

Liu, Z.-H., Qin, L., Li, B.-Z., and Yuan, Y.-J. (2015). Physical and Chemical Characterizations of Corn Stover from Leading Pretreatment Methods and Effects on Enzymatic Hydrolysis. *ACS Sustain. Chem. Eng.* 3, 140–146. doi:10.1021/sc500637c

López Torres, M., and Espinosa Lloréndsdel, M. d. C. C. (2008). Effect of Alkaline Pretreatment on Anaerobic Digestion of Solid Wastes. *Waste Manage.* 28, 2229–2234. doi:10.1016/j.wasman.2007.10.006

Lu, M., Li, J., Han, L., and Xiao, W. (2019). An Aggregated Understanding of Cellulase Adsorption and Hydrolysis for ball-milled Cellulose. *Bioresour. Techn.* 273, 1–7. doi:10.1016/j.biortech.2018.10.037

Ma, Y., Yin, Y., and Liu, Y. (2017). A Holistic Approach for Food Waste Management towards Zero-Solid Disposal and Energy/resource Recovery. *Bioresour. Techn.* 228, 56–61. doi:10.1016/j.biortech.2016.12.090

Malherbe, S., and Cloete, T. E. (2002). Lignocellulose Biodegradation: Fundamentals and Applications. *Rev. Environ. Sci. Biotechnol.* 1, 105–114. doi:10.1023/a:1020858910646

Martín, C., Klinke, H. B., and Thomsen, A. B. (2007). Wet Oxidation as a Pretreatment Method for Enhancing the Enzymatic Convertibility of Sugarcane Bagasse. *Enzyme Microb. Techn.* 40 (3), 426–432. doi:10.1016/j.enzmictec.2006.07.015

Mason, P. E., Darvell, L. I., Jones, J. M., and Williams, A. (2016). Comparative Study of the Thermal Conductivity of Solid Biomass Fuels. *Energy Fuels* 30, 2158–2163. doi:10.1021/acs.energyfuels.5b02261

Meng, X., Foston, M., Leisen, J., DeMartini, J., Wyman, C. E., and Ragauskas, A. J. (2013). Determination of Porosity of Lignocellulosic Biomass before and after Pretreatment by Using Simons' Stain and NMR Techniques. *Bioresour. Techn.* 144, 467–476. doi:10.1016/j.biortech.2013.06.091

Menon, V., and Rao, M. (2012). Trends in Bioconversion of Lignocellulose: Biofuels, Platform Chemicals & Biorefinery Concept. *Prog. Energ. Combustion Sci.* 38, 522–550. doi:10.1016/j.pecs.2012.02.002

Mirahmadi, K., Kabir, M. M., Jeihanipour, A., Karimi, K., and Taherzadeh, M. (2010). Alkaline Pretreatment of spruce and Birch to Improve Bioethanol and Biogas Production. *BioResources* 5, 928–938.

Monlau, F., Latrille, E., Da Costa, A. C., Steyer, J.-P., and Carrère, H. (2013). Enhancement of Methane Production from sunflower Oil Cakes by Dilute Acid Pretreatment. *Appl. Energ.* 102, 1105–1113. doi:10.1016/j.apenergy.2012.06.042

Mustafa, A. M., Poulsen, T. G., and Sheng, K. (2016). Fungal Pretreatment of rice Straw with Pleurotus Ostreatus and Trichoderma Reesei to Enhance Methane Production under Solid-State Anaerobic Digestion. *Appl. Energ.* 180, 661–671. doi:10.1016/j.apenergy.2016.07.135

Neumann, P., Pesante, S., Venegas, M., and Vidal, G. (2016). Developments in Pre-treatment Methods to Improve Anaerobic Digestion of Sewage Sludge. *Rev. Environ. Sci. Biotechnol.* 15, 173–211. doi:10.1007/s11157-016-9396-8

Novarino, D., and Zanetti, M. C. (2012). Anaerobic Digestion of Extruded OFMSW. *Bioresour. Techn.* 104, 44–50. doi:10.1016/j.biortech.2011.10.001

Octavia, S., Purwadi, R., Arsa, I. D. G., and Soerawidjaja, T. H. (2017). Soerawidjaja: Determining the Enzyme Accessibility of Ammonia Pretreated Lignocellulosic Substrates by Simon's Stain Method. *J. Eng. Appl. Sci.* 12, 5307–5312.

Okino, S., Ikeo, M., Ueno, Y., and Taneda, D. (2013). Effects of Tween 80 on Cellulase Stability under Agitated Conditions. *Bioresour. Techn.* 142, 535–539. doi:10.1016/j.biortech.2013.05.078

Pang, J., Zheng, M., Li, X., Sebastian, J., Jiang, Y., Zhao, Y., et al. (2019). Unlock the Compact Structure of Lignocellulosic Biomass by Mild Ball Milling for Ethylene Glycol Production. *ACS Sustain. Chem. Eng.* 7, 679–687. doi:10.1021/acssuschemeng.8b04262

Park, J.-y., Shiroma, R., Al-Haq, M. I., Zhang, Y., Ike, M., Arai-Sanoh, Y., et al. (2010). A Novel Lime Pretreatment for Subsequent Bioethanol Production from rice Straw - Calcium Capturing by Carbonation (CaCCO) Process. *Bioresour. Techn.* 101, 6805–6811. doi:10.1016/j.biortech.2010.03.098

Passos, F., Hernández-Mariné, M., García, J., and Ferrer, I. (2014). Long-term Anaerobic Digestion of Microalgae Grown in HRAP for Wastewater Treatment. Effect of Microwave Pretreatment. *Water Res.* 49, 351–359. doi:10.1016/j.watres.2013.10.013

Patel, V., Desai, M., and Madamwar, D. (1993). Thermochemical Pretreatment of Water Hyacinth for Improved Biomethanation. *Appl. Biochem. Biotechnol.* 42, 67–74. doi:10.1007/bf02788902

Patinvoh, R. J., Osadolor, O. A., Chandolias, K., Sárvári Horváth, I., and Taherzadeh, M. J. (2017). Innovative Pretreatment Strategies for Biogas Production. *Bioresour. Techn.* 224, 13–24. doi:10.1016/j.biortech.2016.11.083

Paudel, S. R., Banjara, S. P., Choi, O. K., Park, K. Y., Kim, Y. M., and Lee, J. W. (2017). Pretreatment of Agricultural Biomass for Anaerobic Digestion: Current State and Challenges. *Bioresour. Techn.* 245, 1194–1205. doi:10.1016/j.biortech.2017.08.182

Peciulyte, A., Karlström, K., Larsson, P. T., and Olsson, L. (2015). Impact of the Supramolecular Structure of Cellulose on the Efficiency of Enzymatic Hydrolysis. *Biotechnol. Biofuels* 8, 56. doi:10.1186/s13068-015-0236-9

Pedersen, M., and Meyer, A. S. (2009). Influence of Substrate Particle Size and Wet Oxidation on Physical Surface Structures and Enzymatic Hydrolysis of Wheat Straw. *Biotechnol. Prog.* 25, 399–408. doi:10.1002/btpr.141

Piven, I., Friedrich, A., Dühring, U., Uliczka, F., Baier, K., and Inaba, M. (2012). Cyanobacterium Sp. For Production of Compounds. Google Patents. US20140178958A1

Prasad, S., Singh, A., and Joshi, H. C. (2007). Ethanol as an Alternative Fuel from Agricultural, Industrial and Urban Residues. *Resour. Conservation Recycling* 50, 1–39. doi:10.1016/j.resconrec.2006.05.007

Rezania, S., Din, M. F. M., Taib, S. M., Sohaili, J., Chelliapan, S., Kamyab, H., et al. (2017). Review on Fermentative Biohydrogen Production from Water Hyacinth, Wheat Straw and rice Straw with Focus on Recent Perspectives. *Int. J. Hydrogen Energ.* 42, 20955–20969. doi:10.1016/j.ijhydene.2017.07.007

Rincón, B., Rodríguez-Gutiérrez, G., Bujalance, L., Fernández-Bolaños, J., and Borja, R. (2016). Influence of a Steam-Explosion Pre-treatment on the Methane Yield and Kinetics of Anaerobic Digestion of Two-phase Olive Mil Solid Waste or Alperujo. *Process Saf. Environ. Prot.* 102, 361–369. doi:10.1016/j.psep.2016.04.010

Safarian, S., and Unnthorsson, R. (2018). An Assessment of the Sustainability of Lignocellulosic Bioethanol Production from Wastes in Iceland. *Energies* 11, 1493. doi:10.3390/en11061493

Saha, B. C., and Cotta, M. A. (2010). Comparison of Pretreatment Strategies for Enzymatic Saccharification and Fermentation of Barley Straw to Ethanol. *New Biotechnol.* 27, 10–16. doi:10.1016/j.nbt.2009.10.005

Santos, V. T. d. O., Siqueira, G., Milagres, A. M. F., and Ferraz, A. (2018). Role of Hemicellulose Removal during Dilute Acid Pretreatment on the Cellulose Accessibility and Enzymatic Hydrolysis of Compositionally Diverse Sugarcane Hybrids. *Ind. Crops Prod.* 111, 722–730. doi:10.1016/j.indcrop.2017.11.053

Sawatdeenarunat, C., Nguyen, D., Surendra, K. C., Shrestha, S., Rajendran, K., Oechsner, H., et al. (2016). Anaerobic Biorefinery: Current Status, Challenges, and Opportunities. *Bioresour. Techn.* 215, 304–313. doi:10.1016/j.biortech.2016.03.074

Scaramuzzino, C., Garegnani, G., and Zambelli, P. (2019). Integrated Approach for the Identification of Spatial Patterns Related to Renewable Energy Potential in European Territories. *Renew. Sustain. Energ. Rev.* 101, 1–13. doi:10.1016/j.rser.2018.10.024

Schroyen, M., Vervaeren, H., Vandepitte, H., Van Hulle, S. W. H., and Raes, K. (2015). Effect of Enzymatic Pretreatment of Various Lignocellulosic Substrates on Production of Phenolic Compounds and Biomethane Potential. *Bioresour. Techn.* 192, 696–702. doi:10.1016/j.biortech.2015.06.051

Sharma, S. K., Mishra, I. M., Sharma, M. P., and Saini, J. S. (1988). Effect of Particle Size on Biogas Generation from Biomass Residues. *Biomass* 17, 251–263. doi:10.1016/0144-4565(88)90107-2

Silva, G. G. D., Couturier, M., Berrin, J.-G., Buléon, A., and Rouau, X. (2012). Effects of Grinding Processes on Enzymatic Degradation of Wheat Straw. *Bioresour. Techn.* 103, 192–200. doi:10.1016/j.biortech.2011.09.073

Singh, R., Shukla, A., Tiwari, S., and Srivastava, M. (2014). A Review on Delignification of Lignocellulosic Biomass for Enhancement of Ethanol Production Potential. *Renew. Sustain. Energ. Rev.* 32, 713–728. doi:10.1016/j.rser.2014.01.051

Soam, S., Kapoor, M., Kumar, R., Gupta, R. P., Puri, S. K., and Ramakumar, S. S. V. (2018). Life Cycle Assessment and Life Cycle Costing of Conventional and Modified Dilute Acid Pretreatment for Fuel Ethanol Production from rice Straw in India. *J. Clean. Prod.* 197, 732–741. doi:10.1016/j.jclepro.2018.06.204

Somerville, C., Bauer, S., Brininstool, G., Facette, M., Hamann, T., and Milne, J. (2004). Toward a Systems Approach to Understanding Plant Cell walls. *Science* 306, 2206–2211. doi:10.1126/science.1102765

Stoffel, R. B., Felissia, F. E., Silva Curvelo, A. A., Gassa, L. M., and Area, M. C. (2014). Optimization of Sequential Alkaline-Acid Fractionation of pine Sawdust for a Biorefinery. *Ind. Crops Prod.* 61, 160–168. doi:10.1016/j.indcrop.2014.06.047

Sun, Y., and Cheng, J. (2002). Hydrolysis of Lignocellulosic Materials for Ethanol Production: A Review. *Bioresour. Techn.* 83, 1–11. doi:10.1016/s0960-8524(01)00212-7

Taherdanak, M., and Zilouei, H. (2014). Improving Biogas Production from Wheat Plant Using Alkaline Pretreatment. *Fuel* 115, 714–719. doi:10.1016/j.fuel.2013.07.094

Taherzadeh, M. J., and Karimi, K. (2008). Pretreatment of Lignocellulosic Wastes to Improve Ethanol and Biogas Production: A Review. *Int. J. Mol. Sci.* 9, 1621. doi:10.3390/ijms9091621

Tamilarasan, K., Kavitha, S., Rajesh Banu, J., Arulazhagan, P., and Yeom, I. T. (2017). Energy-efficient Methane Production from Macroalgal Biomass through Chemo Disperser Liquefaction. *Bioresour. Techn.* 228, 156–163. doi:10.1016/j.biortech.2016.12.102

Thelin, M. H. (1950). De la narcose?? *L'aveu. Schweiz. Med. Wochenschr.* 80, 921. doi:10.1001/archpedi.1950.04040021069025

Torr, K. M., Love, K. T., Simmons, B. A., and Hill, S. J. (2016). Structural Features Affecting the Enzymatic Digestibility of pine wood Pretreated with Ionic Liquids. *Biotechnol. Bioeng.* 113, 540–549. doi:10.1002/bit.25831

Vaidya, A. A., Donaldson, L. A., Newman, R. H., Suckling, I. D., Campion, S. H., Lloyd, J. A., et al. (2016). Micromorphological Changes and Mechanism Associated with Wet ball Milling of Pinus Radiata Substrate and Consequences for Saccharification at Low Enzyme Loading. *Bioresour. Techn.* 214, 132–137. doi:10.1016/j.biortech.2016.04.084

Vasco-Correa, J., and Shah, A. (2019). Techno-economic Bottlenecks of the Fungal Pretreatment of Lignocellulosic Biomass. *Fermentation* 5, 30. doi:10.3390/fermentation5020030

Verardi, A., Blasi, A., Marino, T., Molino, A., and Calabrò, V. (2018). Effect of Steam-Pretreatment Combined with Hydrogen Peroxide on Lignocellulosic Agricultural Wastes for Bioethanol Production: Analysis of Derived Sugars and Other By-Products. *J. Energ. Chem.* 27, 535–543. doi:10.1016/j.jechem.2017.11.007

Vidal, B. C., Dien, B. S., Ting, K. C., and Singh, V. (2011). Influence of Feedstock Particle Size on Lignocellulose Conversion-A Review. *Appl. Biochem. Biotechnol.* 164, 1405–1421. doi:10.1007/s12010-011-9221-3

Viola, E., Cardinale, M., Santarcangelo, R., Villone, A., and Zimbardi, F. (2008). Ethanol from Eel Grass via Steam Explosion and Enzymatic Hydrolysis. *Biomass Bioenergy* 32, 613–618. doi:10.1016/j.biombioe.2007.12.009

Vivekanand, V., Olsen, E. F., Eijsink, V. G. H., and Horn, S. J. (2014). Methane Potential and Enzymatic Saccharification of Steam-Exploded Bagasse. *BioResources* 9, 1311–1324. doi:10.15376/biores.9.1.1311-1324

Wagner, A. O., Lackner, N., Mutschlechner, M., Prem, E. M., Markt, R., and Illmer, P. (2018). Biological Pretreatment Strategies for Second-Generation Lignocellulosic Resources to Enhance Biogas Production. *Energies (Basel)* 11, 1797. doi:10.3390/en11071797

Wahid, R., Nielsen, S. F., Hernandez, V. M., Ward, A. J., Gislum, R., Jørgensen, U., et al. (2015). Methane Production Potential from Miscanthus sp.: Effect of Harvesting Time, Genotypes and Plant Fractions. *Biosyst. Eng.* 133, 71–80. doi:10.1016/j.biosystemseng.2015.03.005

Wang, Q., Kuninobu, M., Kakimoto, K., I.-Ogawa, H., and Kato, Y. (1999). Upgrading of Anaerobic Digestion of Waste Activated Sludge by Ultrasonic Pretreatment. *Bioresour. Techn.* 68, 309–313. doi:10.1016/s0960-8524(98)00155-2

Williams, O., Eastwick, C., Kingman, S., Giddings, D., Lormor, S., and Lester, E. (2015). Investigation into the Applicability of Bond Work Index (BWI) and Hardgrove Grindability Index (HGI) Tests for Several Biomasses Compared to Colombian La Loma Coal. *Fuel* 158, 379–387. doi:10.1016/j.fuel.2015.05.027

Xu, N., Liu, S., Xin, F., Zhou, J., Jia, H., Xu, J., et al. (2019). Biomethane Production from Lignocellulose: Biomass Recalcitrance and its Impacts on

Anaerobic Digestion. *Front. Bioeng. Biotechnol.* 7, 191–212. doi:10.3389/fbioe.2019.00191

Yu, X., Makkawi, Y., Ocone, R., Huard, M., Briens, C., and Berruti, F. (2014). A CFD Study of Biomass Pyrolysis in a Downer Reactor Equipped with a Novel Gas-Solid Separator - I: Hydrodynamic Performance. *Fuel Process. Techn.* 126, 366–382. doi:10.1016/j.fuproc.2014.05.020

Yu, H., Xiao, W., Han, L., and Huang, G. (2019). Characterization of Mechanical Pulverization/phosphoric Acid Pretreatment of Corn stover for Enzymatic Hydrolysis. *Bioresour. Techn.* 282, 69–74. doi:10.1016/j.biortech.2019.02.104

Yuan, Y., Zhao, W., Wang, X., Gao, Y., Niu, L., and Teng, M. (2013). Dimeric Sfh3 Has Structural Changes in its Binding Pocket that Are Associated with a Dimer-Monomer State Transformation Induced by Substrate Binding. *Acta Crystallogr. D Biol. Cryst.* 69, 313–323. doi:10.1107/s0907444912046161

Yunqin, L., Dehan, W., and Lishang, W. (2010). Biological Pretreatment Enhances Biogas Production in the Anaerobic Digestion of Pulp and Paper Sludge. *Waste Manag. Res.* 28, 800–810. doi:10.1177/0734242X09358734

Zeynali, R., Khojastehpour, M., and Ebrahimi-Nik, M. (2017). Effect of Ultrasonic Pre-treatment on Biogas Yield and Specific Energy in Anaerobic Digestion of Fruit and Vegetable Wholesale Market Wastes. *Sustain. Environ. Res.* 27, 259–264. doi:10.1016/j.serj.2017.07.001

Zhang, C., Su, H., Baeyens, J., and Tan, T. (2014). Reviewing the Anaerobic Digestion of Food Waste for Biogas Production. *Renew. Sustain. Energ. Rev.* 38, 383–392. doi:10.1016/j.rser.2014.05.038

Zhang, H., Li, J., Huang, G., Yang, Z., and Han, L. (2018). Understanding the Synergistic Effect and the Main Factors Influencing the Enzymatic Hydrolyzability of Corn stover at Low Enzyme Loading by Hydrothermal And/or Ultrafine Grinding Pretreatment. *Bioresour. Techn.* 264, 327–334. doi:10.1016/j.biortech.2018.05.090

Zhao, R., Zhang, Z., Zhang, R., Li, M., Lei, Z., Utsumi, M., et al. (2010). Methane Production from rice Straw Pretreated by a Mixture of Acetic-Propionic Acid. *Bioresour. Techn.* 101, 990–994. doi:10.1016/j.biortech.2009.09.020

Zheng, Y., Lin, H.-M., and Tsao, G. T. (1998). Pretreatment for Cellulose Hydrolysis by Carbon Dioxide Explosion. *Biotechnol. Prog.* 14, 890–896. doi:10.1021/bp980087g

Zheng, M., Li, X., Li, L., Yang, X., and He, Y. (2009). Enhancing Anaerobic Biogasification of Corn stover through Wet State NaOH Pretreatment. *Bioresour. Techn.* 100, 5140–5145. doi:10.1016/j.biortech.2009.05.045

Zheng, Y., Zhao, J., Xu, F., and Li, Y. (2014). Pretreatment of Lignocellulosic Biomass for Enhanced Biogas Production. *Prog. Energ. Combust. Sci.* 42, 35–53. doi:10.1016/j.pecs.2014.01.001

Zhou, J., Sui, H., Jia, Z., Yang, Z., He, L., and Li, X. (2018). Recovery and Purification of Ionic Liquids from Solutions: a Review. *RSC Adv.* 8, 32832–32864. doi:10.1039/c8ra06384b

Zhu, J., Wan, C., and Li, Y. (2010). Enhanced Solid-State Anaerobic Digestion of Corn stover by Alkaline Pretreatment. *Bioresour. Techn.* 101, 7523–7528. doi:10.1016/j.biortech.2010.04.060

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