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INTERNATIONAL CONFERENCE ON CARBON DIOXIDE UTILISATION (ICCDU) 2016

Topic Editors:
Peter Styring, The University of Sheffield, United Kingdom
Katy Armstrong, The University of Sheffield, United Kingdom
Grant Wilson, The University of Sheffield, United Kingdom

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Carbon dioxide utilisation is a growing field of research that spans early stage laboratory chemistry through to commercial exploitation. In 2013 the CO2Chem Network (www.co2chem.com) made a successful bid to hold the 14th edition of this major conference. This was the first time it was held in the United Kingdom and attracted over 270 delegates from 32 different countries. It was a condition of presentation that all the work submitted was new and novel. We invited submissions of new work for this Research Topic and manuscripts were subjected to deep peer review. We are pleased that these papers are now being collated into an eBook. We value the range and quality of the papers submitted. These range from novel capture, integration and process through to policy, public perception and economic evaluation.

CO2Chem was proud to be chosen to organise this prestigious conference. CO2Chem was founded in 2010 as one of the Engineering and Physical Sciences (EPSRC) Grand Challenge Networks. It is now in its ninth year of operation and its third round of direct funding. It continues to be a forum for discussion and collaboration nationally and globally. We have for a long time associated ourselves with ICCDU and will continue to do so in the future. We hope that the papers presented here serve as a catalyst to further research in CDU and to engagement with ICCDU.

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EDITORIAL
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Editorial: Carbon Dioxide Utilization

Peter Styring and Katy Armstrong*

Department of Chemical and Biological Engineering, UK Centre for Carbon Dioxide Utilization, The University of Sheffield, Sheffield, United Kingdom

Keywords: ICCDU, carbon dioxide, CCU, CDU, carbon dioxide utilization

Editorial on the Research Topic

Carbon Dioxide Utilization

The ICCDU is the foremost conference on Carbon Dioxide Utilization (CDU) on an international stage. The 14th Edition was hosted at the University of Sheffield, the first time it has been hosted by the United Kingdom. The conference was organized by the CO2Chem Network (www.co2chem.com), the largest global network in the field. When this Research Topic was conceived we were very clear that this should not be considered as a set of conference proceedings, but high quality original research papers that reflected the general flavor of the conference. Each paper has had the rigorous peer review that would be expected, as I am sure you will discover.

In the last decade there has been considerable advancement in CDU chemistry and engineering. There has been a transition from bench scale chemistry through to commercial implementation across the world. This Research Topic reflects this transition as it covers areas as diverse as carbon dioxide capture, the chemistry and laboratory scale engineering and even capture free utilization, while also addressing the commercial and social aspects of utilization across the supply chain. While the editors did not impose any barriers to the type of utilization covered, it was noticeable that the majority of papers focused in the conversion of CO_2 into fuels. This demonstrates the need to develop methodologies toward the production of low carbon fuels, particularly for mobility applications, that have superior physical and environmental properties when compared to fossil fuels.

The paper on capture of CO_2 (Reed et al.) offered a new approach to purification through a pressure swing adsorption (PSA) process, based on an ionic liquid coated on to sustainable cellulose fibers. The best materials show capacity similar to aqueous MEA solutions but with reduced costs and faster cycle kinetics. One key finding was that the best performance was achieved for 25% loading of the ionic liquid on to the low-cost cellulose, an effect of the thin film coated on to a highly textured support surface. This was evidenced in SEM studies. The process was further used to integrate the capture unit to a low temperature plasmolysis reactor (Moss et al.) to produce CO, a key constituent of syngas. Different concentrations of CO_2 in the purified flue gas were reacted by plasmolysis, and the results showed that conversion of 80% CO_2 in N_2 into CO was far more efficient than when using pure CO_2. This has potential implications in cost reduction in plasma-catalyzed processes.

In most CDU processes, catalysis is expected to play a major role. This was exemplified in the use of a copper catalyst to convert syngas to methanol in a single pass (Ahoba-Sam et al.). Methanol is not only an important transport fuel or additive, but also a key intermediate in chemicals manufacture. The role of the solvent in the low-temperature process was investigated and it was observed that the best syngas conversion was achieved using diglyme. Indeed, methanol is a key feedstock in the production of butanol, a direct gasoline drop-in fuel, using a non-catalytic process (Dowson and Styring). The novelty of the latter process is that it does not require a CO_2 capture step, instead using the product production to do a reactive capture from flue gas concentrations of CO_2 in nitrogen.

Edited and reviewed by:
Ah-Hyung Alissa Park,
Columbia University, United States

****Correspondence:***
Peter Styring
p.styring@sheffield.ac.uk

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While some might say that the conversion of CO_2 back to a fuel is an energy inefficient process, it is argued that there is a need for synthetic fuels as we move toward a low carbon economy (Wilson and Styring). Synthetic fuels derived from CO_2 are not necessarily the same as those derived from fossil oil as the former have zero sulfur content. Furthermore, they produce far less particulate matter on combustion, because synthetic fuels are low in aromatic and branched hydrocarbons making them more environmentally attractive.

An interesting article from Sweden investigates how synthetic fuels can be produced electrochemically from CO_2 emitted from fossil fuel combustion and biogenic processes (Hansson et al.). This emphasizes the need for local clean energy sources and appropriate CO_2 sources when devising CDU processes. The paper concludes that electro-fuels could be produced from CO_2 but that the limiting factor is a potential supply exceeding demand in Sweden and the availability of clean energy in the country: it is proposed that by 2030 the major market could be derived from lignocellulose-based CDU.

Finally, two papers consider the techno-economic and social aspects of CDU. The first looks at what barriers there are at the present time to the implementation of CDU commercially (Kant). Public acceptance of new technologies is often key to the successful implementation. Carbon Capture and Storage (CCS) has suffered across Europe because of public opposition, to the extent that CCS is not now permitted in countries such as Germany. The second paper considers the best ways to address public concerns (Jones et al.) to present CDU as a truly environmentally-friendly technology, based on an evidential approach. The paper recognizes that research in this area is limited but offers a potential agenda for its continued study and implementation of the data.

It is gratifying to see the level of interest that this Research Topic has generated. At the time of writing this Editorial, 18 June 2018, the combined views recorded for the papers in this topic are over 26,000. Recent developments since the 2016 conference mean that the status of CDU is increasing internationally. A 2018 report from Mission Innovation, supported by the G20 governments and the European Union as a block, has recommended significant increase in funding for CO_2 utilization chemistries and technologies. A number of papers published in this Research Topic featured in the evidence presented to the panels and in the final policy document (https://www.energy.gov/sites/prod/files/2018/05/f51/Accelerating%20Breakthrough%20Innovation%20in%20Carbon%20Capture%2C%20Utilization%2C%20and%20Storage%20_0.pdf). It is becoming clear that the use of CO_2 as a chemical feedstock is becoming an integral tool in a move toward a low carbon future and a circular economy. CDU means that less fossil carbon enters the supply chain, satisfying the top level of the Lansink waste protocol. Furthermore, it also addresses issues of reuse and recycling as part of an industrial carbon cycle.

AUTHOR CONTRIBUTIONS

PS was the primary author of this Editorial paper. KA provided additional information and proof reading of the paper.

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ORIGINAL RESEARCH
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Cellulose-Supported Ionic Liquids for Low-Cost Pressure Swing CO_2 Capture

*Daniel G. Reed, George R. M. Dowson and Peter Styring**

UK Centre for Carbon Dioxide Utilisation, Department of Chemical and Biological Engineering, The University of Sheffield, Sheffield, United Kingdom

Reducing the cost of capturing CO_2 from point source emitters is a major challenge facing carbon capture, utilization, and storage. While solid ionic liquids (SoILs) have been shown to allow selective and rapid CO_2 capture by pressure swing separation of flue gases, expectations of their high cost hinders their potential application. Cellulose is found to be a reliable, cheap, and sustainable support for a range of SoILs, reducing the total sorbent cost by improving the efficiency of the ionic liquid (IL) through increased ionic surface area that results from coating. It was also found that cellulose support imparts surface characteristics, which increased total sorbent uptake. Combined, these effects allowed a fourfold to eightfold improvement in uptake per gram of IL for SoILs that have previously shown high uptake and a 9- to 39-fold improvement for those with previously poor uptake. This offers the potential to drastically reduce the amount of IL required to separate a given gas volume. Furthermore, the fast kinetics are retained, with adsorb–desorb cycles taking place over a matter of seconds. This means that rapid cycling can be achieved, which results in high cumulative separation capacity relative to a conventional temperature swing process. The supported materials show an optimum at 75% cellulose:25% IL as a result of even coating of the cellulose surface. The projected reduction in plant size and operational costs represents a potentially ground-breaking step forward in carbon dioxide capture technologies.

Keywords: carbon dioxide capture, ionic liquid, cellulose, cost reduction, pressure swing adsorption

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Angela Dibenedetto,
Università degli studi di Bari Aldo Moro, Italy

Reviewed by:
Hasmukh A. Patel,
Northwestern University, United States
Hyungwoong Ahn,
University of Edinburgh, United Kingdom
Davide Mattia,
University of Bath, United Kingdom

****Correspondence:***
Peter Styring
p.styring@sheffield.ac.uk

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INTRODUCTION

Carbon dioxide (CO_2) has been shown to be the major contributing gas to global warming and detrimental climate change (IPCC, 2014). Carbon capture utilization and storage (CCUS) is one of the key frameworks being developed to counter this threat. Without further development and subsequent deployment of CCUS and associated technologies, models indicate that warming will not be limited to the previous 2°C target, let alone 1.5°C target contained in the COP21 Paris Agreement (IPCC, 2014; United Nations, 2015).

Within CCUS, once the CO_2 is captured, it may be either sequestered into geological storage or utilized as a feedstock in other products through CO_2 utilization. Both approaches require significant energy input. Either way, both methods first require a CO_2 capture step, although in the utilization processes, this may be a reactive capture directly to a product. One of the key challenges facing CCUS remains the question of which approach to use in order to capture dilute CO_2 from exhaust gases when over 90% of stationary emitters produce emissions concentrations of 15% by volume of CO_2 or even less (Gale et al., 2005).

Removal and capture of CO_2 from these point sources is an area of intense research. Even when only post-combustion removal of CO_2 is considered, approaches range from adsorption and absorption, membrane and cryogenic separation, and microbial or algal biosystems (**Figure 1**) (Chou and Chen, 2004; Figueroa et al., 2008; Stolaroff et al., 2008; Brennecke and Gurkan, 2010; Karadas et al., 2010). Of the overarching technologies listed in **Figure 1**, adsorption and absorption systems are the most advanced and are themselves split into two main types; temperature swing absorption (TSA) and pressure swing adsorption (PSA). TSA processes typically rely on high temperatures in order to regenerate a solvent that readily captures CO_2 liberating a high-concentration CO_2 stream, whereas PSA processes rely on a drop in pressure, most usually from near-atmosphere to vacuum to release the more weakly bound CO_2 (MacDowell et al., 2010; Samanta and Zhao, 2011).

The aforementioned choice between the capture approaches will likely be decided upon relative economic viability of the processes. This hinges on their energy requirements, prospective plant footprint area, and the balance of capital and operating costs. In turn, these economic elements will depend on both the nature of the process and the sorbent taken together. For example, a low-cost sorbent that has exorbitant energy requirements for CO_2 capture and that will require a large plant footprint may struggle to compete with a far higher-cost sorbent that has lower energy requirements and smaller footprint. Location also needs to be considered. If there is surplus low-grade heat available, this can be used in the TSA process to afford desorption of the captured CO_2. However, there are many potential emission sources where surplus heat is not available. In these cases, the PSA process using renewable energy becomes more economically efficient as the heating duty on solvent regeneration by fat outweighs compression duty.

Ionic liquids (ILs) and particularly room temperature ionic liquids (RTILs) are particularly expensive sorbents. Some of these show very promising uptake performance for CO_2 capture such as high selectivity and inherent flexibility, allowing task-specific sorbents to be synthesized (Bates et al., 2002; Ramdin et al., 2012; Moen and Stene, 2014). These RTILs can also bridge both the physisorption and chemisorption classes of sorbent, potentially allowing both high uptake capacity and low regeneration costs in typically TSA processes.

One of the main drawbacks when using RTILs is the very slow rate of CO_2 diffusion through the bulk liquid. Compared with benchmark amines, the diffusion rates of gas through the RTILs is up to 19 orders of magnitude slower (Jassim et al., 2007; Moya et al., 2014). This largely prevents rapid CO_2 sorption and cycling and, therefore, increases the total IL inventory required to treat a given flow rate or volume of gas. Compounding this problem is the high cost of the RTILs. However, in some cases, this might be erroneous as only a few cases of cost modeling have been carried out for IL production. In addition, these are frequently estimates that are based on laboratory-scale syntheses or small-scale production, which can easily imply costs approaching £1 million per tonne (Baltus et al., 2005). A recent full techno-economic analysis of larger scale syntheses have given more likely IL prices ranging from £1,700 to £35,000 per tonne, based on manufacturers estimates but with a strong dependence on the IL structure (Klein-Marcuschamer, 2011). For comparison, the benchmark amine, MEA, has a market cost of £1,100 per tonne. Naturally, it should be noted that the wide range of results is due to scaling assumptions (Chen et al., 2014).

However, what is more certain is that even if the lower-cost figure for the production of ILs is the more accurate, the slow diffusion rate will require infeasibly large inventory supplies to be available at any point source emitter.

SOLID IONIC LIQUIDS (SoILs)

One potential solution to the twin problems of low-gas diffusion rates and high sorbent costs may be to use SoILs as sorbents. While these may appear to be a contradictory name, ILs are

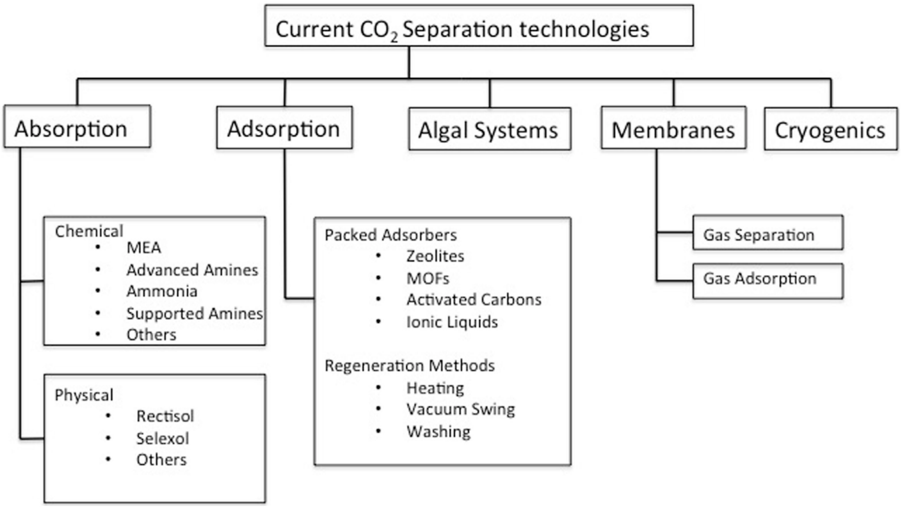

FIGURE 1 | Current leading CO_2 separation technologies.

typically defined as salts with melting points below 120–140°C, allowing organic salts that have high melting points to be entirely solid at room temperature.

Previously published work (Styring et al., 2016) by this group has investigated SoILs and molecular organic salts as an alternative IL approach to CO_2 capture, where PSA is used on finely ground ILs with melting points above room temperature. These solids are often structurally simpler and cheaper to synthesize than RTILs and naturally avoid gas diffusion issues by allowing the gas immediate access to a large IL surface area. They can also potentially avoid sorbent pumping issues as fine powders rather than typically viscous fluids and are significantly easier to dry (Styring et al., 2016).

Through this work, it was found that the high selectivity to CO_2 over nitrogen, which is typical of RTILs, is maintained in the SoILs. However, in contrast with the RTIL capture methods that typically use TSA, PSA is required to counteract the fact that typically crystalline and impermeable SoILs will not allow full gas–solid contacting. As a result, since not all of the IL is available for gas–solid interaction, uptake capacity is limited compared to RTILs. By applying a high pressure swing process, where adsorption and separation occurs at high pressures (5–30 bar) and desorption occurs at atmospheric pressure, uptake capacities can be boosted. Once again, this method reduces the inventory of IL required to treat a given gas stream. An additional benefit of using a high pressure swing process is a potentially reduced capture plant footprint made up of less complex unit operations than those found in a TSA process, and operation at ambient temperature. Overall, there is a small temperature change of less than 1°C over the compression–decompression cycles. Furthermore, it should be noted that if the captured CO_2 is to be transported by pipeline, large-scale compression and pumping equipment will already be present (Pershad et al., 2010).

These positive effects come at the price of the energy costs of pressurization. Costs have been estimated for a model pressure swing capture system using a range of operating pressures and separation performances based on experimental data. Costs estimated by this model compare well with literature examples of high pressure swing systems for CO_2 separation. **Table 1** compares model results with the most prominent separation technologies shown **Figure 1**. This table shows that when considering total energy costs, high pressure swing processes have a decided advantage over other separation technologies.

A frequent comment on this observation is that these overall energy comparisons can be misleading when different energy sources are used for each of the various capture methods (Wilson et al., 2016). For example, in a power plant context, temperature swing processes (MEA and amines primarily) could in principle be powered by low grade and low value heat. This would render the overall energy cost less relevant, especially if assuming this energy might otherwise be wasted. In comparison, the costs of gas compression or vacuum generation, while representing far less total energy, could have a larger associated energy penalty to the power plant if the assumption is made that higher-value electricity is required. This position naturally ignores the possibility that the same low-grade heat that putatively powers MEA capture could be used to power pressurization equipment, which fundamentally requires only mechanical motion and does not necessarily require electricity. Nor does it allow for situations where such waste low-grade heat is unavailable or insufficient for MEA capture to proceed without large economic costs. In such situations, overall energy costs of each approach, as shown in **Table 1**, is a fair basis of comparison. If renewable energy is used for the pressure swing then the situation is further improved.

SUPPORTING SoILs

The action of supporting ILs has previously been used in applications such as supported IL catalysis, a concept that combines the advantages of ILs with those of heterogeneous support materials; and gas separation, where ILs are supported on membranes to improve permeability (Mehnert, 2004; Ilconich et al., 2007). Supporting SoILs to specifically aid CO_2 capture is a relatively unexplored area of research and may allow significantly improved CO_2 uptake per unit mass of IL in the total sorbent. This will further reduce the quantity of IL needed to treat a given gas stream. This would primarily be achieved by coating a thin layer of the SoIL on a support particle with which it has good adhesion and full surface coverage. Assuming the support material is low cost, this in turn may substantially reduce sorbent inventory costs. Further benefits may include unique combinations of properties from both the IL and the support itself.

Supports such as activated carbon, alumina, and cellulose among others, could be considered as viable options. Of these, there is a history of using ILs with cellulose, typically in efforts to separate cellulose from biomaterials as cellulose is known to dissolve well in RTILs (Swatloski et al., 2002). It would, therefore, seem reasonable to assume that SoILs could have a good surface interaction and adhesion to the cellulose particles, allowing the desired thin layer to be deposited, giving total coverage of the

TABLE 1 | Comparison of average reported energy costs for several post-combustion CO_2 capture processes including maximum and minimum reported values (Desideri and Paolucci, 1999; Wong and Bioletti, 2002; Romeo et al., 2008; Zhang et al., 2008; Harkin et al., 2009; Rameshni, 2010; Yang and Zhai, 2010; Belaissaoui et al., 2012, 2013; Krishnamurthy et al., 2014; Kundu et al., 2014; Liu et al., 2014; Xie et al., 2014).

Method	MEA	Advanced amine	Membrane	Vacuum swing	High pressure	Thermodynamic minimum
Type	Temperature swing absorption (TSA)	TSA	Pressure swing adsorption (P SA)	VPSA	PSA	–
Av. capture cost (MJ/t)	3,840	2,690	2,500	1,660	1,170	210
Range (min/max)	2,570/4,600	1,800/3,220	1,900/3,250	1,220/2,100	860/1,580	170/250

support particle. The insolubility of cellulose in other solvents allows easy recovery of any supported SoIL. Furthermore, cellulose is also very cheap, is an abundant bio-renewable material and has only weak interaction with CO_2. The tough fibrous structure of the cellulose support also leads to high mechanical strength, preventing the sorbent particles from breaking up under pressure swing conditions.

As with previous work (Styring et al., 2016), the cations and anions selected for the SoILs focused on low complexity cations with abundant precursor materials. Those chosen for cellulose support were tetraalkylammonium, pyridinium, and imidazolium cations. For the anions, acetate and bromide were chosen. RTILs using acetate have a track-record of high uptake capacity. Bromides, which typically have very low uptake capacities, have a facile synthetic pathway and were chosen to see if supporting them on cellulose would help improve sorption capacity (Shiflett and Yokozeki, 2008). The use of a cellulose support lowers the cost of the materials relative to a pure SoIL while also reducing the inventory of the SoIL. This also improves uptake capacity so has a double benefit. The materials are more expensive than activated carbons but comparable or cheaper than advanced solids such as molecular sieves/zeolites. We have chosen low-cost SoIL materials with market values close to pure MEA for example. These are not highly complex ILs needing exotic anions and cations.

EXPERIMENTAL METHODS

All reagents were purchased at highest available purity from Sigma-Aldrich and used without further purification, other than drying. Amine quaternization reactions were carried out using Schlenk-line techniques under an inert (N_2) atmosphere. Reactions using methyl iodide were carried out using aluminum foil protection on the exterior of the reaction vessel and low lighting. All solvents were HPLC grade. CO_2 and N_2 and were supplied by BOC-Linde. 1-Butyl-4-methylimidazolium bromide ([Bmim][Br]) and tetra-octylammonium bromide ($[N_{8888}][Br]$) were directly purchased from Sigma-Aldrich and thoroughly dried under a flow of 20 mL/min nitrogen at 60°C for 24 h before uptake tests were carried out.

High pressure adsorption experiments were carried out using a bespoke packed-bed adsorption column constructed from Swagelok™ piping and fittings (**Figures 2** and **3**) using a Jasco PU-1580-CO_2 supercritical CO_2 pump, a Jasco BP-1580-81 back pressure regulator, an Omega PX409USB High Accuracy Pressure Transducer, a 42AAV48 Midwest Pressure Systems Gas Pressure Booster, and an AND GF-1000 High Capacity 3 decimal place balance. The reactor was isolated from the system using valves and the assembly weighed on the balance. Desorption was measured by slowly opening the valves while still on the balance. Supported sorbent packed densities were measured using a Micromeritics AccuPyc 1340 Pycnometer and surface area analysis was carried out on a Micromeritics 3Flex gas sorption analyzer. High pressure adsorption capacities were further verified using a Hiden Isochema IGA-0002 adsorption apparatus with a pressure range of 0–10 bar.

IL Syntheses and Cellulose Loading

Tetraethyl ammonium acetate $[N_{4444}][Ac]$ was synthesized by addition of glacial acetic acid (2.00 g, 33.17 mmol) to a 40 wt% aqueous solution of tetraethyl ammonium hydroxide (10.75 mL, 16.58 mmol) followed by evaporation, using heptane to assist in the removal of excess acetic acid by azeotropic distillation. Isopropanol was further used for the azeotropic removal of water. The product was isolated as a free-flowing brilliant white powder that was then further dried under high vacuum. Yield 4.87 g (97%). ^1H NMR, 400 MHz, CD_3OD: δ/ppm 1.05 (t, $J = 7.29$ Hz, 12H $-CH_3$), 1.44 (hex, $J = 7.47$ Hz, 8H, $-CH_2-$), 1.69 (br. m, 8H, $-CH_2-$), 1.95 (s, 3 H, CH_3COO), 3.26 (m, 8H, CH_2-N).

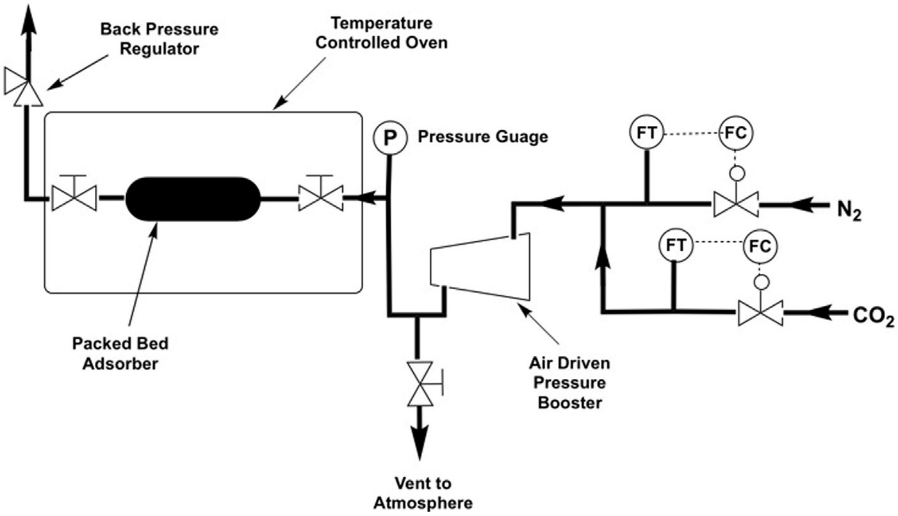

FIGURE 2 | Simplified process flow diagram of the experimental apparatus.

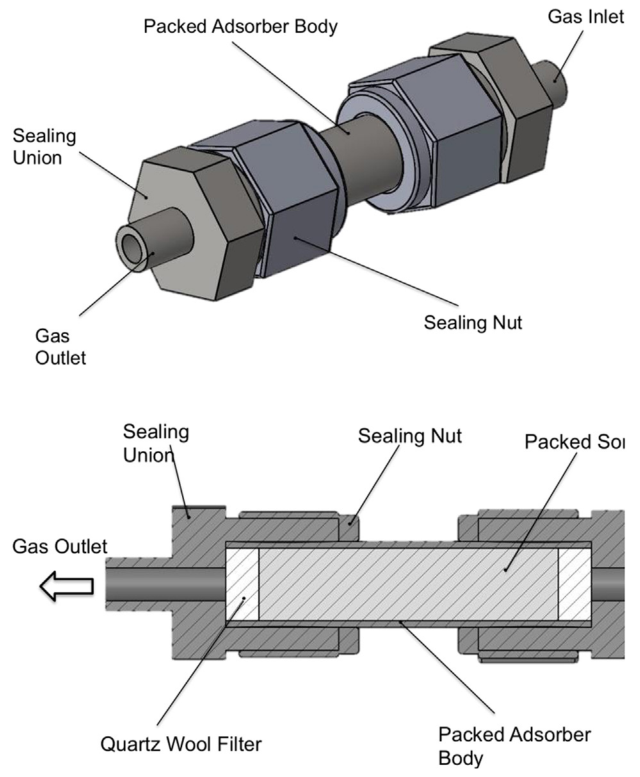

FIGURE 3 | Schematic of the packed bed adsorber with cross-sectional view showing the internal layout and packing configuration.

Methyltrioctyl ammonium acetate $[N_{1888}][Ac]$ was synthesized by the addition of an excess of methyl iodide (5.00 g, 35.25 mmol) to trioctylamine (4.31 g, 11.69 mmol) in acetonitrile (50 mL). The resulting white powder precipitate $[N_{1888}][I]$ (5.62 g) was filtered and then dissolved in a 60:40 mixture of methanol and water (150 mL) and passed through a column of Amberlite® IRN78 Hydroxide Form anion exchange resin, which had been freshly regenerated with an aqueous solution of high purity sodium hydroxide. The resulting methyl trioctyl ammonium hydroxide was then immediately mixed with an excess of acetic acid (2.5 g, 41.6 mmol) in water (30 mL), to prevent decomposition of the unstable ammonium hydroxide species. Samples of both the column eluate and the acetic acid mixture in the receiving flask were periodically taken and shaken with silver nitrate solution, to check for cream or yellow–white precipitating AgI. As with the $[N_{4444}][Ac]$, this was then dried using azeotropic distillation techniques yielding a fluffy white powder. Total yield 4.11 g (82%). ^{1}H NMR, 400 MHz, CD_3OD: δ/ppm 0.93 (t, $J = 7.10$ Hz, 9H, $–CH_3$), 1.38 [br. m. 30H, $–(CH_2)_5–$], 1.73 (m, 6, $–CH_2–$), 2.18 (s, 3H, CH_3COO), 3.02 (s, 3H, $N\text{-}CH_3$), 3.27 (m, 6H, $N\text{-}CH_2–$).

Several attempts were made to synthesize methylpyridinium acetate with anion exchange resin; however, the resulting methylpyridinium hydroxide decomposed as it was formed, leaving only a brown tarry residue on drying.

All ILs were then supported on the cellulose using wet-coating techniques. The IL was first dissolved in equal parts methanol and isopropanol before the cellulose was added at the required amount. The alcoholic solvents were then removed under vacuum using a rotary evaporator heated to 60°C and rotation set at 280 rpm, leaving the IL coated on the cellulose surface. The extent of the coating was confirmed qualitatively by SEM of the resulting free-flowing powders.

Void Space Calculation

Since the gas uptake is quantified gravimetrically, it is important to know the weight of gas that is not interacting with the sorbent: this is known as the void space. The void space was calculated before each run took place. The accurate internal volume of the adsorber (empty) was found by water displacement (V_A). The adsorber rig was then weighed (empty) and under vacuum. Quartz wool was used to ensure that packed ILs were not ejected from the adsorber, and this was also weighed. A portion of quartz wool was packed into one end of the adsorber and the IL to be tested was then packed on top. The second portion of quartz wool was then added at the other end to seal the IL in place and the adsorber was closed and sealed. The adsorber was then re-weighed under vacuum to give the packed sorbent weight. The volumes of the sorbent (V_S) and quartz wool (V_Q) were found using the density data obtained from the pycnometer measurements. These volumes were subtracted from the total internal volume to give the void space as shown in Eq. 1.

$$\text{Void Space} = V_A - (V_S + V_Q) \tag{1}$$

CO_2 Capacity

The CO_2 capacity of the sorbent was calculated using a static gas pressure and was carried out using pure CO_2 gas. The starting weight of the packed adsorber was taken before the gas was introduced. Pure CO_2 then enters the adsorber and the total weight increase of the system was determined (M_T). This was achieved by closing the valves to the reactor, removing it from the system and placing it on the balance, the mass of the empty assembly having previously been measured. The mass increase was attributed to the CO_2 that had been adsorbed onto the sorbent (M_{ads}) and CO_2 in the void space (M_{void}). In order to find the mass of CO_2 in the void space, the density of the gas at that specific pressure and temperature was determined. This void space mass (M_{void}) was removed from the total mass increase (M_T). The remaining mass (M_{ads}) was then attributed to the gas that had adsorbed onto the sorbent (Eq. 2).

$$M_{ads} = M_T - M_{void} \tag{2}$$

This resulting mass of adsorbed gas (M_{ads}) was then used to derive the sorbent capacity, which is reported as a weight percentage of the initial sorbent weight (wt%) as shown in Eq. 3.

$$\text{sorbent capacity (wt\%)} = \frac{\text{mass of gas asorbed}}{\text{initial mass of sorbent}} \times 100 \tag{3}$$

Adsorption and Desorption Kinetics

In order to determine the rate of adsorption, the adsorber was placed under static gas pressure for set periods of time. After each time period, the detached adsorber was weighed to determine the mass of gas adsorbed. Once the adsorbed gas weight plateaued, it was assumed that the sorbent had become saturated. To test desorption rate, the adsorber was placed on the balance and opened to atmosphere. The weight was monitored and recorded at set time intervals until there was no further weight loss. At this point, it was assumed that the desorption of gas was complete.

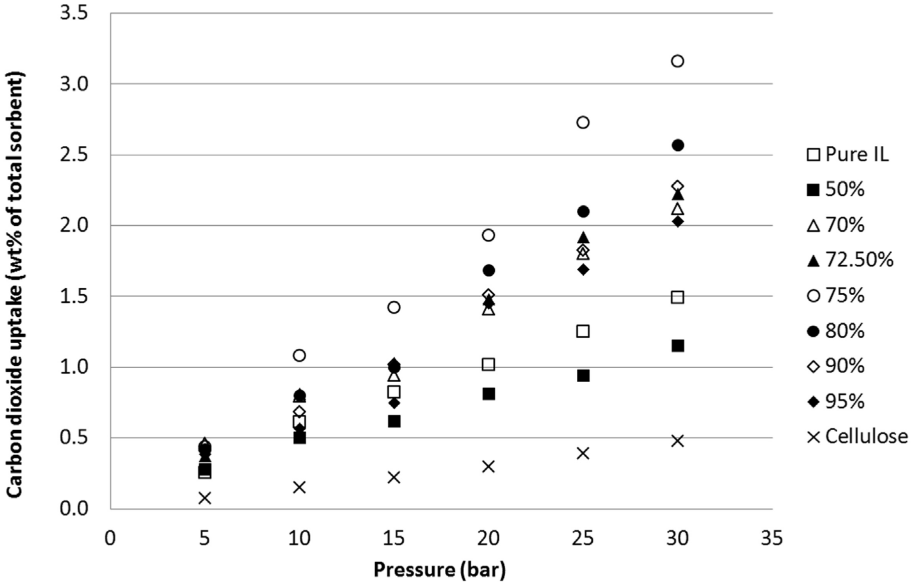

FIGURE 4 | Uptake capacities of CO_2 at various pressures on $[N_{4444}][Ac]$ across a range of cellulose loadings at room temperature.

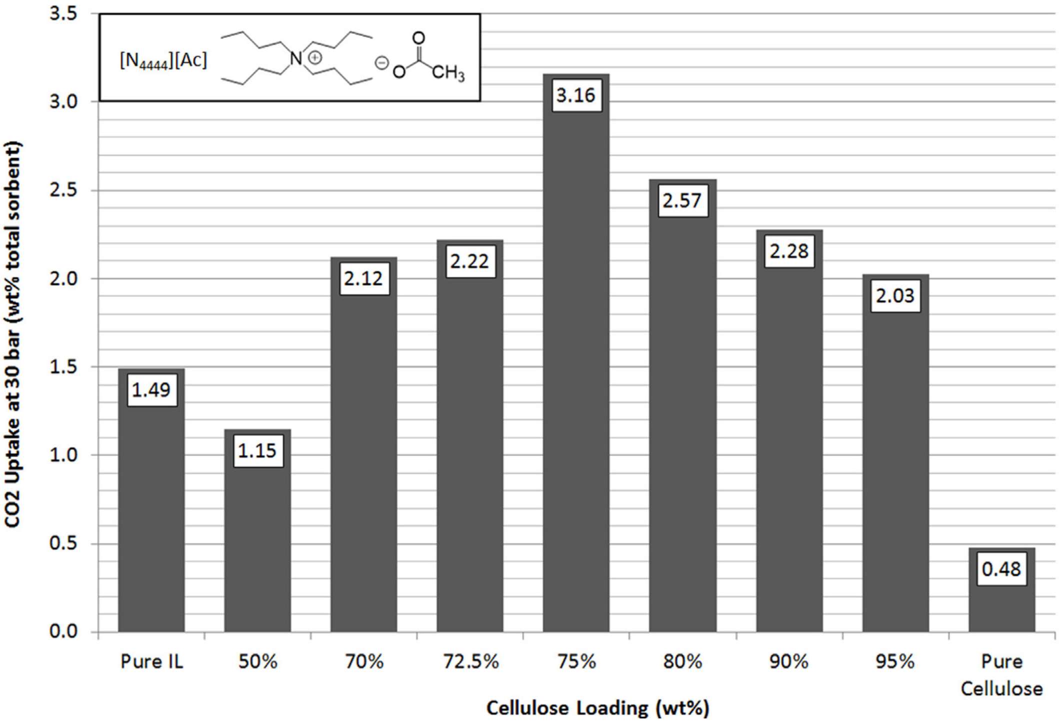

FIGURE 5 | Trends in total sorbent CO_2 uptake at 30 bar of $[N_{4444}][Ac]$ as a function of cellulose loading at room temperature.

RESULTS AND DISCUSSION

CO_2 Adsorption on $[N_{4444}]$[Acetate]

Previous work carried out by this group (Styring et al., 2016) has demonstrated that simple tetraalkylammonium acetate SoILs are suitable low-cost sorbents for use in a pressure swing system. This is due to their rapid adsorption and desorption kinetics, their chemical and mechanical stability, and their high selectivity toward CO_2.

Tetrabutylammonium acetate $[N_{4444}]$[Ac] was chosen for testing due to its ease of handling and low water affinity and was wet-coated onto cellulose powder at various weight loadings, the resultant sorbent powders ranging from 50 to 95% cellulose by mass. These sorbents were then measured for CO_2 uptake (error ±0.01 wt%) over a range of pressures at room temperature (**Figure 4**). While this does not simulate the temperatures that would be expected in flue gas treatment, previous tests on unsupported SoILs have shown minimal effect of temperature on maximum CO_2 capacity at a given pressure (Styring et al., 2016).

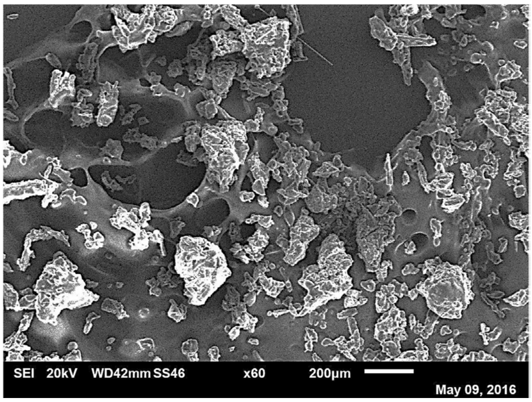

FIGURE 6 | SEM of $[N_{4444}]$[Ac] at 50 wt% cellulose loading showing agglomeration of cellulose particles (white) rather than surface coating.

In line with previous results and expectations, the linear trend of CO_2 uptake with increasing pressure was observed (**Figure 4**). At lower pressures, the ILs have similar uptake capacities so the effect of cellulose loading is less apparent. However, as the pressure was raised to 30 bar, the differences in sorbent performance became greater. Overall, there was a clear and dramatic improvement in uptake as the sorbent trends toward a support loading of 75 wt% cellulose with CO_2 total capacity at 30 bar reaching a peak of 3.16 wt% uptake. This is shown in **Figure 5** in order to clarify the trend that is not immediately evident in **Figure 4**. If this is normalized to 1 g IL, then the adsorption scales to 12.64 wt%, 8.5 times greater than the pure IL. If the low cost of the cellulose is considered, this essentially represents an equal improvement in cost effectiveness. It should be noted that the addition of cellulose initially reduced total CO_2 capacity when support loadings of 50 wt% cellulose were used. This was thought likely to be due to the formation of an aggregated matrix where the cellulose particles are bound together by the SoIL. This was borne out by the SEM images (**Figure 6**). Note also that despite the decrease in total sorbent uptake, when considering the uptake per unit mass IL independent of support, the uptake is still improved by a factor of 1.5 (or 54%).

The uptake at 75 wt% cellulose suggests that, at that loading, there is an optimum condition that allows for greater CO_2 adsorption capacity. This could be due to a variety of reasons; IL layer thickness, surface morphology, and increased total

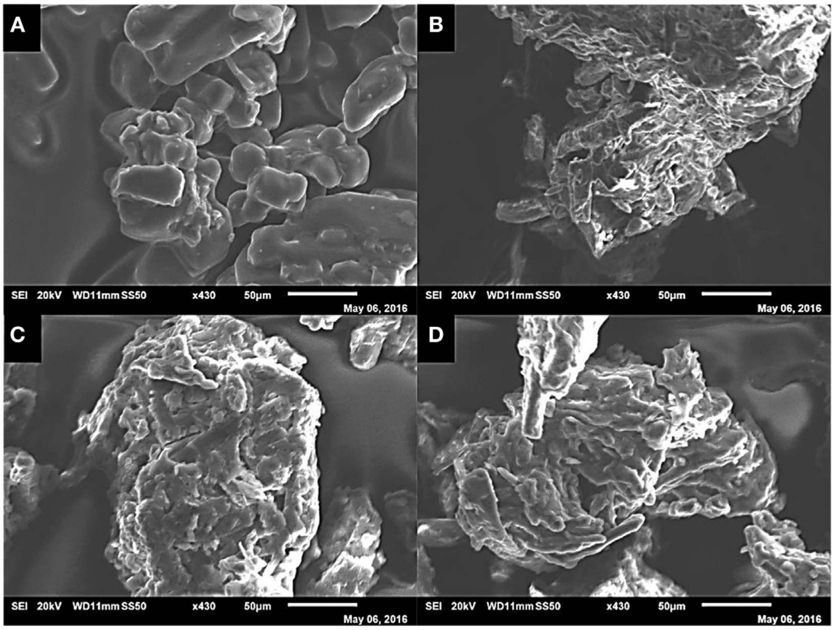

FIGURE 7 | SEM images of unsupported $[N_{4444}]$[Ac] **(A)**, powdered cellulose **(B)**, 75 wt% cellulose $[N_{4444}]$[Ac] **(C)**, and 95 wt% cellulose $[N_{4444}]$[Ac] **(D)** under the same degree of magnification (×430) at 20 kV.

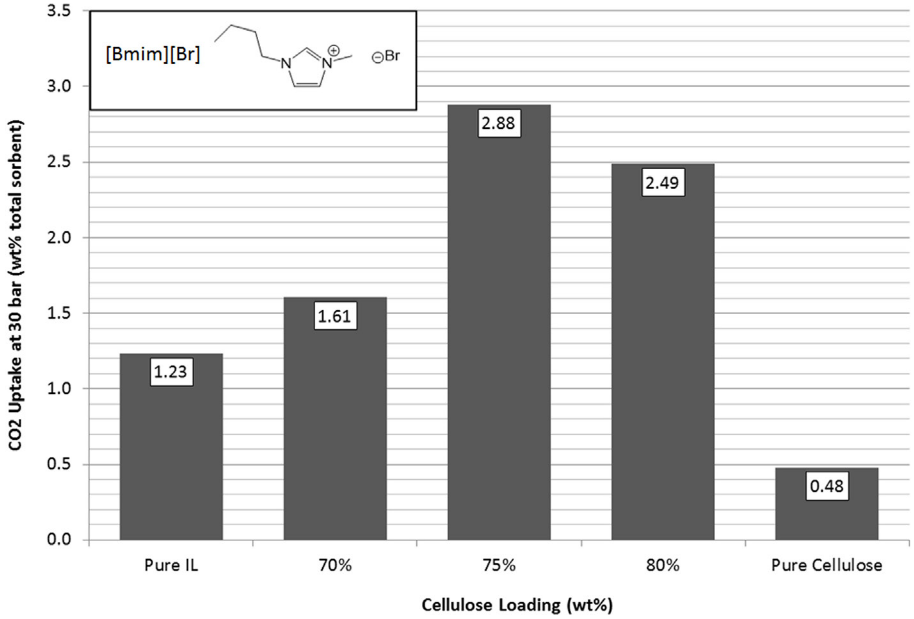

FIGURE 8 | Trends in total sorbent CO_2 uptake at 30 bar for [Bmim][Br] as a function of cellulose loading at room temperature.

TABLE 2 | Selected supported and unsupported sorbent physical properties.

Sorbent	Density (g/cm³)	Surface area (m²/g)
Cellulose	1.595	44.99
[N4444][Ac]	1.059	55.77
[N4444][Ac]—50%	1.261	–
[N4444][Ac]—70%	1.316	–
[N4444][Ac]—72.5%	1.370	–
[N4444][Ac]—75%	1.370	78.20
[N4444][Ac]—80%	1.406	–
[N4444][Ac]—90%	1.460	–
[N4444][Ac]—95%	1.497	–
[N1888][Ac]	1.418	86.32
[N1888][Ac]—70%	1.500	–
[N1888][Ac]—75%	1.525	118.29
[N1888][Ac]—80%	1.550	–
[bmim][Br]	1.395	30.81
[bmim][Br]—70%	1.492	–
[bmim][Br]—75%	1.561	93.95
[bmim][Br]—80%	1.537	–
[N8888][Br]	1.012	60.33
[N8888][Br]—70%	1.294	–
[N8888][Br]—75%	1.300	63.95
[N8888][Br]—80%	1.366	–

surface area. This is further reinforced by the fact that total CO_2 capacity is reduced as higher loadings of cellulose are used. This reduction in CO_2 capacity could be due to issues with adsorption onto thinner IL layers, incomplete coverage leading to reduced IL surface area available for adsorption or simply because there is less IL in the bulk sorbent for CO_2 capture. In order to help determine coverage, further SEM images of the sorbents were taken.

Figure 7 shows tested sorbents at the same magnification (×430) as each other under SEM at 20 kV. The $[N_{4444}][Ac]$ in its pure form shows the crystalline IL particles are very smooth and partially agglomerated, whereas cellulose exhibits a rough and very fine fibrous structure (**Figures 7A,B**). When supported at 75 wt% cellulose loading (image C), a coating of the smoother IL can be seen on the fibrous cellulose particle. However, when comparing **Figures 7A,C**, there is clear introduction of surface roughness to the IL upon loading. At the highest cellulose loading fraction of 95 wt% (**Figure 7D**), the smoothing effect of the IL is still visible; however, the underlying fibrous structure of the cellulose particle is more apparent, leading to areas of incomplete coverage, which would likely have selectivity implications.

The introduction of surface roughness to the IL surface through coating of the cellulose appears likely to be a cause of the observed improvement in CO_2 uptake capacity. This could be explained simply by increased surface area. Alternatively, it is possible that the rough surface provides stronger binding sites that give the IL a pseudo-microporous structure. A combination of these two effects is also possible. Surface roughness causing a sorbent to behave as if microporous has been previously postulated to explain observed effects of gas adsorption onto mesoporous solids (Coasne et al., 2006).

In order to determine if this loading effect is seen with other simple ILs, a small selection of other common SoILs of both high and low capacity were tested. Based on the results of the $[N_{4444}][Ac]$ study, only samples of 70–80% cellulose loading by weight were considered. BET analysis of all SILs was also carried out to determine the effect of loading on surface area. This was performed in order to ascertain whether an increase in surface area was sole reason for increasing CO_2 capacities.

OTHER SoILs

Further testing was carried out to determine whether the trends seen for $[N_{4444}]$[Ac] hold true for other SoILs. $[N_{1888}]$[Ac], [Bmim][Br], and $[N_{8888}]$[Br] were chosen since they are structurally simple, low in cost, have readily available starting materials, and are solids at room temperature. Previous tests with $[N_{8888}]$[Br] have shown it to be particularly poor as a CO_2 capture agent. It was selected in order to indicate whether the increase in CO_2 capacity was proportional to the starting performance of the pure ionic liquid. If so, this would indicate that the improvement seen after cellulose support was simply down to an increase in available surface area of the IL for CO_2 capture and not due to surface effects potentially suggested by SEM images.

[Bmim][Br] had a fairly poor starting capacity when using it in its pure form as it forms large crystals on synthesis and has a high affinity to water making it challenging to handle as fine powder. The resulting large crystals lead to a poor surface area to volume ratio, which was expected to be the reason for its poor uptake performance. However, once supported, [Bmim][Br] showed a similar increase in its CO_2 uptake capacity at 75 wt% loading as was found for $[N_{4444}]$[Ac]. Following the pattern of the $[N_{4444}]$[Ac] (**Figure 8**), 70 and 80 wt% loadings showed poorer total uptake. The 75 wt% cellulose support loading gave an increase of a factor of 2.3 over pure [Bmim][Br], which amounts to an increase of CO_2 adsorbed per unit mass of IL of 9.4, nearly an order of magnitude improvement in the effectiveness of the IL.

Similarly, the 75 wt% cellulose sorbent shows a tripling of surface area by BET measurement (**Table 2**). It should also be noted that it is possible in this case that there is a sharp optimum peak loading for [Bmim][Br] in the 70–75 or 75–80 wt% range that may afford even further improvements in uptake performance. After loading, [Bmim][Br], which is highly hygroscopic, also showed a reduction in its water affinity and remained as a free-flowing powder during handling. This could also be attributed to changes in the surface properties, however, may be due to cellulose acting as a desiccant.

$[N_{1888}]$[Ac] has the highest uptake capacity of the pure ILs that have been previously investigated by this group (Styring et al., 2016). In contrast, $[N_{8888}]$[Br], as previously mentioned, has one of the lowest uptake capacities measured. However, as shown in **Figures 9** and **10**, respectively, $[N_{1888}]$[Ac] showed only very modest improvement at 75 wt% loadings and loadings higher or lower than this amount actually gave a diminished performance. By contrast, $[N_{8888}]$[Br] showed an order of magnitude improvement in total CO_2 capacity, with the highest capacity seen at 70 wt% cellulose loading. Furthermore, $[N_{1888}]$[Ac] exhibited a much larger increase in surface area, of around 40%, when compared to $[N_{8888}]$[Br] after cellulose loading (**Table 2**). However, since its capacity improvement was only marginal, surface area was unlikely to be the driving factor in this case. This perhaps indicates that the surface effects suggested by the SEM images on $[N_{4444}]$[Ac] may be important and, therefore, indicates that surface properties of $[N_{1888}]$[Ac] were already well-suited for CO_2 adsorption. Therefore, the addition of the cellulose support had a negative or near-neutral effect at best. However, it still shows a total improvement, after the loading factor is considered, of a factor of 4.2 times better than the pure SoIL.

On the other hand, the improvement of $[N_{8888}]$[Br] indicates the opposite and that the unsupported salt surface morphology

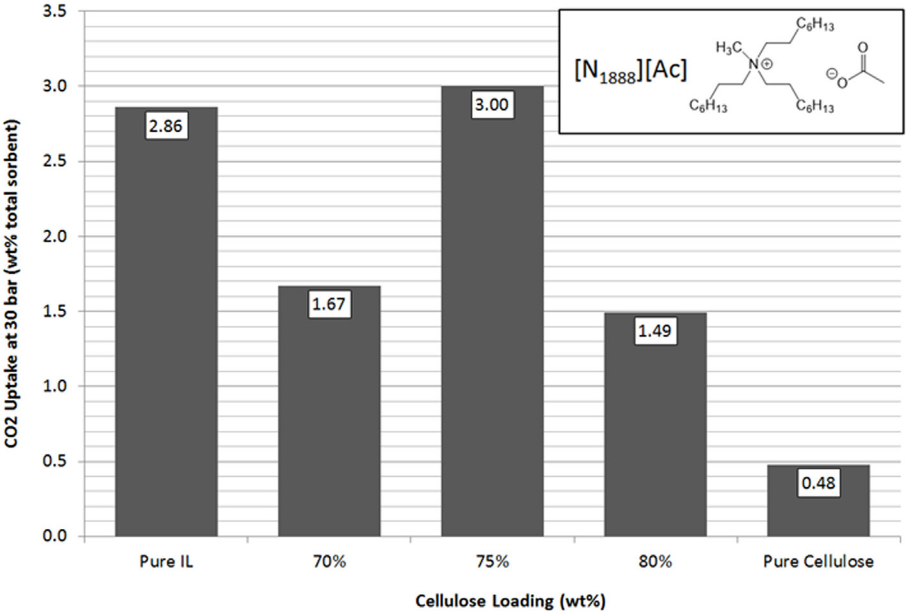

FIGURE 9 | Trends in total sorbent CO_2 uptake at 30 bar of $[N_{1888}]$[Ac] as a function of cellulose loading at room temperature.

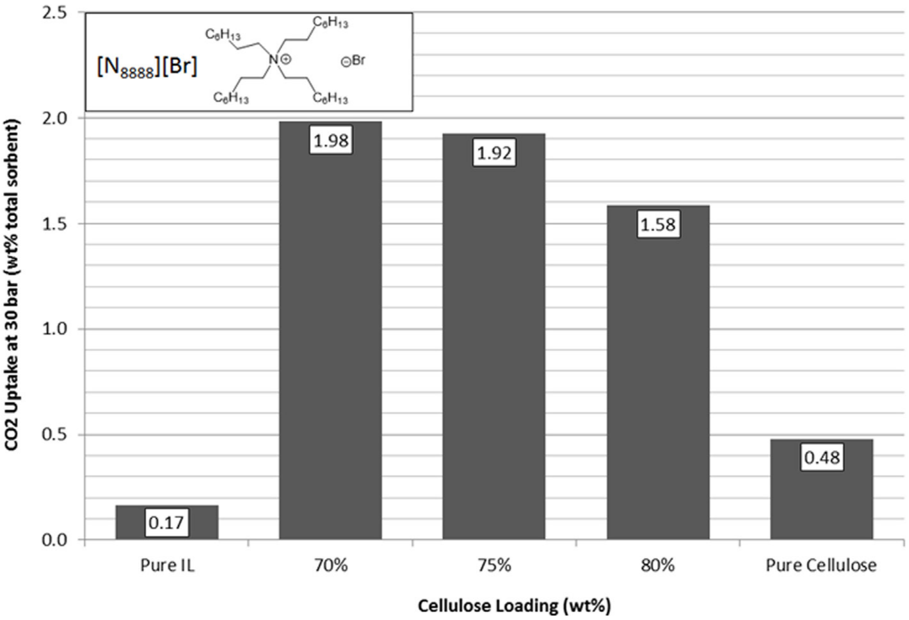

FIGURE 10 | Trends in total sorbent CO_2 uptake at 30 bar of [N_{8888}][Br] as a function of cellulose loading at room temperature.

seems likely to be hostile to CO_2 adsorption, despite its demonstrated capability to perform once supported. This is backed up by the surface area measurements shown in **Table 3** where [N_{8888}][Br] only exhibited a small increase in surface area, yet the increase in performance was large. This further suggests that surface properties play a major role in these cases.

It can be assumed that while the cellulose increases the surface area of the total sorbent, albeit with varying effect, the improvement in CO_2 capacity after cellulose loading is neither proportional to the surface area increase, nor is it proportional to the pure IL uptake and is, in fact, more likely due to the increase in surface roughness imparted by the support. Overall, as cellulose loading increases, the total sorbent uses less and less ionic liquid, meaning the SoIL is used much more efficiently. The previously inaccessible centers of the SoIL particles are now instead spread over the cellulose allowing it to capture more CO_2 per unit of SoIL used. In addition to what appears to be significantly improved surface effects, increased effectiveness at different cellulose loadings can be seen in **Table 3**: depending on the nature of the IL in question. **Table 3** shows the amount CO_2 captured per gram of SoIL within the total sorbent at different cellulose loadings.

Kinetics and Recyclability

In pressure swing systems, the kinetics associated with adsorption and desorption are very important. The faster these two processes can occur, the shorter the adsorb/desorb cycle times can be. This improves the efficiency by reducing adiabatic heat loss and further reduces the total sorbent inventory required to treat a given flow rate of gas. Previous work done using SoILs suggested that the kinetics for CO_2 capture are very favorable (Styring et al., 2016). Pure SoILs have been shown to reach their adsorption capacity in seconds and release the captured CO_2 equally as fast.

TABLE 3 | Maximum CO_2 uptake at 30 bar, as a proportion of IL present in the total sorbent.

Sorbent	Amount CO_2 adsorbed (mgCO_2/gIL)			
	Pure IL	Cellulose loading amount		
	0 wt%	70 wt%	75 wt%	80 wt%
[N_{4444}][Ac]	14.9	70.7	126.4	128.5
[N_{1888}][Ac]	28.6	55.7	120.0	74.5
[Bmim][Br]	12.3	53.7	115.2	124.5
[N_{8888}][Br]	1.7	66.0	76.8	79.0

The pure SoILs tested here have followed the same kinetic trends, all reaching saturation in less than 10 s with desorption being too quick to accurately measure. Cellulose loading did not have any substantial effect on the uptake kinetics, no matter the loading amount of cellulose used.

Sorbent stability was also tested and in **Figure 11**, the highest-capacity sorbent, N_{4444} acetate, loaded with 75 wt% cellulose, was tested through short 1 min adsorb/desorb cycles 40 times each at 15 and 30 bar with weight measurements taken for the first 10 and last 10 cycles to check for any overall changes. There are two scenarios presented: 30 bar adsorption—1 bar desorption and 15 bar adsorption—1 bar desorption. This test was carried out to demonstrate mechanical stability under different pressure loads and multiple cycles. Desorption was carried out at the same rate for each run, with the vessel slowly opened to atmosphere and then allowed to rest for 1 min. Sorbent stability can be shown to be very high under these conditions, with consistent uptake capacities reached. Note that a residual weight of CO_2 remains at the end of each desorb cycle at both pressures. This is the CO_2 that remains in the void spaces of the adsorber such as the valve

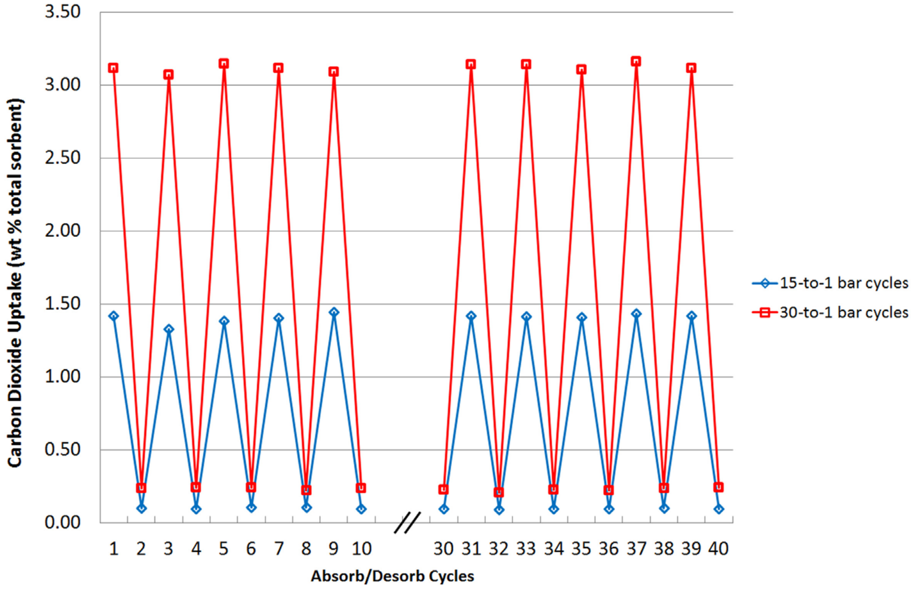

FIGURE 11 | Sorbent stability over repeated 1-min adsorb/desorb cycles at two pressures. Desorption is carried out in each case at 1 bar pressure.

assembly and piping, even after depressurization is complete. Since depressurization occurs over the same time period, the higher pressure runs have proportionately more CO_2 present as less time has passed for atmospheric diffusion. Further diffusion, a flow of nitrogen or application of vacuum for a few seconds all return the starting weight of the sample to 0.

The IL component of the sorbent is also readily recovered in high yield by filtration of a slurry of the sorbent in isopropanol. The isolated IL can then readily be reused with no detectable change in performance, allowing small synthetic batches of each IL to be used to generate a variety of cellulose loading mixtures.

CONCLUSION

It is clear that further advancements in CO_2 capture systems are needed in the near future to develop CCUS in order to help mitigate the potential problems caused by further carbon emissions. Existing state-of-the-art CO_2 capture and separation technologies suffer from high energy costs, primarily associated with the CO_2 desorption inherent in chemisorption-based TSA processes. Alternative PSA processes show many advantages in terms of both cycle speed, energy costs, and sorbent stability, due to the absence of thermal cycling. Therefore, PSA coupled with appropriate solid adsorbents would appear to be a promising alternative gas separation pathway. SoILs show good capacity and excellent adsorption rate, making them desirable for use in a PSA process. However, currently, even simple ILs have a high manufacturing cost, which reduces their attractiveness as large-scale carbon capture sorbents.

Significant reductions in amount of IL required to capture CO_2 have been demonstrated by coating inexpensive cellulose particles with thin layers of IL. In addition, surface characteristics imparted to the IL by the cellulose supports have further increased CO_2 uptake capacity. Together, these two effects may allow even expensive, specialized, and previously overlooked IL sorbents to be used more effectively. Fast sorption kinetics are observed, which results in large capture capacity per unit time when compared to conventional TSA systems, which exhibit significant temperature lag between adsorb and desorb cycles. Further research must be done to show their suitability as a post-combustion capture sorbents.

These studies were fundamental in nature, carried out with pure CO_2 and pure nitrogen. The results of these studies will be used to monitor performance of different gas mixtures ranging from blast furnace top gases at high CO_2 concentrations through to flue gas from power stations down to the parts per million concentrations of atmospheric CO_2. By determining the fundamental data, we are now in a position to test these on low concentration simulated and real waste gas streams.

AUTHOR CONTRIBUTIONS

Each author played a major role in the development of the work and writing the manuscript. PS is the research supervisor and group leader. DGR is a postgraduate research student who undertook the work as part of his Ph.D. programme. GRMD is a postdoctoral research associate who was involved in all aspects of experimentation.

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Integrated CO_2 Capture and Utilization Using Non-Thermal Plasmolysis

Matthew Moss*, Daniel G. Reed, Ray W. K. Allen and Peter Styring

UK Centre for Carbon Dioxide Utilisation, Department of Chemical and Biological Engineering, University of Sheffield, Sheffield, United Kingdom

In this work, two simple processes for carbon dioxide (CO_2) such as capture and utilization have been combined to form a whole systems approach to carbon capture and utilization (CCU). The first stage utilizes a pressure swing adsorption (PSA) system, which offers many benefits over current amine technologies. It was found that high selectivity can be achieved with rapid adsorption/desorption times while employing a cheap, durable sorbent that exhibits no sorbent losses and is easily regenerated by simple pressure drops. The PSA system is capable of capturing and upgrading the CO_2 concentration of a waste gas stream from 12.5% to a range of higher purities. As many CCU end processes have some tolerance toward impurities in the feed, in the form of nitrogen (N_2), for example, this is highly advantageous for this PSA system since CO_2 purities in excess of 80% can be achieved with only a few steps and minimal energy input. Non-thermal plasma is one such technology that can tolerate, and even benefit from, small N_2 impurities in the feed, therefore a 100% pure CO_2 stream is not required. The second stage of this process deploys a nanosecond pulsed corona discharge reactor to split the captured CO_2 into carbon monoxide (CO), which can then be used as a chemical feedstock for other syntheses. Corona discharge has proven industrial applications for gas cleaning and the benefit of pulsed power reduces the energy consumption of the system. The wire-in-cylinder geometry concentrates the volume of gas treated into the area of high electric field. Previous work has suggested that moderate conversions can be achieved (9%), compared to other non-thermal plasma methods, but with higher energy efficiencies (>60%).

Keywords: CO_2, capture, utilization, pressure swing, plasma, CO

Edited by:
Renato Baciocchi,
University of Rome Tor Vergata, Italy

Reviewed by:
Richard Van De Sanden,
Dutch Institute for Fundamental Energy Research, Netherlands
Rafael Mattos Dos Santos,
Sheridan College, Canada

****Correspondence:***
Matthew Moss
mmoss1@sheffield.ac.uk

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INTRODUCTION

Research into carbon dioxide capture and recovery for geological storage (CCS) as a greenhouse mitigation technique has seen a rise in interest over recent years. CCS is a potential mitigation option and could lead to significant reduction of greenhouse gas emissions in the electricity supply system, however, to effectively reduce global CO_2 emissions this technology must be used in conjunction with other methods (Viebahn et al., 2007; Pehnt and Henkel, 2009; Pires et al., 2011). Rather than treating CO_2 as a waste, the ideal solution would be to treat it as a commodity and utilize the ample quantity of CO_2 available for the production of marketable products, or for use in applications where the CO_2 feedstock is generated from fresh sources (Edwards, 1995; Olah et al., 2009; Peters et al., 2011). There are numerous chemical reactions for synthesizing organic molecules from CO_2, some of which are shown in **Figure 1**.

Regardless of the CO_2 end use, be it CCS or carbon capture and utilization (CCU), in most cases the CO_2 must first be captured. The capture step contributes to 75% of the overall cost if CCS is to be used and will increase electricity production cost by around 50%, so finding the most efficient capture method is extremely important (Yang et al., 2008). Targeted large point source emitters such as power stations would benefit from the convenience of a post-combustion capture process due to the ease of retrofitting. Technologies such as cryogenics, membrane separation, and algal-based systems are all potential options; however, they are currently in their infancy and not considered economically viable at this stage (Yang et al., 2008; MacDowell et al., 2010; Bhown and Freeman, 2011). The current state of the art technology for CO_2 capture is by amine absorption in a temperature swing absorption (TSA) process, but this is not without its drawbacks. High sorbent regeneration costs and sorbent losses due to evaporation and degradation mean that further advancements are required. TSA process generally produce a humid stream of pure CO_2 which will require drying before it can be stored or utilized as an intermediate; this drying step is also very energy intensive. More recent research into pressure swing adsorption (PSA) for CO_2 capture using solid sorbents has generated promising results (Ho et al., 2009; Wang et al., 2011; Grande, 2012). PSA has many advantages over traditional systems in that it has a much smaller plant footprint, can accept changing feed compositions and is a stop–start technology making it very flexible with regard to the plant that is supplying it.

Upon capturing CO_2, the main challenge facing utilization is overcoming its thermodynamic stability to form further products. Reactions of CO_2 generally require elevated temperatures and pressures to bring about a reaction and thus can incur large energy penalties, reducing the profitability of the CO_2-derived products.

Centi and Perathoner (2009) have stated that although there are many options to utilize CO_2, including but not limited to, mineralization, chemical production, fuel production, carbonation, and microalgae, the underlying problem is that often these processes require a pure or high purity CO_2 feedstock before conversion can take place. All technologies have their own advantages and disadvantages, but few have successfully made the leap from small to industrial scale. Mineralization is the one of the most widely adopted methods of CCU with an estimated 50 Mt/year of CO_2 used in the production of inorganic carbonates in 2013, according to Aresta et al. (2013). Combined with mineralization, urea production together accounted for over 90% of all utilized CO_2 in 2013; however, they represent a small dent in the global emissions of around 35 Gt/year. It is clear that CO_2 can be used to create all of the products shown in **Figure 1** but cheaper, less energy intensive alternative processes are currently more favorable. If a low energy capture and utilization process

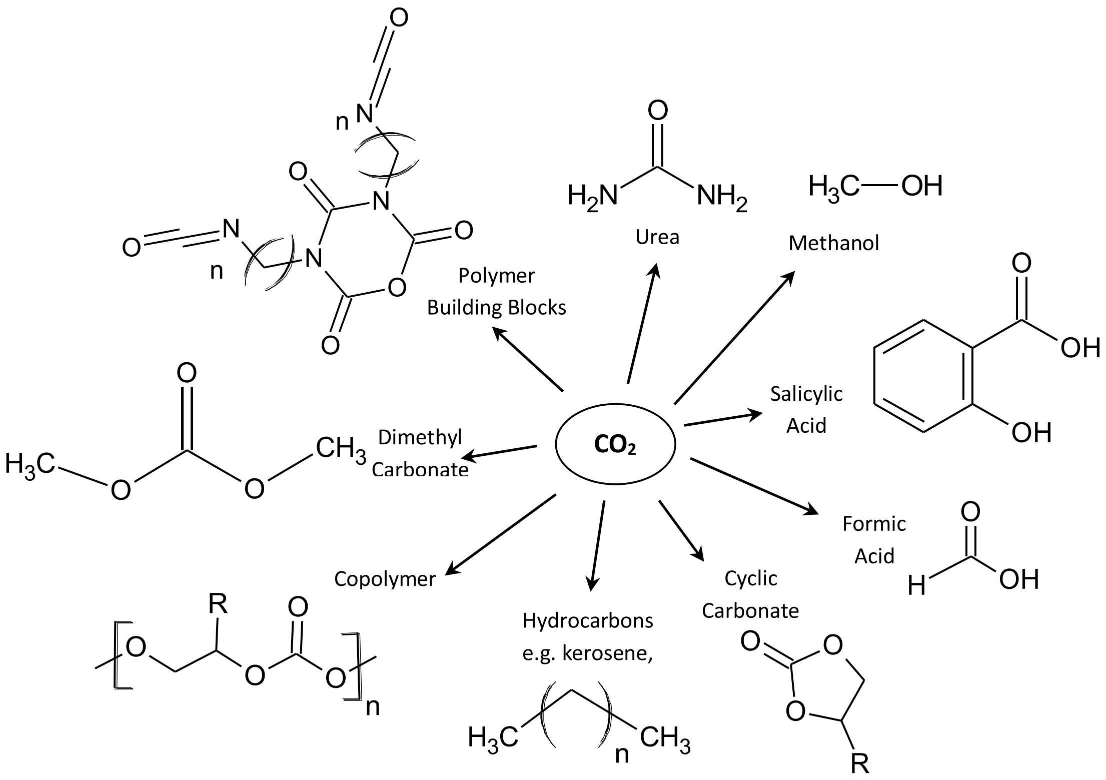

FIGURE 1 | An overview of potential pathways for use of CO_2 as a C1 building block [adapted from Styring et al. (2011)] (CO2Chem Media & Publishing have granted permission for the adaptation of this image for use in this study).

could be found, with the added advantage of being able to turned on and off at will, then surplus renewable energy could be used to power the system as suggested by Goede (2015). If this work, which targets CO as its product, can produce an activated form of CO_2 with minimum energy inputs it goes a long way to addressing the high energy costs associated with CCU.

To overcome the energy barrier to react CO_2 an alternative is to first reduce CO_2 to carbon monoxide (CO); a more reactive molecule. The energy barrier for this reduction can be reduced through the use of non-thermal plasma. Under thermal conditions temperatures in excess of 3,000 K are required to split CO_2 into CO. However, in non-thermal plasma only the electron temperature in the gas is elevated so the reaction can be performed at atmospheric temperature and pressure (Fridman, 2008). Plasma offers an advantage over other utilization methods as it relatively low energy cost to activate CO_2. It is also highly flexible and has been proven to accept a wide range of gas mixtures with conditions tunable to match the provided load. In conjunction with PSA, plasma technology can be easily switched on and off when in demand rather than operate as a continuous process, although it is capable also of doing this. Various studies into CO_2 reduction in non-thermal plasmas have been conducted in different plasma systems (Savinov et al., 2002; Indarto et al., 2007; Aerts et al., 2012; Bogaerts et al., 2015; van Rooij et al., 2015; Sun et al., 2017). However, to-date, there have been no literature reports of any integrated capture and utilization processes detailed in their published work.

To the best of our knowledge, this new whole system approach to CCU has never been reported in the literature and combines together two highly promising technologies that have demonstrated in previous work to be low in energy costs. On paper, both technologies are individually suited to accepting a variable feed composition and intermittent load (which could match fluctuating energy supply if renewable energy was used). Although, in this work, both are currently operated on a small scale, they have good potential for scale-up to process a large quantity of gas. Corona discharge is already established on an industrial scale in electrostatic precipitators, and the PSA system is expected to scale linearly with size; however, further investigation of the ability to manufacture sorbents on large scale must be undertaken (Roth, 2001). This work aims to provide a foundation for future CCU processes and advocates a whole systems approach to assessing these technologies, paying close attention to the purity of CO_2 required for each utilization step.

In this work, a high PSA system is used to first capture, then upgrade the composition of flue gas to high purity. After capture the CO_2 is released and passed through a pulsed corona discharge reactor wherein electron initiated dissociation converts the CO_2 to CO, other products are formed but as the aim of this paper is to provide a proof of concept the detailed kinetical pathway is not discussed further. Using non-thermal plasma technology, this process aims to provide a source of non-fossil fuel derived carbon for chemical feedstocks.

METHOD

Pressure Swing Adsorption

First, a bench scale single bed PSA system was used to extract CO_2 from a simulated flue gas stream containing 12.5% CO_2 and 87.5% N_2. This composition sits well within the range expected as an output from coal fired power stations, for example, found in the UK (Naims, 2016; von der Assen et al., 2016). This PSA system makes use of a cheap and robust solid sorbent, which is based on previously reported poly-ionic liquid sorbents by this group (Supasitmongkol and Styring, 2010; Dowson et al., 2016), which selectively adsorbs CO_2 on pressurization of the gas stream. As the pressure is released, the N_2 and CO_2 desorb from the sorbent surface at different rates, thus creating two separate streams; one rich in N_2 followed by one rich in CO_2. An experimental diagram of the process is shown schematically in **Figure 2**. High-pressure adsorption experiments were carried out in a bespoke stainless steel packed-bed adsorber column constructed using Swagelok™ 1/2″ tubing 100 mm in length. A cross section of which is shown in **Figure 3**. The column is compression sealed and can withstand pressures up to 200 bar. The sorbent is packed inside with quartz wool filters used to avoid sorbent carry over during testing.

Flue gas streams were pressurized to 15 bar and allowed to adsorb for 15-min cycles. Full methodology was as described previously for solid ionic liquid sorbents (Dowson et al., 2016). A two-stage depressurization of the adsorber leads to two gas

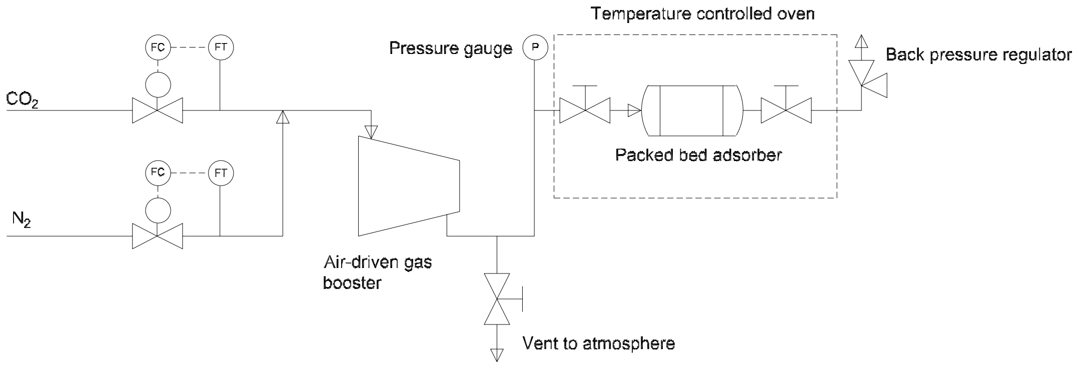

FIGURE 2 | Pressure swing adsorption experimental rig used for measuring sorbent capacity, rate, and separation potential.

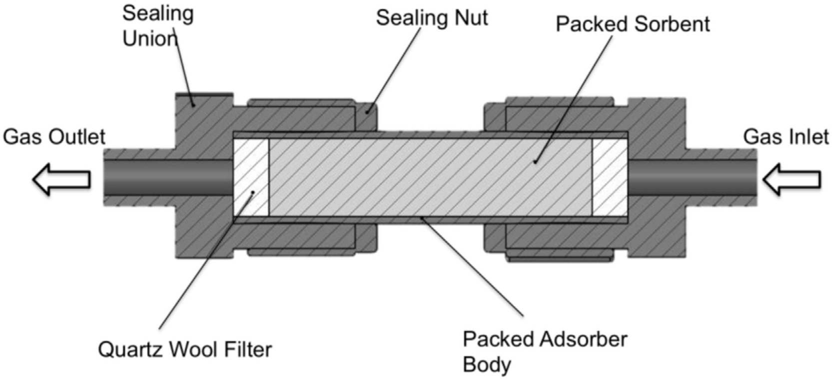

FIGURE 3 | Cross-sectional view of the packed-bed adsorber used for CO_2 separation from simulated flue gas streams.

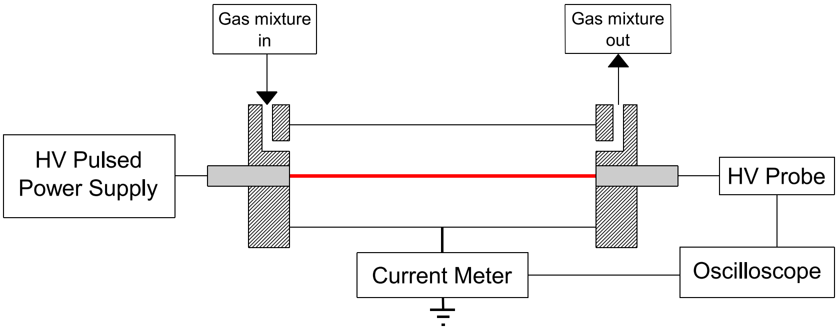

FIGURE 4 | Pulsed plasma experimental schematic.

streams. This CO_2-rich stream would be sent directly to the corona reactor for reduction to CO.

Pulsed Corona Discharge

A simplified experimental diagram of the downstream plasma utilization section is presented in **Figure 4**. Experiments were performed at atmospheric pressure and ambient temperature. The reactor used was a wire-to-cylinder corona discharge reactor constructed using a stainless steel cylinder as the outer ground electrode (R = 17 mm), and a narrow tungsten wire as the inner live electrode (r_0 = 125 μm). The total reactor volume was approximately 300 cm^3.

Plasma ignition was provided by means of a high voltage pulse generator (NPG18-3500N Megaimpulse Ltd.) (Lyublinsky et al., 2013). Electrical measurements were taken using a high voltage probe (Tektronix P6015A) connected to the live electrode to measure the voltage and a wide band current transformer (Pearson 6595) to measure the current. These two parameters enabled the energy and power used during the utilization process to be calculated. The unique aspect of this power supply is the ability to send a series of short pulses approximately 40 ns in width over a microsecond at a repetition rate that can be varied up to 3,200 Hz. These short pulses remove the need for a dielectric layer, prevent gas heating (thus increasing the efficiency of CO_2 splitting), and reduce the possibility of plasma arc development.

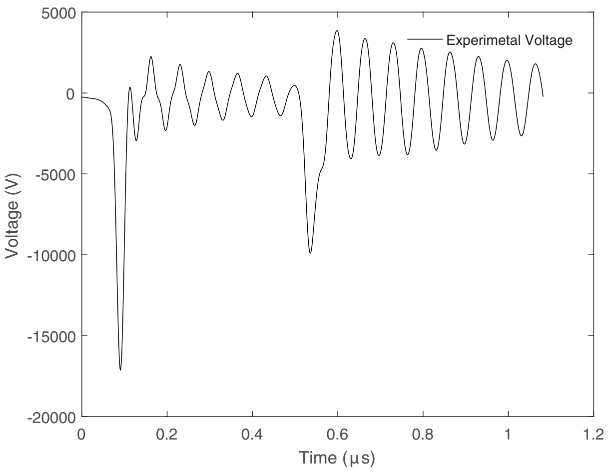

FIGURE 5 | Typical signal of input voltage waveform.

The applied voltage signal is shown in **Figure 5**. It is characterized by a primary short pulse of very high amplitude proceeded by a series of smaller short pulses of lower amplitude. The corresponding output current is also shown in **Figure 6**.

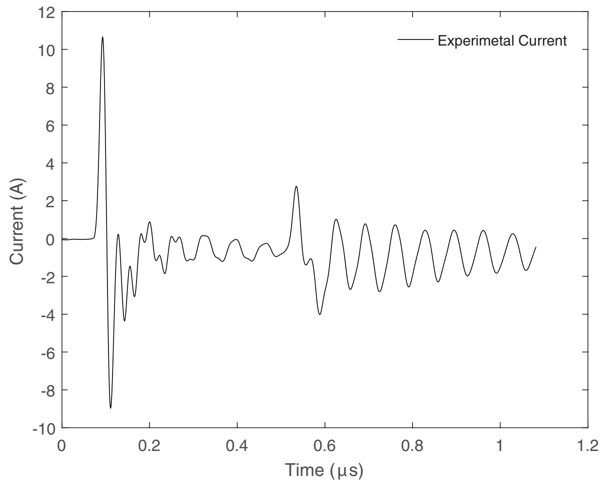

FIGURE 6 | Typical output current waveform.

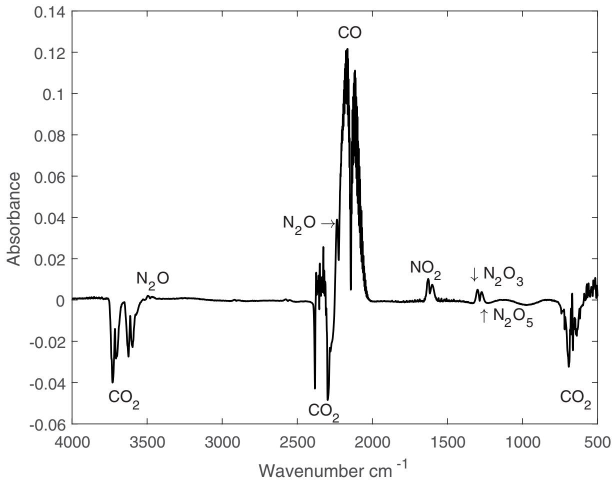

FIGURE 7 | Sample Fourier transform infrared absorbance spectrum subtracted from background spectrum for 50:50 CO_2:N_2 mixture.

Following capture from the PSA rig, the CO_2-rich flue gas was passed to the pulsed plasma reactor wherein it was subjected a corona discharge for varying residence times. The residence time was altered by changing the gas flow rate (Q) into the plasma reactor between 100 and 400 mL/min by using mass flow meters (Bronkhorst) which corresponds to residence times of 37.5, 75, and 150 s. Gaseous products from the corona reactor were measured by means of a Fourier transform infrared (FTIR) spectrometer (Varian 660-IR Agilent) post discharge. No liquid products were observed. A typical absorbance spectrum is shown in **Figure 7**. The method used to quantify the production of CO was performed by calibrating the FTIR with known quantities of CO to generate a calibration curve. Before plasma ignition a background spectrum of the CO_2 or CO_2/N_2 mixture was taken. After being exposed to the plasma, another spectrum was taken, and the background spectrum subtracted to determine the absolute IR absorbance. This absorbance was then compared to a known value along the calibration curve, and the quantity of CO was found. The main products detected were CO, NO, NO_2, N_2O, N_2O_5, and N_2O_3 with CO the dominant product. As the most important species as far as utilization is concerned, only the conversion of CO_2 to CO was calculated. In addition, the values of other products remained in the parts per million range so were viewed as minor importance. Consideration into separation of all the product gases requires further work and is outside the scope of the article. This is in contrast to the works of Heijkers et al. (2015) who observed effective conversions up to 15% of N_2 to other products, although in that work the specific energy input (SEI) peaked at 7.1 eV/molecule compared to the maximum of 0.43 eV/molecule used in this work.

To evaluate the effectiveness of CO_2 utilization, two important and commonly used parameters will be deployed. These are the conversion factor (X) and energy efficiency (η) as defined by Eqs 1 and 2, respectively. The conversion is defined as the change in CO_2 concentration over the initial CO_2 concentration. As the production of other carbon containing species is negligible, this can be said to approximate the CO yield. From this, effective conversion (X_{eff}), which is also used in literature, can be found as a product of X and the relative CO_2 content in the feed. For example, if a gas contains 80% CO_2, the conversion is multiplied by 0.8.

$$X_{\text{abs}}(\%) = \frac{[\mathrm{CO_2}]_{\text{in}} - [\mathrm{CO_2}]_{\text{out}}}{[\mathrm{CO_2}]_{\text{in}}} \times 100 \approx \frac{[\mathrm{CO}]_{\text{out}}}{[\mathrm{CO_2}]_{\text{in}}} \times 100 \tag{1}$$

$$\eta\,(\%) = \frac{\Delta H_R}{E_{\text{CO}}} \times 100 \tag{2}$$

The energy efficiency is defined as a ratio between the dissociation enthalpy of CO_2 (ΔH_R) as shown in Eq. 3 to the energy penalty to produce one molecule of CO (E_{CO}).

$$\mathrm{CO_2} \rightarrow \mathrm{CO} + \frac{1}{2}\mathrm{O_2},\ \Delta H_R = 2.9\ \text{eV/molecule} = 283\ \text{kJ/mol} \tag{3}$$

Equation 2 is usually expressed in the literature in terms of the SEI, or the ratio of discharge power to the gas flow rate (SEI = W/Q) (J/cm^3) (Eq. 4). Discharge power is defined as the total energy supplied over the residence time ($W = E/t_g$) (J/s). For calculation of total energy, see Eq. 6.

To calculate E_{CO} (J), the total energy (E) must be calculated during the residence time of the gas as a ratio to the number of CO molecules that have been subjected to corona discharge (N_{CO}),

$$E_{\text{CO}} = E / N_{\text{CO}} \tag{4}$$

where N_{CO} can be expressed as follows:

$$N_{\text{CO}} = X_{\text{eff}}[\mathrm{CO_2}]_{\text{in}} Q\, t_g. \tag{5}$$

The total energy deposited is calculated as shown in Eq. 6. It is the product of the energy applied during a single pulse (E_{pulse}) (J), the gas residence time (t_g) and the pulse repetition frequency

(f) (Hz). E_{pulse} can be further calculated from the integral of the applied voltage and current over the duration of a pulse (τ).

$$E = ft_g E_{\text{pulse}} = ft_g \int_0^{\tau} V(t) I(t) dt \tag{6}$$

From previous work (Moss et al., 2017), it is known that the shape of the applied voltage waveform heavily influences the energy deposited within the plasma reactor and it can affect the chemical kinetic pathway of CO_2 utilization. Under all experimental conditions, the repetition frequency was fixed at 1,700 Hz, as higher values led to instabilities in the discharge, increasing the temperature of the gas and thus reducing the energy efficiency of utilization. In this work, the energy deposited in the gas was altered by modifying the residence time of the gas only and estimated to be between 1 and 2 mJ across all gas mixtures.

COUPLING OF THE TWO PROCESSES

Bringing the two processes together to create a single utilization system is a simple matter with only the addition of an intermediate storage vessel between the two systems. The proposed system is shown schematically in **Figure 8**.

As separate systems, these two processes effectively work as stop–start technologies, i.e., they can readily be turned on and off. Joining them into a continuous process does not change this and allows the overall system to be highly operationally flexible. Not only operational time but also flexibility is provided in the form of the feed gas accepted into the process. The PSA system can accept variable feed flow rates and compositions with little effect to the process; similarly, the corona reactor can accept various feed flow rates and compositions while still effectively producing the desired product; albeit at the cost of varying separation. The addition of an intermediate storage vessel between the two systems is required to act as a buffer for the cyclic nature of the PSA product stream, thus allowing a constant feed to the corona reactor to be maintained.

RESULTS AND DISCUSSION

Outputs from the Capture Process

To generate the product streams for the corona reactor, the PSA system uses a poly-ionic liquid solid sorbent, which allows separation of CO_2 from a simulated flue gas stream due to the difference in desorption rate of CO_2 and N_2 from the sorbent. N_2 is desorbed instantly, whereas CO_2 is held for longer periods of time giving a clear separation of the two gas streams. Although the exact mechanism of this desorption behavior is not fully understood, the physical nature of the adsorption in this case leads to weak physical interactions with the CO_2 molecule. Although there is some interaction with N_2, it is almost negligible and decreasing the system pressure fully reverses it, allowing almost instantaneous release of N_2 from the system. It is likely that CO_2 desorption rate is a function of the system pressure, and as the pressure drops, the weak interactions formed between the molecules and the surface of the sorbent are continually broken as the pressure is reduced with the most weakly bound molecules leaving the system first. Desorption rate was determined for each gas individually by

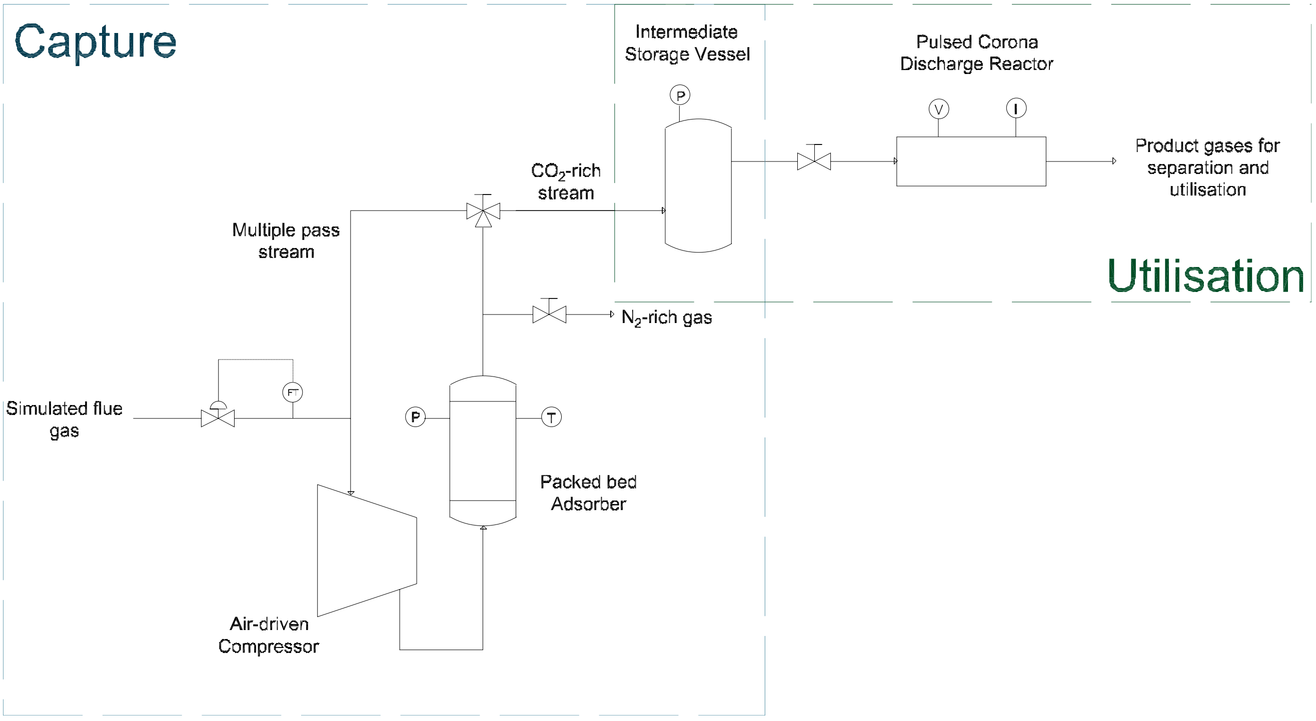

FIGURE 8 | Proposed system for integrated CO_2 capture and utilization.

first allowing gas adsorption for 15 min at 15 bar. Previous work (Dowson et al., 2016) has shown that after this 15-min period, the sorbent will be fully saturated at 100% and will adsorb no more as shown in **Figure 9**. In fact, adsorption rates for some of the ionic liquid sorbents were found to be mere seconds. The pressure was then released from the adsorber and the sorbent weight was tracked until a steady state was reached and desorption was completed.

As can be seen from **Figure 10** during certain points of the desorption step, both gasses will be released at the same time therefore, after one pass, it is clear that a 100% stream of both N_2 and CO_2 cannot be achieved. Further passes would be required to

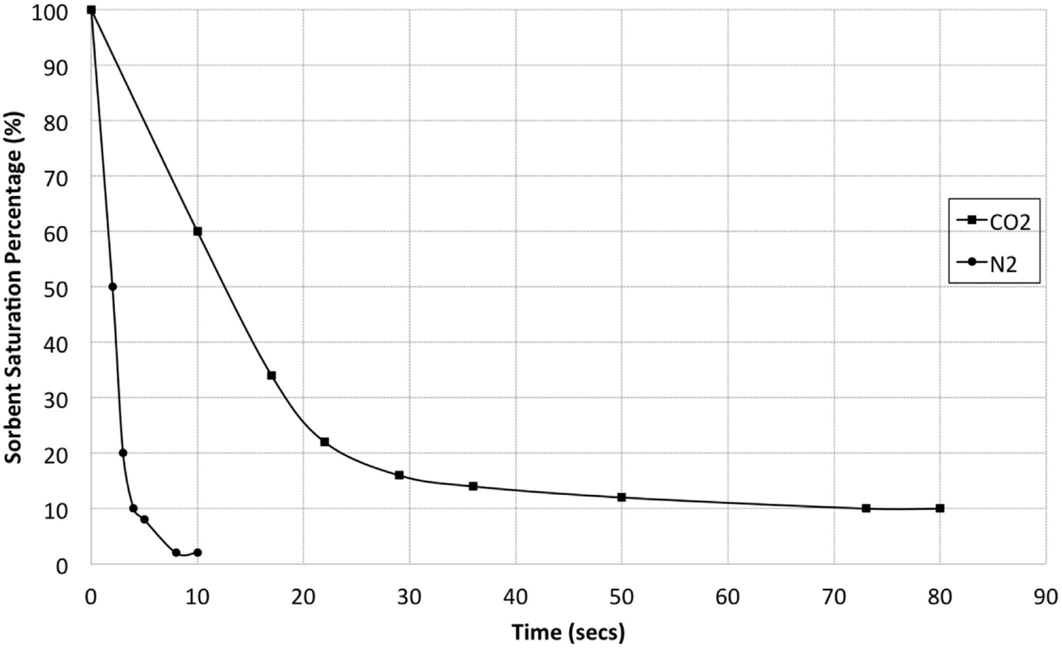

FIGURE 9 | Rate of desorption for carbon dioxide and nitrogen from the sorbent over time during a single pressure drop from 15 bar down to 1 bar.

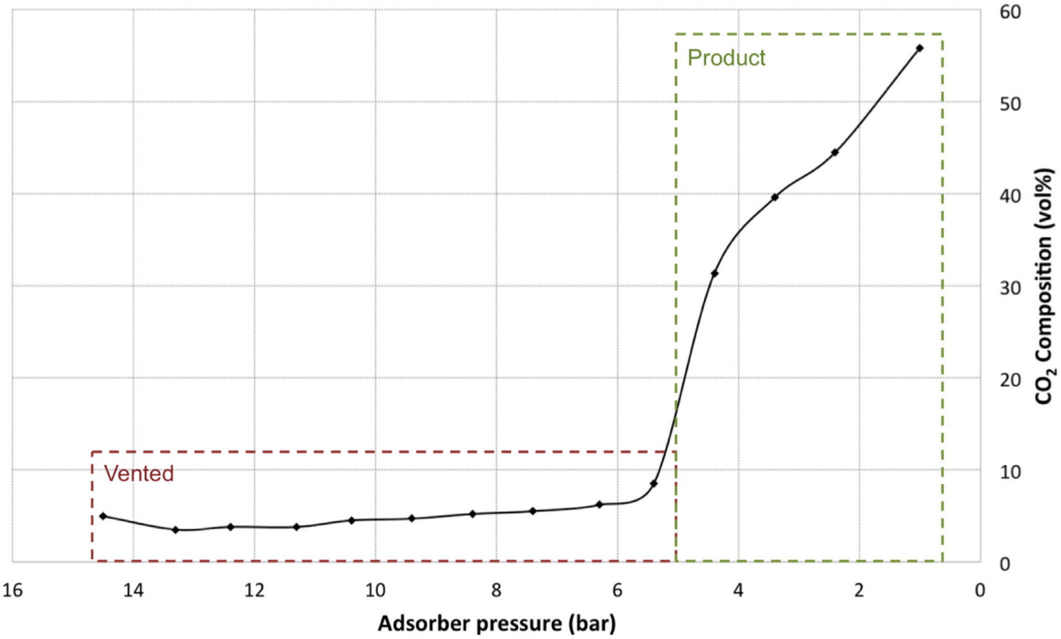

FIGURE 10 | CO_2 composition at the adsorber outlet with a gradual gas desorb of 50 mL/min with pressure dropping from 15 to 1 bar with an initial starting CO_2 concentration of 12.5%.

gradually increase the CO_2 concentration to higher percentages. It is also thought that the instantaneous desorbing N_2 will in fact pull some of the weakly bound CO_2 with it as it flows through the packed bed. To determine the CO_2 composition of the gas in the outlet, a mixed gas stream of 12.5% CO_2 and 87.5% N_2 was produced using Bronkhorst mass flow controllers. This gas mixture was then pressurized using a Midwest Pressure Systems 40 series air driven gas booster to 15 bar and left to adsorb for 15 min with the reactor held at a steady temperature of 25°C. The pressure within the adsorber was then released gradually using a JASCO MODEL BP-1580-81 programmable electronic back pressure regulator with a gas flow rate of approximately 50 mL/min and allowed to flow through a COZIR Sprint IR inline infrared sensor to determine the CO_2 composition.

These initial tests show that there are two distinct stages within the pressure drop, as the pressure drops from 15 down to approximately 5 bar, the CO_2 concentration is low and N_2 desorption dominates, this stage would is vented as a "waste" gas. At 5 bar, there is a sharp gradient shift as CO_2 starts to desorb, this stage is product gas. The peak concentration of the product gas is around 55% CO_2 with an average composition of around 44% CO_2 in the total volume of gas released. This product gas can then be sent to the corona reactor directly, or can be recycled for a second pass of the adsorber. **Figure 11** shows measured gas compositions with ranging CO_2 inputs and outputs to show the flexibility of the system. To generate these data, the pressure was dropped instantaneously using the back pressure regulator to mimic the two stages previously mentioned allowing for a combined adsorption/desorption cycle time of around 5 min to be achieved. The output results shown are the average composition from stage 2 of the pressure drop.

Higher concentrations of product gas were obtained by doing multiple passes of the packed-bed adsorber. It is shown that with some optimization, a product output over 90% CO_2 could be achieved with just two passes of the adsorber if the utilization system required it.

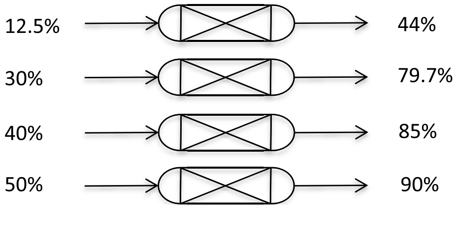

FIGURE 11 | Various composition range inputs and outputs from the pressure swing adsorption adsorber.

Results from Pulsed Corona Reactor

Figure 12 shows the absolute and effective CO_2 conversion produced during pulsed corona discharge against the gas residence time for various gas mixtures of CO_2 and N_2. It is evident that for all gas mixtures increasing, the residence time has a positive effect on the conversion. Initial observation suggests that there is no immediate correlation between gas mixture and conversion; however, it can be seen that a small quantity of N_2 enhances CO_2 conversion, but further increase leads to a reduction in conversion. Examining effective conversion shows raw flue gas (12.5% CO_2) and 100% CO_2 perform the worst across all gas mixtures, which is highly beneficial for the proposed process as it proves raw flue gas to be unsuitable for utilization and that pure CO_2 is not required. Ideally, an upgraded flue gas feed is most suitable in terms of conversion for this non-thermal plasma system, which is exactly what the PSA system used in this work provides.

Peak effective conversions of approximately 8% were found in an 80% CO_2/20% N_2 mixture. Snoeckx et al. (2016) observed a similar effect using a dielectric barrier discharge (DBD) plasma reactor although the reported conversions were slightly higher, peaking at 12% for a 25% CO_2/75% N_2 mixture. However, it should be noted that the conversions reported in that work were achieved at significantly higher SEIs approximately one order of magnitude higher than this work. Transfer of energy from vibrationally excited N_2 has been proven to be effective in enhancing the conversion of CO_2 in DBD systems and it is theorized that the same effects are exhibited in a pulsed corona, although the extent of this requires further investigation. Pontiga et al. (2011) also investigated mixtures of CO_2 and N_2 in a DC corona discharge. However, in that work, the conversion to CO was only in the order of a few percent. They attributed the lower conversion upon increasing N_2 concentration to the formation of nitrous oxides (NO_x), which inhibit the formation of CO through reactions such as Eq. 7, which could prove a limiting factor.

$$NO_3 + CO \rightarrow NO_2 + CO_2 \tag{7}$$

Heijkers et al. (2015) observed a large conversion of N_2, in addition to CO_2, in a microwave plasma. N_2 conversions up to 15%, at peak SEI of 7.1 eV/molecule, was observed, which is significantly higher than those reported in this work where the total NO_x products formed was in the order of hundreds of parts per million. This observation can be attributed to the lower specific input energy used during pulsed corona discharge operation which is typically one order of magnitude lower than other plasma technologies. As less total energy is applied the amount available to convert N_2 is also less; this combined with a higher energy threshold to ionize N_2 over CO_2 results in low NO_x production.

Figure 13 shows the energy efficiency of CO_2 conversion under plasma conditions as a function of the SEI. For all mixtures, except 60% CO_2/40% N_2, the efficiency decreases as the SEI is raised, i.e., the residence time is increased. As demonstrated in previous work (Moss et al., 2017), the efficiency is substantially higher than other reported works at low SEIs, and this remains the case in CO_2/N_2 mixtures, peaking at approximately 90% albeit with a large error. Again compared to the works of Snoeckx et al. (2016), the highest reported efficiency was 13% in a 75% CO_2/25% N_2 mixture. It is noted that the gas mixture containing 60% CO_2 exhibits a different trend compared to the others and this is attributed to a different kinetic pathway of reduction but to validate this would require an in-depth kinetical analysis.

Taking the case of pure CO_2, the energy efficiency is again much higher than other works with a maximum around 35% being achieved at the lowest SEI/longest residence time. Except

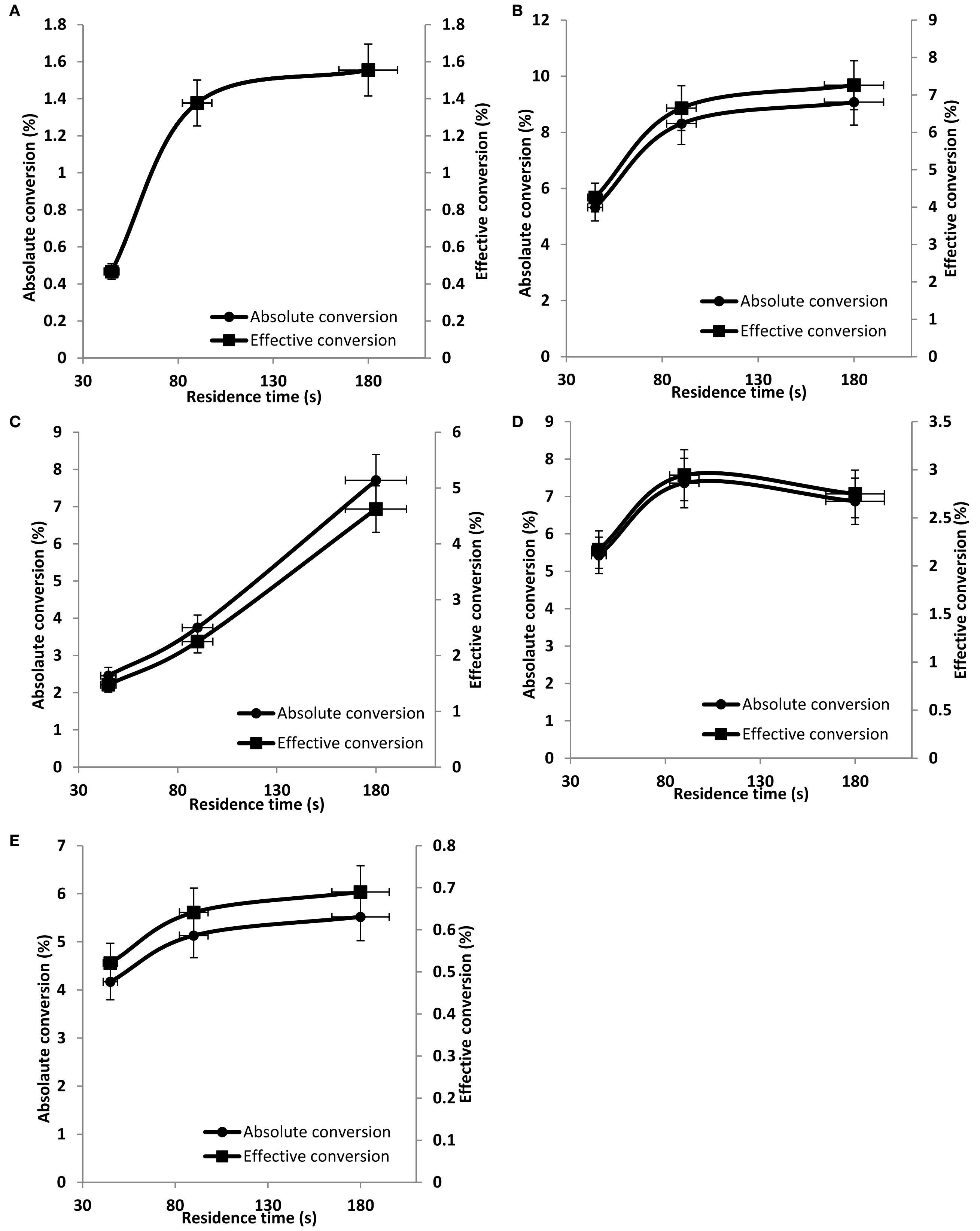

FIGURE 12 | Effec tive and absolute conversion of CO_2 to CO as a function of residence time: **(A)** 100% CO_2, **(B)** 80% CO_2, **(C)** 60% CO_2, **(D)** 40% CO_2, and **(E)** 12.5% CO_2.

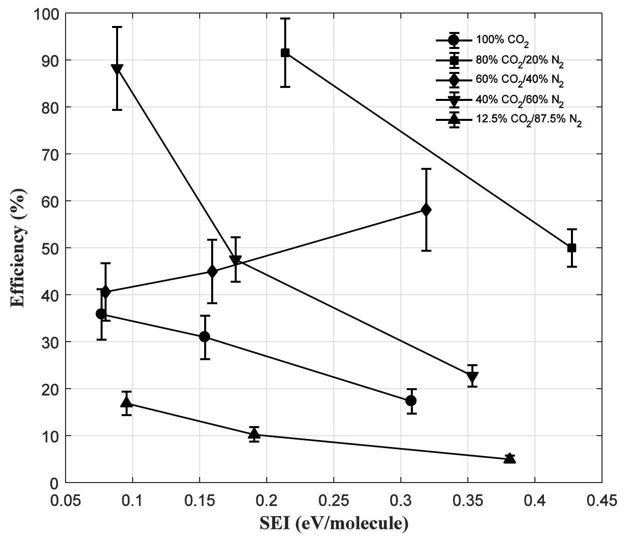

FIGURE 13 | Energy efficiency as a function of specific energy input for different gas mixtures (1 eV/molecule = *ca.* 3.933 J/cm^3 under standard temperature and pressure).

for raw flue gas, N_2 addition has a positive effect on efficiency, and at higher values of SEI, as the N_2 content is decreased the efficiency increases. It is theorized that up to 20% N_2 content in the gas mixture has a positive effect on CO_2 conversion and efficiency owning to the formation of N_2 metastables, which are effective at transferring energy to lower energy states of CO_2. Further increase in N_2 quenches these metastables, and the beneficial effect is no longer observed. Furthermore, as the gas content contains more N_2, a higher energy requirement is needed to ignite and sustain the plasma, and more energy is directed toward reactions of N-containing species and diverted away from CO_2 dissociation. This effect becomes dominating as more N_2 is added as demonstrated in other works (Heijkers et al., 2015).

The main reason for higher efficiencies being achieved has been stated in previous work and proven by means of numerical modeling (Moss et al., 2017). The unique form of the applied voltage pulse, characterized by an initial large amplitude pulse followed by a series of smaller amplitude pulses, allows a two-step pathway of CO_2 utilization to be established. During the high amplitude pulse, ionization and vibrational excitation of the gas are the dominant reactions; however, during the series of smaller amplitude pulses, dissociation of neutral and vibrationally excited CO_2 reactions dominates, which is the most direct route to produce CO. In contrast to other works, the role of vibrational excitation and subsequent dissociation is not expected to play a major role in the formation of CO; as the relaxation times of such species are shorter than the inter-pulse duration. N_2 vibrational species may play a role in enhancing CO_2 conversion as shown in the literature but without a detailed kinetic model of this type of plasma discharge it cannot be conclusively stated. Small quantities of N-containing and O-containing molecules are expected to lower the overall conversion and efficiency as energy will be diverted toward reactions of these components but as the quantity of these is small their effects on conversion and efficiency are minimal.

CONCLUSION

Carbon dioxide capture by pressure swing absorption and conversion by non-thermal plasma has been demonstrated to be a viable process for the production of CO albeit on a small scale, a valuable precursor to many chemicals and key feedstocks for the chemicals industry. CO_2 can be captured from raw flue gas and upgraded to *ca.* 40% purity in only one stage and fed into the corona discharge reactor to achieve approximately 7% absolute conversion to CO across a range of feed rates and with an average energy efficiency of 54%. Alternatively, the upgraded flue gas can enter a second stage in the capture process and be further refined to around 80%. This high purity CO_2 when fed into the corona reactor is capable of producing a product gas containing approximately 8% CO with an average energy efficiency of 71%.

The main advantage over this route to CO, although conversions are relatively low and even for plasma technology this conversion is average but the fact that linking the two processes together allows a variable waste gas stream to be captured and then upgraded to obtain a higher concentration of CO_2 with some conversion to a useful product. For the utilization stage, it has been discovered that, unlike other technologies, a pure CO_2 feed is not only not required but it is unfavorable. Flexibility of feed gases and flexible operating conditions are an additional benefit over most other utilization technologies as they favor continuous/continuous-batch operation. It should be remembered that low conversions are common in the process industries and simply require effective recycling of the unreacted reagents to improve performance. The Haber–Bosch process, which is the main global route to ammonia production, is a prime example of this approach.

Although there needs to be consideration for the separation of CO from the product gas, this process suggests that a low energy route to CO may be achievable. Both the PSA process and pulsed corona reactor are non-intensive in terms of energy usage; however, for the process to be realized on a larger scale, recycling of the unreacted CO_2 in the product gas must be deployed. Membrane separation technology offers a potential solution to this problem.

There will always be concerns about how the effects of impurities such as SO_x and water vapor will have on capture and utilization processes and the sensitivity of the system toward this. Future work examining these effects must be completed before the process can truly be considered for industrial application. The scale-up to pilot scale of these technologies is another step to overcome before a realistic, industrially viable process can be envisaged. It is envisaged that for the PSA system, the scale-up is linearly related to the size of the equipment; however, consideration into the feasibility of manufacturing ionic liquid sorbents on large scales must be undertaken. To successfully scale up the utilization step, it is likely that the corona reactor would employ a modular configuration of multiple reactors; however, it should be noted that increasing the reactor size would exponentially increase the energy costs.

Although this process shows promise, in terms of a complete capture and utilization system, careful consideration into the recycling and separation of the product gas and a techno-economic assessment of the whole process must be performed before larger scales can be achieved. However, it provides a useful conceptual process for forming a low energy route to a highly energetic CO product from a wide range of sources, containing various CO_2 concentrations, including the potential for biogas conversion.

AUTHOR CONTRIBUTIONS

MM was a research student working on the 4CU project and postdoctoral researcher on a CO2Chem Seedcorn Grant and specialized in plasmolysis. DR was a research student working on the 4CU project and specialized in PSA for carbon dioxide capture. PS and RA were research supervisors and investigators on the 4CU project. All the authors contributed to the writing of the paper.

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frontiers in Energy Research

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The Role of Solvent Polarity on Low-Temperature Methanol Synthesis Catalyzed by Cu Nanoparticles

*Christian Ahoba-Sam[1], Unni Olsbye[2] and Klaus-Joachim Jens[1]**

[1] Department of Process, Energy and Environmental Technology, University College of Southeast Norway, Porsgrunn, Norway, [2] Department of Chemistry, University of Oslo, Oslo, Norway

Methanol syntheses at low temperature in a liquid medium present an opportunity for full syngas conversion per pass. The aim of this work was to study the role of solvents polarity on low-temperature methanol synthesis reaction using eight different aprotic polar solvents. A "once through" catalytic system, which is composed of Cu nanoparticles and sodium methoxide, was used for methanol synthesis at 100°C and 20 bar syngas pressure. Solvent polarity rather than the 7–10 nm Cu (and 30 nm Cu on SiO_2) catalyst used dictated trend of syngas conversion. Diglyme with a dielectric constant (ε) = 7.2 gave the highest syngas conversion among the eight different solvents used. Methanol formation decreased with either increasing or decreasing solvent ε value of diglyme (ε = 7.2). To probe the observed trend, possible side reactions of methyl formate (MF), the main intermediate in the process, were studied. MF was observed to undergo two main reactions; (i) decarbonylation to form CO and MeOH and (ii) a nucleophilic substitution to form dimethyl ether and sodium formate. Decreasing polarity favored the decarbonylation side reaction while increasing polarity favored the nucleophilic substitution reaction. In conclusion, our results show that moderate polarity solvents, e.g., diglyme, favor MF hydrogenolysis and, hence, methanol formation, by retarding the other two possible side reactions.

Keywords: methanol synthesis, low temperature, solvent polarity, "once through" reaction, Cu, nanoparticle size, syngas conversion

Edited by:
Peter Styring,
University of Sheffield,
United Kingdom

Reviewed by:
Antoine Buchard,
University of Bath,
United Kingdom
Peter P. Edwards,
University of Oxford,
United Kingdom
Joan Ramón Morante,
Institut de Recerca de l'Energia
de Catalunya, Spain

Correspondence:
Klaus-Joachim Jens
Klaus.J.Jens@usn.no

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INTRODUCTION

Methanol (MeOH) is a multipurpose molecule, which has a high potential as a C_1 building block for both energy and CO_2 storage (Olah, 2005). It stores both carbon and hydrogen in liquid form at ambient temperature and is readily transportable as it is liquid at ambient temperature. Methanol can be directly converted to valuable hydrocarbons, such as light olefins and gasoline, over acidic microporous materials (Olsbye et al., 2012), thereby providing an alternative to the main fossil energy sources and petrochemical feedstocks used today.

The current technology for MeOH synthesis is based on conversion of syngas (made up of $CO/CO_2/H_2$) over a $Cu/ZnO/Al_2O_3$ catalyst, operating around 250°C and 100 bar (Hansen and Højlund Nielsen, 2008; Ali et al., 2015). Although this technology is highly optimized including recycling of unreacted syngas, its thermodynamic restriction limits syngas conversion per pass coupled with operating conditions, such as temperature and pressure, to make the process capital intensive. Since syngas conversion to methanol is an exothermic reaction (Eq. 1), lower temperature is required to achieve full conversion per pass. Moreover, syngas production accounts for more than half of the total capital cost in current methanol processes (Marchionna et al., 1998). The lowest cost of syngas production is by the use of air rather than pure O_2-blown autothermal reformer (Hansen and Højlund Nielsen, 2008). Full conversion per pass will allow the use of N_2 diluted syngas for methanol production since recycling will not be necessary. Hence, there is a need for the development of a low-temperature approach to MeOH synthesis.

$$CO + 2H_2 \rightleftharpoons CH_3OH\ \Delta H = -90.6\,kJ/mol \qquad (1)$$

A low-temperature methanol synthesis (LTMS) reaction presents the possibility for full syngas conversion per pass around 100–120°C at relatively low pressure, for example below 50 bar (Christiansen, 1919). The LTMS reaction is known to occur in two major steps shown in Eqs 2 and 3. CO carbonylation of MeOH to methyl formate (MF) is catalyzed by alkali metal alkoxide (Eq. 2) (Christiansen, 1919; Tonner et al., 1983); hydrogenolysis of MF to MeOH, which is usually the rate-limiting step, is catalyzed by transition metal-based compounds (Turek et al., 1994; Ohyama, 1999).

$$CO + CH_3OH \rightleftharpoons HCOOCH_3 \qquad (2)$$

$$HCOOCH_3 + 2H_2 \rightleftharpoons 2CH_3OH \qquad (3)$$

Several different Cu-based catalysts have been reported to be active for LTMS reaction between 80 and 120°C. Examples of Cu-based materials reported for the hydrogenolysis reaction include CuO/Cr_2O_3, Raney Cu, Cu on SiO_2, $CuCl_2$, and Cu alkoxide (Ohyama and Kishida, 1998; Xing-Quan et al., 1999a; Li and Jens, 2013a,b). Prolonged milling of a physical mixture of CuO and Cr_2O_3, for example, correlated well with the surface area of Cu, which enhanced methanol synthesis activity (Ohyama and Kishida, 1998, 1999). Hence, the particle size of Cu plays an important role in the LTMS reaction, such that syngas conversion increases with decreasing Cu particle sizes.

The LTMS reaction is normally conducted in a "once through" approach, where the two steps are performed simultaneously. A kinetic study by Liu et al. (1988) has shown that when the two steps are performed together, the rate of MeOH formation is higher than when the two steps are separated. The reaction rates of MeOH carbonylation and its reverse rates were observed to occur at about five orders of magnitude faster than the rate of MF hydrogenolysis. A synergistic relationship between the two steps has been proposed (Li and Jens, 2013b) but the actual relationship involved is yet to be understood.

Traditionally, the LTMS reaction is performed in liquid phase in a solvent. The liquid solvent plays an important role as MeOH synthesis is exothermic and the solvent can help to dissipate excess heat generated during the process. However, aside energy dissipation, could there be other roles for the solvent to play? While most attention has been on finding the right LTMS catalyst system, little attention has been placed on the influence of solvent on the LTMS process. Quan et al. (Xing-Quan et al., 1999b) reported on the influence of solvent polarity in a Cu–Cl and Cu–Cr catalyzed LTMS reaction. They observed that as solvent polarity increased MeOH formation decreased; however, an adequate explanation was not given.

We focus on a Cu nanoparticle/alkoxide catalyst system for the LTMS reaction (Li and Jens, 2013a,b). We have recently reported that Cu nanoparticles are responsible for MeOH synthesis, including that particle aggregation led to decrease in activity. Furthermore, when Cu nanoparticles size were varied from 7 ± 2 to 21 ± 1 nm, MeOH yield were observed to decrease linearly with Cu nanoparticles sizes (Ahoba-Sam et al., 2017). In this work, we will revisit the effect of solvent on the reaction. Particularly, we have studied the influence of solvent polarity in a "once through" MeOH reaction as well as the effect on MF intermediate side reactions. Furthermore, the influence of the solvent on Cu nanoparticle synthesis will be discussed. To the best of our knowledge, this influence of solvents with different hydrocarbon chain length and polarity on Cu nanoparticles size has not been reported. In order to eliminate any influence of the different Cu particles sizes on the effect of solvent polarity, a heterogeneous Cu/SiO_2 catalyst containing 30 nm Cu nanoparticles was used as a reference.

MATERIALS AND METHODS

Materials and Experimental Setup

Copper (II) acetate ($Cu[OAc]_2$, 98%), dry sodium hydride (NaH = 95%), methanol (MeOH, anhydrous 99.8%), MF (99%), sodium methoxide ($NaOCH_3$, 95%), $Cu(NO_3)_2{\cdot}3H_2O$, Ludox HS-40 colloidal silica (40 wt% SiO_2 dispersed in water), L-ascorbic acid, and the various solvents used in this work, listed in **Table 1**, were all purchased from Sigma Aldrich. The syngas contained 1CO: $2H_2$ (± 2%) and was purchased from Yara Praxair AS. All chemicals were used as received unless otherwise stated.

Methanol synthesis and some of the catalyst components were prepared in a 200 ml (60 mm diameter) stainless steel high pressure type hpm-020 autoclave batch reactor (Premex Reactor AG). The reactor was equipped with a dip tube for sampling, a pressure sensor, and a thermocouple inserted into the reactor to measure internal pressure and temperature, respectively. A Nupro security valve attached to the reactor was set at 100 bar for safety. A magnetic stirrer head was attached to a stirrer equipped with oblique impeller blades (approximately 30° angle) and reaching near to the bottom of the reactor for adequate mixing. The magnetic stirrer head was externally attached to an electric BCH Servo Motor paired with a lexium 23 drive to give up to 3,000 rpm, with a high degree of precision. The reactor was heated in an oil block controlled by a Huber Ministat 230 thermostat. The internal temperature and pressure in the reactor was independently logged by a PC.

"Once Through" System

Generally, about 3.6 mmol of $Cu(OAc)_2$,18 mmol of dry NaH, and 50 ml solvent were placed in the reactor. This was set under 1 bar N_2 blanket and the mixture stirred at 3,000 rpm and heated to 100°C for 2 h. The resulting reaction mixture was cooled to ambient temperature (<30°C). After degassing the gaseous phase,

TABLE 1 | List of Solvents used and their properties, adopted from CRC (2003–2004) and Wohlfarth (2008) (ε = dielectric constant).

Solvent	Short form	Formula	ε	Boiling point/°C	% Purity
Methylbenzene	Toluene	C_7H_8	2.33	110.6	≥99.5
Diethyl ether	DEE	$C_4H_{10}O$	4.19	35	≥99.9
1-Methoxy-2-(2-methoxyethoxy)ethane	Diglyme	$C_6H_{14}O_3$	7.23	162	≥99.5
Tetrahydrofuran	THF	C_4H_8O	7.36	66	≥99.9
1,2-Dimethoxyethane	Glyme	$C_4H_{10}O_2$	7.55	84.5	99.5
2,5,8,11,14-Pentaoxapentadecane	Tetraglyme	$C_{10}H_{22}O_5$	7.79	275	>99
Acetonitrile	MeCN	C_2H_3N	35.87	82	99.8
Dimethyl sulfoxide	DMSO	C_2H_6OS	47.13	189	≥99

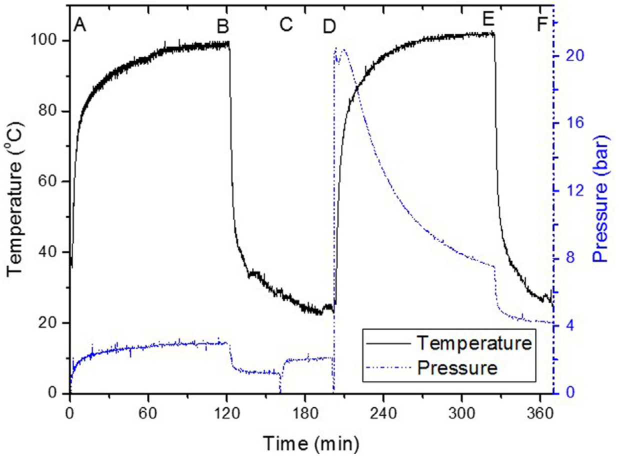

FIGURE 1 | Typical "once through" low-temperature methanol synthesis reaction, (A) 3.6 mmol $Cu(OAc)_2$ + 18 mmol NaH in solvent, (B) rapid cooling in 50 ml solvent, (C) addition of 52 mmol MeOH, (D) 20 bar $CO/2H_2$ charging, (E) rapid cooling, (F) sampled for further analysis.

52 mmol MeOH was added and stirred at ambient temperature for 30 min to ensure that all NaH had reacted to sodium methoxide co-catalyst.

The reactor was purged with syngas and charged to about 20 bar, then stirred at 3,000 rmp and heated to 100°C. After 2 h, the reactor was cooled to about 25°C. Syngas conversion was determined by the difference in pressure between the start of reaction and after reactor cooling to room temperature (~25°C) at the end of reaction (**Figure 1**). The reactor was then degassed, and the liquid portion analyzed. Typically, the amount of carbon products in liquid reaction mixture after cooling as compared to the syngas pressure drop represented about 85% of the syngas consumed, assuming $CO/2H_2$ were proportionally consumed.

The liquid portion of the sample as well as the gas phase were analyzed by a gas chromatograph equipped with both liquid and gas injection valves (Agilent 7890 A). The liquid injection port was connected to a CARBOWAX 007 series 20 M column with dimensions 60 m × 320 μm × 1.2 μm and was programmed as follows; the temperature was ramped at 15°C/min from 40°C initial temperature to 250°C and held at 250°C for 3 min, at 0.47 bar (6.8 psi) constant pressure. The liquid sample was injected *via* an Agilent 7683B autosampler. The products were identified and quantified by an Agilent 5975 mass spectrometer detector (MSD). 0.54 mg heptane was added to each sample vial as internal standard. The gas injection valve was connected to 2.7 m Porapak Q and 1.8 m Molecular Sieve 5 Å packed columns connected to a thermal conductivity detector for analysis of permanent gases including up to C_2 hydrocarbons. This set-up was connected to a 0.9 m Hayesep Q back flush column.

CuO/SiO_2 Catalyst Preparation

CuO/SiO_2 catalyst was prepared by similar steps as reported in Huang et al. (2008) and Xiong et al. (2011) albeit with some modifications. 100 ml of 0.5 M $Cu(NO_3)_2{\cdot}3H_2O$ was prepared in a three-necked round bottomed flask. 100 ml of 1 M L-ascorbic acid was added dropwise while stirring. 49 g of 40 wt% SiO_2 dispersed in water was added to the mixture. This was stirred at 100°C for 3 h. The cooled resulting mixture was then centrifuged and washed three times with distilled water and dried at 70°C in an oven. The dried particles were then calcined at 550°C for 3 h. The calcined CuO/SiO_2 catalyst was used for LTMS reaction in a similar way as was done for the "once through" experiment.

MF Side Reaction Study

11 mmol sodium methoxide dissolved in 97 mmol methanol and 33 mmol MF were added to 20 ml of each solvent. The mixture was stirred under 1 bar N_2 and heated to 100°C for 1 h. The cooled resulting liquid mixture was analyzed using Perkin-Elmer Spectrum One FT-IR spectrometer and Agilent GC.

Catalyst Characterization

The Cu and CuO/SiO_2 catalysts were analyzed by XRD and TEM. A Bruker D8 A25 powder diffractometer using Mo Kα radiation with a wavelength, λ = 0.71076 Å and a Lynxeye detector with "hardened" chip for Mo radiation was used. Total Pattern Analysis Solution (TOPAS) software was employed for quantitative Rietveld analysis of the diffractogram. This software operates by fitting theoretical diffraction pattern to a measured diffraction pattern using non-linear least square algorithms. The samples were analyzed as slurry which was pipetted into a capillary tube with 0.5 mm internal diameter. The tube was centrifuged at 2,000 rmp for 10 min to settle the solid portion at the bottom. The capillary was mounted on the capillary spinner such that the X-ray beam measured around the capillary bottom where the particles were concentrated. The X-ray diffractogram was determined at 0.023° step/s for an interval of 15–35° 2 theta.

The TEM imaging was performed with a Joel 2100F instrument. Samples were diluted in methanol, and particles were dispersed in an ultrasound bath for 30 min. The solution was then deposited onto a carbon film on a copper grid. Cu particles were ascertained to be present using EDS and electron diffraction. Generally, particle size distributions were determined by measuring the diameters of the TEM images as the particles sizes using MATLAB assuming that the Cu particles were circular droplets. Typically, an average of 30-particle diameters ± SD from the TEM images for each sample was used for particle size determination.

RESULTS AND DISCUSSION

Typical "Once Through" LTMS

Figure 1 shows the steps involved in the LTMS reaction using diglyme as solvent. Typically, Cu nanoparticles were made by hydride reduction of Cu^{2+} ($Cu(AOc)_2$) in steps A and B with NaH at 100°C (Glavee et al., 1994). Addition of MeOH at step C led to the formation of $NaOCH_3$ (sodium methoxide) and $H_{2\,(g)}$ which resulted in an increase in pressure. Syngas was added at step D, where after an induction period due to increase in temperature, pressure declined rapidly with time. After 2 h (E), the reaction was stopped by cooling to about 25°C at F. We deliberately stopped the reaction after 2 h and so the activity of the catalyst was not optimized for determining TOF or TON. Moreover, our batch reactor system did not allow for time on steam analysis of individual products except the changes in pressure and temperature, which were continuously monitored during the reaction. The pressure drop represented 89% syngas conversion. The liquid products composition after 2 h showed 96 and 4% C selectivity to MeOH and MF, respectively.

The slurry was further analyzed by XRD to determine oxidation state and crystallite size of the Cu catalyst involved in the LTMS reaction. **Figure 2** shows the X-ray diffractogram of the slurry at steps B, C and E as illustrated in **Figure 1**. The XRD samples were taken right after steps B, C, and D were completed, respectively. The diffractogram after step B showed mainly Cu_2O and NaH phases, while that after step C showed Cu_2O and Cu^0 phases [X-ray powder diffraction files referenced from Neuburger (1930), Wyckoff (1963), Smura et al. (2011)]. The diffractogram after E showed predominantly Cu^0 oxidation state.

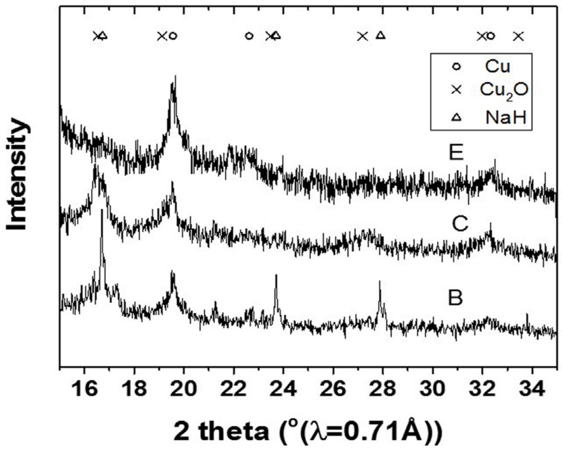

FIGURE 2 | X-ray diffractogram of the slurry after the steps B, C, and D in **Figure 1.**

This indicated that reduction of the Cu^{2+} precursor took place during the process by hydride reduction during step B. Moreover, all NaH was reacted upon the addition of methanol since no NaH pattern was observed in the diffraction at step C. The steps C to D resulted in the pressure rise illustrated in **Figure 1**, as H_2 was released in the process. Furthermore, the LTMS reaction under highly reducing environment of CO and H_2 led to Cu^0 oxidation state at E. The average Cu crystallite sizes were estimated by Reitveldt analysis. The slurry at step C was composed of about 50/50% Cu^0/Cu_2O with average crystallite sizes of about 7.5 ± 0.7 nm. After the LTMS reaction, the Cu^0 crystallite sizes at step E was 9.5 ± 0.9 nm. This showed about 2 nm increase in the average crystallite size of the Cu after methanol synthesis occurred. **Figure 3** shows TEM image of the Cu particles. The Cu particle size was about 10 ± 3 nm. Electron diffraction also confirmed [111] and [311] Cu^0 planes present.

Solvent Variation in "Once Through" Synthesis

As indicated in **Table 1**, different aprotic solvents were employed to study the influence of solvent polarity on the LTMS reaction. Aprotic solvents were used because of the presence of NaH, which can react easily with protons. Moreover, the $NaOCH_3$ co-catalyst may be consumed in the presence of protic solvent. Five out of the chosen solvents were ethers with different chain lengths and polarity.

Figure 4 shows the activity of the catalyst system in the "once through" reaction plotted versus dielectric constant (ε) of the solvents. 51% syngas conversion was observed when diethyl ether (DEE) was used as solvent with the least $\varepsilon = 4.19$. In diglyme with $\varepsilon = 7.23$, 89% syngas conversion was observed. Then after, syngas conversion decreased to 85, 80, and 74% in tetrahydrofuran (THF), glyme, and tetraglyme, respectively, following the order of slight decreasing in ε. Thereafter, syngas conversion sharply declined to 30 and 14% in acetonitrile (MeCN) ($\varepsilon = 36$) and dimethyl sulfoxide (DMSO) ($\varepsilon = 47$), respectively. Despite the more noticeable changes in the syngas conversion in the various solvents, selectivity to MeOH was always >90% indicating that selectivity was barely affected by the solvents' dielectric constant or polarity.

The chosen ether solvents differ in polarity (represented by their ε), boiling point, and chain length (or molar mass) which is shown in **Table 1** [from CRC (2003–2004), Wohlfarth (2008)]. The dielectric constant is known to be proportional to the solvents polarity (Rabaron et al., 1993). Among these properties, the observed syngas conversion pattern followed the ε of the solvents with the optimum around $\varepsilon = 7.2$ for diglyme. Notably, slight differences in the ε with regards to diglyme, THF, glyme, and tetraglyme depicting the slight differences in their polarity, such that syngas conversion followed the order

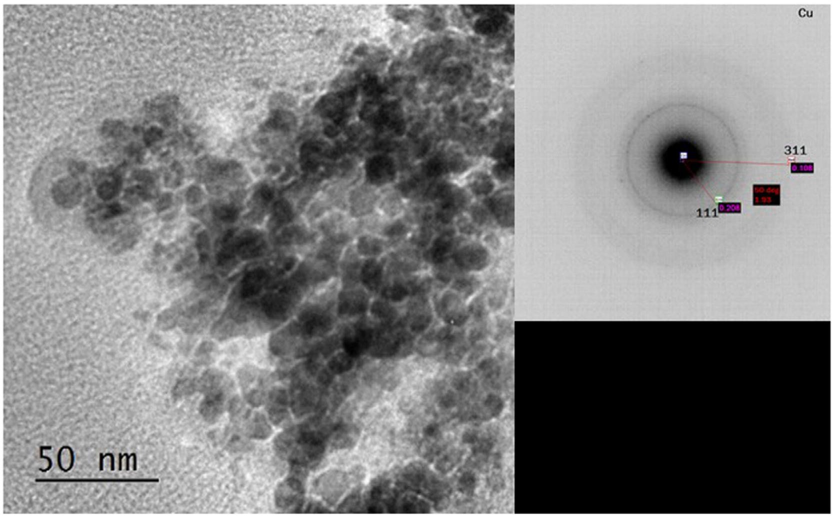

FIGURE 3 | TEM image and electron diffraction of Cu from step F with 10 ± 2 nm particles sizes and [111] and [311] Cu^0 planes.

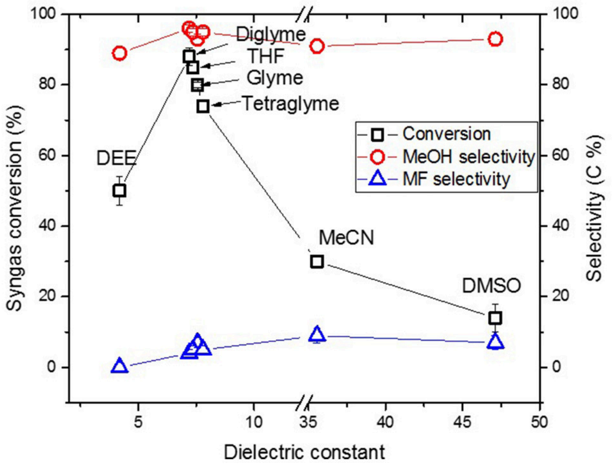

FIGURE 4 | Syngas conversion and selectivity versus dielectric constant of solvent in the "once through" Cu nanoparticles catalyzed reaction.

diglyme > THF > glyme > tetraglyme. On the other hand, the order of increasing solvent chain length as well as boiling point is THF < glyme < dilgyme < tetraglyme. Clearly, the syngas conversion did neither follow solvent's chain length nor their boiling point, but preferred less polar solvents among these ether solvents.

The solvent polarity range was extended beyond the ethers, such as MeCN and DMSO with $\varepsilon = 36$ and 47, respectively. These two, which are more polar than diglyme showed a very sharp decline in syngas conversion. Solvents with higher polarity than that of diglyme led to even lower MeOH formation. On the contrary, DEE with lower ε ($\varepsilon = 4.2$) than diglyme also showed lower syngas conversion, suggesting that lower polar solvents than diglyme may also lead to lower amount MeOH formation in LTMS reactions. This, therefore, suggest that solvent polarity plays an important role in the "once through" LTMS reaction such that solvents with similar polarity with diglyme showed higher MeOH formation.

Solvent Effect on Cu Nanoparticles in the "Once Through" Reaction

Copper nanoparticles were synthesized as described in Section "Typical "Once Through" Low Temperature Methanol Synthesis" for the "once through" catalyst. However, since different solvents were involved, there is a possibility that nucleation and crystallite growth of Cu nanoparticles will differ in the different reaction media. It is also important to note that Cu nanoparticles size plays an important role in MF hydrogenolysis (Ohyama and Kishida, 1998). This section, therefore, focuses on the effect of the different chosen solvents on Cu nanoparticles size.

Figure 5 shows the slurry X-ray diffractogram of the different solvents after LTMS reaction. Generally, a Cu^0 phase was predominately observed but with varying reflex intensity. The broadness of the reflexes confirm formation of nanoparticles in all employed solvents. **Figure 6** shows the Cu nanoparticle TEM images of the different solvents. **Figure 7** shows a summary of **Figures 5** and **6** in relation to the ε value of the solvents. Generally, the Cu crystallites and particles sizes in each particular solvent were about the same, considering the fact that the XRD measures the bulk average while the TEM images only show a few particles. On average, Cu particles in all ether solvents were within 9–10 nm, while in MeCN and DMSO solvents approximately 7 nm particle size was observed.

Cu particles sizes do not seem to have been influenced by the different ether solvents. Considering that, the ethers have different chain lengths as well as different amounts of oxygen per mole capable of forming chelates around a Cu atom, one could expect the particle size to vary with chain length. However, this was not observed which could be due to the fact that, the excess amount of solvents used might have provided enough oxygen for dative bonding if chelate formation was necessary in tuning the particles sizes.

Cu nanoparticles sizes prepared in the non-ether solvents were smaller as compared to those made in ether solvents. DMSO with higher polarity ($\varepsilon = 47$) showed smaller Cu particles sizes than was observed for MeCN ($\varepsilon = 36$). The difference of the ether solvents ε values were relatively small ($\varepsilon = 4.2$–7.8) as compared to DMSO and MeCN. There is a possibility that the polarity difference in the solvents played a subtle role in the formation of Cu nanoparticles size, particularly when the polarity difference is larger. It has been reported that nucleation slows down with solvents polarity (Zhao et al., 2004; Wei et al., 2008). The consequence of slower rate of nucleation is that, larger crystals may be formed if longer growth time (>24 h) is allowed. However, we observed the opposite, which might be due to an inadequate aging time of 2 h in our system.

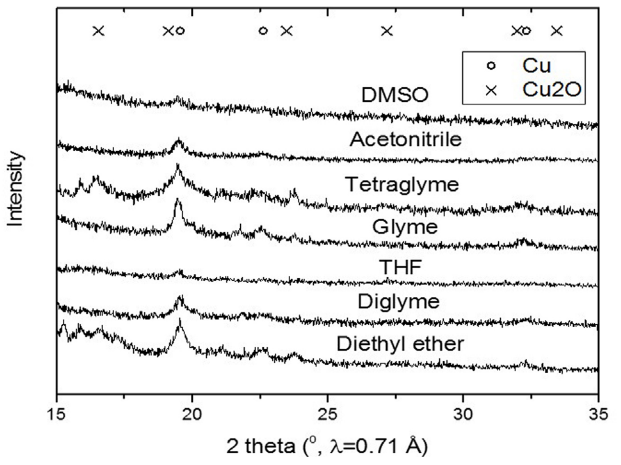

FIGURE 5 | X-ray diffractogram of the slurry after low-temperature methanol synthesis reaction for the different polar solvents.

The use of solvents with higher polarity in the LTMS reaction, despite generating smaller Cu nanoparticles, led to the least amount of MeOH formation. However, it is expected that the smaller the Cu nanoparticles the faster the hydrogenolysis of MF which is usually the limiting step in the LTMS reaction. Smaller Cu nanoparticles should, therefore, lead to higher MeOH formation. This on the contrary was not the case when solvents polarity was varied, suggesting that the solvent polarity was the bottleneck in our case rather than just the Cu particles sizes.

Solvent Variation using CuO/SiO_2 Catalyst

In Sections "Solvent Variation in "Once Through" Synthesis" and "Solvent Effect on Cu Nanoparticles in the "Once Through" Reaction," the lowest methanol formation was observed in the more polar solvents despite the fact that the smallest Cu nanoparticles were made in these solvents. The two main components that varied before LTMS reaction were the type of solvent used and slight changes in Cu NP sizes. A dry CuO/SiO_2 catalyst with larger particle size as compared to the 7–10 nm Cu NP slurry used above was prepared and used for the LTMS reaction as a control. This will help to differentiate between the influence of Cu nanoparticles size as against that of the solvents, as solvent polarity will be varied but with the same CuO/SiO_2 catalyst size.

Figure 8 shows the XRD diffractogram of the calcined CuO/SiO_2 catalyst. Crystalline CuO and amorphous SiO_2 were

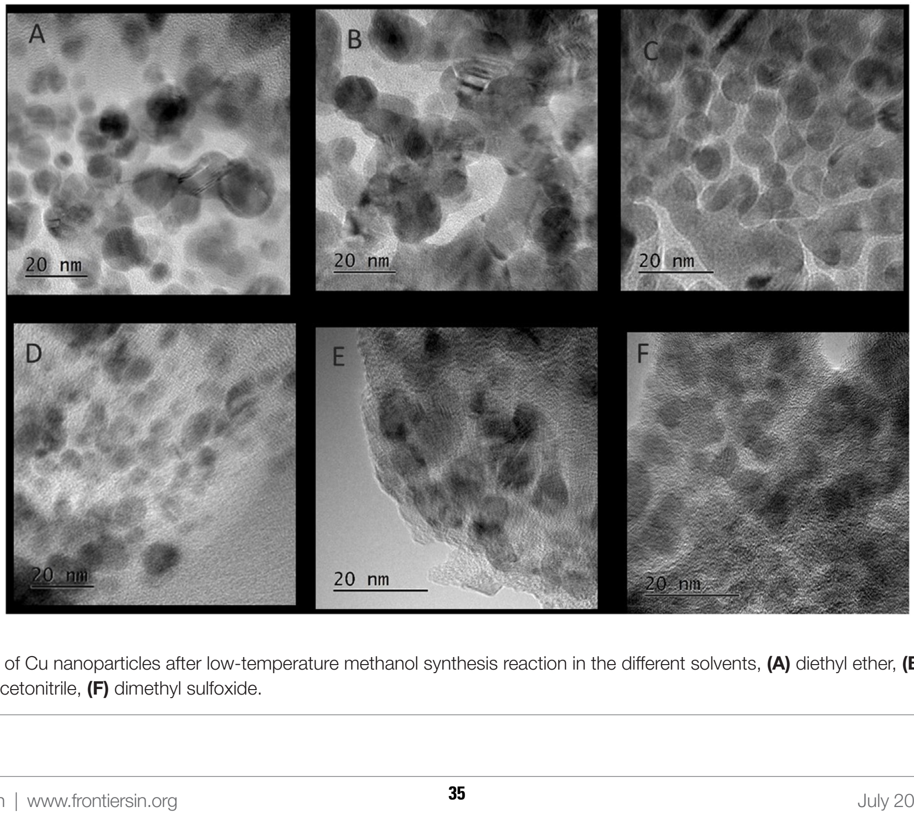

FIGURE 6 | TEM images of Cu nanoparticles after low-temperature methanol synthesis reaction in the different solvents, **(A)** diethyl ether, **(B)** glyme, **(C)** tetraglyme, **(D)** tetrahydrofuran, **(E)** acetonitrile, **(F)** dimethyl sulfoxide.

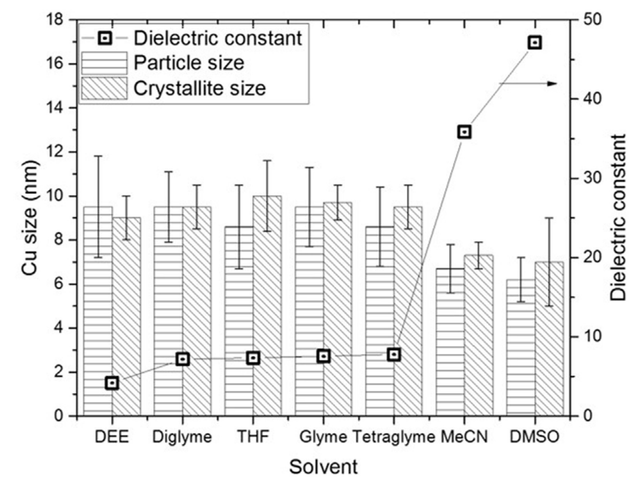

FIGURE 7 | Comparison of the Cu particles sizes and dielectric constants in the different solvents after low-temperature methanol synthesis reaction.

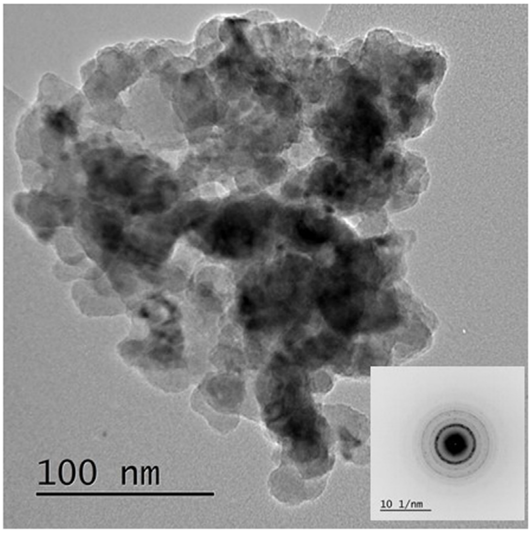

FIGURE 9 | TEM image and an inserted electron diffraction of the calcined CuO/SiO_2 catalyst.

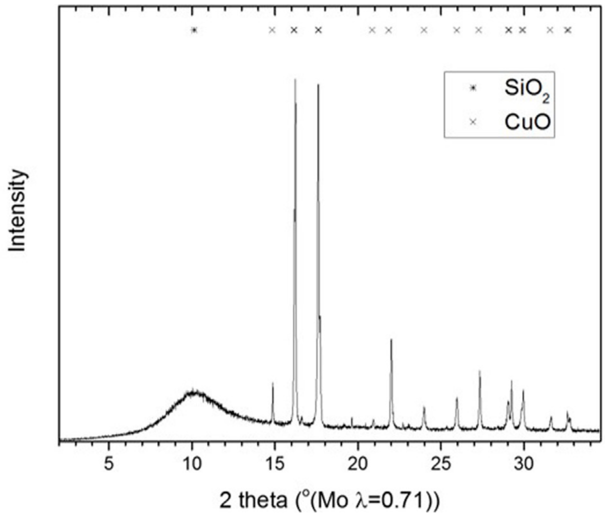

FIGURE 8 | X-ray diffractogram of calcined CuO/SiO_2 catalyst.

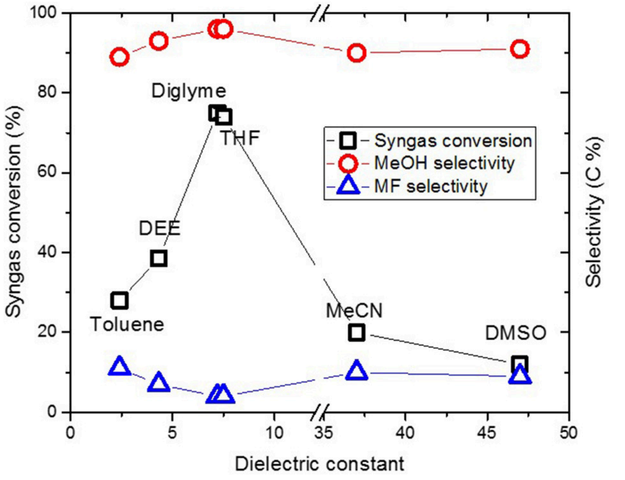

FIGURE 10 | Syngas conversion and selectivity versus dielectric constant of solvent in the CuO/SiO_2 catalyzed reaction.

observed [powder diffraction files referenced from Barth (1932), Tunell et al. (1935)]. The line broadening analysis indicated that, the CuO crystallite size was 30 ± 5 nm. **Figure 9** shows the TEM image and an inserted electron diffraction diagram of the CuO/SiO_2 catalyst. The TEM showed a good dispersion of the crystalline CuO on the SiO_2 support. The electron diffraction showed mainly [110], [002], [11-2], and [112] planes of CuO.

The CuO/SiO_2 catalyst was used for methanol synthesis, in a similar way to Section "Typical "Once Through" Low Temperature Methanol Synthesis," except that, the very first step for making Cu nanoparticles (**Figures 1A,B**) was omitted since the synthesized CuO/SiO_2 catalyst was used. **Figure 10** shows catalyst activity versus ε value for solvents of various polarity. Syngas conversion increased from 28 and 39%, respectively, in toluene and DEE, to 76% in diglyme but slightly decreased to 74% in THF and then sharply to 20 and 12% in MeCN and DMSO, respectively. Despite the large differences in syngas conversion, selectivity to methanol remained ≥90% and MF ≤10% in the different solvent.

Generally, syngas conversions were higher in the "once through" system for the Cu nanoparticles slurry as compared to the CuO/SiO_2 catalyst system. This is not surprising since the Cu catalysts involved in the two scenarios were different in support material and particles sizes. The CuO in the CuO/SiO_2 catalyst was about 30 nm compared with the ≤10 nm Cu particles made in the "once through" system. Moreover, our earlier report showed that within 7–21 nm sizes, methanol formation decreased with Cu particle size (Ahoba-Sam et al., 2017). Therefore, the observed lower syngas conversion can be related to the larger Cu particle size. Despite this, selectivity to MeOH and MF as well as the trend in syngas conversion followed the same path as was observed in the **Figure 4** for the "once through" system. A similar trend has been reported for a CuO/Cr_2O_3 system with varying solvent polarity (Xing-Quan et al., 1999b). Therefore, solvent polarity plays an important role in LTMS reaction, such that solvents with ε values around 7.2 appear to give improved MeOH synthesis results.

The observed effect of solvent polarity on the LTMS reaction needs an explanation. What is the exact role of polarity in the LTMS reaction? Syngas is known to be less soluble in polar solvent compared to apolar solvents (Vogelpohl et al., 2014). This is so because strong interaction exists between polar molecules, which makes it difficult for relatively non-polar H_2 and CO to enter. However, while solubility cannot be totally ruled out in gas–liquid systems, the solubility explanation may only hold for solvents with ε values >7. Syngas conversion decreased with decreasing solvents' polarity in $\varepsilon = 4.2$ and 2.3 in DEE and toluene systems, respectively. Our recent results showed that increasing Cu nanoparticles sizes from 7 to 21 nm led to decrease in both conversion and selectivity to MeOH in diglyme. This coupled with similar trends observed for the different Cu sources suggests that hydrogenation was not the main step responsible for the above observation. The Section "Influence of Solvent Polarity on Side Reactions of the LTMS Reaction,"therefore, seeks to address the possible side reactions, which could limit the LTMS reaction in the different solvents.

Influence of Solvent Polarity on Side Reactions of the LTMS Reaction

The LTMS reaction involves two major steps, carbonylation and hydrogenolysis of MF (illustrated in Eqs 2 and 3, respectively). However, the main intermediate product, MF can also undergo possible side reactions as shown in Eqs 4 and 5. It has been reported that the formation of MF from MeOH and CO (Eq. 2) is highly reversible (Christiansen, 1926; Liu et al., 1988). Moreover, it has also been observed that MF can react with $NaOCH_3$, to form dimethyl ether (DME) and NaOOCH (sodium formate) (Christiansen, 1926; Jogunola et al., 2012). Therefore, during the LTMS reaction, if MF hydrogenolysis is not fast enough, MF can either decarboxylate back to CO and MeOH and/or react with $NaOCH_3$ to give DME and NaOOCH.

$$CH_3OOCH \rightleftharpoons CO + CH_3OH \quad (4)$$

$$CH_3OOCH + NaOCH_3 \rightleftharpoons CH_3OCH_3 + NaOOCH \quad (5)$$

The influence of solvents' polarity on the possible side reactions involved in the LTMS reaction was then studied. This was done by heating MF in the presence of $NaOCH_3$ in a predetermined solvent under 1 bar N_2 gas. The IR spectrum of the resulting liquid mixture is shown in **Figure 11**. The gray lines in **Figure 11** (B–G) represent the pure solvent while the black lines represent the reaction mixture. These were compared with MeOH, MF, and NaOOCH shown in **Figure 11**A. Typically, bands observed at 2,830, 2,770, 1,650, 1,570, 1,360, and 770 cm^{-1} were not observed in pure solvent or in methanol and MF. These bands were typical NaOOCH bands when compared with standard spectra from NIST data base (Stein, 2016). The NaOOCH bands appeared in all the spectra of the different solvents, which indicated that formate was formed in all the different solvents.

Table 2 shows the rise in pressure and relative amount of CO released for the different solvents tested. Although DME and methanol were present in the gas phase, it was difficult to separate them on the Porapak Q column as their peaks superimposed on each other leading to a shoulder peak. Therefore, only N_2 and CO, which were well separated on the mol sieve column, were quantified for this analysis. The CO equivalence in these chromatograms should be regarded as a relative measure to N_2 and not as an absolute measure. The amount of CO released generally decreased with increasing solvent polarity.

The amount of MF drastically decreased from 33 mmol initial amount to less than 4 mmol in the side reaction test for all solvents. Trace amounts of DME were observed in the liquid sample analysis (using the MSD) of all solvents. MF was, therefore, involved for all solvents in the two reactions; (i) decarbonylation into CO and MeOH and (ii) nucleophilic substitution to form DME and NaOOCH, as illustrated in Eqs 4 and 5. Although DME and NaOOCH were observed, we were not able to quantify them. However, assuming that decarbonylation and nucleophilic substitution are the main MF side reactions occurring and considering the high MF reactivity in the solvent tests, the relative amount of CO released in these reactions can be used to determine which of the two pathways is predominant for the different solvents.

The released CO amount decreased with increasing polarity of the solvent. This suggested that decarboxylation was enhanced in less polar solvents. The decreasing amount of CO released with increased solvent polarity suggested that the nucleophilic substitution pathway is enhanced with increased solvent polarity which appears logical since this reaction pathway involves ionic salt formation which is expected to be stabilized by polar rather than non-polar solvents (Parker, 1969).

Maximum syngas conversion was observed for a solvent ε value around 7.2 (see Solvent Variation in "Once Through" Synthesis and Solvent Variation using CuO/SiO_2 Catalyst). Considering the nucleophilic substitution pathway to be favored by polar solvents and the decarbonylation pathway to be favored by low polarity solvents, a relatively moderate polar solvent is a good compromise to supress unwanted side reactions, maximizing the MF hydrogenolysis pathway. The above results indicate that the different MF reaction pathways in the LTMS reaction, i.e., hydrogenolysis, decarboxylation, and nucleophilic substitution, may have comparable activation barriers. Changing the polarity might influence the path which intermediates are better favored by the polarity of the solvent. Hence, MF is a transient intermediate, which will always be present at relatively low concentration in the reaction mixture.

NaOOCH formation is detrimental to the overall catalytic cycle because $NaOCH_3$, the co-catalyst, is consumed by this reaction. Previously, we observed Cu catalyst agglomeration to be a major source of LTMS reaction deactivation as Cu particles growth corresponded to a lower activity. Our current study indicates that the nucleophilic substitution side reaction is also

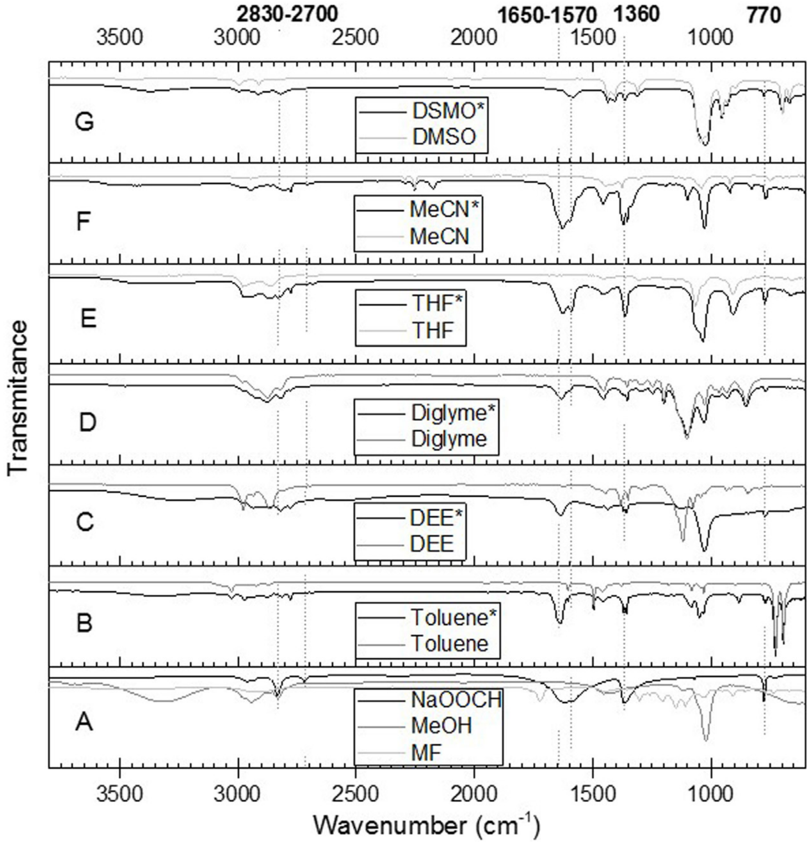

FIGURE 11 | ATR-IR spectra of solvent (B–G in gray), and reaction mixture (B–G, black with *). The spectra A is for MeOH, methyl formate, and NaOOCH. The NaOOCH (in black) was adopted from NIST data base (Stein, 2016).

TABLE 2 | Solvent effect on side reaction, CO equivalent = CO/(CO + N_2) × Pressure rise, CO and N_2 was determined from gas analysis while the MF was determined from liquid analysis.

Solvent	Pressure rise/bar	CO equivalent/bar	MF remaining/mmol
Toluene	3.00	1.91	3.43
Diethyl ether	2.94	1.66	2.12
Diglyme	2.46	1.23	1.77
Tetrahydrofuran	1.95	0.90	2.33
Acetonitrile	1.23	0.59	1.00
Dimethyl sulfoxide	0.82	0.32	0.41

a potential source of LTMS reaction deactivation which will increase in importance especially in more polar solvents.

CONCLUSION

The liquid-phase LTMS reaction is influenced by solvent polarity. Solvents with moderate polarity similar to diglyme with $\varepsilon = 7.2$ give highest syngas conversion among eight different selected solvents covering a wide range of polarity. MeOH formation increased with increasing ε value until that of diglyme (7.2) and decreased thereafter with further increase of the ε value. This trend was independent of Cu catalyst nanoparticle size. Our results indicated that MF, the main intermediate LTMS reaction product undergoes two side reactions (i) decarbonylation to form CO and MeOH and (ii) a nucleophilic substitution reaction to form DME and sodium formate. Solvent polarity distinguishes between these side reactions such that decarbonylation is favored as solvent polarity decreases while nucleophilic substitution is favored as solvent polarity increases. Our results show that moderate polarity solvents, e.g., diglyme favor MF hydrogenolysis by retarding the other two possible side reactions.

Safety Warning

Large amount of compressed CO and H_2 gas were used, with potential poisoning and flammable hazards, respectively, and hence, the appropriate equipment and detectors must be used to avoid unwanted releases. The solvents used especially diglyme and glyme are toxic and must be handled with care.

AUTHOR CONTRIBUTIONS

CA-S was involved in conception and design of experiment, acquisition of data, and analysis and interpretation of data for this work. He drafted the work, approved the final version of the work to be submitted and agreed to be accountable for all aspects of the work in ensuring that questions related to accuracy or integrity of any part of the work are appropriately investigated and solved. UO was involved in conception of experiment and interpretation of data for this work. She approved the final version of the work to be submitted and agreed to be accountable for all aspects of the work in ensuring that questions related to accuracy or integrity of any part of the work are appropriately investigated and solved. K-JJ was involved in conception and design of experiment and analysis and interpretation of data for this work. He was involved in revising the draft of the work and approved the final version of the work to be submitted and agreed to be accountable for all aspects of the work in ensuring that questions related to accuracy or integrity of any part of the work are appropriately investigated and solved.

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Demonstration of CO_2 Conversion to Synthetic Transport Fuel at Flue Gas Concentrations

George R. M. Dowson[1] *and Peter Styring*[1,2]*

[1] *Chemical and Biological Engineering, The University of Sheffield, Sheffield, United Kingdom,* [2] *UK Centre for Carbon Dioxide Utilisation, Department of Chemistry, The University of Sheffield, Sheffield, United Kingdom*

A mixture of 1- and 2-butanol was produced using a stepwise synthesis starting with a methyl halide. The process included a carbon dioxide utilization step to produce an acetate salt which was then converted to the butanol isomers by Claisen condensation of the esterified acetate followed by hydrogenation of the resulting ethyl acetoacetate. Importantly, the CO_2 utilization step uses dry, dilute carbon dioxide (12% CO_2 in nitrogen) similar to those found in post-combustion flue gases. The work has shown that the Grignard reagent has a slow rate of reaction with oxygen in comparison to carbon dioxide, meaning that the costly purification step usually associated with carbon capture technologies can be omitted using this direct capture-conversion technique. Butanol isomers are useful as direct drop-in replacement fuels for gasoline due to their high octane number, higher energy density, hydrophobicity, and low corrosivity in existing petrol engines. An energy analysis shows the process to be exothermic from methanol to butanol; however, energy is required to regenerate the active magnesium metal from the halide by-product. The methodology is important as it allows electrical energy, which is difficult to store using batteries over long periods of time, to be stored as a liquid fuel that fits entirely with the current liquid fuels infrastructure. This means that renewable, weather-dependent energy can be stored across seasons, for example, production in summer with consumption in winter. It also helps to avoid new fossil carbon entering the supply chain through the utilization of carbon dioxide that would otherwise be emitted. As methanol has also been shown to be commercially produced from CO_2, this adds to the prospect of the general decarbonization of the transport fuels sector. Furthermore, as the conversion of CO_2 to butanol requires significantly less hydrogen than CO_2 to octanes, there is a potentially reduced burden on the so-called hydrogen economy.

Keywords: carbon dioxide utilization, butanol, energy storage, carbon avoided, transport fuel, Grignard reagent

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Robert J. Farrauto,
Columbia University,
United States

Reviewed by:
Edward J. Rode,
DNV GL, Norway
Xuezhong He,
Norwegian University of
Science and Technology,
Norway

***Correspondence:**
Peter Styring
p.styring@sheffield.ac.uk

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INTRODUCTION

Carbon capture and storage (CCS) and carbon dioxide utilization (CDU) are two potential approaches to address mitigation of the ever-rising CO_2 levels in the atmosphere, which have alarming climate implications (IPCC, 2014). For either approach to be effective in limiting or mitigating emissions, three key criteria have to be achieved. Sufficient amounts of CO_2 must be stored or converted, or otherwise prevented from atmospheric release. The CO_2 must be stored or converted for a sufficient period of time, and this must be achieved at a reasonable cost. For CCS, the overall storage capacity and intended storage time are potentially sufficient with estimates of total storage capacity exceeding 10 Tt, corresponding to centuries of current-level emissions (IEA, 2009). However, achieving this storage at practical cost is the major challenge facing CCS worldwide, with the exception of enhanced oil recovery (EOR) operations which have questionable total climate impacts given carbon footprint of the CO_2 released on use of the additional oil that is produced (Jaramillo et al., 2009). While a handful of geological storage CCS projects without EOR have been initiated, and more are planned, these typically operate where high concentrations of CO_2 are available (reducing capture/purification costs) or are reliant on significant government support or subsidy (Global CCS Institute, 2016). In the case of CO_2-EOR and CO_2 utilization, there is an additional complicating factor that storage is not long term as 92% of the recovered oil will be burned through combustion, with a similar fate for some, but not all of the utilization products.

Therefore, perhaps a better way to look at CO_2 utilization is not through the mitigation potential of waste, but in the use of CO_2 as a valuable C-1 resource. The latter approach, therefore, considers the utilization as avoiding new fossil carbon entering the supply chain and so indirectly reduces new emissions by mitigation and avoidance (von der Assen and Bardow, 2014). The carbon dioxide is converted for the production of chemicals with higher economic value, which results in a much more favorable immediate economic case than that with CCS. The resulting added-value from the CO_2 ideally offsets some or all of the processing costs. This leaves CDU at a decided advantage over CCS in terms of economics, with several commercial processes based on CDU already in operation worldwide (Langanke et al., 2014; Gunning and Hills, 2015; Styring et al., 2015).

However, even with indirect effects included, the maximum amount of CO_2 that may be utilized remains very small compared to total emissions. For example, if the entire global annual production of ethylene, the most widely manufactured commodity chemical containing carbon atoms, was carried out using carbon sourced exclusively from CO_2, this would result in direct utilization of less than 1.5% of total global CO_2 emissions (Stratas Advisors, 2016; Olivier et al., 2017). Even with other commodity chemicals included and assumptions made of indirect mitigation, theoretical utilization could represent only a small proportion of total emissions (**Figure 1**). Naturally, this further neglects the fact that direct conversion of CO_2 into hydrocarbons, and especially aromatics, are not likely to become commercial processes in the near future.

It should be noted that while this demonstrates that CDU may only have minor or limited impact on total emissions mitigation, even when imagining a hypothetical sustainable route for the production of the most common commodity chemicals from CO_2, profitable CDU processes may provide finance for CCS initiatives, thus offsetting further public or governmental costs (Hendricks et al., 2013). However, if CDU is only considered in isolation from CCS, other potential products in which to sink the emitted carbon must be made to allow for substantial reductions in CO_2 emissions. In this context, the only carbon-containing materials that are used on sufficient scale for CDU to impact on total emissions are fuels themselves (**Figure 2**).

LOW-CARBON FUELS FROM CARBON DIOXIDE

In the case of CDU-derived fuels, which re-release the CO_2 that was initially trapped when they are combusted, the efficacy of the

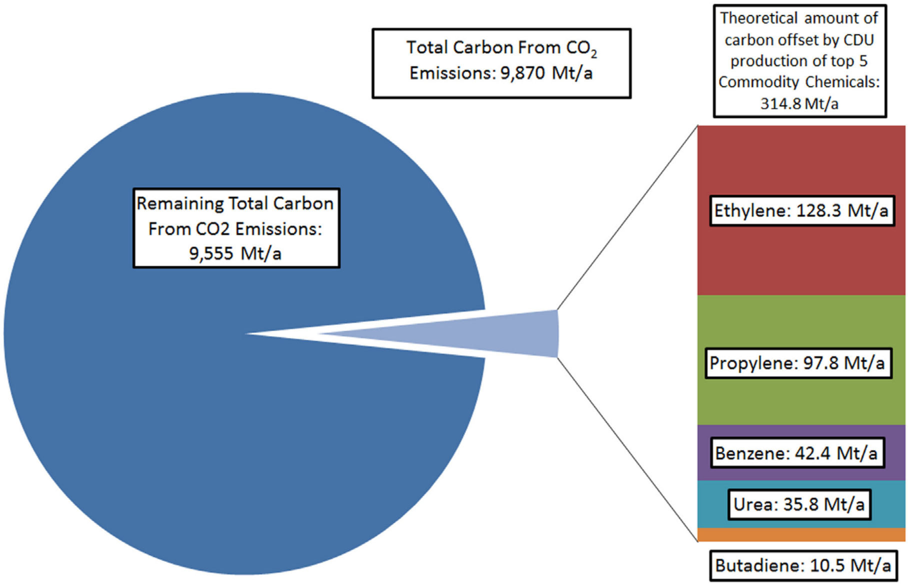

FIGURE 1 | Comparison of total carbon in global CO_2 emissions compared to carbon atoms contained in five major carbon-containing commodity chemicals, avoiding derivatives such as ethylene oxide. 2015 figures used (Levdikova, 2014; Yennigalla, 2015; Heffer and Prud'homme, 2015; Coombs, 2016).

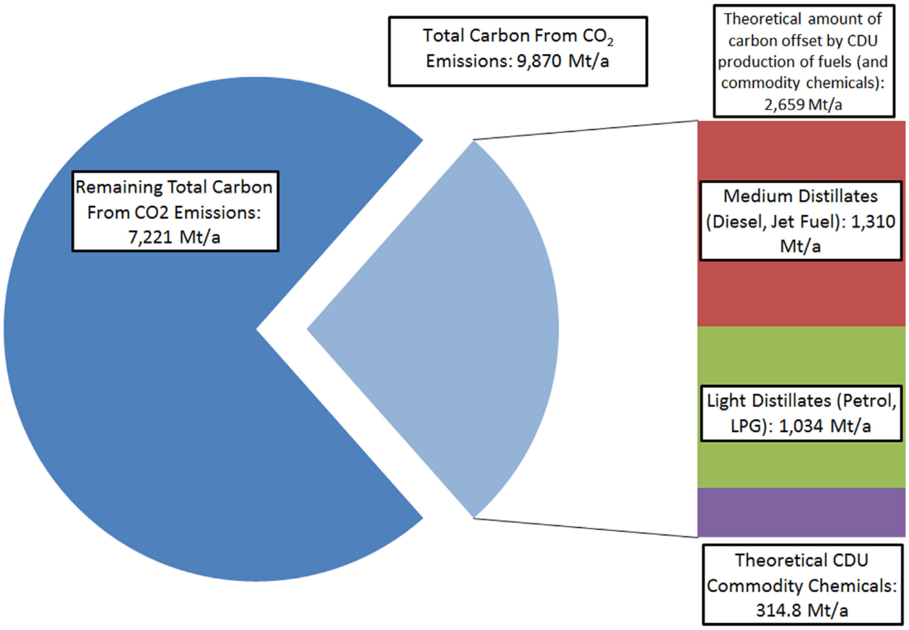

FIGURE 2 | Comparison of total carbon in global CO_2 emissions compared to carbon atoms contained in major liquid fuels and the theoretical collective commodity chemicals shown in **Figure 1**. 2015 Figures used (Dudley, 2015).

process in terms of emissions relies on observing the emissions *avoided* by the use of such a fuel. Since the CDU fuel itself may be seen as carbon neutral, provided all carbon atoms contained within the liquid fuel come from emission CO_2 and no further emissions are generated in production, upon combustion useful work is extracted without the use of new fossil carbon. In the extreme scenario where all major liquid fuels are synthesized from CO_2, the result is that road, water, and air vehicles essentially become indirectly powered by renewable electricity. By using synthetic fuels of this kind, it is possible to still use liquid fuel combustion engines and the existing fuels infrastructure. Thus, a 23% reduction/utilization of total emissions could be theoretically achieved (Mobility, 2015). Furthermore, with the large shift in the energy-generation sector toward renewable and lower carbon energy sources, this figure will rise as the total relative share of the emissions from the transport sector grows. It should be noted that other than widespread vehicle electrification, which is strongly limited for long-distance haulage, shipping and air-travel, or dramatic societal change, CDU fuels production represents one of the few potential strategies able to reduce transportation carbon emissions in the short-term future. Furthermore, it is the only strategy that may offer such reductions in transport emissions without significant disruption or onerous infrastructure redevelopment in the short and medium term, provided the CDU fuels are drop-in replacements for existing fossil analogs.

Unlike certain commodity or fine chemicals that can be generated from CO_2 without significant energy input, such as polyurethane foams, fuels synthesis by definition requires a large energy input, naturally exceeding the combustion energy of the resulting product. Furthermore, the energy must necessarily be renewable or low carbon and as cheap as possible. In this respect, the conversion of CO_2 into fuel may be better considered as an energy-vectoring strategy to balance electricity demand and supply as increasing amounts of renewable energy capacity is installed worldwide. Spot negative energy prices, once very rare, are now becoming more frequent even in large economies like Germany, Australia, UK, and parts of the United States (Martinez-Anido et al., 2016). Furthermore, renewable energy curtailment has grown dramatically. Germany, for example, has had to dramatically increase curtailment of renewable energy supplies in recent years, with over 1.5 GWh of renewable energy curtailed in 2014 (Morris, 2015). This wasted energy alone (not including a much larger amount of ultra-low and negative cost energy generated that year) would have been sufficient energy to produce approximately 50,000–80,000 l of CDU-gasoline, assuming the overall energy efficiency of the conversion of electricity to chemical energy in the fuel to be 30–50% with respect to the combustion energy density of petrol. Although this amount is relatively small in terms of the German liquid fuel market, with nearly 15,000 TWh per year of additional renewable energy expected to be produced worldwide by 2035, production of CDU fuels may be an important tool to balance periods of low demand and high generation in certain areas (BP Statistics, 2015; International Energy Agency, 2016).

It should be noted that even if a high-efficiency pathway to transform CO_2 into a liquid fuel can be developed and deployed, the overall use of the energy will have poor efficiency due to the limitations of the combustion engines that use these fuels. Furthermore, since liquid fuels are relatively cheap per liter, if a competitive economic price is desired, the CDU fuel pathway would only be viable when energy prices are very low. Although a simple energy calculation shows that the absolute maximum energy price that allows CDU fuel production at around €1/L is €105/MWh (readily achievable by most low-carbon generation methods), the real energy price will have to be much lower to account for process inefficiencies and further issues such as the cost of capturing and purifying the CO_2 from the waste streams to begin with.

THE COST OF CARBON CAPTURE

The high cost of capturing carbon dioxide from waste streams is a major challenge for both CDU and CCS strategies. Despite the thermodynamic de-mixing costs being relatively low in flue gas streams (approximately 150–250 MJ/t CO_2 depending on concentration), CO_2 capture and purification processes have much larger energy costs stemming from the sorption/desorption process. This is evident where an energetic driving force is required for either the sorption of the carbon dioxide, such as in high pressure adsorption and membrane separation, or for the desorption step, such as in amine-based chemisorption or vacuum swing adsorption. This results in a range of energy costs from approximately 1 to 4 GJ/t CO_2 with the lower range consisting mainly of immature techniques and the upper range consisting of benchmark amine processes such as monoethanolamine (Dowson et al., 2016). Further issues associated with the capture processes involve the challenges of retrofitting existing plants and the footprint size of the capture process facility, which must be sited near to the point source, as well as the interactions between the sorbent materials and trace gases in the waste stream which are often corrosive or deleterious, especially to the benchmark amine sorbent materials (Uyanga and Idem, 2007; Soosaiprakasam and Veawab, 2008). Furthermore, temperature swing processes such as the benchmark amine-based processes require a substantial amount of waste heat to desorb the captured CO_2 which may be available in sufficient quantity for a capture from certain point sources such as power plants although at a high parasitic energy cost (Lin et al., 2016). However, similar waste heat may not be available in industrial manufacturing waste streams, for example.

One potential method to avoid these issues is to directly react the low partial pressure CO_2 with a reagent that provides a platform for further product generation. This approach has superficial similarities with amine-based chemisorption processes, in that a new chemical bond is formed with the flue gas CO_2. However, such a direct utilization route has the benefit of not requiring large energy expenditure to re-release the CO_2 into the gas phase, but instead takes the "capture product" and directly converts it further to form value-added compounds. By necessity, this will require a stoichiometric quantity of the reagent, which must therefore be able to be generated using environmentally benign processes.

Previous work carried out by this group has identified organometallics and particularly Grignard reagents as being suitable for the direct conversion of flue gas concentration of CO_2 into value-added products such as acetic, terephthalic, and adipic acids (Dowson et al., 2015). The organomagnesium reagent, which was shown to react readily with CO_2, even at low partial pressures, can then be regenerated from the by-product magnesium dihalide (MgX_2). Electrolysis of the dihalide produces magnesium metal and the elemental halogen, which can then either directly halogenate certain hydrocarbons or be "burned" in hydrogen and subsequently reacted with an alcohol to produce the organohalide starting precursor (RX) to the initial Grignard reagent (**Figure 3**). In this way, the Grignard reactant is "looped" making the overall process akin to post-combustion chemical looping, which is typically carried out using calcium oxide as a reactive capture agent (Blamey et al., 2010). Again, the difference in this case is that the looping process produces a value-added compound containing the captured CO_2 rather than low-value CO_2 gas, combining both capture and utilization in one step.

As a result, the reduced magnesium consumed during the reaction provides the driving force for the overall process, rendering all other steps exothermic, and readily carried out at ambient pressures and temperatures. The hydrogen-halide burning process in particular is extremely exothermic and can also allow for surplus energy recovery (Group, 2014). The crucial magnesium electrolysis step, while highly energy intense, is also highly efficient in industrial magnesium production from sea salts. Faradaic efficiencies approaching 90% have been reported, and energy costs may be further reduced if the expensive magnesium chloride drying process can be avoided by using non-aqueous hydrogen halide for the post-Grignard reaction quench step (Polmear, 1999).

Naturally, it should be noted that Grignard reagents are highly sensitive to water, requiring that any incoming flue gas stream that supplies the CO_2 for the first step in **Figure 3** must

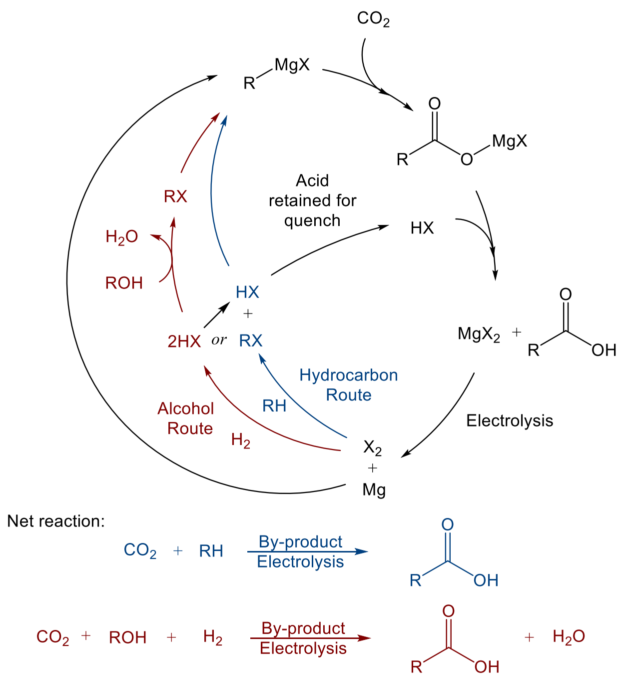

FIGURE 3 | General Grignard CO_2 reaction/cycle scheme including Grignard regeneration using alcohols or hydrocarbons as starting reagents.

be vigorously dried. While this would normally represent a considerable energy penalty for the process in terms of more standard capture approaches, compared with the electrolysis of one molecular equivalent of magnesium salt per molecule of CO$_2$ captured, the energy cost is relatively small. Furthermore, there is the possibility that the drying process could be carried out using the otherwise non-recoverable portion of the exothermic heat (waste heat) from the reaction process to thermally cycle drying agents. In any case, the flue gas will need to be dried irrespective of the capture process, either post-capture in the case of amines or pre-capture for membranes or direct CDU.

Trace levels of water that are carried through to the Grignard reaction will cause the formation of methane and Mg(OH)X. The methane could potentially be recycled to increase the CO$_2$:O$_2$ ratio in the flue stream or otherwise utilized/reclaimed. The other product, Mg(OH)X, would be converted to the standard MgX$_2$ by-product after the general Grignard quench with HX. Some care would have to be taken to avoid the formation of MgO, which is not typically reduced by electrolysis in the same way as MgX$_2$, although this too is relatively easily converted back to MgX$_2$. Overall, the presence of small quantities of water would primarily serve to only reduce reaction yield. Previous work carried out by our group has indicated that the reaction of Grignard reagents with oxygen is relatively slow compared to its reaction with CO$_2$, although flue gas streams with very high oxygen levels may see trace amounts of the oxygen products, MgO, methanol, and possibly dimethyl ether (Goebel and Marvel, 1933; Dowson et al., 2015).

Without these undesirable reactions, the post-quench products of the reaction of Grignard reagents with CO$_2$ are carboxylic acids, which are not typically used as liquid fuels, although they can be used to generate biodiesel esters. Further conversion steps are therefore required for the generation of a more conventional advanced fuel. One potential advanced fuel target would be butanol. Butanol is well recognized to be a potential drop-in replacement for petrol in road vehicles as well as a suitable blending agent for diesel engines (Yao et al., 2010). Unlike ethanol, which can only be blended with hydrocarbon fuels up to certain limits due to its corrosivity and hydrophilicity, butanol is lipophilic and non-corrosive (New Zealand Ministry of Transport and SGS Industrial, Penrose 2009). Furthermore, it has a slightly higher energy density (36.0 MJ/L) than gasoline (34.2 MJ/L), and similar burn rate and octane number, allowing completely unmodified vehicles to run on both butanol alone and butanol/petrol fuel blends (Szulczyk, 2010; Xu and Avedisian, 2015). Butanol further allows higher ethanol concentrations to be used within blended fuels, as it solubilizes ethanol in the bulk petrol and prevents ethanol volatilization (Yanowitz et al., 2011).

As a CDU fuel, butanol is also attractive as it requires significantly less hydrogen to produce it from CO$_2$ than the proposed synthetic hydrocarbons suitable for petrol engines. This is due to its relatively high density, partial oxidation, and shorter chain length. Simple stoichiometric calculations show that 15% less hydrogen per liter and 26% less hydrogen per kilogram is required in the product fuel than for synthetic octanes. Given the limitations in energy efficiency of hydrogen generation from water electrolysis, this presents a potentially significant energy advantage for butanol production (Dincer and Acar, 2015). Furthermore, as a single-component fuel, it does not encounter issues with the absence of branched and aromatic compounds in synthetic hydrocarbons that reduce the octane numbers of methanol-to-gasoline and Fisher–Tropsch products to unsuitable levels (Dry, 2002). The fact that it can be used as a single-component fuel potentially allows for higher general engine efficiency to be achieved even than conventional petrol as the combustion characteristics are entirely uniform and not disrupted by variations in low-octane components, when the butanol is being used alone (Irimescu, 2012). The other advantage is that mixtures of butanol isomers can be directly used as drop-in fuels, meaning that isomer mixtures do not need to be separated prior to use.

However, the production of butanol from carbon dioxide, other than *via* biological processes or syngas, has previously only been reported as trace production in the high temperature/pressure hydrogenation of CO$_2$ in water by platinum/cobalt catalysts (He et al., 2016). Here, we report a route to produce butanol-based fuel that is suitable for petrol-based applications in a multi-step-moderate-yield process. This has the potential to become a moderate-to-high yield process from CO$_2$ once fully optimized. The reported process is demonstrated under near-ambient conditions for the major synthesis steps.

EXPERIMENTAL METHODS

All reagents and deuterated solvents were purchased from Sigma-Aldrich at the highest available purity and were used without further purification. Schlenk-line techniques, used where indicated, were carried out using furnace-dried glassware under a dry nitrogen atmosphere. The apparatus was purged at least three times prior to handling of air-sensitive Grignard reagents. All solvents were purchased from VWR at HPLC grade or higher and were used without further purification. H$_2$, CO$_2$, N$_2$, O$_2$, and dry synthetic flue gas (12% CO$_2$, 88% N$_2$) were supplied by BOC-Linde. Catalyst pre-treatment and hydrogenation experiments were carried out in a 250-mL stainless steel Parr autoclave with heating mantle and glass insert and were stirred magnetically using an IKE stirrer hot-plate.

^{1}H NMR spectra were recorded on a Bruker Avance 400 spectrometer operating at 400 MHz. All samples were dissolved in deuterochloroform and TMS added as the internal standard. Quantitative analysis of the butanol mixtures was performed by ^{1}H NMR using mesitylene (10 μL) as an internal standard against 0.2 mL of reaction products diluted with deuterochloroform.

BUTANOL SYNTHESIS: GRIGNARD REACTION AND ESTERIFICATION

Magnesium Acetate Chloride ($CH_3COOMgCl$)

A 250-mL two-necked, round bottom flask with magnetic stirrer bar attached to a reflux condenser and Schlenk-line apparatus with large silicone oil bubbler, under an atmosphere of dry nitrogen was cooled in an ice-water bath. Methylmagnesium chloride (50 mL, 3.0 M solution in THF, 150 mmol) was added under a flow of dry nitrogen. A further 100 mL of dry THF was added to maintain solubility of Grignard reagent throughout the reaction. After liquid additions were complete and the reaction vessel sealed, the nitrogen flow was stopped. Dry synthetic flue gas (12% CO_2, 88% N_2) was admitted at a slow flow rate that maintained positive overall pressure through a needle adapter and sparging needle inserted as deeply as possible into the liquid layer. Flow was monitored using the oil bubbler. Maintaining low gas flow rates and the use of a reflux condenser was important to limit the evaporative loss of solvent and formation of a gel-like solid within the reaction vessel, indicative of poor initial solubility or inverse solubility of the magnesium chloride acetate salt intermediate product in THF. The latter effect can become pronounced, particularly if temperatures become elevated. Complete reaction was indicated by a stable internal pressure when gas flow was paused (monitored by oil bubbler) or by the reaction remaining cold or cooling even when the ice bath was temporarily removed. The resulting product, magnesium acetate chloride, was used directly in solution without isolation.

Ethyl Acetate by Direct Esterification of Magnesium Acetate Chloride

The Grignard reaction mixture was quenched by the very slow addition of a small excess of sulfuric acid (30 mL, 166 mmol) dissolved in ethanol (100 mL). The resulting mixture was then fractionally distilled, using a long fractionating column due to the relatively close boiling points of THF and the ethyl acetate/ethanol azeotrope (66 and 71.8°C). The resulting product was dried using anhydrous magnesium sulfate and stored over molecular sieves. Crude product yield was 13.62 g, indicating an ethyl acetate yield of approximately 9.41 g (71% overall yield from the starting Grignard agent) with an azeotropic composition of 71.8% ethyl acetate. Separation of the azeotrope was not attempted as neither ethanol nor trace THF would adversely affect subsequent reaction stages.

Ethyl Acetoacetate

A Claisen condensation was carried out using a previously published procedure which emphasized the importance of ensuring the alkoxide salt was of highest purity possible to achieve maximum yield (Fisher and McElvain, 1934). Therefore, freshly prepared sodium ethoxide (1.3 g, 19 mmol) was added to the azeotropic mixture from the previous reaction and heated under reflux for 24 h. The mixture was then cooled and aqueous acetic acid added slowly to quench the base. The product, ethyl acetoacetate was extracted using diethylether, with additional distilled water added to the reaction mixture to limit ethanol contamination of product yield. 4.80 g of very pale yellow ethyl acetoacetate (69% yield from ethyl acetate) was isolated and characterized by ^{1}H NMR spectrometry, comparing the resulting spectrum to reference spectra: δ_H (ppm) 400 MHz, $CDCl_3$: 1.30 (t, 3 H), 2.28 (S, 3 H), 3.45 (S, 2 H), and 4.20 (q, 2 H).

HYDROGENATION CATALYST (Cu/ZnO) PREPARATION

ZnO (32.55 g, 400 mmol) was added to a 1 M aqueous solution of $Cu(NO_3)_2$ (100 mL, 100 mmol) and stirred to form a well-dispersed slurry. The suspension was dried under vacuum using a rotary evaporator and the moist solid further dried using the same method with the addition of 2-propanol to drive off moisture by azeotropic evaporation. The resulting solid was placed in a furnace at 500°C for 16 h to yield a gray-black powder of CuO supported on ZnO. 2 g of the resulting powder was placed in a 250-mL Parr autoclave and heated to 200°C under 10 bar H_2 for 4 h. During cooling, the autoclave was evacuated to remove any generated water, yielding a copper-orange powder of Cu on ZnO with a loading of 20 wt% Cu determined by the initial molar ratio of the reactants.

HYDROGENATION AND HYDROGENOLYSIS

Ethyl acetoacetate (4.80 g, 36.9 mmol) and ethanol (5 mL) were added to the catalyst contained in the 250-mL Parr autoclave which was then sealed and purged using H_2 to a pressure of 20 bar. Reaction was continued for 16 h. The reaction mixture was cooled and filtered, then dried over anhydrous magnesium sulfate to yield 10.5 mL of mixed alcohols, which were analyzed by ^{1}H NMR spectroscopy (**Table 1**) with quantitative analyses carried out using mesitylene [δ_H(ppm) 400 MHz, $CDCl_3$: 2.25 (s, 9 H), 6.75 (m, 3 H)] as an internal standard. The branched methyl group on the 2-butanol appears as a doublet at a shift of 1.12 ppm was cleanly away from the bulk of the signals. The combined integral of the terminal CH_3 groups (at δ_H 0.7–0.8 ppm) where the 1- and 2-butanol signals overlap was determined and the amount of 1-butanol was determined by subtracting the amount of 2-butanol based on the amount determined from the 1.12 ppm doublet. A small doublet was observed next to the 2-butanol doublet which did not fit with being a carbon satellite and fitted the reference spectrum for 1,3-butane diol (the terminal CH_3), which was used to calculate the butanediol concentration. The combined butanol isomers, butanediol and acetone were isolated in 98% conversion from ethyl acetoacetate with 95% selectivity to the butanol isomers. The overall four-step conversion from methyl magnesium chloride (chloromethane) to butanol isomers is 44%.

RESULTS AND DISCUSSION

Producing butanol entirely and directly from CO_2 using the Grignard process would not be possible without additional steps

TABLE 1 | Composition of total product mixture, determined by ^{1}H NMR, 400 MHz, $CDCl_3$.

Composition	1-butanol	2-butanol	Ethanol	1,3-butanediol	Acetone
Mass (%)	69	26	4	1	<1
Volume (%)	70	25	4	1	<1

and starting reagents. First, the Grignard process requires a hydrocarbon or alcohol to form the initial Grignard reagent and the product of the Grignard reaction would have to be converted from a carboxylic acid to the final alcohol product. With CDU processes in mind, the two obvious candidates for the starting hydrocarbon and alcohol shown in **Figure 3** would be methane and methanol, both readily synthesized by the hydrogenation of CO_2 (**Figure 4**) (Mikkelsen et al., 2010; Saeidi et al., 2014). The selective formation of methyl halide from the reaction of methane and the elemental halogen is somewhat challenging, due to the higher reactivity of the products than starting materials, although appropriate choice of rare-earth or precious metal catalyst can yield the desired product (Olah et al., 1985; Podkolzin et al., 2007). By comparison, the conversion of methanol into any of the methyl halides is rather trivial using the hydrogen halide to carry out nucleophilic substitution. The former pathway remains potentially interesting as it does not require the addition of hydrogen to the process shown in **Figure 3**, although additional hydrogen would be needed in the CDU production of methane over methanol. With either of these compounds used as starting materials, the product of the Grignard process, after quenching, is acetic acid. This would have to then be condensed and hydrogenated to form the desired product, butanol.

Condensing two equivalents of smaller molecules such as ethanol, to produce butanol has previously been reported by Guerbet chemistry (Koda et al., 2009; Dowson et al., 2013; Ho et al., 2016). However, production of butanol from acetic acid has not previously been reported. Although butanol has previously been made directly from CO_2, the yield was limited (Irimescu, 2012). Acetic acid can be condensed in the Claisen self-condensation *via* ethyl acetate to produce the desired four-carbon chain product, as shown in **Figure 5**.

While this reaction is readily carried out in the presence of a strong base, the final alkyl acetoacetate (ethyl acetoacetate in the case shown in **Figure 5**) product cannot be isolated without an acid quench, requiring a stoichiometric equivalent of base to be consumed to drive the otherwise mildly endergonic reaction. Care must also be taken that the acid quench does not hydrolyze the alkyl ester to produce the oxobutanoic acid (acetoacetic acid), as this is not stable, particularly at room temperature, decomposing to produce acetone and carbon dioxide (Hay and Bond, 1967).

Hydrogenation of the produced acetoacetate ester to directly yield butanol had not been previously reported in the scientific literature but similar hydrogenation processes using supported Cu(0) catalysts have been reported, particularly in the reduction of highly oxidized species such as low-molecular weight esters, glycerol, dimethyl maleate, and carbon dioxide (**Figure 6**) (van de Scheur and Staal, 1994; Brands et al., 1999; Schlander and Turek, 1999; Bienholz et al., 2011).

By including all compounds generated and consumed during the overall reaction process, a basic energetic pathway of the generation of butanol from the reaction of methanol with CO_2 and hydrogen, as described in the experimental section can be constructed using the available reaction enthalpy data (**Figure 7**).

Note that this energy calculation in **Figure 7** excludes the initial formation of the methanol (or methane) starting reagent, previously illustrated in **Figure 4**, for clarity.

From the starting methanol, the reaction profile clearly demonstrates the strongly exothermic nature of the overall reaction pathway, but naturally does not show the energy required to regenerate the Grignard agent, which provides the majority of the driving force for the overall process, with the remaining steps driven by the by-production of water in the esterification and hydrogenation steps. Furthermore, it should be noted that

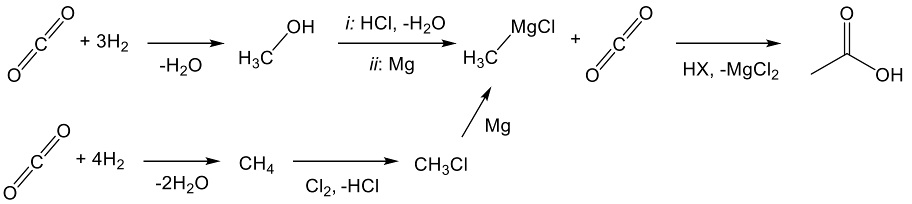

FIGURE 4 | Overall preparation of acetic acid *via* CO_2 hydrogenation followed by Grignard reaction.

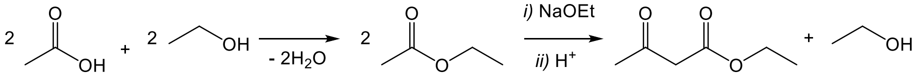

FIGURE 5 | Esterification of acetic acid and Claisen condensation of ethyl acetate.

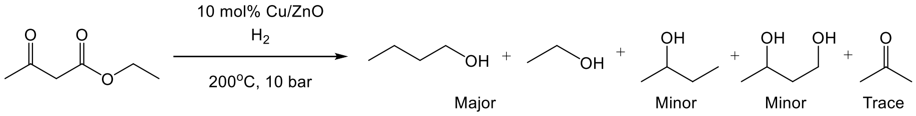

FIGURE 6 | Hydrogenation of ethyl acetoacetate to produce butanol, ethanol, and minor by-products.

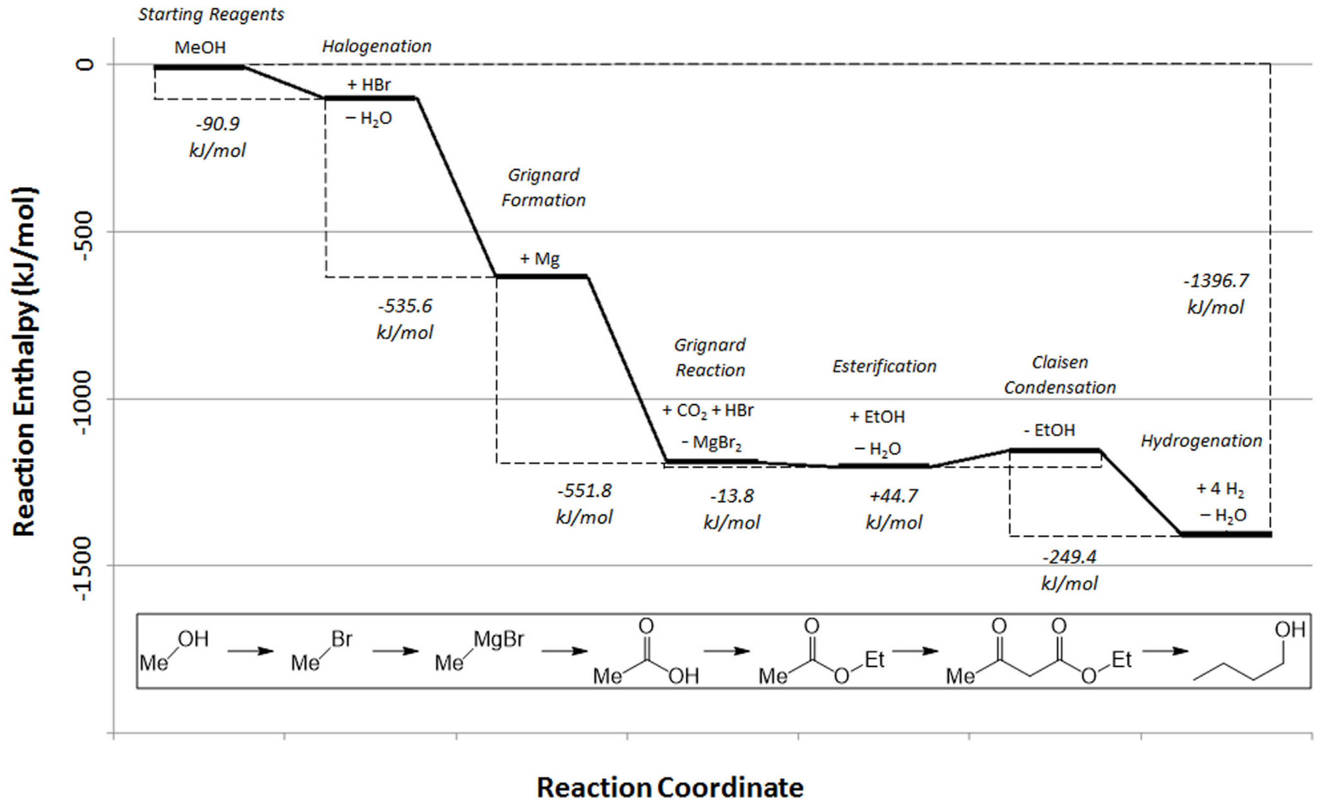

FIGURE 7 | Reaction enthalpy profile for the synthesis of butanol from methanol in a carbon dioxide utilization process (NIST, 2017).

the Claisen condensation has a slightly positive overall enthalpy of reaction. This, in combination with the reaction entropy, renders this step of the reaction non-spontaneous without consumption of one equivalent of base by use of acid work-up (Davis and Garratt, 1991). However, given the exothermic nature of the overall reaction pathway, a broad estimation of the overall energy cost of the reaction, starting from methanol or methane, can be calculated from the energy requirements of magnesium regeneration, hydrogen production, and Claisen base/acid. Note that this calculation does not include energy costs associated with the drying of the carbon dioxide source and assumes 100% reaction yield. Simultaneously, potential energy recovery of the 15.26 MJ/L exotherm from the reaction process shown in **Figure 7**, has not been included, which would make the overall process more favorable. While the drying costs will be small in comparison with the other energy requirements such as magnesium electrolysis, reaction yields may be limited. In fact, magnesium electrolysis costs can be minimized by realizing that the process operates commercially at large scale and so it would be economically more favorable to batch process the regeneration of magnesium as part of that process rather than using dedicated electrolysers. At this stage, energy costs associated with the process alone are considered. A full life-cycle analysis is being carried out to account for all impacts, including the impact of methanol production and transport of the by-product to the electrolysis site. However, a full scope three LCA falls outside the scope of this paper due to the complexity of the analysis.

TABLE 2 | Minimum energy cost per liter of butanol fuel produced from methanol and methane.

Reaction component	Required amount	Alcohol route	Hydrocarbon route
Magnesium electrolysis[a]	531.2 g/L	13.37 MJ/L	13.37 MJ/L
Hydrogen production[b]	88.1 and 66.1 g/L	16.80 MJ/L	12.60 MJ/L
Claisen base/acid[c]	437.1 g/L	1.53 MJ/L	1.53 MJ/L
Total energy cost	–	31.7 MJ/L	27.5 MJ/L
Increase in fuel energy[d]	–	15.4 MJ/L	9.74 MJ/L
Energy efficiency	–	48.6%	35.4%

[a] *Calculated using magnesium electrolysis cost of 25.2 MJ/kg (Demirci and Karakaya, 2012).*

[b] *Hydrogen electrolysis efficiency of 75% used.*

[c] *Chloralkali process for base (NaOH) production (Thannimalay et al., 2013).*

[d] *Calculated by difference in energy density of butanol compared to 2 M equivalent quantities of methanol and methane, respectively.*

By comparison of the specific energy of the starting materials (methanol and methane, respectively) with the energy density of the butanol product, and then comparing this difference with a reasonable minimum overall energy cost of conversion (including magnesium regeneration, hydrogen generation, and the stoichiometric acid and base required to complete the Claisen condensation) a calculation of the efficiency of the transformation *via* this route, with the assumptions listed above, can be made (**Table 2**).

It should be emphasized that **Table 2** represents the *minimum* energy cost of butanol production calculated with the assumptions

TABLE 3 | Minimum energy cost per liter of butanol fuel produced from CO_2 and hydrogen only.

Reaction component	Required amount	Reaction energy costs
Magnesium electrolysis[a]	531.2 g/L	13.37 MJ/L
Hydrogen production[a]	264.4 g/L	50.41 MJ/L
Claisen base/acid[a]	437.1 g/L	1.53 MJ/L
Total energy cost	–	65.31 MJ/L
Product fuel energy	–	29.2 MJ/L
Energy efficiency	–	44.7%

[a]*Calculated as in* ***Table 2***.

listed below the table and assumes 100% chemical yields for all steps but with realistic energy requirements for the reagent costs. While such maximal yields are implausible, near-quantitative yields for each step should be possible in principle.

Note also that this calculation omits the production of methanol/methane from CO_2 as with **Figure 7**. A calculation including the energy costs of the additional hydrogen required to form the methanol and methane required for the Grignard route are shown in **Table 3**. However, it should be noted that these figures omit any costs of capture and purification of CO_2 from a waste gas stream, which would be required for the initial step of this route.

These two tables illustrate that the energy costs associated with chemical looping of magnesium to capture CO_2 and upgrade methanol or methane to drop-in petrol replacement does not significantly outstrip the energy gain in the content of the produced fuel. In addition, it can be seen in the two tables that the conversion of CO_2, methanol or methane into butanol by a CDU approach, and without any additional energy recovery but with optimistic reaction yields, could in principle convert nearly half of a given quantity of electrical energy into a storable fuel that is directly compatible with existing infrastructure. While it is tempting to therefore make comparisons with the efficiencies of existing energy storage methods such as pumped hydroelectric storage and compressed air energy storage (which are higher), these approaches would have a completely different role in energy storage than a CDU-based fuel.

Overall, we believe that it is not unreasonable to suggest that CDU fuel production could realistically represent a new tool in balancing electricity demand and supply and could, with sufficient installation of renewable energy, make a tangible impact in reducing the carbon footprint of liquid fuel transportation.

CONCLUSION

Butanol can be produced using a multi-step synthetic approach from methane or methanol *via* a Grignard reagent that reacts with dilute carbon dioxide in nitrogen to give an acetate intermediate. Classic synthetic organic chemistry then allows homologation to give a four-carbon backbone that is partially hydrogenated to yield a mixture of 1- and 2-butanol. Each isomer has a higher octane number and energy density than octane itself and can be used as a direct drop-in fuel for gasoline-based combustion engines. This means the fuel can be used directly in existing automobile engines without blending or modification of those engines. The transformation, which is overall exothermic from the Grignard reagent, is facilitated by the high energy of the organometallic starting material. Energy is therefore required to regenerate the magnesium from the stoichiometric amount of magnesium halide by-product. If this is reprocessed using standard high-efficiency industry electrolysis techniques using renewable energy then the cost of this step is minimized.

The methodology allows liquid fuels to be produced from renewable, weather-dependent electricity at times where it would otherwise be curtailed, or in situations where dedicated generation is installed. This provides a potentially excellent method for chemical energy storage across seasons, otherwise not possible using other storage methods. The process also adds value to the system by removing carbon dioxide from primary emissions sources, storing otherwise curtailed excess renewable energy and by avoiding new fossil carbon from entering the supply chain when the fuel is used. While current projected utilization quantities are expected to fall short of the vast quantities of CO_2 anthropogenically emitted, it provides a tool in the arsenal for the production of low-carbon fuels and to balance energy demands in an increasingly intermittently powered world. It is recognized that the fuel will eventually lead to CO_2 emissions, but this will not be new carbon but second generation, upcycled carbon.

The fact that flue gas concentration carbon dioxide is used means that the costly carbon capture step can be omitted, although it would be required in some form for total synthesis of fuel from CO_2 and hydrogen alone. In the original case where methanol or methane are used as starting reagents, this is an example of reactive capture of CO_2 where the gas is chemically removed from the flue gas stream, thereby purifying the waste stream while at the same time producing a value-added product. The process has a number of steps including the esterification and Claisen condensation where improvements can be made through more precise definition of the reaction parameters. The overall carbon avoidance can also be improved by using methanol sources from CO_2 to prepare the Grignard reagent through methanol bromination and by preparing the methyl rather than the ethyl ester. We will also look at using real flue gases from industrial emissions to test the robustness of the methodology and product purity.

AUTHOR CONTRIBUTIONS

GRMD was the Postdoctoral Research Associate who carried out the laboratory work. PS was the academic supervisor and Principal Investigator. There were equal contributions to the production of this paper.

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Why Synthetic Fuels Are Necessary in Future Energy Systems

I. A. Grant Wilson[1,2] and Peter Styring[1]*

[1]UK Centre for Carbon Dioxide Utilisation, Chemical & Biological Engineering, Sir Robert Hadfield Building, The University of Sheffield, Sheffield, United Kingdom, [2]UK Energy Research Centre (UKERC), London, United Kingdom

We propose a hypothesis that fuels will continue to be critical elements of future energy systems. The reasons behind this are explored, such as the immense benefits conferred by fuels from their low cost of storage, transport, and handling, and especially in the management of the seasonal swing in heating demand for a country with a summer and winter season such as the UK. Empirical time-series data from Great Britain are used to examine the seasonal nature of the demand for liquid fuels, natural gas, and electricity, with the aid of a daily Shared Axis Energy Diagram. The logic of the continued need of fuels is examined, and the advantages and disadvantages of synthetic fuels are considered in comparison to fossil fuels.

Keywords: synthetic fuels, CO_2 fuels, seasonal storage, low-carbon fuels, TWh storage

Edited by:
Youngjune Jason Park,
Gwangju Institute of Science and Technology (GIST),
South Korea

Reviewed by:
Sune Dalgaard Ebbesen,
Innovation Fund Denmark, Denmark
Dong-Yeun Koh,
Georgia Institute of Technology,
United States

****Correspondence:***
I. A. Grant Wilson
grant.wilson@sheffield.ac.uk

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INTRODUCTION

Nearly all modern energy systems are critically dependent on fossil fuels. Part of this is due to the cost and availability of fossil fuels versus other primary and secondary energy sources, but an often-overlooked reason is from the intrinsic benefit that these fuels bring. The ability to store terawatt hours (TWhs) of chemical energy economically allows the supply of primary energy to be decoupled from the demand of energy on a grand scale, both in terms of the timeframe and in terms of the location. For a country like Great Britain, with distinct summer and winter seasons, the ability to store TWhs of fuels for heating helps to balance out this major seasonal demand swing. The move toward ever-greater amounts of primary energy sourced from weather-dependent renewables (primary electricity[1]) brings challenges in the ongoing balance of supply and demand over different timescales, and over different distances, with the interseasonal swing in heat demand being one of the greatest.

The global deployment of weather-dependent renewable generation such as wind generation and solar PV seems set to continue, as costs decrease, and increased knowledge is gained on how to successfully integrate greater amounts of primary electricity within electrical systems (as a subset of wider energy systems). In 2014, 2015, and 2016 renewable generation (excluding large hydro) was 45.3, 51.3, and 55.3%, respectively, of the annual global electrical generation change in capacity (Frankfurt School-UNEP Centre, 2017), compared to a value of just 19.5% in 2007. This level of increase over a decade justifies that weather-dependent renewables can be considered a mainstream technology choice for many countries, which has helped to bring costs down, but like other mature forms of generation there are still several areas where technology development could bring additional cost improvements.

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[1] Electricity that is harvested directly from nature without the need for a fuel, *inter alia* solarPV, solarThermal, wind, wave geothermal, and tidal.

The major historical driver, at a time when the costs were higher for wind and solar PV generation, was for countries to encourage investment/deployment as a means to reduce their carbon emissions. This growth in markets led to manufacturing and technological advances that provided cost reductions, which itself helped greater investment and further growth. The original focus on carbon reduction is now being augmented by additional drivers such as the security of supply, diversification of primary energy sources away from fossil fuel imports, and increasingly the benefit of deploying renewable energy as an economic form of generation. In a similar vein to exploiting their fossil resources for the twin benefits of domestic economic activity and a decrease in imports, or even an increase in exports, the increase in experience and drop in generation prices allows countries to consider exploiting their renewable energy resources at greater scales than previously imagined. With countries singing up to the COP21 Paris Climate change agreement and submitting Intended Nationally Determined Contributions with lower-carbon targets, the decarbonization of the electrical system will continue to be a priority over the medium term: precisely because experience around the world shows that it is possible. In Great Britain, for example, a combination of demand reduction, increased low-carbon renewable generation, and fuel switching from coal to natural gas generation has provided an emissions reduction of 61% in 2016 from a 1990 baseline.

With the level of direct subsidies for renewable generation reducing, and capacity auctions growing increasingly common, the direct government costs of subsidizing renewable energy are becoming more controlled and understood; however, the indirect costs of accommodating higher and higher levels of primary electricity are still subject to considerable uncertainty. A major part of this is due to the increased costs of balancing electrical generation and demand in future systems that have less of a role for fuel-based generation. The ability to balance future energy systems (not just electrical energy systems) is hard to imagine without the benefit of fuels of some sort, and if fossil fuels are limited either for climate or other reasons, then there would seem to be a strong case for synthetic fuels to take their place.

The contribution of this article is to propose the critical ongoing need for fuel-based storage to overcome seasonal variations in energy demands for Great Britain, evidenced by using multi-year empirical time-series data for liquid fuels, natural gas, and electricity.

This paper is divided as follows: first, the levels of stored fuels in Great Britain are outlined, their levels discussed, and the initial case for fuels is put forward. Next, the seasonal variation in Great Britain's energy demand for liquid fuels, natural gas, and electricity is presented with a top-level look at the synergy between solar and wind generation using empirical data. Next, the discussion and conclusion parts indicate the main findings of the paper and the consideration of these for a wider audience of policy makers and existing or potential bulk electrical storage operators.

Hypothesis

The hypothesis described in this article proposes that due to the sheer scale of fuel use that provides the interseasonal stores of energy that modern energy systems require, that the use of fuels will still be justified in future energy systems too. It is difficult to conceive of energy systems moving to a just-in-time provision of energy from non-fuel-based primary energy sources to final energy demand, as the challenges of balancing this over seasons without the benefit of fuels are insurmountable. Fuels confer immense energy system benefits due to their low cost of storage, transport, and handling and in any decarbonized future energy system, having low cost means of storing and transporting TWhs of energy will still be critical to the successful delivery of energy over an annual basis. The hypothesis is grounded in the belief that there will be a continued requirement to decouple primary energy supplies from demands at a grand scale on both a temporal scale and location. At an estimated 240 TWh of average stored energy in fossil fuels in Great Britain over the 2012–2016 period analyzed, the scale of this is compared to the seasonal nature of the demand for liquid fuels, natural gas, and electricity, with the aid of a daily Shared Axis Energy Diagram. The logic of the continued requirement of fuels is examined, and the advantages and disadvantages of synthetic fuels are considered in comparison to fossil fuels.

AVERAGE AMOUNT OF STORED ENERGY IN GREAT BRITAIN

Table 1 shows the approximate average amount of stored energy in Great Britain for the main solid (coal), gaseous (natural gas), and liquid fuels (crude oil and oil products) over the period from 2012 to 2016. There is a seasonal variation in the amount of coal and natural gas held in storage, but the total inventories of crude oil and oil products has less of a seasonal component. This is thought to be due to the underlying demand for the fuels themselves, with electricity (coal and natural gas) and heating (natural gas) having strong seasonal swings, which is less apparent with transport (crude oil and oil products); in addition, crude oil and oil products are traded internationally both import and export to a much greater degree than coal and natural gas.

At an approximate average level of 240 TWh, the levels of stored energy available in Great Britain's fossil fuel stocks are vast. As a member of the IEA and the European Union (for the time period of the data), over half of this is in liquid fuels that is subject to some mandatory level of stored energy, the rest is not mandated and is therefore a market decision. These average levels of stored energy have provided a structurally adequate level of energy supply that has kept Great Britain away from the spectre of running out of energy. The energy supply shocks that have happened have been limited to other types of supply chain

TABLE 1 | Average amounts of stored energy in fuels in Great Britain from 2012 to 2016.

Fossil fuel	Average amount of stored energy (approximate), 2012–2016 (TWh)
Coal	80
Natural gas	30
Crude oil and oil products	130
Total	240

Coal and crude oil values from BEIS Energy Trends monthly data. Natural gas values from National Grid.

disruptions such as pay disputes by tanker drivers, rather than the stores of energy themselves being completely depleted (although March 2013 was a close call for natural gas).

As Great Britain moves to secure more and more of its primary energy needs from renewable electricity sources, there is a shift to weather dependency not only for demand but also for the supply of primary energy. This is said to bring new challenges to balance the difference between supply and demand over different timescales, which is undoubtedly true. However, energy systems have *always* required balancing over different timescales, so this is not a new challenge in and of itself, although the technologies and tools to do so are likely to be. Historically, fuels have allowed this decoupling of primary energy supply from demand on a grand scale at a temporal scale and location.

The question of whether this average stored level of energy at 240 TWh is optimized is explored in the next section.

ARE THE LEVELS OF STORED FUELS OPTIMIZED?

All energy systems benefit from having stores of energy that act as buffers along their supply chain from the collection of primary energy to the final energy use. This is driven by a desire for a certain level of "energy security," which itself is a challenging term to conceptualize (Kiriyama and Kajikawa, 2014; Cox, 2016). The question of how much stored energy should actually be available to an energy system such as Great Britain is an open research question, as it is not optimized at a whole system level between the electrical, natural gas, and liquid fuel networks. Even if it was, the level of stored energy of different fuels can change relatively quickly driven by the difference in demand created by switching fuels, e.g., the "dash for gas" building of natural gas generation in Great Britain (Winskel, 2002) had a major impact on the demands for coal and natural gas. In 2016, the price differential between coal and natural gas as a fuel for electrical generation, coupled with an effective carbon price, provided the market conditions for a fuel switch from coal to natural gas at an unprecedented rate (Wilson and Staffell, 2017).

The additional expense of having stores of energy is accepted and accommodated ultimately by the increase in price to end users, to provide a degree of resilience and reliability to reduce the impact of energy supply chain shocks. When supply shocks do happen to energy systems, economic activity is interrupted, with possible wider sociopolitical consequences too. For countries that have grown used to having high availability of energy systems, the lack of energy (or even the thought of the lack energy) for heating, transport, or provision of electricity looms as a major fear rather than a mere inconvenience. Depending on how long, how widespread, and how arduous an energy supply shock might be, there would be a widespread desire to hold someone to account, and from past experience in Great Britain, this is very likely to initially be the incumbent government of the day.

The amount of stored energy is influenced by market frameworks, such as the regulated market-based approaches used in Great Britain, and on the type of fuel and its cost of storage. Dependent on a complex interplay of factors, each market player will look to their own profitability for storing energy and may choose to physically store energy, e.g., coal or biomass somewhere along its supply chain, or to contractually purchase the delivery of fuel from a third party at a given timeframe, who therefore has the difficulty and expense of storing the fuel until it is required. Third party merchant facilities exist for the storage of fuels, for example, in Great Britain the natural gas grid has access to short-, medium-, and long-term (seasonal) storage facilities that all help smooth out the natural gas demand variation by having gas that is already "in-country," and many of these are available to third parties to store natural gas.

If the individual companies' self-interests align with the needs of the wider system, then this can provide system level benefits, but due to the costs of purchasing and storage of fuels, there are pressures to keep the stores of energy to acceptable levels, which are influenced by factors such as the anticipated change in price of the fuels. Thus, levels of stored fuels are influenced by the current and expected future costs of the fuel versus the cost of storing it, and companies may decide to have a physical hedge of fuel in the form of a stockpile to compliment or reduce the need for a financial hedge against increasing prices. There is a commercial interplay between these different costs and benefits, which is not well understood; however, the main point remains that the levels of stocks of fuels are unlikely to represent an optimized amount to provide a system level benefit.

There may be more opportunity of a system level benefit when there is a monopoly provider of the energy system to dictate the levels of storage, e.g., electricity in a state-owned monopoly, but again, the reason for the amounts of stored energy in fuels are not well understood. Even if there is logic to the level of stored energy on one of the energy systems in a country, such as the electrical system, it is highly unlikely that this will take account of the level of stored energy required in the natural gas or liquid fuels systems too. This lack of a whole systems appreciation of the amount of stored energy across all energy vectors in any country is endemic, but there are positive signs that this whole systems approach is gaining more interest at a policy level (Scottish Government Energy Consultation, 2017; http://www.gov.scot/Publications/2017/01/3414). As more primary energy is harvested using primary electricity, and parts of heating and transport demands are transferred over to the electrical system, this provides policy makers and regulators an opportunity to reconsider energy systems in a more holistic or whole systems manner; meaning that the different primary energy sources, energy vectors, and final energy demands are considered together.

Regardless of the ownership or operation of an energy system, energy stores can be mandated as a matter of political will, typically driven by the overall imperative to reduce the impact of supply chain shocks. A major example of these are the level of inventories of crude oil held by members of the International Energy Agency, equivalent to at least 90 days of their net oil imports. Joining the organization as a member places a legal requirement to hold a minimum inventory of crude oil, which will have a cost. Another example is the level of stocks of petroleum products under European Union legislation, which is based on the average daily consumption of the previous year (Bielecki, 2002). To the authors' knowledge, there is no similar widespread *legal* obligation to hold a certain level of solid or gaseous fuels;

liquid fuels have therefore attracted more political interest than solid or gaseous fuels, as the inventories of these are left up to the market, i.e., it is a market decision.

THE CONTINUED NEED FOR FUELS

It is of little surprise that countries including Great Britain continue to be utterly dependent on fuels for their stored energy requirements; however, a question arises what it would use in the future if not fossil fuels? Large reductions in coal generation have already happened, falling below 10% of all electrical generation in 2016; the first time in Great Britain's electrical history. Data suggest that even less electricity will be produced from coal in 2017, as the first quarter of 2017 shows coal generation to be 11% of the total, down from 16% of the total in the first quarter of 2016. This reduction, mainly due to an effective carbon price, is strengthened by a stated aim of the UK Government to remove unabated coal from Great Britain's electrical system by 2025. If carbon capture and storage (CCS) does not provide coal generation with a lower-carbon future, then the stockpiles of coal, and the energy that they contained, will no longer be available to the system. This means the average of 80 TWh of energy contained in coal stocks between 2012 and 2016 will have gone; a large reduction has already been recorded for the first quarter of 2017 with an average level of below 40 TWh of stored chemical energy in coal (BEIS, 2017). As the first quarter is typically when stocks of coal are at their lowest, it remains to be seen how the levels will rise over the summer and autumn period in 2017.

Assuming that the stored energy of coal is therefore unavailable in Great Britain's future energy systems (without CCS), the same might be argued for natural gas too, as this will come under increasing pressure to move off the system in a deeply decarbonized future. There is a large difference between the two fuels, with natural gas providing 80% of the heating demand of Great Britain as well as providing primary energy for the electrical system. Coal in comparison provides very little heating supply and is primarily used in the electrical and industrial sectors. Moving away from natural gas therefore brings the grand challenge of how to decarbonize the heating sector, as well as part of the electrical sector.

If coal and natural gas are no longer available to Great Britain, it is an open research question how it would balance its energy demand over the year. Due to costs or resource constraints, it is difficult to imagine how tens or hundreds of TWhs of energy can be stored in any energy form that is not a fuel. Non-fuel methods of storing energy are orders of magnitude more expensive than storing fuels, and although they will have vital roles to play in terms of balancing shorter and medium term supply and demand (within day, and days to weeks), they are ill suited to provide the TWh levels of seasonal balancing required by heating demand in particular.

The comparison of the average amount of stored energy of 240 TWh is compared to the daily energy demands of Great Britain in the next section.

DAILY SHARED AXIS ENERGY DIAGRAM FOR GREAT BRITAIN

Figure 1 shows the different energy vectors that Great Britain used on a *daily* basis from 2014 to early 2017. The background and

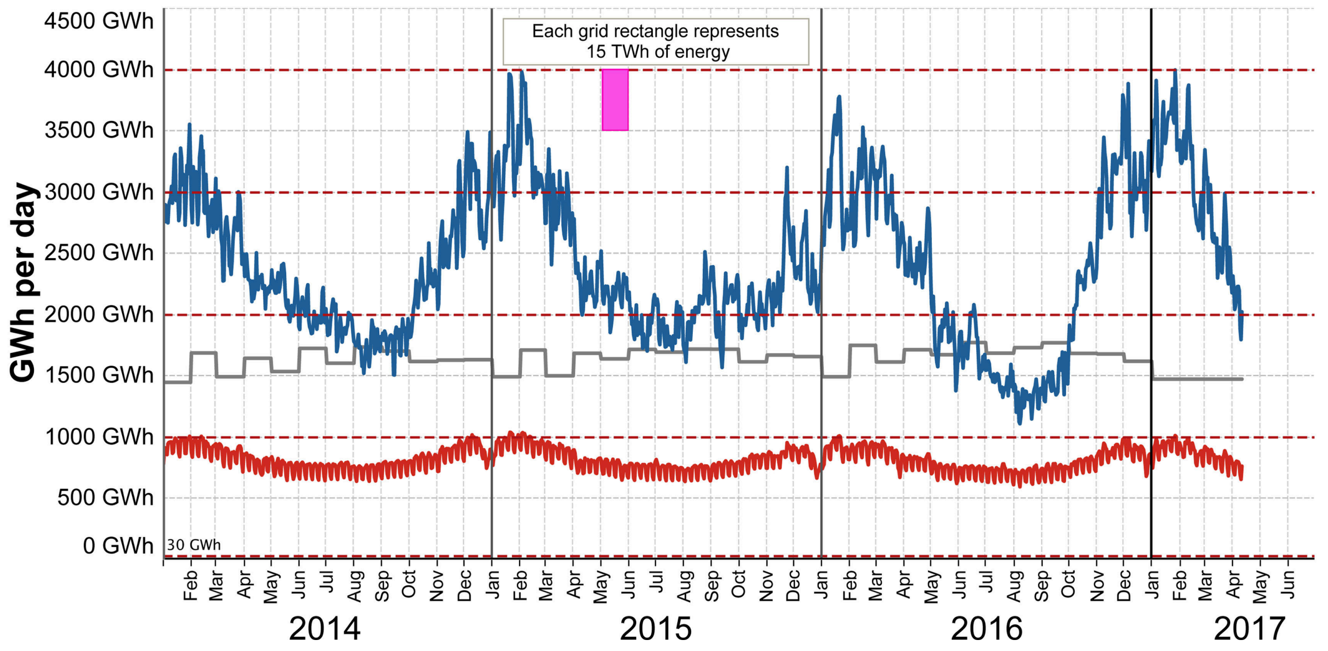

FIGURE 1 | Daily Shared Axis Energy Diagram for Great Britain 2014–2016. Data sources, National Grid, Elexon, and BEIS. Data sources are described in Wilson et al. (2014).

evolution of this daily Shared Axis Energy Diagram is described in Wilson (2016).

The dark blue line is the natural gas demand in Great Britain less the amount exported through interconnectors to mainland Europe. The blocky gray line is the total of motor spirit (petrol), DERV (diesel), and aviation fuel. These are reported on a monthly basis by the department of Business, Energy and Industrial Strategy and are then calculated on a *daily* basis to be comparable with other data in the diagram; the flat end to this line over 2017 is an extension of the January values into February and March (as the reporting of liquid fuels has a time lag). The red line is the amount of electrical demand in Great Britain, which is calculated as the total of INDO (Initial National Demand Out-turn) and the amount of embedded wind and solar generation estimated by National Grid.

The red dotted line, close to the *x*-axis and marked as 30 GWh, is an approximation of the amount of energy that could be stored each day in Great Britain's four pumped storage schemes in total (Wilson et al., 2010), and the magenta box is the size of one grid box in the figure and represents 15 TWh of energy.

Figure 2 replicates **Figure 1** with the magenta box now showing the average amount of stored energy in Great Britain in fossil fuels. From **Table 1**, the value for coal is 80 TWh, natural gas is 30 TWh, and crude oil and oil products are 130 TWh, which total the 240 TWh shown.

It is clear from both figures that the average amount of energy contained in fossil fuels over the 2012–2016 time period is large enough to provide seasonal levels of balancing, whereas the scale of pumped storage at 30 GWh is simply too small to operate over seasonal timeframes. Scaling this up to a global level by considering that in 2015 the primary energy demand of Great Britain was only *ca.* 1.5% of global primary energy demand (BP, 2017), the amount of stored energy in fossil fuels at a global level stored within countries is likely to be in the multi petawatt hour scale (as an order of magnitude estimate). If one were to consider the fossil fuels that are *in situ* in working reserves at the very start of their fossil fuel supply chains, then the stored energy at a global level could be into the exawatt hour range. However, as discussed by McGlade and Ekins (2015), many of these underground stores of energy are likely to come under increasing pressure *not* to be exploited and remain unused and underground.

The next section examines an amount of storage for the non-fuel sources of primary energy.

DAILY CUMULATIVE DIFFERENCE DIAGRAM FOR RENEWABLE ELECTRICAL GENERATION

Figure 3 shows the cumulative difference of the storage required to firm up renewable generation of solar, wind, and solar + wind over the years from 2010 to 2016. The energy generated on each day is averaged over a year per technology, and this annual average is then subtracted from the daily generation value. If the daily output is below average then this gives a negative daily difference value, conversely if the daily output is above average then this will be a positive daily difference value. The annual charts in **Figure 3** are the cumulative total of this daily difference, which starts and finishes the year at a zero amount. Conceptually, the maximum and minimum values for the running total are the amount of storage required to provide a flat average output over the year, given a 100% efficient electrical storage device. Although this top-level

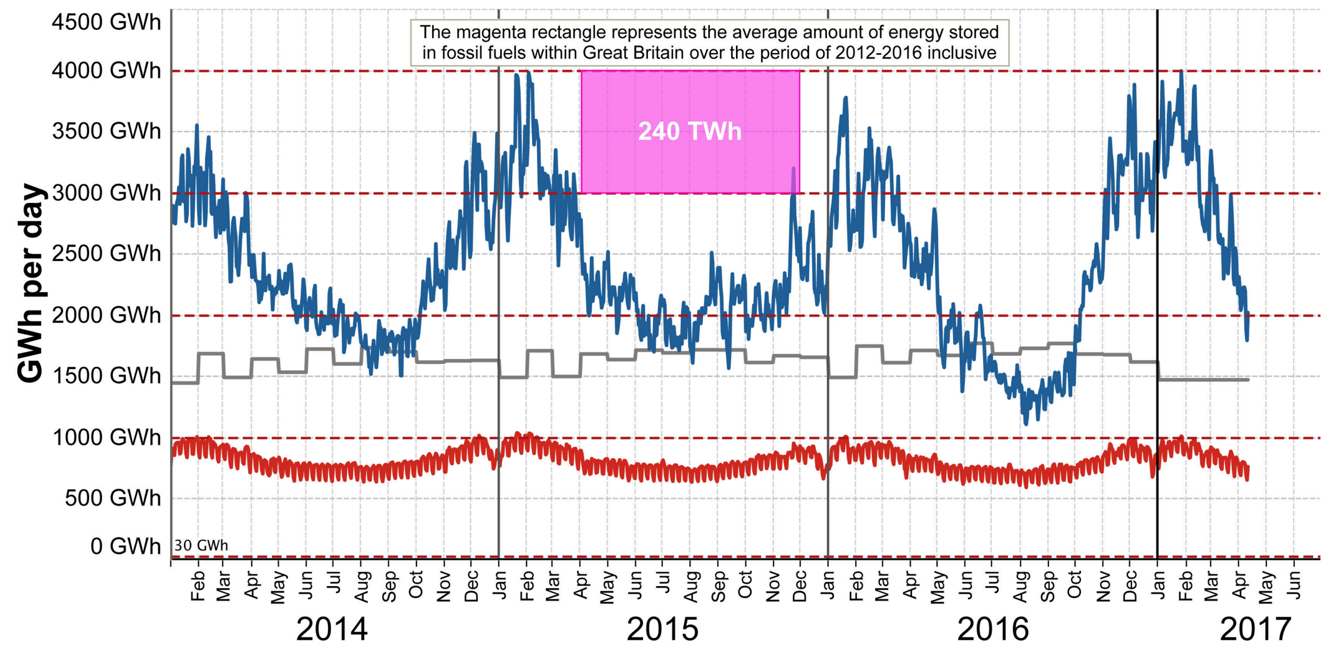

FIGURE 2 | This figure shows the average amount of stored energy in fossil fuels within Great Britain over the period 2012–2016.

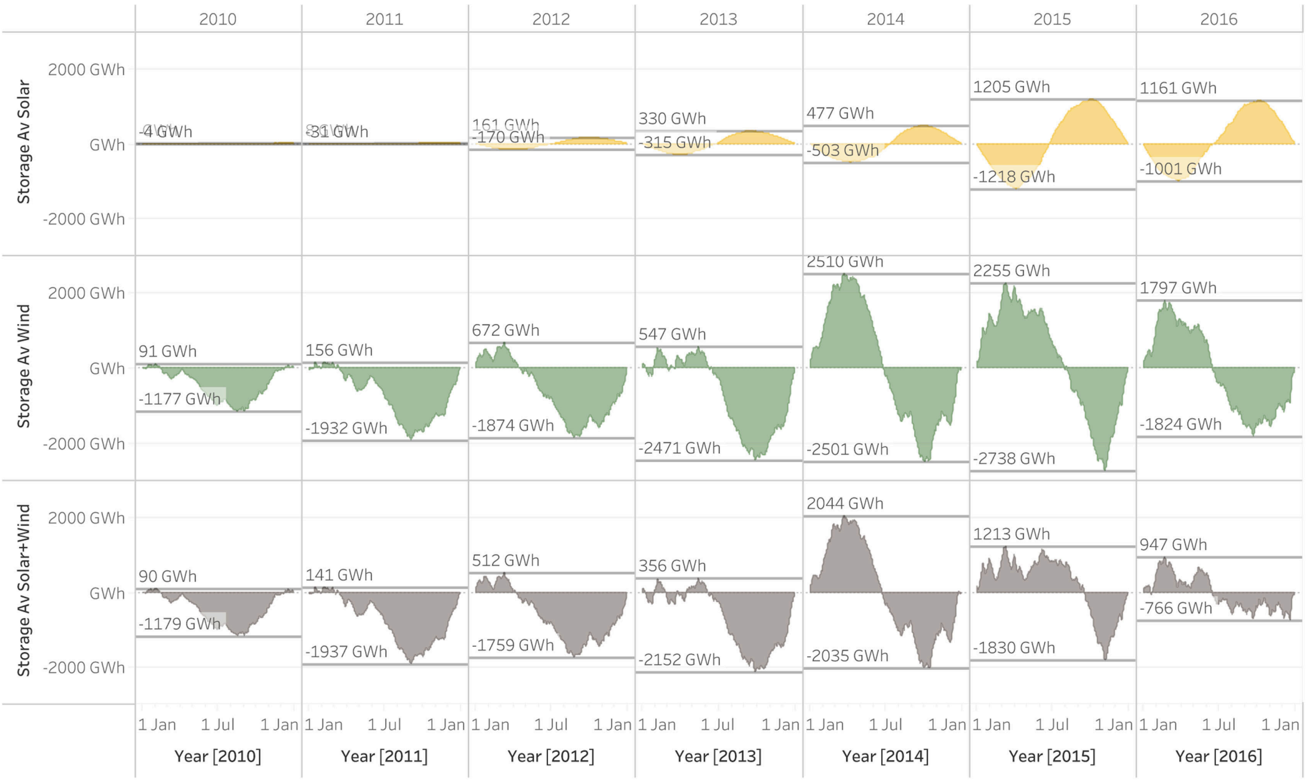

FIGURE 3 | Cumulative difference between Great Britain daily and average annual output from solar, wind, and solar + wind.

assessment is instructive, it is also unrealistic for a number of reasons: the calculation supposes an energy storage device with no efficiency losses, the calculation supposes an energy system that would want to have a flat output over a year from a renewable source. Nonetheless, the calculation shows the benefits of a combination of solar and wind that considerably reduces the need for an amount of storage for either generation type alone. The negative correlation of wind and solar therefore has a positive impact on the amount of storage required to provide a flat annual output and is indicative of the benefits of a diversified electrical generation portfolio.

This exercise also displays the differing range of outputs of weather-dependent renewable generation, with wind having many days considerably above average (high positive slopes in **Figure 3**), and concentrated in the winter and spring periods. As renewable generation capacity continues to be deployed, it brings with it an increased risk of times where curtailment is used to protect the electrical network itself, and the electrical equipment connected to it. The alternating current frequency of the network requires to be kept within strict limits, and curtailment of renewable energy is a method that is used by the system operator to manage the system by turning down or switching off the output from renewable generators. Historical balancing of electrical networks using thermal generation allowed the chemical energy in fuels to be kept in the fuel (by not combusting it) until it was required. This is not possible with wind generation, as the only ability to store the energy of the wind is after it is harvested as electricity. It is simply not feasible to store the wind as wind. The same is true of solar PV generation, as sunlight cannot feasibly be stored as sunlight, but there are technological avenues such as artificial photosynthesis (AP) that provide a route to stored energy without an electrical vector. The global solar PV capacity at the end of 2016 was 303 GW (IEA, 2017); however, this was on a steep trajectory being only 3.7 GW 10 years previously. Wind capacity at the end of 2016 was 486.8 GW (GWEC, 2016). Strictly speaking, AP does not use solar PV but chromophores within the AP system to directly harvest and use the photons. AP converts photons directly to products in a multistage process that mimics natural photosynthesis. This can be categorized into two main phases: hydrogen generation through water splitting (the light cycle) and the photocatalytic reduction of carbon dioxide using that hydrogen (the dark cycle, analogous to the Calvin cycle). If we decouple the two processes to say that the hydrogen is produced from any weather-dependent source (such as wind), then the term solar fuels is also used. Natural photosynthesis is highly inefficient, producing only enough of a particular product to maintain its survival, growth, and reproduction. This is typically around 1% solar efficiency for most plants. However, if we aim to produce fuels, this efficiency must increase significantly and the product must suit our energy needs. AP systems have been shown to operate an order of magnitude higher than a natural system. If wind power is used, then AP efficiency can be at least doubled due to the higher conversion efficiency of wind over solar PV. There are many studies and reviews of AP, and a recent European Commission study has highlighted the potential for further exploitation. While the water splitting reactions are well developed, effort is now focusing on the CO_2 reduction step using catalytic and photocatalytic systems.

The deployment of AP, and solar fuels in general, will not only depend on the availability of the energy source but also on the availability of other resources necessary to the process. The message is that when designing any process, we must consider "location, location, location" (Styring, 2016). Solar PV and solar thermal energy is more suited to southern Europe, for example, while wind power is more suited to northern latitudes. It has also been suggested that due to the particularly high solar flux in the Sahara Desert, this would provide an ideal location. However, AP also needs water, a scarce commodity in such an environment; it also requires a source of carbon dioxide and again a desert is not an industrialized area. This would need water and CO_2 to be piped in, at high cost, or in the case of CO_2, direct air capture to be employed.

USE OF STORAGE AND COST

If one wishes to store the output of weather-dependent electrical generation at scale to allow for seasonal levels of storage in the TWh range, then this is challenging for non-fuel systems of storage in terms of cost.

First, if one considers the target price from the US Department of Energy for batteries of \$100 per kWh, then the cost for 1 TWh of batteries would be \$100 billion. Second, the nature of seasonal storage is such that it might only be charged and discharged a handful of times a year. Due to the upfront cost of the batteries, there would be an understandable desire to use them more often than the handful of times a year, to reduce the per unit storage cost of a unit of electrical energy. As a broad example, \$100 per kWh, 100% efficiency, and an estimated lifespan of 5,000 charge/discharge cycles would provide a per kWh unit of energy storage cost of 100/5,000 = 2 cents per kWh, in essence, the more batteries or for that matter any other storage device that has a high capital cost are utilized, the more favorable it is for the eventual unit price of stored energy.

Different forms of energy storage are better suited to storing energy over different timeframes. Electrochemical forms of storage are rapidly developing in terms of cost, and these are highly suited to storing electrical energy over a cycle that may last anywhere from minutes to hours to days up to weeks. However, as the previous paragraph makes clear—they are ill suited to cycles that last from weeks to months to seasons, precisely because the capital cost makes it desirable to utilize them often to reduce the unit cost of energy that is stored.

This desire to increase the charge/discharge cycles of a storage technology is *incompatible* with the characteristics required for seasonal levels of storage, which may need the energy to be held over months until it is required. This challenge is however ideally suited to fuels, as these are orders of magnitude cheaper to store on a unit price of stored energy. This is the reason that they have historically been used as seasonal stores of energy and is one of the main foundations of the hypothesis that fuels will continue to have a critical role to play in future energy systems.

If this basis of the hypothesis is accepted, then there is still the question of which types of fuels might be suited to this in the long term.

SYNTHETIC FUELS VERSUS FOSSIL FUELS

The overriding benefit of fossil fuels versus synthetic fuels is due to their cost advantage on an energy basis. Fossil fuels are the most traded physical commodities in the world, leading to a highly competitive environment. Technology advancements in the oil, natural gas, and coal sectors have allowed new deposits to be exploited, e.g., tight oil/gas and shale oil/gas, and the competitive nature of these hydrocarbon markets brings constant pressures to supply chains to limit cost increases or drive further cost savings.

After many decades and trillions of US dollars of investment in supply chain improvements and generation of knowledge, it is nearly impossible for synthetic fuels to compete economically with fossil fuels purely on a cost per unit of energy basis (Pérez-Fortes et al., 2016). It can be argued that with significant levels of investment to encourage synthetic fuel supply chains to develop and innovate, that synthetic fuels can seek to close this cost gap to fossil fuels. However, the perennial cost challenge is not only due to the maturity and scale of supply chains but also and maybe more importantly due to where the actual energy stored in the fuels comes from in the first place.

The main environmental problem with fossil fuels is with their unabated combustion that releases fossil carbon back into the atmosphere, which will become increasingly expensive in a carbon-constrained world. Fossil fuels by statistical convention are classed as primary energy, when in fact, they could be classed as secondary energy carriers, as the original energy is due to sunlight that created the original biogenic material that subsequently became a fossil fuel. The overall conversion for this is extremely low, from the photon to eventual energy contained in the fossil fuel, but this is of little concern, as the reserves of fossil energy reserve are available in a concentrated form that can be harvested with the expenditure of some energy. For most fossil fuels the energy returned on energy invested (EROI) is high, as one only needs to expend a small part of the energy contained in the fossil fuel to actually harvest the fossil fuel itself. In a comprehensive meta-analysis on EROI for various fuels and energy harvesting (Hall et al., 2014), coal is reported to have an EROI of 46:1, oil and gas at 20:1, nuclear at 13:1, hydroelectric power generation at 84:1, wind power 18:1, and solar power 10:1. These reported values are subject to a range of uncertainties but give an indication of the relative EROI of different energy sources. Interestingly, the EROI of fossil fuels and nuclear, the mainstay of most electrical systems, is reducing over time as the easier won deposits (the high EROI reserves of these fuels and mineral ores) continue to be depleted, leaving lower EROI reserves to take their place. This contrasts with the technology and supply chain improvements in renewables such as wind and solar generation, where the EROI for these technologies has steadily improved, albeit from a low starting point.

The EROI from the harvesting of fossil fuels is the fundamental basis of the energy leverage that has driven economic and population growth since the industrial revolution. All societies at any level of advancement are utterly dependent on their access to energy, without it, their societies collapse (Hall et al., 2009). So, this period of human history leading to unprecedented increases in population is directly linked to this return on energy invested (McKevitt and Ryan, 2014).

Synthetic fuels, on the other hand, have much lower EROIs if they are derived from biomass, and in the case of power-to-fuels have EROIs that are less than one. All routes to creating synthetic fuels have process efficiency losses, which means that the amount of energy put into synthetic fuels to create them is always going to be less than the energy eventually stored in the fuels. This, above all else, means that power-to-fuels have a cost disadvantage compared to harvested fuels such as fossil fuels with higher EROIs. In short, power-to-fuels will *always* have an EROI below 1, whereas fossil fuels will *continue* to have EROIs well above 1. Having an EROI below 1 combined with a renewable energy source provides a combined generation and storage EROI above 1, which in the long-run is the basis of a sustainable energy system.

There are a wide range of fuels that can be synthesized using power (electricity) to provide the energy to be stored in the fuels. The creation of hydrogen from electrolytic splitting of water is a typical starting point for power-to-fuels and can itself be an energy vector. The challenge with hydrogen however lies with its storage, with hydrocarbon fuels proving much easier to store due to their physical characteristics. The concept of transporting hydrogen through natural gas infrastructure has undergone a renaissance in Great Britain in 2016, as evidenced by the interest at a policy and industry level generated around the Leeds Citygate H21 project (Sadler, 2016). Prior to a changeover to using natural gas from the North Sea, the gas networks of Great Britain used to supply town gas (also known as synthesis gas) as a mixture of hydrogen and carbon monoxide produced from the gasification of coal. The Citygate H21 project considers whether a repurposing of the natural gas network to transport 100% hydrogen would be feasible, and the challenges involved in undertaking this transition. One of the major challenges of the identified is in the manufacture of approximately 6 TWhs of hydrogen on an annual basis. This is felt to require the mature process of producing hydrogen at scale, the steam reformation of natural gas to strip the hydrogen from natural gas to leave CO_2. If this CO_2 from the steam methane reforming process were not sequestered, there would be a carbon increase for the final energy delivered, so the concept is critically dependent on having a CCS infrastructure available. However, there is room for the growth of hydrogen from electrolysis, but the sheer volumes of energy needed and existing costs of electrolysis are thought to preclude this pathway to provide significant levels of hydrogen in the short term. The project is interesting as it contains many of the considerations for the continued use of fuels, be they natural gas itself, or hydrogen derived from this natural gas (with CCS) or from hydrogen created by electrolysis using low-carbon electricity.

The owners and operators of natural gas infrastructure clearly have a vested interest in the continued use of their assets but are grappling with the challenges of meeting deep decarbonization targets with the continued use of unabated natural gas.

Over the long term, the use of synthetic fuels versus the creation of low-carbon fuels from fossil fuels using CCS will be determined by price, which will itself be determined by policy. One area where synthetic fuels have an advantage is being able to help balance the electrical grid, which as mentioned earlier is likely to suffer from the ever-greater risks of the excess supply of electrical energy. This is a complex area to understand in detail due to the interaction between future demands and the portfolio of future electrical generation, but the principle is that power-to-gas can provide flexibility to the electrical system as a highly controllable demand, and in addition provide a source of storable fuels for the electrical, gaseous, or even liquid fuels systems. This is one of the reasons that power-to-gas is being actively investigated to gain a better understanding of the potential of the sector to be a key element in the flexibility of future energy systems.

CO_2 Fuels

The existing infrastructure to handle, transfer, and store fuels is primarily built for hydrocarbon fuels, which have carbon atoms bonded to hydrogen. Given this, there is a deep experience and knowledge base of the costs and the risks of these fuels in markets and in the regulatory and safety frameworks that surround them. Building this knowledge using fuels other than hydrocarbons takes time, and the costs of developing infrastructure for non-hydrocarbon fuels is likely to be costly, with valid questions arising around path dependency for future energy systems. As one of the main problems with fossil fuels is due to their unabated combustion and therefore the release of carbon dioxide into the atmosphere, which increases greenhouse gas concentration, several potential solutions have been proposed and developed. The main solution is CCS, where the carbon dioxide is captured by one of several techniques, and then stored back underground in a suitable geological repository. Depending on the technique used, this can capture upwards of 90% of the carbon that otherwise would have been released to the atmosphere without CCS. Due to the economy of scale benefits of CCS, these are suited to larger scale point source emitters of CO_2 such as industrial and power sector plants.

A related concept that is garnering greater interest is the technique of using captured carbon to produce synthetic hydrocarbons or other forms of CO_2 fuels that are easier to store than hydrogen. This is not a replacement for CCS, as the fuels created *via* this route will likely be combusted and the CO_2 released to the atmosphere. Synthetic methane and methanol are of particular interest, with demonstration projects in power-to-methane using hydrogen produced by electrolysis and carbon from CO_2 to create methane that is injected into existing natural gas infrastructure. There are disadvantages to this approach in terms of additional efficiency losses introduced by the extra step of adding carbon to hydrogen, as opposed to the creation of hydrogen itself. However, the concept is of interest as it allows the continued use of the natural gas infrastructure, with all the benefits in terms of handling, transport, and storage.

Even though there may be clear benefits for the use of synthetic fuels in terms of an extended lifetime of existing hydrocarbon fuel infrastructure, and potentially a security of supply benefit of creating fuels within a country's national borders, the climate benefits of synthetic fuels are challenging to analyze. A full life cycle analysis needs to be undertaken for each synthetic fuel, which takes account of the source and therefore the carbon footprint of the energy inputs; which is complex, as the carbon footprint of grid electricity is constantly changing due to the underlying mix of generation plant at any moment in time. The other important consideration is where the carbon itself came from, and how this is accounted for. There should instinctively be a difference if the carbon came from a biogenic source and therefore was already above ground when it was captured by the biomass (thus reducing atmospheric CO_2), as opposed to carbon that was captured from a fossil fuel-based power plant, where the carbon has come from underground. If the fuel is eventually combusted without the carbon being captured again, then the carbon from the biomass can be argued to be rereleased back to the atmosphere without the addition of a further carbon atom. In comparison, if the carbon atom was originally from a fossil fuel source, if the synthetic hydrocarbon is eventually combusted without the carbon being captured again, then this will provide an additional carbon atom into the atmosphere. There is an ongoing debate around the climate benefits of biomass itself (Brack, 2017), and also when a carbon atom in the atmosphere stops being fossil based, and is merely considered just another carbon atom in the mixture of atmospheric CO_2. In short, there are likely to be a range of climate benefits to synthetic fuels (especially, if one considers the potential reduction in the use of fossil fuels), but these are particularly sensitive to a range of input conditions.

CONCLUSION

The hypothesis of this article proposes that the benefits to energy systems from the stores of fossil fuel-based energy will not be able to be replaced without some other form of fuel-based energy storage; the question should therefore be what type of fuel-based storage, not whether it is required. All energy systems (not just electrical energy systems) have benefited from the TWhs of stored chemical energy intrinsic in fossil fuels that has allowed a decoupling of primary energy supplies from the final use demand on a grand scale. The hypothesis is that this will continue to be the case.

As an example, Great Britain's primary energy demand was explored using daily data, and as a northern European country with a range of inefficient building stock, its primary energy demand can be seen to be highly seasonal due to the demand for heating through the winter period; this is shown in **Figure 1**. With effective policies and investment to increase the efficiency of building envelopes, the seasonal variation of the heat demand for primary energy supplies should reduce between the summer and the winter, but even so, there will still be a significant difference between the primary energy required on a daily basis in the winter versus the summer. In the past, fuels have provided the TWh buffers of energy required to provide seasonal levels of stored energy, and it is highly likely that in the future Great Britain will continue to require TWhs of storage to provide security of supply buffers of energy to provide system resilience. Widening this, it seems clear that all energy systems of any country will still require some part of their TWh levels of stored energy into the long-term, what is less clear is the form that these might take.

This scale and use of seasonal levels of storage at a national scale that are well into the TWh region points to the use of fuels rather than other forms of storage, due to the unit cost of storing energy that is only stored and utilized a handful of times a year.

Given the cost disadvantages of synthetic fuels, if policy makers wish to encourage them to grow in market share, then they could consider providing protected markets for them to compete within, provide subsidies, or by costing fossil fuels with a carbon price that helps to close the cost gap.

The creation of synthetic fuels also provides a highly dispatchable demand to help integrate greater levels of weather-dependent renewables, which will be increasingly desirable in future energy systems that rely on primary electricity from renewables to a much greater degree.

The question simply put is not whether we will continue to need fuels in future energy systems, but the type of fuels that will be suitable in a highly decarbonized world.

AUTHOR CONTRIBUTIONS

Dr. Grant Wilson is the main author for the article. Professor Styring provided comments and input to several sections. Both authors approve it for publication.

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The Potential for Electrofuels Production in Sweden Utilizing Fossil and Biogenic CO_2 Point Sources

Julia Hansson[1,2]*, **Roman Hackl**[1], **Maria Taljegard**[3], **Selma Brynolf**[2] **and Maria Grahn**[2]

[1] Climate and Sustainable Cities, IVL Swedish Environmental Research Institute, Stockholm, Sweden, [2] Division of Physical Resource Theory, Department of Energy and Environment, Chalmers University of Technology, Göteborg, Sweden, [3] Division of Energy Technology, Department of Energy and Environment, Chalmers University of Technology, Göteborg, Sweden

This paper maps, categorizes, and quantifies all major point sources of carbon dioxide (CO_2) emissions from industrial and combustion processes in Sweden. The paper also estimates the Swedish technical potential for electrofuels (power-to-gas/fuels) based on carbon capture and utilization. With our bottom-up approach using European databases, we find that Sweden emits approximately 50 million metric tons of CO_2 per year from different types of point sources, with 65% (or about 32 million tons) from biogenic sources. The major sources are the pulp and paper industry (46%), heat and power production (23%), and waste treatment and incineration (8%). Most of the CO_2 is emitted at low concentrations (<15%) from sources in the southern part of Sweden where power demand generally exceeds in-region supply. The potentially recoverable emissions from all the included point sources amount to 45 million tons. If all the recoverable CO_2 were used to produce electrofuels, the yield would correspond to 2–3 times the current Swedish demand for transportation fuels. The electricity required would correspond to about 3 times the current Swedish electricity supply. The current relatively few emission sources with high concentrations of CO_2 (>90%, biofuel operations) would yield electrofuels corresponding to approximately 2% of the current demand for transportation fuels (corresponding to 1.5–2 TWh/year). In a 2030 scenario with large-scale biofuels operations based on lignocellulosic feedstocks, the potential for electrofuels production from high-concentration sources increases to 8–11 TWh/year. Finally, renewable electricity and production costs, rather than CO_2 supply, limit the potential for production of electrofuels in Sweden.

Keywords: carbon dioxide, CO_2 recovering, carbon capture and utilization, carbon recycling, power-to-gas, alternative transportation fuels

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Katy Armstrong,
University of Sheffield, UK

Reviewed by:
Hyungwoong Ahn,
University of Edinburgh, UK
Adam Hughmanick Berger,
Electric Power Research Institute,
USA

Correspondence:
Julia Hansson
julia.hansson@ivl.se

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HIGHLIGHTS

- Sweden emits 50 million metric tons of CO_2 per year from different types of point sources, the vast majority of which is emitted at low concentrations.
- Of this, 65% is from biogenic sources, most of which are located in southern Sweden.
- Currently, the high-concentration sources of CO_2 in Sweden can provide a potential 1.5–2 TWh electrofuels/year (2% of current transportation demand).

- The Swedish potential for electrofuels is currently limited by the electricity required and production costs rather than the amount of recoverable CO_2.

INTRODUCTION

Anthropogenic greenhouse gas (GHG) emissions need to be reduced in order to limit global climate change and reach ambitious climate targets (Pachauri et al., 2014). Carbon dioxide (CO_2) emissions can be reduced by using less fossil fuels or by using fossil fuels in combination with carbon capture and storage (CCS) or carbon capture and utilization (CCU) [e.g., Cuéllar-Franca and Azapagic (2015), Wismans et al. (2016)]. In Sweden, the overall national vision is for zero net emissions of GHG to the atmosphere by 2050 (likely to be changed to 2045), along with a fossil fuel-independent vehicle fleet by 2030 (Government offices of Sweden, 2009; Swedish Government Official Reports, 2016). An extensive official investigation commissioned by the Swedish government has concluded that a range of options are needed to reduce CO_2 emissions from the transport sector, including biomass-based liquid and gaseous fuels (biofuels) along with hydrogen and electricity produced from renewable energy sources (Swedish Government Official Reports, 2013).

However, neither government nor academia have explored electrofuels (i.e., power-to-gas/fuels or synthetic hydrocarbons produced from CO_2 and water using electricity), extensively. Interest in electrofuels is on the rise, both in the literature (Graves et al., 2011; Mohseni, 2012; Nikoleris and Nilsson, 2013; Taljegård et al., 2015)[1] and in terms of demonstration plants in the EU, in some cases, including CO_2 capture (Gahleitner, 2013). Studies mainly investigate electrofuels as a (i) technology for storing intermittent electricity [e.g., Streibel et al. (2013), de Boer et al. (2014), Vandewalle et al. (2014), König et al. (2015), Qadrdan et al. (2015), Varone and Ferrari (2015), Zakeri and Syri (2015), Zhang et al. (2015), and Kötter et al. (2016)], (ii) fuel for transport [e.g., Connolly et al. (2014), Ridjan et al. (2014), Larsson et al. (2015)], or (iii) means of producing chemicals [e.g., Ganesh (2013), Perathoner and Centi (2014), and Chen et al. (2016)]. Different types of energy carriers [e.g., methane, methanol, DME (dimethyl ether), gasoline, and diesel] can be produced, which makes electrofuels a potentially interesting option for all transport modes, especially shipping, aviation, and long distance road transport, where the potential for other renewable fuel options, such as electricity and hydrogen, may be limited. Electrofuels may allow increased use of biofuels, if the CO_2 associated with their production is used for production of electrofuels instead of being emitted to the atmosphere (Mignard and Pritchard, 2008; Mohseni, 2012; Hannula, 2015, 2016).

CO_2 emissions can be captured from various point sources, including industrial processes that produce CO_2, such as biofuel production (including anaerobic digestion and fermentation), natural gas processing, steel plants, and oil refineries, fossil and biomass combustion in heat and power plants, or directly from the air.

Many studies have estimated CO_2 emissions from point sources in China [e.g., Chen and Chen (2010), Liu et al. (2010), Zhang and Chen (2014)]. Zhang and Chen (2014) used a bottom-up approach to estimate CO_2 emissions from fuel combustion and the main industrial processes at 7.7 Gt CO_2 per year in 2008, with coal as the main source. The potential global supply of CO_2 from point sources is estimated in Naims (2016). The total estimated global capturable CO_2 supply from point sources amount to approximately 12.7 Gton of CO_2 (Naims, 2016). High purity point sources (e.g., fermentation of biomass and ammonia production) and other low cost sources (e.g., bioenergy, natural gas, and hydrogen production) represent in total approximately 0.3 Gton of CO_2. Naims (2016) further indicates that there is enough CO_2 to meet the estimated global CO_2 demand in the near and long term.

In Austria, the iron and steel, cement industry, and power and heat industries are the largest point sources of CO_2 emissions (Reiter and Lindorfer, 2015). Biofuel production, a relatively modest point source at about 113 kton in 2013, is considered the most suitable Austrian source for power-to-gas application by Reiter and Lindorfer (2015). A German feasibility study by Trost et al. (2012) identifies a large potential for biogenic CO_2 sources, including biogas upgrading, bioethanol plants, and sewage treatment plants. Trost et al. (2012) also found a substantial electrofuels potential of over 130 TWh fuel per year in the form of methane produced using CO_2 from industrial processes and biogenic sources. Reiter and Lindorfer (2015) and Trost et al. (2012), both conclude that availability of CO_2 will not be a limiting factor for using power-to-gas as a balancing strategy for intermittent renewable power sources (wind power and photovoltaics) in Austria or Germany.

In Sweden, carbon capture is currently implemented at, for instance, Agroetanol in Norrköping. Agroetanol produces grain-based ethanol; the resulting CO_2 is purified and sold to the AGA Gas AB. Detailed quantification of current and/or future Swedish CO_2 emissions from point sources is, however, lacking in the scientific literature, and there are no assessments of the technical potential for Swedish production of electrofuels. Electrofuels may represent an interesting option in Sweden, that is a forest-rich country, due to the ambitious GHG emission reduction targets in general and specifically in the transport sector. Assessing the Swedish potential for CCS and CCU requires detailed knowledge of the stationary CO_2 emissions. The overall impact on CO_2 emissions of the production and use of electrofuels mainly depends on the electricity-related CO_2 emissions. The Swedish electricity production consists mainly of hydro power and nuclear power implying relatively low GHG emissions.

The overall aim of this paper is to map and quantify stationary Swedish CO_2 emissions by concentration, origin, and geographical distribution, as well as investigate the potential for CCU. Specifically, we aim to (i) map and quantify the major point sources of CO_2 emissions from industrial and combustion processes in Sweden with a bottom-up approach and estimate the technical potential for CO_2 capture or recovery and (ii) estimate the technical potential for production of electrofuels

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[1] Brynolf, S., Taljegård, M., Grahn, M., and Hansson, J. (2017). Electrofuels for the transport sector: a review of production costs. *Renew. Sust. Energ. Rev.* (Submitted).

in Sweden, as an example of CCU. We analyze the potential for biofuels-related CO_2 in the future (a 2030 scenario), since the use of biomass and biofuels is expected to increase and use of fossil fuels decrease. Additionally, we estimate the potential demand for CO_2 and electricity corresponding to the use of electrofuels for road transport, heavy trucks, and shipping, at scale, in order to give a first indication of the potential role for electrofuels in transportation in Sweden.

MATERIALS AND METHODS

This section describes the methodology for estimating both CO_2 emissions from major point sources and the potential for capturing and using the emissions.

Assumptions about the CO_2 Sources Included

CO_2 emission sources can be divided into diffuse sources (e.g., transport and agriculture) and point sources (e.g., factories and power production). This study uses a bottom-up approach to estimate CO_2 emissions from the following point sources in Sweden:

- Industrial process plants (including iron and steel, non-ferrous metal, oil and gas refineries, lime and cement, pulp and paper, chemical, metal, and other similar plants)
- Heat and power production (including biomass, waste, and fossil fuel-fired plants)
- Biofuels production facilities (including ethanol, biogas, and more advanced biofuels).

Emissions data for year 2013 from the European Environment Agency's "European Pollutant Release and Transfer Register" (European Environment Agency, 2015) was used to estimate (i) the available amount of CO_2 and (ii) the share of fossil and biogenic CO_2, for Swedish point sources, including all sources emitting 0.1 million metric tons of CO_2 per year or more. Other CO_2 sources are assumed to be negligible (except in the case of biofuels production). The concentration of CO_2 for each type of sources was estimated using (Chapel et al., 1999; Bosoaga et al., 2009) (see **Table 1**). For the purposes of analysis, the concentrations were divided in three ranges: low (<15 vol%), medium (15–90 vol%), and high (>90 vol%).

For biofuels plants, the CO_2 estimates are based on data gathered by Swedish Energy Agency and Energigas Sverige (2015) and Grahn and Hansson (2015) in 2012–2013. Also, the sources emitting less than 0.1 million metric tons of CO_2 per year are included in the case of biofuels since these are relatively pure and, therefore, well suited for electrofuels production. In most biofuels production processes, there is a surplus of CO_2 and the CO_2 is of high purity (Xu et al., 2010). When biogas is upgraded to transport fuel quality, a cleaning step to remove CO_2 is included, resulting in a relatively pure stream of CO_2. The CO_2 emissions from domestic biofuel production in a 2030 scenario are estimated based on biofuels production scenarios from Grahn and Hansson (2015) and on scenarios for anaerobic digestion and gasification-based biogas production from Dahlgren et al. (2013). Grahn and Hansson (2015) assessed the potential contribution of domestically produced biofuels for transport in Sweden in 2030 based on a mapping of the prospects for current and potential Swedish biofuel producers. Some of the planned biofuels production plants included in the scenario for 2030 have been canceled or put on hold and are, therefore, excluded in this study.

The 2030 scenario was constructed exclusively for biofuel plants because these represent a relatively pure stream of CO_2 of particular interest in electrofuels production, and because the use of biofuels is expected to increase in the future. For many biofuels, no extra major purification step is needed in the capture process, which leads to a relatively low capture cost. This can also be assumed for the case of biogas since CO_2 is already removed when biogas is upgraded to transport fuel quality. This can be compared to the CO_2 capture cost linked to processes requiring an extra purification step like steel and iron, ammonia, refinery, cement, and fossil or biomass combustion plants estimated at $20€_{2015}$–$170€_{2015}$/ton CO_2 in the short term (10–15 years) and $10€_{2015}$–$100€_{2015}$/ton CO_2 in the more long term (Damen et al., 2007; Finkenrath, 2011; Kuramochi et al., 2012, 2013; IEA, 2013). Even though it has been

TABLE 1 | The type of CO_2 stream, CO_2-concentration range, range of CO_2 emissions per unit, and share of recoverable CO_2, for different point sources in Sweden based on European Environment Agency (2015).

Production facility and location	Type of CO_2 stream	Typical concentration	Process CO_2 emissions (kton/year) for smallest and largest plant	Recoverable share (%)
Oil and gas refineries	Flue gases, by-product	3–13 vol%[a]	122–1,573	90
Power and heat production	Flue gases	3–13 vol%	104–1,990	90
Iron and steel production	Flue gases	Approx. 15 vol%	102–1,540	90
Non-ferrous metal production	Flue gases	Approx. 15 vol%	101–256	90
Cement and lime production	Flue gases, by-product	Approx. 14–33 vol%	110–1,940	90
Production of chemicals	Flue gases, by-product	3–13 vol%[a]	13–620	90
Pulp and paper production	Flue gases	Approx. 15 vol%	165–1,740	90
Waste treatment or incineration	Flue gas	Approx. 10 vol%	105–837	90
Fermentation-based biofuels	By-product	Pure stream	0.11–154	100
Anaerobic digestion-based biofuels	By-product	>90 vol-%	0.14–21	54
Gasification-based biofuels	By-product	>90 vol-%	1.84–37	100
Other	Flue gas	3–13 vol%	134	90

For CO_2 concentration and recoverability references, see Section "Availability of CO_2 for Carbon Capture and Utilization."

[a] *Minor amounts of CO_2 are available at higher concentrations (up to 100 vol%).*

indicated that the cost for carbon capture represents a relatively modest share (a few percent) of the total electrofuel-production cost unless air capture is assumed (Graves et al., 2011; Tremel et al., 2015; Varone and Ferrari, 2015; see text footnote 1), using CO_2 from biofuel production represent an attractive source for electrofuel production since more pure streams will likely be used first for economic reasons and the domestic biofuel actors, representing a considerable biofuel production capacity, in order to comply with sustainability requirements need to improve their production processes in terms of CO_2 emissions.

Table 1 presents the type of CO_2 stream, typical concentration of CO_2, the range of CO_2 emissions per unit, and the amount of recoverable CO_2, for different point sources. **Table 2** includes a list of all the biofuel production facilities in operation in 2015, their production capacity and associated CO_2 emissions, and the corresponding information for the biofuels plants planned by 2030. **Table 3** summarizes the main assumptions used in estimating the amount of CO_2 that is available for recovery from current and future biofuels plants.

Availability of CO_2 for CCU

In order for CO_2 to be used to produce electrofuels, the gas needs to be separated from other substances in emissions from industrial and combustion processes, such as sulfur dioxide. The concentration of CO_2 in power plant flue gases is relatively low (<15 vol%) (Chapel et al., 1999); for process-related emissions, e.g., in the lime and cement industry, CO_2 concentrations are somewhat higher (14–33 vol%) (Bosoaga et al., 2009) (see **Table 1**). In this study, we assume that 90% of the CO_2 from medium- (15–90 vol%) and low- (<15 vol%) concentration CO_2 sources is recoverable (Chapel et al., 1999). Current CO_2 capture technologies do not usually capture all the CO_2 as this is too expensive and requires too much energy.

In biofuels production processes (fermentation, anaerobic digestion, gasification), relatively pure streams (>90 vol%) of CO_2 are available in latter cases due to the demand for high fuel purity in the transport sector. We assume that 100% of the CO_2 from biofuel plants is recoverable and could be converted into fuel. Approximately 54% of the biogas produced in Sweden is upgraded for the transportation sector (Swedish Energy Agency and Energigas Sverige, 2016), which means that CO_2 capturing technology already exist on several Swedish anaerobic digestion facilities. Another opportunity for anaerobic digestion-based biogas plants is to feed raw biogas to a methanation reactor, thereby combining biogas upgrading and electrofuels production (Johannesson, 2016). Biogas plants that currently do not upgrade their gas are generally small implying high costs for upgrading and currently supplying other markets than the transport sector, making them less suitable as a source of CO_2 for electrofuels production. Therefore, only CO_2 from biogas-upgrading plants is considered in this study. For simplicity, we assume that the share of upgraded biogas of total biogas production by 2030 remains at 54%.

Geographic Distribution of CO_2 Emissions

The CO_2 emission sources have been mapped and categorized by concentration and geographical area. The geographical areas are those used for the Swedish electricity market, i.e., four price areas (SE1, SE2, SE3, and SE4) (Swedish Energy Markets Inspectorate, 2014) (see **Figure 1**). The electricity price areas were implemented in Sweden in order to control the transmission of electricity between regions and to promote the construction of power generation and transmission capacity in and to areas with electricity deficits. On average, the northern parts of the country (SE1 and SE2) are characterized by an excess of electricity production due to the available hydropower resources and relatively

TABLE 2 | Biofuels production facilities and associated CO_2 emissions.

Production facility and location	Biofuel	Biofuel production (GWh/year)	Process CO_2 emissions (ton/year)	Reference[a]
Facilities operational in 2015				
Agroetanol, Line 1, Norrköping	Ethanol	391	53,466[b]	Axelsson et al. (2014) and Grahn and Hansson (2015)
Agroetanol, Line 2, Norrköping	Ethanol	1,126	154,014[b]	Axelsson et al. (2014) and Grahn and Hansson (2015)
ST1, Göteborg	Ethanol	34	4,617	Axelsson et al. (2014) and ST1 (2016)
SEKAB, Örnsköldsvik	Ethanol	64	7,807	Arvidsson and Lundin (2011) and Grahn and Hansson (2015)
SP, pilot plant, Örnsköldsvik	Ethanol	0.9	109	Arvidsson and Lundin (2011) and Grahn and Hansson (2015)
LTU Green Fuels, pilot plant, Piteå[c]	DME	6	1,836	Pettersson and Harvey (2012) and Grahn and Hansson (2015)
GoBiGas, Göteborg Energi, Göteborg	Gasification-based biogas	180	36,900	Heyne (2013) and Grahn and Hansson (2015)
Swedish anaerobic digestion-based biogas production (277 plants)	Biogas	1,686	245,680	SGC (2012) and Swedish Energy Agency and Energigas Sverige (2016)
Additional production capacity until 2030				
Fermentation	Ethanol	3,300	402,033	Hansson and Grahn (2013)
Anaerobic digestion	Biogas	4,600	672,342	SGC (2012), Dahlgren et al. (2013), and Hansson and Grahn (2013)
Gasification	Biogas, methanol, DME	4,050	1,023,260	Dahlgren et al. (2013) and Hansson and Grahn (2013)

[a]References for the amount of biofuels produced and the estimated CO_2 emissions per unit of fuel are provided here.

[b]CO_2 produced at Agroetanol in Norrköping is currently purified and sold to the AGA Gas AB.

[c]The closure of this pilot plant was announced in April 2016.

TABLE 3 | Main assumptions for assessing CO_2 availability from current and future biofuels plants in Sweden.

Production technology	Assumed amount of available CO_2 per GWh biofuel
Fermentation	Cereal based: 136.8 ton CO_2/GWh (Axelsson et al., 2014) Lignocellulose based: 121.7 ton CO_2/GWh (Arvidsson and Lundin, 2011)
Anaerobic digestion	Upgraded biogas: 145.7 ton CO_2/GWh (SGC, 2012)
Gasification	Black liquor gasification: 305 ton CO_2/GWh (Pettersson and Harvey, 2012) Indirect gasification: 206 ton CO_2/GWh (Heyne, 2013)

low overall power consumption. In the southern parts (SE3 and SE4), electricity consumption often exceeds production, which leads to relatively higher electricity prices in these areas (Nord Pool, 2016).

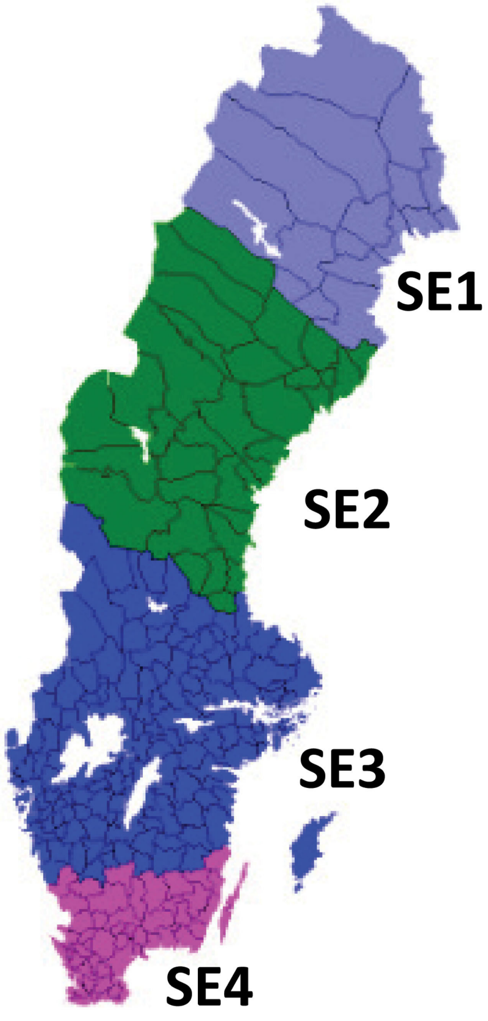

FIGURE 1 | The electricity price areas (SE1, SE2, SE3, and SE4) in Sweden, which are used to illustrate the geographic distribution of the CO_2 emissions. Figure based on SCB (2015).

Electrofuel-Production Efficiency and Cost

The focus in this study is on electrofuels in the form of methane, methanol, and DME since these are the most discussed electrofuels in the literature (see text footnote 1), are of interest for the relevant transport sector (shipping and trucks), and include fuels in liquid and gaseous form. The amounts of CO_2 and electricity necessary for the types of electrofuels included in this study are given in **Table 4** and are based on lower heating value (LHV).

Table 4 also presents cost ranges for 2015 and 2030 estimated in the base case reference scenario in Brynolf et al. (see text footnote 1). The electricity-to-fuel efficiency of the electrofuel-production process strongly depends on the type of electrolyzer and the future development of production technologies. Alkaline electrolysers have efficiencies in the range of 43–69% today, while the most efficient electrolysers are expected to reach efficiencies above 80% based on LHV (Smolinka et al., 2011; Benjaminsson et al., 2013; Grond et al., 2013; Mathiesen et al., 2013; Bertuccioli et al., 2014; Hannula, 2015; Schiebahn et al., 2015). Combining this with the efficiency for fuel synthesis yields electricity-to-fuel efficiencies in the 30–75% range for methane, methanol, and DME, this corresponds to an electricity demand of 1.33–3.33 MWh electricity/MWh electrofuel.

Brynolf et al. (see text footnote 1) suggest costs for different electrofuels (methane, methanol, DME, gasoline, and diesel) in the span of 120€$_{2015}$–1,050€$_{2015}$/MWh$_{\text{fuel}}$ and 100€$_{2015}$–430€$_{2015}$/MWh$_{\text{fuel}}$ in 2015 and 2030, respectively. However, in the base case of the reference scenario representing average data, the same costs are 200€$_{2015}$–280€$_{2015}$/MWh$_{\text{fuel}}$ and 160€$_{2015}$–210€$_{2015}$/MWh$_{\text{fuel}}$ in 2015 and 2030, respectively. The most important factors affecting the production cost of electrofuels are the capital cost of the electrolyzer, the electricity price, the capacity factor of the unit, and the lifetime of the electrolyzer. The base case reference scenario assumes alkaline electrolyzer with a capital cost of 600€$_{2015}$/kW$_{\text{el}}$, capacity factor of 80%, lifetime of the electrolyzer at 25 years, carbon capture cost at 30€$_{2015}$/ton, and electricity price of 50€$_{2015}$/MWh. A capacity factor at 80% implies that the plant is run the major part of the year. However, if electrofuels are used to balance intermittent renewable power production (i.e., there is production only when there is a surplus of power from these sources), the capacity factor will be reduced. This will not influence the estimated technical potential for production of electrofuels in Sweden in this study, but it will lead to increased electrofuel-production costs [which is further assessed in Brynolf et al. (see text footnote 1)]. In the case of a carbon capture cost at 10€$_{2015}$/ton representing more pure streams like biofuels operation, the production cost of electrofuels is reduced by approximately 3%. In their review of the literature, Brynolf et al. (see text footnote 1) also found that the cost of capturing CO_2 generally is a minor factor in the total production cost of electrofuels representing less than 10% (when not considering CO_2 capturing from air). CO_2 can be captured from various industrial sources with costs ranging from about 10€$_{2015}$ to 170€$_{2015}$/ton CO_2, depending on the CO_2 concentration (Damen et al., 2006, 2007; Finkenrath, 2011; Goeppert et al., 2012; Kuramochi et al., 2012, 2013; IEA, 2013; see text footnote 1). This indicates that from an economic point

TABLE 4 | Estimated values for CO_2 and electricity demand per unit of electrofuel and production cost for 2015 and 2030 (based on literature review and base case reference scenario by Brynolf et al. (see text footnote 1) representing average data and based on lower heating value, for assumptions see the text).

Electrofuel	Fuel synthesis efficiency (%)	CO_2 per unit of fuel (t/MWh_{fuel})	Electricity per unit of fuel (MWh_{el}/MWh_{fuel})	Production cost 2015 ($€_{2015}/MWh_{fuel}$)	Production cost 2030 ($€_{2015}/MWh_{fuel}$)
Methane	77[a]	0.21	2.00	200	160
Methanol	79[b]	0.28	1.93	210	160
DME	80[b]	0.27	1.95	210	160

[a] *Mohseni (2012), Grond et al. (2013), Schiebahn et al. (2015),* and *Tremel et al. (2015).*

[b] *Hannula and Kurkela (2013)* and *Tremel et al. (2015).*

of view, all CO_2 sources (except from pure air) might be of interest for electrofuel production in the future.

RESULTS

CO_2 Emissions in Sweden

In Sweden, major stationary point sources currently emit approximately 50 Mton CO_2 per year. Of this, about 45 Mton CO_2 is recoverable (see **Figure 2**). Our analysis includes 148 facilities, with 14 U emitting more than 1 Mton CO_2/year, 88 U emitting between 1 Mton and 100 kton CO_2/year, and 47 U emitting less than 100 kton/year.

Figure 2 shows the distribution of CO_2 emissions among different types of point sources. Pulp and paper plants and heat and power plants are the two major types of point sources, corresponding to 23 Mton CO_2 (45% of the total) and 11.5 Mton CO_2 (23% of the total) per year, respectively. In total, biogenic sources account for 65% or 32 Mton of CO_2 emissions per year. The high share of biogenic CO_2 is mainly due to the extensive use of biomass in producing pulp, paper, heat, and power and from waste treatment and incineration. Emissions from biofuel production represent a small share of the current total amount of available CO_2, with approximately 0.5 Mton of recoverable CO_2 per year. According to Andreas Gundberg, Innovation manager at Lantmännen Agroetanol, CCU has already been implemented at the main Swedish ethanol producer representing approximately 90% of the total Swedish ethanol production capacity. The emissions from this ethanol production (about 100 kton/year) are included in the analysis.

Figure 3 shows the amount of CO_2 available and the corresponding potential production of electrofuels in the form of methanol at different CO_2 concentrations in Sweden in 2013 and in 2030. The majority of the CO_2 is available at low and medium concentrations, equally spread between the categories low and medium but mainly below 20 vol%. A small share of the CO_2, mainly from the biofuels industry, is available at higher, significantly more accessible, concentrations.

About 90% of the high-concentration emissions come from sources in geographic region SE3, along with about 60% of the rest of the CO_2 emission sources (see **Figure 4**). Anaerobic digestion and ethanol production from agricultural crops currently dominate biofuels production, and these are mostly located in densely populated areas (producing biogas from digestion of sewage sludge and food waste) or in proximity to agricultural operations (farm-based ethanol and biogas production), which are mainly found in southern Sweden. However, electricity prices in the southern parts are currently less favorable than further north where hydropower resources and lower demand create

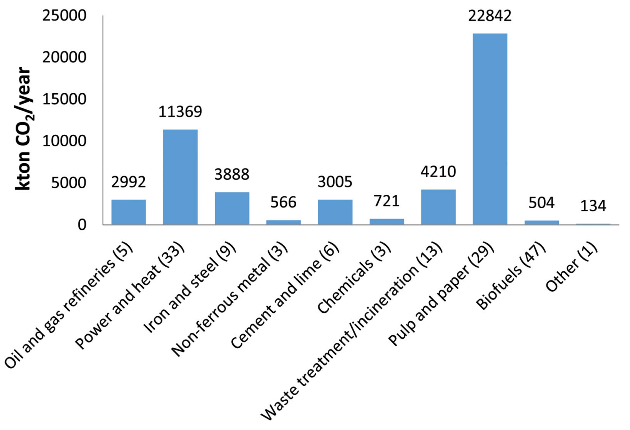

FIGURE 2 | Current recoverable CO_2 from major point sources in Sweden, based on European Environment Agency (2015), Grahn and Hansson (2015), and Dahlgren et al. (2013). In total, 149 point sources are included; the number of plants in each category is given in parenthesis.

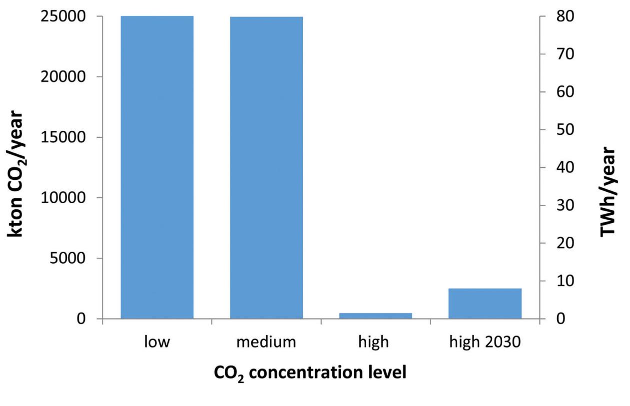

FIGURE 3 | Recoverable CO_2 and potential for production of electrofuels in the form of methanol at three different concentration levels (low: <15 vol%, medium: 15–90 vol% and, high: >90 vol%) in 2013 and at high concentration in 2030.

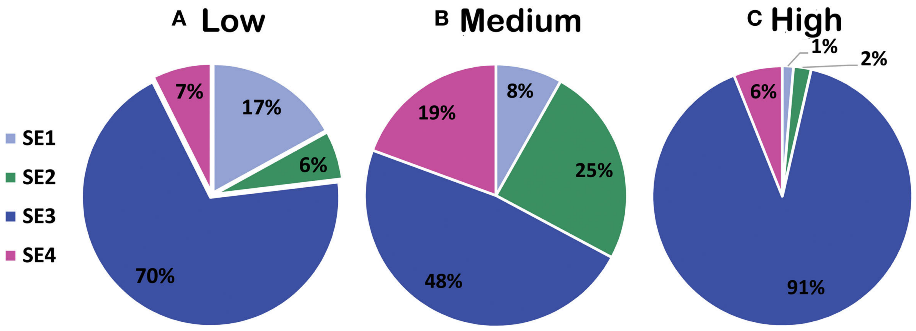

FIGURE 4 | **CO₂ point sources by region and concentration level**. **(A)** Low, **(B)** medium, and **(C)** high.

an excess of electricity while the transmission capacity to the southern industrial and population centers is limited.

The projected large-scale introduction of biofuels based on lignocellulosic feedstocks should entail higher shares of high-concentration CO_2 emissions in the northern regions, SE1 and SE2, if plants are located near feedstock resources.

The biofuels sector is expected to grow significantly in Sweden during the coming years in order to achieve national climate and transport targets. **Figure 5** illustrates the current and estimated amount of CO_2 available for electrofuels production from different biofuel production technologies and a minor share of others sources available by 2030 in Sweden based on Dahlgren et al. (2013) and Hansson and Grahn (2013). Only CO_2 from the production of upgraded biogas is included. In 2030, the CO_2 originates mainly from gasification, anaerobic digestion, and fermentation-based biofuels production (utilizing both cereals and lignocellulosic biomass and considering recent implementation plans). In 2030, these sources could potentially yield 2.2 Mton CO_2 for electrofuels production (approximately 5.5 times the amount currently available). The largest increase in production capacity is expected with the large-scale implementation of a variety of biomass-gasification-based biofuels, such as synthetic natural gas, DME, or methanol from lignocellulosic biomass. Ethanol produced from lignocellulosic feedstocks could also potentially generate large amounts of highly concentrated biogenic CO_2.

Swedish Production Potential for Electrofuels

Using all the currently recoverable CO_2 from the point sources identified in this study to produce electrofuel in the form of methane would yield approximately 224 TWh per year. This corresponds to approximately 2.5 times the current Swedish demand for transportation fuels [approximately 85 TWh per year in 2014 (Swedish Energy Agency, 2015b)]. For electrofuels with lower conversion efficiencies (e.g., methanol and DME), production could instead cover about twice the current demand. Producing 224 TWh per year of electro-methane requires about 448 TWh of electricity (assuming 2 MWh_{el}/MWh_{fuel}), which corresponds to three times the current Swedish electricity generation [149 TWh (Swedish Energy Agency, 2015a)].

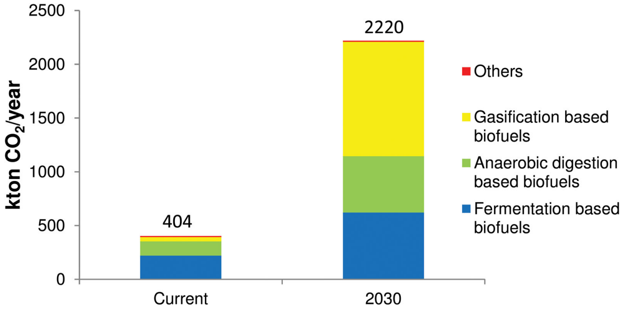

FIGURE 5 | **CO₂ from high CO₂ concentration sources (>90 vol-%) today and in 2030**.

The high-concentration sources, represented mainly by biofuel plants, suffice to provide only about 2% of the current demand for transportation fuels (corresponding to 1.5–2/year, see **Figure 6**). Converting the high-concentration emissions to electrofuels would require about 3–4 TWh of electricity (2–3% of the current national production). In 2030, the potential production of electrofuels in the form of methane, methanol, and DME from high-CO_2 sources is 8–11 TWh (see **Figure 6**). This corresponds to approximately 9–13% of the current demand for transportation fuels and would require about 15–21 TWh of electricity (10–14% of current electricity production).

Table 5 shows the requirements for meeting the current Swedish fuel demand for (non-air) transport with electrofuels in the form of methanol. As seen in **Table 5**, about half of the recoverable CO_2 (23 Mton) would be needed to supply the entire current Swedish road transport demand with electrofuels in the form of methanol (assuming a conversion factor of 0.275 ton CO_2/MWh methanol). The corresponding amount of CO_2 needed to satisfy the entire fuel demand from heavy trucks and all domestic and international shipping currently bunkering in Sweden is estimated to be about 5 and 6 Mton CO_2, respectively. This implies that in the case of large-scale introduction of electrofuels for road transport (including heavy trucks), heavy trucks only, or shipping in Sweden, the supply of CO_2 is not a limiting factor.

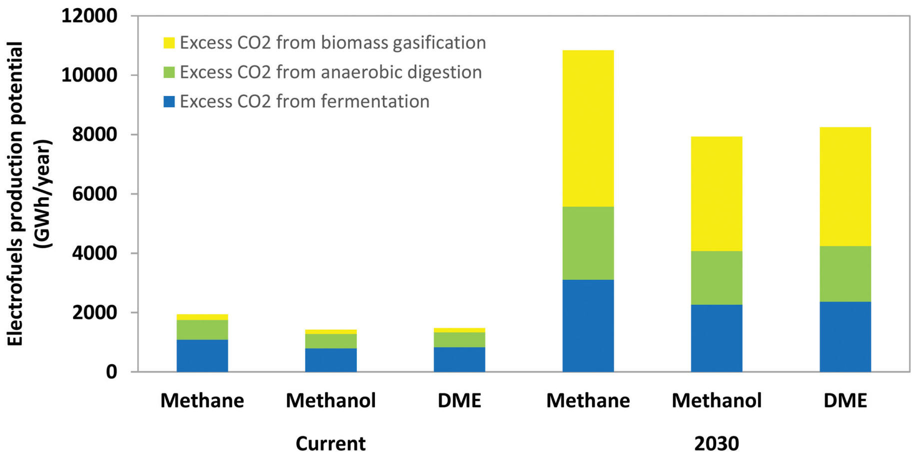

FIGURE 6 | **Production potential for electrofuels in the form of methane, methanol and DME from current and future biofuel plants with high CO_2 concentrations**.

TABLE 5 | **Outputs and inputs to electrofuels production if fulfilling the fuel demand with electrofuels in the form of methanol in three different transport modes.**

	Road transport	**Heavy trucks**	**Shipping**
Fuel demand 2014 (TWh)	85 (Swedish Energy Agency, 2015b)	18 (Swedish Government Official Reports, 2013)[a]	21 (Swedish Energy Agency, 2015b)[b]
Electrofuel replacement (%)	100	100	100
Electrofuel production			
Methanol (TWh)	85	18	21
Electrofuel requirements			
Electricity (TWh)	164	35	41
Carbon dioxide (Mton)	23	5	6

*For electricity and CO_2 demand per unit of electrofuel see **Table 4**.*

[a] *Expected to increase to approximately 25 TWh by 2050.*

[b] *Represents the total Swedish use of bunker fuels in 2014 of which 96% was used for international sea transport.*

However, meeting the entire current road transport demand with electrofuels would require about 164 TWh_{el} of electricity (with methanol at 1.93 MWh_{el}/MWh_{fuel}). This would more than double the current demand for electricity. To meet the current Swedish fuel demand for passenger cars (at about 41 TWh) (Swedish Government Official Reports, 2013) with electrofuels in the form of methanol would require approximately 11 ton CO_2 and 79 TWh_{el} of electricity. For comparison, if the entire passenger car fleet were replaced by electric vehicles, the increased demand for electricity would be approximately 10 TWh (based on Swedish Government Official Reports, 2013).

Using electrofuels for the heavy truck sector and for shipping bunker fuel sold in Sweden would require about 35 and 41 TWh_{el}, respectively. For comparison, in 2014, domestic power generation was 150 TWh (SCB, 2016). Further, the goal is to increase domestic generation from renewable sources by about 30 TWh by 2020, compared to 2002 figures and current production of renewable electricity is approximately 85 TWh (SCB, 2016). Large-scale introduction of electrofuels would require a major increase in the supply of electricity from renewable energy sources.

DISCUSSION AND CONCLUSION

This study shows that Swedish point sources emit approximately 50 million metric tons of CO_2 per year, 65% of which is biogenic in origin. The potentially recoverable emissions amount to 45 Mton. The main point sources are in the pulp and paper industry along with heat and power, while emissions from biofuel production (with relatively high concentrations of recoverable CO_2) amounted to 0.5 Mton CO_2 in 2015, with an estimated potential for 2.2 Mton CO_2 in 2030. Thus, the potential streams of relatively pure CO_2 are modest, at least in the near term. Currently, the potential yield from these sources is 1.5–2 TWh of electrofuels per year, corresponding to approximately 2% of the current Swedish demand for transportation fuels.

However, in Sweden, all types of CO_2 emissions, whether fossil or biogenic, and whether low-concentration or high, are of interest in terms of CCU (although carbon capture can be expected to first be applied to systems with higher concentrations of CO_2 because capture costs are somewhat lower for these, generally speaking). In the case of electrofuels, as mentioned earlier, it has been indicated that the cost for carbon capture represents a relatively modest share of the total electrofuel-production cost which makes the purity of the CO_2 sources less important. However, CO_2 from biofuel operations seem like an attractive source since biofuel actors strive to reduce their CO_2 emissions due to sustainability requirements. Further, biomass-related CO_2 emissions are expected to increase in the future, since the use of biomass for energy is expected to increase while fossil CO_2 emissions are expected to decrease.

We conclude that the Swedish supply of CO_2 does not have to be a limiting factor for the potential future production of electrofuels for the Swedish transport sector, even if the current supply of pure CO_2 streams is limited. However, there might be other limiting factors such as the associated electricity demand.

As indicated in the introduction, electrofuels represent a potential long-term energy storage option and could, therefore, be of interest in terms of managing grid-integration of more intermittent renewable energy sources (e.g., wind and solar power). But large-scale introduction of electrofuels in the transport sector would in turn represent a huge new demand for electricity. The direct use of electricity needed to supply the entire current transport demand for passenger cars would increase current electricity demand by 10%, while using electrofuels would require increasing the Swedish electricity generation by about 60% to meet the same transport demand (Swedish Energy Agency, 2015b). The electrofuels production process and combustion engine are simply that much less efficient than electric motors. Therefore, large-scale introduction of electrofuels might potentially increase the challenge of balancing intermittent renewable generation, rather than help solve it with long-term energy storage, since an increased demand for power would most likely be met with new wind power installations in Sweden. Producing electrofuels only part of the year is one option to limit this problem. However, according to Brynolf et al. (see text footnote 1), the production cost of electrofuels increases drastically per megawatt hours fuel when the capacity factor (i.e., actual production as share of total production capacity) of the wind turbines is decreased. Thus, the benefit of using electrofuels for balancing renewable energy need to be further assessed.

The production cost of different electrofuels is also a limiting factor for the potential future production of electrofuels in Sweden. The literature contains a fairly broad range of estimates, but the most important factors in the production cost of electrofuels are the capital cost of the electrolyzer, the electricity price, the capacity factor of the unit, and the lifetime of the electrolyzer (see text footnote 1).

The majority of the current CO_2 sources are located in southern Sweden, which is also the case for the current CO_2 sources with relatively pure CO_2 emissions. However, from the perspective of the electric-grid, electrofuels production may be more suitable in the northern parts of Sweden where there is generally a surplus of power generation and lower electricity prices. An increasing demand for electricity in southern Sweden might put additional pressure on the transmission capacity from north to south. Future biofuel plants based on forest biomass (as included in the 2030 scenario) are expected to be located mostly in northern Sweden and, therefore, represent an interesting source of CO_2 for production of electrofuels.

From a climate perspective, it might be preferable to capture and store CO_2 underground, using CCS technology, and not convert CO_2 into a fuel that after combustion will be released to the atmosphere again (van der Giesen et al., 2014; Sternberg and Bardow, 2015). If the CO_2 has been captured from burning fossil fuels, CCS will avoid increased CO_2 concentration, and if the CO_2 is captured from burning biomass (or from air), CCS will decrease the atmospheric CO_2 concentration, *ceteris paribus*. Today, however, there are several obstacles that have to be overcome before CCS could be available at a large scale, including public acceptance (Oltra et al., 2010; Dütschke, 2011). CCS is also only applicable for relatively large CO_2 sources and storage possibilities depend on geological prerequisites.

The overall impact on CO_2 emissions of the production and use of electrofuels mainly depends on the electricity-related CO_2 emissions and what the fuels replace (van der Giesen et al., 2014; Sternberg and Bardow, 2015). van der Giesen et al. (2014) conclude that for some production paths, the climate impact is worse than for fossil fuels, and achieving a net climate benefit requires using renewable electricity and renewable CO_2 sources. Sternberg and Bardow (2015) evaluate electrofuels relative to the case in which the same amount of CO_2 is instead either emitted or stored. They find that electrofuels can at best only make a small contribution to mitigation compared to other available solutions and that using CO_2 emissions for electrofuels is worse from a climate perspective compared to storing them. It would be interesting to more thoroughly study the environmental impact of electrofuels compared to other CCU technologies with a lifecycle perspective. For example, the amount of CO_2 emissions from electricity production will depend on (i) the time perspective (for example using a marginal or average electricity mix) and (ii) the geographical boundaries of the electricity supply. However, GHG emissions from electricity production are expected to decrease significantly as a consequence of stringent energy and climate policies changing the mix of energy sources.

To summarize, electrofuels are limited by electricity demand rather than the demand for CO_2 and, at scale, require a substantial amount of renewable electricity at relatively low cost. The GHG impact of electrofuels compared to other options, in particular CCS, needs to be further assessed.

AUTHOR CONTRIBUTIONS

JH is the main author; planned the work and led the writing. RH was responsible for the mapping and quantification of the major Swedish point sources of CO_2 emissions and contributed to further assessments and paper writing. SB, MT, and MG contributed with the electrofuel-production characteristics, participated in the assessment, and contributed to paper writing.

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REVIEW
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The Social Acceptance of Carbon Dioxide Utilisation: A Review and Research Agenda

Christopher R. Jones[1,2]*, Barbara Olfe-Kräutlein[3], Henriette Naims[3] and Katy Armstrong[1]

[1] UK Centre for Carbon Dioxide Utilisation (CDUUK), University of Sheffield, Sheffield, United Kingdom,
[2] Environment and Behaviour Research Group (EBRG), Department of Psychology, University of Sheffield, Sheffield, United Kingdom, [3] Institute for Advanced Sustainability Studies (IASS), Potsdam, Germany

CO_2 utilisation technologies—also called carbon dioxide utilisation (CDU) and carbon capture and utilisation (CCU)—convert CO_2 *via* physical, chemical, or biological processes into carbon-based products. CO_2 utilisation technologies are viewed as a means of helping to address climate change and broadening the raw material base for commodities that can be sold to generate economic revenue. However, while technical research and development into the feasibility of CO_2 utilisation options are accelerating rapidly; at present, there has been limited research into the social acceptance of the technology and CO_2-derived products. This review article outlines and explores three key dimensions of social acceptance (i.e., socio-political, market, and community acceptance) pertaining to innovation within CO_2 utilisation. The article highlights the importance of considering issues of social acceptance as an aspect of the research, development, demonstration, and deployment process for CO_2 utilisation and explores how key stakeholders operating on each dimension might affect the innovation pathways, investment, and siting decisions relating to CO_2 utilisation facilities and CO_2-derived products. Beyond providing a state-of-the-art review of current research into the social acceptance of CO_2 utilisation, this article also outlines an agenda for future research in the field.

Keywords: carbon dioxide utilisation, carbon capture and utilisation, social acceptance, public perception, review

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United States
Julia Van Heek,
RWTH Aachen University, Germany

****Correspondence:***
Christopher R. Jones
c.r.jones@sheffield.ac.uk

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INTRODUCTION

Carbon dioxide utilisation (CO_2 utilisation or CDU) technologies—also called Carbon Capture and Utilisation (CCU) technologies—utilise CO_2 as a valuable carbon resource. CO_2 utilisation technologies can be defined as converting CO_2 *via* physical, chemical, or biological processes into carbon-based products (see **Figure 1**). Thus, these technologies can be thought of as a new synthetic carbon cycle, which uses and releases CO_2 back to the atmosphere or sequesters it in products. By sequestering CO_2 and/or reducing the direct reliance on extracted fossil fuels as a carbon-feedstock for the manufacture of commodity products, CO_2 utilisation technologies are seen as a means of helping to mitigate climate change, while simultaneously creating useful, saleable products that can potentially offset the costs associated with the capture and/conversion processes (Styring et al., 2014).

CO_2 utilisation is often directly compared and contrasted with Carbon Capture and Storage (CCS); however, they are two distinct technology paths and so it is necessary to treat and evaluate these technologies individually, especially with regard to environmental policy targets (Bruhn et al., 2016). Specifically, CCS is a CO_2 mitigation strategy; its objective is to deal with large volumes of CO_2

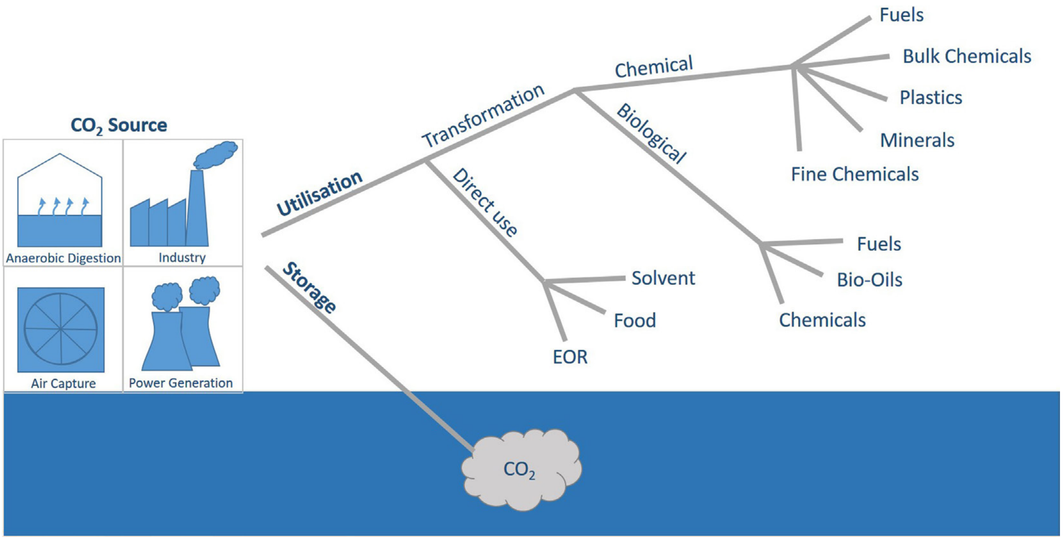

FIGURE 1 | **Carbon dioxide storage and utilisation options**. Carbon dioxide from point source emitters (e.g., fossil fuel power generation or other large industrial emitters) or *via* direct air capture or biological processes can be geologically stored (*via* carbon capture and storage) or used. Use of CO_2 can be direct (e.g., for use in "enhanced oil recovery") or the captured CO_2 can be transformed *via* chemical or biological processes for use as a carbon feedstock (e.g., for the manufacture of fuels, chemicals, plastics, etc.).

emissions by capturing and sequestering the gas in geological formations for periods of hundreds of years (Intergovernmental Panel on Climate Change, 2005). CO_2 utilisation on the other hand uses CO_2 as a feedstock for the creation of new, value-add products; it can promote sustainability and a circular economy, encourage industrial symbiosis and economic growth and enable the storage of renewable energy. Thus, while both technologies "capture" CO_2, the subsequent treatment of the gas is very different.

While the majority of CO_2 utilisation options remain at low technology readiness levels (or TRLs) (Wilson et al., 2015), some CO_2-derived products are beginning to emerge on to the market [e.g., synthetic methane (or "e-gas") produced by Audi; polyols manufactured by Covestro and Novomer (under the trade names Cardyon and Converge, respectively) and construction aggregates from the accelerated mineralisation of waste ashes by Carbon8 Aggregates]. Importantly, as the commercialization of products and processes continues, there will be an associated growth in the interactions that a diversity of social stakeholders (including policy-makers, businesses, the general public, etc.) will share with CO_2 utilisation facilities and products. For example, consumer purchase decisions may help to determine whether products containing CO_2 succeed in a competitive marketplace. Thus, developing a firm understanding of the factors and actors likely to shape the "social acceptance" of CO_2 utilisation should be a priority for research. Interestingly, however, to date there has been very little systematic research in this area (Jones et al., 2015). This is a situation that contrasts markedly with the rich literature that now exists relating to the key factors and actors likely to govern the "social acceptance" of CCS technologies (see, e.g., L'Orange Seigo et al., 2014).

Within the current article, we directly address this knowledge gap by first outlining a key framework for conceptualizing the social acceptance of technological innovation, before summarizing and synthesising the findings from the extant literature pertaining to the social acceptance of CO_2 utilisation technologies. Where relevant, inferences about the factors and actors likely to shape the future commercial success of CO_2 utilisation are also made. We end by outlining a research agenda for future academic inquiry into the social acceptance of CO_2 utilisation technologies; highlighting the key questions that need addressing and the methodological considerations that should be kept in mind in the pursuit of such research.

THE IMPORTANCE OF SOCIAL ACCEPTANCE

Social acceptance, or the extent to which an innovation (e.g., a policy, technology) is endorsed or rejected by key social actors (e.g., politicians, financiers, and publics), is recognised as being necessary for the successful introduction and commercial success of such innovation (e.g., Wüstenhagen et al., 2007; Perlaviciute and Steg, 2014; Upham et al., 2015). This is particularly the case within Western democracies, where policy or institutional change typically requires the support of individuals and communities (Peterson et al., 2015). Indeed, there are a growing number of examples of where failures to appropriately engage with, assess and accommodate the opinions of key social actors at a general, regional and/or local level has led to delays or curtailments to the introduction of innovations (e.g., GM technology, Horlick-Jones et al., 2006; renewable energy technologies, Devine-Wright, 2011).

Formal investigations into the social acceptance of new technologies date back to the 1980s where, at the time, a growing recognition of the governing influence that myriad stakeholders could exert upon the path of technological innovation, investment, and deployment led to a realisation that understanding (and influencing) the factors affecting the success of such innovation demanded more than a simple assessment of general public opinion (Wüstenhagen et al., 2007; Fournis and Fortin, 2017). Since then, respect for the importance of understanding and addressing the issue of social acceptance (and social acceptability[1]) of technologies has grown rapidly (Fournis and Fortin, 2017).

Logically, a diversity of frameworks of social acceptance have followed—stemming from a number of psychological, sociological, and technical perspectives—aiming to provided working definitions of "acceptance" and showcase the important dimensions and stakeholders (and their associated relationships) that underpin whether or not technological or policy innovations are accepted (e.g., Szarka, 2007; Wüstenhagen et al., 2007; Shove, 2010; Huijts et al., 2012; Upham et al., 2015).

For example, Huijts and colleagues (2012), from a *psychological* perspective, propose a comprehensive framework of *public* acceptance of sustainable energy technologies (SETs). This framework considers an individual's intentions to support or oppose SETs to be a product of their attitudes, personal norms, perceived behavioural control, and subjective norms; concepts which are in turn predicted by other factors (e.g., perceived costs, risks, and benefits of the SET). However, while Huijts et al.'s (Huijts et al., 2012) framework provides a helpful take on the issues of *public* acceptance (see also Gupta et al., 2012), it fails to acknowledge that the *social* acceptance of innovation is governed by manifold social stakeholders (including but not limited to publics) working at multiple levels (macro, meso, and micro). Furthermore, the model cannot accommodate the epistemological differences of research stemming from other disciplinary perspectives (e.g., sociological accounts of technology acceptance, e.g., Shove, 2010).

With this in mind, the introduction to the social acceptance of CO_2 utilisation within the current article is structured in accordance with Wüstenhagen et al.'s (Wüstenhagen et al., 2007) "triangle of social acceptance" (see also Wolsink, 2012); a broader, conceptual framework, which characterizes the three levels of acceptance typically thought to shape the fate of technological and policy innovation (Upham et al., 2015). According to this framework, social acceptance of innovation to be the product of three dimensions: socio-political, market, and community acceptance (see **Figure 2**). While originally designed to profile the factors and actors influencing the social acceptance of renewable energy policy and technologies; the "triangle" framework has been applied within other policy domains, such as waste management and climate change adaptation (Wolsink, 2010).

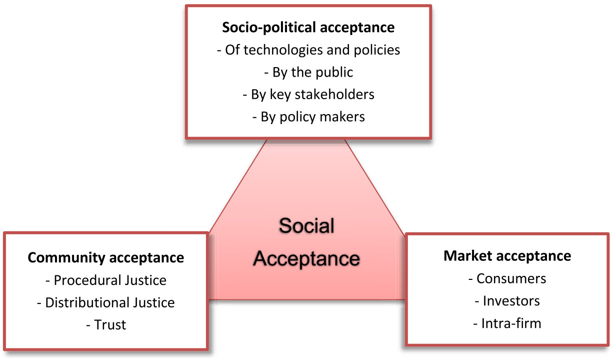

FIGURE 2 | **The "Triangle of Social Acceptance."** The "triangle" framework proposes that the social acceptance of policy and technology innovation is determined by the opinions and actions of stakeholders operating on three dimensions (i.e., socio-political, market, and community acceptance). The figure is adapted from Wüstenhagen et al. (2007) and is reproduced with the permission of the copyright holder.

According to Wüstenhagen and colleagues (2007), *socio-political acceptance* refers to the acceptance of technologies and policies at the broadest, most general level by major social actors (e.g., the general public, policy-makers). By contrast, *market acceptance* is more specific and integrates considerations of the diffusion of innovation among consumers and the interactions and investment decisions of technology investors (e.g., the chemical industry or plant engineers); operating as both competitive and collaborative entities within both national and/or multinational contexts. Finally, *community acceptance* is the acceptance of specific projects at a local level by stakeholders (particularly residents and local authorities) living proximal to the development. It is at this level that trust in decision-makers and perceptions of procedural and distributive justice (i.e., the extent to which decision-making processes and the distribution of risk and benefits are thought to be fair and equitable) are believed to shape the ability to deploy specified projects.

According to the "triangle" framework, the three dimensions of social acceptance are often interrelated (i.e., the decisions made by key actors on one dimension can have ramifications for acceptance of innovation on the other dimensions). For example, failures to institutionalize frameworks to promote market and community acceptance at the socio-political level (e.g., procurement mechanisms, decision-making protocols) can mean that general support for a technology may fail to translate into business and consumer investment and/or local support for the construction of specified projects. Similarly, it is possible that existing market path-dependencies can provide inertia to the adoption of technological innovations endorsed at a socio-political and/or community level. Further, it is the differences in acceptance recorded at the socio-political (i.e., general) and community (i.e., local) level that has given rise to extensive research into so-called NIMBYism (not in my backyard, e.g., van der Horst, 2007; Jones and Eiser, 2010) and ongoing debates around the benefits and drawbacks of devolved versus centralised decision making (e.g., Bouffard and Kirschen, 2008).

While some researchers have critiqued the general concept of "social acceptance" (e.g., Batel et al., 2013) or have criticized Wüstenhagen et al.'s framework for failing to fully and explicitly

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[1] There is ambiguity around the use of the terms "acceptance" and "acceptability." While often used interchangeably they are noted to be different concepts (Fournis and Fortin, 2017). We favour use the term "acceptance" within the current article, not only because it is used by the "triangle" framework (i.e. the conceptual framework around which we structure the current review) but it is also a term that simplistically refers to whether something is accepted or not, as opposed to mapping to more complex, dynamic and hierarchical discussions of collective choice (Szarka, 2007).

define the assumptions upon which it rests and/or recognize the complexities around the stakeholder relationships it identifies (Fournis and Fortin, 2017); the "triangle" framework is widely cited and provides a good basis from which to foster a global understanding of the people and processes that are likely to determine whether or not innovations are socially accepted and therefore succeed or fail. Moreover, the proposed key dimensions of acceptance (i.e., socio-political, community, and market acceptance) have been confirmed by other commentators (e.g., Upham et al., 2015).

In the following sections, then, we explore each of the three dimensions of the "triangle" in turn; outlining the factors and actors that are likely to influence decisions about the acceptance of CO_2 utilisation (both in general and with regard to specific products or siting of facilities) and summarising the nature and findings of any extant research that has been conducted. The review ends by proposing a number of key research questions that we feel should form the basis of future investigation in the field.

THE SOCIAL ACCEPTANCE OF CO_2 UTILISATION

Socio-Political Acceptance

General socio-political support for (or rejection of) a given innovation can fundamentally shape its success. There are numerous examples of where failures to secure appropriate socio-political support for a technology has delayed or curtailed its introduction. This is exemplified, for example, by resistance to the introduction of E10 (10% ethanol) automotive fuel in a number of countries due to concerns about its effect on fuel prices and the perceived risks it poses to the operation of some older vehicles (Hauke, 2014). Also, the introduction of CCS technologies in some countries (e.g., Germany) has been stymied by a strong resistance to the concept among stakeholders and the general public (Brunsting et al., 2011; L'Orange Seigo et al., 2014). The following section outlines some of the key factors and actors at the socio-political level that are likely to shape the development and deployment of CO_2 utilisation technologies.

The primary driver behind socio-political interest in CO_2 utilisation to date has been climate change mitigation. This interest has arisen in response to national and international legislation regarding greenhouse gas emissions (e.g., European Union Emission Trading System, the Renewable Energy Directive, and the Fuel Quality Directive). Policy-makers are concerned with reducing the "carbon footprint" of their individual countries and industrial emitters are concerned with the possibility of economic penalties that could result from their emissions. These growing pressures (alongside other concerns, e.g., ensuring the security of raw resources) have led to accelerated innovation in technology and policy relating to CO_2 utilisation.

Within this space, one can assume that the views of societal opinion leaders and industrial-sector decision-makers about whether or not to invest in CO_2 utilisation (or particular technology or product options)—shaped by, for example, individual expertise, personal opinions, "bottom line" considerations, policy support, and media coverage (e.g., Kepplinger, 2007)—will influence the broader socio-political acceptance of CO_2 utilisation and, hence, investment and development of the technology. However, while there have been informal efforts to engage with and network interested actors (e.g., by SCOT and CO2Chem)[2,3] to date there has been no formal systematic research in this area. As such, we argue that formal stakeholder analysis (e.g., Hemmati, 2002; Roloff, 2008; Freeman, 2010) in order to identify the key industrial (and other) stakeholders within the sector (both emitters and users) and to establish their motivations and requirements for investment should be a priority. This will identify levers, synergies, and courses of action which can be undertaken from both a policy and industrial perspective.

Public funding schemes and research-programme investment are a key means by which synergies can be formed and innovation encouraged. They provide a high level of facilitation for innovative technologies and, in turn, can positively steer internal decision making processes. There are currently around 34 governmental programmes for research into CO_2 utilisation worldwide.[4] The pre-requisites for the establishment of such programmes are manifold but appear to include, for instance, the existence of a strong chemical industry (e.g., Germany, Netherlands, Korea), the existence of an extractive oil or gas industry that has an interest in "enhanced recovery" applications (e.g., Canada, USA), or, in countries that plan to continue to use fossil fuel resources for their energy supply, the existence of coal-fired plants aiming at installing "Clean Coal" systems (e.g., China) (Olfe-Kräutlein et al., 2016, for a full outline of current programmes).

Interestingly, there often appears to be a disjunction between what developers see as the primary purpose of CO_2 utilisation technology and the motivations driving governmental research-programme investment in the sector. That is, while industrial and academic actors involved in the development of CO_2 utilisation technologies emphasise the fairly limited contribution that such technologies can make to climate change mitigation efforts (e.g., due to a dependency on the availability of renewable energy, see e.g., Bringezu, 2014); research programme investment is often rooted in this "climate change mitigation" context. There are evident questions as to the long-term consequences that any difference in the purported versus perceived rationale for CO_2 utilisation might have for future public investment in the sector. Arguably, policies for investment need to evolve and realign to recognise the wider use-value of CO_2 utilisation technologies (e.g., contributions to the sustainability and breadth of the raw material base of a country); this is something which has been recognised by the German government through their CO_2Plus initiative (funded as part of the broader "Green Economy" initiative).[5]

Relatedly, there are questions as to how wider socio-political confidence in CO_2 utilisation might be affected by any misalignment in the perceived versus stated rationales for investment in the technology. For example, the way in which CO_2 utilisation is

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[2] http://www.scotproject.org/

[3] http://co2chem.co.uk/

[4] http://database.scotproject.org/

[5] https://www.ptj.de/co2plus

publicly "framed" might have consequences for support among a number of socio-political actors including, notably, the general public. Indeed, not only does research into framing reveal how the manner in which technological innovation is presented can exert a large impact on public opinion (e.g., Chong and Druckman, 2007; Jones et al., 2012; de Vries et al., 2016) but also that perceived discrepancies between the purported and perceived rationale for investment in technology can negatively affect public trust (e.g., Terwel et al., 2011).

While the views of the general public are a known determinant of the success of technological and policy innovation; research into the public acceptance of CO_2 utilisation is currently sparse. This reflects the early technology readiness level of many CO_2 utilisation options and low level of public awareness of the technology at the present time. The few studies that do exist have tended to use discursive methods (e.g., focus groups, semi-structured interviews) to assess initial understanding of the technology and gain initial insights into the factors that might underpin acceptance (e.g., Jones et al., 2014, 2016; van Heek et al., 2017a,b). That said, recently, details of findings from larger scale surveys are beginning to emerge (Perdan et al., 2017). In combination with formative research into the opinions of selected experts (Olfe-Kräutlein et al., 2016; van Heek et al., 2017a,b) and *via* monitoring participation in stakeholder discourse events (Olfe-Kräutlein et al., 2016), a picture of public perceptions of CO_2 utilisation technologies (and how these map to and/or diverge from those of experts) is beginning to build.

The results of these studies generally confirm that awareness of CO_2 utilisation is currently very low and while there is some scepticism about the long-term environmental benefits of the technology, there is tentative overall support for the concept as a "bridging technology" in the fight against climate change (Jones et al., 2015, 2016). This support is, however, strongly caveated by people's self-professed lack of knowledge of the technology, questions over the techno-economic feasibility of the processes and uncertainty over the societal consequences of investment in the technology. For example, some people question whether or not investment in CO_2 utilisation could detract from investment in more preferable low-carbon technologies (e.g., renewables) or conflict with broader sustainability goals (e.g., CO_2 utilisation is seen by some as being predicated on the continued use of fossil fuels) (e.g., Jones et al., 2016). A summary of the formative research that has been conducted to date into general public perceptions of CO_2 utilisation can be found in **Table 1**.

To some extent, the results of this initial research into public perceptions can be seen to be a product of the pro-environmental focus of the framing used to introduce the technology to participants. The power that such framing is likely to have on opinions is likely to be further enhanced by the novelty and unfamiliarity of the technology (Druckman and Bolsen, 2011). An obvious starting point for future research in this area, then, is to investigate the role that different framing of CO_2 utilisation (e.g., to focus on alternative costs, benefits, or risks) might have on public opinion. Moreover, there are related questions pertaining to how emerging mental models and/or affective evaluations of CO_2 shape how communications regarding CO_2 utilisation are perceived among lay-publics (e.g., Montijn-Dorgelo and Midden, 2008).

TABLE 1 | Summary of the key studies conducted into emerging perceptions of CO_2 utilisation technologies and product options.

Study (location)	Year	Aim
Jones et al. (2014) (UK)	2014	Qualitative focus group study with follow-up information-choice questionnaire, designed to (a) test a methodology for assessing public perceptions of CO_2 utilisation and (b) elucidate new understanding of people's attitudes to the technology
Jones et al. (2015) (UK)	2015	Qualitative focus group study (with questionnaire), building on 2014 study, designed to investigate and assess emerging lay public perception of CO_2 utilisation among groups of adults and high school students
Olfe-Kräutlein et al. (2016) (Germany)	2016	Semi-structured interview and participant observation study, designed to explore the potential for and barriers to communication about CO_2 utilisation. Study provides (a) an analysis of expert and other stakeholder perspectives and (b) strategic comments for future communications regarding CO_2 utilisation
Jones et al. (2016) (UK/Germany)	2016	Focus group study (with questionnaire), designed to investigate and compare and contrast laypeople's opinions towards CO_2 utilisation technologies in the UK and Germany
Arning et al. (2017) (Germany)	2017	Qualitative focus group and online survey study, designed to (a) conceptualize CO_2-utilisation risk perception; (b) evaluate the relationship between risk perception and product acceptance and (c) provide a breakdown of the factors affecting responses within different user-groups
van Heek et al. (2017a) (Germany)	2017	Qualitative interview study designed to assess acceptance of different CO_2-derived plastic products. Study compares layperson and scientific expert attitudes and perspectives
van Heek et al. (2017b) (Germany)	2017	Combination of qualitative and quantitative methods with the aim to deliver insights into acceptance drivers and barriers connected to CO_2 utilisation technology
Perdan et al. (2017) (UK)	2017	Quantitative survey of 1213 UK adults, designed to establish the extent of people's awareness and acceptance of CO_2 utilisation and to elicit the importance they put on different sustainability issues relevant to the technology

Full references for the studies can be found in the reference section.

One of the mooted benefits of research into public perception is that the knowledge gleaned from such activity could be used in order to inform public engagement and communication materials by helping to identify possible misperceptions and/or key concerns and benefits. Parallel research conducted into public perceptions of carbon capture and storage (CCS), for example, has been used to provide a scientifically sound basis for communication relating to this technology (Brunsting et al., 2011). Intriguingly, early evidence shows that the conceptual relatedness of CCS to CO_2 utilisation (and the fact it is often called CCU) could have implications for the public acceptance of CO_2 utilisation technology (Jones et al., 2016), particularly in countries or contexts where CCS has proven to be controversial and/or rejected at a socio-political level (e.g., Germany) (L'Orange Seigo et al., 2014).

A key shaper of public opinion at the socio-political level is the media. Media coverage (e.g., news reports) continues to play an important role in spreading information and raising awareness about technological innovation (Hampel and Zwick, 2016; Weitze and Weingart, 2016). While a full analysis of media coverage of CO_2 utilisation technologies has yet to be published (and remains a priority for future research), informal analysis indicates that media coverage at present tends to be positive. Although, negative connotations have been reported in some contexts where CO_2 utilisation is considered alongside CCS technologies (Bruhn et al., 2016). A number of interesting questions exist regarding how media coverage will develop and shape public opinion going forward. For example, there are questions as to whether or not media exaggeration of the purported benefits of CO_2 utilisation might raise false expectations among the general public and other socio-political stakeholders (Olfe-Kräutlein et al., 2016).

In summary, how technological innovation is received and responded to at the socio-political level has key implications for investment decisions and public support. The studies that have been conducted to date have provided first insight into some of the factors likely to govern acceptance at a socio-political level. These indicators should now serve as a starting point for more comprehensive research in the field. An option for such research—and one that would allow for a wider precis of the key non-technical factors and actors likely to foster acceptance or rejection of CO_2 utilisation at this level—is to use a multi-stakeholder approach (e.g., Freeman, 2004, 2010). This approach would allow for a wider and more diverse group of stakeholders to participate in the dialogue about the future of CO_2 utilisation; as well as helping to highlight the dynamics of decision making regarding acceptance at the socio-political level.

Market Acceptance

Wüstenhagen et al. (2007), p. 2685 define market acceptance as "*…the process of market adoption of an innovation*" and examine it in regard to acceptance among consumers, investors, and intra-firm actors. In this market perspective, the decision to accept or reject an innovation is based on *diffusion theory* (Rogers, 1995). Diffusion theory separates the uptake of innovation into five steps: (1) knowledge, (2) persuasion, (3) decision, (4) implementation, and (5) confirmation (see **Figure 3**). The success of diffusion is assessed as *"the number of individuals who adopt a new idea in a specified period"* (Rogers, 1995, p. 206). This measure is influenced by a variety of factors, including the perceived attributes of the innovation, the type of innovation decision and the communication channels available (Rogers, 1995). Consequently, for any group of market actors (consumers, investors, and intra-firm actors) these factors should be considered to better understand the adoption process steps and the resulting acceptance or rejection of an innovation. In the following section, we use diffusion theory as a lens to explore the factors that might affect the market acceptance of CO_2 utilisation technologies among consumers, investors, and intra-firm actors.

Consumers

To date, limited studies have focused specifically on consumer acceptance of CO_2-derived products. The current exceptions

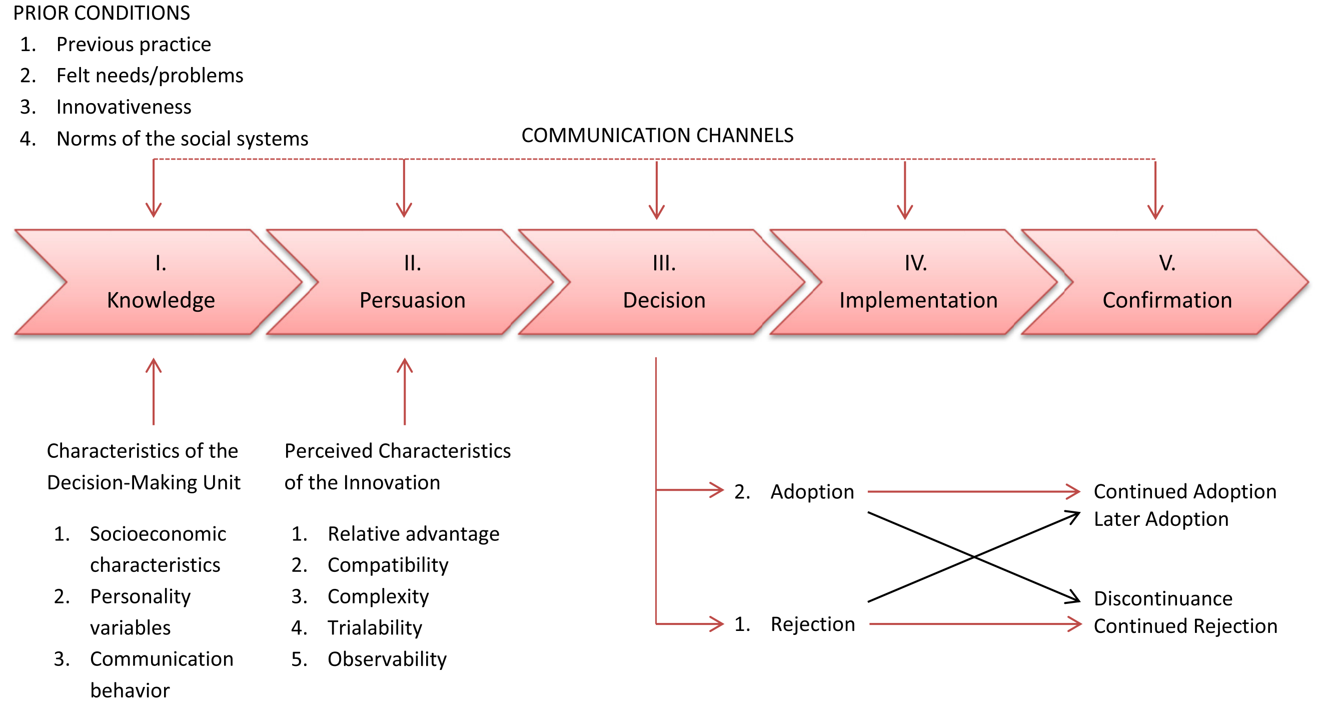

FIGURE 3 | **A model of stages in the innovation-decision process**. According to the model, adoption or rejection of innovation proceeds through five consecutive stages. Source: Rogers (1995), p. 165. This is an adapted version of the original figure that is reproduced with the permission of the copyright holder.

include two small qualitative studies that have focused on assessing potential consumer perceptions of CO_2-derived mattresses and plastics (Arning et al., 2017; van Heek et al., 2017a,b). Both studies reveal that the risk is deemed to be relatively low and that people tend to have positive perceptions of the products. However, while these findings are encouraging for proponents of CO_2 utilisation (e.g., investors); as both studies asked people to consider the purchase of hypothetical (rather than actual) products, there are limitations to the conclusions that can be derived regarding actual real-world consumer acceptance. As more "real" CO_2-derived consumer products reach the marketplace, it will be possible to analyse the specific effects of how, for instance, advertising, product pricing, and labelling will affect purchasing behaviour. Presently, though, learning more about the processes by which consumer opinions are liable to be formed and shaped—particularly prior to the decision to adopt or reject an innovation—is essential.

In most cases, materials derived from CO_2 utilisation will be retailed to intermediaries (e.g., product manufacturers or distributers) rather than directly to end-consumers. It is currently unclear to what extent the final retailers of consumer goods will seek to label their products as being "CO_2-derived" or with other possible messages in attempt to gain competitive market advantage (Olfe-Kräutlein et al., 2016). While there are open questions as to whether certain consumers will accept or reject CO_2-derived products on principle (e.g., irrespective of labelling or advertising); there are particularly interesting questions relating to how end users will respond in those cases where products *are* explicitly marketed as CO_2 derived. It is in these cases where the opinions of consumers will exert a particularly strong influence on the ultimate success or failure of the product(s) in question.

According to diffusion theory, because few CO_2-derived products are available to consumers on the open market and so limited numbers of consumers have ever had to face the explicit decision for or against buying a CO_2-derived product; the majority of end consumers can be considered as either having no exposure to such products or, at most, as being early in the *knowledge* stage of the model.

Perception of an innovation at the *knowledge* stage is shaped strongly by the characteristics of the socioeconomic system the consumers are part of, the communication behaviours relating to the innovation and consumers' individual attitudes (see **Figure 3**). While learning of the existence of an innovation can provide a basis for its later adoption; whether or not consumers develop this knowledge is strongly shaped by their values, beliefs, and attitudes (Rogers, 1995). For instance, consumers are more likely to seek out information on CO_2-derived products if such products are deemed to gel with their extant belief systems (e.g., if such products are seen as being congruent with their aspirations to live more sustainably).

At present, there are questions regarding the adequacy of the information that is available to consumers regarding CO_2 utilisation (and more specifically CO_2-derived products) in order to develop an informed understanding at the knowledge stage. Much of the information on the nature of CO_2 utilisation (e.g., its consequences, advantages, disadvantages) remains in scientific publications that are inaccessible to most consumers. Moreover, while all companies distribute communication materials to their own customers, the current efforts largely target at business customers since most CO_2-derived products are intermediates. The research community is thus increasingly aware of a need for neutral and evidence-based communication about CO_2 utilisation innovations for a broader public; information that is aimed at improving the base knowledge of potential future consumers—for some existing examples, see Olfe-Kräutlein et al. (2014) and Krämer et al. (2015).

Once knowledge of an innovation has developed, the *persuasion* stage of Rogers's (Rogers, 1995) model becomes relevant. Whether or not efforts to persuade people regarding an innovation translates to the decision to adopt (or reject) it is strongly influenced by the communicated characteristics of the innovation, e.g., the relative advantage the innovation will afford consumers (i.e., how useful it will be) and the perceived compatibility of the innovation with existing lifestyle practices (see **Figure 3**).[6] The decision over how CO_2-derived products are promoted to consumers ultimately rests with the producers and/or retailers consumer goods. As such, their marketing decisions about which product characteristics are emphasised will strongly influence how a product is received and whether or not it is later adopted or rejected.

Investors

In the context of CO_2 utilisation, investors include public and private R&D funding programs (aiming to promote the general development and implementation of the technologies) and private companies that see a need to capture and/or use CO_2 (e.g., large CO_2 emitters, the chemical industry). In contrast to end-consumers, investors are currently significant market actors; however, decision making at the level of investors is usually a confidential and non-public process. While the *knowledge* stage in investment decision making is generally professionalised, it is nevertheless influenced by the characteristics of the decision making unit (e.g., a profit-focused hedge fund will set different preferences than a welfare-oriented public investor.) Whether an investor is then *persuaded* to invest in CO_2 utilisation is likely to be rationally driven by strategic motives (such as the optimisation of profits or other desired KPIs) and, hence, progression through the latter stages of the diffusion model (decision, implementation, and confirmation) will depend largely on the defined targets and measurable outcomes of the investment.

While information on specific investment decisions is likely to remain largely confidential, it is nevertheless recommended to conduct research into the factors and actors driving these investment decisions. There are a few studies focussed on start-up companies (e.g., Zimmerman and Kant, 2016) or public investments (e.g., Olfe-Kräutlein et al., 2016), but a more detailed and systematic analysis of acceptance issues among investors would be beneficial. There is a further need for research into future path dependencies, for example, relating to infrastructure decisions and interfaces with the socio-political system (e.g., relevant regulation and frameworks) in order to better understand and

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[6] Similar constructs are recognised in other key models of technology acceptance (e.g. the Technology Acceptance Model, e.g. Venkatesh and Davis, 2000).

improve investment security for investors. While formative studies that touch upon some of the issues pertinent to investment decisions have been published (e.g., Bringezu, 2014; Wilson et al., 2015; Naims, 2016; Piria et al., 2016), there is need to continuously review and update these according to the evolving expectations of investors and changing regulatory and policy environments.

Crucially, there is a role for the academic community in providing evidence-based support for investors in their process of decision making. These are studies that evaluate the potential and risk of different CO_2 utilisation innovations from an ecologic, economic and/or societal perspective; providing insight into the suitability and acceptability of different technologies in various future scenarios. Helpfully, the first of such studies, which not only largely focus on the environmental aspects and life cycle assessment of CO_2 utilization (e.g., Bennett et al., 2014; von der Assen and Bardow, 2014; von der Assen et al., 2016) but also with regard to the circular economy (e.g., Styring et al., 2011; Bringezu, 2014) and socioeconomic context (e.g., Naims, 2016; Olfe-Kräutlein et al., 2016) have now been published. However, as with the research into path dependencies, there will be a need for further and/or updated studies as new technologies and markets develop.

Intra-Firm Actors

Intra-firm actors are the individuals (e.g., developers, managers) or groups of individuals (e.g., departments, boards) within a company who will also play a major role with regard to acceptance and diffusion of CO_2 utilisation technologies and products. Research indicates that firms with a proactive environmental strategy tend to be more likely to invest in R&D, technology, and human resources to develop their capabilities, even in uncertain business environments (Aragón-Correa and Sharma, 2003). Thus, it can be assumed that environmentally proactive firms, in addition to those with a comfortable competitive position, are more likely to advance the development and introduction of CO_2 utilisation in comparison to those with more tentative innovation strategies and/or a weaker market position.

Within organisations, so-called "change agents" play an integral role in shaping the path of innovation. Change agents act through all stages of the diffusion process; in the best cases outlining the need for and increasing knowledge of innovations, before promoting the favourable characteristics of an innovation and expediting decision-making processes (Rogers, 1995). Consequently, the abilities of individual change agents, alongside the support systems provided to them within firms and the firms willingness and/or ability to shift extant intra-firm path dependencies (e.g., Alänge et al., 1998), will play a crucial role for the acceptance and diffusion at the intra-firm level.

At the current time, the principal intra-firm change agents for innovation in CO_2 utilisation are technically trained R&D professionals, project managers and/or business development managers. Currently, very little is known about how these individuals are operating within firms to shape the agenda for CO_2 utilisation and the development, use and/or marketing of CO_2-derived products. For example, what barriers do they face to implementing their ideas and how successful are they in communicating the need for change to their managers?

In sum, a number of factors and actors stand to shape the market acceptance of CO_2 utilisation technologies and/or CO_2-derived products. While investors are already significant actors in this arena, the first studies into their role and behaviour are ongoing and so only speculative conclusions can be drawn as to the processes driving their decisions to invest. Furthermore, while intra-firm environments and actors (e.g., change agents) are known to shape the uptake and diffusion of innovation; first studies in this field are also ongoing. Further attempts to assess their role for the diffusion and intra-firm acceptance of CO_2 utilisation will be useful. Also, formal investigations into the nature of decision making within firms seeking to invest in the CO_2 utilisation sector remains a priority for future research.

Similarly, while there is emerging intelligence on consumer attitudes towards CO_2-derived products, there are currently significant limitations to this research. To the extent that (a) there will be increased number of CO_2-derived products available to consumers in the future and (b) efforts will be made to gain competitive market advantage by communicating the source of carbon within these products, there needs to be increased research focus on the antecedents of consumer acceptance.

Community Acceptance

"Community acceptance" refers to "*…the specific acceptance of siting decisions and […] projects by local stakeholders, particularly residents and local authorities*" (Wüstenhagen et al., 2007, p. 2685). Thus, according to Wüstenhagen and colleagues (2007), this dimension is the most specific dimension of acceptance and refers to the rejection or acceptance of particular facilities or projects within geographically defined "host" communities (see also Sovacool and Ratan, 2012).

While one could choose to debate this relatively narrow definition of community—e.g., one could seek to define "community acceptance" more liberally so as to recognise that "non-local" stakeholders (e.g., global NGOs) and "communities of interest" can still exert influence over the fate of specific projects (Young, 1986; Walker and Devine-Wright, 2008)—it is certainly the case that the opposition or support received for specified projects at a local level is a key contributor to their success or failure (e.g., Devine-Wright, 2011).

Social scientific research has revealed a considerable amount about the factors likely to affect community acceptance of any array of (proposed) industrial and/or other facilities. This research has not only registered the differences that can (apparently) exist between the acceptance of facilities when considered at a general (i.e., socio-political) versus a local (i.e., community) level but has also provided key insight into the myriad explanations that can account for these differences (e.g., van der Horst, 2007; Jones and Eiser, 2010; Bell et al., 2013). This has included efforts to investigate how project acceptance might differ in different countries and cultures (e.g., Toke et al., 2008; Pietzner et al., 2011).

Taken together, it can be concluded on the basis of research conducted to date, that issues of "place" (including social, cultural, and technological characteristics) and "process" (i.e., engagement and decision-making practices) are of central importance when it comes to understanding how proposed projects or facilities are received and responded to at a local level. This is particularly the case within Westernised democracies, where "policy and institutional changes require support from both individuals and communities" (Peterson et al., 2015, p. 1).

Community Acceptance of CO_2 Utilisation Facilities

While there is a rich literature charting community acceptance of a large number of locally unwanted land-uses (LULUs) (e.g., prisons, power plants, and mental hospitals) (Schively, 2007) relatively little (if any) published research has specifically investigated opinions towards the prospect of CO_2 utilisation facilities. This is despite the fact that there are existing examples of commercial CO_2 utilisation facilities currently in operation (e.g., the Carbon Recycling International "Vulcanol" production plant, Grindavik, Iceland; Carbon8 "accelerated carbonation" facility, Brandon, UK).

To the extent that CO_2 utilisation facilities are affiliated with (and are hence sited alongside) existing industrial operations, one could anticipate that the likelihood of prohibitive local opposition forming to earmarked facilities could be very low. Indeed, for communities living adjacent to such sites, who are familiar with and/or reliant on the extant plant for employment, the prospect of additional operations (and opportunities) might be viewed quite positively (e.g., Van Der Pligt et al., 1986; Jones et al., 2015). It is, however, by no means guaranteed that the presence of extant development will mean that further development will be condoned. For example, concerns over fairness and distributive justice (i.e., the distribution of benefits and burdens) or failings in the inclusivity and/or transparency of the decision-making process, might also shape community level acceptance (e.g., Dobson, 1998; Jones et al., 2011; Ottinger, 2013). Moreover, as technologies, product options and their associated markets develop, diversify, and mature; there is an increased likelihood that more (and more diverse) communities will face the prospect of hosting CO_2 utilisation facilities. This will likely bring much less "familiar" populations into direct contact with such facilities.

We argue that the impact that the attitudes and behaviours of prospective host communities can have on the fate of such facilities, necessitates bespoke research into the nature and determinants of community acceptance towards CO_2 utilisation facilities.

The Risks of Drawing Conclusions Based on CCS Research

It would be relatively easy to draw speculative conclusions about likely community responses towards prospective CO_2 utilisation facilities by accessing the rich literature on "local" CCS development (e.g., Oltra et al., 2012; L'Orange Seigo et al., 2014). However, while there is some logic to this enterprise—bearing in mind the similarity in the terms and the fact that CCS and CO_2 utilisation facilities are both industrial plant designed to treat or "sequester" carbon dioxide—there is also good reason to be cautious due to the abovementioned differences in nature, scale, and intended purpose of these technologies (Bruhn et al., 2016). Moreover, where research has provided participants with the opportunity to consider their opinions of CO_2 utilisation in comparison with CCS (e.g., Jones et al., 2015, 2016), there is evidence of a number of fundamental differences in the perceived risks, costs, and benefits, including at the level of individual facilities, of these technology options.

Crucially, the formative research into public perception that has been completed to date (e.g., Jones et al., 2015, 2016) suggests that it is the transportation and storage of carbon dioxide—as opposed to the capture and/or conversion processes *per se*—that appear to be of most concern to those interviewed. This concern would appear to principally stem from the anticipated risk of CO_2 leakage, which is deemed to at the very least undermine the purpose of the technology or at worst to pose a direct risk of death or illness through contamination of drinking water, explosion and/or asphyxiation (e.g., L'Orange Seigo et al., 2014). While this research does reveal that people do see some risks with CO_2 utilisation facilities (e.g., risks from chemicals, explosion, etc.); currently, it appears that such facilities are likely to be viewed as any other form of generic industrial facility. Thus, it would appear that community level objections to CO_2 utilisation facilities are likely to be grounded in concerns over the prospect of local industrial development *per se*, as opposed to any bespoke risks posed by the CO_2 utilisation facility. It appears as though this tempered risk perception stems from both a trust in operators to run the facilities safely, as well as the comparatively benign, confined, and controlled nature of the processes being proposed; perhaps offset further by the prospect of local economic benefits (e.g., new jobs) (Jones et al., 2015).

Is the Current Indifference to CO_2 Utilisation Facilities a Positive Sign?

The relative indifference regarding the prospect of local development indicated in the studies conducted to date should not be taken to mean that it is guaranteed that there will be no opposition to local facilities. As previously outlined, local opinion towards actual development can differ from that registered when facilities are considered in a more general, abstract and/or hypothetical sense (e.g., Jones and Eiser, 2010; Devine-Wright, 2011; Bell et al., 2013). The fact that the research conducted to date has only focused on the opinions of general, unaffected publics is thus a weakness in making specific predictions about the likely acceptance or rejection of specific projects. Moreover, the findings that have been accrued to date are based upon the responses of a relatively ill-informed public (i.e., people with a low awareness and knowledge of the technology). It is possible that as people learn more about benefits and drawbacks of CO_2 utilisation and/or the prospect of local development becomes more real that "unexpected" local objections could arise (e.g., Bell et al., 2005, 2013).

Taken together, the extant research on LULUs indicates that developers and investors should pay close attention to matters of "place" and "process" (Peterson et al., 2015) when seeking to site facilities. CO_2 utilisation facilities are not a special case in this regard. While there are certain "unique" features of such technologies that might particularly resonate with host communities (e.g., specific perceived risks and benefits), the need to be (a) cognisant and responsive to the specific features and demands of a place and its people; and (b) make decisions in a fair, inclusive, and (ideally) participatory way, is now customary advice for finding common ground with potential host communities (e.g., Beierle and Cayford, 2002; Manzo and Perkins, 2006). That said, bespoke research into the community level acceptance of CO_2 utilisation facilities does not yet exist and this should be a priority for future research.

SUGGESTED RESEARCH AGENDA

In the context of CO_2 utilisation, the factors and actors relating to each of the three dimensions of the triangle of social acceptance (i.e., socio-political, market, and community acceptance) raise a number of novel and interesting research questions. While many of these questions have been outlined in the preceding sections; the following research agenda pulls out *some* of the priorities for future research in this field. This is not intended to be an exhaustive list of research questions but rather an outline of a handful of important avenues for initial inquiry, which are based upon the themes identified within this review article.

Socio-Political Acceptance

Socio-political support among the general public and other stakeholders can fundamentally shape the successful introduction of products and/or deployment of CO_2 utilisation facilities. As such, key CO_2 utilisation stakeholders should be identified as targets for future research (e.g., industry decision-makers, national, and international policy-makers, publics, and the media), and systematic programmes of investigation should be conducted in order to gain deeper insight into the antecedents and consequences of acceptance at this level. This research should seek to recognise and chart regional differences in socio-political acceptance of CO_2 utilisation.

Recommended studies relating to socio-political acceptance include

- A systematic, issue- and organisation-focussed stakeholder analysis in order to identify and clarify the range of stakeholders with connections to the development and deployment of CO_2 utilisation technologies and products (in different regions), as well as the reasons for their interest and/or investment in CO_2 utilisation at the socio-political level.
- A broader and more-detailed analysis of the international media coverage of CO_2 utilisation in order to assess emerging perceptions of CO_2 utilisation technologies (among the media and reported stakeholders) and how these are influencing the public agenda on CO_2 utilisation.
- A systematic analysis of the broader political agenda regarding CO_2 utilisation and how it might influence the investment in and the further research and development of technologies and products. This research should model different investment and development pathways in different policy and legislative scenarios.

Market Acceptance

A number of stakeholders will affect the market acceptance of CO_2 utilisation technologies and products. Notably, these include market actors, whose decisions to invest in CO_2 utilisation technologies and/or to produce, purchase, utilise, or retail CO_2-derived products will significantly shape innovation within the sector. Also, as more CO_2-derived products become available on global markets, the opinions, and choices of consumers will necessarily have an influence of growing importance.

Future research in the area of market acceptance should include

- Detailed identification of market-stakeholders and analysis of their perceptions of CO_2-derived products (including end-consumers) as they become commercially available. This research should seek to compare and contrast preferences for different CO_2-utilisation options and analyse how the preferences are formed, spread and how they affect choice among different consumer-groups.
- A more-detailed and systematic analysis of the acceptance and diffusion of different CO_2 utilisation technologies and products among investors. Studies should specifically investigate how the socio-economic environment and extant path dependencies affect behaviour among different investors.
- Research into intra-firm perception, attitudes, acceptance, and diffusion of CO_2 utilisation technologies and products. In particular, the role that "change agents" have in influencing intra-firm decision making is a relevant area for research.

Community Acceptance

Whether or not specific CO_2 utilisation facilities are welcomed at a local level could have implications for the overall success of the concept. While inferences can be drawn from analogous technological innovation, we currently know little about the community-level acceptance of CO_2 utilisation facilities and less about how opinions might evolve following construction and (successful or interrupted) operation. While some CO_2 utilisation facilities do currently exist, it is only a matter of time before more (and more diverse) communities will be invited to host facilities, either in isolation or in association with other industrial developments (e.g., CCS projects).

Two key questions that should form the basis of systematic future research in this area are:

- To what extent is the relative agnosticism (or indifference) currently shown towards hypothetical CO_2 utilisation facilities mirrored within communities actually hosting facilities and/or facing actual development (i.e., to what extent is there a "social gap" in CO_2 utilisation facility siting, see Bell et al., 2005, 2013)?
- Which of the many "place" and "process" factors identified as influencing local project acceptance (Peterson et al., 2015) are most important in shaping people's attitudes (and behavioural responses) to CO_2 utilisation facility development? For example, how does the presence and reliance on extant industrial development in a community affect acceptance of CO_2 utilisation facilities?

In addition to shedding light on the extant nature of more specific, "local" opinion towards CO_2-utilisation facility development, the findings of such research hold the potential to help inform public communication and engagement activities for use in relation to subsequent projects. Importantly, though, one needs to think carefully about the methods used in this research in order to ensure that a representative sample of community stakeholders are questioned and that informed opinions are assessed (e.g., de Best-Waldhober et al., 2009).

Interactions between the Dimensions of Social Acceptance

Finally, while specific consideration of interactions between the socio-political, market, and community dimensions was beyond the scope of this initial review, it is evidently the case that these three forms of acceptance are often interrelated (Wüstenhagen et al., 2007; Sovacool and Ratan, 2012). As such, a focus of future research should be to develop a better and more comprehensive understanding the nature of these interactions (and implications of thereof) within the context of CO_2 utilisation. For example, one could reflect on how the opinions registered by local stakeholders at the community level (e.g., local authorities, affected publics) might serve to affect more general socio-political level acceptance (e.g., national government) decision making (or vice versa). Similarly, one might investigate how general socio-political acceptance might translate into consumer uptake or rejection of specific CO_2-derived products.

CONCLUSION

Research into the social acceptance of the CO_2 utilisation is currently at an embryonic stage (the first article was published in 2014); however, perceptions of CO_2 utilisation among diverse social stakeholders (e.g., investors, policy-makers, the public) will fundamentally shape the path of CO_2 utilisation technologies and CO_2-derived projects. The aim of the current article was to outline the importance of considering the "social acceptance" of CO_2 utilisation technologies and products, while simultaneously identifying some of the key factors and actors likely to shape this acceptance. We utilised the "triangle of social acceptance" (Wüstenhagen et al., 2007) as a framework for structuring the article in order to help "carve up" this complex and multi-faceted concept into more digestible pieces. Crucially, this review was not designed to be an exhaustive precis and synthesis of *all* of the specific stakeholders and issues that should be considered in this arena, but was rather designed to elucidate the most important players and considerations that should be kept in mind when seeking to broach the subject of social acceptance in the context of CO_2 utilisation.

It is intended that this review and research agenda should form the basis for increased collaborative research between social scientists, pure scientists and engineers around CO_2 utilisation technologies and products; such that development and deployment decisions appropriately recognise and respond to the social context for their introduction (e.g., Jones and Jones, 2016).

AUTHOR CONTRIBUTIONS

All named authors have contributed to all aspects of the writing process, including the initial conception of the review and the drafting and revision of the article. All authors approved the final the version of the article and agreed to be accountable for what it contains.

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Overcoming Barriers to Successfully Commercializing Carbon Dioxide Utilization

*Marvin Kant**

Department of Entrepreneurship and Innovation Management, Technische Universität Berlin, Berlin, Germany

The successful transition to a low-carbon economy hinges on innovative solutions and collaborative action on a global scale. Sustainable entrepreneurship is thereby recognized as a key driver in the creation and transformation of ecologically and socially sustainable economic systems. The purpose of this article is to contribute to this topic by understanding commercialization barriers for strong sustainability-oriented new technology ventures and to derive recommendations to overcome them. A qualitative multilevel approach is applied to identify barriers and drivers within the internal dynamic capabilities of the organization and within the organization's external stakeholders. A model of barriers has been developed based on semi-structured interviews with new carbon dioxide utilization ventures and associated industry players in Canada, the USA, and the European Economic Area. Resulting recommendations to facilitate the (re-)design of a dedicated support system are proposed on four levels: (a) actors, (b) resources, (c) institutional settings, and (d) the coordination of the support system.

Keywords: sustainable entrepreneurship, sustainability transition, barriers to commercial success, CO_2 utilization, new technology venture, commercialization, sustainability-oriented innovation, support system

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University of Sheffield,
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Meng Lu,
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Luca Coscieme,
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****Correspondence:***
Marvin Kant
marvin.kant@tu-berlin.de

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INTRODUCTION

Paris's COP21 (UNFCCC, 2015) and the G7 Summit (G7 Germany, 2015) in 2015 emphasize the need for a transition to a low-carbon economy. Moreover, increasing amounts of money will be invested in clean technologies over the next decades (UNFCCC, 2015), potentially boosting sustainable-oriented innovation. However, effective allocation and support systems to leverage the sustainability transition of entire industries are still relatively unexplored.

In recent years, sustainable entrepreneurship (SE) has been recognized as key in the creation and transformation of ecologically and socially sustainable economic systems (Pacheco et al., 2010) such as a low-carbon economy. Furthermore, SE is identified as an essential driving force in the sustainability-oriented innovation (SOI) process (Jay and Gerard, 2015): the multidirectional sequence of inventing, developing and diffusing new sustainability-oriented technologies and ideas.

This work uses Schaltegger's and Wagner's definition of SE, because it ties SE and SOI together: "Sustainable entrepreneurship is in essence the realization of sustainability[-oriented] innovations aimed at the mass market and providing benefit to the larger part of society" (Schaltegger and Wagner, 2011, p. 225). The following section focuses on SE (realization of SOI) and its role in the sustainability transition (environmental and social benefits to society and market impact).

Literature increasingly deals with SE (cf. Schaefer et al., 2015), and entrepreneurship has been proposed as a solution to environmental problems (York and Venkataraman, 2010). SE identifies market opportunities and addresses market failures by aligning environmental, social, and economic aspects of sustainability (Cohen and Winn, 2007; Hall et al., 2010; Parrish, 2010; Thompson et al., 2011). Elkington (1998) coined this alignment as the "triple bottom line" principle. Porter and Kramer (2011) put Elkington's triple bottom line in a business perspective, arguing that business should deal with society's environmental and social issues such as resource depletion and climate change to create a shared value. The participation of multiple stakeholders and actors in the innovation process is required to create such a shared value. Hence, the involvement of stakeholders outside the organization becomes paramount for SOI and SE (Paech, 2007). This leads to the multilevel perspective on all stakeholder along the innovation value-added chain of this study to realize SOI.

The sustainability-orientation of an innovation determines the provided benefits for society, the environment, and the economy. Scholars often distinguish the degree of sustainability in two to three ascending categories (Klewitz and Hansen, 2014; Jay and Gerard, 2015; Muñoz and Dimov, 2015). The highest degree of sustainability may be achieved by radical (cf. Christensen, 1997) rather than incremental change (Roome, 2012). Therefore, this research focuses particularly on radical innovation which is either "(…) explicitly directed at a sustainability goal" or implicitly adhered to sustainability goals without having sustainability issues as a primary target (Blowfield et al., 2008, p. 2). Thus, strong sustainability-orientation and meaningful impact on sustainability transformation may be attained.

Although large incumbents struggle with radical innovation, incumbents seem key in diffusing sustainability innovations to mass markets because they have the necessary assets at their disposal (Schaltegger and Wagner, 2011) and often directly sell to other businesses (Parker, 2011). Hockerts and Wüstenhagen (2010) investigated the interplay of large incumbents and new technology ventures. Their work on "Greening Goliaths" and "Emerging Davids" describe the necessary interaction to attain sustainability transformations. Therefore, this study focuses on radical new technology ventures and their endeavor to bring sustainability-oriented products/services to the market whilst particularly acknowledging the interaction with external stakeholders such as large industry players.

The radical nature of an innovation is quite often best depicted in hardware-based technologies. The problem with hardware-based technologies is that a proof-of-concept on a technically relevant scale is essential when attracting external resources to sustain business operations and business growth. These proofs of a scale-up production for hardware-based sustainability-oriented technology applications range from demonstrators over pilot production facilities to large commercial plants and are mostly very capital-intensive (Bossink, 2014). Capital intensity, in turn, greatly influence investment risks for sustainability-oriented technologies such as renewable energy (Tietjen et al., 2016).

In this regard, Bürer and Wüstenhagen (2009) (based on Grubb, 2004) refine Murphy's and Edwards' (Murphy and Edwards, 2003) concept of the cash flow valley of death and describe this technology valley of death as the middle phase between publicly funded R&D and self-sustaining funding from (private) partners/customers, where a successful prototype needs to scale-up further to introduce a product/service to the market successfully. When this valley of death is not bridged, sustainability-oriented ventures are lacking and current societal challenges such as resource depletion and climate change are not being tackled through radical innovation.

Carbon dioxide (CO_2) utilization technology ventures typically combine the underlying problem of high capital intensity and the preconditions for a sustainability transition due to a high level of technology radicalness for a strong sustainability-orientation and mass application potential. The author defines CO_2 utilization as innovative approaches to convert CO_2 molecules to other molecules. This definition builds on Styring' and Jansen's (Styring and Jansen, 2011) definition by adding the innovation aspect of not being fully commercialized yet.

The sustainability effect of CO_2 utilization is reflected by the fact that the use of CO_2 as a raw material may not only be a door-opener for large emission abatement technologies but may also be a potent resource efficiency technology because it feeds CO_2 back into the carbon-based economic system (Armstrong and Styring, 2015; Styring et al., 2015; Naims, 2016). Furthermore, CO_2-based products such as CO_2-based fuel are about to reach larger markets (Aresta et al., 2013) and thereby gaining increasingly importance for sustainability transitions.

However, a successful diffusion of a technology in society is crucial to have meaningful SOI (Hall and Clark, 2003; Boons and Lüdeke-Freund, 2013). Hence, this article has a particular focus on the commercialization phase (cf. Pellikka, 2014) and looks at the critical process step between product development and commercialization, as it is at this stage that most sustainable entrepreneurs fail.

Barriers, drivers, and success factors of SE have already been drawn to the center of attraction of business scholars (Bernauer et al., 2007; Walker et al., 2008; Pinkse and Dommisse, 2009; Kennedy et al., 2013; Pinkse and Groot, 2015). Pinkse and Groot (2015), for example, focus on market barriers, namely inefficiency, externalities and imperfect information, identifying SE as a possible way to overcome these barriers. They argue that market barriers, once overcome by entrepreneurs, who are involved in political collective activities via industry associations, can reveal entrepreneurial opportunity (ibid). However, most of these research findings are adding sustainability-specific characteristics to findings from conventional innovation or entrepreneurship studies (Walker et al., 2008; Driessen et al., 2013; Jay and Gerard, 2015).

This article contributes to the literature by addressing the following primary research question: *What are the barriers and drivers for successful commercialization of strong sustainability-oriented new technology ventures?*

The aim of this work is twofold: firstly, to gain a better understanding of the internal and external barriers to the commercial success of new CO_2 utilization technology ventures; and secondly, to use the identified barriers to derive hands-on recommendations to (re-)design a dedicated support system for these technologies. It brings together different research on SE in the light of sustainability transition to illustrate the complex and dynamic process to commercialize new sustainability-oriented technologies. By researching new CO_2 utilization ventures in Canada, the USA, and the European Economic Area (EEA) a broad set of barriers and drivers have been identified. Subsequently, detailed recommendations for strong sustainability-oriented new technology ventures, policy makers, and support providers are derived to facilitate the implementation of strong SOI such as CO_2 utilization.

BARRIER FRAMEWORK METHODOLOGY

Previous research noted that the commercialization process of a small firm has both an internal (e.g., managerial actions and decision making) and an external (e.g., interaction with commercialization environments) dimension of activities (cf. Pellikka, 2014). Especially, the dependency of small firms, such as new technology ventures on external resources, has been recognized (e.g., Oakey, 2007). Pellikka's (Pellikka, 2014) framework of the commercialization process in small high-technology ventures sheds light on the interface between internal and external commercialization dimensions and thus may help to discover how firms can receive these external resources.

Other scholars also acknowledge these internal and external dimensions. Walker et al. (2008), for example, performed a literature review on barriers and drivers of small and medium enterprises to engage in good environmental practice. They point out two perspectives how barriers are perceived: the firm perspective, representing the internal dimension and the government perspective, as one of the main representations of the external dimension (ibid). Acknowledging such of a multilevel perspective can also help to better understand ambiguous findings such as barrier of company A is a driver for company B (Hueske and Guenther, 2015). Hueske and Guenther (2015) propose a barrier framework that enables a more encompassing identification, on different level of analysis, of innovation barriers and draws from theory.

This work builds on a multilevel perspective from current relevant research (Hueske and Guenther, 2015) to investigate all barriers to commercial success. A dynamic capabilities approach (Teece et al., 1997; Eisenhardt and Martin, 2000), in combination with stakeholder theory (Freeman, 2004; Tantalo and Priem, 2016), was chosen to analyze both internal and external barriers that exist alongside the innovation value-added chain. Applying this analysis on multiple levels enables a focus on interactions of barriers within and across the levels of analysis. Furthermore, it acknowledges the specificity of context and thereby allows for a broad set of recommendations (Hueske and Guenther, 2015) and an increased contextual understanding. Both, the organizational and the external level define (cross-)barrier categories and subcategories are set out within the different levels. **Figure 1** pictures the applied barrier framework.

Freeman et al. (2007, 2010) argue that stakeholders have competing goals when creating value that need to be addressed by managerial trade-off decision making. In contrast to Freeman's mind-set, the stakeholder synergy approach addresses how value can be created simultaneously for stakeholder groups that are essential for a firm (Tantalo and Priem, 2016). This approach helps to identify value creation opportunities both within and across relevant stakeholder groups (ibid). Seven key stakeholder groups can be observed: (1) investors, (2) future employees, (3) partners and suppliers in research, engineering and manufacturing, (4) competitors, (5) customers, (6) governments, and (7) society (Hueske and Guenther, 2015).

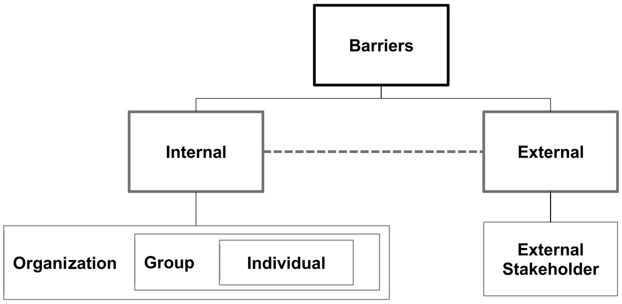


FIGURE 1 | Applied barrier framework (adapted from Hueske and Guenther, 2015).

Dynamic capabilities may be used to create new resource configuration and update the competitive position of an organization. Furthermore, dynamic capabilities include processes such as collaboration and product development that may turn resources into value-creating strategies (Eisenhardt and Martin, 2000).

An explorative qualitative interview study was used to investigate the new CO_2 utilization venture landscape worldwide. This research approach is suitable for early stage research such as SE in CO_2 utilization (Silverman, 2013). Furthermore, the approach was chosen to enable the enfoldment of existing theory by analyzing capability-driven, internal barriers and stakeholder-driven, external barriers (Eisenhardt, 1989).

The empirical setting is carefully chosen and looks specifically on the EEA, Canada, and the USA. This choice was made to exclude too much variation due to differences between industries.

SAMPLE AND DATA COLLECTION

The author choses a theory-based purposeful sampling approach to identify and select information-rich interviews (Palinkas et al., 2015; Patton, 2015). Experienced and knowledgeable individuals, which were available and willing to participate, have been identified to make an effective use of limited research resources (Palinkas et al., 2015). New CO_2 utilization ventures were identified globally via (1) the author's participation at several events (such as conferences and workshops) with a CO_2 utilization theme and (2) an extensive online desk research on past conferences, privately and publicly funded projects/programmes/prizes, and aggregated news platforms. A population of $N = 48$ existing new CO_2 utilization venture companies (as of October 2015) were identified with a great concentration in the EEA, Canada, and the USA.

Smit et al. (2014) divide carbon utilization into four sections: enhanced oil recovery, CO_2 to chemicals, CO_2 to fuels, and incorporating CO_2 into construction and building material. This categorization is based on the output of the various CO_2 utilization technologies (Peters et al., 2011; see also Styring and Jansen, 2011; Hendriks et al., 2013). The author of this work adapted the categorization by application class of CO_2 utilization technologies, but included only those categories that are in line with the CO_2 utilization definition of this paper. Incorporating CO_2 into construction and building material is mainly carried out by mineralization of CO_2. Hence, the population and sample were divided into CO_2 to chemicals, CO_2 to fuels, or CO_2 mineralization.

Typically, these categories contain various technologies that address different industry sectors:

- CO_2 mineralization turns CO_2, minerals, and industrial waste mainly into aggregates or fillers for the building industry (Styring et al., 2015).
- CO_2 to chemicals primarily cover applications such as intermediates, specialty chemicals or precursors such as polyols for the plastic production (ibid).
- CO_2 to fuels include primary power-to-x technologies. Power-to-x processes—in the context of CO_2 utilization—use electricity to transform CO_2 into liquid or gaseous fuels, e.g., for the transportation sector or as seasonal storage for the energy market (ibid).

Other possible transformation pathways of power-to-x are chemicals with more complex molecular structure such as pharmaceuticals (ibid). Hence, also a hybrid category of "CO_2 to chemicals" and "CO_2 to fuels" is possible. The use of micro-organisms is another method to convert CO_2 into fuels and/or chemicals (Styring and Jansen, 2011).

Within the population of $N = 48$ companies, 19 initial interviews were conducted with 18 different ventures. The geographical distribution and the shares within the categories of the identified CO_2 utilization ventures of the population were well reflected in the sample (cf. **Figure 2**). The interviewees' position ranged from CEOs, CTOs, and CFOs to R&D managers, business developers, and operations and sales persons. Most of the interviewees were intentionally the (co-)founders of the company because they potentially have the best overview of the company and can share in-depth insight into business operations and strategies. 30- to 80-min (Ø 45 min) interviews were conducted face-to-face and/or via telecommunication between October 2015 and April 2016. In addition to the initial 19 interviews, two more interviews with new CO_2 utilization ventures were conducted in July and November 2016, adding up to $n = 20$ companies with a total of 900 min of recording time. This enabled further insights and the ability to test propositions derived from previous interviews. All interviews were semistructured and a semiopen questionnaire was adapted from interview studies on similar technology fields (e.g., Matus et al., 2012). The semiopenness allowed for an ongoing adjustment of the questionnaire in the course of the interview series; in combination with the sequenced interview process over several months, interviews were carried out until no new phenomenon were discovered and therefore theoretical saturation was reached (Strauss and Corbin, 2015). In addition, a ranking of perceived

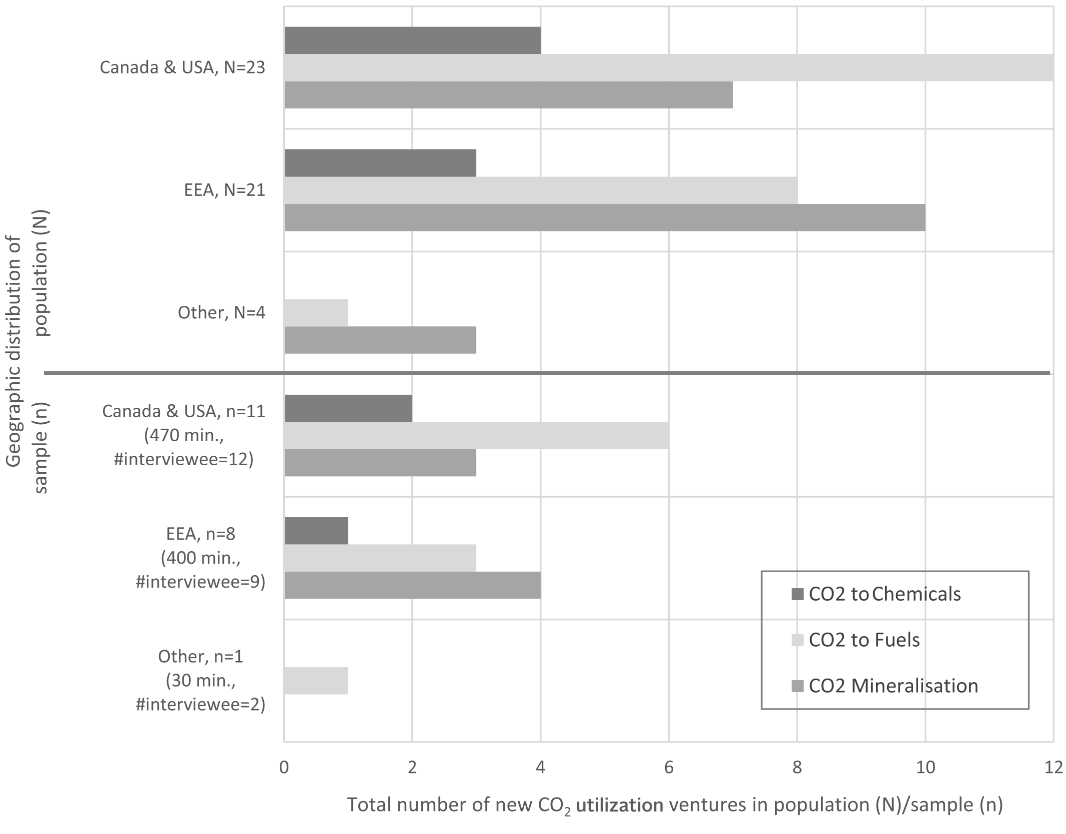


FIGURE 2 | Overview of the identified population and sample.

success factor categories, which were identified in the literature, was carried out in twelve interviews. All initial interviews were recorded, transcribed, and send to the respective interviewee for validation prior to the anonymized data analysis process. The study was carried out in accordance with the German law. No ethics approval was required for this type of research as per German laws and regulations. In compliance with these laws and regulations, oral informed consent was obtained from all research participants. Their answers were anonymized and it is not possible to link the statements back to individual subjects. **Figure 2** provides further aggregated information about the sample on the ordinate.

To enhance contextual understanding, additional data sources such as publicly available reports were used to triangulate the venture's positions (proposition testing). Furthermore, during the data collection process four interviews with a steel producer, utility, infrastructure provider, and chemical company were conducted in the EEA to give a broader perspective from additional stakeholders. These four interviews with five interviewees were surveyed over a total of 140 min.

DATA ANALYSIS

Data were analyzed using the software Atlas.ti 7 (ATLAS.ti, 2016). An open and axial coding process (Strauss and Corbin, 2015) was performed to extract internal and external commercialization barriers and increase the reliability of the analysis. Following the coding process, codes of each code family were manually extracted. The codes were further aggregated and duplicates were removed. This extraction revealed cross-family and cross-level occurrences of barriers and contextualized the data from the interview by comparing institutional settings and company types: the EEA vs. Canada and the USA, and large incumbents vs. new technology ventures. **Table 1** states an exemplary overview of the data analysis process.

RESULTS

A qualitative multilevel model on the internal and external barriers to successful commercialization has been developed based on the families from the coding process (cf. **Figure 3**). External barrier categories focus on the external stakeholders of the value-added chain of SOI and the internal categories reflect the sustainability-oriented venture itself. External stakeholder are public and private investors, future employees, partners in R&D and manufacturing, competitors, customers, governments, and society. The internal organization is divided into strategy, size and structure, and resources of the organization. Resources can be further broken down into infrastructural, technological and financial resources, knowledge and networks, and management and team in terms of social and human capital. Furthermore, a third main category was derived from the analysis, because of the reoccurring nature of three barrier categories at the immediate interface of internal and external barriers: promoter, location, and risk. They are referred to as cross-linkage barriers.

The following part provides an overview of the barriers of each category and their main drivers. Moreover, it indicates cross-barrier relationships across the three main categories: external, internal and cross-linkage barriers and compares the predominant institutional settings and company types.

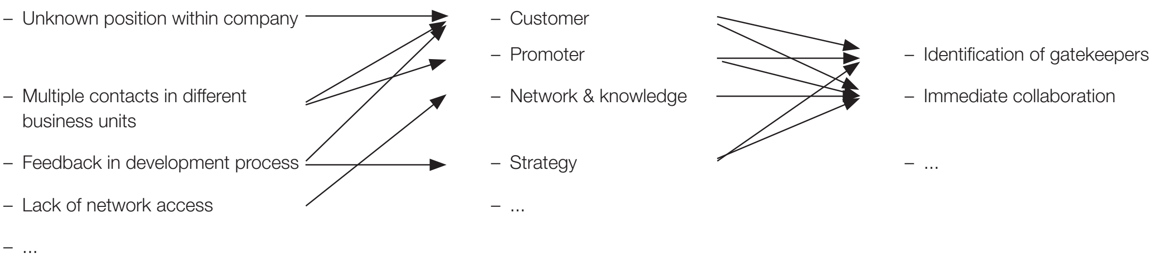
All barriers and drivers in this section are extracted from the underlying data of the qualitative research, unless stated otherwise. They represent the individual perception of the new CO_2 utilization ventures and industry player.

External Stakeholder

New CO_2 utilization ventures encounter various commercialization barriers in their external environment (cf. **Table 2**). This environment is mainly determined by investors, future employees, partners in R&D and manufacturing, competitors, customers, governments, and society.

TABLE 1 | Exemplary overview of the data analysis process (adapted from Hahn and Ince, 2016).

Data analysis process →		
Open coding process:	*Axial coding process:*	*Extraction process:*
Transcripts are coded with different phenomena related to barriers and drivers	Codes are aggregated into structured theory-based code families; first relations within and across barrier family are revealed	Extraction and further condensation within the families, and identification of core barrier categories with drivers and cross-barrier relations
Iteration	⇄	
Results: Coded phenomena	Results: Barrier categories	Results: Barrier model with cross-barrier linkages
Example:	Example:	Example:
– Unknown position within company – Multiple contacts in different business units – Feedback in development process – Lack of network access – ...	– Customer – Promoter – Network & knowledge – Strategy – ...	– Identification of gatekeepers – Immediate collaboration – ...



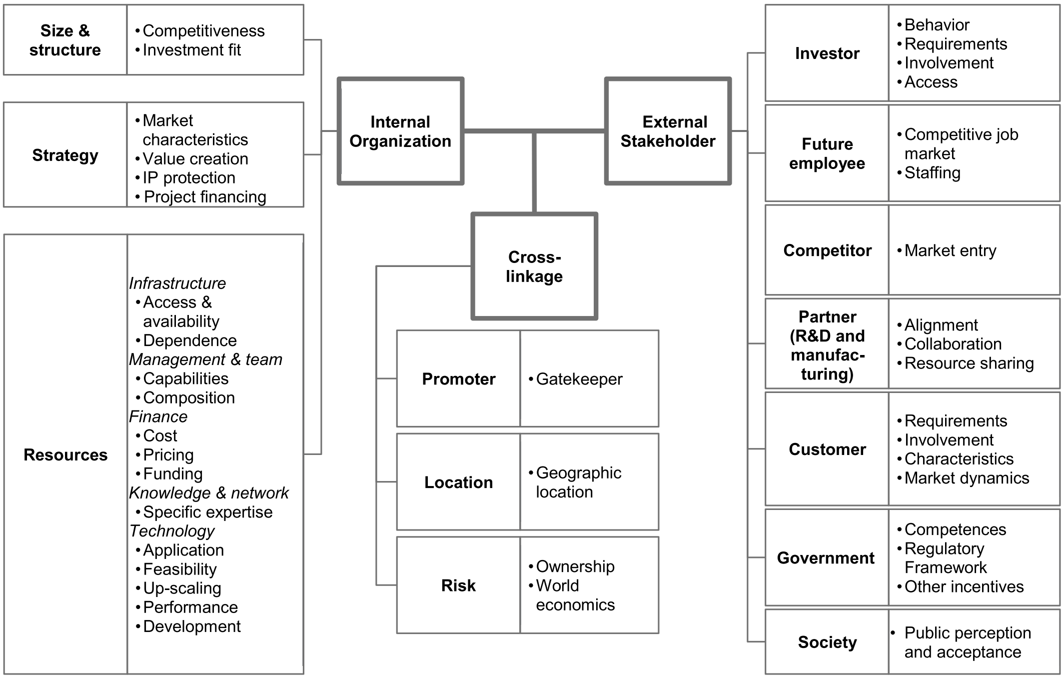


FIGURE 3 | Multilevel barrier model.

Barriers when dealing with investors in the field of CO_2 utilization fall within investment behavior, requirements dilemma, operational and strategic involvement, and in access to investments. The risk taking of investors is not much different to other hardware-based technology investments. However, uncertainties in regulations, the preference for asset-backed investments, and the fact that there is often yet no market with a minimum assurance were reported to discourage the risk affinity for CO_2 utilization further. In addition, study participants stated that the clean tech sector still suffers from a loss of reputation due to investment decisions during the mid-2000s: institutional investors without suitable sector-specific experience invested heavily into clean energy technologies (e.g., Rai et al., 2015) contributing to poor financial returns between 2000 and 2010 (e.g., Bygrave et al., 2014).

These experiences led to a set of requirements that put new technology ventures to the test. A proof-of-concept on an industrial scale (actual system prototype or proven technology in its final form) is often mandatory and existing agreements with off-takers/customers are required as described by the interviewees.

Moreover, the degree of an investor's involvement can result in a trade-off decision: the investor may bring crucial market and management expertise but might also curtail the new venture's freedom and fail to acknowledge its expertise as reported differently by the study participants. Either way, the interviewees highlighted that institutional investors are necessary to scale-up and grow. Hence, access to these investments were noted to be of upmost importance and new CO_2 utilization ventures stated to often lack the network to gain that investment access.

Barriers in the context of future employees are competitive job markets and the staffing process. Job markets like any other market are influenced by world economics. Especially the oil market developments pre and post the 2000s were pointed out to have shaped the availability of technical personal in the USA and also in Europe. In general, the risk affinity of future employees and thereby the willingness to work in a firm with a high probability to fail is claimed to be low. New CO_2 utilization ventures also began to strategize and move to certain locations to get access to greater talent pools. Close ties to university can facilitate the staffing process. However, there is also a trade-off between proximity for partnerships and recruitment. Overall, fluctuation in the management, and the internal development of necessary skillsets and the organizational fit of future employees were described to remain challenging.

Additional barriers related to external stakeholders concern partners in R&D and manufacturing. The partner's alignment with new CO_2 utilization ventures emerges as a barrier, when it comes to the strategy for a technology development that takes at least 3–5 years and the motivation that depends on the position within the value chain. Furthermore, there are proclaimed challenges in collaboration and resource sharing (knowledge transfer and infrastructure). New CO_2 utilization ventures need to assess and identify potential partnerships to engage in a collaboration. The roles of partner, however, are not necessarily easy to define, the coordination of partnerships is resource intensive and the matchmaking process requires the presence of extensive networks as described by the interviewee. Nevertheless, outsourcing strategies and approaches

TABLE 2 | Overview of external stakeholder barriers and drivers.

Category	Barrier	Driver
Investor	Investment behavior	Past investments Risk taking
	Set of requirements	Proof-of-concept Existing agreements
	Involvement[a]	Decision making[a] Management
	Access	Network Staged project financing
Future employee	Competitive job market	Market development Risk taking Geographical location
	Staffing	Skillset and organizational fit Fluctuation in management Close tie to university
Partner	Alignment[a]	Strategy alignment Motivational alignment[a]
	Collaboration[a]	Consortium coordination Identification and division of potential roles Partnership assessment Matchmaking[a] Outsourcing Ecosystem and joint projects
	Resource sharing (knowledge transfer and infrastructure)	Market and industry intelligence transfer Infrastructure provision (availability and access) IP portfolio Management experience Testing capabilities
Competitor	Market entry	Lock out Scale effect Subsidization
Customer	Proof of concept	Quantity and quality of the sample Offtake agreements Multiple risk profiles Risk/burden sharing
	Problem acknowledgment and solution understanding	Early customer involvement in the development process
	Specific characteristics[a]	Compliance to industry requirements: – Ownership model – Investment inability – Intrinsic motivation to lower carbon footprint[a]
	Global market dynamics[a] and policy intervention	Decentralized energy production Carbon market
Government	Competences	Lack of foresight Responsibility
	Regulatory framework	Translation Harmonization Sovereignty Complexity Volatility Market perversion
	Other incentives[a]	General sponsorship[a] Long-term strategies
Society	Public perception and acceptance[a]	Marketing strategies[a] Educational programmes

[a] *Perceived main barrier reported.*

to build entire synergetic ecosystems with crucial value chain stakeholders involved were identified as attempts to overcome shortcomings in resources. Knowledge transfer—by means of market and industry intelligence, and management expertise—and the provision of infrastructure, offer opportunities for building up intellectual property (IP) portfolios and testing capabilities under real life conditions, but were recognized as very challenging to establish.

The competitor category reveals market entry barriers in form of lock out, subsidization and scale effects. New CO_2 utilization ventures claim to face threats of being locked out of the market by competitors temporarily lowering prices for commoditized products. Such entry deterrence strategies of large incumbents in high volume markets with little product margins are reported to require significant price advantages of new technology ventures over current prices to be competitive. Furthermore, inconsistencies within the subsidization of renewable energy or fossil fuels directly influence competing technologies when certain technologies are favored (e.g., Victor, 2009; Hope et al., 2015) or exemptions for certain companies are made [e.g., the special equalization scheme under the renewable energy sources act in Germany (§§ 63 ff. Erneuerbare-Energien-Gesetz—EEG 2017)]. Aside from these subsidies, scale effects cater for low costs of mature technologies such as fossil-based productions as described by the interviewees.

During the interaction with customers new CO_2 utilization ventures encounter barriers regarding a proof-of-concept, the participation of potential customers, specific customer characteristics, and global market dynamics. A proof-of-concept in form of a pilot production facility with a high quality of product samples is mandatory for most potential customers to sign any kind of offtake agreement; this in turn is often necessary for investors as recurrently pointed out by the study participants. However, risk profiles of customers are reported to vary depending on the position within the value chain (e.g., 1/10 of scale for several months vs. full scale for several years). Moreover, new CO_2 utilization ventures can share customers' risks by issue commissioning warranties. A financial challenge yet remains: either as a proof-of-concept or as the backing of warranties. Furthermore, customer's problems need to be acknowledged and the solutions need to be understood from both, the customer and the new CO_2 utilization venture as pointed out by the participants. To do so, an early participation and specific customer characteristics are identified drivers that must be addressed. New CO_2 utilization ventures have experienced challenges in complying with industry requirements such as ownership models, investment abilities, and customers' intrinsic motivations to lower the environmental impact. Policy intervention and market dynamics were described to further influence these specific characteristics and to be potential barriers in themselves. Overall there is little perceived willingness to pay a premium for environmentally and socially superior products in the field of CO_2 utilization: Only one out of 14 interviewees sees a general willingness to pay a premium for carbon-based products; one interviewee does not know and 12 interviewee see no or very limited willingness of a small fraction of customers to pay premium prices.

Further barriers that are related to governments are in the categories competences, regulation, and other incentives. In terms of competences, the study participants claim that there is a lack of foresight and most regulation is based on current rather than novel technologies. Moreover, responsibilities are often not clearly defined and passed on between different authorities (e.g., between the different Directorate-Generals of the European Union). With respect to regulatory frameworks translation, harmonization, and sovereignty is often an issue for rolling-out CO_2 utilization technologies globally. Regulation frameworks are perceived as too complex, volatile, and can even create market perversion, e.g., by encouraging the generation of more and more energy rather than focusing on a more efficient use (e.g., via storage). The barriers for funding applications are noted to be considerable for small companies and thereby limit the funding access. Other incentives like a general sponsorship for the implementation of CO_2 utilization technologies are underrepresented and long-term strategies and global agendas for CO_2 utilization were identified as still missing by the interviewees.

When it comes to society, the main barrier is public perception and acceptance. There is a perceived negative misconception of CO_2, especially when new CO_2 utilization ventures are connected to the emitting industries. Dedicated marketing strategies and education programmes are identified as widely missing.

Internal Organization

New CO_2 utilization ventures experience also barriers within their organization (cf. **Table 3**). These barrier categories range

TABLE 3 | Overview of internal organization barriers and drivers.

Category		**Barrier**	**Driver**
Size and structure		Competitiveness	Pricing capabilities Scale effects Regulatory complexity Multiple roles
		Investment fit	Understanding investment rationale
Strategy		Market characteristics	Application focus Market entry strategy
		Added value	Targeting strategy for value chain Balancing R&D relevance and marketability Value capture Build on and acknowledge existing competencies
		IP protection	Rigid patenting strategy
		Project financing	Staged project approach
Resources	Knowledge and networks	Specific expertise	Management and market expertise Access to extensive network
	Management and team	Capabilities	Adaptation abilities
		Management composition	Set-up and fluctuation
	Infrastructure	Access and availability	Modification capabilities Outsourcing capabilities In-house R&D infrastructure External infrastructure
		Dependence	Centralized production systems Influx of required inputs
	Finance	Cost	Capital expenditure for proof-of-concept and testing Scaling capabilities Location dependency of input costs
		Pricing	Capabilities to compete on price
		Funding[a]	Location dependency of funding availability[a] Fundraising capabilities
	Technology	Application[a]	Technology platform Application determinants[a] Adaptability to input sources
		Feasibility	Testing and sampling compliance
		Up-scaling	Proof-of-concept expertise
		Performance	Compliance to industry requirement Product superiority
		Technology development	Customer involvement Duration

[a] *Perceived main barrier reported.*

from size and structure over strategy to resources. Like other new technology ventures, CO_2 utilization ventures encounter challenges because of their size. The competitiveness is affected by capabilities to compete on market prices and even below-market (dumping) prices as reported by the study participants. Moreover, scale effects such as the fossil industry built up over decades, complex regulatory framework, and limitations to take on multiple roles simultaneously such as investor, owner, manufacturer, and operator influence the perceived competitiveness even further. The internal structure of new CO_2 utilization ventures greatly influence the decision making of investors. An understanding of the investment rationale is noted to enhance the chances of survival and future growth.

Strategy-related barriers relate to market characteristics, value creation, IP protection, and project financing. The market entry strategy must meet the specific market requirements and characteristics. Hence, a focus on the technological application is observed to be necessary. Opportunities may arise when focusing on bridging applications to decarbonize the transportation sector or to store energy. New CO_2 utilization ventures need to target customers that are at a particular stage in the value chain, even though their technology can have different outlets for different value chain positions. Moreover, they need to balance relevance in R&D and marketability of their technology and need to decide on how much value they want to capture and how to acknowledge and build on the existing competencies of their potential customers as reported by the interviewees. When approaching a customer, study participants noted that challenges regarding the IP arise. A rigid patenting strategy might help to facilitate immediate interaction, but is also very capital intensive as pointed out by the interviewees. Having a sound strategy to finance and to implement collaborative projects holds further perceived hurdles that may be driven by staged project approaches.

Internal barriers in the resource domain are grouped into knowledge and networks, management and team, infrastructure, finance, and technology. New CO_2 utilization ventures encounter challenges to obtain certain expertise such as management and market expertise, and application know-how. They often report to lack access to networks to build-up knowledge and approach key persons for innovation processes in external organizations, so-called gatekeepers (Allen, 1970). Within the management and team category, capabilities such as adaptation abilities for dynamic team settings and changing environments and the management composition were reported by the study participants to hinder successful commercialization.

Furthermore, infrastructure availability and dependence on existing infrastructure cause perceived internal challenges. In this regard, modifying existing equipment or using external facilities to rapidly deploy new technologies was described as greatly beneficial. However, compliance requirements from customers to build-up R&D facilities internally and the access to external infrastructure hinders the development of new CO_2 utilization ventures. Moreover, centralized production systems with established infrastructure and the upkeep of an influx of required inputs such as CO_2 and energy apply further pressure on these ventures.

Financial barriers are reflected by costs, pricing, and funding. The capital costs for proofs-of-concepts and other testing actions are noticed as very high in the field of CO_2 utilization. In addition, new CO_2 utilization ventures report to be often incapable of either scaling down at capital expenditure rates that would enable technological applications (see economies of scale) or building the facilities large enough to make the capital expenditure feasible, because raw materials are not available in sufficient quantities. Furthermore, their pricing capabilities are limited and they are unable to compete on under-market (dumping) prices. Funding opportunities and cost or availability of inputs such as CO_2 and energy were stated to vary from one geographic location to another (see also Hendriks et al., 2013). Moreover, it is the experience of CO_2 utilization ventures that the availability of funding sources is limited and that the exploitation of these sources is also challenging in terms of administration.

The last categories of internal barriers are of technological nature. They are related to application, feasibility, up-scaling, performance and technology development. Some new CO_2 utilization ventures in the sample use platform technologies and therefore have a broad range of possible technological applications. This application range was identified by interviewees to bring challenges; research expertise and experience often determine the focus on an initial product rather than marketability or other market drivers. The study participants observed that new CO_2 utilization ventures need to focus on a market driven applications whilst ensuring a maximized flexibility to adapt to different CO_2 sources such as diluted or concentrated and large or small CO_2 sources. Furthermore, when showing the feasibility of their CO_2-based products and processes they must comply with time and resource-intensive testing and sampling requirements (e.g., life-cycle assessments, large simulations or pretests under real life conditions) of potential customers. Moreover, to get to a so-called proof-of-concept new CO_2 utilization ventures have to up-scale their lab-scale processes over demonstrators to pilot plants. In the light of experiences from the participants, this up-scaling requires extensive engineering expertise and necessary capital.

A poor performance of CO_2-based products can hinder a successful commercialization as well. Industry requirements such as the reported high level of reliability of power plant operations must be acknowledged. The willingness to pay a premium for CO_2-based products was highlighted as very limited, hence, the interviewees conveyed product performance needs to be superior to be competitive. Developing CO_2-based products takes time, especially when involving other stakeholders in the development process, coordination, and feedback loops (e.g., external evaluation rounds). These stages were reported to be time consuming and very challenging.

Cross-Linkage

The third main category of the identified barriers is referred to as cross-linkage barriers (cf. **Table 4**). Barriers in this category can relate to both, internal and external barriers. They are re-occurring connecting elements within the commercialization process and are grouped into three sub-categories: location, risk, and promoter.

TABLE 4 | Overview of cross-linkage barriers and drivers.

Category	Barrier	Driver
Location	Geographical location[a]	Incentives and des-incentives[a] Proximity to portfolio venture Possibilities for joint ventures Market existence for exit
Risk	Ownership	Asset ownership Risk/burden sharing
	World economics	Decentralized energy production Economic crisis
Promoter	Gatekeeper[a]	Identification and conviction[a]

[a]*Perceived main barrier reported.*

New CO_2 utilization ventures face various challenges in terms of the geographic location. The location does not only determine incentives and des-incentives such as regional or national regulation and funding opportunities, but it also feeds into the requirements for partnerships: the proximity to portfolio venture, the possibilities for joint ventures, and the existence of markets for a potential exit depend on the location of a collaboration as study participants have reported.

When it comes to risk, the barriers are ownership and world economics. Owning capital-intensive assets is described to be too risky for most new CO_2 utilization ventures, whereas the interviewees stated large industry players often own too many assets to take risks. Furthermore, the perceived risk averseness of their potential customers (and investors) can corner them into additional risk taking via warranty agreements. Global market developments and dynamics such as the economic crisis and the shift of the energy sector toward decentralized energy production were found to create further uncertainties and hinder long time commitments of several stakeholders.

Promoters are individuals that actively and intensively support the innovation process (cf. Witte, 1973) and thus are playing an important role in the commercialization process of CO_2 utilization. However, they are most of the times noted to be absent and identifying and convincing gatekeepers at any stakeholder organization was recognized as considerably challenging. New CO_2 utilization ventures reported that they face multiple organizational levels approaching large companies and find it difficult to identify key contacts. Hence, not only the identification but also the advocacy for a collaboration represent main barriers for these ventures. However, promoters for CO_2 utilization do already exit internally within the founding and management teams of new technology ventures and externally among investors, partners and governments. Examples of this highlighted by the study participants include:

- Founders of new CO_2 utilization ventures can have proven entrepreneurial skillsets and vast industry knowledge and networks from previous work experiences to enable the access to investors and potential customers and partner. Moreover, they cannot only bring specific know-how, but also have intrinsic sustainability-oriented motivation from previous experiences and see CO_2 as (market) opportunity.
- Effective technology and market knowledge transfer can also be performed by investors and partners. Moreover, investors and universities can provide R&D infrastructure or universities can grant access to extensive IP portfolios and talent pools.
- Manufacturing partners can manufacture to the specific requirements of new CO_2 utilization ventures. Existing expertise and equipment allows for a quicker project implementation, bigger scale-up, and more value capture by being able to offer turnkey solutions.
- Government can administer sponsorship for new CO_2 utilization ventures. This sponsorship may cover different forms, from R&D funding schemes, to dedicated knowledge transfer and infrastructure programmes.

Cross-Barrier Relations and Comparisons

The study results do not only identify the internal, external and cross-linkage barriers of new CO_2 utilization ventures, but also indicate the (perceived) relevance of the barrier categories. Cross-barrier relations were discovered first, by triangulating the reported barriers of new CO_2 utilization ventures with the reported barriers of the four industry players (steel producer, utility, infrastructure provider, and chemical company). Second, by comparing two geographic location, representing two different institutional settings: Canada, the USA, and the EEA. Third, by considering ties between internal, external, and cross-linkage barriers. Fourth, by having four categories of success factor (Song et al., 2008) ranked by the new CO_2 utilization ventures. Lastly, by comparing the sample on an application class level.

Barriers in the categories customer, partner, technology, government, finance, infrastructure, and strategy were reported the most by both new technology ventures and large incumbents, whereas there was less reporting in the categories society, risk, and knowledge and network. Differences were mainly in the categories investor and competitor, and promoter and team and management. The industry players reported more barriers in the first two categories, while the new ventures reported more in the latter two. **Figure 4** gives a graphical overview of this data triangulation by plotting the relative reported barrier categories of the industry players against the relative reported barrier categories of new ventures.

Comparing the two regions, the reported barrier categories are primarily similar. However, the categories risk and society were more often reported in the EAA and the categories team and management, investor, competitor, knowledge and network and future employee more often in Canada and the USA (cf. **Figure 5**). **Figure 5** shows the relative reported barrier categories with regard to the two observed regions. Categories that are closer to the ordinate (EEA) than to the abscissa (Canada and the USA) indicate a higher importance/relevance in the EEA and vice versa. The closer a category is to the bisector, the less distinct its importance/relevance for one region is.

The amount of cross-barrier relationships between the three main categories are also depicted in **Figures 4** and **5**. The external categories customer, investor, government, partner; the internal categories strategy and all resource subcategories; and the cross-linkage categories promoter and location have the most links with ties to more than 50% of the other main categories.

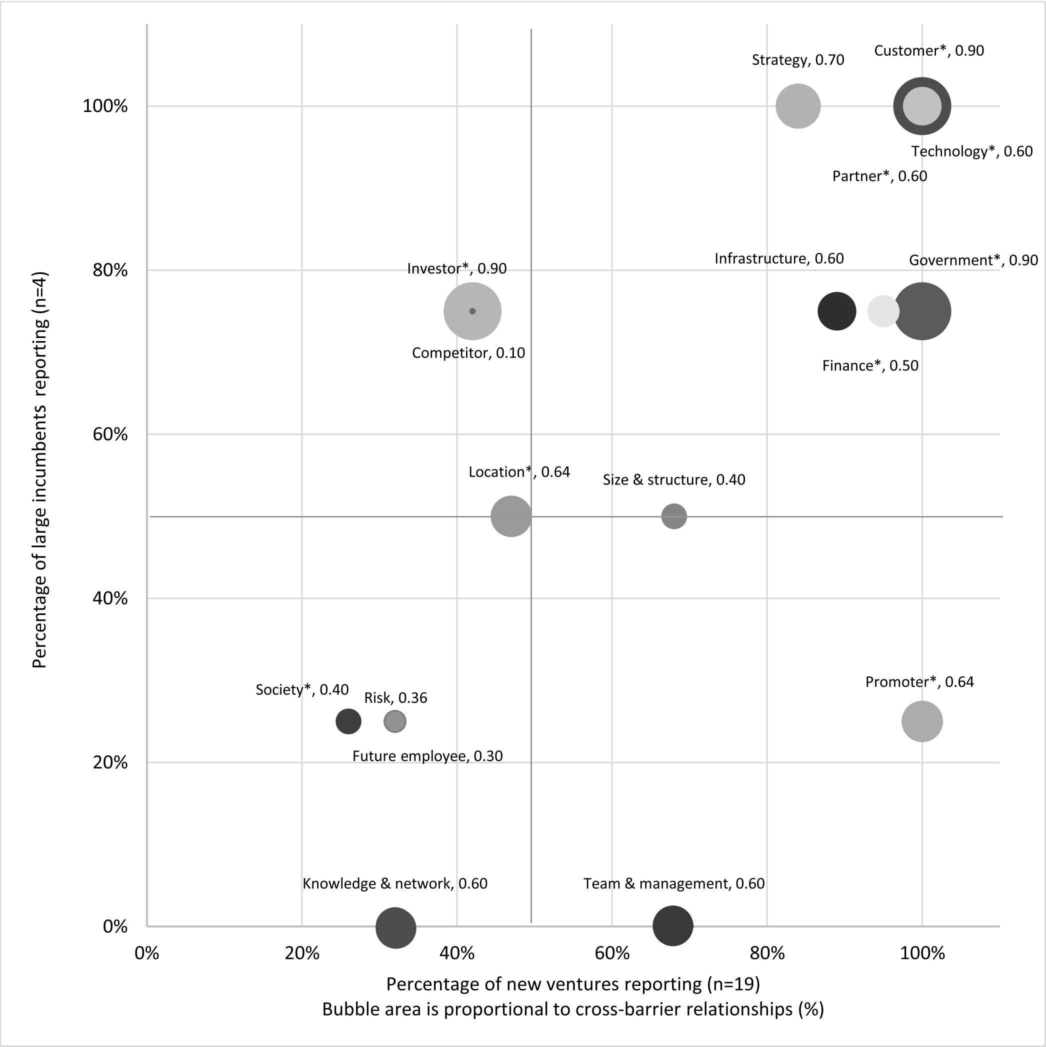


FIGURE 4 | Reported barrier category matrix: new ventures vs. incumbents. *Perceived main barrier reported in category.

The emphasis on main barriers has been captured by coding terms such as "challenge," "hurdle," "issue," "barrier," or "problematic" in combination with "main," "biggest," or "most." These perceived main barriers are in the categories partner, customer, investor, government, society, promoter, location, finance, and technology (cf. **Tables 2–4**). Moreover, the perceived main barrier categories cover those barrier categories that have been reported by all new CO_2 utilization ventures in the sample and include those barrier categories that have the most cross-barrier relationships (cf. **Figures 4** and **5**). However, the perceived main barrier category society is only reported by the minority of new CO_2 utilization ventures in the sample and has little relationships to other barrier categories.

Figure 6 reveals the ranking of success factor categories. Thus, market and opportunity are the highest ranked categories followed by team, resources, and strategic and organizational fit. The ranking slightly changes when breaking it down to the two geographic locations. For Canada and the USA, the entrepreneurial opportunity is on the same rank as entrepreneurial team.

Other comparisons can be made between the different application classes. For this matter the application class CO_2 to fuels was further broken down, when a new CO_2 utilization venture aimed at technological outlets in CO_2 to fuels and CO_2 to chemicals. These ventures often pursue platform technologies that allow for the conversion of CO_2 to synthetic fuels and other more complex chemicals such as pharmaceuticals. **Table 5** shows differences and relations of technology readiness level (TRL) and application classes. CO_2 mineralization has the highest technological maturity, on average, followed by CO_2 to fuels, and CO_2 to chemicals.

Pursuing multiple application classes CO_2 to fuels and CO_2 to chemicals seem to impact the TRL. In most of these cases the venture has not decided on a business model or initial product yet. This is also depicted in the lowest averaged venture age of 4.8 years in this application class.

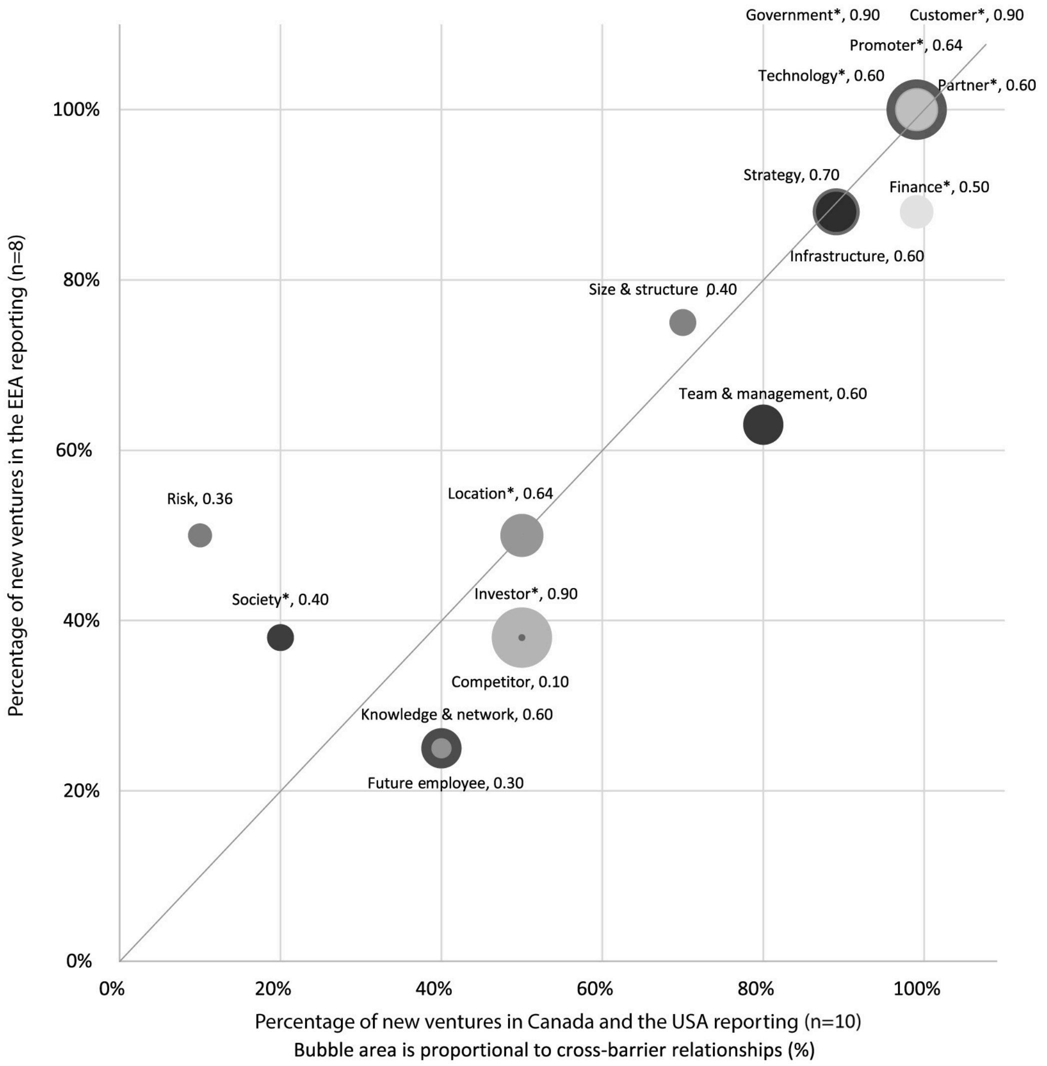


FIGURE 5 | Reported barrier category matrix: Canada and USA vs. EEA. *Perceived main barrier reported in category.

On average, the CO_2 mineralization class has the highest TRL but less capital has been attracted and fewer employees are working in this field than in the CO_2 to fuels class.

Overall, the evaluation via various comparisons of the observed barrier phenomena remains challenging because of the qualitative nature of this study. However, the results at least indicate different levels of relevance. **Figures 4–6** and **Table 5** thereby provide an effective way to highlight these indications.

DISCUSSION

For all the identified barrier categories, the interviewees provided several barriers and drivers. However, some categories have been reported more frequently than others and may be contextualized with Song et al.'s (Song et al., 2008) ranking:

> Song et al.'s (ibid) market and opportunity factors are mainly determined by the external environment of new CO_2 utilization ventures. Hence, the proportion of reported barriers in the external categories as well as the emphasis on them are consistent and indicate the relevance of these categories. Song et al.'s interpretation of entrepreneurial team is best reflected in the internal barrier categories of team and management and knowledge and networks. Both seem especially relevant in Canada and the USA (cf. **Figure 4**). This fact is also being backed by the higher ranking of entrepreneurial team in this region (cf. **Figure 6**). Although, the resource-related categories cannot be clearly distinct from Song et al.'s entrepreneurial resources: Whereas factors such as financial resources are clearly related to the financial barrier category, patent protection and supply chain integration are more related to the strategy category. However, both internal categories (finance and strategy) seem to be of high relevance as well as technology and infrastructure. The less prominently ranked strategic and organizational fit would be best connected to the internal size and structure category. Even though cross-linkage barriers cannot being clearly related

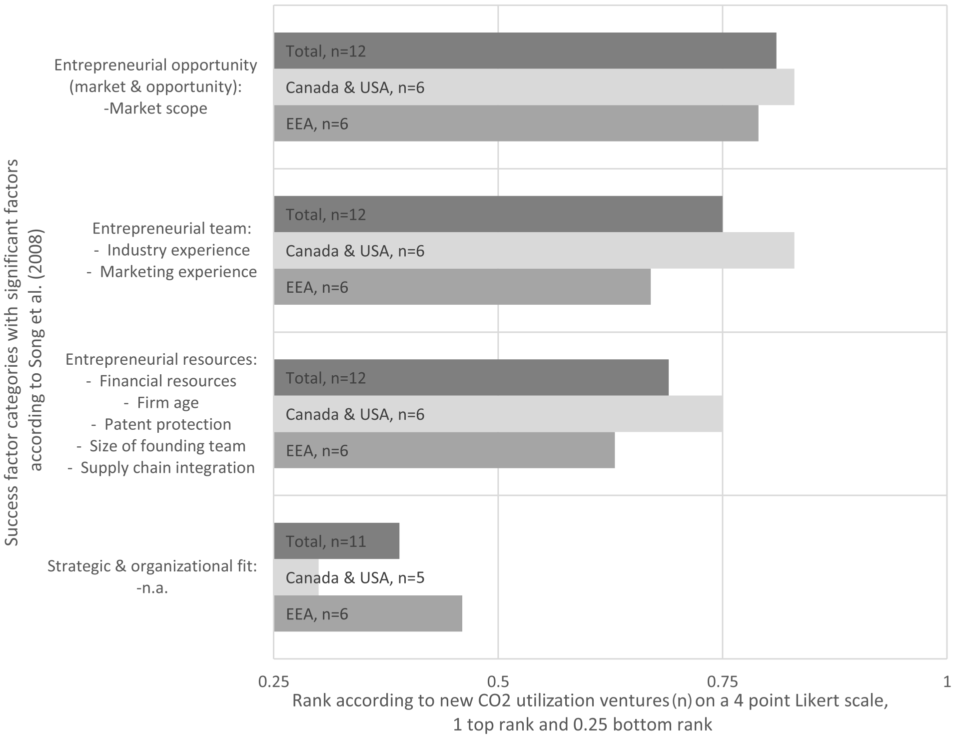


FIGURE 6 | Success factor ranking according to Song et al. (2008).

TABLE 5 | Overview of sample comparison.

Application class	TRL of lead process (interview)	Capital attracted (in mUSD)	# employees	Venture age in 2015 (in years)	Years in company (average, if more than one interviewee; as of 2015)
CO_2 to chemicals	2–3	n.a.	4	3	3
CO_2 to chemicals	4–5[a]	n.a.	n.a.	4	0.5
CO_2 to chemicals	7–8[a]	50	30	11	2.5
Average CO_2 to chemicals	4–5	50	17	6	2
CO_2 mineralization	3–4	n.a.	n.a.	5	5
CO_2 mineralization	3–4	0.16	2	6	6
CO_2 mineralization	6–8	5	10	3	3
CO_2 mineralization	7	30	9	15	10
CO_2 mineralization	7–8[a]	n.a.	n.a.	6	6
CO_2 mineralization	8–9	130	75	10	5
CO_2 mineralization	8–9[a]	n.a.	n.a.	7	7
Average CO_2 mineralization	6–7	40	24	7.4	6
CO_2 to fuels	4–5	200	130	8	3
CO_2 to fuels	4–5	1.6	5	6	4
CO_2 to fuels	5	n.a.	12	4	4
CO_2 to fuels	5–6	20	14	13	13
CO_2 to fuels	9	12	20	6	6
Average CO_2 to fuels	5–6	58	36	7.4	6
CO_2 to fuels, CO_2 to chemicals	3–4	14	13	5	5
CO_2 to fuels, CO_2 to chemicals	4	5	7	1	1
CO_2 to fuels, CO_2 to chemicals	5	1	5	6	6
CO_2 to fuels, CO_2 to chemicals	5–6	200	140	10	10
CO_2 to fuels, CO_2 to chemicals	5–6	n.a.	10	2	2
Average CO_2 to fuels, CO_2 to chemicals	4–5	55	35	4.8	3.6
Average CO_2 to fuels+	5–6	57	36	6.1	4.8
Average total	**4–5**	**53**	**30.4**	**6.55**	**4.8**
Standard deviation (of the sample)	**n.a.**	**74.3**	**44.4**	**3.7**	**2.9**

[a] *Retained from third party information.*

to Song et al.'s success factors, location and promoter seem to play a mediating role.

A support system in the context of entrepreneurship is defined as a system that "[…] comprises all actors, institutional settings and resources that help entrepreneurs in innovating successfully" (Fichter et al., 2016).

The barriers of new CO_2 utilization ventures relate to their stakeholders or actors (perceived main categories: partner, customer, and investor), their internal organization including resources (perceived main categories: finance, strategies, and technology), specific contextual settings such as institutional settings (perceived main categories: government and society), and relational settings (perceived main categories: promoter and location). Hence, the concept of a coordinated, dedicated support systems could be applied to provide effective leverage for a sustainability transformation of industries (Fichter et al., 2013).

Capital-Intensity: Collaboration, Compliance, and Alignment (Actors)

The capital intensity is paramount in CO_2 utilization technologies. New CO_2 utilization ventures need to proof their technology in costly demonstrators and pilot plants. Shared infrastructure and cost-efficient business models have been recognized to be of help in overcoming capital challenges for these kind of technologies (Cleantech Incubation Europe, 2014). New CO_2 utilization ventures that invest primarily in people and not in bricks may be better able to adapt an organizational structure that comply with conventional requirements of institutional investor such as investment volumes.

Furthermore, there is a need for an immediate collaboration to enhance knowledge transfer and facilitate learning for new CO_2 utilization ventures. Regional collaborative alliances with multiple stakeholder alongside the CO_2 value chain from CO_2 emission, capture, and utilization to the consumption of CO_2-based products are wanted. Entire partnership systems could bring together (local) stakeholder to create specific business opportunities for CO_2 utilization.

However, new CO_2 utilization ventures also seem to lack the effective coordination of these approaches. Intermediating third parties (cf. van Lente et al., 2003; Altenburg and Pegels, 2012; Kivimaa, 2014) could ensure motivational and strategic alignment of different partners and coordinate the collaboration. Furthermore, these parties could help to overcome the (causality) dilemma where both, potential off-taker and investor, require a proof-of-concept and existing contracts by mediating between the different actors.

Disruptive Nature of Radical CO_2 Utilization Innovation: Product Performance and Staged Project Approaches (Resources)

New CO_2 utilization ventures face challenges when approaching conservative industries with radical solutions. The potentially disruptive nature of these solutions (Christensen, 1997) may be the reason for a restraining behavior of customers, investors, and other partners (cf. Gauthier and Gilomen, 2016).

Large incumbents do not only hesitate when developing sustainability-oriented solutions themselves (cf. Ihlen and Roper, 2014), but also are often reluctant to establish new facilities for a CO_2-based production. Building-up a new production can be disruptive for established companies, whereas retrofitting an existing production line is rather sustaining for them.

These different innovation natures may also be represented in the sample: an application class with a higher TRL and, at the same time, fewer capital attracted than another class could indicate that, e.g., capital efficient retrofitting approaches are more prominent in the first class (cf. **Table 5**: CO_2 mineralization vs. CO_2 to fuels). However, differences in TRL, attracted capital and number of employees could also be explained by different technology requirements (e.g., exothermic vs. endothermic) or market conditions (e.g., resource availability).

Beside the disruptive or sustaining nature, the degree of the sustainability-orientation of an innovation seems to influence the commercial success of new CO_2 utilization ventures. Hockerts and Wüstenhagen (2010) identified two dimensions of entrepreneurial activity that can lead to a sustainability transition of an industry: environmental and social performance, and market share. Hörisch (2015) builds on these dimensions and argues that sustainability-oriented new technology ventures need to master a coordinated interplay between sustainability effect and market impact to meaningfully contribute to sustainability transitions.

However, the findings of this study show that these dimensions tend to have a negative effect upon each other. An optimum CO_2 reduction is often not economically viable and market impact is achieved at the expense of the sustainability effect.

Consequently, new CO_2 utilization ventures need to initially focus on the product's performance (economic value creation) rather than on its sole sustainability aspect (ecological and social value creation) to successfully commercialize their products in competitive mass markets. This focus may diminish the strong sustainability-orientation by emphasizing innovation which does not have sustainability as a primary target, but even products or materials with very high sustainability effect could be positioned as more durable, robust, or cheaper (cf. Driessen et al., 2013) to attain greater market impact.

Nevertheless, staged approaches such as a staged market entry strategy (cf. Clay, 2013) could help to target niche markets with a high sustainability effect and move toward mass markets with increased economies of scale and knowledge about industry requirements. Trade-offs between sustainability dimensions may thereby be avoided.

However, some technologies cannot be economically viable on a niche-market scale. That is why an early application focus in consideration of the market circumstances is crucial. Platform technologies with various application options might help to diversify and dynamically adapt to new market developments, but the choice often overburdens new CO_2 utilization ventures. Staged project strategies can help to generate initial revenue and get a better understanding of customers by starting with advisory projects on a potential CO_2 utilization implementation.

Dependencies, Policy Interventions, and Public Perception: Dedicated Long-term Support and Marketing Strategies (Institutional Settings)

The acknowledgment of regulatory systems and institutional settings are essential for CO_2 utilization and shape support systems for entrepreneurship (Fichter et al., 2013). In this work two geographic regions with different institutional settings have been looked at: Canada and the USA and the EEA. However, there were more similarities than differences. Whereas risk averseness and societal acceptance seemed to play a bigger role in the EEA, institutional investors, human capital and knowledge transfer seemed to be more prominent in Canada and the USA.

The public perception of CO_2 utilization influence new technology ventures. Even though only the minority of the new CO_2 utilization ventures reported barriers in the society category, social acceptance has been recognized as a necessity for a successful commercialization of SOI such as CO_2 utilization (Jones et al., 2017). Dedicated marketing strategies enable these ventures to counteract the misperception of CO_2 utilization, especially in the EEA (cf. van Heek et al., 2017).

Policy interventions and regulatory pressure might be another way to overcome barriers (Jaffe and Palmer, 1997; Brunnermeier and Cohen, 2003; Parker et al., 2009; Kneller and Manderson, 2012) but represent dependency on rather short-term mechanism. Interventions such as feed-in tariffs for renewable energy technologies affect institutional investors in clean technologies (cf. Bürer and Wüstenhagen, 2009; Ghosh and Nanda, 2010). Due to the larger number of private investments in the clean technology sector in Canada and the USA than in the EEA, a different importance of institutional investors might be attributed to the two institutional settings.

CO_2-based products can substitute fossil-based products, however, the technologies for the substitution are often not yet economically viable without evolving production systems or new regulations (Bocken et al., 2014). Some of these CO_2 utilization technologies currently need excess energy from renewable energy production. This dependency of current inefficiencies in the distribution systems of renewable energies can lead to a shorten vision as interim solutions.

However, clear responsibilities within existing regulatory frameworks and less complexity could already reduce barriers regardless of the institutional setting and the time horizon.

Cross-Linkage Barriers: Tailor-Made Solutions and Local Facilitation (Coordination)

The cross-linkage barrier categories of promoter and location especially stress the relevance of context and mediation for new CO_2 utilization ventures.

Not only proximity aspects when dealing with external stakeholders (for investments: cf. Knight, 2012; for partnerships: cf. Hansen, 2014) and location-dependent (des-)incentives, but also the technological diversity within CO_2 utilization call for a dynamic adoption to the specific needs of a new CO_2 utilization venture. Hence, tailored support solutions for individual technological and geographic context are needed (see also Fichter et al., 2016).

The promoter model is a recognized concept to overcome innovation barriers (Gemünden et al., 2007). In this work, gatekeepers are key people in any commercialization process of an external organization whereas promoters are key to drive a specific innovation on different levels (Hauschildt and Schewe, 2000).

With regard to the four person promoter model (Gemünden et al., 2007), the identified promoters in CO_2 utilization are mainly power and expert promoters. Process and relationship promoters remain mainly unidentified or are missing. This is especially reflected in the challenge to identify and engage with gatekeepers outside the new CO_2 utilization venture's organization.

An intermediating third party could step in to facilitate the matching process and act as relationship promoter (ibid).

Limitations and Future Research

The population size was determined by the fact that CO_2 utilization is a relatively new and emerging field. The population of new CO_2 utilization ventures was identified with little under 50 worldwide and the companies within the sample are on average 6.5 years old (cf. **Table 5**). The sample size made a full comparison of the application classes challenging and led to a lack of contrasting juxtaposition within the classes.

Additionally, comparisons between different conversion processes such as catalysis, artificial photosynthesis, photocatalysis, and electrochemical reduction (cf. Styring and Jansen, 2011) for the same product and different sustainable business models such as create value from waste or substitute with renewables and natural processes (cf. Bocken et al., 2014) are missing.

Comparisons of top management and operating staff within a single new CO_2 utilization venture to view the phenomena from different perspectives (Eisenhardt and Graebner, 2007) were rarely performed, because of the limited amount of knowledgeable people (cf. Palinkas et al., 2015) for this study. From the 23 interviewees, nine had not been with the company since its start, accounting for an average of being 4.8 years with the venture (cf. **Table 5**). Therefore, internal barriers have been aggregated to the organizational level only.

Although theoretical saturation was reached in the course of this analysis, future research should look at sustainability-oriented organizations in their growth phase in-depth to identify differences in the individual, group and organizational level (cf. Hueske and Guenther, 2015). Such an in-depth analysis could also enrich data on the social dimension of sustainability, that is currently underrepresented due to the predominant focus on the technology development of most of the investigated new technology ventures.

In addition, qualitative comparisons could shed light on the differences in location and output- and process-based categorizations of new CO_2 utilization ventures and longitudinal studies on sustainability-oriented ventures could contribute to a better understanding of success and failure factors of strong sustainability-oriented new technology ventures.

Furthermore, case studies on system intermediaries for the sustainability transition and their role in supporting these new ventures could help to further shape effective support mechanism.

CONCLUSION

Theoretical Implications

This work brings together SE, sustainability transition and barriers to successful commercialize radical SOI. These radical SOI show increased complexity when compared to conventional innovation. Multidimensional (economic, environment, and social) focal points such as the coordinated interplay of sustainability effect and market impact (cf. Hörisch, 2015) or the problem of "double externalities" (cf. Beise and Rennings, 2005) and an extended external orientation toward more diverse stakeholders (including society or partnership ecosystems), e.g., to overcome resource constraints, to bring novel technology to the market or to share risks (cf. Jay and Gerard, 2015) differentiate the commercialization process of strong sustainability-oriented new technology ventures from conventional new technology ventures. Hence, this study supports the notion of describing radical SOI processes by adding sustainability-specific characteristics to conventional innovation processes (cf. Walker et al., 2008; Driessen et al., 2013; Jay and Gerard, 2015).

An internal and external barrier framework (Hueske and Guenther, 2015) has been applied and further developed for strong sustainability-oriented new technology ventures based on a qualitative interview study with 24 new ventures and large incumbents in CO_2 utilization. A new cross-linkage barrier category has been added to the main barrier categories to highlight the relevance of connections between internal and external barriers. This category contributes to a better understanding of the importance of context for strong SOI such as CO_2 utilization.

Stakeholder synergies and the creation of shared values (cf. Tantalo and Priem, 2016) are experienced throughout the barrier analysis but especially in the partner category where entire stakeholder ecosystems drive the successful commercialization of CO_2 utilization. Hence, stakeholder synergies (Tantalo and Priem, 2016) rather than stakeholder theory (Freeman et al., 2007, 2010) could be supported by strong sustainability-oriented new technology ventures for external barriers.

Value-creating strategies through collaboration also occur internally with external interactions (Eisenhardt and Martin, 2000). Organizational learning (cf. Teece et al., 1997) is represented foremost as driver in expertise gain in the knowledge and network category. Thus, dynamic capabilities seem appropriate for internal barriers of strong sustainability-oriented new technology ventures.

Both, synergies and learnings can be facilitated by cross-linking promoters that can reveal gatekeepers and mediate between stakeholder groups (cf. Hauschildt and Schewe, 2000). In combination with the proximity dimension (Knight, 2012; Hansen, 2014) these intermediaries can lay the groundwork for local new venture support systems paving the way for multilevel perspectives on the entire system of strong SOI such as CO_2 utilization (cf. Geels, 2011).

Strategies and Recommendation

Recommendations for a dedicated support system are derived from a commercial barrier analysis of new CO_2 utilization ventures in the institutional settings of Canada and the USA, and the EEA. There are four levels of recommendations for strong sustainability-oriented new technology ventures, policy makers, and support providers: on (a) actors, (b) resources, (c) institutional settings, and (d) the coordination of a support system.

a. Strong sustainability-oriented new technology ventures and other actors from the entire value adding path of CO_2 utilization (e.g., from CO_2 and energy supplier, R&D and upscaling partners to off-taker/customers) should take part in partnership ecosystems that are aligned and facilitated by intermediating third parties to exploit synergies such as increased value capture and knowledge transfer. Policy makers can encourage these ecosystems by providing necessary resources and means to pursue fruitful collaborations.
b. Strong sustainability-oriented new technology ventures should foster their focus on the CO_2-based product's performance, for example, by managing platform technologies and facilitate staged project approaches such as staged market entry strategies.
c. Policy makers should pursue in sponsorship for CO_2 utilization such as regulatory frameworks with clear responsibilities and little complexity, for example, to ease access to funding opportunities and encourage internationalization for strong sustainability-oriented new technology ventures.
d. Intermediaries should coordinate support systems, for example, to identify gatekeepers, spark collaboration by aligning strategies and motivations and enable support providers to tailor support solutions to the specific needs of a new CO_2 utilization venture in a given environment.

AUTHOR CONTRIBUTIONS

MK: main/single author, main contribution to the conception and execution of the work.

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Edited and reviewed by:
Katy Armstrong,
University of Sheffield,
United Kingdom

***Correspondence:**
Marvin Kant
marvin.kant@tu-berlin.de

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*Marvin Kant**

Department of Entrepreneurship and Innovation Management, Technische Universität Berlin, Berlin, Germany

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A corrigendum on

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There was a mistake in the title of the x axis of **Figure 5** as published (the sample size [n] was incorrect). The correct title of the x axis of **Figure 5** is: "Percentage of new ventures in Canada and the USA reporting ($n = 10$)." The author apologizes for the mistake. This error does not change the scientific conclusions of the article in any way.

The original article has been updated.

Conflict of Interest Statement: The author declares that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

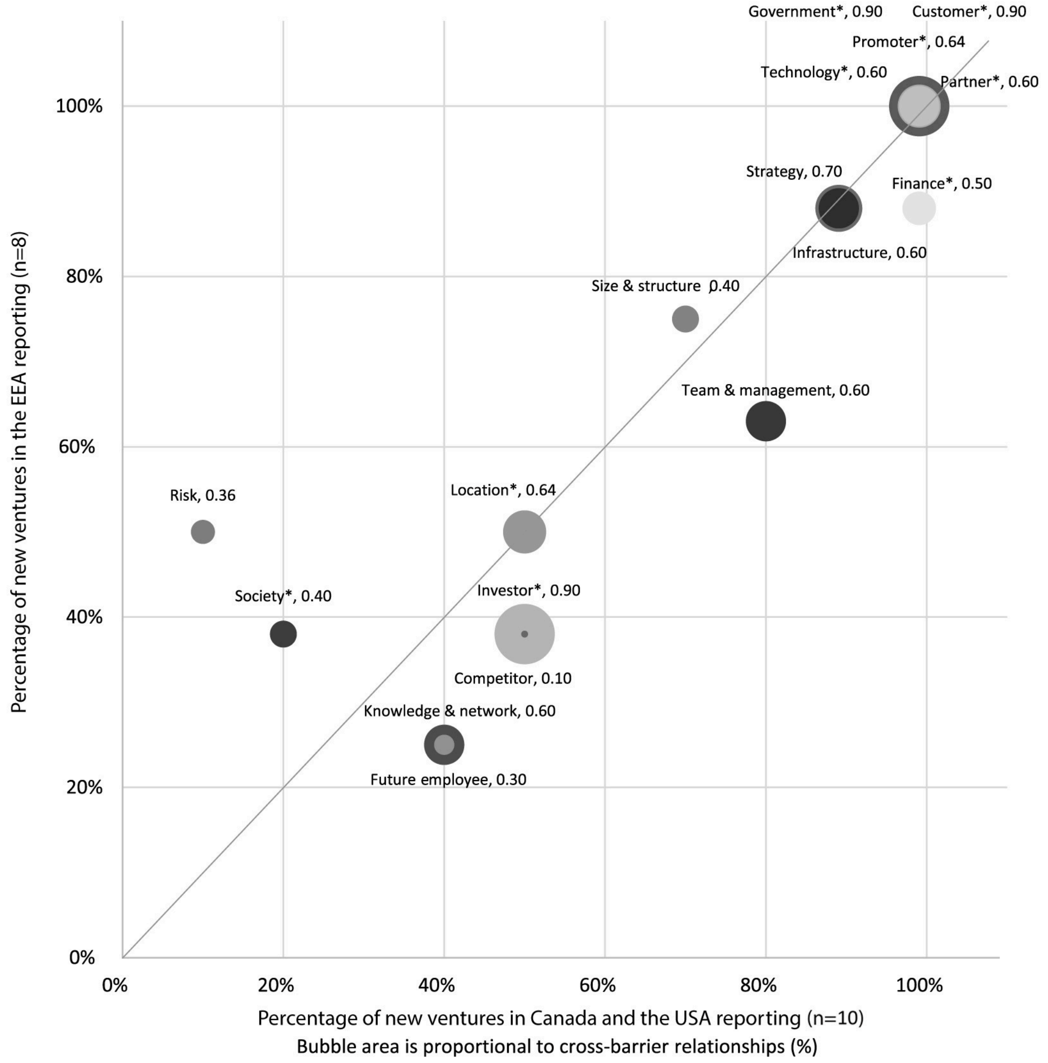

FIGURE 5 | Reported barrier category matrix: Canada and USA vs. EEA. *Perceived main barrier reported in category.

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