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Integrated waste biorefineries: Achieving sustainable development goals, 2nd Edition

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Integrated waste biorefineries: Achieving sustainable development goals, 2nd Edition

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Editorial: Integrated waste biorefineries: achieving sustainable development goals

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Editorial on the Research Topic
Integrated waste biorefineries: achieving sustainable development goals

Introduction

The Sustainable Development Goals (SDGs) established by the United Nations provide a comprehensive framework for a brighter tomorrow, encompassing crucial aspects such as renewable energy, clean water and sanitation, and responsible consumption. However, accomplishing these goals requires dedicated efforts over an extended period. An innovative and effective solution to waste management and energy issues is the emergence of waste biorefineries. These advanced systems not only provide sustainable waste management and energy solutions, but they also have the potential to reduce poverty and hunger while supporting global economic growth initiatives.

As our world faces critical environmental concerns, such as climate change and serious health issues, a major shift in our production and consumption paradigms seems inevitable. One solution to achieve that would be extending waste-oriented biorefineries, converting waste into energy, power, and useful products in a circular economy context. In light of the

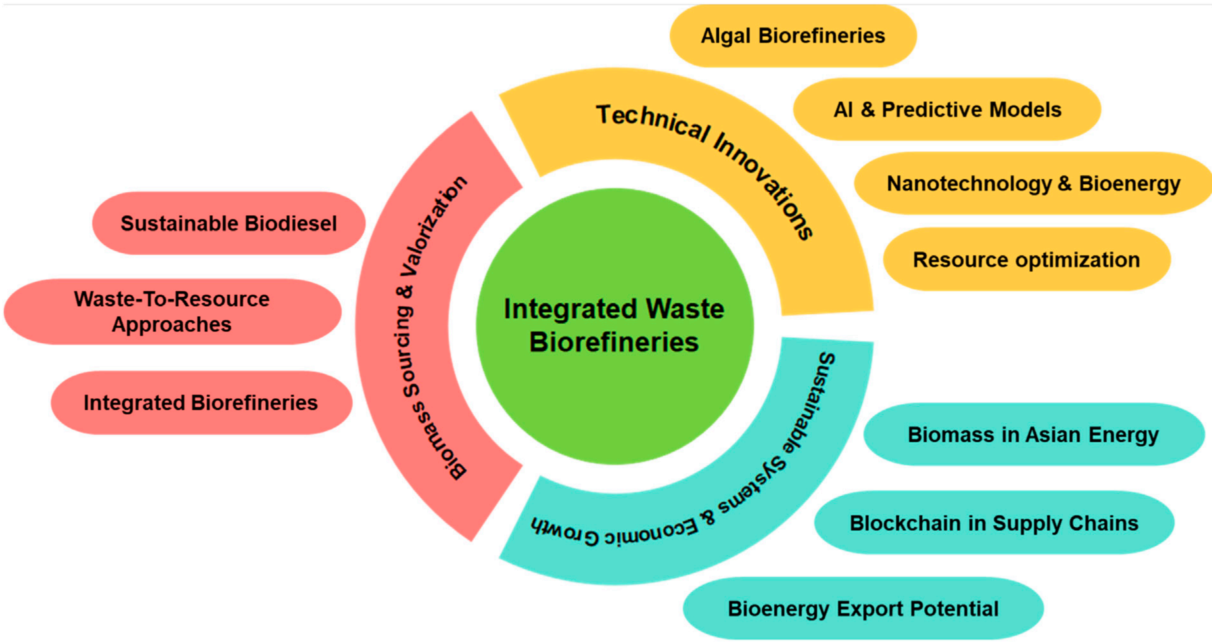

FIGURE 1
Categorization of articles in this Research Topic.

above, this Research Topic focuses on the role of waste biorefineries in meeting the SDGs, where respected scientists share their insights on waste biorefineries' status, advancements, and prospects. Through their contributions, readers can explore how these innovative systems can play a vital role in achieving SDGs, tackling pressing environmental and health issues, and creating a better future. The accepted articles in this Research Topic are categorized under the sections of (1) Technological innovations and advancements in biorefineries, (2) Biomass sourcing, characterization, and valorization, and (3) Sustainable systems, economic growth, and policy implications based on the relevancy of their Research Topic and aims (Figure 1).

Technological innovations and advancements in biorefineries

In today's world, technology has become essential in driving progress and achieving a sustainable future, especially in the biorefinery industry. Combining scientific research and innovation creates a more environmentally friendly and efficient energy landscape, which tackles current challenges and prepares for future requirements. Following are the 4 articles published under this subsection and their details.

The article by Nagi et al. highlights the untapped potential of microalgae as a platform for developing algae-based biorefineries. Microalgae present an environmentally friendly alternative to traditional fuels, but several challenges hinder their large-scale production, including nutrient requirements and water costs. The study emphasizes the necessity for coupling biofuel production with high-value or mid-value products, highlighting the industries' shift towards utilizing algae by-products in cosmetics, nutraceuticals, and animal feed. The review comprehensively analyses the status, challenges, and prospects of cost-effective microalgae biomass production. It also emphasizes the potential for valorizing high-value co-products to advance microalgal biofuel commercialization. This work aligns with "SDG 7: Affordable and Clean Energy", and "SDG 13: Climate Action", as the authors emphasize on the use of renewable energy sources and thereby reducing greenhouse gas emissions.

The research conducted by Ayub et al. emphasizes the high potential of alternative renewable fuels, particularly biomass, for electricity generation as a sustainable substitute for fossil fuels. It reveals an innovative Artificial Neural Network (ANN) model to forecast crucial process parameters for the integrated biomass gasification power plant: gasification temperature and air-to-fuel ratio. Using data from thermodynamic equilibrium model simulations across 86 different biomass feedstocks, this ANN model stands out for its impressive accuracy, reflected in an MSE score of 1,497 and a test R of 0.9976. Notably, this research offers a powerful tool for enhancing power generation efficiency and productivity of biomass gasification.

Khan et al. examined the role of nanotechnology in enhancing biogas yield from various wastes in bioenergy production. The study investigates the impact of diverse nano-additives on anaerobic digestion, from metal oxides to carbon-based nanomaterials. Based on a bibliometric analysis of 14,000 articles, it has been revealed that there has been a surge in biogas research over the last decade. Nanomaterials have revolutionized methane production and waste treatment. However, the environmental challenges of nanomaterial disposal post-process are also noted, emphasizing the need for further advancements before broad industrial application.

The potential to increase lactic acid (LA) yields from food waste fermentation was investigated by incorporating nitrogen as NH_4Cl

or digestate and augmenting with sucrose. The research by Bühlmann et al. demonstrates that while NH_4Cl and digestate boost LA formation rates, NH_4Cl also advances the final LA concentration. Crucially, introducing sucrose amplified the LA concentration and promoted desired *Lactobacillus* growth, suppressing undesired microbial communities. This shows that biorefineries can benefit by using digestate as a nutrient and sucrose as a carbon source, improving the feasibility of lactic acid-anaerobic digestion biorefinery models.

Biomass sourcing, characterization, and valorization

Biomass is a renewable resource that is crucial to our future energy needs. By improving our understanding of its sources, refining its characterization, and maximizing its value, we can move closer to a more sustainable energy paradigm that minimizes waste and prioritizes efficiency. Following are the 3 articles published under this subsection and their details.

Bukhari et al. delved into the potential of Dodonaea plant oil as a biodiesel source, a tropical shrub known for its high-fat content. Transesterification and esterification reactions were performed at 60°C for 70 min using a 1:6 M oil-to-alcohol ratio, resulting in a 90% biodiesel yield. The fuel characteristics of the derived biodiesel were promising when evaluated against the ASTM standards. Dodonaea presents an excellent non-edible source for biodiesel production. Its cultivation on marginal lands ensures a consistent feedstock for the bioenergy sector. Thoroughly monitoring its production quality highlights Dodonaea's potential for large-scale biodiesel commercialization.

Kopperi and Mohan examined a novel approach to an algal-biorefinery system that combines dairy wastewater treatment, hydrothermal liquefaction (HTL) of defatted algal biomass, and acidogenic processes in a closed-loop system. The study used Coelestrella sp SVMIICT5 microalgae and achieved 87% wastewater treatment, along with notable biomass growth of 3.2 g/L of DCW. After extraction, the HTL process optimized the algal residue to produce an impressive 52% bio-crude yield, which holds potential for jet fuel production. Dark fermentation of the resulting HTL stream led to significant bio-hydrogen generation. This innovative research highlighted the potential of integrating biological and thermochemical processes in developing sustainable biorefineries. The work stresses the potential benefits of algal-biorefinery using the non-arable land and wastewater recycling, which contributes to the "SDG 6: Clean Water and Sanitation" as well as "SDG 15: Life on Land".

Qian et al. proposed blending alkaline black liquor, a biomass pretreatment by-product, directly with polyvinyl alcohol (PVA). This unique combination resulted in composite films that showcased outstanding UV-shielding and enhanced physical properties. Adding 3.0% of alkaline BL to the PVA reduced the film's UV transmittance to below 20%, boasting physical strengths surpassing films derived from commercial alkaline lignin. This method minimizes environmental impact and promotes biomass efficiency by eliminating costly lignin extraction, marking a step towards zero-waste biorefinery.

Sustainable systems, economic growth, and policy implications

Sustainability, economy, and policy are the major factors in global energy. Our energy future depends on understanding the connections between these different elements. Following are the 3 articles published under this subsection and their details.

Considering growing environmental concerns and resource depletion, researchers are delving into the transformative potential of blockchain technology for sustainable supply chain management. The study by Munir et al. systematically assesses blockchain's contribution to sustainability in supply chains across economic, environmental, and social dimensions, using 136 articles. The study highlighted blockchain's potential to improve economic sustainability through its traceability, transparency, and decentralization features. Blockchain can support sustainable supply chains, but its strategic significance is unclear. Developed nations have adopted it, but developing countries lag. Regulatory interventions are needed to promote green practices. Future studies should merge blockchain with big data IoT and consider the learnings from COVID-19. By the adoption of sustainable technologies and best practices, such as blockchain in the supply chain is crucial for achieving environmental and social sustainability aligns with SDGs such as "SDG 9: Industry, Innovation, and Infrastructure", "SDG 12: Responsible Consumption and Production", and "SDG 17: Partnerships for the Goals".

Biomass has historically been a primary source of cooking and heating in Asia, especially in countries like Bangladesh, China, India, Mongolia, Nepal, Pakistan, Sri Lanka, and Laos. However, traditional cookstoves (TCS) emit harmful substances like CO_2 and $PM_{2.5}$, leading to various health risks and showcasing low thermal efficiency. The review by Ahmad et al. synthesizes the fragmented information on biomass cookstoves in the mentioned Asian countries, highlighting the improved thermal efficiency and reduced emissions of improved biomass cookstoves (ICS). Although China leads to ICS adoption, financial constraints, lack of awareness, and infrastructural challenges are notable barriers across Asia. To address the issue, future interventions should prioritize the development of efficient and affordable stoves while promoting their use through targeted workshops, collaborations, and regular quality evaluations.

Ayub et al. explore bioenergy production and export potential in biomass-rich countries using the Product Space Model (PSM). Key findings highlight Pakistan's abundant biomass resources, with canola oil, leather flesh wastes, and poultry fattening showing the highest income potential. In contrast, goat manure and cashew nutshell presented lower income potential, suggesting their optimal use within local energy generation plants. According to a study, the U.S. is a major producer of sophisticated biowaste products. The study recommends that countries like Pakistan and Argentina broaden their export offerings by concentrating on underutilized products closely associated with their current exports. The potential for diversification is higher in the US, China, and India. The study demonstrates how biomass-rich nations can attain sustainable economic growth via optimized bioenergy production and export strategies.

Outlook

As we strive to overcome the global crises, the importance of integrated solutions like waste biorefineries for sustainability becomes clearer. These systems represent ideal opportunities within the circular economy by transforming waste into valuable resources. Moving forward, we must synchronize technological progress with evolving policies and changing economies. Need to raise public awareness about the potential benefits and applications to ensure the sustainability of biorefineries. Future research is required to explore the integration of biofuel systems with industrial commodities production to achieve economically sustainable outcomes. The application of blockchain technology in the supply chain should be further investigated to enhance environmental and social sustainability. Finally, emphasizing collaboration, informed decisions, and continual innovation will create a sustainable legacy for future generations.

Author contributions

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Integration of Algal Biofuels With Bioremediation Coupled Industrial Commodities Towards Cost-Effectiveness

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Microalgae offer a great potential to contribute significantly as renewable fuels and documented as a promising platform for algae-based bio refineries. They provide solutions to mitigate the environmental concerns posed by conventional fuel sources; however, the production of microalgal biofuels in large scale production system encounters few technical challenges. High quantity of nutrients requirements and water cost constrain the scaling up microalgal biomass to large scale commercial production. Crop protection against biomass losses due to grazers or pathogens is another stumbling block in microalgal field cultivation. With our existing technologies, unless coupled with high-value or mid-value products, algal biofuel cannot reach the economic target. Many microalgal industries that started targeting biofuel in the last decade had now adopted parallel business plans focusing on algae by-products application as cosmetic supplements, nutraceuticals, oils, natural color, and animal feed. This review provides the current status and proposes a framework for key supply demand, challenges for cost-effective and sustainable use of water and nutrient. Emphasis is placed on the future industrial market status of value added by products of microalgal biomass. The cost factor for biorefinery process development needs to be addressed before its potential to be exploited for various value-added products with algal biofuel.

Keywords: biofuels, biorefinery, grazers, microalgae, integrated pest management

INTRODUCTION

The development of renewable energy resources has become a priority due to climate change and dwindling fossil fuel reserves. Algae holds much promise as a potential feedstock for biofuels because of their higher capacity for productivity per unit land area than conventional terrestrial feedstocks (Chisti, 2007; Wijffels et al., 2010; Georgianna and Mayfield, 2012; Khrunyk et al., 2020). Algal biofuel is immediately compatible with our existing transportation infrastructures like refineries, fuel stations, and the engines of cars (Hannon et al., 2010). If a profitable and sustainable algal biofuel process can be developed, the potential benefits of the technology are compelling including the use of non-arable land, recycling wastewater, and carbon dioxide.

An extensive research program on algal biofuels was sponsored more than 40 years ago by the US Department of Energy (DoE) at the National Renewable Energy Laboratory during the oil crisis of the 1970s. Despite being a successful demonstration of the feasibility of algal biomass as a source of oil, this Aquatic Species Program (1978–1996) was discontinued due to the decreasing federal budget and lower crude oil market (Hu et al., 2008). In the last decade, microalgae reemerged as a source of biofuel and concerted effort has been made towards isolating potential microalgal strain, strain improvement, elucidating biosynthesis pathways, optimize growth and cultivation parameter, harvesting, coproduct development, fuel extraction, refining and residual biomass utilization (Garrido-Cardenas et al., 2018; Wood, 2021). Like academic research, huge claims about the promise of algal biofuel (Chisti, 2007) and the high crude oil price at that time motivated a large number of companies to take an interest in microalgal biofuel, investing significant amounts of money to pursue that objective. Recent technoeconomic analysis has demonstrated that with existing technological readiness, algal biofuel is cost competitive with fossil fuel if combined with the production of high-value co-products (Ruiz et al., 2016; Cruce and Quinn, 2019). Today, most algae based companies have adopted parallel business plans that focus more on the expensive algae byproducts such as cosmetic supplements, nutraceuticals, specialty oils, natural color, and animal feed.

In this review, we provide a perspective on developing sustainable algal cultivation practices and bioproducts from microalgae to make the process of algal biofuel efficient and economically competitive. We have restricted this review to the photoautotrophic microalgal biomass production and to process them into biodiesel or converting them into biocrude at high temperature and pressure through hydrothermal liquefaction but does not include any other form of algal biofuel like bioethanol, biogas, or biohydrogen. The worldwide commercial production of microalgal products is also discussed.

CHOICE OF THE MICROALGAE PRODUCTION SYSTEM

Large capital investment in microalgae cultivation still limits economic biomass production (Acién et al., 2012; Ruiz et al., 2016; Kaur Nagi et al., 2021). Microalgae are not growing at a scale (<5 ha) that is required for the level of cost economy analysis of biofuels. To make "high-volume, low-cost" product like biofuel, microalgal production system must be increased several orders of magnitude, and it demand strategies to reduce the capital expenditure. A considerable variety of systems are available for photoautotrophic production of microalgal biomass, and they are broadly categorized into open raceway ponds and closed photobioreactor systems. Despite the challenge of biological contamination and water loss, raceway ponds are the major commercial production systems of algae biomass because of their large scalability, lower capital, and operational costs (Borowitzka and Vonshak, 2017; Schipper et al., 2021). To balance the strengths and weakness of open and closed systems, algae is cultivated in combined setup of photobioreactor and raceway, called as hybrid system. For production of microalgal biodiesel, two-stage hybrid system could be suitable where exponentially growing algal biomass is transferred from photobioreactor to open raceway ponds under nutrients replete condition to induce higher lipid yield (Liyanaarachchi et al., 2021).

Various research attempted to reduce the capital as well as the expenditure cost of the production systems (**Table 1**). Capital investment although about one order magnitude lower in an open pond than photobioreactor and again, the construction costs can be reduced by 24–75% if self-sealing layers are developed, rather than using synthetic liners, at the soil-water interface by microalgae and associated organisms through bioclogging process (Coleman et al., 2014; Pattullo et al., 2019). Sapphire Energy demonstrated stable microalgal productivity in an unlined pond (2,000 m^2 surface area, 500,000 L volume, 10 $cm s^{-1}$ flow rate) at the Las Cruces test facility, New Mexico without any issues with suspended materials or major water loss through soil (McBride and Merrick, 2014). High-value products like eicosapentaenoic acid (EPA) and omega-3 fatty acid are produced in the unlined pond of Qualitas Health in Imperial, Texas (Efroymson et al., 2020). Greenhouse gas emissions associated with synthetic pond liner manufacture and transportation could be eliminated by using unlined ponds and which eventually will make technology more sustainable (Canter et al., 2014; Greene et al., 2020). Closed raceway ponds were also designed by enclosing a normal raceway ponds with transparent cover that prevents escaping supplied CO_2 into atmosphere and consequently reduce the expenditure of CO_2. Instead of using paddle wheel, airlift-driven raceway can reduce around 80% power consumption for algal production (Kumar Singh et al., 2021).

A considerable variation exists in data in literature and opinions among experts about the selecting the suitable production system for algal bioenergy. However, a general consensus of several life cycle assessment (LCA) studies indicates raceway ponds are better than photobioreactor in terms of net energy ratio and global warming potential (Ketzer et al., 2018; Herrera et al., 2021). The use of expensive photobioreactor system can be justified for making high-value products. Furthermore, the location of the production facility is one of the divers for selecting a commercial production system. For instance, astaxanthin is produced in raceway ponds in Hawaii, United States by Cyanotech Corporation, but it is not feasible under the sun of the Arava desert due to high water evaporation. Therefore, Algatech in Israel uses photobioreactors for the same product. However, substantial energy is used for cooling the photobioreactor. To minimize the cost associated with temperature control, reactor design or strain improvement should be considered in future research. Similar to NASA's OMEGA (Offshore Membrane Enclosures for Growing Algae) system, microalgae can be grown in floated plastic tubes in seawater which functions as a temperature buffer (Wiley et al., 2013).

An alternative to the traditional cultivation systems, biofilm-based systems have tested for biofuel production as summarized by Gross et al., in 2015 (Gross et al., 2015). Algal biofilm-based technology was first developed by Walter Adey in the 1980s called Algal Turf Scrubber™ (ATS) in which naturally seeded filamentous algae grow on a screen in a shallow basin through

TABLE 1 | Comparison of cost analysis of microalgal cultivation systems.

Cost factor		Photobioreactor	Raceway ponds	Hybrid system	Unlined pond	OMEGA (Offshore Membrane Enclosures for Growing Algae) system	Algal turf scrubber
Capital cost	Land cost	Land occupation low	High	Moderate	High	Low	High
	Building cost	High	Low	Moderate	Low (linear cost is eliminated)	High	Low
Operation cost	CO_2 purging efficiency	High (CO_2 loss low)	Low	Moderate	Low	High	Not applicable
	Energy input for mixing	High (High)	Low	Moderate	Low	High	Low
	Energy for maintaining temperature	High	Nil	Moderate	Nil	Nil	Nil
	Water cost (water evaporation lost)	Low	High (water evaporation high)	Modarate	Very high (chances of water leaking through soil)	Low	High
	Productivity	High	Low	High	Low	High	Moderate
	Biomass quality	Reproducible	Variable	Reproducible	Variable	Reproducible	Variable (ash content high)

(Chisti, 2007; Adey et al., 2011; Wiley et al., 2013; Narala et al., 2016; Borowitzka and Vonshak, 2017; Efroymson et al., 2020; Liyanaarachchi et al., 2021)

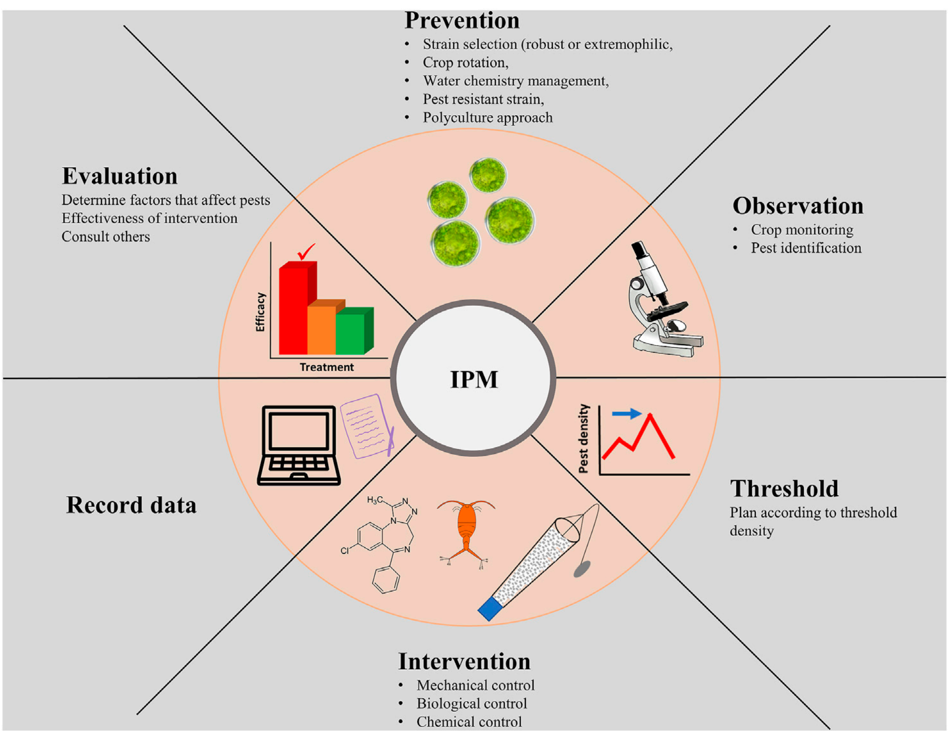

FIGURE 1 | Integrated pest management process for microalgae cultivation.

which water is pumped (Adey et al., 2011). This is used to treat wastewater and was commercialized it through a company Hydromentia based in Florida. Rather than in suspension, algae are attached to the surface and harvested through scraping and thus avoid the expensive harvesting procedures in traditional microalgal cultivation. Although ATS is a robust system for algal biomass production and its productivity comparable to the raceway ponds, higher ash (30–50%) and lower lipid in algal biomass are major challenges to use them for biofuel (DeRose et al., 2019). ATS could be a viable option for biofuel production coupling with wastewater treatment if the ash content can be reduced by growing desired algal communities especially by avoiding silica containing diatoms which contribute up to 65% of the total ash (Adey et al., 2011; Kim et al., 2021).

SUSTAINABLE CULTIVATION PRACTICES

Maintaining long-term, stable, and highly productive algal biomass production in large scale outdoor conditions is the most significant barrier in algal biofuel commercialization. Much like terrestrial crops, microalgal cultivation systems are invaded by weeds, pests, and pathogens, making crop protection a major challenge in the commercialization effort. It is estimated that 30–40% of annual algal crop production is lost to pond crashes (Newby et al., 2016). In this section, we discuss integrated pest management practices (IPM) for healthy algal crop cultivation and a sustainable crop protection process against undesirable biomass losses (**Figure 1**).

IPM uses proactive strategies rather than controlling the pests in the production system. Selection of robust strain in terms of adaptability in varying water chemistry, tolerant to a wide range of field temperature is an essential criterion for any successful algal field cultivation (Lee and White, 2019; Harmon et al., 2021). A robust stain can withstand the variation of water quality parameters that is common in industrial effluents. Selection of suitable microalgal candidates is crucial for recycling flue gases that has high temperatures, fluctuating gas composition, and the presence of toxic chemicals (Kondaveeti et al., 2020). It is often argued that indigenous strains have better fitness to grow in that local environment (Winckelmann et al., 2015; Mutanda et al., 2020). Sero and colleagues reported that the microalgal strains isolated from extreme urban wastewater environments have inherent biological traits to proliferate in stress and capable of producing high biomass yield using wastewater (Sero et al., 2021). Adaptive evolution, mutagenesis, genetic engineering, and systems biology approaches have been used now for microalgal strain improvement with desired traits (Arora and Philippidis, 2021; Kumar Singh et al., 2021; LaPanse et al., 2021). Growing extremophilic microalgae have a successful commercial history. For example, *Dunaliella* is used for commercial β-carotene production in extreme salinity, and widely cultivated microalgal species *Spirulina* is grown in a highly alkaline solution. Extreme conditions help in reducing contaminations from other algal weeds or pests (Varshney et al., 2015; Lafarga et al., 2021). Alkaliphilic *Chlorella* used for biofuel also showed resistance to grazers in high alkaline cultures (Vadlamani et al., 2017). In addition to pest management, alkaliphilic microalgae can grow efficiently without external sparging of CO_2 as alkaline solutions scavenge atmospheric CO_2 at high rates. If a direct air capture technology is established with those microalgae, the capital expenditure, as well as around 65% of total operational cost associated with the recovery of CO_2 from flue gases and delivery to the production unit, can be eliminated (Davis et al., 2016).

Amoeba, ciliates, rotifers, flagellates and crustaceans are the commonly found grazers in microalgal cultivation (Rajvanshi and Sayre, 2020). Infections from fungi like chytrid, bacteria and virus may affect productivity (Grivalský et al., 2021). Crop rotation over the year is quite essential to prevent pest population buildup. The development of a microalgal cell line resistant to pests is another preventive approach that was demonstrated in *Synechococcus elongatus* against amoeba attack (Simkovsky et al., 2012). Pesticides or chemicals are often used to mitigate the challenges of contamination like traditional agriculture. Extensive application of insecticide to maintain productivity causes burden of the maintenance cost, development of insecticide resistant pest and water quality loss of nature. More than 550 species of insects were found resistant to insecticide in agriculture, albeit there is no report from algal cultivation (Whalon et al., 2008; Smith and Crews, 2014). However, commercial production of microalgae has the capacity to repeat the same environmental damage if we do not follow the IPM practice. Thus, identification of pests and understanding their life cycle are primary steps to develop a controlling measure. It is possible to forecast pest attacks and take preventive measures if we have clear knowledge about pest biology and their interactions with algae and the environment. Pest monitoring through microscopy is a common practice in algae cultivation. On several occasions, algae crashes were reported within 2–5 days after detection of pests. Thus, increasing the detection sensitivity and developing early detection tools are essential for algal crop protection techniques. Besides monitoring pests through molecular techniques, algal phenotypic response to pests was employed for early detection. For example, rapid decline in quantum yield (Fv/Fm) and non-photochemical quenching in microalgae were reported prior to pond crashes due to parasitic and grazers attack, respectively (McBride et al., 2014; Deore et al., 2020). Infochemicals released by *Microchloropsis salina* due to the grazers attack was used as a marker for pond health monitoring (Reese et al., 2019; Roccuzzo et al., 2020).

The use of mechanical or biological control rather than conventional chemical treatment is the essential component of IPM strategy (Lee and White, 2019; Al-Jabri et al., 2021). The pest types and their density often determine control operation. Mechanical treatments like pump cavitation or filtering through plankton net are applied to remove larger grazers like rotifers (Kim et al., 2017). Selective feeding of invertebrate consumers can be used to control grazers in algal ponds. Smith and colleagues experimentally demonstrated that introducing zooplanktivorous fish can control the negative impact of grazers and increase lipid productivity in open raceway ponds (Smith et al., 2010). This concept stems from the trophic cascade principle of ecology, which posits that the biomass of primary producers can be maintained by top predators that reduce the population density of primary consumers (Shurin et al., 2014). Invasion of undesired algal strains affects the community structure and alters the biomass productivity and composition that have an impact on the biorefinery process. Maintaining high density cultures in the field is an effective approach to protect against invading algal weed in field cultivation (Richmond et al., 1990). Like pest prevention, biological control was applied to treat small unicellular contaminants such as *Chlorella vulgaris* and *Monoraphidium minutum* in *Spirulina* culture. Herbivorous rotifer *Brachionus plicatilis* that can selectively ingest only small single-celled algae because of their small mouth opening were introduced in long filamentous *Spirulina* culture (Mitchell and Richmond, 1987).

Microalgal consortia have the potential to offer crop protection and increase the stability of yields (Smith et al., 2010; Newby et al., 2016; Mattsson et al., 2021). The use of consortia makes the biorefinery process more complex for extracting any species-specific product, however, managing microbial consortia could be a viable industrial practice for biofuel with higher productivity and stability. Consortia benefit from the "portfolio effect", whereby some species populations will increase in response to pest or environmental fluctuations even if others decline (Shurin et al., 2014). Algal consortia could enhance the nutrients-use efficiency, eventually reducing the fertilizer cost of algal biomass production (Mandal et al., 2018b). In addition, consortia increase productivity in the field through niche partitioning, facilitation, and complementarity (Cardinale et al., 2007; Mandal et al., 2018a). However, random inclusion of species in algal consortia showed success or failures in previous algal biofuel studies. We urge here to design consortia based on the algal complementary traits. Whether it is intentional or nuisance, microbial consortia is the reality for open pond raceway and even in a photobioreactor. Molecular 16S and ITS2 regions analysis of year-long cultivation of industrial microalgal cultivation showed how the diversity of prokaryotic and eukaryotic communities changes over time, and pond productivity and stability positively linked with eukaryotic species diversity of the pond (Beyter et al., 2016). Analogous to rhizosphere in plants, phycosphere is proposed, but it is not studied systematically in commercial production (Wirth et al., 2020). Besides parasitic microbes, many microbes observed in the cultivation have a mutualistic relationship with microalgae and provide essential vitamins for microalgal growth (Kazamia et al., 2012; Yao et al., 2019; Kaur Nagi et al., 2021). Thus, careful management of microbial food-web structure can maximize crop protection and improve crop yield for industrial algal biofuels production (Yun et al., 2016).

In IPM, strong record-keeping and making a correlation of data between yield and operational activities over seasons is a common practice. The factors that determine pest pressure must be identified to predict the pest development time in future operations. The evaluation of the effectiveness of pest control treatments guides selecting the best crop protection strategy. Importantly, translating laboratory-scale results to farm-scale production is a shortcoming in the scaling up of algae cultivation. Field cultivation faces different selection pressures like variable irradiance, temperature, and additional biological challenges—most of which are not seen in the bench-scale studies. To close the lab-to-field yield gap for reliable biomass production, those variables can be tested at a small laboratory scale in more controlled environments before tested at a pilot scale.

WASTEWATER RECYCLING AND NUTRIENT UTILIZATION

Considering the large amounts of wastewater generated globally, around 28–38% of wastewater is treated in developing countries and it became down to almost 8% in underdeveloped ones (Sato et al., 2013). Nitrogen, phosphorus, other macro or micronutrients, the organic carbon in wastewaters is being used for the growth of microalgae. To produce each metric tonne of dry algal biomass requires around 88 kg of elemental N and 12 kg of elemental P, which in turn puts a significant impact on the economy of algal biomass production (Pate et al., 2011). Algal cultivation and wastewater treatment can be integrated to accomplish improved environmental and economic stability. This will not only save the cost of the nutrients of algal biomass production but also surplus the wastewater treatment cost. Techno-economic suggests the production cost can be reduced to more than five times when coupled with wastewater treatment (Acién et al., 2012).

The concept of treating municipal wastewater using microalgae was initiated in the 1950s by Oswald and colleagues at the University of California, Berkeley using high-rate algal ponds with shallow depth and paddlewheel mixed (Oswald and Golueke, 1960; Benemann, 1980; Benemann et al., 1980). Later, it advanced to different types of cultivations systems like photobioreactors, earthen lagoons, concrete tanks, corrugated raceway ponds, biocoils, for use (Craggs et al., 1997; Park et al., 2011; Posadas et al., 2015; Randrianarison and Ashraf, 2017). The advantages and limitations of using an algal turf scrubber system for treating wastewater and biofuel production were described in earlier section. The nutrient removal efficiency of different microalgal strains and their productivities varied in different cultivation systems and wastewater types as illustrated in **Table 2**. The treatment efficiency of algae-based system and biomass productivity can be improved by operating parameters such as mode of cultivation (batch or continuous), aeration, changing water chemistry (pH, adding require nutrients) (González-Camejo et al., 2021). Further, different stresses like pH, temperature, salinity changes or nutrients reduction in growth media have been suggested to increase lipid yield for biofuel production (Bélanger-Lépine et al., 2018).

The essentials for evaluation of wastewater treatment schemes involving algae include a clear understanding of the standard steps of treatment to justify the expense of such developmental efforts and more importantly, the characteristics of the wastewater with large flows (Laurens, 2017). These wastewaters are highly turbid, often polluted by algal growth inhibitors like organic compounds in highly toxic concentrations, salt accumulations, and allelopathic agents excreted by algae themselves (Bacellar Mendes and Vermelho, 2013). Be it a monoculture or polyculture of microalgal strains, efficient pilot harvesting of biomass is vital, especially when the treated wastewater must be brought to re-use. Leaving back the traditional concept of drying, solvent extraction of lipids, and transesterification for the production of fatty acid methyl esters, all the time more interest is being directed towards the hydrothermal liquefaction (HTL) process for bio-oil productions (Al-Jabri et al., 2021; Chen and Quinn, 2021). This aqueous phase from the HTL process contains high concentrations of nutrients like nitrogen, phosphorus, and other elements that can be recycled for microalgal growth. While varying compositions of the algal biomass in wastewater

TABLE 2 | Microalgal nutrients removal efficiency and biomass productivity in different wastewater treatment.

Algal species	Wastewater source	Algal cultivation system	Uptake/Removal efficiency	Biomass productivity	Commodity (Product/ Co-product)	Reference
Scenedesmus sp.	Domestic wastewater	Pilot scale study (20 days)	NH_4-N: 80% NO_2-N: 99% NO_3-N: 86% PO_4-P: 66% SO_4: 76% Ca: 84%	0.68 g/L–0.84 g/L	43.3% SFA, 44.4% MUFA, 12.3% PUFA	Baldev et al. (2021)
Chlorella vulgaris, Chlorococcum vitiosum, Chroococcus turgidus, Desmococcus olivaceus, Scenedesmus acutus, Scenedesmus dimorphus and *Oocystis solitaria*	Coke plant waste water	Bioreactor in lab scale semi-continuous mode (5 L—1,400 rpm)	NH_4-N: 42.7% (46 mg L^{-1}) Total CN: 47.83% (3.73 mg L^{-1}) TDS: 22.1% (1896 mg L^{-1} O_2)	NR	NR	Kaur Nagi et al. (2021)
Isochrysis sp.	Sewage discharge	500 ml flasks operating as photo bioreactor	TN: 5.57% TP: 84–94% COD: 89–93% NH_4-N: 9.31%	55.5 × 105 cells ml^{-1}	63.0, 16.92% MUFA, 20.00% PUFA	Kumar Singh et al. (2021)
Desmodesmus sp. PW1	Piggery wastewater	Laboratory scale 30 L photobioreactor	TN: 79.2% TP: 65.3%	0.81 g L^{-1}–1.76 g L^{-1}	Total fatty acid/dry weight (%): 29.4 ± 0.17 28.3 ± 0.21 SFA 39.9 ± 0.93 MUFA 31.3 ± 1.74 PUFA	Chen et al. (2020)
Scenedesmus obliquus FACHB-276	Municipal wastewater	1 L Erlenmeyer flasks	TN: 96% TP: 80% COD: 85%	0.83 g L^{-1}	Lipid content: 56%	Qu et al. (2020)
Chlorella sorokiniana CY-1	Palm oil mill effluent (POME)	5 L Novel-designed photobioreactor (NPBR) and glass-made vessel photobioreactor	COD: 93.7% TN: 98.6% TP: 96.0%	NPBR: 408.9 mg L^{-1} d^{-1}	Lipid content: 14.43% (NPBR)	Cheah et al. (2020)
Tetraselmis indica BDU 123	Pharmaceutical wastewater	250 ml flasks	COD: 66.30% TOC: 78.14% NO_3-N: 67.17% PO_4-P: 70.03%	46.85–61.25 mg L^{-1} d^{-1}	Lipid Productivity (mg L^{-1} d^{-1}): 15.69–17.15	Amit and Ghosh., (2020)
Dunaliella FACHB-558	Anaerobically digested poultry litter wastewater	500 ml flasks operating as photo bioreactor	TN: 63.8% TP: 87.2% TOC: 64.1%	678 mg L^{-1}	7.26 mg L^{-1} β-carotene	Han et al. (2019)
Hindakia tetrachotoma ME03	Municipal wastewater	Flat airlift photobioreactor (PBR) (1 L)	NR	0.72 ± 0.01 g L^{-1}	0.11 g of bioethanol/g of microalgal Biomass	Onay (2019)
Chlorella vulgaris	Dairy wastewater effluent	Photobioreactor set-up (10 L)	BOD: 85.61% COD: 80.62% SS: 29.10% TP: 65.96% TN: 85.47%	1.232 dry weight g L^{-1}	22.65% SFA 77.35% UFA	Choi (2016)

(NR—Not Reported, TDS—Total Dissolved Solids, COD—Chemical Oxygen Demand, BOD—Biological Oxygen Demand, TN- Total Nitrogen, TP—Total Phosphorus, TOC—Total Organic Carbon, SS- Suspended solids, SFA—Saturated Fatty Acids, UFA—Unsaturated Fatty Acids, PUFA—Polyunsaturated Fatty Acids, MUFA—Monounsaturated Fatty Acids).

is a shortcoming in the refinery process, converting the carbohydrates, proteins, and lipids agnostically to bio-oil would be a feasible choice.

POSSIBLE CO-PRODUCTS WITH BIOFUEL AND THEIR MARKET

Amongst various non-conventional sources, microalgae are promising microorganisms that play a key role in the biobased economy, since they serve as a continuous and reliable source of several bioactive natural products (Fabris et al., 2020). Microalgae are factories for producing various compounds other than the only lipid for making biofuel. Lipid is converted into biodiesel through transesterification process in which triglycerides react with alcohol in the presence catalyst. In thermochemical process like pyrolysis, gasification, combustion or hydrothermal liquefaction biomass is thermally breakdown into organic chemicals which reform into various types of biofuels (**Figure 2**). The biochemical conversion involves the hydrolysis of biomass by bacteria into fermentable sugars which is converted into bioethanol, biogas and biohydrogen (Saad et al., 2019). As shown in **Figure 2**, the algal biomass residue after high-value co-products and biodiesel production can be route into thermochemical or biochemical process for maximal valorization of algal materials. However, most microalgal companies focus on single product development. Recently, the focus of microalgae biomass delivering a single product is shifting towards delivering multiple products along with lipid derived biofuels in a biorefinery approach (Wijffels et al., 2010; Ansari et al., 2017). The current production of microalgae derived products (more than 75%) are finding their way towards food,

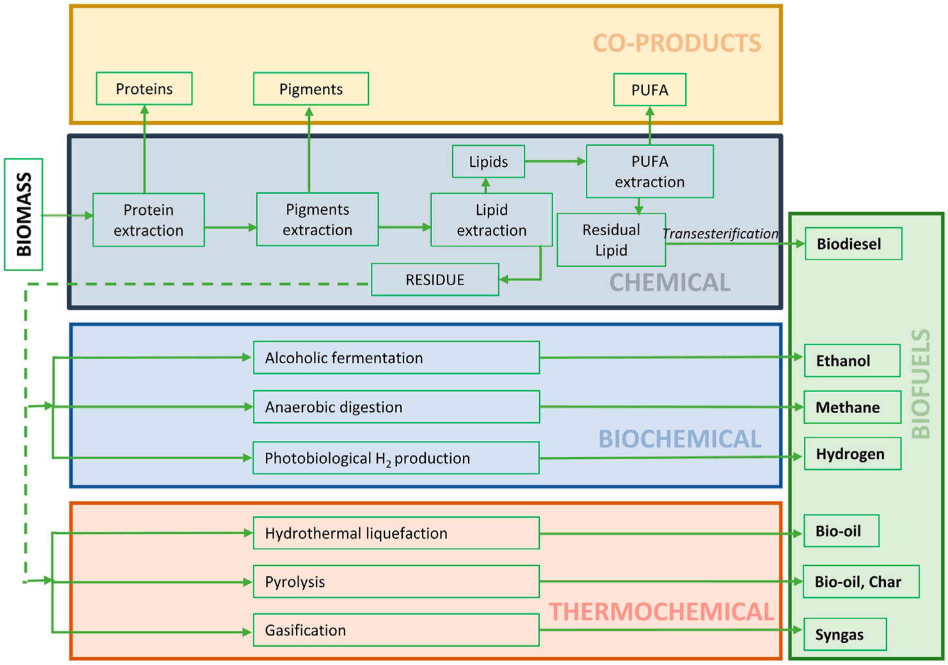

FIGURE 2 | Integrated algal biorefinery process for biofuels and other value added co-products.

feed, nutraceutical, and cosmetic industries (Nethravathy et al., 2019; Rahman, 2020). Thus, if algal biofuel is combined with the production of bulk chemicals, food, and feed ingredients, the cost gap between biofuel and fossil fuel would be closed (Shukla and Kumar, 2018). The proposed biorefinery approach, on other hand, may cause the market saturation of high-value products. Thus, the market niche and demand of such algal high-value products must be analyzed critically. However, nowadays people are trending towards natural products, especially in the COVID era. In the following section, we analyzed the algal products that can zeal with algal biofuel, their potential, current industrial situation, future market (**Table 3**).

Pigments

Microalgal pigments is a profitable business nowadays. Pigments from algae such as *Dunaliella, Scenedesmus, Nannochloropsis, Haematococcus, Muriellopsis, Chlorella, Phaeodactylum, Spirulina, Porphyridium* have gained more popularity in the health food industry as they produce carotenoids, chlorophylls, and phycobiliproteins in high amounts (Noreña-Caro and Benton, 2018; Arashiro et al., 2020; Silva et al., 2020). Currently, the global demand for pigments produced from natural sources is growing rapidly with great health benefits to humans ("BCC Research: Market Research., 2021 Reports and Industry Analysis"). In terms of commercialization, pigments from microalgae have a high revenue generation > USD 1 billion (selling price—USD 400/kg) and the global carotenoid market is expected to be USD 2.0 billion by 2026. The lutein and zeaxanthin eye health care market from microalgae crosses USD250 million per year. The market for canthaxanthin and zeaxanthin is still in its developing stages (Lin et al., 2015; Pereira et al., 2021). On other hand, the average market size of astaxanthin and β-carotene from *Dunaliella* for food supplements is in the range of 2,500 USD per kilograms and 75 million USD (Hejazi and Wijffels, 2004; BIOPRO, 2013; Levasseur et al., 2020). Astaxanthin is considered the leading molecule propelling microalgal biorefinery (Dawidziuk et al., 2017; Khoo et al., 2019) with production costs shifting between 300 and 3600 USD/kg depending upon the purity (Li et al., 2011; Dawidziuk et al., 2017). Algae Health Science, Yunnan, China is one of the biggest producers of astaxanthin from *Haematococcus pluvialis* (Schultz., 2020). Numerous pigments such as astaxanthin from marine algae, xanthophylls, and phycobiliproteins from red algae, have a great potential in cosmetic application (Morocho-Jácome et al., 2020).

According to a recent study, mainly *Spirulina* and *Chlorella* are the key algal strains that top the algal market worldwide in health and nutrition with a production of 12,000 tons per year and 5,000 tons per year, respectively (Koyande et al., 2019; Nethravathy et al., 2019; Wang et al., 2020). Chlorophyll and phycobiliproteins have been widely used as coloring agents and fluorescent markers in both strains due to their high stability (Pulz and Gross, 2004; Dasgupta, 2016). Fucoxanthin product named fūcoTHIN® was used as a supplement in body weight products (Liu J., 2016; Liu Q., 2016). Moreover, this valuable pigment can be used in animal feed products as it is regarded as safe (Yi et al., 2015). Algal Technologies Ltd., Israel (2018) reported the fucoxanthin production from microalgae with a growing global market of approximately USD 600 million during 2018–2025 (Global Fucoxanthin Market, 2020). The effective use of microbial pigments depends on high productivity, production costs, pigment characterization, and stability at a broader range of

TABLE 3 | Microalgal products and their commercialization potential.

Compound	Marketed products	Microalgae species	Production cultivation scale	Productivity	Price	Global market	Industrial importance	Producer/Suppliers	References
β-Carotene	Betatene, Spray dried powder	*Dunaliella salina*	Closed PBRs and open raceway, 1,200 tons/year	27 mg/g β-carotene	US $ 300–3,000/kg	280 million US$ USD 618.94 million by 2026	Health food Dietary supplement Pharmaceuticals and Cosmetics	Cognis Nutrition and Health Co. (Australia); Nature Beta Technology ltd. (Israel); Aquacarotene ltd. (Australia)	Figueroa-Torres et al. (2020), Harvey and Ben-Amtoz. (2020)
Carotenoids	Whole-cell dietary supplements, Biomass, pigments	*Chlorella vulgaris*	Closed PBR, 4,000 tons/year	51–58% protein, 22.6 mg/g total chlorophyll 2.7 mg/g total carotenoid, 10–12% EPA	$10–20/kg (Health food)	USD 210.15 million by 2024	Health food and Nutritional supplement	Chlorella manufacturing and Co. (Taiwan); Ocean Nutrition (Canada); Chlorella manufacturing and Co. (Taiwan) BlueBiotech International GmbH (Germany)	Bhattacharya and Goswami. (2020), Figueroa-Torres et al. (2020), Market Data Forecast, (2021)
Astaxanthin	Bioastia® extract, Naturose Powder Astafactor® (meal extract) AstaPure®	*Haematococcus pluvialis*	Closed and semi-closed photobioreactors, Open raceway, 300 tons/year	23.2 mg/g astaxanthin 2.8 mg/g beta-carotene 10.2 mg/g lutein	Nutraceutical grade astaxanthin originating from *Haematococcus pluvialis* can reach 6000 USD/kg	770 million USD by 2024 and reach 800 million by the end of 2026	Human Dietary, supplement (Sports nutrition, Suncare, general health); Aquaculture and feed; nutraceuticals; antioxidant	Cyanotech Corporation (United States); Mera Pharmaceuticals Inc.(United States); BioReal. Inc. (United States); Aquasearch agatechnologies (Israel)	Bhattacharya and Goswami. (2020), ALGATECH (2020), Niizawa et al. (2018)
Fucoxanthin	FucoVital™	*Phaeodactylum tricornutum*	PBR, flat-panel airlift (FPA) reactor	42.0% protein; C20:5 30.2%; Fucoxanthin,0.18	168.62 USD/kg	Fucoxanthin: USD 600 million during 2018–2025	Food supplement, Antioxidant, feed	Algatech (Israel) (ALGATECH 2020)	Figueroa-Torres et al. (2020), Global Fucoxanthin Market. (2020), Mutanda et al. (2020), Branco-Vieira et al. (2018)
Allophycocyanin	Spirulysat® Electric Sky® Bloo Tonic®	*Arthrospira platensis*	Open raceway pond and photobioreactor, 10,000 tonnes/year	62.0% protein; 90 mg/g phycocyanin 67 mg/g	200 to $2.2 million per kilogram	Phycocyannin232.9 million USD by 2025 (Mu et al., 2019); Spirulina USD 779 million by 2026	Food supplement or bio colorant application, beverages (Food/cosmetic industry)	Nature Beta Technologies Cognis (Australia); Panmol/Madaus (Austria); yanmar Spirulina Factory (Myanmar); ikken Sohonsha Corp. (Japan)	www.spirain.com; AlgoSource., (2020), Bachchhav, et al. (2020), Bioeconomy. (2020), Horizon. (2020)
Phycoerythrin	Fluorescent label	*Porphyridium spp.*	Closed PBR	47.1% protein; 15% EPA	$10000/kg (Phycoerythrin) $15/mg (Fluorescent label)	10–50 million USD in 2019	Food supplement; Food additives, Nutrition	BlueBiotech International GmbH (Germany); Cyanotech (Hawaii, United States); InnovalG (France)	Figueroa-Torres et al. (2020), Nwoba et al. (2020), Li, et al. (2019)

(Continued on following page)

TABLE 3 | (*Continued*) Microalgal products and their commercialization potential.

Compound	Marketed products	Microalgae species	Production cultivation scale	Productivity	Price	Global market	Industrial importance	Producer/Suppliers	References
Eicosapentaenoic acid (EPA)	Almega®PL	*Nannochloropsis oculata*	Closed PBR	40% protein; EPA 18.0%	$128.15/kg	2.5 billion USD in 2014; 5 billion USD by 2020	Cholesterol Lowering, Omega-3 supplements	Cleanalgae SL (Spain); Astaxa (Germany)	Rao et al. (2020), Figueroa-Torres et al. (2020), Wang et al. (2020), Chouhan et al. (2021)
Docosahexaenoic acid (DHA)	Maris DHA oil	*Schizochytrium sp*	Fermentor, 10 tonnes DHA oil	DHA content: ≥ 22.5% EPA content: ≥ 10%	$60/g	USD 435 Million by 2026	Dietary supplement; Health food supplements as defined in Directive 2002/46/EC for adult population excluding pregnant and lactating women, Nutritional supplements., additive for infant formula, Rheumatoid arthritis	OmegaTech (United States), BlueBiotech International GmbH (Germany) Spectra Stable Isotopes (Maryland, United States) Martek Biosciences (Maryland, United States)	Molino et al. (2020); Dawczynski, et al. (2018)

temperature and light (Morales-Oyervides et al., 2017). Being the most revenue generating compounds in algal biorefinery pigments can play a major role in the economy of biofuel production (Ruiz et al., 2016; Mutanda et al., 2020).

Proteins

Microalgae are known for producing proteins with a healthy balance of essential amino acids and widely used for decades as a feedstock in the pharma and nutrition sectors. In past years, proteins from microalgae have now been investigated thoroughly in food sciences as a cheap and more sustainable source, qualifying as proven alternatives to conventional ones, thus meeting the global demands of protein in nutrition (Kay and Barton, 1991; Becker, 2007). Several microalgal strains have a protein content higher than conventional plant or animal sources. For example, protein content in *Spirulina platensis* is 65%, higher than that in meat (45%), soy flour (37%), milk (24%), or fish (24%) (Younes et al., 2011; Barka and Blecker, 2016; Ritala et al., 2017).

Algal proteins from *Chlorella* and *Spirulina* are recognized as safe for human consumption. The market for algae protein has witnessed a huge upsurged demand, due to their high nutritional value, exploration by the vegan population, and being a sustainable source. Currently, among the algal sources of protein, blue-green algae hold the largest market share with revenue surpassing USD 300 million in 2019. Asia- Pacific algal protein market is expected to witness 6.5% CAGR till 2026. In 2019, Swiss food manufacturer Nestle made a strategic partnership with Corbion for the development of commercial microalgae-based protein products. The microalgae proteins and peptides hold anticancer, immunosuppressive, anti-hypertensive, and antioxidant properties (Wang and Zhang, 2013). Microalgal proteins are mostly being used as supplements, and are available in the market in form of tablets, capsules, or liquid. The use of microalgae as a bulk commodity in human food is rare because of their unfavorable sensory attributes like the smell, color, and texture; a smaller part is applied as an ingredient in pasta, baked goods, snacks (Ritala et al., 2017). Microalgal protein is now used as an ingredient of meat analogs through modifying texture and flavor in food processing techniques (Fu et al., 2021). Microalgae or protein are proven feedstock for the animal. For instance, *Scenedesmus obliquus* protein extracted from a sequential refinery process was used as an alternative to a fish meal before converting biomass into biodiesel (Patnaik et al., 2019).

Extracting the protein from algal biomass before processing it into biofuel can make the microalgal biofuels economically viable. Several researchers have reported the production of proteins along with advanced biofuels from *Chlorella* and *Scenedesmus* (Illman et al., 2000). However, a technoeconomic analysis of the algal biorefinery process revealed the extraction and purification of soluble protein with chemical extraction followed by diafiltration membrane purification encompassed about 75% of refinery cost (Suarez Ruiz et al., 2018). Thus, developing a suitable technology for this refinery cost reduction is one of the critical challenges in the bioprocess.

Polyunsaturated Fatty Acid

Microalgae are well known for being the source of PUFA such as γ-linolenic acid, arachidonic acid, eicosapentaenoic acid (EPA), and docosahexaenoic acid (DHA) (Ratledge, 2010). Although, both EPA and DHA from fish oil dominate the market, the demand for microalgal sources is increasing because of the vegan characteristic of algal oil. The presence of persisting contaminants such as dioxins, heavy metals such as methyl mercury, and polychlorinated bisphenols in fish oil is also a challenge (Ruiz-Rodriguez et al., 2010; Ryckebosch et al., 2014). Advantages of fatty acids from microalgae were also observed against inflammation and cardiac related disease such as myocardial infarction, hypertension, thrombosis, etc. (Nauroth et al., 2010; Adarme-Vega et al., 2014). PUFAs, particularly DHA and EPA, are reported to have a therapeutic role in a variety of inflammatory pathologies, for instance, arthritis, Alzheimer's disease, and lupus (Yates et al., 2014). There is an increasing market potential for long chain polyunsaturated fatty acids (LC-PUFAs) due to their intense application in health (Saini and Keum, 2018). PUFA market is likely to expand at an annual growth rate of 13.5% globally (Rahman, 2020). Several microalgal species like *Schizochytrium, Crypthecodinium,* and *Ulkenia* have been cultivated heterotrophically for DHA production at an industrial scale. The company, DSM which is the major driver in this particular oil market, commercialized a DHA rich oil from "*Crypthecodinium cohnii*". called DHASCO™ (Wynn et al., 2010). This is popularly used in infant formula, supplements, and products for pregnancy and nursing. DSM commercialized another DHA and EPA rich algal oil, Life's ™ OMEGA, which is approved for use as a novel food ingredient in specific food categories and dietary supplements. Martek Biosciences commercialized DHA production from the microalgae *Crypthecodinium*.

Green alga *Parietochloris incisa* (Bigogno et al., 2002) comprises a higher amount of arachidonic acid content; though, the total content of lipid is lower when compared to other existing commercialized fungus for arachidonic acid production. *Spirulina platensis* is the best source for linolenic acid production (Tanticharoen et al., 1994). EPA producing microalgal strains, in particular, *Nitzchia, Nannochloropsis,* and *Phaeodactylum tricornutum* are widely cultivated (Spolaore et al., 2006). Almega PL™, an EPA-rich product is marketed by Qualitas Health by using autotrophic production of microalgal biomass. In a sustainable biorefinery approach, omega-3 fatty acids can be separated from microalgal lipids, while the rest of the lipid or other components of the biomass could be used for making food, fuel, or other valuables. For example, after the separation of omega-3 fatty acids from *Nannochloropsis salina* oil, the waste oils were used to produce flexible polyurethane foam (Phung Hai et al., 2020). This biodegradable polyurethane foam is an alternative to petroleum-based polymer and showed its application in making footwear and surfboard. In recent years, concurrent production of fucoxanthin and docosahexaenoic acid from *Isochrysis* strain has been examined with encouraging effects (Sun et al., 2019).

Cosmetics

Next to pigments and fatty acids, microalgae have long been of interest as sources of bioactive compounds to use in cosmetics. Bioactive compounds from microalgae have potential applications like water-binding, thickening, and antioxidant agents, prevention of hyperpigmentation, stimulation of bleaching, modulation of melanogenesis in hair, melanocyte proliferation, improvement and stimulation of keratinocyte differentiation, growth of human hair follicles, improvement or maintenance of skin's barrier function, improvement of aged skin appearance, collagen stimulation, and improving skin's firmness and elasticity (Levasseur et al., 2020; Randhir et al., 2020; Chouhan et al., 2021). Several protective and efficient systems against the free radicals and reactive oxygen species are developed in algae because of the natural exposure to oxidative stress. This, in turn, produces compounds that can be used to replace the currently employed organic and inorganic filters against the damaging effects of UV radiation (Wheeler et al., 2008; Gouveia et al., 2009).

Both *Nannochloropsis* and *Isochrysis* have been found effective against UVA and UVB transmissions with the same profile as any formulation containing SPF15 fighting organic and inorganic filters (Lotan, 2012). Compared to the sunscreen formulations used commercially, cyanobacteria showed better absorption in the visible spectral region and UV A, UVB region as well, i.e., 290–650 nm (Ariede et al., 2017). Mycosporine-like amino acids such as asterina, palythene, palythine, and porphyra have been reportedly produced by cyanobacteria of *Nostoc sp*. R76Dm and have shown *in-vivo* reactive oxygen species (ROS) scavenging potential and *in-vitro* dose-dependent antioxidant potential (Rastogi et al., 2016).

Pentapharm in Basel, Switzerland launched a commercial product called Pepha-Tight using a compound from *Nannochloropsis oculata* for short-term and long-term skin-tightening properties and other called Pepha-Ctive using extracts from *Dunaliella salina* to positively influence the energy metabolism of the skin and to stimulate cell proliferation (Spolaore et al., 2006). The cosmetic industry is growing worldwide with a market size was valued at $380.2 billion in 2019, and is projected to reach $463.5 billion by 2027, registering a compound annual growth rate of 5.3% from 2021 to 2027 (Chouhan et al., 2021). Rapid growth in this industry can make a market niche for algal cosmetics when combined with biofuel.

Microalgae are also a source of several minerals and vitamins like vitamin A, vitamins of the B group like B1, B2, B3, B5, B6, B8, B9, B12, vitamin C and E. Phytohormones like abscisic acid, gibberellins, auxin, cytokinin, ethylene, polyamines, salicylates, signal peptides, and brassinosteroids are produced by most of the microalgal lineages (Bajguz and Piotrowska-Niczyporuk, 2013; Galasso et al., 2019; Levasseur et al., 2020). Algae derived bioactive compounds have been suggested for treating COVID-19 disease (Chia et al., 2021). Approximately 73,000 algal species have been identified but few reached the commercial scale (Guiry, 2012). However, there is numerous germplasm that need to be explored for the production of valuable products. Despite the suitability of algae for biorefining, holding the functionality of the different compounds in the refinery process is a challenge. Research is needed to explore the compatibility of the compounds in down streaming processing and to reduce the materials and energy consumption in the process. Economics of microalgal downstream processing including cell disruption, extraction, purification, and biomass conversion must be evaluated for the sustainability of biorefinery process.

ALGAL BIOFUEL COMMERCIALIZATION EFFORT

Commercial microalgae production was started with the cultivation *Chlorella* for the single-cell protein in the early 1960s in Japan, followed by Spirulina in the US, and then in China and Thailand (Lee, 1997; Borowitzka, 2013). In the 1980s, efforts were initiated to produce microalgal pigments, predominantly beta-carotene and astaxanthin, through the cultivation of *Dunaliella sp*. and *Haematococcus sp*. In the 1980s, commercial production of PUFAs, especially EPA and DHA, was started for nutraceuticals application. In the early of this century around 2005, a number of companies like Algenol, Cellana, Origin Oil, Aurora Biofuel, PetroAlgae, PowerFuel.de, Shell Oil, Solix Biofuel, Sapphire Energy, and Solazyme raised remarkable private sector investment with a promise of producing algal biofuel competitive with the fossil fuel (Waltz, 2009). In India, Reliance Industries invested with Algenol, United States to recycles carbon dioxide into fuels through its direct-to-ethanol process near Jamnagar petroleum refinery. Sapphire Energy used hydrothermal liquefaction technology to make "crude-like oil" that can be refined into gasoline or jet fuel. The estimated minimum price for algae biofuel was \$2.1 per liter which weighs high than regular gasoline (Gu et al., 2020). Today, most algae companies except for ExxonMobil and Synthetic Genomics shifted their business model into high-value products. ExxonMobil and Synthetic Genomics reported the doubling of lipid production without compromising growth through genetic modification in *Nannochloropsis gaditana* using CRISPR–Cas9 genome editing techniques (Ajjawi et al., 2017). Their joint algae biofuel research program targets to produce 10,000 barrels of algae biofuel per day by 2025 using genetically modified strain. However, the phenotype stability of engineered strain in the field along with the concern of environmental risk growing often raised the question of the genetically engineering approach for microalgal biofuel research. The finding of the first field trial of genetically modified algae by researchers from the University of California San Diego and Sapphire Energy, United States was encouraging as genetically modified *Acutodesmus dimorphus* conserved the genetically modified phenotypes in field cultivation without impacting the phytoplankton communities in native lakes (Szyjka et al., 2017).

After few years from 2005 when microalgae did not reach the economic target, the potential of microalgae for biofuel was debated and called "hype" (Waltz, 2009). In a reply to the news feature "Biotech's green gold?" in Nature Biotechnology (Waltz, 2009), Stephens and colleagues demonstrated microalgae are capable of producing ~60–100 kl oil ha^{-1} y^{-1} on a practical conservative scale (Stephens et al., 2010). Algae-based transportation fuels have already demonstrated their ability to drive personal automobiles, fly commercial planes, and power Navy ships. In our view, it not about the potential of algae, it is all about technological readiness to compete with fossil fuel.

Although algal biofuel didn't reach yet the economic target, Life cycle assessment (LCA) of algal biofuel from the pilot-scale facility of Sapphire Energy was found to have lower greenhouse gas (GHG) emissions than corn ethanol and petroleum fuels (Liu et al., 2013). Interestingly, Energy Return on Energy Investment (EROI) which is the key for measuring the sustainability of any energy technology was above one in their pilot-scale analysis and varied between one and four depending on the scale of production.

CONCLUSION AND FUTURE PERSPECTIVES

Microalgal biofuel remains in an early stage of development. In our view, we invested only a few years from capital injection to demonstrating large-scale commercial production. Venture capitalists should consider the challenges and barriers that need to be overcome before this technology is commercialized. Even, the demonstration plants (at <5 ha) that were used for estimating the cost analysis were well weighed below the size threshold for economic viability. To make "high volume, low-cost product" like biofuel, scaling up microalgal cultivation system to a commercial level is a key in the process development. Although microalgae are an excellent feedstock of multiple products, maintaining the stability of all chemicals with their bioavailability is critical challenge in adapting biorefinery approach. A substantial innovation is required in downstream processing steps like milder cell disruption technologies, solvents or supercritical fluid extraction to ensure the functionality of the products reserve in the process. Research should be carried out to find the appropriate sequence of products extraction from microalgal biomass in refinery process. As of now, current market values of algal nutraceutical are quite high when the global production of microalgae is inadequate. Apparently integrating biofuel systems with industrial commodities production looks economically sustainable but replacing only a part of fossil fuel with biofuel can make a surge of high-value products in the market and affect product prices. Awareness among people about algal products must be improved to reach a sustainable biorefinery. Improving downstream processing certainly is an essential step, but to produce enough biomass to feed the process is more critical in algal biofuel commercialization. Successful algae cultivation in the field demands a more ecological approach rather than industrial microbiology. Algae need to be considered as an agricultural crop, and robust agronomic and integrated pest management practices must be developed as cheaply as possible. Indeed, the 2018 Farm Bill classified algae as a crop in US policy and support the algae program. Research investment, policy development, and new scientific discoveries will pave the way for the development of viable microalgal biofuel platforms in the near future. In the meantime, valorizing high-value co-products is a feasible option for microalgal biofuel commercialization.

AUTHOR CONTRIBUTIONS

Each author contributed to the literature review and analysis and to the writing of the paper. SM was the research supervisor and conceptualized the manuscript. All authors have read and agreed to the published version of the manuscript.

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Blockchain Adoption for Sustainable Supply Chain Management: Economic, Environmental, and Social Perspectives

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Due to the rapid increase in environmental degradation and depletion of natural resources, the focus of researchers is shifted from economic to socio-environmental problems. Blockchain is a disruptive technology that has the potential to restructure the entire supply chain for sustainable practices. Blockchain is a distributed ledger that provides a digital database for recording all the transactions of the supply chain. The main purpose of this research is to explore the literature relevant to blockchain for sustainable supply chain management. The focus of this review is on the sustainability of the blockchain-based supply chain concerning environmental conservation, social equality, and governance effectiveness. Using a systematic literature review, a total of 136 articles were evaluated and categorized according to the triple bottom-line aspects of sustainability. Challenges and barriers during blockchain adoption in different industrial sectors such as aviation, shipping, agriculture and food, manufacturing, automotive, pharmaceutical, and textile industries were critically examined. This study has not only explored the economic, environmental, and social impacts of blockchain but also highlighted the emerging trends in a circular supply chain with current developments of advanced technologies along with their critical success factors. Furthermore, research areas and gaps in the existing research are discussed, and future research directions are suggested. The findings of this study show that blockchain has the potential to revolutionize the entire supply chain from a sustainability perspective. Blockchain will not only improve the economic sustainability of the supply chain through effective traceability, enhanced visibility through information sharing, transparency in processes, and decentralization of the entire structure but also will help in achieving environmental and social sustainability through resource efficiency, accountability, smart contracts, trust development, and fraud prevention. The study will be helpful for managers and practitioners to understand the

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procedure of blockchain adoption and to increase the probability of its successful implementation to develop a sustainable supply chain network.

Keywords: blockchain, sustainable supply chain, green supply chain, triple bottom-line, circular supply chain, traceability

1 INTRODUCTION

In the past, the economic benefit was the main focus of supply chain professionals. However, due to a high rate of environmental degradation, the emphasis is shifted from economic to social and environmental sustainability (Tseng et al., 2019; Gupta et al., 2020). The pressure from stakeholders such as government organizations, regulatory bodies, and customers is forcing the firms to redesign their internal and external supply chain structures, according to environmental concerns and social needs (Srivastava, 2007; de Oliveira et al., 2018; Manupati et al., 2019). Green supply chains and sustainable practices are an important area of research, and it includes a series of green initiative activities in all processes (Silvestre et al., 2018; Rezaei Vandchali et al., 2021). The supplementary concepts used in sustainability are the reuse, recycle, and circular supply chain (Koberg and Longoni, 2019). The green and sustainable practices are adopted by different firms to ensure the welfare of society through waste reduction, emission reduction, and energy usage optimization (Agyabeng-Mensah et al., 2020). There are many innovative technologies that provide a competitive advantage to firms (Kamble S. S. et al., 2021). Advancement in technologies is very extensive, and each of these technologies has effects on the green initiative and social sustainability of the firms (Kouhizadeh and Sarkis, 2018). Among all recently developed technologies, blockchain (distributed ledger) has significant effects on the sustainability (Kouhizadeh and Sarkis, 2018).

Blockchain is a distributed accounting system with automatic transaction execution, which is used to maintain the growing data (Wu et al., 2017). Its main characteristics are high consistency, data veracity, traceability, and cybersecurity. Blockchain is considered as a technology that will bring breakthrough in the supply chain as it is a transparent and temper proof system, which will improve the tracking and tracing system (Badia-Melis et al., 2015; Wu et al., 2017; Wang Y. et al., 2019a; Pournader et al., 2019; Behnke and Janssen, 2020; Feng et al., 2020; Ozdemir et al., 2020; Xu et al., 2020; Garaus and Treiblmaier, 2021). Blockchain can be beneficial for the food supply chain in many aspects such as quality preservation, fraud prevention, anti-counterfeiting, and cost reduction (Coronado Mondragon et al., 2020). Effective traceability is required in a complete value chain as lack of transparency in one firm will affect the entire supply chain (Hu et al., 2013). The other factors which drive for the adoption of blockchain are consumer trust, risk management practices, regulatory requirements, high consistency, and data veracity (Bosona and Gebresenbet, 2013). Blockchain will shift the "product-based economy" to an "information-based economy" (Pazaitis et al., 2017).

There are various studies published in the field of blockchain in the supply chain under different titles. The main objective of these studies was to analyze the effects of blockchain adoption on the overall performance of the supply chain. Galvez et al. (2018) examined the capability of blockchain and concluded that traceability and transparency can be improved using blockchain. Kamilaris et al. (2019) reviewed the effects of blockchain in the agri-food supply chain and concluded that blockchain is a step toward transparency in the food supply chain. Feng et al. (2020) provided review of different characteristics of blockchain and proposed a framework for adoption of blockchain in the food traceability system. Hosseini Bamakan et al. (2021) and Han et al. (2021) provided the deep insights into the application of blockchain in pharmaceutical cold chain and identified the different challenges of blockchain adoption. Lim et al. (2021) used descriptive analysis and explored different themes and methodologies used for the adoption of the blockchain. Niknejad et al. (2021) conducted a review on the blockchain using graphical mapping of the bibliographic information. Main emphasis of researchers is the traceability of products, through emerging modern technologies. Wamba and Queiroz (2020) discussed the techniques by which different sectors such as agriculture, e-commerce, and public services gained a competitive advantage through the effective use of blockchain. Liu et al, (2021) examined the literature about the information and communication technologies in agriculture. Rejeb and Rejeb, (2020) and Park and Li, (2021) concluded that all the indicators of sustainability can be improved using blockchain.

Blockchain adoption in the supply chain is at a very early stage, although its application in different sectors is increasing rapidly (Choi et al., 2018; Kuo and Kusiak, 2019). Blockchain has a potential to reshape the entire supply chain by incorporating sustainable activities with a special focus on environment protection and social reforms (Tsai et al., 2021). There is limited literature available which covers that how blockchain will impact the supply chain in terms of its sustainability (Khanfar et al., 2021). The previous literature only covers the economic aspects of blockchain in the supply chain. Moreover, application areas for most of the literature reviews of blockchain are the food and agriculture supply chain and cold supply chain, in which transformational capabilities of blockchain through different attributes such as traceability, transparency, and cybersecurity are analyzed (Sunmola et al., 2021). Challenges and financial barriers in adoption and implementation of the blockchain are widely discussed in the previous literature. There exists a research gap as limited literature is available on the impact of blockchain on green practices in the supply chain. Similarly, the social impacts and challenges of blockchain adoption are discussed in the past, but the concept of social sustainability is very broad, which includes other dimensions such as community welfare, regional development, and employability. The

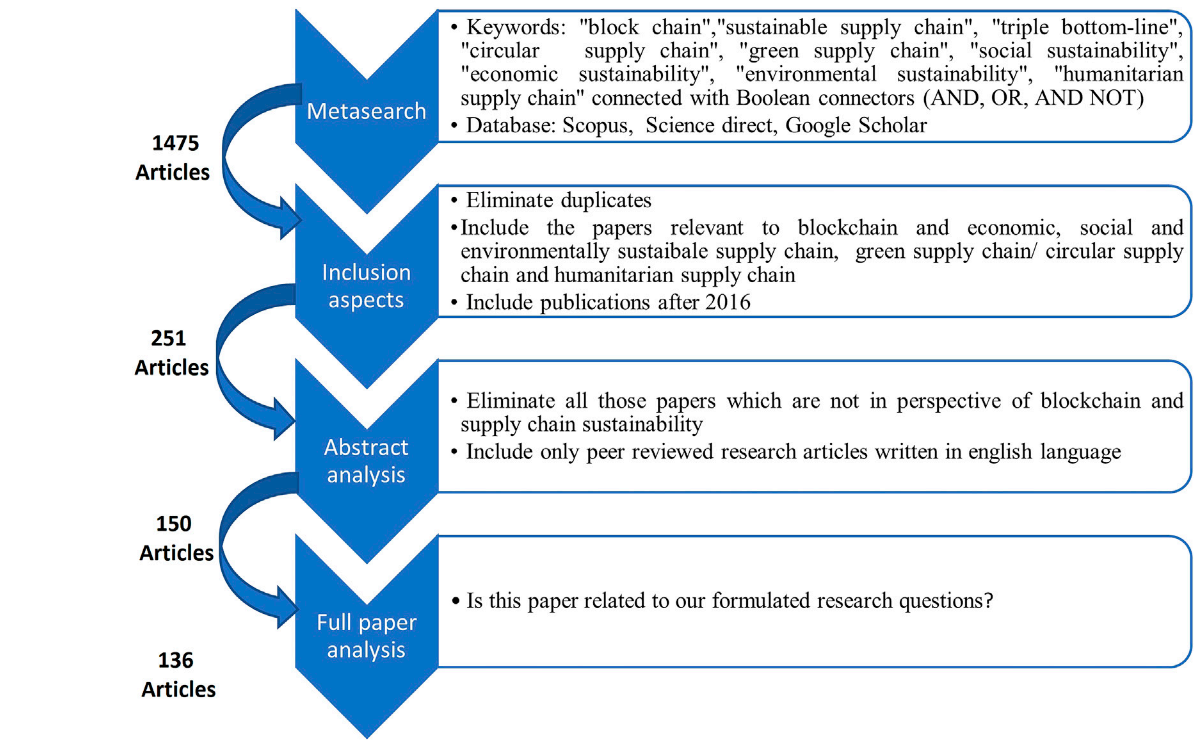

FIGURE 1 | Protocol for the systematic literature review.

humanitarian supply chain is the core topic of researchers, and the effects of digitalizing the supply chain on risk management and sustainability are still need to be explored, especially during the time of crisis. These research gaps are addressed in the current study.

The main objective of this study is to collect the articles from leading journals on the theme of blockchain in perspective of the sustainable supply chain. In this research, articles were collected and categorized on the basis of three basic indicators of (economic, environmental, and social) sustainability. Different models, frameworks, and case studies are included under the paradigm of sustainability. The scope for social sustainability is widened, and articles related to social welfare and the humanitarian supply chain are also included. The main contribution of this study is that it will not only provide the insights about the use of blockchain for the development of the green supply chain but also will help the researchers to evaluate this new technology for its environmental and social impacts as well. The article has the following structure. **Section 2** covers the methodology of the systematic literature review. **Section 3** is about the basic overview on the supply chain sustainability and blockchain. **Section 4** has a detailed review about the economic sustainability in the supply chain using blockchain. **Section 5** covers all the contents of the green supply chain/circular supply chain. **Section 6** describes the advantages of blockchain in the humanitarian supply chain and its social aspects. **Section 7** covers the practical implications of blockchain. **Section 8** is about conclusion.

2 METHODOLOGY OF THE SYSTEMATIC LITERATURE REVIEW

A literature review should be systematic in methodology, explicit in explaining the procedures, comprehensive in scope for all the included material, and reproducible for the people who are reviewing the same topic (Okoli and Schabram, 2010). The difference between traditional literature review and systematic literature review is that systematic review has clearly defined questions, comprehensive relevant study, and properly evaluated and synthesized results, and its main purpose is to make a summary of the best available research on a relevant topic transparently (Habib et al., 2016). Systematic literature review is a rigorous method to assess and evaluate the research in any area. For this research, systematic literature review (SLR) was adopted. There are four steps in a systematic literature review. These steps include planning, searching on a particular topic, screening, and extraction. Protocol for the systematic literature review is given in "**Figure 1**."

Planning: it is the phase in which research questions are formulated. The questions should be clear and explicit. The research questions in this research are the following:

RQ 1: What is the current literature on the intersection of blockchain and the sustainable supply chain?
RQ 2: What are the gaps and future research trends in improving the sustainability of the supply chain using

blockchain from economic, social, and environmental perspectives?

Searching: keywords were developed to search the articles relevant to blockchain and the sustainable supply chain, and these keywords were based on research questions. These articles were collected by using keywords: "blockchain" AND "logistics" OR supply chain" AND "social sustainability, AND "environmental sustainability," OR "green supply chain," AND "economic sustainability," AND "circular supply chain" AND "humanitarian supply chain". Scopus-indexed journals and the Scopus database were selected for data collection. Other forums such as Google Scholar and ScienceDirect were combined for search. The publications were selected from 2016 to 2022 because the concept of blockchain is at its early development stage.

Screening: the inclusion and exclusion criteria were used for the objectivity of research.

Inclusion criteria: the scope of this work was to study about blockchain and sustainability of the supply chain, so all articles are relevant to the application of blockchain in the green supply chain, circular supply chain, and the effects of blockchain on social sustainability. Moreover, articles related to economic sustainability through traceability, transparency, and visibility were also selected. We have included articles from peer-reviewed journals and limited conference articles, which are relevant to the previously described questions.

Exclusion criteria: the main emphasis of this study was on blockchain and triple bottom-line aspects of sustainability in the supply chain. The articles which do not fall in this category were excluded from the list.

Extraction: in the extraction phase, the articles are divided into three categories based on three dimensions of sustainability. The first category of articles is based on blockchain and economic sustainability in the supply chain. In this category, different characteristics of blockchain such as traceability, visibility, and transparency are discussed in detail. The second category is the blockchain-based green supply chain and circular supply chain. In the third category, articles are relevant to social sustainability and humanitarian supply chain management.

3 RESEARCH ON THE INTERFACE OF BLOCKCHAIN AND SUSTAINABLE SUPPLY CHAIN MANAGEMENT

Blockchain helps in achieving environmental sustainability as it helps companies to reduce carbon emissions (Xu et al., 2019). It creates a reputation-based mechanism that encourages participants to find the long-term solution to emissions because all the participants are fully aware of financial benefits of being a well-reputed organization (Esmaeilian et al., 2020). Blockchain can help in the detection of all counterfeit products (Duan et al., 2020). Tracking the products can help in reducing the rework which will help in reducing resource utilization and gas emissions (Badia-Melis et al., 2015; Li et al., 2020). If the manufacturing process becomes green, then environment friendly customers will prefer to purchase the green products (Martins and Pato, 2019). One method to achieve environmental sustainability is the imposition of a carbon tax as the product becomes expansive with a high tax of the carbon footprint, then the customer will prefer the product with a lower price (Lim et al., 2021). Blockchain can help in reducing the carbon footprint in the journey of products toward the end user (De Sousa Jabbour et al., 2018). The supply chain environmental analysis tool (SCEnAT) recommends an outline that will evaluate the emission of carbon of all entities used in supply chains, and its latest version is integrated with Internet of Things (IoT), blockchain, and artificial intelligence (Koh et al., 2013). IBM is developing green assets based on blockchain, which will help the organizations to track, measure, and reduce carbon emissions (Meyer et al., 2019; Upadhyay et al., 2021). The main framework for this research is shown in "**Figure 2**." The features of blockchain include consensus among partners, cybersecurity, immutability, smart contracts, and decentralization of information on a distributed ledger (Viriyasitavat et al., 2018). This excellent information sharing system will improve the traceability, transparency, trust, and responsiveness of the supply chain. Through smart monitoring and controlling of carbon emissions, the environmental sustainability can be improved. Similarly, through smart contracts, carbon taxation policy can be imposed and monitored regularly. The traceability of products and responsiveness of the supply chain will increase the trust of customers (Rodríguez-Espíndola et al., 2020; Thakur and Breslin, 2020). All of these characteristics of blockchain will be useful for monitoring and controlling the overall process of the humanitarian supply chain and firms involved in the supply chain will become socially more responsible. Total articles in this research article are divided into three categories.

1) Articles related to economic sustainability through different features of blockchain such as traceability, transparency, accountability, and visibility.
2) Articles relevant to the model development, theoretical framework, case studies, adoption challenges for blockchain in the supply chain, emissions reduction, green supply chain, and circular supply chain.
3) Articles related to the challenges in implementation of blockchain in the supply chain, its societal impacts, and humanitarian supply chain.

4 ECONOMIC SUSTAINABILITY IN THE SUPPLY CHAIN

Digitalization is transforming the supply chain; specifically, the food supply chain and consumer are more focused on environmental and socially sustainable products (Kittipanya-ngam and Tan, 2019). As a result, traceability, sustainability, and safety have become the core issues (Queiroz and Fosso Wamba, 2019; Wang Y.et al., 2019b). Blockchain technology is regarded as a disruptive and innovative technology and is considered to be the primary tool in the industry 4.0 (Ramadurai and Bhatia, 2019; Thylin and Duarte, 2019). The various features of the blockchain include traceability,

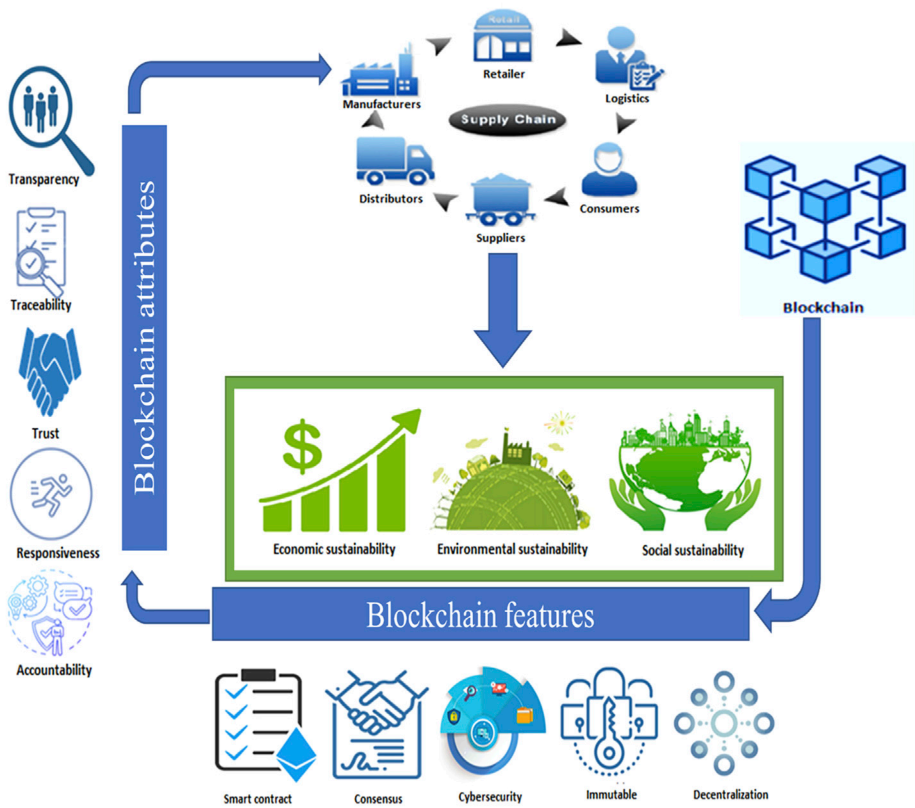

FIGURE 2 | Conceptual framework of transformation of the supply chain to attain triple bottom line through blockchain.

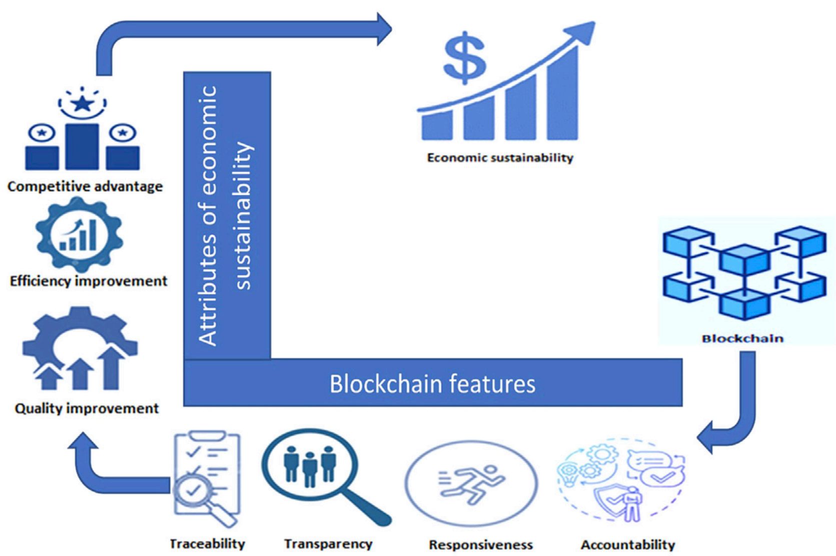

FIGURE 3 | Conceptual framework of economic sustainability of the supply chain through blockchain.

TABLE 1 | Models and framework development for the blockchain-based supply chain with economic sustainability in the agriculture, food, and healthcare sectors.

	Author	Objective	Solution approach	Area of application	Limitations and future research direction
1.	Feng, (2017)	The authors have built traceability system "HACCP" using blockchain.	Hazard analysis and critical control	Agriculture and food sector	Blockchain technology is rudimentary, and its main challenge is a scalability issue.
2.	Caro et al. (2018)	Authors developed and used a case in which they used two different blockchain implementation domains, Ethereum and Hyperledger.	Blockchain implementation through Hyperledger	Agriculture and food sector	Single-language in smart contracts and static structure for a record are the limitations.
3.	Shangping Wang et al. (2019)	Authors have proposed a blockchain-based traceability system.	Prototype development	Agriculture and food sector	The model should be tested through a large-scale practical case study.
4.	Dasaklis et al. (2019)	The researchers have developed a framework that defines the granularity levels of products based on the unique characteristics.	Conceptual framework using smart contracts	Agriculture and food sector	The proposed research is conceptual and requires empirical validation.
5.	Bechtsis et al. (2019)	This research is based on the two-stage supply chain of containerized food.	Hyperledger Fabric framework	Agriculture and food sector	The cost for the implementation of this framework is very high.
6.	Ronaghi, (2020)	The study is about the development of a model which evaluates the maturity of blockchain in the field of the agricultural supply chain.	Ranking the dimensions of blockchain	Agriculture and food sector	Their research is limited to a single-developing country.
7.	Machado et al. (2020)	A framework based on blockchain for effective project management is devised to solve the complexity of the record-keeping issue.	Architectural development using smart contracts	Agriculture and food sector	The developed framework should be empirically validated.
8.	Thakur and Breslin, (2020)	Authors have developed a product serialization method for the security of the supply chain of perishable goods.	Development of the product serialization method	Agriculture and food sector	Future research should be based on the use of this method for the automation of the product recall system.
9.	Liu et al. (2020)	This article proposes a structure of the supply chain based on integration of big data and blockchain.	Operation research	Agriculture and food sector	The proposed model does not explain the complex supply chain.
10.	Sensen Hu et al. (2021)	Researchers have constructed a framework of the organic agriculture supply chain (OASC) by leveraging the immutability of blockchain.	Conceptual framework	Agriculture and food sector	Blockchain technology must be explored for the balance between cost and efficiency.
11.	Eluubek Kyzy et al. (2021)	This article is about the establishment of the consortium through blockchain with the cybersecurity system.	Establishment of consortium based on blockchain	Agriculture and food sector	Future study should be based on economic and environmental aspects of sustainability.
12.	Maity et al. (2021)	The authors have developed and optimized a model of the supply chain of sausage.	Operation research	Agriculture and food sector	The research should be expanded to a large scale by considering the network of suppliers.
13.	Varriale et al. (2021)	The authors investigated the improvement in order and disruption event through modern technologies.	Simulation-based research	Agriculture and food sector	Technology implementation, management, and personal costs were not considered in the study.
14.	Kim and Laskowski, (2018)	In this research, the authors have analyzed the traceability ontology to convert some of its representation to smart contracts.	Conceptual research	Pharmaceuticals	This is conceptual research and requires validation through a case study.
15.	Yong et al. (2020)	The purpose of this article is to develop a "vaccine blockchain" system.	Machine learning	Pharmaceuticals	Future work should be based on real data sets.
16.	Yang, (2021)	In the medical field, the false report spreading trend is increasing, so tracing and tracking is required to gain credibility in the supply chain.	Prototype development	Healthcare sector	Validation of the prototype on a larger scale is required in future research.
17.	Zhu et al. (2021)	Authors have developed a method for the tracing of information on infectious diseases.	Programming using Python 3.7	Healthcare sector	The extension of this research may be based on the use of Hyperledger Fabric.

privacy, immutability, decentralization, and consensus mechanism (Sikorski et al., 2017). The outcomes of the blockchain are agility, resilience, responsiveness, and sustainability (Stranieri et al., 2021). The conceptual framework of economic sustainability of the supply chain using blockchain is shown in "**Figure 3**." The main features of blockchain are its transparency, effective traceability, responsive supply chain, and accountability as discussed in previous sections. By incorporating these features in supply chain processes the quality of products or services will be improved (Chang Y. et al., 2019; Bechtsis et al., 2019). It also will improve the process efficiency and thus will provide the competitive advantage.

4.1 Model Development, Framework Related to Economic Sustainability, and the Blockchain-Based Supply Chain in Agriculture, Food, and Healthcare Sectors

Blockchain is an excellent mechanism of sharing information. Its applications in the food, agriculture, and healthcare sectors

TABLE 2 | Models and framework development for the blockchain-based supply chain and economic sustainability for different sectors.

Sr	Author	Objective	Solution approach	Area of application	Limitation and future research direction
1.	Sahebi et al. (2022)	The authors have identified the enablers of blockchain in the renewable energy supply chain.	Fuzzy interpretive structural modeling	Energy sector	Validation through a case study should be conducted in future research.
2.	Francisco and Swanson, (2018)	The unified theory of acceptance and use of technology was used to develop a framework.	Conceptual framework	Technology sector	The impact of company culture and social acceptance should be analyzed for blockchain adoption.
3.	Longo et al. (2019)	Authors have designed a software connector for the blockchain and enterprise information systems.	Developed software connector	Technology sector	A comprehensive study is required to explore the benefits of blockchain.
4.	Fan et al. (2020)	Successful adoption of blockchain depends on the awareness of customers about traceability issues.	Operation research	Technology sector	Empirical validation is required for a proposed model.
5.	Bai and Sarkis, (2020)	This article presents the performance measures of blockchain in terms of sustainability.	Hybrid group decision, integrated hesitant fuzzy set	Technology sector	It is a conceptual model, and it lacks the real-world practical application.
6.	Yadav and Singh, (2020b)	The main task of this article is to justify that blockchain is more sustainable.	Quantitative research methodology	Technology sector	The findings of this article cannot be generalized due to the limited number of respondents.
7.	Helo and Shamsuzzoha, (2020)	This article is about the development of the portal system for effective tracing and tracking.	Cloud-based portal	Technology sector	Integration of blockchain with ERP and transport management systems should be tested empirically.
8.	Budak and Çoban, (2021)	The purpose of this article is to evaluate the impacts of blockchain adoption in the supply chain.	Cognitive maps method	Technology sector	Future studies should be based on the use of cognitive maps in different industrial sectors.
9.	Erol et al. (2022)	The authors have ranked the most beneficial critical functions of the sustainable supply chain.	Fuzzy SWARA	Technology sector	The research has employed very limited number of criteria and experts.
10.	Figorilli et al. (2018)	This research is about the development of architecture for the wood supply chain.	Conceptual architecture	Wood supply chain	This conceptual architecture should be empirically validated.
11.	Shuchih Ernest Chang et al. (2019)	The authors have proposed a framework of blockchain using smart contracts.	Conceptual framework	Supply chain re-engineering	The future study should be based on using this proposed framework in different industries.
12.	Li et al. (2019)	The authors have developed a prototype-automated customer service based on automated machine learning and blockchain.	Automated machine learning	Customer service sector	Their proposed platform was lacking privacy issues.
13.	Montecchi et al. (2019)	They have developed the framework for the provenance knowledge based on blockchain.	Development of framework	Risk mitigation	This is a conceptual research study and is not validated empirically.
14.	Helo and Hao, (2019)	Authors developed a solution for the tracking of parcels.	Development of the logistics monitoring system	Postal services	Scenario analysis will measure the qualitative and quantitative effects of this proposed model.
15.	Liu and Li, (2020)	The focus of this research is e-commerce.	"Hierarchical deterministic wallet" technique	E-commerce	The research is not empirically validated.
16.	Naderi et al. (2021)	This article is about the calculation of the consumed energy in the sustainable supply chain.	Exergy analysis	Energy sector	Uncertainties in the supply chain network are not considered.
17.	Tian et al. (2020)	Authors used the algorithm of long- and short-term memory to predict the satisfaction of customers.	Machine learning algorithm	Urban logistics	A limited number of indicators are used to measure customer satisfaction.
18.	Wu et al. (2017)	They provided a crowd-validated framework that balanced the problems of contemporary enterprises.	Conceptual framework	Shipment industry	For complex networks in real scenarios, several challenges may be encountered for this model.
19.	Yiu, (2021)	Blockchain is considered the best solution for counterfeiting and malicious modifications.	Conceptual research	Supply chain industry	This is conceptual research and is not validated empirically.
20.	Asuncion et al. (2021)	Authors have performed an assessment for the different layers of blockchain for identification of different challenges.	Graph-based approach	Defense industry	In this research, the used case study was very simple at the pilot phase.
21.	Yousefi and Mohamadpour Tosarkani, (2022)	The study is about the relation of blockchain and supply chain sustainability through smart contracts, traceability, and transparency.	Fuzzy cognitive map	Mineral supply chain	Blockchain is at a very early stage, and it lacks experience experts.

are rapidly increasing due to the traceability system. Perishable foods, vaccines, and cold supply chains require this disruptive technology to control the wastage of food and temperature-controlled pharmaceutical products (Óskarsdóttir and Oddsson, 2019). The researchers have developed different models and frameworks in the perspective of economic sustainability through transparency, traceability, visibility, and accountability in supply by using blockchain. A list of differently proposed frameworks and models related to blockchain and economic sustainability in the supply chain is given in "**Table 1**." The main features of these models are as follows:

1) Most of the developed models and proposed frameworks are based on the agriculture and food sectors, and there are some articles relevant to the pharmaceutical and healthcare sectors.
2) The main emphasis is to develop models and frameworks based on smart contracts and for traceability solutions as contracts can help develop and improve the relationship among all the network of the supply chain. It improves data sharing among all the actors, and it is a continuous improvement process.
3) Some articles are based on the conceptual study and other solution approaches are used including Ethereum and Hyperledger Fabric, machine learning, programming using Python, "SWARA" method, serialization method, mathematical modeling, and prototype development.

For many years, food security has been a large problem. The old methods for logistics and transportation of agri-food are not feasible to match the demands of the market. The traceability system, based on radio frequency identification, for the agri-food value chain should be designed for the safety of food. In this perspective, Bechtsis et al. (2019) presented a framework that integrates all the information of containerized food on a single and secured platform of sharing information called the blockchain. Ronaghi (2020) researched in three stages: in the first phase, they used the SWARA method for ranking different dimensions of blockchain: in the second phase, they designed a model for the evaluation of maturity of blockchain for the agriculture sector. In the third phase, they evaluated their model using a questionnaire. Their findings showed that transaction records and smart contracts are of higher importance in all dimensions of the supply chain.

4.2 Model Development, Framework Related to Economic Sustainability, and the Blockchain-Based Supply Chain in Different Sectors

One of the basic benefits of blockchain is the reliable transaction of payment and money transfer (Rubio et al., 2018). There are a large number of examples for the successful implementation of blockchain in the industrial sector, product development, and governance mechanism. The main purpose for using this application is to restructure the supply chain (Sundarakani et al., 2021). Different models and framework development based on blockchain in perspective of economic sustainability for different sectors are listed in "**Table 2**." Some important points are as follows:

1) Specific articles are related to the technology implementation, software development, or different characteristics of blockchain. These are categorized as the technology sector.
2) The other areas of applications are postal services, wood supply chain, energy sector, urban logistics, and defense industry.
3) Various articles are conceptual; other solution approaches used are fuzzy cognitive map, automated machine learning, hierarchical deterministic wallet, cloud-based portal, graph-based approach, development of blockchain-based logistics monitoring system (BLMS), fuzzy MICMAC, fuzzy analytic network process, quantitative analysis, and operation research techniques.

The main features of the blockchain are decentralization, audibility, and cybersecurity (Hu D. et al., 2021). Blockchain is a transparent system across the whole supply chain as data cannot be manipulated due to minimum role of mediators. In this background, Yadav and Singh (2020b) compared the performance of a blockchain-based supply chain and a traditional supply chain. They identified the characteristics of blockchain and analyzed them through modeling on fuzzy-interpretative structural modeling. Naderi et al. (2021) provided an optimized model which was multi-objective and based on exergy analysis for the sustainable supply chain. The model was simulated on real-time data in the dairy sector of Iran. The rapid changing of the demand of consumers due to urbanization is continuously affecting the logistics industry, which is a challenge for a logistic service provider. In this background, Tian et al., (2020) proposed an evaluation approach for customer satisfaction based on blockchain. A simulation based on experimental work was performed, and the feasibility was evaluated for the proposed model.

4.3 Case Studies Relevant to Economic Sustainability in the Blockchain-Based Supply Chain in the Agriculture, Food, and Healthcare Sectors

The basic characteristic of blockchain is the shared information on equality base as no individual has access to change the information without the approval of other participants (Liu et al., 2020). Case studies and empirical pieces of evidence of blockchain are not in the mature stage; however, different researchers have conducted case studies and developed theoretical inferences. Different case studies conducted in the agriculture, food, dairy, aquaculture, and pharmaceutical sectors are listed in "**Table 3**."

1) The different solution approaches used in these case studies are Ethereum smart contracts, conjoint analysis, analytical hierarchy process, qualitative and quantitative research methodology, and prototype development.

TABLE 3 | Case studies related to economic sustainability in the blockchain-based supply chain in agriculture, food, and healthcare sectors.

Sr	Author	Objective	Solution approach	Area of application	Limitation and future research direction
1.	Paul et al. (2021)	A conceptual framework was developed related to the tea supply chain.	Quantitative research methods	Agriculture and food sector	It should be explored that how blockchain will solve the legal and ethical issues in the tea supply chain.
2.	Salah et al. (2019)	The authors have used smart contracts for the traceability of soybean in agriculture.	Framework development	Agriculture and food sector	Future work should be based on governance structure, scalability, standards, and regulations of blockchain.
3.	Kittipanya-ngam and Tan (2019)	The researchers have proposed a framework of the food supply chain and validated by a firm in Thailand.	Case studies	Agriculture and food sector	The validation of their framework requires a comprehensive study on other types of food supply chains.
4.	George et al. (2019)	The authors developed a prototype for the restaurants.	A prototype implementation	Agriculture and food sector	The prototype is specific to the food supply chain of restaurants.
5.	Behnke and Janssen, (2020)	This article recognized the boundary conditions to enhance traceability.	Qualitative methods	Agriculture and food sector	Short-term solutions are not discussed for quick implementation of blockchain.
6.	Bumblauskas et al. (2020)	The main goal of this article is to explain the adoption of blockchain in the supply chain of eggs.	Case studies	Agriculture and food sector	It is difficult to quantify the benefits of blockchain.
7.	Köhler and Pizzol, (2020)	This article provides insights about the benefits of social and environmental sustainability.	Qualitative research methodology	Agriculture and food sector	A longitudinal study is required for the validation of conclusions.
8.	Saurabh and Dey, (2021)	The research is based on a case study of the grape wine supply chain.	Rating-based conjoint analysis	Agriculture and food sector	Their proposed architecture should be expanded at the multistage level.
9.	Cao et al. (2021)	The main aim of this study is to analyze the trust development through blockchain in the beef supply chain.	Case-based prototype development	Agriculture and food sector	Future studies should consider a large number of producers, consumers, and other stakeholders.
10.	Stranieri et al. (2021)	Authors have proposed the conceptual framework based on performance dimensions such as flexibility, food quality, responsiveness, efficiency, and transparency.	Qualitative research methodology	Agriculture and food sector	The research is specific to only three firms with an already well-structured supply chain.
11.	Niu et al. (2021)	Researchers have investigated the effects of blockchain on suppliers and retailers.	Model development	Agriculture and food sector	The developed model has not considered the output uncertainty.
12.	Mukherjee et al. (2021)	The objective of this article is to highlight the benefits of blockchain in terms of sustainability and resilience.	Analytical hierarchy process	Agriculture and food sector	The proposed method should be used for the multi-tier supply chain.
13.	Masudin et al. (2021)	The finding of authors is that blockchain affects the traceability system, and effective tracing has positive effects on the performance.	Quantitative research methodology	Agriculture and food sector (cold supply chain)	A comprehensive study is required to determine different variables required to measure the performance.
14.	Casino et al. (2020)	The authors have developed secure architecture for the food supply chain.	Validation through a case study	Dairy sector	Blockchain technology has a limitation as it cannot store a large amount of data.
15.	Tan and Ngan, (2020)	The study is specific to the dairy sector where blockchain is used to solve the traceability issues.	Qualitative research methodology	Dairy sector	The research is conducted in the prospect of only a single country, Vietnam.
16.	Kshetri, (2018)	The study explains the different benefits of the implementation of blockchain.	Case studies	Retail, defense, fishing, and pharmaceuticals	The study did not consider the dynamic capabilities of all the companies.
17.	Azzi et al. (2019)	The authors have conducted case studies to analyze how blockchain can provide a reliable, authentic, and transparent system.	Validation through case studies	Food and pharmaceutical industry	A longitudinal study is required to validate the long-term benefits.
18.	Tönnissen and Teuteberg, (2020)	The authors have conducted case studies to analyze the effects of blockchain for the logistics industry.	Validation through case studies	Multiple sectors	Case studies only consider the static view and do not consider the dynamic models.
19.	Kshetri, (2021)	In this article, multiple case studies are analyzed in developing countries.	Case studies	Retailers and the food sector	Framework should be developed integrating IoT, RFID tags, and satellite imagery.
20.	Dwivedi et al. (2020)	The presented blockchain-based scheme is about the pharmaceutical supply chain.	Development of the blockchain-based mechanism	Pharmaceutical industry	The proposed scheme does not consider the traceability of temperature-controlled drugs.
21.	Badhotiya et al. (2021)	This study is about blockchain in the supply chain of pharmaceuticals.	Assessment model	Pharmaceutical industry	A longitudinal study is required to analyze long-term use of blockchain.
22.	Uddin, (2021)			Pharmaceutical industry	

(Continued on following page)

TABLE 3 | (*Continued*) Case studies related to economic sustainability in the blockchain-based supply chain in agriculture, food, and healthcare sectors.

Sr	Author	Objective	Solution approach	Area of application	Limitation and future research direction
		In this article, the authors have proposed a blockchain-enabled Medledger system to track and trace the drugs.	Drug traceability framework		Hyperledger Fabric technology is facing challenges such as governance, scalability, and privacy.
23.	Adarsh et al. (2021)	The research is based on the integrated technology of big data and blockchain.	Development of mobile application	Healthcare sector	The extension of a proposed application in developed countries is the future scope.
24.	Garrard and Fielke, (2020)	The authors have explored the ability of blockchain to the provenances of the supply chain.	Qualitative research methodology	Aquaculture enterprises	The concept of traceability is partially applied in this research.
25.	Tsolakis et al. (2021)	The research is about the design of a food supply chain based on blockchain.	Case study	Aquaculture enterprises	There was limited participation of respondents.

2) The main characteristics of blockchain in the supply chain such as flexibility, efficiency, responsiveness, and transparency are discussed in detail.

Blockchain is used to keep the record of each activity in the supply chain. This record is shareable, traceable, authentic, and legitimate. In this background, Kshetri (2021) conducted multiple case studies and assessed the environmental and social impacts of blockchain. Blockchain technology also uses diverse technologies such as IoT, QR codes, RFID tags, and satellite imagery (Kshetri, 2017). Cao et al. (2021) have conducted a study with a partnership of Australian agricultural processors and developed a mechanism of human–machine reconciles with an overall focus on traceability in the beef supply chain system. Different challenges faced by the pharmaceutical industry involve counterfeit and other operational issues. (A et al., 2021) worked on traceability problems of vaccines and developed a model based on blockchain and big data to track the handling of vaccine in cold storage in India. Digitalization has played an important role in the sustainable agriculture supply chain but there is limited research about the factors which motivate to adopt digital technologies (Davis, 1993). In this perspective, Saurabh and Dey (2021) identified some drivers which are the motivators to adopt blockchain. These drivers are price, trust, traceability, disintermediation, compliance, coordination, and control. Köhler and Pizzol (2020) conducted the six case studies on blockchain-based food supply chains and developed a framework for its assessment using components including the technique, organization knowledge, and product (Seawright and Gerring, 2008).

4.4 Case Studies Relevant to Economic Sustainability in the Blockchain-Based Supply Chain in Different Sectors

A blockchain-based system can reduce the intermediaries and need for centralized authority because it provides the transaction record, efficiency, and transparency (Pournader et al., 2019). The sustainability effects are linked to visibility and traceability in the supply chain. The articles related to the case studies in different sectors are listed in "**Table 4**."

1) The area of application of these case studies is supply chains of chemical, cargo, shipping, logistics, retail, aviation, textile, construction, automotive, trading, mineral, and oil sectors.
2) Some articles are conceptual based; however, different solution approaches used in some case studies are action research through case studies, quantitative research methodology, qualitative research methodology, and prototype development.
3) Some case studies are based on the development of Ethereum-based consortiums, algorithm based on small contract, simulation-based models, and operation research techniques.

4.5 Critical Success Factors, Barriers, and Challenges in Adoption of Blockchain for Economic Sustainability in the Supply Chain

Blockchain is continuously gaining the attention of researchers and practitioners, and it has a potential to bring breakthroughs in the entire supply chain (Kamble et al., 2018). Some case studies of blockchain in different supply chain fields including agriculture, food, health, and manufacturing sectors are discussed in previous sections. Improvement in sustainability includes different dimensions including transparency, traceability, visibility, efficiency, and green practices (Yadav et al., 2020). The adoption of this technology has not gained much acceptance for several years (Dutta et al., 2020). The barriers and challenges for adoption of blockchain for an economically sustainable supply chain are critically examined, and its critical success factors are discussed. Details of relevant articles are given in "**Table 5**."

1) These challenges and barriers are in different areas of applications such as the agriculture and food sectors, pharmaceutical, manufacturing sector, maritime industry, fashion industry, small and medium enterprises, and local and global supply chains.
2) Most of the researchers have used the solution methodology for identification and ranking of challenges and barriers, which is the decision-making trial and evaluation

TABLE 4 | Case studies related to economic sustainability in the blockchain-based supply chain for different sectors.

Sr	Author	Objective	Solution approach	Area of application	Limitation and future research direction
1.	Sikorski et al. (2017)	The objective of this study was to find the applications of blockchain in industry 4.0.	Process flowsheet models	Chemical industry	A longitudinal study is required for validation of the proposed model.
2.	Sundarakani et al. (2021)	A case study of different industries is undertaken to analyze the effects of blockchain adoption.	Action research	Cargo and chemical industry	Future research should employ the techniques of primary data collection.
3.	Yang, (2019)	The study is about the application of blockchain.	Quantitative methodology	Shipping industry	The research is limited to only one industry.
4.	Ahmad et al. (2021)	The authors have developed an architecture to highlight the components and participants to automate the logistics of ports.	Blockchain-based architectures	Logistics of ports	There is a need to expand the usage of developed architecture in other sectors.
5.	Min, (2019)	This article unveils the charisma of blockchain to increase resilience.	Conceptual research	Technology sector	It is a conceptual research study and requires a case study for its validation.
6.	Fosso Wamba et al. (2020)	The main aim is to validate the performance of a blockchain-based supply chain.	Quantitative research methodology	Technology sector	More attributes as moderators or mediators should be explored.
7.	Lahkani et al. (2020)	In this research, blockchain was incorporated into the B2B global supply chain.	Conceptual research	E-commerce sector	It is a conceptual research study and requires a case study for its validation.
8.	Xu et al. (2020)	The authors have discussed the different characteristics of blockchain such as transparency and traceability.	Case studies	Retail sector	Technical and regulatory constraints for the adoption of blockchain are not discussed.
9.	Sund et al. (2020)	The authors have developed a prototype to manage the supply chain efficiently.	Prototype development	Retail sector	The developed prototype is not optimized for best performance.
10.	Di Vaio and Varriale, (2020)	This research contributes by reviewing the literature about the implications of blockchain in operation management.	Airport collaborative decision making	Aviation industry in Italy	Future studies must also take into account the other international airports.
11.	Ho et al. (2021)	This research brings a system for the accurate traceability of spare parts to improve the inventory management.	Blockchain-based system architecture	Aviation industry	The proposed architecture only focuses on information gathering and does not explain data analytics.
12.	Donghui Hu et al. (2021)	Researchers have proposed a blockchain-based system for the data sharing.	Development of data trading platform	Trading sector	Empirical validation of this architecture is required.
13.	Agrawal et al. (2021)	A framework is proposed for the traceability of organic cotton through a mass-balancing validation mechanism.	Simulation-based model	Textile sector	Future research should be focussed on formulating a customized smart contract for different sectors.
14.	Kusi-Sarpong et al. (2022)	The study investigates the relation of blockchain, intellectual capital, and sustainable production.	Quantitative research methodology	Textile sector	Use of cross-sectional data is a further limitation of this study.
15.	Aslam et al. (2021)	The study is based on the sustainable supply chain practices in Pakistan for the oil industry.	Quantitative research methodology	Oil industry	The relationship between features of blockchain and supply chain practices should be empirically validated.
16.	Zhaojingang et al. (2020)	The authors have developed a framework based on blockchain. They have used an algorithm of smart contracts.	Development of algorithm	Construction industry	The concept of blockchain in the construction industry is in the early stage, and it should be further validated.
17.	Calvão and Archer, (2021)	The authors have conducted qualitative research from different people of the mineral supply chain.	Qualitative research methodology	Mineral supply chain	The benefits of digitalization should be the quantified mineral supply chain.
18.	Kuhn et al. (2021)	An architecture is proposed to gain transparency in the automotive supply chain.	Prototypical development	Automotive sector	The concept should be used in manufacturing to automate the tracing system.
19.	Kamble et al. (2021b)	The main objective of this study is to investigate the effect of the information-enabled supply chain on its sustainable performance.	Quantitative research methodology	Automotive sector	The study emphasizes only on economic aspects of sustainability.
20.	Gopalakrishnan et al. (2021)	This study is about the application of blockchain in solid waste management.	Operation research	Solid waste management	Cost aspects in this model of a supply chain are not considered.

laboratory (DEMATEL); the other methodologies used are the analytic hierarchical process, a fishbone diagram and Political, Economic, Social, Technological, Legal, and Environmental (PESTLE) analysis, intuitionistic fuzzy AHP (multi-criteria decision making), fuzzy VIKOR, qualitative research methodology, and quantitative research methodology "interpretive structural modeling (ISM)."

3) Most of the identified barriers can be categorized into technical, organizational, and environmental barriers.

Blockchain is a revolutionary technology that will transform the entire supply chain, but there are many challenges and barriers in its implementation. In this context, Farooque et al. (2020) have collected the data from three organizations of China

TABLE 5 | Article list about different challenges in adoption of blockchain for an economically sustainable supply chain.

Sr	Author	Objective	Solution approach	Area of application	Limitation and future research direction
1.	Kamble et al. (2020)	Authors have identified the enablers of blockchain.	Decision-making trial and evaluation laboratory	Agriculture and food sector	Future studies should include the cause-and-effect diagram for these enablers.
2.	Tayal et al. (2021)	In this article, a total of nine critical success factors are identified for the food supply chain.	Quantitative research methodology	Agriculture and food sector	A limited number of critical success factors are considered.
3.	Alharthi et al. (2020)	The main objective of this article is to evaluate the role of blockchain for the pharmaceutical industry.	Conceptual model	Pharmaceutical industry	The research is KSA-based and it has considered only three health providers.
4.	Nayak et al. (2019)	In this article, different success factors for adoption of blockchain for the green supply chain are identified.	"Interpretive structural modeling (ISM)"	Small and medium enterprises	These identified success factors are for the developing country India and cannot be generalized.
5.	Lohmer and Lasch, (2020)	The authors have conducted semi-structured interviews from experts of the industry to analyze the barriers during the adoption of blockchain.	Qualitative research methodology	Manufacturing sector	A comprehensive study is required on identified barriers.
6.	Farooque et al. (2020)	In this article, researchers have prioritized the barriers of blockchain adoption.	Fuzzy decision-making trial and evaluation	Manufacturing sector	Data are gathered only from three China-based organizations.
7.	Zhou et al. (2020)	The researchers have conducted a case study in the Singapore's maritime industry to identify critical success factors in the adoption of the blockchain technology.	Analytic hierarchical process, a fishbone diagram, and PESTLE analysis	Maritime industry	Their study is limited to the Singapore maritime industry.
8.	Ar et al. (2020)	This research is a framework that guides the decision makers for the adoption of blockchain in logistics.	Intuitionistic fuzzy AHP and fuzzy VIKOR	Large-scale logistics company	A more comprehensive study is required to consider all the required criteria for blockchain adoption.
9.	Caldarelli et al. (2021)	The main objective of this article is to identify different barriers in adoption of blockchain for a sustainable fashion supply chain.	Qualitative research methodology	Fashion industry	There should be some case studies based on quantitative studies to address the gaps in research.
10.	Saberi et al. (2018)	In this article, blockchain and smart contracts are examined.	Conceptual research	Supply chain management	Research is more focused on economic sustainability only.
11.	Yadav and Singh, (2020a)	The authors have identified critical successful factors.	Quantitative research methodology	Supply chain management	Data are collected from 195 respondents only, and the study has considered only 12 critical factors.
12.	Hastig and Sodhi, (2020)	Critical success factors for the implementation of blockchain are companies' capabilities, technical maturity, and governance.	Descriptive research	Supply chain management	Research is on a descriptive base and requires empirical validation.
13.	Ghode et al. (2020)	The authors identified different challenges for the implementation of blockchain.	Quantitative research methodology	Supply chain management	The research considered the participation of only five researchers and practitioners.
14.	Kouhizadeh et al. (2021)	This article presents a comprehensive overview of barriers for adoption of blockchain.	Decision-making trial and evaluation laboratory	Supply chain management	Interdependencies of sub-factors of these barriers need to be explored.
15.	Bischoff and Seuring, (2021)	Authors have presented a summary of barriers in the implementation of traceability systems.	Conceptual research	Supply chain management	The research is conceptual-based and not empirically validated.

about the experience of blockchain implementation. Their findings were that technological immaturity, poor organizational policies, and lack of government regulations are the main barriers. Saberi et al. (2018) examined the applications of blockchain in the context of sustainability. The important part of this critical examination is that how blockchain can overcome the barriers during its adoption. These barriers are categorized as intraorganizational, interorganizational, technical, and external barriers. Alharthi et al. (2020) explored the challenges in the adoption of blockchain for the pharmaceutical industry. The main issues found are lack of integration of this technology in the health system, lack of coordination among stakeholders, and poor demand forecasting of medicines (Zhou et al., 2020). Data were gathered from the 30 maritime professionals, and the analytical hierarchical process ("AHP") (and PESTLE analysis were applied to identify critical success factors.

The future work should be based on the development of a model or framework which considers all dimensions of sustainability including social, economic, and environmental perspectives. The model should be empirically validated for multiple sectors to draw a generalized conclusion, and all the benefits should be quantitatively measured. These frameworks and architecture should consider the other technologies which will be integrated with blockchain for data collection such as the Internet of Things, QR codes, RFID, and artificial intelligence.

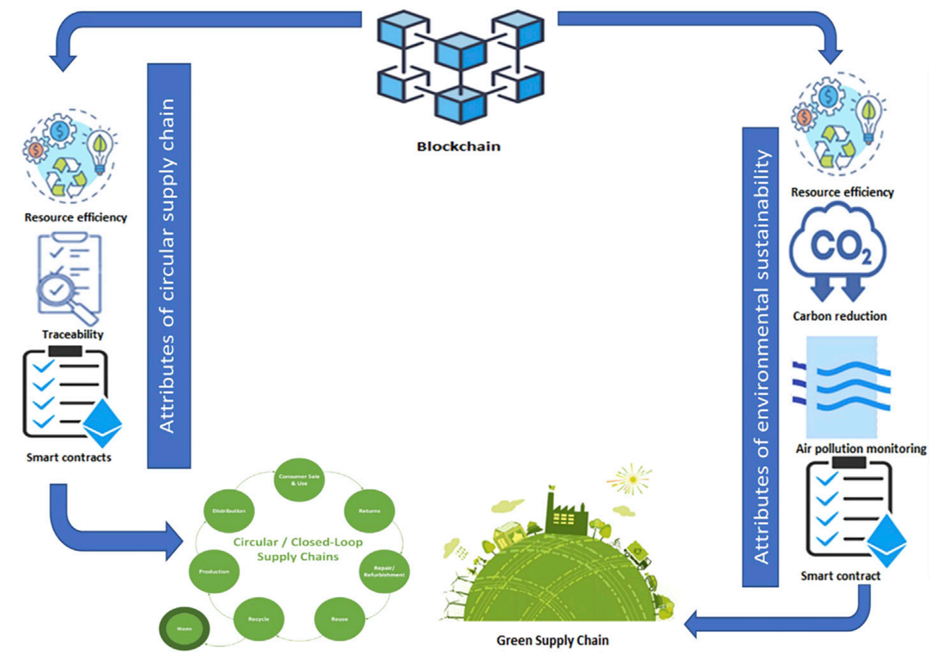

FIGURE 4 | Conceptual framework of transformation of the supply chain to the green/circular supply chain.

TABLE 6 | Models and frameworks related to the blockchain-based green/circular supply chain.

Sr	Author	Objective	Solution approach	Area of application	Limitation and future research direction
1.	Casado-Varaa et al. (2018)	In this article, the author proposes a model of the supply chain.	Conceptual framework	Agriculture and food sector	In their model, they did not perform any economic evaluation.
2.	Bai et al. (2021)	This article proposes a framework of the green supply chain, which is based on a non-cooperative game.	Bayesian formula	Agriculture and food sector	The research is simulation-based and did not provide validation.
3.	Manupati et al. (2019)	The main aim of the research is to develop a blockchain-based model, with the main purpose to monitor the performance of the supply chain.	Mixed integer non-linear programming	Technology sector	The proposed model should be validated in different sectors such as hospitals, railways, and education.
4.	Treiblmaier, (2019)	This article is a framework about the integration of the physical internet and blockchain.	Conceptual framework	Technology sector	The effects of the blockchain technology for the triple bottom line should be quantified and measured.
5.	Bill Wang et al. (2020)	This article presents a system architecture of a circular supply chain integrated with blockchain for the fast fashion industry.	Conceptual architecture	Fashion industry	The input data should be obtained from multiple stakeholders.
6.	Tan et al. (2020)	The main objective of this article is to develop a green logistics-based framework integrated with blockchain.	Conceptual framework	Logistics	There is also a need to assess the risks while adopting the blockchain.
7	Centobelli et al. (2021)	The article suggests a framework called integrated Triple Retry to design the circular supply chain.	Conceptual framework	Waste management	It is a conceptual framework and requires validation.

5 BLOCKCHAIN-BASED CIRCULAR/ GREEN SUPPLY CHAIN MANAGEMENT

A sustainable supply chain is the flow of resources and information from supplier to end customer while considering the financial, societal, and environmental performances (Chen et al., 2014). The firms are focusing to increase the technical capabilities without affecting the triple bottom-line (Casino et al., 2019). Blockchain is used in different countries to control carbon generation efficiently. The conceptual model for the blockchain-based green supply chain or circular supply chain is shown in **Figure 4**. The two concepts discussed in this model are to form the circular supply chain and green supply chain by using the blockchain technology. The model of the circular supply chain urges the producers and manufacturers to remake and reuse the discarded material to make it more economical and environmentally

TABLE 7 | Case studies for the blockchain-based green/circular supply chain.

Sr	Author	Objective	Solution approach	Area of application	Limitation and future research direction
1.	Friedman and Ormiston, (2022)	The findings of authors reveal that blockchain can ensure traceability, sustainability, and fair food supply chain.	Qualitative research	Agriculture and food sector	The food supply chains are very diverse. The findings of this study cannot be generalized.
2.	Kouhizadeh and Sarkis, (2018)	The article enlists the core dimensions of blockchain for the green supply chain.	Conceptual research based on the case study	Green supply chain	Their research provides only a conceptual overview of blockchain and the green supply chain.
3.	Mastos et al. (2021)	The waste-to-energy concept is proposed, developed, and used in a case study for its evaluation.	ReSOLVE model (regenerate, share, optimize, loop, virtualize, and exchange)	Supply chain management	Future studies should also consider the monitoring of the effects of the circular supply chain on air pollution.
4.	Park and Li, (2021)	Authors conducted case studies to compute the effects of blockchain on triple bottom line of sustainability.	Case study	Supply chain	The impact of blockchain should be investigated from the lens of suppliers, customers, and distributors.
5.	Czachorowski et al. (2019)	The study is about the proposed methods for the effective utilization of the blockchain technology.	Conceptual research based on case study	Maritime industry	The research did not quantify the effects of blockchain on sustainability.
6.	Esmaeilian et al. (2020)	The authors summarized the literature on the industry from the perspective of a sustainable supply chain.	Conceptual research	Social manufacturing	Future studies should be based on the optimization of business strategies to achieve sustainable goals.
7.	Khan et al. (2021)	The research examines the effect of blockchain on sustainable practices in the supply chain.	Quantitative research	Manufacturing sector	A comprehensive cost/benefit analysis is required for the adoption of blockchain in different sectors.
8.	Ajwani-Ramchandani et al. (2021b)	In this article, multiple and in-depth case studies are conducted to analyze the effectiveness of blockchain.	Empirical validation through a case study	Packaging waste	The main research focus was on emerging economies only.
9.	Ajwani-Ramchandani et al. (2021a)	The main objective of this research is to develop a concept that how blockchain and the circular supply chain can be integrated into the framework of linear economy.	Qualitative research methodology	Solid waste management	Future studies must consider artificial intelligence along with blockchain to develop the framework of circular economy.
10.	Nandi et al. (2021)	In this article, the author provides insights to form a resilient, sustainable, and transparent supply chain affected by COVID-19.	Conceptual research based on case study	COVID-19	Future research should be based on multiple studies for the use of blockchain and circular economy.

sustainable. Different characteristics of blockchain such as traceability and smart contracts are useful for the monitoring, controlling, and reducing the carbon footprints during different stages of supply chain. The air pollution monitoring will be useful for the carbon reduction. Similarly smart contracts can be developed to impose the carbon tax policies. For example, blockchain is used in Northern Europe to motivate the people for financial rewards in exchange for depositing the recyclables' plastic bottles or cans. Proper traceability of products through blockchain and resource efficiency can be useful to develop the complete structure of the close loop supply chain.

5.1 Model Development, Framework, and Architecture Related to Blockchain-Based Green and Circular Supply Chains

Blockchain is an assurance of transparency and human rights. The research on blockchain for the environmentally sustainable supply chain is in an early phase, but it is evolving rapidly. A list of articles for different models, architecture, and frameworks by different researchers are given in "**Table 6**" and discussed in detail. The main features of these research articles are as follows:

1) These models and frameworks are developed in different sectors such as waste management, the fashion industry, and the food and agriculture sectors.
2) Some articles are conceptual-based; other methodologies used are Bayesian formula, mixed integer non-linear programming (MINLP) model, and mathematical modeling techniques.
3) The main theme of these frameworks is a green supply chain, circular supply chain, and carbon reduction policies through smart contracts, recycling, and rework.

The new emerging technology including blockchain and physical internet (PI) can improve the sustainability by restructuring the entire supply chain. Bai et al. (2021) presented a framework of the green supply chain, which is based on a non-cooperative game, and they designed a model which was based on the Bayesian formula. They evaluated their work through simulation on Python 3.5. Manupati et al. (2019) developed a model to optimize carbon emission levels and operational cost. The circular supply chain is a transition from disposal to reuse and is a step toward a sustainable economy. Wang B. et al. (2020) presented system architecture of a circular supply chain. Their study analyzed the challenges related to sustainability. Casado-Varaa et al, (2018) proposed a new model of an agricultural supply chain using blockchain. They used the multi-agent system based on smart contracts. The main advantage of the model was that through blockchain, the traceability of all the stages is possible.

5.2 Case Studies and Theoretical Developments of Blockchain in the Green/ Circular Supply Chain

Sustainable practices are implemented by the firms to mitigate the negative environmental and social effects in their supply chain (Rejeb and Rejeb, 2020; Gupta et al., 2021). The development in sustainability is the opportunity for all the firms to redesign their supply chain. The integration of big data, blockchain, and artificial intelligence can improve the sustainability goals linked to traceability, security, environmental degradation, and social ethics. Case studies and theoretical developments for the green/circular supply chain are listed in "**Table 7**." The main features of these case studies are as follows:

1) The different areas of applications of these case studies are the maritime industry, packaging waste, solid waste, agriculture, forestry, and fisheries industries; one article is written based on the background of COVID-19.
2) Many research articles are based on conceptual models validated through case studies; however, one research article is based on the ReSOLVE model (regenerate, share, optimize, loop, virtualize, and exchange).
3) Most of the themes are about the circular supply chain, waste-to-energy concepts, packaging waste, and integration of IoT and RFID technologies with blockchain.

The concept is the circular economy is evolving in recent times, which focuses to transform the products into new products after their useful life. In this context, Mastos et al. (2021) developed the waste-to-energy model and validated it by three case studies of the wood waste supply chain in the paradigm of industry 4.0. The knowledge of circular economy is still very limited, although it is adopted in developing countries (Kalmykova et al., 2018). Ajwani-Ramchandani et al. (2021a) provided the concept that how blockchains can be used for social and environmental sustainability in a circular supply chain. Modern society is more focused on social and environmental aspects. In this perspective, Kouhizadeh and Sarkis (2018) discussed the core dimensions of blockchain including decentralization of the database, secured transaction, information transparency, and smart contracts (Leng et al., 2019). The maritime industry is producing environmental degradation rapidly. Czachorowski et al. (2019) presented the insights on blockchain in the maritime industry for the reduction of pollution. Packaging waste is the most critical problem, which is a barrier for the implementation of sustainable development programs (Dahlbo et al., 2018).

5.3 Critical Success Factors, Barriers, and Challenges of Blockchain for the Green/ Circular Supply Chain

The most important success factor of blockchain is the awareness of customers. If manufacturing becomes green, then the environmental friendly customer will prefer purchasing the product. In this section, the barriers and adoption of blockchain for green/circular supply chains are critically examined, and its critical success factors are discussed. Details of relevant articles are given in "**Table 8**."

1) One of these articles is from the procurement section, and it has used quantitative and qualitative research methodology to find the challenges during blockchain adoption.
2) The second article is from the manufacturing sector, and it has used the decision-making trial and evaluation laboratory "DEMATEL" method, which is used to evaluate the critical success factors.

There were many limitations in articles relevant to case studies and theoretical developments in the blockchain-based green supply chain/circular supply chain. One common problem among all these studies is that these studies were cross-sectional studies and were unable to completely assess the effects of blockchain in different industrial sectors. A longitudinal study is needed to evaluate the long-term impacts of this nascent technology. Similarly, most of the studies were for a specific sector in a specific region. The geographic location, culture, laws, and people can affect the results and conclusions drawn from these studies. Another observation is that most of the studies were qualitative, and interviews conducted were structured or semi-structured. More quantitative studies should be included to get some quantifiable results and effects for all the attributes.

6 BLOCKCHAIN-BASED SOCIAL SUSTAINABILITY IN THE SUPPLY CHAIN

One major issue in the global supply chain is to protect the rights of workers and to provide them with a safe environment. There are a lot of standards for their rights, but it is common to violate the rules and regulations even in reputable organizations. Blockchain provides a commitment to achieve social sustainability. The parameters to measure the social sustainability include regional development, the welfare of workers, humanitarian supply chain, animals' health, transparency, fraud mitigation, trust development, and food security. A list of articles about the impacts of blockchain on social sustainability and for the humanitarian supply chain is given in "**Table 9**." The conceptual framework is given in "**Figure 5**." The main areas discussed in this framework are social sustainability and social welfare. Social welfare also includes the humanitarian supply chain management. The different attributes of blockchain such as accountability, transparency, and traceability will be beneficial for the fraud

TABLE 8 | Article related to challenges and barriers in the blockchain-based green/circular supply chain.

Sr	Author	Objective	Solution approach	Area of application	Limitation and future research direction
1.	Rane and Thakker, (2019)	This article is about to analyze the impacts of blockchain on the green supply chain.	Qualitative and quantitative research	Procurement section	There is a need to form regulatory authorities for blockchain implementation in developing countries.
2.	Rane et al. (2020)	Authors evaluated the critical factors for the success of the green supply chain.	Quantitative research	Manufacturing sectors	The results of the study are useful only for the automobile industry.
3.	Huang et al. (2022)	In this study, authors evaluated the critical success factors for the implementation of blockchain for green supply chain management.	Analytical hierarchy process	Supply chain management	The data are collected only from researchers. Experts from the industry should be part of the evaluation system in future work.

prevention and trust development of all stakeholders. Traceability of products will improve the safety of food. Similarly, effective tracing and tracking will lead toward the transparency in humanitarian supply chain management. Important points of these research articles are as follows

1) Some articles are relevant to humanitarian supply chain management, in which used solution approaches are quantitative research methodology (partial least squares structural equation modeling), fuzzy delphi and best–worst method, fuzzy decision-making trial and evaluation laboratory, intuitionistic fuzzy analytic network process, and fuzzy best–worst method.
2) The area of application of other articles includes the agriculture and food sector, dairy sector, small and medium enterprises, manufacturing sector, social media, the fashion industry, and global supply chain. The methodologies used in these articles are quantitative research methodology (ISM-DEMATEL), qualitative research methodology, mathematical modeling, and conceptual research.

Food safety is the main concern of the developing world. In this perspective, Yadav et al. (2020) have got the opinion of experts in the agriculture industry in India. Their finding revealed that government regulations and lack of trust are the main barriers for blockchain adoption. Benzidia et al. (2021) developed a conceptual model based on the ambidexterity theory of dynamic capability. The organization strategy of ambidexterity with a balanced approach of social and technological factors between suppliers and customers will enhance the capabilities of digitalization and innovation potential of the buyer, while considering the sustainable processes. Patil et al. (2020) identified 14 barriers for blockchain in the humanitarian supply chain. The identified barriers are organizational, technological, and financial. Blockchain can increase transparency, which is the need for a halal food value chain. In this perspective, Ali et al. (2021) explored that the supply chain of halal food can achieve sustainability through blockchain technology. The strategic fit in the supply chain and regulatory intervention are the enablers in the success of blockchain. Mangla et al. (2021) collected the data from the dairy farmers and evaluated the social impacts of the blockchain technology on farmers and communities using different parameters such as rural area development, food fraud, animals' health, food security, healthy food, and transparency.

Supply chains are very complex nowadays, and customer satisfaction is very challenging in this era of globalization. Most of the work is carried out for economic sustainability, and research for environmental and social sustainability is scarce. Most of the experts of the supply chain do not recognize the new technology, so their responses are not as reliable to be considered for further analysis. Future research should be based on the data from multiple sectors from multiple regions, so a comparative analysis may be performed to identify and prioritize the challenges and barriers for blockchain implementation.

7 PRACTICAL IMPLICATIONS

This extensive review will provide insights about recent advances at the interface of blockchain and the supply chain to all the managers, researchers, practitioners, and policy makers who are involved in the supply chain. Blockchain can revolutionize different industrial sectors such as banking and finance, health and medicine, retail, agriculture, and logistics. The review is focused on different models' development, conceptual frameworks, and case studies about the implementation of blockchain. This research is useful by summarizing all the latest developments of blockchain and its effects on the sustainability of the supply chain for various sectors including agri-food, pharmaceuticals, manufacturing, automobiles, aviation, and many other national and international companies. Different attributes of blockchain are evaluated in this article, which include fraud mitigation, workers' welfare, animal health, food security, transparency, traceability, and resilient supply chain. It also sheds light on the social aspects of blockchain such as food safety, trustful collaboration, humanitarian logistics, and social welfare. Firms will be able to improve their strategies and policies using blockchain to broaden their eco-friendly practices, sustainable consumption of energy and natural resources,

TABLE 9 | Article related to blockchain use for social sustainability in the supply chain and humanitarian supply chain.

Sr	Author	Objective	Solution approach	Area of application	Limitation and future research direction
1.	Sander et al. (2018)	The objective of the article is to evaluate the acceptance of blockchain as a traceability system in the meat supply chain.	Quantitative research methodology	Agriculture and food sector	Future research should be based on a more complicated network of the supply chain.
2.	Yadav et al. (2020)	The authors have investigated the barriers in implementation of blockchain in the agriculture supply chain in India.	Quantitative research methodology	Agriculture and food sector	The study is based on a developing country. The social and cultural values of developed countries are different.
3.	Ali et al. (2021)	This article presents sustainable framework for the blockchain-based supply chain of halal food.	Qualitative research methodology	Agriculture and food sector	Future research should be based on the identification of challenges in the complex supply chain.
4.	Mangla et al. (2021)	This article evaluates and assesses the impacts of blockchain, fraud mitigation, welfare, animal health, food security, and transparency.	System dynamics modeling	Dairy sector	Different optimization models should be used to minimize the losses in the supply chain.
5.	Pazaitis et al. (2017)	The research exploits the potential of blockchain to facilitate the social sharing dynamics.	Conceptual framework	Sharing economy	The study is only on the theoretical background.
6.	Patil et al. (2020)	Authors have identified 14 barriers of blockchain for humanitarian supply chain management.	Fuzzy best–worst method	Humanitarian supply chain	Interrelation between different barriers should be explored.
7.	Queiroz et al. (2020)	Authors developed a model about the social influence on blockchain adoption and empirically validated it by Brazilian professionals.	Partial least squares structural equation	Humanitarian supply chain	It is difficult to present a comparison of different countries for implementation challenges of blockchain.
8.	Dubey et al. (2020)	Authors explored the effect of collaboration between all actors of disaster relief operations.	Fuzzy best–worst method	Humanitarian supply chain	Future research must include the interaction effect of organizational culture.
9.	Sahebi et al. (2020)	The authors identified barriers for blockchain adoption in the humanitarian supply chain.	Fuzzy delphi and best–worst method	Humanitarian supply chain	Lack of published data in the domain of blockchain and the humanitarian supply chain are the limitations of this study.
10.	Ozdemir et al. (2020)	This study aims to analyze the role of blockchain in mitigating the effects of barriers in the humanitarian supply chain.	Intuitionistic fuzzy analytic network	Humanitarian supply chain management	The sample size of data is very small.
11.	Wong et al. (2020)	The objective of this study is to investigate the impacts of top management participation, competitive pressure, market dynamics, and regulatory issues on the adoption of blockchain.	Quantitative research methodology "PLS-ANN"	Small and medium enterprises	The research is based on Malaysian companies, and future studies should include a cross-country evaluation.
12.	Kopyto et al. (2020)	The authors used the delphi method to get judgments from experts to analyze the influence of blockchain on societal, technical, and economic aspects of a supply chain.	Delphi method	Small and medium enterprises	The research is based on the qualitative study only.
13.	Benzidia et al. (2021)	The study is about the social effect of blockchain adoption on the relationship between the supplier and buyer.	Quantitative research methodology	Manufacturing sector	Research must be extended longitudinally by the involvement of more stakeholders.
14.	Queiroz and Fosso Wamba, (2019)	This study helps to understand the individual behavior on blockchain adoption in the supply chain in the United states and India.	Partial least squares structural equation modeling	Logistics	The developed construct does not consider the effort expectancy and unified theory of acceptance and the use of technology.
15.	Venkatesh et al. (2020)	In this article, system architecture is developed by the integration of big data, blockchain, and Internet of Things.	Conceptual architecture development	Process flow industries	Detailed research is required for challenges involved in the adoption of blockchain in different industries.
16.	Choi et al. (2020)	This article explores how blockchain can improve the transparency and trust of social media analytics.	Conceptual research	Social media	A multi-methodological approach can be used for research methodology.
17.	Nikolakis et al. (2018)	This article develops a verifiable framework to explain that blockchain can increase social sustainability.	Conceptual framework	Global value chains	The governance mechanism of information handling is still a big question in the adoption of blockchain.
18.	Choi and Luo, (2019)	A theoretical model is established about the effect of poor-quality data on sustainability of supply chain operations.	Operations research	Fashion industry	Future model should be price-dependent for realistic results.

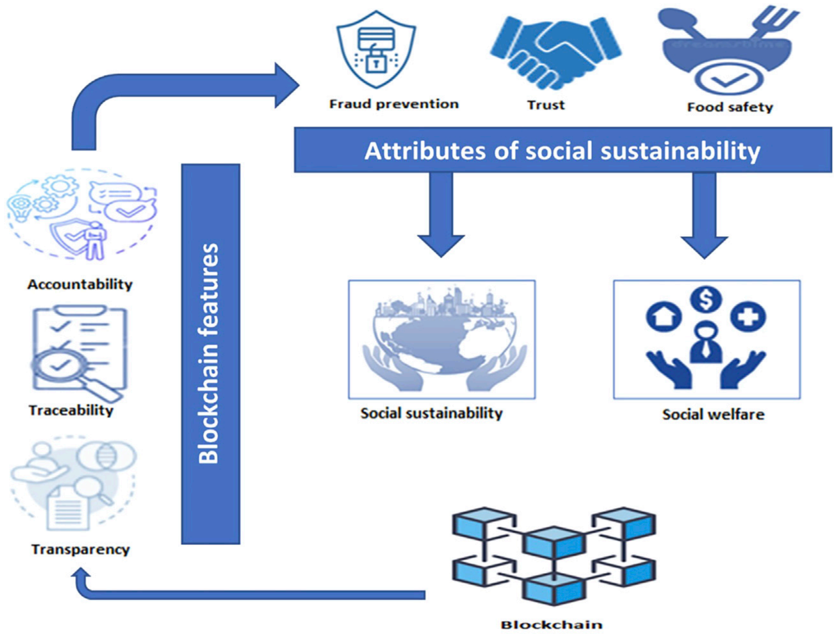

FIGURE 5 | Conceptual framework of transformation of the supply chain to attain social sustainability through blockchain.

and social vitality. Blockchain can foster the green supply chain by the traceability of products in an effective way and by monitoring the environmental compliance throughout the entire supply chain. Through efficient tracing, it will improve energy wastage and resource consumption. Finally, it will be helpful in transaction cost reduction through smart contracts and will increase the accuracy, speed, and efficiency of the supply chain.

8 CONCLUSION

After conducting the extensive literature review, it is being concluded that the supply chain has entered the era of blockchain and big data, and these technologies have great potential to revolutionize the entire network. The research was categorized into three domains. In the first category, blockchain and economic sustainability through different attributes of blockchain such as traceability, transparency, decentralization, visibility, smart contracts, accountability, immutability, and cybersecurity were evaluated through relevant literature studies. In the second category, the role of blockchain for the circular and green supply chains was assessed through a review of relevant articles. The benefits of blockchain in the humanitarian supply chain and its social aspects through trust development, fraud prevention, and food safety were critically examined in the third category. Different constructive characteristics of blockchain provide resilience, mutual trust, fraud mitigation, social welfare, and risk mitigation in the supply chain.

However, the scope of the present study is very broad, as it not only covers the triple bottom-line aspects of sustainability but it also lists the articles relevant to the humanitarian supply chain. Still, the study has limitations such as the research is conducted only from sustainability perspective and other aspects of supply chain such as resilience, agility, and robustness are not the scope of this study. The articles were selected only from Scopus-indexed journals, and some important information sources such as book chapters were neglected. Blockchain has a capability for the traceable, authentic, and reliable information flow using the smart contract, but the main question is still unanswered that is blockchain a real disruptive technology for social innovation or is it just an incremental technology that has very low strategic significance in supply chain sustainability. At present, several countries have adopted the blockchain technology in several sectors. Developed countries such as the United States and Japan are among the top countries for the acceptance and implementation of blockchain. Many African and Asian countries are also part of leading countries in blockchain adoption. In developing countries, blockchain adoption and green practices in procurement and the supply chain are at a very early stage, and there is a need to develop regulatory authorities at the government level to implement these practices. The effective use of the blockchain technology in developing countries with focused improvements will not only strengthen the economic aspects of the supply chain but will also improve its performance to comply with the environmental regulations and social aspects.

Future research direction in perspective of developmental research should be a joint function of blockchain with big data, life cycle assessment techniques, Internet of Things, and RFID. Future research should consider the limitations of blockchain in information handling, governance framework, and workability of smart contracts. Many unaddressed questions should be explored, for example, what non-technological aspects such as company regulations, culture, and social acceptance will impact the adoption of blockchain? The basic lesson learned from the COVID-19 crisis is to manage the resilience and risk. It should be investigated that how blockchain will affect the cost, risks, and uncertainties during the operation and disruption. Future research should also consider the government's role in the adoption of blockchain. Overall, this article will provide an opportunity to academicians and researchers, for the complete understanding of the blockchain-based supply chain in paradigm of triple bottom-line aspects.

DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding authors.

AUTHOR CONTRIBUTIONS

Each author contributed to the literature review, analysis, and to the writing of the manuscript. MAM (1st author) conceptualized and drafted the manuscript. AH, TM, and MH were the research supervisors and provided guidance for the collection of relevant articles. CS and AQ helped in developing frameworks, while MS, MAM (8th author), and SI contributed to the graphical abstract and figures.

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Biodiesel from Dodonaea Plant Oil: Synthesis and Characterization—A Promising Nonedible Oil Source for Bioenergy Industry

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In this work, Dodonaea oil was studied as a potential biodiesel source. Dodonaea (*Dodonaea viscosa* Jacq.) is an evergreen shrubby plant that thrives in tropical and subtropical conditions. The plant produces high-grade biodiesel in terms of both quantity and quality despite its naturally high fat content. In the transesterification followed by esterification reaction, varied ratios of oil to methanol, constant temperature (60°), reaction duration (1 h), and different catalyst concentrations (0.25–0.75% (w/w) were utilized. A maximum biodiesel yield of 90% was achieved. For fuel characteristic analysis, the prepared biodiesel was specified and compared to ASTM criteria. The chemical composition was verified using analytical techniques such as FT-IR and NMR spectroscopy. As a result of the foregoing, Dodonaea is considered a possible bioenergy source, particularly in the transport sector.

Keywords: dodonaea plant, nonedible oil source, biodiesel, fuel properties analysis, spectroscopic studies

1 INTRODUCTION

Traditional energy supplies such as natural gas, coal, and petroleum currently meet the increasing global energy demand, but these resources are rapidly decreasing and are at the point of extinction (Demirbas 2007; Mahmood et al., 2014). Due to the uncertainty of fossil-based fuels and mounting environmental harms, the world's interest in alternative, clean, and sustainable energy options has shifted (Barnwal and Sharma 2005).

The primary sources of electricity are petroleum-based fuels such as oil, coal, and natural gas. However, as humanity's reliance on fossil fuels has grown, the rate of asset exhaustion and the threat of global warming have also increased. As a result, the issue persists; alternative fuels must be developed to reduce fossil fuel consumption, while also reducing greenhouse gas emissions. In this circumstance, biomass derivative fuels, which are renewable, sustainable, and environmentally benign, may be a superior option.

Biodiesel plays a key role in reducing greenhouse gas emissions in the transportation sector, and the European Union is increasing its relevance for sharing, which is equivalent to an emission reduction of nearly 85% in this sector. Few actions are required to achieve sufficient progress in the transportation area, given the existing circumstances of strong political support and market expansion. The use of biodiesel in transportation is critical for reducing greenhouse gas emissions and the European Union's understanding of the role biofuels must play in the automobile sector, particularly in street transportation, is established. To establish trust, a

FIGURE 1 | Matured plant of dodonaea (*Dodonaea viscose*).

positive working relationship with all stakeholders, including vehicle manufacturers and oil corporations, was established with the goal of transferring technical know-how, producing fundamental data on cultivation and extraction, marketing strategies, capacity development, coordination, and the execution conduct of necessary research on all the elements of new generation biofuels, and international cooperation.

Because of its long-term viability and environmental benefits, biodiesel derived from vegetable oil is now a viable alternative to petro-diesel (Fernando et al., 2006). Various biodiesel production sources are chosen depending on their accessibility in a given region or country (Sadia et al., 2013). Initially, researchers were interested in edible vegetable oil sources for biodiesel production, such as soya bean, palm, rapeseed, sun flower, canola, and safflower, but these oil sources pose a severe danger to food security (Ghadge and Raheman 2006; Vicente et al., 2004; Kulkarni et al., 2006; Meka et al., 2007). To overcome this obstacle, researchers began investigating the non-edible oil sources in order to develop biodiesel, which proved to be a cost-effective and efficient alternative. Researchers have been already working on a number of nonedible oil sources, such as cotton, rubber, Jatropha, Pongamia, tobacco, and Calophyllum (Kansedo and Lee 2009; Ramadhas et al., 2005; Berchmans and Hirata 2008; Naik et al., 2008; Veljkovic et al., 2006; Sahoo and Das 2009). In this context, the Dodonaea plant was studied quantitatively and qualitatively for biodiesel production, and the results were unexpected.

Dodonaea belongs to the Sapindaceae family (*Dodonaea viscosa* Jacq.). It is an evergreen shrub or small tree that grows throughout the tropics and subtropics of the world from the coast to an altitude of more than 2000 m, as shown in **Figure 1**. It is an Australian native, but it can also be found in New Zealand, Mexico, Florida, Africa, the Virginia Islands, Arizona, South America, and India. In Pakistan's subtropical regions, Dodonaea is prolific, generating a dense population (Venkatesh et al., 2008; Rani et al 2009; Barkatulla and Ibrar 2010; Prakash et al., 2012; Lawal and Yunusa 2013).

The therapeutic benefits of Dodonaea are well-known. The locals utilize its leaves, blossoms, and roots to treat a number of ailments, including skin infections, fever, pain, swelling, diarrhea, toothache, and headache (Cribb and Cribb 1981; Rojas et al., 1996). Dodonaea leaves are used to cure bone fractures because they have antibacterial, anti-inflammatory, antifungal, antiulcer, antihyperglycemic, antidiarrheal, antimicrobial, antioxidant, analgesic, and antipyretic qualities (Prakash et al., 2012). In India, it is used as a wood fuel source, and the seeds are used as a fish poison (Jain and Singh 1999; Wagner et al., 1987; Parihar and Dutt 1947). The seeds contain 20.23% fixed oil, according to the literature. However, due to their poisonous nature, they are not used for cooking or other purposes. Apart from the previous discussion, Dodonaea oil has been proposed for biodiesel production in various industries in this research work.

Many seed-bearing plant species are grown for the purpose of production in the world (Mushtaq et al., 2009), but less systematic data on Dodonaea seed oil and its usage in qualitative biodiesel production are available due to its nonedible qualities. In this work, Dodonaea oil was researched systematically for qualitative and quantitative biodiesel synthesis. Taking into consideration the abovementioned statement, Dodonaea oil is recognized as a low-cost source for the bioenergy industry.

2 MATERIALS AND METHODS

2.1 Materials

The taxonomic study and biodiesel synthesis were conducted in the Department of Plant Sciences, Quaid-i-Azam University and Islamabad's Biofuel & Biodiversity and Anatomy Labs, respectively. The raw materials used in this study were Dodonaea seed, oil, methanol, potassium hydroxide, and anhydrous sodium sulfate. All the reagents and chemicals were provided by Merck (Germany), Schrlau (Spain), and Sigma-Aldrich and were used without any purification.

2.2 Oil Extraction

Dodonaea seeds were purchased from a local agriculture sale (**Figure 2**). The oil was extracted from the oven-dried seeds using a mechanical oil expeller (KEK P0015, 10127 Germany). The oil was extracted and processed before being utilized to make biodiesel. To remove contaminants, the crude oil was filtered *via* Whatman filter paper. For further testing, the filtered oil was stored in glass bottles and kept at room temperature (Hussain and Mezan 2010).

2.3 Biodiesel Synthesis

2.3.1 Experimental Setup

Biodiesel was made from Dodonaea crude oil using the alkaline transesterification mechanism. For the transesterification procedure, a 250-mL conical flask, a multiple heating magnetic stirrer (Am4, VELP SCIENTIFICA), and a thermometer were used.

FIGURE 2 | Seed sample of Dodonaea plant species.

2.3.2 Alkaline Transesterification

On a hot plate, the filtered oil was heated to 120°C to remove any moisture and then cooled to 60°C. KOH was dissolved in methanol and stirred for 30–35 min to produce methoxide. At 60°C, methoxide was added to the oil and swirled for 60 min. The mixture was allowed to settle for 8–10 hrs or overnight at room temperature after an hour. Three lyres were discovered in the end. In the base of crude biodiesel, a gelatinous material known as glycerin was produced in the shape of tiny spots floating on the surface. The lyres were isolated using simple handling devices. The crude biodiesel was rinsed in warm water to remove the contaminants. The method was performed two to three times to remove all the contaminants. Anhydrous sodium sulfate was added after washing to remove any leftover moisture. The biodiesel was distilled after purifying it and rotated at 55°C for 1 h to remove any extra methanol.

2.4 Optimization of Biodiesel

A number of transesterification processes were carried out with the changing oil-to-methanol molar ratios, different kinds of catalyst concentrations, reaction time, and temperature to determine the best conditions for the maximum conversion of oil to biodiesel.

The process of the transesterification reaction was carried out in a 1/2 liter three-necked round-bottom flask equipped with a sampling outlet, reflux condenser, thermometer, and magnetic stirrer. Approximately, 250°ml dodonaea filtered oil was heated. The temperature was maintained up to 120°C for 1 h. The moisture and degraded mono, di-glyceride were removed from the acylglycerole. The transesterification reaction of dodonaea oil was carried out with various oil molar ratios and catalyst concentrations (w/w). The temperature (60°C), reaction time (2 h), and stirring velocity (600 rpm) were kept constant for the reactions. The resultant product after the complete reaction was allowed to cool down at room temperature. The upper phase contained a thin spot of soap and the middle part biodiesel, while the base phase contained a gelatinous mass of glycerin, and the mixture was separated by simple decantation. The main dogma of biodiesel preparation is presented in the flow chart of the biodiesel (**Figure 3**).

In the end, the mixture was separated into two layers: the upper layer contain dodonaea crude biodiesel having an excess amount of methanol. The crude biodiesel was purified by residual methanol distillation at 65°C for 60 min by a moderate rotary evaporator. The remaining catalyst together with other inorganic impurities formed soap, and some catalyst was removed by consecutive washing steps with distilled water by adding three to four drops of weak acid (CH_3COOH) to neutralize the remaining catalyst. The extra water molecule was removed with the help of anhydrous sodium sulfate (Na_2SO_4) followed by filtration (Ullah et al., 2014; Ullah et al., 2015a).

2.5 Determination of Biodiesel Fuel Properties Analysis

This article also looks at the qualities of the prepared biodiesel fuel. Quantitatively, the fuel properties test such as color, flash point, density, kinematic viscosity, pour point, cloud point, cetane number, sulfur content, and acid number of the prepared biodiesel sample in contrast to petro-diesel were analyzed and matched with the American Society for Testing and Materials (ASTM) standards (Ullah et al., 2014; Ullah et al., 2015b; Ullah et al., 2015c).

2.6 Profiling and Characterization of Biodiesel Using FT-IR and NMR Spectroscopy

The biodiesel that had been prepared was profiled and classified using analytical experiments. FT-IR spectroscopy (Perkin Elmer-TENSOR27) in the 6000–600 cm^{-1} region was used to monitor the reaction. NMR spectroscopy, which includes ^1H NMR and ^{13}C NMR, was used to determine the maximal conversion and presence of proton and carbonyl carbon groups in the synthesized biodiesel (**Figure 4** and **Table 1**).

3 RESULTS AND DISCUSSION

3.1 Oil Contents

The presence of 20.27% oil content in Dodonaea seeds has been documented in the literature (Parihar and Dutt 1947), but the percentage of oil expression present in Dodonaea seeds was 23% using the Soxhlet operations. Oil with a concentration of more than 20% is regarded as suitable for biodiesel processing, according to the research. Due to its low cost and accessibility, Dodonaea oil is within the proposed margin and may be used simply for biodiesel production (Fernando et al., 2006).

3.2 Conversion of Dodonaea Seed Oil to Fatty Acid Methyl Esters

Dodonaea oil can be converted to fatty acid methyl esters (FAMEs) using a variety of methods. In our current research, we performed transesterification reactions. Transesterification

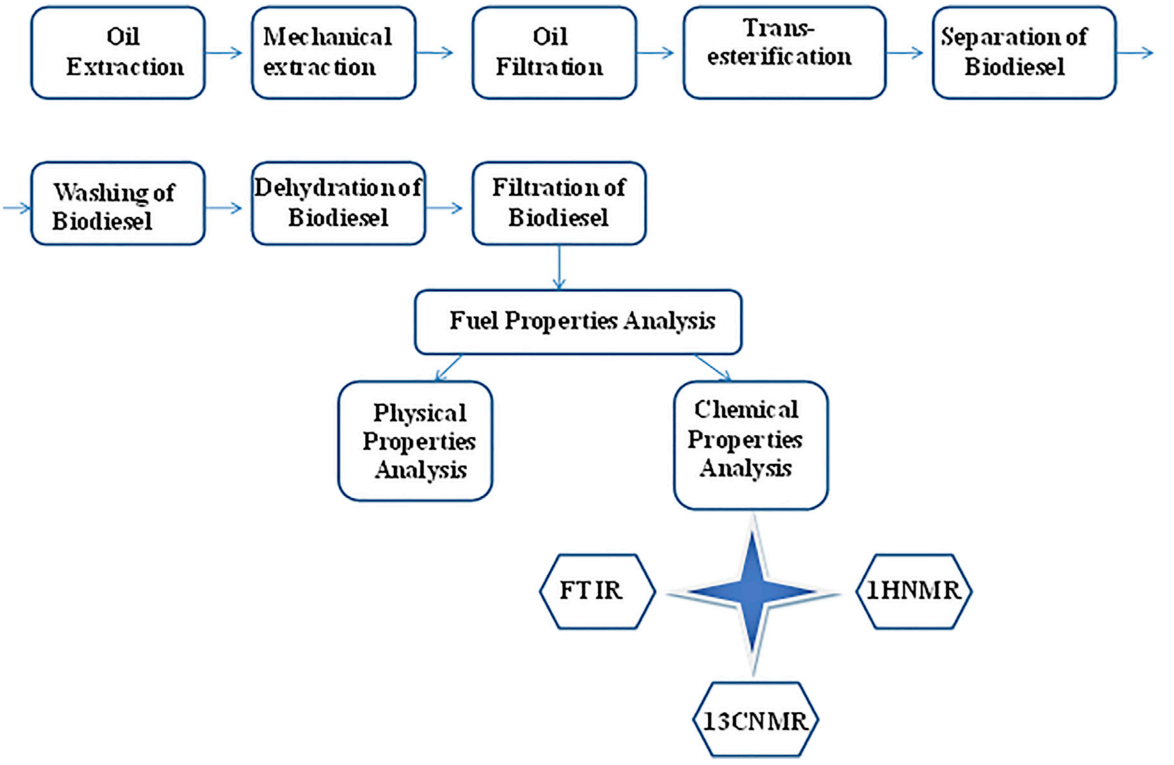

FIGURE 3 | Flow chart of the biodiesel synthesis techniques adopted for experimental work.

with potassium hydroxide is used to achieve the best output of biodiesel (Karmaker et al., 2010). The main goal of the research was to see if it was possible to convert Dodonaea oil to biodiesel under perfect circumstances for maximum yield. Because of its short chain and quick conversion time, methanol was utilized to repair the reaction. Before the transesterification process, the oil was heated to 120°C and then cooled to 60°C at room temperature.

Moreover, methoxide is produced by dissolving KOH in methanol and stirring for 30–35 min at 600 rpm (Mushtaq et al., 2009). The resulting biodiesel production is higher when methoxide is used instead of hydroxide catalyst pellets. At 65°C, methoxide was added to the oil and agitated for an hour, allowing the reaction mixture to settle and isolate the newly formed chemical. The mixture was allowed to sit for 8–10 h. The results revealed two noticeable lyres and a few tiny soap spots on the surface. The layer base was built of gelatinous glycerin and crude biodiesel. A maximum yield of the biodiesel (90%) was reached using proton NMR spectroscopy.

3.3 Effect of Variables on Biodiesel Production

As illustrated in **Figures 5–8**, a series of tests were conducted in order to obtain the best output of biodiesel from non-edible Dodonaea oil. The impacts of the following parameters were explored and their ideal circumstances.

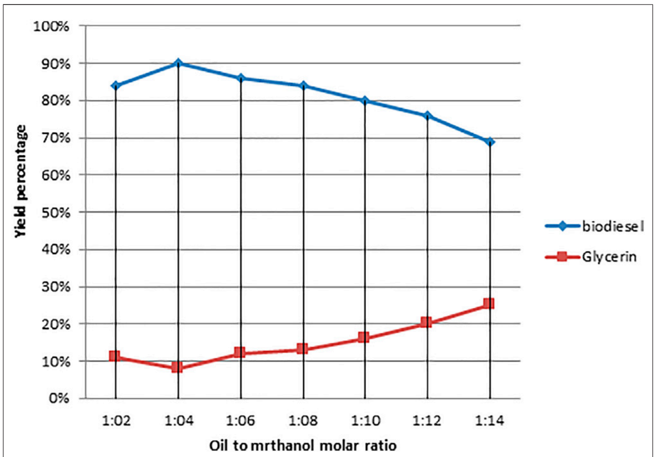

FIGURE 4 | Effect of variation in the molar ratio of oil to alcohol on biodiesel production yield.

3.3.1 Effect of Molar Ratio of Oil to Methanol

The molar ratio of oil to methanol in the transesterification process is an important factor that determines the yield of methyl ester (Lin et al., 2009). In the following transesterification operations, the oil-to-methanol ratio was changed as follows: The rest of the parameters were held constant during the reaction: 1:4, 1:6, 1:9, 1:12, 1:15, and 1:18.

TABLE 1 | Fuel property analysis of the Dodonaea biodiesel.

Fuel properties	Method	Results	ASTM
Colour	ASTMD-1500	2	2.0
Flash point °C (PMCC)	ASTM D-93	102	60–100
Density @15°C Kg/L	--------------	0.863	0.86–0.90
K. Viscosity 40°C cSt	ASTM D-445	3.97	1.9–6.0
Pour point °C	ASTM D-97	−12	−15 to 16
Cloud point °C	ASTMD-2500	−15	−3 to 12
Sulfur % wt	ASTMD-4294	0.0043	0.05
Total acid no. mg/KOH/gm	ASTM D-974	0.73	0.5

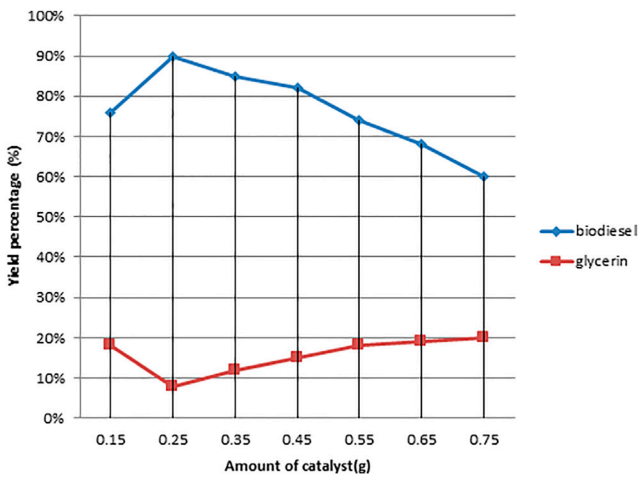

FIGURE 5 | Effect of variation in catalyst (KOH) concentration on the Dodonaea biodiesel production.

Table 1 demonstrates that at 1:6 M ratios, the greatest conversion of triglycerides to methyl esters occurred, with a yield of 90%. At 1:6 oil-to-methanol molar ratio, Freedman found a 90–97% conversion of triglycerides to methyl esters, which is similar to our findings (Freedman et al., 1984). According to Freedman's observations, increasing the molar ratio of oil to methanol initially increases the conversion percentage, but further increasing the molar ratio of oil to methanol reduces the conversion of glycosides to methyl esters (Patil and Deng 2009; Sharma and Singh 2010).

3.3.2 Effect of Catalyst Concentration on Conversion

In the oil with the freest fatty acids, the use of a base catalyst outperforms the use of an acid catalyst, and potassium hydroxide outperforms sodium hydroxide in the transesterification reaction. Moreover, because of the emulsion and soap formation, if the free fatty acid level is higher than 3%, the final product will not contain biodiesel (Fukuda et al., 2001).

To generate the largest yield of biodiesel, the basic catalyst potassium hydroxide was chosen for transesterification in this investigation (Shahid and Jamal 2011). In the extraction of glycerol from crude biodiesel, potassium hydroxide outperformed sodium hydroxide, according to Encinar et al. (Encinar et al., 2005). Other researchers converted Turkish safflower oil to biodiesel using potassium hydroxide, attaining a biodiesel output of 97.7%. (Isigigur et al., 1994).

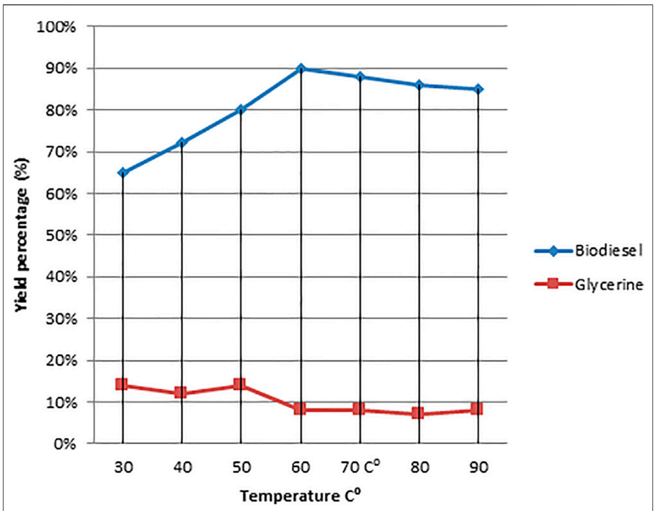

FIGURE 6 | Effect of temperature variation on the Dodonaea biodiesel production yield.

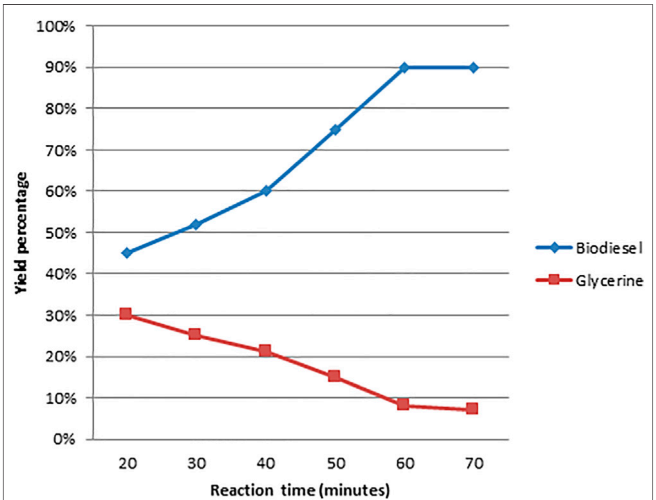

FIGURE 7 | Effect of reaction time on the production of biodiesel from Dodonaea.

To convert Dodonaea oil to biodiesel, a base catalyst was used in the transesterification reactions. Different potassium hydroxide concentrations were utilized in different processes (0.15, 0.25, 0.35, 0.45, 0.55, 0.65, and 0.75). The maximum conversion percentage of the biodiesel was achieved at 90 percent using 0.25% potassium hydroxide. The potassium hydroxide concentration continuously rises as a result of saponification, lowering the conversion percentage. Because of emulsion formation, utilizing a greater concentration of potassium hydroxide catalyst in the transesterification reaction has a detrimental impact on methyl ester yield and consistency (**Figure 6**) (Meher et al., 2006; Rashid et al., 2008).

3.3.3 Effect of Temperature on Conversion

Transesterification can occur at a variety of temperatures depending on the oil used in the reaction (Ma and Hanna

1999). The lowest temperature range has a significant impact on the rate of transesterification reaction and, ultimately, the end product. The temperature increases the lower oil viscosity proportionally and directly increases the reaction rate because the reaction receives more energy (Koh and Ghazi 2011). Saponification was accelerated until alcoholysis was completed if the reaction temperature was above the boiling point of methanol (Dorado et al., 2004). The influence of temperature on fatty acid methyl ester yield from Dodonaea oil during the transesterification reaction was investigated using different temperatures (30, 40, 50, 60, 70, 80, and 90°C). The ideal temperature range for these reactions was discovered to be 60–65°C.

According to the data, increasing the temperature to 60°C boosted the biodiesel yield significantly, as shown in **Figure 7**. The production of biodiesel decreased as the temperature rose. The best temperature for the optimal conversion of cotton seed oil to biodiesel, according to Rashid et al., is 65°C (Rashid et al., 2008). At 60°C, Pongamia, Jatropha, and sesame all had the highest biodiesel yields, with Jatropha having the maximum yield of 99% (Mushtaq 2009). It was observed that the highest yield of biodiesel could be attained at room temperature by simply increasing the reaction time. As illustrated in **Figure 6**, the maximum temperature has an impact on the saponification reaction, resulting in a low biodiesel output (Reference Deleted by mistake).

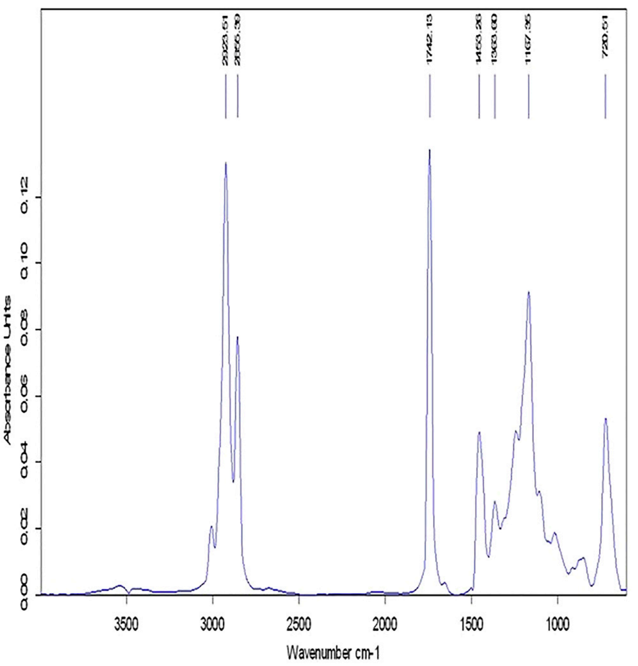

FIGURE 8 | FT-IR spectrum showing various peaks in the Dodonaea prepared biodiesel.

3.3.4 Effect of Reaction Time on Conversion

The length of the transesterification reaction has a significant impact on the production of biodiesel. They must be swirled well at a consistent rate to achieve complete contact between the catalyst and the triglycerides during the transesterification reaction. A series of tests were carried out using Dodonaea seed oil to assess the effect of reaction time on biodiesel yield. The reaction time was increased from 20 to 70 min by including a 10-minute break. A response time of 60–70 min was determined to be optimal, resulting in a biodiesel yield of 90%. As the reaction temperature was raised, the production of biodiesel increased, as illustrated in **Figure 8**. (Mushtaq and colleagues, 2009).

3.4 Biodiesel Characterization

Color, flash point, viscosity, density, pour point, cloud point, sulfur percentage, and acid quantity were all examined in the biodiesel generated from Dodonaea plant oil. The fuel characteristics of Dodonaea biodiesel were investigated and compared to those of ASTM in **Table 1**.

3.4.1 Flash Point

When handling, storing, and transporting fuel, the flash point is an important factor to consider. This is the temperature at which the biodiesel can ignite when exposed to flame. A greater flash point is generally regarded to reduce the risk of fire (Syam et al., 2009; Krisnangkura and Simamaharnop). The biodiesel's key advantage over petroleum-based fuel is its flash point (Anwar et al., 2010). In this study, the flash point of Dodonaea biodiesel was estimated using ASTM D-93 and was found to be 102°C. This fuel has a greater flash point than the regular petro-diesel, indicating that it is safe for use in transportation.

3.4.2 Density

According to **Table 1**, the density of Dodonaea biodiesel @150°C kg/L was found to be 0.863 kg/L in this investigation using the ASTM D-1298 procedure. The density of Dodonaea biodiesel was found to be higher than that of petroleum diesel, but still within the ASTM criteria.

3.4.3 Kinematic Viscosity

The viscosity of a fuel influences its atomization upon injection into the combustion chamber and the development of soap and engine deposits (Knothe and Steidley 2005). Viscosity, which appears to oppose any dynamic change in fluid motion, is used to quantify the internal fluid friction of the fuel to flow. Injector lubrication and atomization are affected by the viscosity of the fuel.

Low-viscosity fuels do not offer adequate lubrication for fuel injection pumps to fit perfectly, causing leakage or increased wear. If the viscosity is low, the leakage will result in engine power loss. If the viscosity is high, the injection pump will be unable to supply enough gasoline to fill the pumping chamber, resulting in engine power loss once more. Kinematic viscosity (1.9–6.0 mm2/s in ASTM D 6751 and 3.5–5.0 mm^2/s in EN 14214) is one of the biodiesel specifications [49]. As indicated in **Table 1**, the kinematic viscosity of Dodonaea biodiesel was tested using ASTM D-445 at 40°C and was determined to be 3.97 mm^2/s. The

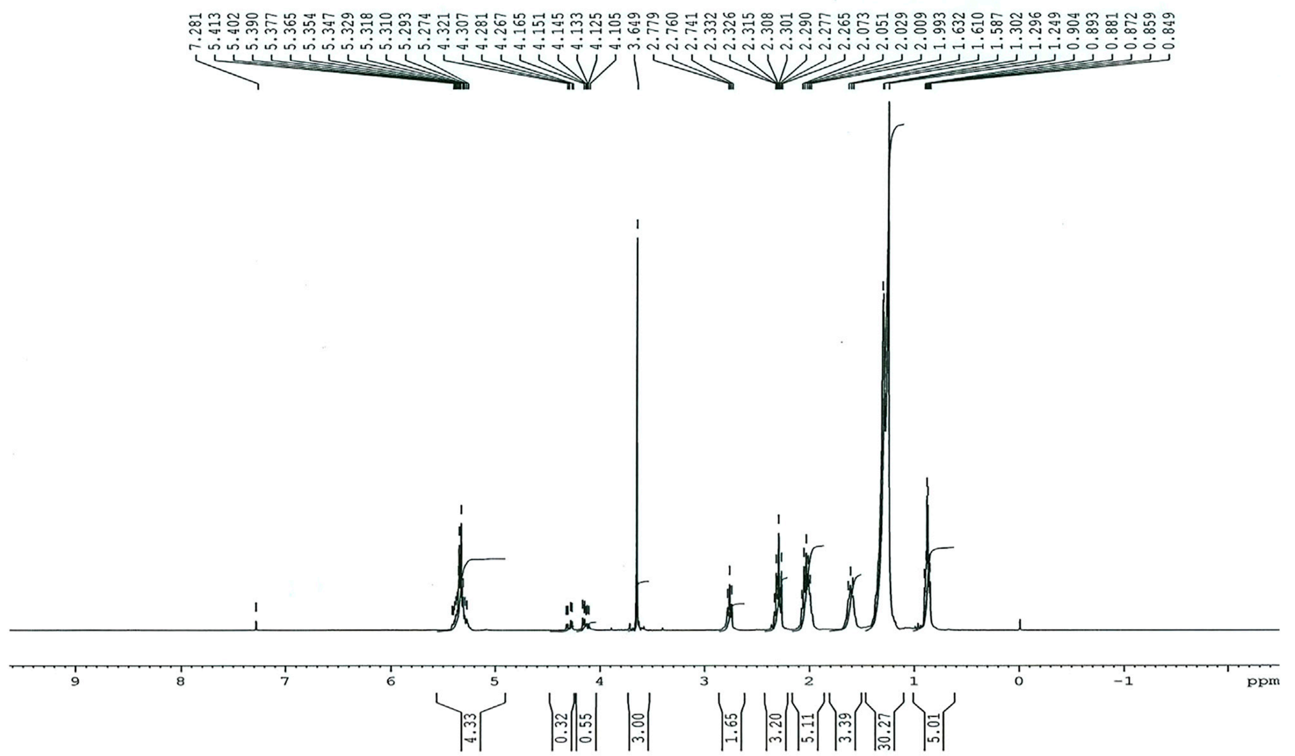

FIGURE 9 | [1]H NMR spectrum showing the chemical bonding in the Dodonaea plant prepared biodiesel.

measured value fell within the ASTM D-445 standard range (1.9–6.0 mm2/s). The lower viscosity of the biodiesel makes it easier to pump and atomize (Knothe and Steidley 2005).

3.4.4 Pour Point

The pour stage is the lowest temperature at which a fuel can pour or flow when cooled under particular conditions. A high pour point is frequently associated with poor fuel characteristics [47]. The pour point of methyl ester generated from Dodonaea oil according to ASTM D-97 was determined to be −12°C, which is nearly comparable to the pour point of Pongamia [44]. This value is within the ASTM biodiesel requirement ranges. The type of fatty acid branched chain contained in the original oil has an impact on the pour point (Lee et al., 1995).

3.4.5 Cloud Point

When gasoline is refrigerated under certain conditions, the cloud point is the temperature at which paraffin (wax) crystallizes. A fuel's high cloud point also indicates that it has poor characteristics. In this study, the cloud point of Dodonaea methyl ester, as determined by ASTM D-2500, was found to be −15°C (**Table 1**).

3.4.6 Sulfur Content

The sulfur concentration was evaluated using ASTM D-4294 in this study. The biodiesel generated from Dodonaea oil has an extremely low sulfur level of 0.0043%, as reported in **Table 1**. The range of sulfur is less than 1 ppm, unlike the normal petro-diesel fuel, which has a sulfur level of 50 ppm. The fact that biodiesel has a sulfur percentage of less than 1 ppm is a major benefit to both engine life and the environment. The low sulfur content of the biodiesel makes it a good fuel for extremely polluted areas as SO_2 levels in biodiesel are substantially lower than in conventional diesel. Traditional diesel has a lower pour point, flash point, and sulfur content. Biodiesel has a greater pour point, flash point, and sulfur content (Anwar et al., 2010).

3.4.7 Acid Number

The total acid number is the amount of potassium hydroxide required to neutralize the free fatty acids in biodiesel (Arjun et al., 2008). The most straightforward method for determining fuel content is to examine the acid value. The total acid number of Dodonaea biodiesel was estimated using ASTM D-974 and was found to be 0.73 mg KOH/gm (**Table 1**). As the acid value increases, the rubber components of the older engine fuel supply systems degrade.

3.5 Biodiesel Chemistry

The current research study used analytical methods to analyze Dodonaea biodiesel. The conversion of Dodonaea oil to methyl esters was validated using these methods. The functional group and conversion percentage were determined using ^{1}H and ^{13}C NMR, respectively, and the transesterification reaction was tracked using FT-IR.

TABLE 2 | FT-IR spectroscopy showing various peaks in the Dodonaea biodiesel.

Peaks	Frequency range (cm^{-1})	Bond	Functional group
2923.51	3000–2850	C-H stretch	Alkanes
1742.13	1750–1735	C=O stretch	Ester, saturated aliphatic
1453.26	1470–1450	C-H bend	Alkanes
1167.36	1300–1150	C-H Wag (–CH_2X)	Alkyl halide
720.51	725–720	C-H rock	Alkanes

3.5.1 FT-IR Study

Fourier-transform infrared spectroscopy was used to identify the functional groups and peaks corresponding to distinct stretching and bending vibrations in the Dodonaea biodiesel. The production of fatty acid methyl esters was confirmed by the FT-IR measurements.

FT-IR analysis, which is created by transesterification from their peaks, also confirms different functional groups (Knothe 1999). This study approach can also be utilized to assess the oil content in the adulterated biodiesel–petrodiesel mixture with minor modifications (Mahamuni and Adewuwi 2009). There were two primary distinctive bands for detecting methyl esters: one was carbonyl carbon, which had a peak at 1735–1750 cm^{-1}, and the other was C-H, which had a peak at 2850–3000 cm^{-1}. (**Figure 9**). The carbonyl carbon (C=O) and alkane (C-H) peaks of the ester occurred at 1742.13 cm^{-1} and 2923.51 cm^{-1}, respectively. As demonstrated in **Table 2**, the alkyl halide peak was at 1167.36 cm^{-1}, while the C-H rock peak was at 720.1 cm^{-1}. In the same way, the C-H bending peak was found at 1453.26 cm^{-1}. The place of the carbonyl group in FT-IR is sensitive to substituent effects and to the structure of the molecule (Bianchi et al., 1995).

3.5.2 NMR Study

3.5.2.1 ^{1}H NMR Spectroscopy

^{1}H NMR was used to assess the yield of Dodonaea biodiesel (**Figure 9**). Proton nuclear magnetic resonance spectroscopy was recently used to study the kinetics and product distributions of the transesterification reactions (alcoholysis) between vegetable oils and alcohols (^{1}H NMR). Because a tiny aliquot of the batch reaction may be collected at any time and the ^{1}H NMR spectrum analysis offers extensive details about the chemical species participating in the reaction, using ^{1}H NMR to monitor a reaction is simple and quick (Morgenstern et al., 2006). Using ^{1}H NMR spectroscopy, the protons in the alcohol moiety of the resulting methyl esters and the protons of the methylene group

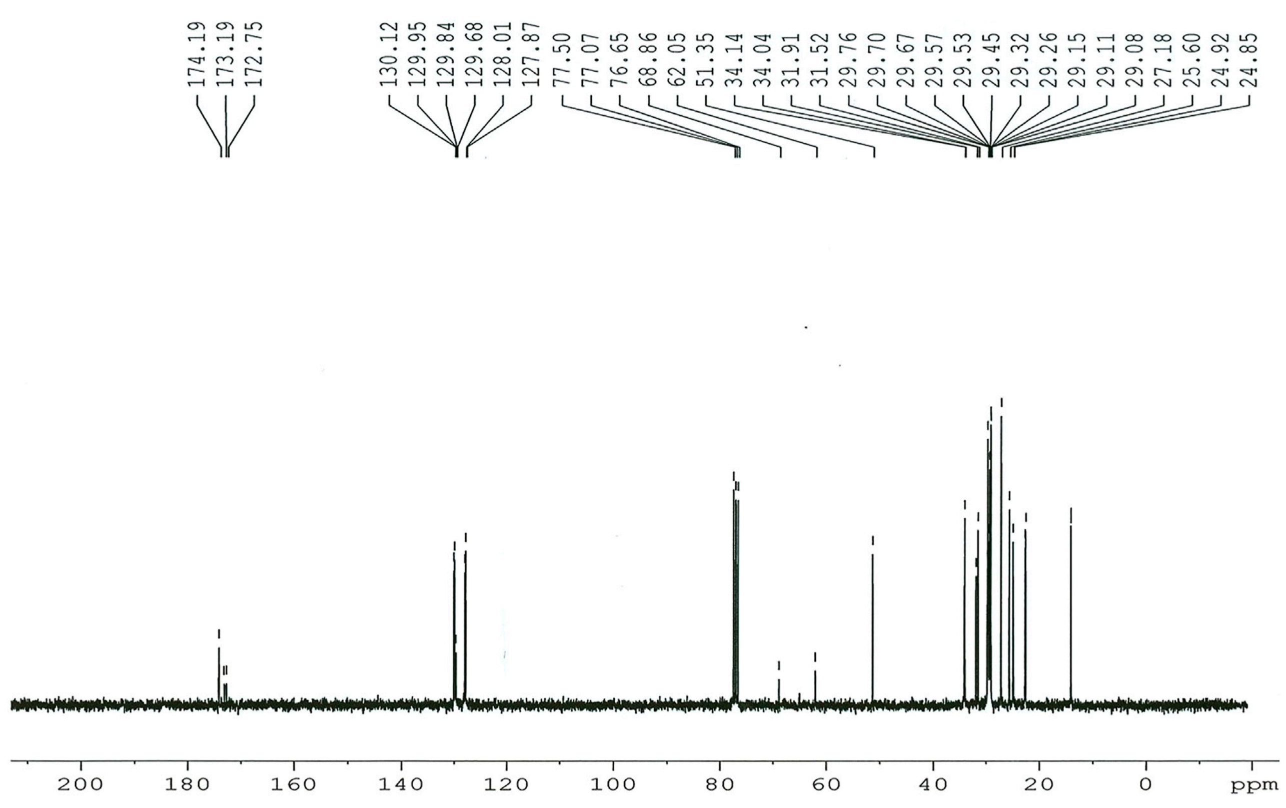

FIGURE 10 | ^{13}C NMR spectrum of the Dodonaea biodiesel.

next to the ester moiety in TAG were used to track the yield (Ullah et al., 2014). The ^{1}H NMR spectra of the methyl ester product obtained by the transesterification of Dodonaea oil are shown in **Figure 10**. The methoxy proton's distinctive peak was found at 3.649 ppm. The methylene triplet was discovered at 2.332 ppm. These two peaks at 3.649 and 2.332 ppm demonstrate the presence of methyl esters in the Dodonaea biodiesel. At 1.249 ppm, a strong singlet was detected, and at 0.904 ppm, a peak for the terminal methyl proton was detected. The signal at 5.274 indicates the existence of carbonyl methylene protons and olefinic hydrogen. ^{1}H NMR was also used to validate the conversion percentage of triglycerides to the biodiesel using equation 1. (Gelbard et al., 1995; Knothe 2009).

$C = 100 \times 2AMe/3ACH_2$ .... *Eq. (1)*

C = Percentage conversion of triglycerides to the corresponding methyl esters.

AMe = Integration value of the methoxy protons of the methyl esters.

ACH_2 = Integration value of the α-methylene protons.

3.5.2.2 ^{13}C NMR Spectroscopy

The presence of carbonyl esters (-COO-) and the C-O group in the Dodonaea biodiesel was determined using ^{13}C NMR. The distinctive peaks at 130.12 and 127.87 ppm in ^{13}C NMR spectra (**Figure 10**) indicate the existence of unsaturation. Methylene esters in the Dodonaea biodiesel have unsaturation bonds of 131.92 and 127.10 ppm [56–58]. The peaks at 24.85 and 34.14 ppm correspond to the terminal carbon of the methyl group and the methylene carbon of the long chain, respectively.

CONCLUSION

According to the current study on Dodonaea plant oil, this plant provides a promising and innovative source for biodiesel manufacturing. When the following criteria were met, the biodiesel output was reported to be 90% in this study: A 1:6 M oil-to-alcohol ratio, a temperature of 600°C, a reaction period of 70 min, and a concentration of 0.25% potassium hydroxide catalyst was used. The fuel characteristics of the Dodonaea plant biodiesel were analyzed and compared to the American Society for Testing and Materials standards. Dodonaea plant oil is nonedible and a promising source for biodiesel production, based on the fuel qualities and physico-chemical analyses outlined previously. It is also suggested that Dodonaea plant species be grown readily on the marginal and barn land to increase the supply of feedstock for the bioenergy industry. The main theme of various studies and the fuel properties test in the Dodonaea plant oil biodiesel was to monitor and control the quantity and quality of the prepared biodiesel and its potential for reliable commercialization.

DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/Supplementary Material, Further inquiries can be directed to the corresponding author.

AUTHOR CONTRIBUTIONS

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

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Prediction of Process Parameters for the Integrated Biomass Gasification Power Plant Using Artificial Neural Network

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Alternative renewable fuels like biomass have the potential to be considered for electricity generation by replacing the utilization of fossil fuels and reducing the greenhouse gas emissions into the environment. An integrated biomass gasification power plant is the best suitable option to generate electricity from different biomass feedstocks. Several modeling and simulation techniques have been utilized for the integrated biomass gasification power generation process. These models are utilized to predict the power output from the different gasifier types, designs, and feedstocks. In this study, An Artificial neural network (ANN) model is developed to estimate the process parameters of the Integrated biomass gasification power plant. This ANN model predicts the gasification temperature (T) and air to fuel ratio (AFR) for the gasification process integrated with the power plant at the atmospheric pressure. There is a total of ten input parameters such as moisture content of biomass (M), volatile matter (VM), fixed carbon (FC), ash content (A), element composition of carbon (C), oxygen (O), hydrogen (H), nitrogen (N), sulfur (S) and required power (KW) are used to predict the two key gasification process parameters T and AFR. The data generated from thermodynamic equilibrium model simulations are employed in the developed ANN model for the different 86 biomass feedstocks. The proposed ANN model was optimized for the Mean Squared Error (MSE) loss function and evaluated using MSE and R score metrics. It is observed that the best predicted for a hidden layer size was of 60 neurons. The best test score was achieved as an MSE score of 1,497 and test R 0.9976. This study can be implemented for any kind of biomass feedstock for the power generation system.

Keywords: biomass gasification, power generation, artificial neural network, parameter prediction, logistic regression

1 INTRODUCTION

In recent decades, the global energy demand and consumption have increased due to the rapid increase in population and industrial developments, which have also raised environmental issues worldwide (Hanchate et al., 2021). Fossil fuels provide about 80% of the world's overall total energy needs that cause significant environmental and health problems (Iea, 2011). Various energy sources,

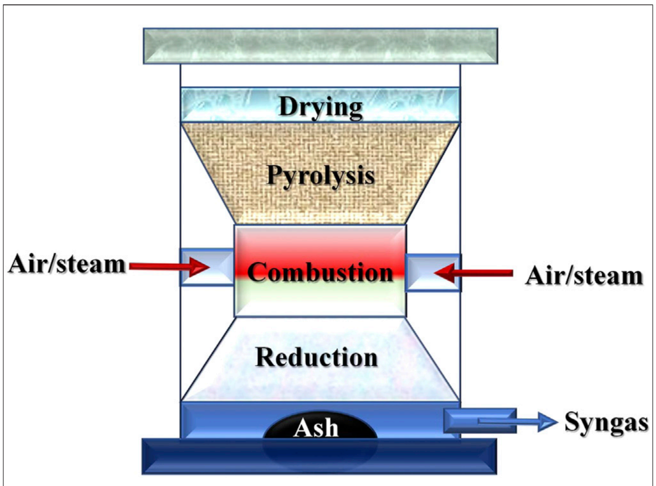

FIGURE 1 | A schematic of downdraft gasifier.

including renewable and non-renewable, are being taken into consideration to help meet the world's energy demand and environmental issues (Anwar et al., 2021; Kanwal et al., 2021). Combustion of primary conventional fossil fuel-based energy sources is the leading cause of pollutant emissions into the environment. Renewable energy options have the great potential to overcome emission problems of carbon-based energy systems to produce environmentally friendly clean fuels (Mofijur et al., 2013b; Sansaniwal et al., 2017). Biomass is considered one of the most suitable alternative energy resources of green energy that has the great potential to generate renewable energy in the form of electricity, bio-oil (biodiesel), biohydrogen, and biogas (Mofijur et al., 2013a; AlNouss et al., 2020; Ayub et al., 2022). Thermochemical and biochemical technologies are being adopted mainly to produce biofuels from biomass conversion (Wahlen et al., 2020; Tawfik et al., 2021). The former technologies are more efficient as compared to the biochemical technologies due to the fast reaction time and high energy efficiency (Sansaniwal et al., 2017). The biomass gasification process is one of the most suitable thermochemical conversion methods to produce the energy from the various biomass feedstocks for the different integrated energy systems (Ayub et al., 2021).

Biomass gasification is recognized as a sustainable conversion method since it produces clean syngas for effective heat and power generation and utilization while emitting comparatively less amount of pollutants (Mofijur et al., 2013a; Nguyen et al., 2020). The syngas formed from biomass gasification mainly consists of hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2), water (H_2O) vapors, methane (CH_4), and nitrogen (N_2) (Ayub et al., 2020a). During the gasification process, some minor products such as tar, solid char, nitrogen, and Sulphur compounds such as NOx and SOx can be seen alongside the primary components of syngas (Karmann et al., 2019). The high composition of H_2, low content of N_2, the minimal amount of impurities and contaminants, and high heating value (HHV) of the syngas can all be used to determine their suitability for use in thermal combustion systems for power production (Gambarotta et al., 2018).

The biomass gasification process is divided into four steps due to the apparent complexity of the chemical processes involved: biomass drying, pyrolysis, oxidation, and reduction (Mohapatra and Phale, 2021). The biomass feedstock is heated in the first step at a very low-temperature range (100°–150°C) to remove the moisture contents. At the second step, this feedstock is heated at high temperatures (150°–700°C), the pyrolysis phase, and turned into volatile and solid carbon-rich components, commonly called char or unconverted byproducts. At this point, a high viscosity black liquid called tar is formed that contains heavy components of organic and inorganic materials. Finally, the gasifier undergoes oxidation and reduction reactions, converting solid char, heavy organic, and volatile components into syngas at extremely high temperatures (800°–1,100°C) (Ayub et al., 2020b). The biomass gasification process and stages involved are schematized in **Figure 1**.

Many researchers have presented studies for the efficiency improvement of the biomass gasification process. The biomass properties, reactor design, and operational conditions are the key factors that determine gasifier efficiency, product gas composition, and overall system effectiveness in the gasification process. Moisture content (MC), volatile matter (VM), ash (A), fixed carbon (FC), and elemental composition of organic and inorganic components are all the key components that influence feedstock characteristics (Ferreira et al., 2019). Inside the gasifier, exceedingly complex thermochemical processes have also been observed. As a result, experimentation could provide practical information about the optimum process parameters and appropriate feedstock of selected biomass for the reactor, but they take a lot of time and are more expensive than modeling (Binns and Ayub, 2021). When it comes to numerical modeling, Biomass gasification models are divided into kinetic-based models (Inayat et al., 2012), computational fluid dynamic (CFD) models (Liu, 2014), thermodynamic equilibrium models (Zainal et al., 2001), and artificial neural network (ANN) models (Li et al., 2019). There is also a research dimension making progress in resolving CFD model to predict via machine learning using physics informed neural networks (Rafiq et al., 2022a; Rafiq et al., 2022b), that has the potential to make CFD predictions tasks faster from days to just seconds.

Kinetic models have been formulated on the basis of the reaction kinetics taking place within the reactors. Consequently, formulating more realistic models requires a detailed understanding of gasification processes and phase conversion transfer mechanisms. These models have the ability to estimate syngas gas composition, the temperature of the reactor, and gasification efficiency (Dang et al., 2021). CFD models are more complicated as compared to the kinetic and thermodynamic modeling approaches because they require a very long computing time and comprehensive knowledge about the reactions involved. Comprehensive numerical evaluations of feedstock components, mechanism of fluid flow, mass and energy transport, chemical expressions, particle structure and dimensions, and a set of parametric correlations and equations

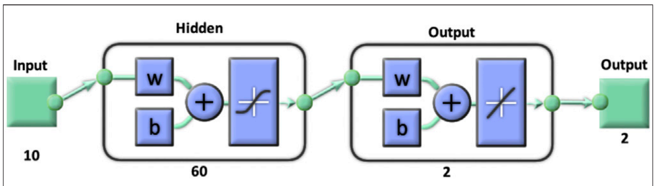

FIGURE 2 | Matlab ANN setup and configuration.

were accomplished employing CFD models. Various previous studies concentrated on equilibrium models, artificial neural networks, and other empirical or semi-empirical models that allow for quick computation, parametric analysis, and optimization of the gasification process to avoid the complexity and errors accompanying kinetic and CFD models (Kumar and Paul, 2019). Thermodynamic equilibrium models are categorized into stoichiometric and non-stoichiometric equilibrium models (Zainal et al., 2001). These models are based on the equilibrium constants of the gasification reactions involved, or the composition of syngas is calculated based on the Gibbs free energy minimization method. These models are simpler and provide faster computation than the kinetic and CFD models (Ayub et al., 2021). ANN models are developed based on the mathematical principles that correlate the input and output streams to predict the required output. An ANN model impersonates the functioning of the human brain to process the data quickly and effectively based on a system of neural networks provided to the model some human attributes. The application of ANN models for the biomass gasification process or integrated power generation system is very limited. Generally, input data set of ultimate and proximate analysis or process parameters are required to predict the outcomes. Hence, these models are more appropriate as compared to complex reaction-based problems. These models can be applied to the different types of reactor configurations (Li et al., 2018). Yucel et al. (2019) employed the ANN networks to estimate the gasification product gas composition from the biomass gasification process data. Li et al. (2018) presented a study based on the ANN model for the biomass gasification processes considering the heating rate and reactor length to predict the hydrogen composition. However, ANN models are not very attractive options for biomass gasification processes or integrated power generation systems due to the limitation of experimental data. Safarian et al.(2020a) developed the ANN model for power generation, and the data is generated from the integrated thermodynamic equilibrium model. They predicted the net power output from various biomass feedstocks under the equilibrium conditions.

In this study, an ANN model is developed and implemented for an integrated thermodynamic equilibrium power generation system to predict the required power's critical influencing gasification process parameters that have not been predicted before through ANN. This study aims to estimate the process conditions like gasification temperature (T) and air to fuel ratio (AFR) through ANN model development by using 86 different

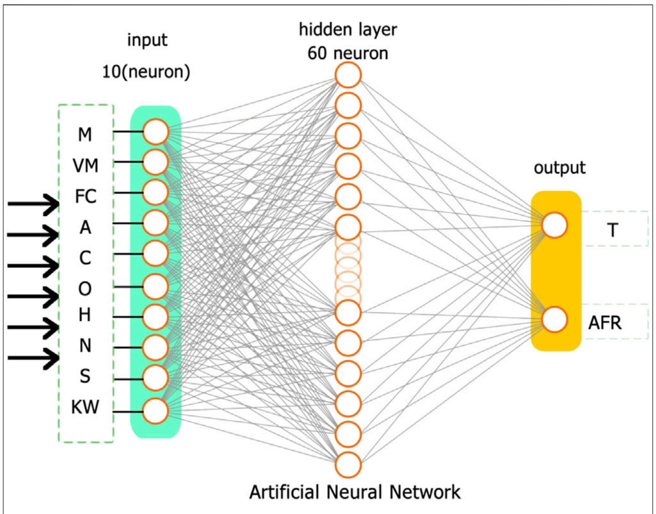

FIGURE 3 | ANN model architecture to estimate the process parameters for the integrated downdraft biomass gasification process with a power generation system.

biomass samples for the larger dataset of 1,032 observations. Moreover, this developed ANN model was tested and validated against the original data set, which has shown the effective utilization of the ANN model for the integrated biomass gasification power generation system to predict the critical process parameters. The model is optimized using the Mean Squared Error (MSE) loss function and evaluated our proposed model using two evaluation metrics, i.e., MSE and R score, using a hidden layer with 60 neurons. This model can be used for any kind of biomass feedstocks for the integrated power generation system.

This article is organized in the following sections. The proposed method is detailed in **Section 2**, whereas results and discussion are covered in **Section 3**. In the final section of the article, the conclusion of the study has been presented.

2 PROPOSED METHODS

Artificial Neural Network (ANN) (McCulloch and Pitts, 1943) is proposed to estimate the parameters of the biomass gasification system. The proposed model consists of an input layer, a hidden layer, and an output layer. The following sections cover the details of each component in detail.

2.1 Model Architecture

The ANN model is developed based on the thermodynamic equilibrium model simulated with ASPEN Plus integrated power generation systems. There are 1,032 data points of 86 different biomass feedstocks utilized in the ASPEN Plus model to estimate the power generation for the specific operating conditions (Safarian et al., 2020a; Safarian et al., 2020b). In this study, an ANN model for the downdraft biomass gasification process integrated with a power generation system is developed to estimate operating conditions-gasification

TABLE 1 | Proposed model layer configuration.

Layer (type)	Shape	Param #
Input	(10)	-
h1 (Dense)	(60,10)	660
output (Dense)	(2,60)	122
Total params	-	782
Trainable params	-	782

temperature (T) and air to fuel ratio (AFR)- for the required power output. This ANN model is developed and implemented in MATLAB utilizing Neural Network Toolbox, as shown in **Figure 2**.

Figure 3 presents the structure of the developed ANN model to predict operating conditions such as gasification temperature (T) and air to fuel ratio (AFR). All the ANN schemes have only one input layer containing ten input variables: moisture content (M), volatile matter (VM), fixed carbon (FC), Ash content (A), the elemental composition of carbon (C), oxygen (O), hydrogen (H), nitrogen (N), sulfur (S) and power (KW) produced and one hidden layer and one output layer containing process parameters or operating conditions that are gasification temperature (T) and air to fuel ratio (AFR).

We employ one hidden layer employed empirically, considering the size and complexity of the dataset. We conducted various experiments with hidden layer sizes and reported the observations explained in the results section. The best selection of model consisted of the hidden layer size of 60 neurons. Therefore, we have considered a single hidden layer with varying nodes from 10 to 120. The model early stopped at various epochs for various hidden layer sizes to keep from overfitting. We recorded epochs and obtained Mean Squared Error (MSE). The layer configuration is listed in **Table 1**.

2.1.1 Multi-Target Regression

Machine Learning classifiers usually support only one target variable. Regression models have a real value target, while classification models have a binary or multivalued target. The multiple regression model is one in which multiple independent variables are used to predict a dependent variable. Multi-target regression (Reyes and Ventura, 2019) is the term used when there are multiple dependent variables. If the target variables are categorical, then it is called multi-label or multi-target classification, and if the target variables are numeric, then multi-target (or multi-output) regression is the name commonly used.

2.1.2 Activation Function

The Rectified Linear Unit (ReLU) (Agarap, 2018) is an activation function for tensor output and makes the model training process nonlinear. In the convolution process, output tensors may contain positive and negative values, so before forwarding the output to the next layer, an activation function is applied. Positive values of ReLU remain unchanged, while negative values are converted to 0 values. The procedure is called rectification. From a range of negative and positive values, a non-saturating function $f(x) = max(0, x)$ returns zero or a positive value. Negative values are removed from the output feature map. During the convolution process, it increases the nonlinearity of the model without affecting the quality of classification in receptive fields. ReLU function can be expressed as follows.

$$Y(x,y) = \begin{cases} 0, & \text{if } X(x,y) < 0 \\ X(x,y), & \text{otherwise} \end{cases} \tag{1}$$

For a specific neuron at x and y positions, X (x, y) is the input to ReLU, and Y (x, y) is the output of ReLU activation.

2.2 Training Method

Our network is fed by the ten best input parameters, including M, VM, FC, A, C, O, H, N, S, and KW, while T and AFR are output parameters. First, the data are normalized by limiting the values to 0 and 1. Following normalization, 80% of the data were allocated for training, 10% for validation, and 10% for testing and evaluation. . For training data selection, we used the hold-out (Sammut and Webb, 2011) strategy.

A maximum of 500 training epochs were used to train the model. The training system was configured to stop when there is no further improvement to using an early stopping (Prechelt, 1998) technique with early-stopping patience of ten epochs. Levenberg-Marquardt optimizer (Moré, 1978) with a learning rate of 0.001 was used. Performance was optimized based on the choice of learning rate. Then, we optimized MSE as a loss function during training, which is a metric for regression prediction systems. A complete list of simulation parameters is listed in **Table 2**.

2.3 Dataset and Exploratory Data Analysis

The dataset consists of 1,032 experiments recorded for 86 feedstock available from (Safarian et al., 2020a). We conduct exploratory data analysis of the values from the experiments for more insights about the data. **Table 3** lists down the dataset statistics for each input component: M, VM, FC, A, C, O, H, N, and S, as well as precondition adjustment parameters: T and AFR.

Figure 4 depicts the inter-parameter correlation density. The parameter correlation matrix shows the correlation between each pair of parameters. The parameter correlation is measured before the task execution. A strong correlation exhibits a high degree of dependency of input parameters on each other. To best

TABLE 2 | Simulation parameters.

Param name	Value (range)
Model type	Artificial neural network
Model category	Multivariate Regression
Activation method	ReLU, Linear
Run Epoch	500
Stopping patience	10 epochs
Optimization Algorithm	Levenberg-Marquardt Algorithm
Learning rate	0.001
Loss method	MSE
Evaluation score	MSE, R
Training method	Hold out

TABLE 3 | Dataset statistics.

	M	VM	FC	A	C	O	H	N	S	KW	T	AFR
mean	14.43	75.38	17.79	6.84	47.69	38.44	5.86	1.01	0.16	148.53	1,050	2.03
std	13.5	7.22	4.91	7.98	4.37	6.21	0.88	1.2	0.23	87.26	335.57	0.21
min	2.5	47.8	0.5	0.1	27.33	11.18	2.94	0.1	0	0	600	1.8
25%	7.2	73.1	15.8	2.7	45.92	37.83	5.53	0.38	0.09	80.37	825	1.8
50%	8.75	76.8	17.6	4.2	48.43	39.74	5.88	0.66	0.1	148.78	1,050	2
75%	12.1	80.4	20	7.8	50.5	42.12	6.07	1.16	0.19	208.31	1,275	2.3
max	62.9	86.3	37.9	46.3	55.8	46.95	9.77	9.27	1.29	436.79	1,500	2.3

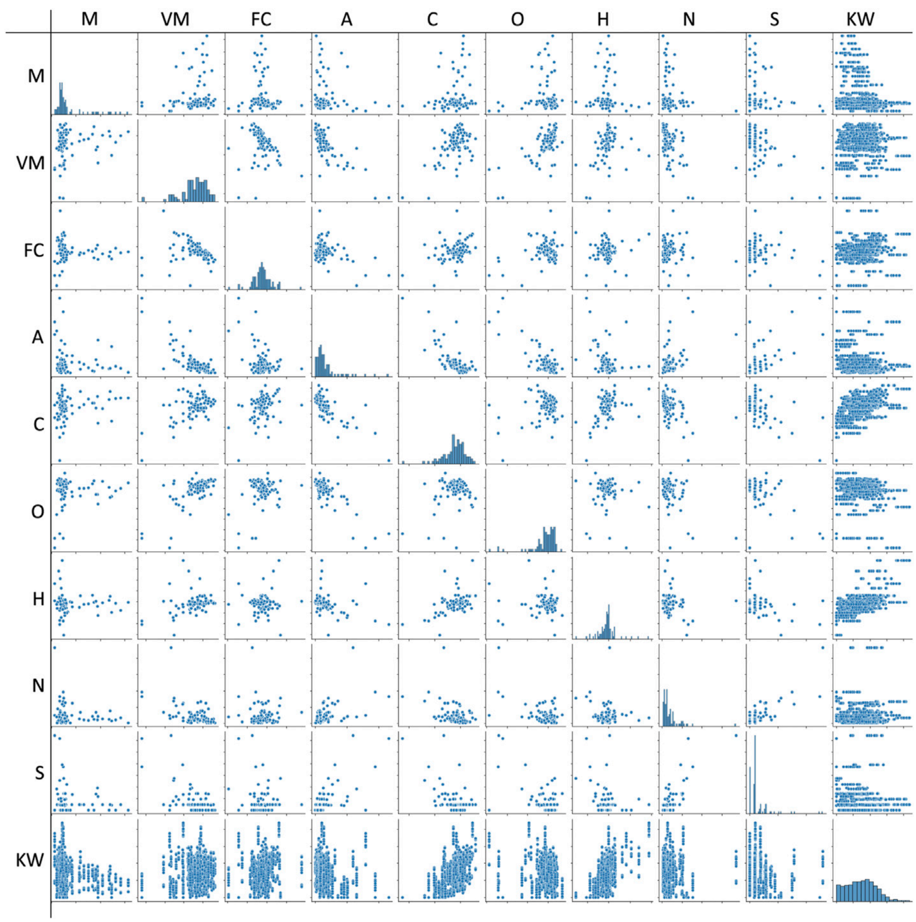

FIGURE 4 | Dataset inter-parameters correlation.

understand the relation between parameters, we compute the inter-parameter correlation heatmap as presented in **Figure 5**.

3 RESULTS AND DISCUSSION

3.1 Evaluation Metrics

A Mean Squared Error (MSE) (Sammut and Webb, 2011) and R score (Ribas et al., 2013) were used to evaluate the proposed model. The evaluation metrics are expressed in the following equations.

$$MSE = \frac{1}{n}\sum_{i=1}^{n}\left(Yi - \hat{Y}i\right)^2 \tag{2}$$

$$R^2 score = 1 - \frac{\sum_{i=1}^{n}\left(Yi - \hat{Y}i\right)^2}{\sum_{i=1}^{n}\left(Yi - \bar{Y}i\right)^2} \tag{3}$$

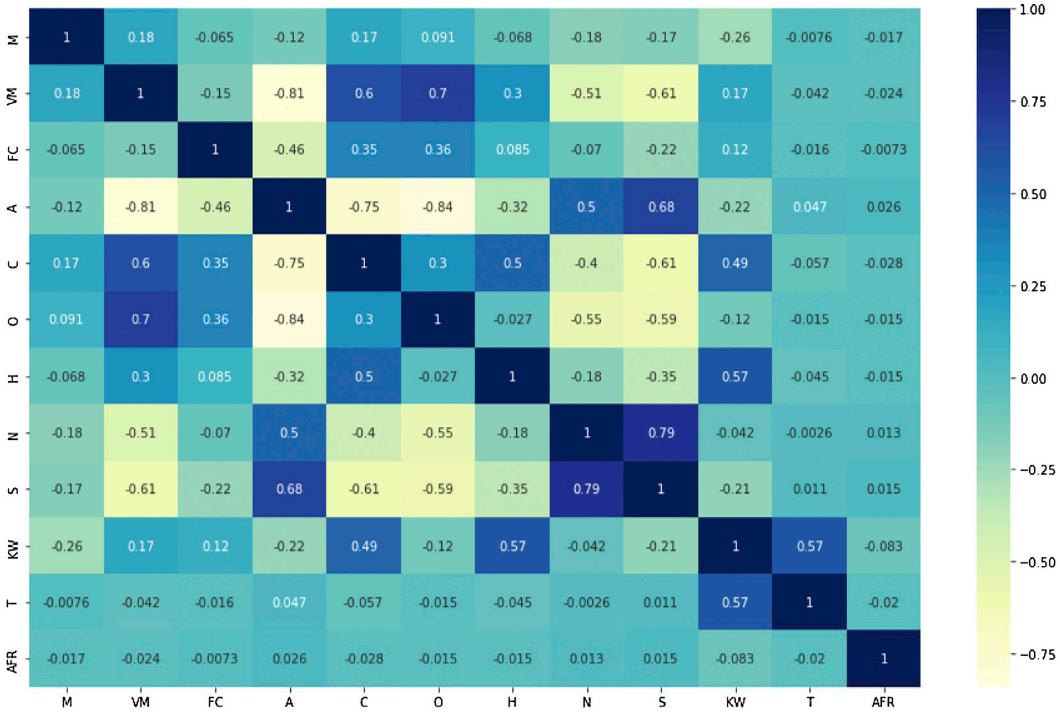

FIGURE 5 | Parameter correlation heatmap.

TABLE 4 | MSE loss at various neurons at the hidden layer. Bold values represent the best configuration for the model.

Model: Artificial neural network

Optimizing Algorithm: Levenberg-Marquardt Algorithm

Hidden layer size	Early Stop Epoch	Best?	MSE (test)	R (test)
10	61	-	3,549	0.9948
20	77	-	3,091	0.9952
30	58	-	2859	0.9952
40	50	-	3,310	0.9949
50	26	-	1913	0.9972
60	**16**	**Yes**	**1,497**	**0.9976**
70	16	-	1953	0.9972
80	45	-	4,049	0.9939
90	15	-	4,868	0.9929
100	16	-	6,160	0.9908
110	15	-	3,603	0.9942
120	14	-	3,662	0.9948

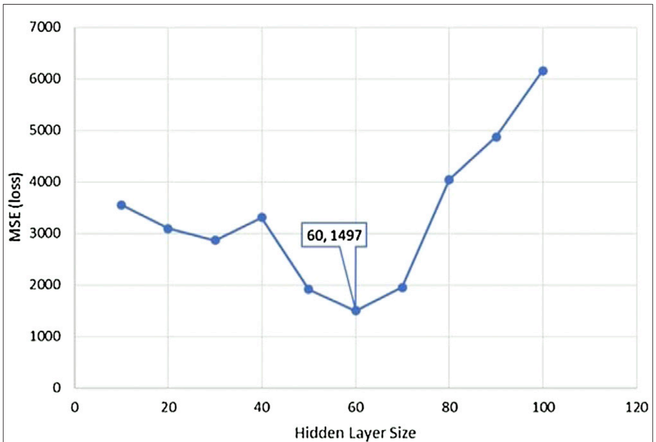

FIGURE 6 | Loss plot at various number of neurons at the hidden layer.

The values of $\bar{Y}$ and $\hat{Y}$ represent the predicted value and mean value of Y, respectively.

3.2 Model Validation

A model performance evaluation is presented in **Table 4**. As the model is optimized to minimize MSE loss, we compute train and test set metrics to show overfitting and bias. The applied dataset showed excellent performance. The scatter plot in **Figure 7** compares predicted values with actual test values. Testing, validation, and training plots showed a significantly stable output with minor outlier predictions, whereas most of the data were predicted correctly and followed the optimal line.

Table 4 shows the test MSE and R score for various hidden layer sizes. We observe that the given observation is best predicted for a hidden layer size of 60 neurons. The best score achieved reads as a test MSE score of 1,497 and test R 0.9976. Therefore, we recommend a network size of 60 neurons at the hidden layer. **Figure 6** graphically plots the loss behavior for different neurons at the hidden layer.

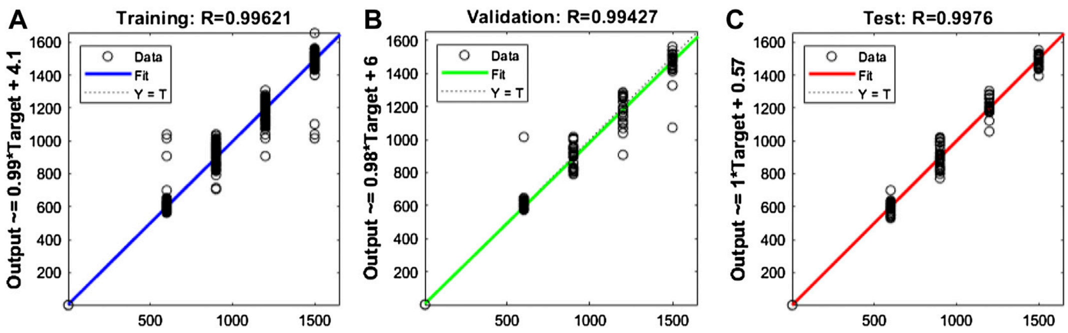

FIGURE 7 | Scatter plot for **(A)** training **(B)** validation, and **(C)** test dataset distributions.

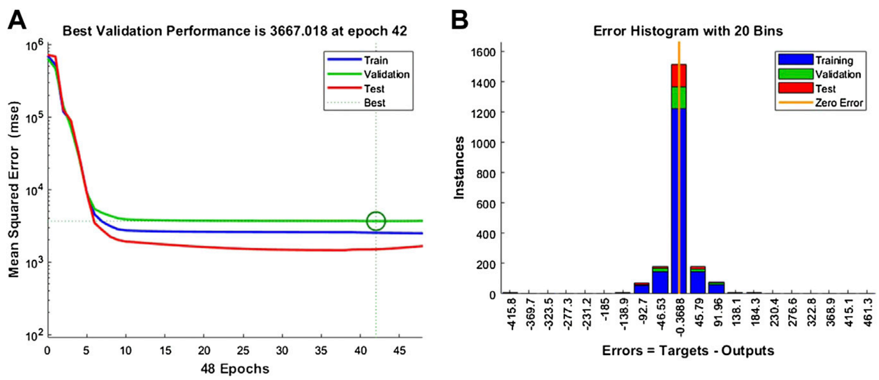

FIGURE 8 | **(A)** Training history and **(B)** error histogram.

We trained the model using a dataset split of 80% training, 10% validation, and 10% test set. We collected loss plots for each of the splits, as shown in **Figure 7**. Here (A) represents the training split, (B) depicts the validation split scatter plot, and (C) shows the test split performance. All of the split plots were generated at an optimal layer size of 60 neurons with dataset splits described earlier in this section.

The proposed model training, validation, and test performances are depicted in **Figure 8**. Where (A) plots the MSE loss over running epochs, it is evident that the model performed a smooth training without any overfitting and underfitting. Similarly, (B) depicts the error histogram with 20 bins, where sample instances are the highest concentration peak at zero with a small error spread.

The performance of the developed model is measured using standard performance metrics, i.e., MSE and R score. It is evident that the proposed model fits the presented data and estimates the process parameters. We record the bias and weights of the best-performing model in **Supplementary Table S1** with a bi-color heatmap for the quick perception of the model states.

The dataset employed is obtained by using the ASPEN Plus process simulator which is widely used for near-perfect process parameters and production environment simulations. Data reliability is highly dependent on experiments conducted to generate data and the process design and conditions. Since the dataset is peer-reviewed in a recent research article (Safarian et al., 2020a; Safarian et al., 2020b) therefore, we consider it safe to believe the reliability. We use actual data for training and validation, and we have tested our predictions on a subset of actual data separated using the holdout model evaluation method.

3.3 Practical Implications

The ANN models are historically known to perform best when sufficient data is present, whereas physical sciences lack experimental data due to the nature of experiments and the efforts required in collecting the data. Inspired by evolving influence and successful track record of artificial intelligence and machine learning in physical sciences, we have introduced the proposed model. We expect this approach to be more progressive and succeed by employing larger datasets and trying new approaches. Our proposed has significant benefits over the conventional physical science experimental approach to predict process parameters without trivial experiments for new materials. This approach makes it more useful in further study of biomass gasification for power generation and a good start for the production environment to try starting parametric conditions of temperature and air to fuel ratio. The recommended parameters from the model can save setup time and materials and reduce overheads in initializing an integrated gasification process for power generation.

4 CONCLUSION

An ANN model is developed for the integrated biomass gasification power plant in this study. Gasification temperature (T) and air to fuel ratio are the two key process parameters that influence the efficiency of the gasification process and the power output. Therefore, an ANN model is proposed to predict these process parameters to increase the efficiency of the integrated biomass gasification power generation system. For this purpose, 1,032 simulated data points for the 86 biomass feedstocks are used to develop, train, test, and validate the developed ANN Model. In this model, 80% of the data were allocated for training, 10% for validation, and 10% for testing and evaluation. It is observed that the given observation is best predicted for a hidden layer size of 60 neurons. The best test score was achieved as an MSE score of 1,497 and test R 0.9976. Therefore, we recommend a network size of 60 neurons at the hidden layer. We further suggest to employ the proposed approach for pre assessment of process parameters to quick start the biomass gasification production process. The model intend to increase the productivity and save the fuel and time to smoothen out the biomass gasification production.

DATA AVAILABILITY STATEMENT

Publicly available datasets were analyzed in this study. This data can be found here: https://www.sciencedirect.com/science/article/pii/S2352340920312701.

AUTHOR CONTRIBUTIONS

HA: Data collection, conceptualization, methodology, investigation, writing—original draft, software. MR: Data collection, conceptualization, methodology, investigation, writing—original draft, software. MQ: Formal analysis, writing—review and editing, GR: Writing—review and editing. GC: Supervision, writing—review and editing. ML: Supervision, writing—review and editing.

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SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fenrg.2022.894875/full#supplementary-material

Supplementary Table S1 | The bias and weights recorded for best performing model.

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Nanomaterials for biogas augmentation towards renewable and sustainable energy production: A critical review

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Nanotechnology is considered one of the most significant advancements in science and technology over the last few decades. However, the contemporary use of nanomaterials in bioenergy production is very deficient. This study evaluates the application of nanomaterials for biogas production from different kinds of waste. A state-of-the-art comprehensive review is carried out to elaborate on the deployment of different categories of nano-additives (metal oxides, zero-valent metals, various compounds, carbon-based nanomaterials, nano-composites, and nano-ash) in several kinds of biodegradable waste, including cattle manure, wastewater sludge, municipal solid waste, lake sediments, and sanitary landfills. This study discusses the pros and cons of nano-additives on biogas production from the anaerobic digestion process. Several all-inclusive tables are presented to appraise the literature on different nanomaterials used for biogas production from biomass. Future perspectives to increase biogas production via nano-additives are presented, and the conclusion is drawn on the productivity of biogas based on various nanomaterials. A qualitative review of relevant literature published in the last 50 years is conducted using the bibliometric technique for the first time in literature. About 14,000 research articles are included in this analysis, indexed on the Web of Science. The analysis revealed that the last decade (2010–20) was the golden era for biogas literature, as 84.4% of total publications were published in this timeline. Moreover, it was observed that nanomaterials had revolutionized the field of anaerobic digestion, methane production, and waste

Abbreviations: AD, Anaerobic Digestion; AGS, Anaerobic Granular Sludge; CM, Cattle Manure; COD, Chemical Oxygen Demand; DIET, Direct Interspecies Electron Transfer; EGSB, Expanded Granular Sludge Bed; EPS, Extracellular Polymeric Substance; HRT, Hydraulic Retention Time; ICZ, NZVI coated zeolite; MEG, Mono-Ethylene Glycol; MSW, Municipal Solid Waste; MWCNT, Multi-Walled Carbon Nanotubes; NC, Nano-composite; NM, Nanomaterials; NP, Nanoparticles; NW, Nanowires; NZVI, Nanoscaled Zero-Valent Iron; OMS, Octahedral Molecular Sieve; SWCNT, Single-Walled Carbon Nanotubes; TS, Total Solids; TSS, Total Suspended Solids; UASB, Up-flow Anaerobic Sludge Blanket; VFA, Volatile Fatty Acids; VS, Volatile Solids; WAS, Waste Activated Sludge.

activated sludge; and are currently the central pivot of the research community. The toxicity of nanomaterials adversely affects anaerobic bacteria; therefore, using bioactive nanomaterials is emerging as the best alternative. Conducting optimization studies by varying substrate and nanomaterials' size, concentration and shape is still a field. Furthermore, collecting and disposing nanomaterials at the end of the anaerobic process is a critical environmental challenge to technology implementation that needs to be addressed before the nanomaterials assisted anaerobic process could pave its path to the large-scale industrial sector.

KEYWORDS

anaerobic fermentation, biogas, nanotechnology, nanoparticles (NPS), waste, biomass, biohydrogen, nanomaterial

Introduction

Exponential growth in the world population has raised the energy demand drastically (Hagos et al., 2017). Meeting the energy requirement has now become an area of prime importance for all nations. At present, the world is highly dependent on conventional energy sources, i.e., fossil fuels (Palaniappan, 2017). The available reserves for fossil fuels are diminishing rapidly; one study indicated that existing reserves would last till 2050 (Satyanarayana et al., 2011). Besides, these conventional fuels contribute much to environmental pollution and ecological destruction. Along with fluctuating fuel prices, these factors have led the fuel industry to move towards sustainable renewable resources to fulfill the energy demand (Malik and Sangwan, 2012). Currently, fossil fuels fulfill almost 90% of world energy demands, and it is expected to minimize it to 50% by 2040 via incorporating more sustainable renewable energy sources such as solar, wind, geothermal, tidal, and biomass (biofuels) (Hussein, 2015).

Biofuels can be produced by utilizing locally available organic feedstock. Various methods are available for organic matter to energy conversion, but AD (Anaerobic Digestion) is among the most preferable, specifically for biogas production (Hao et al., 2019; Feng et al., 2021). In this process, the absence of O_2 provides a favorable environment for bacteria to decompose organic matter by breaking it into methane and other by-products (Seadi et al., 2008). AD finds its implications for waste treatment on a broad category of waste, including sludge, wastewater, and municipal waste (Vasco-Correa et al., 2018). It is also mentioned among widely considered methods for converting complex waste to biogas (Holm-Nielsen et al., 2009; Feng et al., 2014). Additionally, applications of AD in the treatment of animal manure (Bidart et al., 2014), energy crops (Lönnqvist et al., 2013), organic food waste (Zhang et al., 2016), microalgae (Park et al., 2009), and agricultural residues (Mushtaq et al., 2016) make it stand among other methods.

In the mentioned process of organic waste conversion to biogas, four main phases are usually included; (i) hydrolysis, (ii) acidogenesis, (iii) acetogenesis, (iv) methanogenesis (Christy et al., 2014), see Figure 1. These four phases highly dependent upon the extent of interactions between microorganisms during each phase. In the first phase, hydrolytic bacteria are in action. They transform complex organic matters such as proteins, fats, and carbohydrates into organic monomers. Most organic matters contain complex macromolecules that cannot be directly used by acidogenic microorganisms. Therefore, hydrolysis is needed to break complex structures into small molecules (monomers), which ultimately can be used in the second phase of anaerobic digestion. In the second stage, acidogenesis, thus formed monomers are transformed into Volatile Fatty Acids (VFAs) with the help of fermentative bacteria. In the third phase, acetic acid is formed accompanied by evolving hydrogen gas by the action of acetogenic bacteria. Among four phases of anaerobic digestion, acidogenesis is considered the fastest one. The last stage is methanogenesis, where products of the last phase are transformed into methane and carbon dioxide (Mao et al., 2015; Zaidi et al., 2021a). Thus, formed methane significantly varies in quality based on a few factors such as biomass composition, additives, selection of conversion process, and precursors. Typically, the composition of biogas is specified by methane and carbon dioxide contributing 50–75% and 25–45%, respectively. A minute amount of other gasses can be there, usually of calorific values of 21–24 MJ/m^3 (Ganzoury and Allam, 2015).

Biogas, as a renewable energy source, is an emerging sector globally with consecutive increments in the production capacity over the years. Figure 2 represents the regional breakdown, not only reflecting the overall increment but also every region is showing growth over the years, which is a promising motivation for scientists and investors for the biogas augmentation utilizing all the available technologies to pursue state-of-the-art solutions for biogas production. Nanotechnology, which can be defined as interpolation of matter at very small dimensions (less than or equal to 100 nm), is in its emerging phase. At this small scale, material properties change (such as melting point and chemical changes) that has made this technology pivot to researchers (Antonio et al., 2017). Nanotechnology can be used in many fields such as materials engineering, life sciences, electronics, biotechnology, information technology, and cognitive sciences

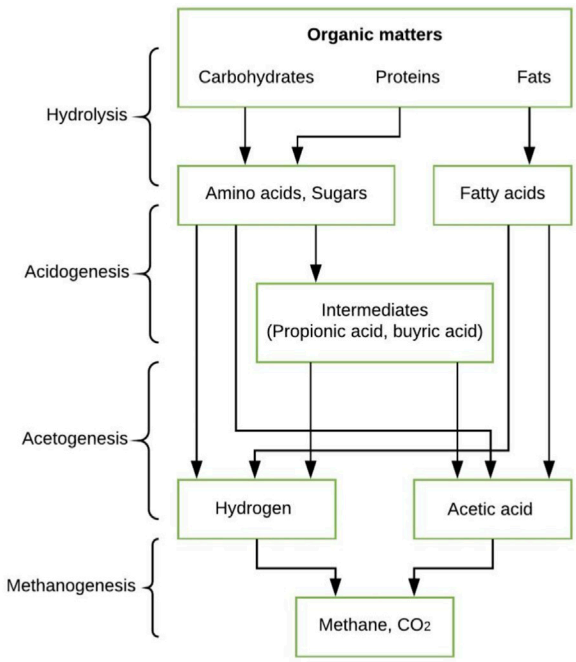

FIGURE 1
Common major sequential processes during anaerobic digestion (Feng et al., 2018).

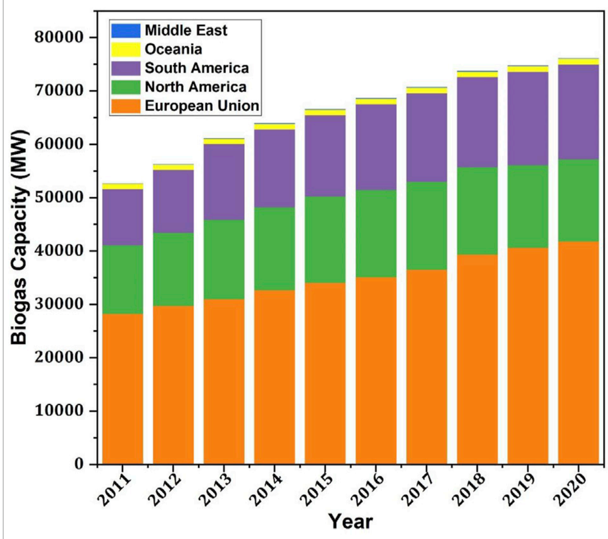

FIGURE 2
Regional breakdown of global biogas capacity (RENA, 2021).

(Khan et al., 2009; Demetzos, 2016). The bioenergy field can be revolutionized by improving catalytic conversions and enhancing catalytic efficiency. Literature is evident from the recent implications of nanoparticles (NPs), nanomaterials (NMs), nanosheets, and others in bioenergy production (Rahman et al., 2016). Wu et al. (2021) recently conducted a literature review to highlight the importance of different operating parameters on biogas production and to understand the importance of different auxiliary technologies in optimizing these operational parameters. The study finds that the addition of NPs is a promising option, especially for mainstream biogas production plants, to enhance biogas production. However, some challenges (such as high investment cost, strict control of NPs concentration, energy demand, and disposal risks) need to be minimized before introducing NPs in the industrial sector (Zaidi et al., 2021b). In another review study (Jadhav et al., 2021), the authors studied the impact of metallic NPs on microbial direct interspecies electron transfer for biogas production enhancement. The use of metallic NPs was found to be cost-effective, efficient, and sustainable for biogas production. Hassanein studied the role of electro-conductive NPs. NPs were found to be promising for AD process stability and efficiency enhancement (Zaidi et al., 2019a; Kumar et al., 2021). Specifically, metallic NPs were highlighted as the most famous NPs for their potential to decrease lag time and improve the biogas production and process stability. Moreover, studying the role of size, type, and concentration of metallic NPs is still a challenge (Hassanein et al., 2021). After conducting a literature review, Ellacuriage stipulated that to increase volumetric efficiency and reduce initial capital cost, NPs augmentation is the most suitable approach (Ellacuriaga et al., 2021).

The economic feasibility of large-scale AD has always been a prime concern for the research community. The application of NPs has contributed to the economic feasibility of AD by enhancing catalytic efficiency (Faisal et al., 2019). However, the disposal of these NPs after biogas production is still a significant environmental challenge. Therefore, there is a dire need to find environmentally friendly disposing methods for NPs being used in AD. Moreover, the main challenge in understanding nanomaterial's augmentation with biogas is their kinetics. The root cause of lower biogas production in the absence of NPs is a cellular wall that restrains the interaction of catalysts with the substrate. Studying the impact of different NPs, through the lens of their positive and negative aspects could improve our understanding of biogas production.

This paper presents a comprehensive state-of-the-art review highlighting the direct influence of nano-additives and nano-nutrients on either biogas production enhancement or adverse effects during anaerobic digestion. Future perspectives to enhance biogas production via nano-additives are also presented. The focus has been placed on classifying available literature according to the type of nanomaterial employed during AD. The detailed discussion shows how nanomaterials can be effectively used for biogas augmentation to improve biomass

TABLE 1 Classification of nanomaterials.

Classification	Examples
One dimensional NMs	Nanolayers
Two dimensional or 2D NMs	Nanowire, nanotube, nanorod, Graphene
Three dimensional NMs	Quantum dots, fullerenes, metal and metal oxides NPs

utilization as a renewable and sustainable energy source. Furthermore, this study reports a bibliometric analysis of biogas literature published in the last 50 years. To the best of the authors' knowledge, it is the first study based on a detailed quantitative literature review.

Nanomaterials role in chemical reactions

Nanomaterials (NMs) are materials having one or more dimensions smaller than 100 nm. This resulted in a much high surface area of the material just because of the size. A spherical NP of 1 nm diameter will have approximately 100% of its atoms on the surface. Whereas an NP having a diameter of 10 nm would have only 15% of its atoms on the surface. It would be expected from a particle having a higher surface area to be more reactive than the same mass of material consisting of larger particles, as chemical reactions typically take place at surfaces (Rao et al., 2001).

NMs can be classified into three categories contingent on a number of dimensions at the nanoscale as per the British Standards Institution (BSI, 2007). Table 1 depicts some NMs from each group. In the literature, nanoparticles are specified as 3D particles having at least one dimension of less than 100 nm. They could have various morphologies and shapes. As discussed earlier, the surface properties and high reactivity of the NPs are due to the increased surface area to volume ratio. This distinctive feature of NPs makes them popular in products and techniques where chemical reactions are important. In this text, nanomaterials and nanoparticles are used as interchangeable terms, both referring to the nano-scale materials in the context of the discussion.

There are numerous benefits of NMs for biogas production. NMs provide more exposed sites available for anaerobic bacteria (Rahman et al., 2016). It also helps in the solubilization of organic matter to release intercellular polymeric substances. The control over surface features aids in catalyzing animal fats, plant cell membranes, and cellular remains. They also help a chemical modification of organic matter (Nyberg et al., 2008). The application of NMs for biogas production can be one of the possible ways to sustain this renewable energy source for large-scale production. Several NMs are used as an additive to enhance biogas production.

Research trends in biogas studies: Past and contemporary

In order to find out a pattern, sequence, and significant research trends, quantitative analysis is performed using the web of science database, as shown in Figures 3,4. To conduct the analysis, 14,000 journal articles (research papers only) were explored from the web of science database, and content analysis was performed to determine the main keywords used by researchers. These keywords define the mainstream of research within a field. The colors depict different eras of research. The diameter of bubbles denotes the impact of that keyword, i.e., the occurrence of a keyword. These bubbles are interconnected using links. Link strength is evident in the relation between two keywords, i.e., co-occurrence in the same research article.

The survey was divided into two eras for analysis purposes, the first 1970–2016 and the second 2017–2020. The purpose of this division was first to understand research evaluation within the field and second to determine the current topics of research to define future directions. Figure 3 revealed that anaerobic digestion and biogas production are among the most used keywords throughout the era 1970–2020. In addition, these keywords find their most implications in the last 5 years as denoted by red color. Therefore, it is concluded that anaerobic digestion and biogas production are among hot topics of research.

In order to further understand the main streams of research within anaerobic digestion and biogas production, data from the last 4 years were evaluated. It is pertinent to mention that 2010–2020 is observed as the main era of research rise in this field. A total of 84.4% of the publications have been published in the last 10 years. Out of this, 84.4%, 54.7% of publications belong to the last 4 years, 2017–2020. Therefore, 2017–2020 can be mentioned as a research-intensive period of biogas production. This high research interest is due to the emergence of new technologies and their implications for biogas production.

The analysis of research keywords used in the last 3 years depicts that the emergence of NP is the main technology that evolved in this era and got incredible attention from the research community. The yellow color of the keyword NP is evident to a sharp contrast and shift towards effective implementation of NP in producing biogas during 2019–2020. The strong link of NPs

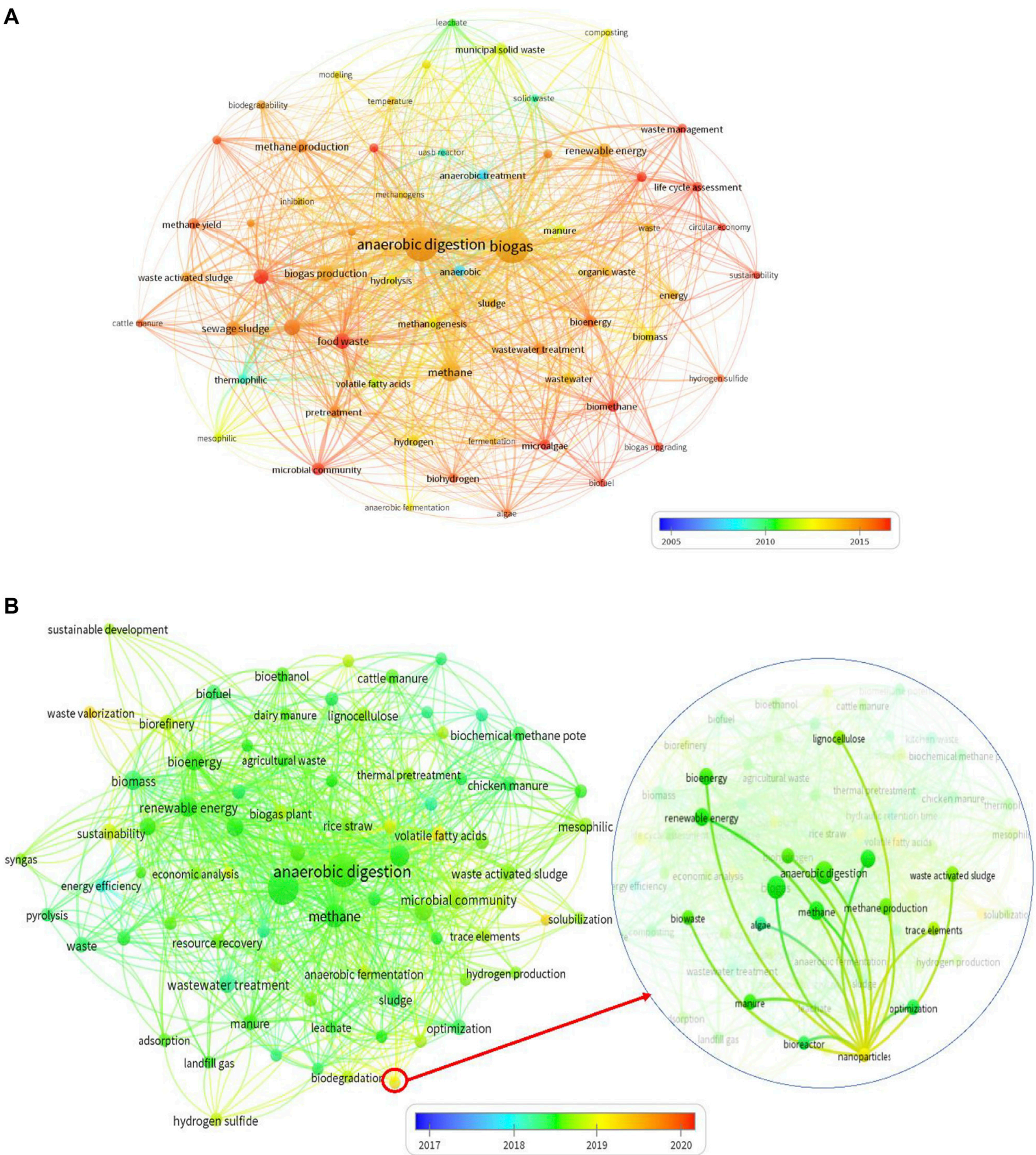

FIGURE 3
Major research terms used by researchers from **(A)** 1970–2020 **(B)** 2017–2020.

with anaerobic digestion, methane production, and waste activated sludge represents NPs' reputation for mentioned technologies with in short duration. Owing to this reputation, NPs implications for biogas production can be regarded as the central pivot to the research community.

The most important aspect to note is the emergence of nanoparticles in the last decade and their strong connection with biogas production. Therefore, based on research trends, it can be concluded with confidence that nanoparticles and biogas production starting from sludge have gotten significant attention in recent years. In this regard, this review is conducted to update how nanomaterials have contributed to biogas production.

Application of nanomaterials for biogas production

This section presents a comprehensive review of the recently reported studies on biogas production based on the class of materials used for a different kind of feedstock. Nanomaterials are a vital candidate to enhance biogas production from different inorganic waste. Basically, at the nanoscale, the surface area of the material is high, making the reaction relatively fast (Zaidi et al., 2019a). In addition, these NPs interact with the cell membrane of sludge, leading to structural changes in the cells that finally make it bacteria permeable membranes. In this way, more bacteria find their way to attack sludge and hence increase overall biogas production (Faisal et al., 2019). Nevertheless, attention has been focused on the use, effects, and outcomes of various NMs for biogas production.

Trace metal nanomaterials for biogas enhancement

Trace metals are essential for methanogenic bacteria growth in an AD reactor (Qiang et al., 2013). Metals nutrients such as iron, cobalt, nickel, etc., are found to influence the AD process significantly (Kelly and Switzenbaum, 1984; Zaidi et al., 2018). Zero-valent iron has been widely employed to treat various kinds of waste. The literature showed that it releases electrons for methanogenesis during the AD process, resulting in biogas augmentation. Nanoscaled Zero-Valent Iron (NZVI) has a high surface-to-volume ratio; this characteristic increased the chemical reaction sites and positively influenced the AD. Su et al. (2015) investigated the influence of 0.05, 0.10, and 0.20 wt% NZVI (60–120 nm) on the AD of Waste Activated Sludge (WAS) for 20 days at the mesophilic temperature (32 ± 1°C). The results indicated that 0.05 wt% and 0.10 wt% NZVI increased the methane production by 9.8% and 4.6%, respectively. However, 0.20 wt% NZVI decreased methane production by 8.8%. The authors suggested that NZVI stimulates methanogenic populations and sulfate reducers. It also accelerates sludge stabilization in AD resulting in increased biogas and methane production. The metallic iron core caused a slow release of soluble Fe^{2+} acting as a donor and caused the formation of reactive oxygen species. The hydrogen sulfide reacted with NZVI oxide shell on the surface and resulted in the formation of FeS and FeS_2, which was regarded as the main reason for decreasing H_2S and an increase in methane. These findings agree with Carpenter et al. (2015), who reported that cytotoxicity of NZVI to the microorganism in the AD with varied particle size and reactivity could improve the degradation increase biogas production while decreasing CO_2. The observed decrease in biogas production at a higher concentration of NZVI by Su et al. (2015) was confirmed by the study conducted by Suanon et al. (2016). According to the authors, improvement in biogas and methane production is dose-dependent, and a higher dose of NZVI could result in an inhibitory effect. Another study conducted by Suanon et al. (2017) investigated the effect of 0.1 wt% NZVI on methane yield from wastewater sludge at mesophilic conditions (37 ± 1°C) for 50 days. Results showed an increase of 25.2% in methane production.

The production efficiency of biogas and methane yield from Cattle Manure (CM) slurry were discussed under the influence of various concentrations of NZVI, ranging from 5 to 20 mg/L. Batch-wise, anaerobic fermentation of CM was conducted at 37 ± 0.3°C, 90 rpm of rotating speed, and 50 days of Hydraulic Retention Time (HRT). This study concludes that the addition of NZVI is favorable for biogas production. The addition of minute amount, amounting to only 5 mg/L, incremented biogas and methane production by 1.44 and 1.38 times, respectively. The best concentration was found to be 20 mg/L which increases biogas and methane volume by 1.45 times and methane production by 1.59 times. The authors mentioned that the addition of these NPs improves the startup of biogas production and hence reduces the lag phase in comparison with control. The optimal NZVI concentration found in this study was further experimented with by the same authors (Abdelsalam et al., 2016).

The influence of NZVI on the AD of WAS was studied by Wang et al. (2016) at concentrations of 1, 10, 100, and 500 mg/g Total Suspended Solids (TSS), respectively. Batch anaerobic digesters were used for the AD with working volume, operating temperature, and mixing rate of 1 L, 35 ± 1°C, and 120 rpm, respectively, for HRT of 30 days. The study indicated that 10 mg/g TSS increased methane production to 120% of the control, whereas other concentrations had no considerable effect, see Figure 5. This is also in agreement with results obtained by Su et al. (Su et al., 2015) and Suanon et al. (Suanon et al., 2016).

In contrast, Amen et al. (2017b) investigated different concentrations of NZVI (50, 100, and 250 mg/L) on anaerobic activated municipal sludge and showed 25% and 62% enhancement in biogas and methane, respectively, by 250 mg/L. In another study conducted by Amen et al. (2017), a novel method of coating NZVI on zeolite and mixing NZVI with zeolite is investigated for improving biochemical methane potential and the lag phase from the AD of anaerobic sludge at 37°C for 14 days of HRT. Zeolite is a mineral compound (a mixture of silica, aluminum, and oxygen). It is a non-cytotoxic mineral having a systematic structure containing channel and pore cavities. The authors worked on the idea that zeolite can trap NZVI inside channels and immobilize the NZVI particles on its surface. Using zeolite as an absorbent carrier for NZVI may be a suitable

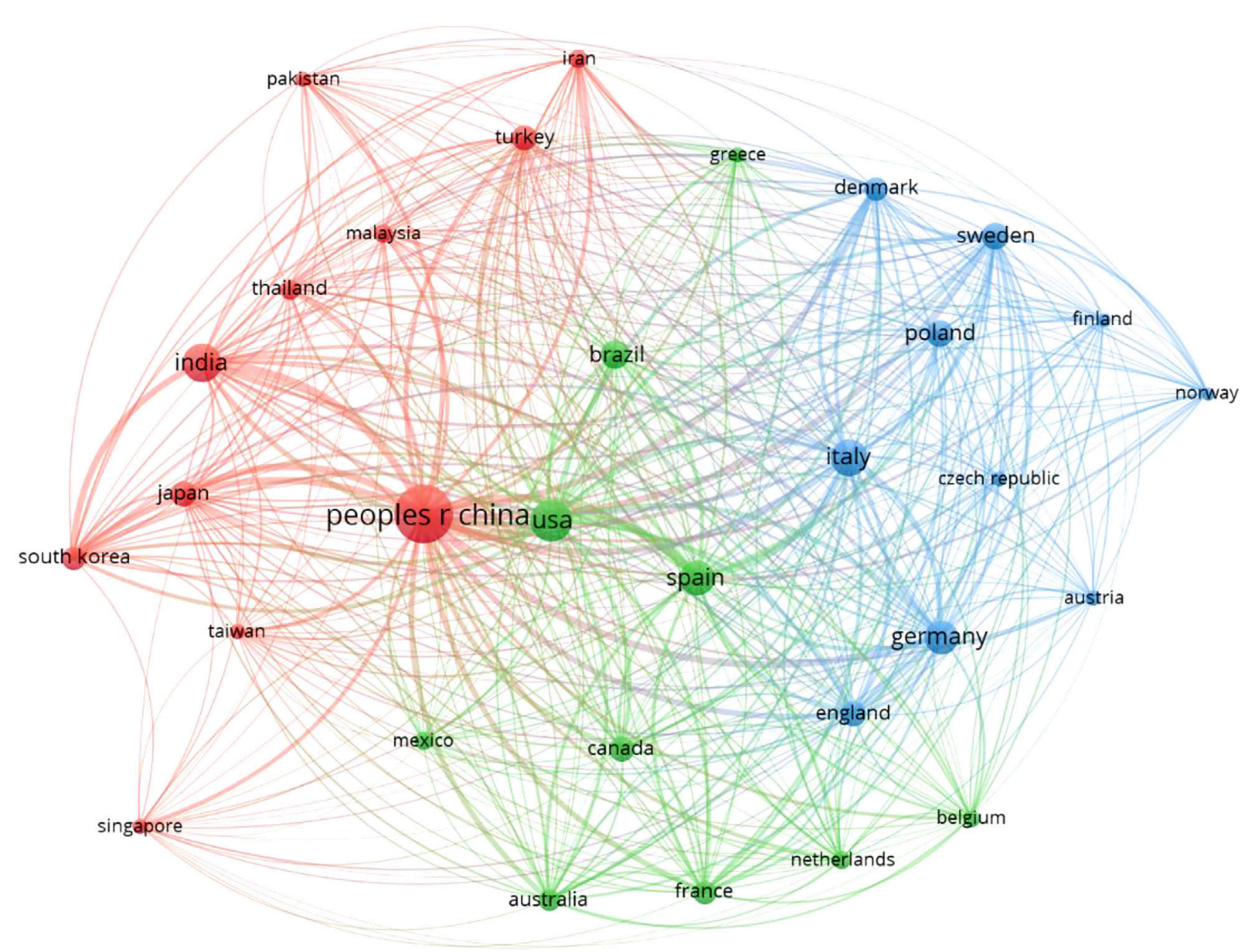

FIGURE 4
Currently active countries on nanotechnology-based biogas production on the basis of the number of citations.

way to stimulate microorganisms and prevent cell membrane disruptions caused by NZVI. The authors used this method to examine the overall performance of the AD process. It can be observed that till day 8, ICZ caused a lag period, and then from day 9 to day 14, it caused significant biogas enhancement (Amen et al., 2017b). The lag phase is attributed to the time required by anaerobic sludge for the adaptation of ICZ. Results showed that 500 mg/L NZVI and 4 g/L zeolite mixture produced 130.87% increase in cumulative biogas production, whereas NZVI alone (45nm, 1000 mg/L) gave a 105.46% increase in cumulative biogas production. The NZVI coated zeolite (ICZ) with 500, and 1000 mg/L concentrations produced the highest amount of biogas in comparison with other additions and control. Cumulative biogas increase of 149.95% and 286.75% is observed for 500 and 1000 mg/L ICZ, respectively. The study concluded that the higher ICZ concentrations generated more biogas and positively affected the AD process.

The influence of NZVI on wastewater sludge AD was also studied by Jia et al. (2017). The impact of the different concentrations of NZVI (500, 1000, 1500, 2000 mg/L) on wastewater sludge at mesophilic conditions (35°C) for 35 days was investigated. The results showed that the group with 500 mg/L and 1000 mg/L NZVI increased cumulative biogas production by 7.30% and 18.11%, respectively, as shown in Figure 6. The higher concentrations of 1500 mg/L and 2000 mg/L NZVI decreased biogas production by 27.30% and 46.45%, respectively., The higher concentration of NZVI resulted in counter-productive, as observed in other studies (Su et al., 2013; Su et al., 2015; Wang et al., 2016). Therefore, in general, it is critical to find the optimal concentration of the NZVI with the specific waste to achieve the goal, i.e., enhancing biogas generation.

The long and short-term impact of Ag NPs on the AD of waste activated sludge (WAS) was investigated by Ünşar et al. (2016). During the short-term test, Ag NPs did not show any

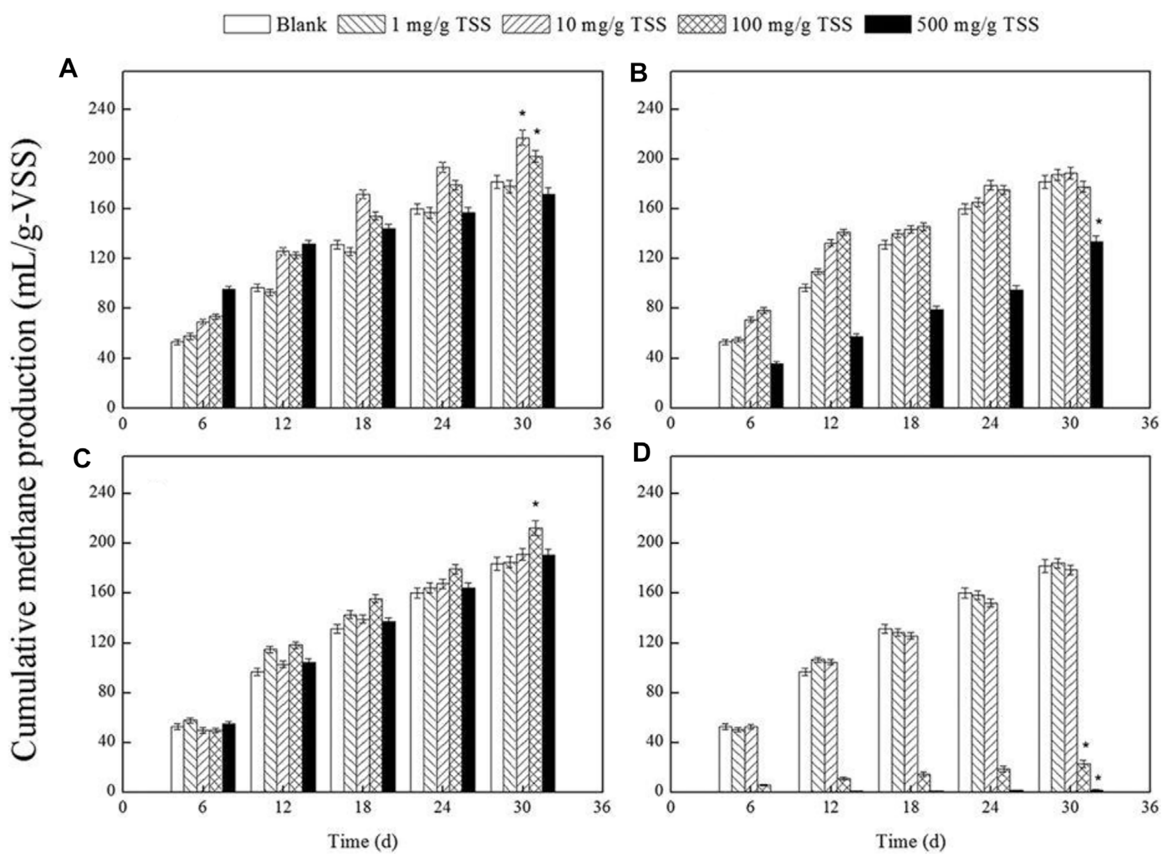

FIGURE 5
Influence of various concentrations of nZVI **(A)**, Ag NPs **(B)**, Fe_2O_3 NPs **(C)** and MgO NPs **(D)** on cumulative methane production during AD of WAS (Wang et al., 2016).

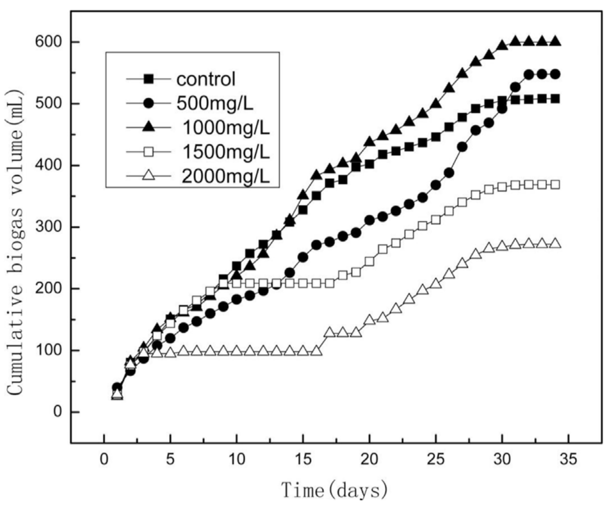

FIGURE 6
Cumulative biogas production by NZVI (Jia et al., 2017).

effect on biogas production. However, during the long-term test, high concentrations (150, 250, and 500 mg/g TS) of Ag NPs showed almost 5% inhibition in methane production, see Figure 7. Wang et al. (2016) studied the influence of Ag NPs on the AD of WAS at concentrations of 1, 10, 100, and 500 mg/g TSS, respectively. The study concluded that Ag NPs had no significant effect on biogas production. The 500 mg/g TSS concentration decreases methane production by 73.52%, as shown in Figure 5. Higher concentrations of Ag NPs decrease the biogas yield because they impede the microbes and activities of key enzymes for the AD process. Gitipour et al. (2016) studied the toxicity of cationic Ag NPs on bio-solids from the wastewater treatment plant to examine the antibacterial impacts of different Ag NPs on the AD process and compared to that of Ag^+. Negatively charged citrate-coated Ag NPs (citrate-Ag NPs), minimally charged polyvinylpyrrolidone coated AgNPs (PVP-Ag NPs), and positively charged branched polyethyleneimine coated AgNPs (BPEI-Ag NPs) were investigated. BPEI-Ag NPs showed a significant increase (almost double the amount) in biogas production than control, as shown in

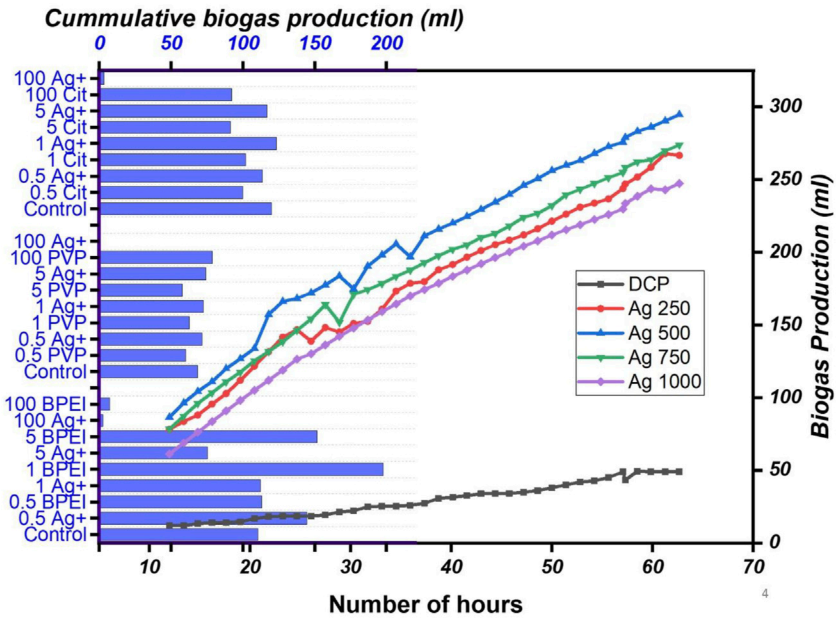

FIGURE 7
Biogas production for different concentrations of Ag NPs (Ünşar et al., 2016) and Cumulative biogas production (horizontal bar) resulted in different concentrations of Ag NPs or Ag^+ (Gitipour et al., 2016).

Figure 7. Toxicity examination showed that at lower concentrations of Ag NPs, functional redundancy built within the microbial community resulted in low toxicity. However, at high doses, BPEI-Ag NPs resulted in eminent toxicity compared to PVP-Ag NPs and citrate-Ag NPs.

Abdelsalam et al. (2017a) studied the effects of various concentrations (0.5, 1, and 2 mg/L) of Co. and Ni NPs on the production capability of methane and biogas from the conversion of CM (Abdelsalam et al., 2017a). AD of CM was carried out batch-wise at operating temperature and mixing rate of 37 ± 0.3°C and 90 rpm, respectively, for HRT of 50 days. The study indicated that adding 1 mg/L Co. NPs increases the biogas and methane volume by 1.64 and 1.86 times, respectively. The optimal concentration of Ni NPs was found to be 2 mg/L, which increases biogas and methane volume by 1.74 and 2.01 times, respectively. The authors mentioned that the addition of Ni and Co. NPs improved the startup of biogas production and reduced the lag phase compared to control. Co. and Ni NPs showed increased decomposition of organic matter as more decomposition of Total Solids (TS), and Volatile Solids (VS.) observed at the end of the experiment. Elreedy et al. (2017) also investigated the influence of Ni NPs (60 nm) at much higher concentrations compared to the work in (Abdelsalam et al., 2017a). The Ni NPs concentration in this study was 20, 30, 60, and 100 mg/L on the AD of industrial wastewater containing Mono-Ethylene Glycol (MEG). Results showed that 60 mg/L of Ni NPs produced an increase of 23% in hydrogen production. This result suggested that a higher dose of NPs is required for industrial waste to enhance biogas production. It would be interesting to see that similar waste has been tested for lower NPs concentration for industrial waste, but the authors of this review were unable to find it.

Our previous work (Zaidi et al., 2018) explored the influence of Ni and Co. NPs on biogas yield from the AD of green microalgae (*Enteromorpha*), which was the first study to discover the significance of NPs on microalgae. Results indicated that 1 mg/L of Ni and Co. NPs produced 26 and 9% cumulative increase in biogas production. It was observed that during the less effective domain (see Figure 8), NPs revealed no significant result to improve biogas production. However, approximately 60 h of the digestion process, NPs showed the cumulative effect on biogas production. The increase in biogas production was credited to the release of extracellular polymeric compounds (proteins, carbohydrates, and cellulose) after the dissolution of the microalgae cell wall. In order to understand the effectivity of NPs on the AD of microalgal biomass, measurement of soluble indexes such as Chemical Oxygen Demand (COD), reducing sugar, pH and VFA were measured. It was found that COD and VFA increased for the groups with NPs, whereas reducing sugar decreased as NPs stimulated bacteria to consume more sugar during the AD.

An exhaustive list and summary of the reported metal NPs including size, concentration, type of feedstock used, anaerobic temperature, HRT, and their effect on biogas and methane production, is shown in Table 2.

Various metal NPs effect on biogas production from different feedstock is presented in this section. NZVI was the most reported one, along with Ni and Co. NPs, which showed an

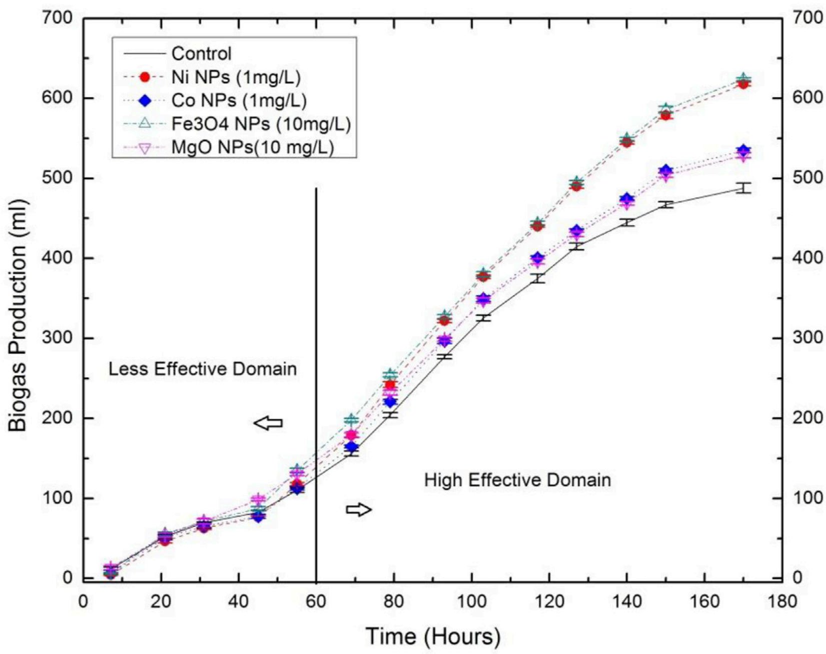

FIGURE 8
Biogas production influenced by nanoparticles (Zaidi et al., 2018).

increase in biogas production. On the other hand, Ag, citrate-Ag, PVP-Ag, BPEI-Ag, Au, and Zn silica nanogel showed adverse effects on the biogas production rate, resulting in a dramatic decrease in the amount of biogas produced. This decrease was attributed to the toxicity of the materials.

Utilization of metal oxide nanoparticles for biogas production

The effect of ZnO and CeO_2 NPs with different concentrations (10, 100, 500, and 1000 mg/L) on anaerobic sludge from an Up-flow Anaerobic Sludge Blanket (UASB) reactor was studied by Nguyen et al. (Nguyen et al., 2015) under mesophilic temperature (30°C) for 40 days. Results showed that all investigated concentrations of ZnO and CeO_2 NPs produce biogas less than the control except 10 mg/L CeO_2 NPs sample, which produced only an 11% increase in biogas, as shown in Figure 9. This study remotely suggested that the role of oxides may be limited to use for biogas production; fortunately, this is not the case. The authors performed a bacterial toxicity test to explore the biogas inhibition effect. They found that ZnO NPs are more highly toxic to *Escherichia coli* than CeO_2 NPs and caused 99% cell death at 100 mg/L and so the same at higher concentrations. The authors attributed the positive effect of 10 mg/L CeO_2 NPs on the bacterial viability of sludge digestion as their ability to act like free radicals.

The long and short-term inhibition impacts of CuO and CeO_2 NPs was studied by Ünşar et al. (2016) on the AD of WAS. The AD inhibition effect was observed from 5.8% to 84% when CuO NPs concentration increased from 5 mg/g to 1000 mg/g TS. CeO_2 NPs with dosages of 150, 250, and 500 mg/g TS enhanced the methane yield to 18.8%, 25.5%, and 9.2%, respectively (Ünşar et al., 2016). Fluorescence *in situ* hybridization (FISH) analysis exposed a decrease in archaea in CuO NPs samples, whereas the abundance of these bacteria was found in CeO_2 NPs.

Casals et al. (2014) also performed an anaerobic experiment under mesophilic conditions by applying Fe_3O_4 NPs (100 ppm) to organic waste for about 2 months. It was concluded that this set of conditions promises an increment in the production of methane and biogas by 234% and 180%, respectively, as shown in Figure 9. In addition, Fe^{2+} was identified as the main contributing factor as it serves to disintegrate waste fabulously in anaerobic conditions. This is probably one of the highest increments of biogas and methane production one can find in the available literature.

In the AD process, metal distribution conversion is another important aspect, as discussed by Suanon et al. (Suanon et al., 2016). The effect was studied by employing Fe_3O_4 NPs in an anaerobic batch chamber with mesophilic conditions. The methane production was incremented by 1.5 gm per 500 ml of Fe_3O_4 NPs. It was concluded that the presence of Fe_3O_4 NPs is favorable for metal stabilization in

TABLE 2 Reported metal NPS and their influence on biogas generation.

NPs type	NPs size	NPs concentration	Feedstock	Temp (°C)	HRT	Result	References
NZVI	60–120 nm	0.05 wt% 0.10 wt% 0.20 wt%	WAS	32 ± 1	20 days	0.05 and 0.10 wt% NAZI increased methane production by 9.8 and 4.6%, respectively. 0.20 wt% NZVI decreased methane production by 8.8%	Su et al. (2015)
	50 nm	0.5 g/L, 1.0 g/L, 2.0 g/L, 4.0 g/L	WAS	35	100 days	Biogas enhanced by the addition of 1 g/L of Fe_3O_4 by 21.66%	Xiang et al. (2019)
	50 nm diameter	0.5 g/L, 1 g/L, 2 g/L, 4 g/L	Waste sludge	35.0 ± 2°C	20 days	The optimum dosage for biogas generation was 0.5 g/L of nZVI, promoted the process of hydrolysis-acidification of sludge	Yanru Zhang et al. (2019)
	10 nm	0.04–5000 ppb	Anammox sludge	25.3 ± 1.9°C	310	Ammonium and nitrite utilization rates increased apparently with continuous nZVI addition	Erdim et al. (2019)
	 119–42 nm 123–51 nm	1.25 g/L cNZVI 2.5 g/L cNZVI 5 g/L cNZVI 1.25 g/L sNZVI	WWTPS	30	10 days	Reactors dosed with 2.5 and 5.0 g/L cNZVI resulted in equally increased methane production. 1.25 g/L NZVI, both cNZVI, and sNZVI gives 28.3% increase in methane production as compared to respect	Carpenter et al. (2015)
	9 ± 0.3 nm	20 mg/L	CM	37 ± 0.3	40 days	1.5 times and 1.67 times increase in biogas and methane production respectively as compared with control	Abdelsalam et al. (2016)
	50 nm	0.75 and 1.5 g per 500 ml	WWTPS	37 ± 1	12 days	Methane production increases by 1.45 times of the control by 0.75 g dose 70.3% decrease in methane production by 1.5 g dose	Suanon et al. (2016)
	<50 nm	1 mg/g TSS 10 mg/g TSS 100 mg/g TSS 500 mg/g TSS	WAS	35 ± 1	30 days	1 mg/g TSS had no measurable effect. 10 mg/g TSS gives 120% of the control. 100 and 500 mg/g have no considerable effect	Wang et al. (2016)
	7–9 nm	5 mg/L 10 mg/L 20 mg/L	CM	37 ± 0.3	50 days	5 mg/L NZVI Increase biogas production by 1.44 times and methane production by 1.38 times. 10 mg/L NZVI Increase biogas production by 1.45 times and methane production by 1.53 times. 20 mg/L NZVI Increase biogas production by 1.45 times and methane production by 1.59 times	Abdelsalam et al. (2017b)
	60 nm	50, 100 and 250 mg/L	MSW	37 ± 3	14 days	25.23 and 62.67% increase in biogas and methane production respectively by 250 mg/L	Amen et al. (2017b)
	160 nm	0.1 wt%	WWTPS	37 ± 1	30 days	25.2% increase in methane yield	Suanon et al. (2017)
	45 nm	1000 mg/L	WWTPS	37	14 days	105.46% increase in cumulative biogas production	Amen et al. (2017a)
	50–70 nm	500, 1000, 1500, 2000 mg/L	WWTPS	35	35 days	7.30% increase in biogas production 18.11% increase in biogas yield 27.30% decrease in biogas yield 46.45% decrease in biogas yield	Jia et al. (2017)
	55 nm	56, 560, and 1680 mg/L	Digested sludge	37	14 days	20% decrease in methane production	Yang et al. (2013a)
	20 nm	10 mg/L	Sewage sludge	37	17 days	30.4% increase in biogas production, 40.4% increase in methane production	Su et al. (2013)
	128 nm	10 mg/g TSS	Waste activated sludge	35 ± 1 °C	30 days	Increase 120% of methane production	Wang et al. (2016)
	46–60 nm	1500 mg/L	Granular sludge	30 C	-	No toxic effects on the methanogenic activity	

(Continued on following page)

TABLE 2 (*Continued*) Reported metal NPS and their influence on biogas generation.

NPs type	NPs size	NPs concentration	Feedstock	Temp (°C)	HRT	Result	References
NZVI and zeolite mixture (IMZ)	—	500 mg/L nZVI and 4 g/L zeolite	WWTPS	37	14 days	130.87% increase in cumulative biogas production	Amen et al. (2017a)
NZVI coated zeolite (ICZ)	24.1 µm	500 and 1000 mg/L	WWTPS	37	14 days	149.95% and 286.75% increase in cumulative biogas yield for 500 and 100 mg/L respectively	Amen et al. (2017a)
Ag	20–40 nm	5 mg/g TS 50 mg/g TS 150 mg/g TS 250 mg/g TS 500 mg/g TS	WAS	37	48 days	No substantial decrease in methane yield was detected at 5 and 50 mg Ag per g TS dosages. Dosages of 150, 250, and 500 mg Ag per gTS resulted in more than 5% inhibition. The detected inhibitions as per the investigated dosages are 6.5, 7.8 and 12.1%, respectively	Ünşar et al. (2016)
	170 ± 7.9	1 mg/g TSS 10 mg/g TSS 100 mg/g TSS 500 mg/g TSS	WAS	35 ± 1	30 days	1, 10, and 100 mg/g TSS had no measurable effect. 500 mg/g decreased methane production by 73.52%	Wang et al. (2016)
citrate-AgNPs	10–15 nm	0.5 mg/L 1 mg/L 5 mg/L 100 g/L	WWTPS	37	30 days	No substantial enhancement in biogas	Gitipour et al. (2016)
PVP-AgNPs	10–15 nm	0.5 mg/L 1 mg/L 5 mg/L 100 g/L	WWTPS	37	30 days	No substantial enhancement in biogas	Gitipour et al. (2016)
BPEI-AgNPs	10–15 nm	0.5 mg/L 1 mg/L 5 mg/L 100 g/L	WWTPS	37	30 days	No significant increase in biogas. At 100 mg/L, nearly complete inhibition occurred	Gitipour et al. (2016)
Co.	28 ± 0.7 nm	1 mg/L	CM	37 ± 0.3	40 days	1.7 times and 2 times enhancement in biogas and methane production respectively as compared with control	Abdelsalam et al. (2016)
—	<100 nm	0.16 mg/g TSS	Sludge	264 h	37	Co. NPs + MW pretreatment gave 42% cumulative rise in biogas yield	Zaidi et al. (2019b)
—	30–80.9 nm	1.4, 2.7, 5.4 mg/L	Poultry litter	35	69 days Exp. A, 79 days Exp. B	NPs increased CH4 production by 23.8–38.4% compared to poultry litter only AD The highest increase in CH_4 was observed 29.7% at 5.4 mg/L	Hassanein et al. (2019)
—	<100 nm	1 mg/L	Green algae	37	264 h	For Co. NPs along MW pretreatment enhanced biogas yield by 42.36%	Zaidi et al. (2019b)
—	28 ± 0.7 nm	1 mg/L	Manure slurry	37 ± 0.3°C	50 days	1.64 times and 1.86 times increase in biogas and methane production, respectively as compared with control	Abdelsalam et al. (2017a)
—	17–28 nm	0.5 mg/L 1 mg/L 2 mg/L	CM	37 ± 0.3	50 days	0.5 mg/L Co. NPs Increase biogas production by 1.36 times and methane production by 1.43 times. 1 mg/L Co. NPs Increase biogas production by 1.64 times and methane production by 1.86 times. 2 mg/L Co. NPs decrease biogas production by 0.95 times and methane production by 0.87 times	Abdelsalam et al. (2017a)
—	100 nm	1 mg/L	Microalgae	37 ± 0.3	7 days	9% increase in biogas production	Zaidi et al. (2018)

(Continued on following page)

TABLE 2 (*Continued*) Reported metal NPS and their influence on biogas generation.

NPs type	NPs size	NPs concentration	Feedstock	Temp (°C)	HRT	Result	References
—	20 nm	75 mg/L	Cellulose	37 C, 55 C	50 days	Zero or slight toxicity effect on ordinary heterotrophic organisms, ammonia-oxidizing bacteria, and anaerobic bacteria	García et al. (2012)
—	20–40 nm	5, 9, 13 mg/L	SW	35	5 days	The optimum concentration of 9 mg/L was observed with additive 202.46 NL/kg VS., consequently enhanced methane yield by 45%	Yazdani et al. (2019)
—	40–60 nm	9 mg/gVS	Sewage sludge	—	40 days	The 9 mg/gVS increased methane yield by 186% along 2.6 times more VS. removal with respect to the control	Lizama et al. (2019b)
—	40–60 nm	7 mg/ gVS+15,000 kJ/kgTS	Sewage sludge	35	30 days	Biogas yield of 190% enhanced while methane of 242.8% increased	Lizama et al. (2019a)
—	30–80.9 nm	15, 50, 100 mg/L	Poultry litter	35	69 days Exp. A, 79 days Exp. B	NPs increased CH4 production by 23.8–38.4% compared to poultry litter only AD Highest increase in CH_4 was observed 29.1% at 100 mg/L	Hassanein et al. (2019)
	70 nm	2 mg/μg chlorophyll a	Cyanobacte-rial bloom	-	-	promotes flocculation of cyanobacterial biomass	Marsalek et al. (2012)
—	55 ± 11 nm	1680 mg Fe/L (30 mM)	digested sludge	—	—	quick dissolution of Fe NPs NZVI so as to produce hydrogen more	Yang et al. (2013b)
—	<212 μm	1680 mg Fe/L (30 mM)	digested sludge	—	—	By releasing the slow hydrogen from ZVI increases the methane yield higher and sulfate yield gets reduced	Yang et al. (2013b)
—	<50 nm	10 mg/g TSS	waste activated sludge	37	—	In the vicinity of 10 mg/g total suspended solids (TSS) nZVI and 100 mg/g TSS Fe_2O_3 NPs enhanced methane yield to 120 and 117% of the control, respectively	Yang et al. (2013b)
—	9 nm	20 mg/L	Raw manure	37 ± 0.3°C	5 days	Methane production was enhanced by 67%	Abdelsalam et al. (2016)
—	0.05 m^2/g surface area	0.4 g ZVI/g SFW	Food waste	35	30 days	Butyric acid was 30–40% achieved of the VFAs in the acidogenic reactor	Kong et al. (2016)
Ni	17 ± 0.3 nm	2 mg/L	CM	37 ± 0.3	40 days	1.8 times and 2.17 times increase in biogas and methane production, respectively, as compared with control	Abdelsalam et al. (2016)
—	<50 nm	0.004 g/g SS	microalgal biomass	37	15 days	36% enhancement was seen of biomass solubilization	Kavitha et al. (2019)
—	58.3–79.7 nm	1.34 mg/g VS.	Poultry litter	35	69 days Exp. A, 79 days Exp. B	NPs increased CH4 production by 23.8–38.4% compared to poultry litter only AD The highest increase in CH_4 was observed 38.4% at 12 mg/L	Hassanein et al. (2019)
—	<100 nm	1 mg/L	Green algae	37	264 h	For Ni NPs along with MW pretreatment of enhanced biogas yield by 31.73%	Zaidi et al. (2021b)
—	17 ± 0.3 nm	2 mg/L	Manure slurry	37 ± 0.3°C	50 days	1.74 times and 2.01 times increase in biogas and methane production, respectively, as compared with control	Abdelsalam et al. (2017a)
—	17–28 nm	0.5 mg/L 1 mg/L 2 mg/L	CM	37 ± 0.3	50 days	0.5 mg/L Ni NPs Increase biogas production by 1.46 times and methane production by 1.49 times. 1 mg/L Ni NPs Increase biogas production by 1.72 times and methane production by 1.96 times. 2 mg/L Ni NPs Increase biogas production by 1.74 times and methane production by 2.01 times	Abdelsalam et al. (2017a)
—	60 nm	20, 30, 60, and 100 mg/L		55	10 days	60 mg/L dosage caused 23% increase in hydrogen production	Elreedy et al. (2017)

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TABLE 2 (*Continued*) Reported metal NPS and their influence on biogas generation.

NPs type	NPs size	NPs concentration	Feedstock	Temp (°C)	HRT	Result	References
			industrial wastewater containing MEG				
—	100 nm	5 and 10 mg-Ni/kgVS	Sewage sludge	37 ± 1 °C	20 days	increased methane yield up to 10%	Tsapekos et al. (2018)
—	100 nm	1 mg/L	Microalgae	37 ± 0.3	7 days	26% increase in biogas production	Zaidi et al. (2018)
Zn silica nanogel	—	—	Manure	-	56 days	Overall, cumulative gas volumes were decreased by 92.73–95.83%	Sarker et al. (2019)
Mixed NPs	20–21 nm Ag, ZnO, TiO_2	0.25 mg/g Ag, 2 mg/g TiO_2, 2.8 mg/g ZnO	Primary activated sludge	35 ± 2°C	300 days	maximum of 73% (control), 71% (ENPs) and 70% (metal salts) methane content in the biogas was observed	Eduok et al. (2017)

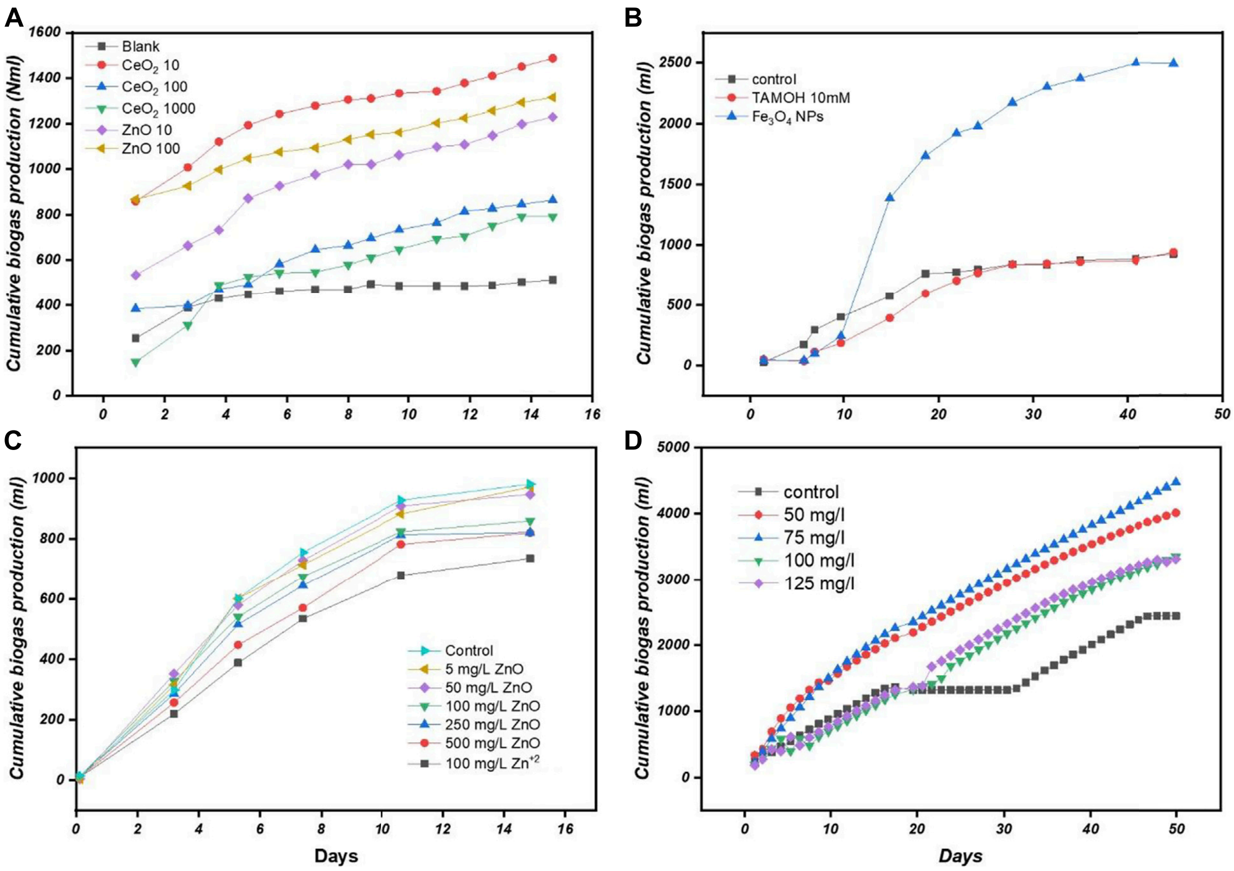

FIGURE 9
(A) Influence of Ce O 2 and ZnO NPs on biogas production (Nguyen et al., 2015) **(B)** Effect of 100ppm Fe3 O 4 on biogas production (scale bar is 20 nm) (Casals et al., 2014) **(C)** Effect of ZnO ENMs on production after 14 days (Zhang L. et al., 2017) **(D)** Cumulative methane production by Fe3 O 4 NPs (Ali et al., 2017).

the digestate as it ultimately results in an improvement in biogas production. However, it promotes the immobilization of phosphorus in digestate. The information mentioned in the paper was not conclusive to support the immobilization hypothesis, and the authors have acknowledged this to suggest further research.

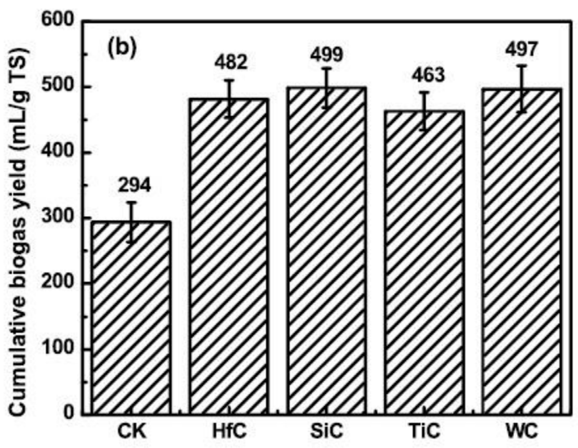

FIGURE 10
Cumulative biogas yield by nano-scale transition metal carbides (Li et al., 2018).

Abdelsalam et al. (2017b) also contributed by studying the effect of Fe_3O_4 NPs on biogas production. By employing different concentrations on CM slurry, mixing temperature of 37 ± 0.3°C at an rpm of 90 and HRT of 50 days; biogas and methane production was incremented by 1.66 and 1.96 times, respectively, by adding just 20 mg/L Fe_3O_4 NPs as shown in Figure 9.

Wang et al. (2016) studied the influence of MgO and Fe_2O_3 NPs on the AD of WAS at concentrations of 1, 10, 100, and 500 mg/g TSS, respectively. The concentration of 100 mg/g TSS of iron oxide NPs gives 117% of the control, whereas other concentrations had no measurable effect on biogas; see Figure 5. MgO NPs had no significant effect on biogas production (Shi et al., 2020). The 500 mg/g TSS concentration inhibited methane production by 1.08%. Higher concentrations of MgO NPs decrease the biogas yield because they impede the microbes and activities of key enzymes for the AD process, see Figure 5.

Li et al. (2017) studied the fate and long-term exposure of CuO, TiO_2, and ZnO NPs (50 mg/L) on the AD of Anaerobic Granular Sludge (AGS) for 90 days. The results showed that CuO NPs stopped the methane production on the 39th day. Long-term exposure resulted in inhibited methanogenesis strongly and quickly. The exposure of TiO_2 NPs lowered the biogas and methane production by 30.70% and 14.01%, respectively. The study suggested that TiO_2 NPs had an adverse effect on the acidogens and acetogens than methanogens. The effect of TiO_2 NPs on anaerobic sludge from the UASB reactor was also investigated by Yadav et al. (Yadav et al., 2017). Outcomes of their study indicated a slight biogas inhibition in line with the results obtained by Li et al. (2017).

Syntrophic oxidation of butyrate (intermediates in the transformation of complex organics to methane) was studied by Zhang and Lu (2016) in two different lake sediments. The authors used conductive Fe_3O_4 NPs to accelerate the reaction kinetics. Results indicated that methane yield was substantially increased, and the lag phase reduced significantly under the presence of NPs. 25μmol CH_4/liter was produced from 10 μmol of butyrate addition. The authors performed Direct Interspecies Electron Transfer (DIET) and found that cell-to-cell distance in enrichments amended with NPs was larger than control. They suggested that conductive NPs form cell-nanomaterial-cell networks and facilitate DIET, which contributed to an enhancement in methane.

The response of iron oxide NPs on AGS during AD of beet sugar industrial wastewater was investigated by Ambuchi et al. (2017). Three Plexiglas Expanded Granular Sludge Bed (EGSB) reactors were used under a mesophilic temperature of 36 ± 1°C for an incubation period of 74 days. More biogas was produced during the first 24 h than in the control reactor. The initial increase in biogas production was also observed in another study (Abdelsalam et al., 2017b). Results showed 1.25 times increase in biogas and 28.9% more ml/g-VSS CH_4 gas. The authors stated that the employment of iron oxide NPs as conduits for electron transfer toward methanogens resulted in biogas enhancement.

A comparative study of Fe_3O_4, Co_3O_4, NiO, and MoO_3 micronutrient and NPs with CM slurry in the single and bi-phasic AD at 37 ± 2°C for 20 days was carried out by Juntupally et al. (2017). During a single-phase AD, Fe_3O_4 NPs produced 0.16 L/(g VS. reduced) biogas. An increase in biogas production with enhanced methane (70–80%) is reported during single-phase, whereas in bi-phase, AD Fe_2O_3 and its corresponding NPs showed a 76% increase (Juntupally et al., 2017). NiO NPs yielded peak biogas of 0.3 L/(g VS. reduced) in the biphasic AD compared to Co_3O_4 and MoO_3 NPs. During single-phasic AD, NiO and Co_3O_4 NPs provided the same biogas yield of 0.15 L/(g VS. reduced).

The effect of different concentrations of ZnO NPs (as shown in Figure 9) on VFAs and biogas production during AD of WAS investigated by Lingling Zhang et al. (2017). Results showed that VFA production is inversely correlated to ZnO NPs concentrations. ZnO NPs inhibited the waste sludge hydrolysis-acidification, mainly protein. ZnO NPs' impact on protein hydrolysis slowed down the VFA accumulation during AD and decreased biogas production, as shown in Figure 9. This action also changed bacterial community structure and was identified to be the main reason for biogas reduction.

Temizel et al. (2017) investigated the influence of ZnO NPs on sanitary landfills for biogas production. They used landfill bioreactors operated at 35°C for 1 year. The results obtained indicated that reactors inoculated with ZnO NPs produced less biogas than the control reactor. The authors mentioned that the release of Zn^{2+} might adversely affect the methanogenic archaea activity, and hence inhibition in biogas yield occurred. Biogas from landfills is being

TABLE 3 Reported metal oxide NPs and their influence on biogas generation.

NPs type	NPs size	NPs concentration	Feedstock	Temp (°C)	HRT	Result	Ref
CeO_2	—	10 mg/L 100 mg/L 500 mg/L 1000 mg/L	UASB Reactor Sludge	30 ± 1	40 days	A decrease in biogas was observed. 10 mg/L increase biogas generation by 11%	Nguyen et al. (2015)
—	15–30 nm	5 mg/g TS 50 mg/g TS 150 mg/g TS 250 mg/g TS 500 mg/g TS	WAS	—	48 days	CeO2 dosages of 150, 250, and 500 mg per gTS enhanced methane generation to 18.8, 25.5, and 9.2%, respectively	Ünşar et al. (2016)
—	12 nm	640 mg/L	Cellulose	37, 55	50 days	Toxicity effect, decrease nearly 100% biogas production	García et al. (2012)
—	<25 nm	5, 50, 150 mg/g VSS	GS	35	6	No effect was observed	Ma et al. (2013)
—	50 nm	1500 mg/L	Granular sludge	30	80 h	No toxic effects on the methanogenic activity. Acetoclastic MA is reduced by 80%, while hydrogenotrophic reduced by 82%	Gonzalez-Estrella et al. (2013)
—	192 nm	10 mg/L	Anaerobic sludge	30	40 days	NPs could increase the biogas production by 11%	Hou et al. (2017)
ZnO + Cip	119.7 nm ZnO	0.015, 0.300, and 3.000 mg/g DW ZnO 10,100 mg/kg DW Cip	Sludge	35 ± 2°C	20	Complex inhibition rate of ZnO + C_{ip} decreased by 23.3%	Lin Zhao et al. (2018)
ZnO + C_{60}	119.7 nm ZnO 129.5 nm C_{60}	0.015, 0.300, and 3.000 mg/g DW ZnO 100 mg/kg DW C_{60}	Sludge	35 ± 2°C	20	ZnO + C_{60} gave an inhibition rise of only 3.9% Complex inhibition rate was 18.5%	Lin Zhao et al. (2018)
ZnO	—	10 mg/L 100 mg/L 500 mg/L 1000 mg/L	UASB Reactor Sludge	30 ± 1	40 days	Inhibition in biogas production was observed	Nguyen et al. (2015)
—	119.7 nm	30 mg/g	Sludge	35 ± 2°C	35 days	The inhibition rate of ZnO was 26.7%	Zhao et al. (2019)
—	119.7 nm	0.015, 0.300, and 3.000 mg/g DW of sludge	Sludge	35 ± 2°C	20	Only ZnO inhibited CH4 yield by 49.5% at 14 h and 15% after 35 days	Lin Zhao et al. (2018)
—	531 nm	0.4 mg/L	seed sludge	35	(SRT = 120 days and HRT = 6 h)	biogas production reduced from 0.36 to 0 L/g COD removal within 40 days	Chen et al. (2019)
—	140 nm	10, 300, 1500 mg/L	waste activated sludge	35	20 days	1 mg/g-TSS of ZnO NPs not affected methane production, 30 and 150 mg/g-TSS of ZnO NPs enhanced 18.3% and 75.1% of inhibition respectively	Mu and Chen, (2011)
—	140 nm	10, 50 mg/g TSS	Aerobic granule	35 ± 1°C	—	No effect noticed	Mu et al. (2012)
—	140 nm	100, 200 mg/g TSS	Aerobic granule	35 ± 1°C	—	Effect of −25.1%,−44.5% were observed	Mu et al. (2012)
—	<100 nm	100 mg nano-ZnO/kg of dry waste	Sanitary Landfills	35 ± 2	1 year	The decrease in biogas production of about 15%	Temizel et al. (2017)
—	<100 nm	6, 30, 150 mg/g TSS	WAS	35	18	6 mg/g, 30 mg/g, 150 mg/g TSS affected methane production by no effect, 23% and 81% repectively	Mu et al. (2011)
—	120–140 nm	42, 210, 1050 mg/L	Mixed primary and excess sludge	35	8 days	Decreased the abundance of methanogenic archaea, inhibition of methane production	Haining Huang et al. (2019)

(Continued on following page)

TABLE 3 (*Continued*) Reported metal oxide NPs and their influence on biogas generation.

NPs type	NPs size	NPs concentration	Feedstock	Temp (°C)	HRT	Result	Ref
—	50–70 nm	7.5–480 mg/L	Cattle manure	36	14 days	Inhibition of biogas production up to 74%	Luna-delRisco et al. (2011)
—	10–30 nm	10–1500 mg/L	Granular sludge	30	80 h	highly inhibitory to acetoclastic and hydrogenotrophic methanogens with IC50 values of 87 and 250 mg/L	Gonzalez-Estrella et al. (2013)
—	<100 nm	0.32, 34.5 mg/L	WAS	30	90	In addition to 0.32 mg/L, a slight decrease in methane yield was observed while adding 34.5 mg/L shows complete inhibition in 1 week	Otero-González et al. (2014a)
—	850 nm	10 mg/L 1000 mg/L	Sludge out of UASB reactor	30	40 days	Biogas reduced by 8% using 10 mg/L while 65% reduction is seen when 1000 mg/L added	Hou et al. (2017)
—	90–200 nm	0, 5, 50, 100, 250 and 500 mg/L	WAS	37 ± 1	14 days	Inhibition in biogas and methane was observed with increasing dosages of ZnO NMs. 25% reduction on biogas and 50% reduction on methane production	Lingling Zhang et al. (2017)
—	15 micro.m	120 mg/L	Cattle manure	36	14	18%, 72% reduction in biogas by addition of 120 mg/L, 240 mg/L	Luna-delRisco et al. (2011)
—	<100 nm	50 mg/L	AGS	35 ± 1	90 days	Inhibition effect on biogas and methane yield	Li et al. (2017)
—	200 nm	0, 5, 30, 100 mg/g-TSS	WAS	37 ± 1°C	-	Enzyme activity decreased, thus inhibition reduced in the vicinity of TiO_2	Lingling Zhang et al. (2019)
CuO	30–50 nm	5 mg/g TS 50 mg/g TS 150 mg/g TS 250 mg/g TS 500 mg/g TS	WAS	—	48 days	CuO NPs inhibited methane from 150 mg CuO per gTS concentration. 150, 250 and 500 mgCuO per gTS dosages resulted in strong inhibition	Ünşar et al. (2016)
—	<50 nm	50 mg/L	AGS	35 ± 1	90 days	Inhibition effect on biogas and methane production	Li et al. (2017)
—	30 nm	7.5–480 mg/L	Cattle manure	36	14 days	Inhibition of biogas production up to 96%; 120 mg/L, 240 mg/L show decreasing effect in Biogas production by 19% and 60%	Luna-delRisco et al. (2011)
—	30 nm	15 mg/L	Cattle manure	36	14	30% reduction in biogas in noticed	Luna-delRisco et al. (2011)
—	40 nm	10–1500 mg/L	Granular sludge	30	80 h	Inhibited acetoclastic methanogens with IC_{50} value of 223 mg/L	Gonzalez-Estrella et al. (2013)
—	37 nm	1.4 mg/L	AGS	30	83	Methane yield reduced by 15%	Otero-González et al. (2014b)
Fe_3O_4	7 nm	100 ppm	WWTPS	37	60 days	180% increase in biogas production and 234% increase in methane production	Casals et al. (2014)
—	—	10 g/L	waste activated sludge	37 ± 1°C	22 days	Methane yield out of ZVI + Fe3O4 in digester was 68.9% greater than Fe-free digester	Zisheng Zhao et al. (2018a)
—	—	10 g/L	Waste activated sludge	37 ± 1°C	22 days	Fe_3O_4 obviously enhanced the sludge's solubilization, hydrolysis, and acidification	Zisheng Zhao et al. (2018b)
—	20–30 nm	75 mmol	Swine manure	37 ± 0.1°C	38 days	Nano magnetite improved the methane yield by a maximum 6.0%; the maximum methane	Junya Zhang et al. (2019)

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TABLE 3 (*Continued*) Reported metal oxide NPs and their influence on biogas generation.

NPs type	NPs size	NPs concentration	Feedstock	Temp (°C)	HRT	Result	Ref
						production may be increased by 47.8% on a daily basis	
—	100–150 nm	50 mg/g	Lignocellulos-se degradation	37%	60 days	HA enhanced by 54% Fe_3O_4 were observed more random after solid-state fermentation	Danlian Huang et al. (2019)
—	7 nm	100 mg/L	Wastewater sludge	—	480 days	Short term exposure of AgNPs evidently decreased nitrogen removal Long-term exposure to AgNPs had no rigorous effects	Juan Huang et al. (2019)
—	7.2 nm	120 ppm (12 mg/ g VS.)	Rice straw	37	15 days	2% NaOH with 120 ppm NPs increase CH_4 production nanoparticles increased methane yield by 129%.	Khalid et al. (2019)
—	94–3400 nm	15, 50, 100 mg/L	Poultry litter	35	69 days Exp. A, 79 days Exp. B	NPs increased CH4 production by 23.8–38.4% compared to poultry litter only AD The highest increase in CH_4 was observed 27.5% at 15 mg/L	Hassanein et al. (2019)
	100 nm	0.162 mg/g VS.	canola straw and banana waste plant with buffalo dung	37 ± 0.1	40 days	Maximum methane yield of 256 mLCH$_4$/gVS and 202.3 mLCH4/gVS at a dosage of 0.81 & 0.5 mg for CS and BPW	Noonari et al. (2019)
	20 nm diameter	0.5 g/L, 1 g/L, 2 g/L, 4 g/L	Waste sludge	35.0 ± 2°C	20 days	The optimum dosage for biogas generation was 1 g/L of Fe_3O_4	Yanru Zhang et al. (2019)
	7 ± 0.2 nm	20 mg/L	CM	37 ± 0.3	40 days	1.7 times and 2.16 times increase in biogas and methane production respectively as compared with control	Abdelsalam et al. (2016)
	1212.6 ± 109.4 nm	1.43–17.1 mg/g MLSS	synthetic wastewater	25	57 days	Fe_3O_4 NPs at 5–60 mg/L showed no substantial effect on N removal, moreover on COD removal with a slight -decrease	Ma et al. (2017)
	20 nm	0.75 and 1.5 g per 500 ml	WWTPS	37 ± 1	12 days	Methane production increases by 1.25 times of the control by 0.75 g dose 0.9 times increase in methane production by 1.5 g dose	Suanon et al. (2016)
	-	10 Mm	lake sediments	-	40 days	CH_4 production was about 60–90% larger	Zhang and Lu, (2016)
	7–9 nm	5 mg/L 10 mg/L 20 mg/L	CM	37 ± 0.3	50 days	5 mg/L Fe3O4 NPs Increase biogas production by 1.63 times and methane production by 1.82 times. 10 mg/L Fe3O4 NPs Increase biogas production by 1.64 times and methane production by 1.90 times. 20 mg/L Fe3O4 NPs Increase biogas production by 1.66 times and methane production by 1.96 times. 66% increase in biogas production, 96% increase in methane production	Abdelsalam et al. (2017a), Abdelsalam et al. (2017b)
	10–35 nm	50, 75, 100, 125 mg/L	MSW	37 ± 0.5	60 days	The concentration of NPs 50 and 75 mg/L was found to be more effective in improving the methane production as compared to increased concentrations at 100 and 125 mg/L	Ali et al. (2017)
	7 nm	100 mg/L	crystalline cellulose	37	60 days	180% increase in biogas production, 8% increase in methane production	Casals et al. (2014)

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TABLE 3 (*Continued*) Reported metal oxide NPs and their influence on biogas generation.

NPs type	NPs size	NPs concentration	Feedstock	Temp (°C)	HRT	Result	Ref
	15–22 nm	50–125 mg/L	Municipal solid waste	37	60 days	Up to 117% increase in methane production	Ali et al. (2017)
	<100 nm	10 mg/L	CM	37 ± 2	20 days	Increase in biogas production with enhanced methane (70–80%)	Juntupally et al. (2017)
	20 nm	750 mg/L	BSIWW	36 ± 1	74 days	1.25 times increase in biogas. 28.9% more ml/g-VSS CH4 gas	Ambuchi et al. (2017)
	<100 nm	10 mg/L	Microalgae	37 ± 1	7 days	26% increase in biogas production	Zaidi et al. (2018)
Fe_2O_3	<30 nm	1 mg/g TSS 10 mg/g TSS 100 mg/g TSS 500 mg/g TSS	WAS	35 ± 1	30 days	1, 10 and 500 mg/g TSS had no influence. 100 mg/g TSS gives 117% of the control	Wang et al. (2016)
	20 nm	0.5 g/L, 1.0 g/L, 2.0 g/L, 4.0 g/L	WAS	35	100 days	Biogas enhanced by the addition of 0.5 g/L of Fe_3O_4 by 24.44%	Xiang et al. (2019)
	20–40 nm	20 mg/L 100 mg/L	Cattle Manure	38	30 days	production of biogas and CH_4 was 336.25 and 192.31 ml/gVS, respectively, at max Fe_2O_3 NPs improved anaerobic digestion, resulting in higher production of methane	Farghali et al. (2019)
	140 ± 30 nm	500 mg/g TS	Waste activated sludge	25	48 days	Methane production was decreased by 289%	Kökdemir Ünşar and Perendeci, (2018)
	-	750 mg/L	Granular sludge	36	84, 96 h	Increase 38% of methane production	Ambuchi et al. (2016)
	40 nm	1500 mg/L	Granular sludge	30	80 h	No toxic effects on the methanogenic activity	Gonzalez-Estrella et al. (2013)
TiO_2	<100 nm	100 mg/L	UASB Reactor Sludge	37	15 days	No substantial effect on biogas production	Yadav et al. (2017)
	4–8 nm	0, 500, 1000, 1500, 2000 mg/L	wastewater, waste sludge	35 ± 1°C	28 days	methane production increased by an average of 14.9%	Cervantes-Avilés et al. (2018)
	25 nm	50 mg/L	AGS	35 ± 1	90 days	Decreased biogas and methane yield by 30.70% and 14.01%, respectively	Li et al. (2017)
	25 nm	1500 mg/L	Granular sludge	30	80 h	No toxic effects on the methanogenic activity	Gonzalez-Estrella et al. (2013)
	150–170 nm	42, 210, 1050 mg/L	Mixed primary and excess sludge	35	8 days	No measurable impact on methane production	Zheng et al. (2015)
	7.5 nm	840 mg/L	Cellulose	37, 55	50 days	No effects	García et al. (2012)
	<25 nm	6, 30, 150 mg/g TSS	WAS	35	48 h	No effect was seen	Mu et al. (2011)
	185 nm	150 mg/g TSS	WAS	35	105	No effect was observed	Chen et al. (2014)
MgO	<50 nm	1 mg/g TSS 10 mg/g TSS 100 mg/g TSS 500 mg/g TSS	Waste activated sludge	35 ± 1	30 days	1, 10 and 100 mg/g TSS had no measurable effect. 500 mg/g decreased methane production by 108%	Wang et al. (2016)
—	<100 nm	10 mg/L	Microalgae	37 ± 1	7 days	8% biogas enhancement	Zaidi et al. (2018)
—	<50 nm	500 mg/g TSS	WAS	35 ± 1°C	2 days	MgO NPs created up to lower levels of methane yield by 1.08% than of the control	Wang et al. (2016)
Co_3O_4	<100 nm	10 mg/L	CM	37 ± 2	20 days	Increase in biogas production with enhanced methane (70–80%)	Juntupally et al. (2017)
NiO	<100 nm	10 mg/L	CM	37 ± 2	20 days	Increase in biogas production with enhanced methane (70–80%)	Juntupally et al. (2017)

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TABLE 3 (*Continued*) Reported metal oxide NPs and their influence on biogas generation.

NPs type	NPs size	NPs concentration	Feedstock	Temp (°C)	HRT	Result	Ref
—	—	20 mg/L	Sludge from wastewater	50	7–14 days	30% increment compared to the control, which can be elaborated by the prevalence of acetic acid production	Elreedy et al. (2019)
Ni-Ferrite and Ni-Co-Ferrite	~11 nm	20, 70 and 130 mg/L of both	Cow manure	(15°C)	35-days	Ni-Ferrite NPs achieved biogas enhancements of 30.8%, 28.5%, and 17.9% at concentrations of 20, 70 and 130 mg/L, respectively	Abdallah et al. (2019)
Ni/Co. oxide to palm oil mill effluent	~14 nm (NiO) ~16.79 nm for CoO	0.41–0.69 g/L (test) and 0.66 g/L (control)	palm oil mill effluent	35°C	110 h	H_2 gas production was enhanced by 37%	Mishra et al. (2019)
Fe/GAC	50 nm	1000 mg/L	tetracycline wastewater	51 days	35 ± 1 C	The biogas production and methane content were enhanced by 21.2% and 26.9%	Zhang et al. (2018)
Mn_2O_3	-	1500 mg/L	Granular sludge	30	80 h	No toxic effects on the methanogenic activity	Gonzalez-Estrella et al. (2013)
SiO_2	10–20 nm	1500 mg/L	Granular sludge	30	80 h	No toxic effects on the methanogenic activity	Gonzalez-Estrella et al. (2013)
—	10–20 nm	630,150 mg/g TSS	WAS	35	Different time	No significant effect is noticed	Mu et al. (2011)
Al_2O_3	<50 nm	1500 mg/L	Granular sludge	30	80 h	No toxic effects on the methanogenic activity	Gonzalez-Estrella et al. (2013)
—	270 ± 10 nm	250 mg Al_2O_3/g TS	waste activated sludge	—	—	14.8% increase in methane production	Kökdemir Ünşar and Perendeci, (2018)
—	<50 nm	6, 30, 150 mg/g TSS	WAS	35	Several fermentation time	No effect was observed	Mu et al. (2011)
ɤ-Al2O3	20–50 nm	100 g/L	Granular sludge	27	12 h	Much reduction in methane yield up to 60%	Alvarez and Cervantes, (2012)
Fe_2NiO_4	—	100 mg Ni^{2+}/L	Wastewater	30	7 days	positive effect of Fe_2NiO_4 nanoparticles on AD activity	Chen et al. (2018)
Fe_2NiO_4Zn	—	100 mg Ni2+/L	Wastewater	30	7 days	negative effect of Fe_4NiO_4Zn nanoparticles on AD activity	Chen et al. (2018)
MoO_3	<100 nm	10 mg/L	CM	37 ± 2	20 days	Increase in biogas production with enhanced methane (70–80%)	Juntupally et al. (2017)

recognized as one potential source for bioenergy production; the authors suggested that the presence of ZnO NPs in a waste matrix of landfills may become a hurdle to its application. The toxic effect of ZnO NPs indicated in this study agrees with Li et al. (2017), who also investigated the effect of ZnO NPs on the AD of AGS and found that methane and biogas yield was suppressed. They mentioned that long-term exposure resulted in inhibited methanogenesis vigorously and quickly.

The effect of bio-compatible Fe_3O_4 NPs (10–35 nm) at four different concentrations (50, 75, 100, and 125 mg/L) on the AD of Municipal Solid Waste (MSW) was investigated by Ali et al. (2017) at 37 ± 0.5°C for 60 days of HRT. Results indicated that concentration of 50 and 75 mg/L was found to be more effective in improving the methane production as compared to increased concentrations at 100 and 125 mg/L, see Figure 9. This is in contrast with the results obtained by Abdelsalam et al. (2017b).

In one of our previous studies, the experience of studying green microalgae's anaerobic digestion (*Enteromorpha*) for biogas production by employing Fe_3O_4 and MgO NPs have been promising (Zaidi et al., 2018). A cumulative increase of 28% for 10 mg/L of Fe_3O_4 NPs and 8% for 10 mg/L of MgO NPs was noticed. As a controlled sample, an additional effect of NPs approaches zero in the less effective domain. Nevertheless, after observation of 60 h, a substantial effect incrementing biogas production was noticed. The increase in biogas production was credited to the release of extracellular polymeric compounds (proteins, carbohydrates, and cellulose) after the dissolution of the microalgae cell wall. Table 3 comprehensively summarizes the metal oxide NPs and their effect on biogas generation.

This section discussed the addition of different metal oxide NPs during the AD for biogas production. Fe_2O_3, Fe_3O_4, Co_3O_4, NiO,

TABLE 4 Reported nano-scale Nb-based compounds and their influence on biogas generation.

NPs type	NPs size (nm)	NPs concentration	Feedstock	Temperature (°C)	HRT	Result	References
NbO_2	200	7.5, 15, 30, 60, and 120 mg/L	DM	36 ± 1	35 days	1.3 times increase in biogas by 60 mg/L concentration	Lingling Zhang et al. (2017)
$Nb_{3.49}N_{4.56}O_{0.44}$	500	7.5, 15, 30, 60, and 120 mg/L	DM	36 ± 1	35 days	1.1 times increase in biogas by 15 mg/L concentration	Lingling Zhang et al. (2017)
NBN	100	7.5, 15, 30, 60, and 120 mg/L	DM	36 ± 1	35 days	60 mg/L NbN improved cumulative biogas by 1.1 times	Lingling Zhang et al. (2017)

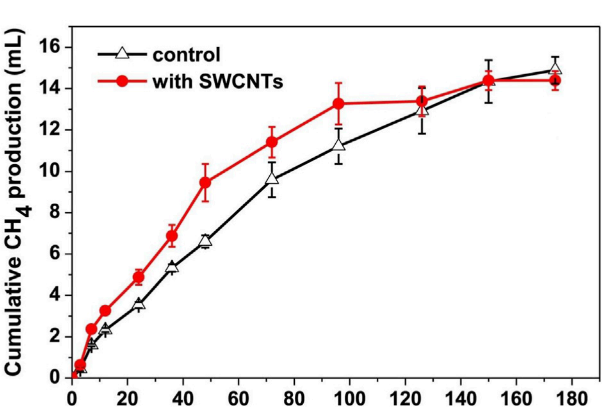

FIGURE 11
The influence of SWCNTs on methane production in Hours (Li et al., 2015).

MoO_3 showed an increase in biogas production. On the other hand, CeO_2 showed mixed effects depending on their concentration in the reactor as well as the digestion time. The addition of nano-iron oxide (Fe_3O_4) enhanced methane production by 234% due to the presence of the non-toxic $Fe3^+$ and $Fe2^+$ ions. ZnO, CuO, TiO_2, MgO, MnO_2 showed a decrease or no change in biogas production rate (Mishra et al., 2018).

Nano-scaled Nb-based compounds in biogas

The functionality of Nb-based compounds (NbO_2, $Nb_{3.49}N_{4.56}O_{0.44}$, and NbN) with various concentrations (7.5, 15, 30, 60, and 120 mg/L) at mesophilic condition (36 ± 1°C) in the AD of dairy manure was investigated by Taihong Zhang et al. (2017). This is the first study discussing the application of these compounds for AD. The results showed that Nb-based compounds worked as efficient catalysts in the AD process. They improve the fermentation condition and stimulate the bacterial activity inside the digester. The cumulative biogas production by NbO_2, $Nb_{3.49}N_{4.56}O_{0.44}$, and NbN produced was 522.7, 437.1, and 455.7 ml/g VS., respectively (Zhang T. et al., 2017). Table 4 summarizes reported Nb-based compounds and their effect on biogas production.

Nano-scaled transition metal carbides for biogas enhancement

The effect of nano-scale transition metal carbides (HfC, SiC, TiC, and WC) at a concentration of 0.25 wt% on the AD of CM was investigated by Li et al. (2018) batch-wise under mesophilic temperature. The experiments were performed in triplicates and average data was presented. Results showed that all these four carbides worked as accelerants in the AD process. HfC, SiC, TiC and WC increased biogas production by 63.9, 69.7, 57.5 and 69%, respectively, as compared to control check (CK), see Figure 10. We found that this is the first and maybe the only report on using metal carbides to inoculate in AD digesters. Table 5 summarizes nano-scale transition metal carbides and their influence on biogas generation.

Utilization of carbon and carbon-based nanomaterials for biogas

The one and the only study discussing the influence of Single-Walled Carbon Nanotubes (SWCNTs) on AD of AGS, with average diameters of 1–2 nm and length of 5–20 nm at a concentration of 1000 mg/L, under mesophilic conditions (35°C) for 8 days was examined by Li et al. (2015). SWCNTs did not reflect any significant enhancement in biogas and methane generation, see Figure 11. In the presence of 1000 mg/L SWCNTs, the volume of generated CH4 was significantly larger ($p < 0.05$) than that in the control reactor for the initial 48 h. However, it slowly decreased and ended at almost the same or little lower cumulative production as control, showing no effect. The authors attributed this zero effect of SWCNTs as a decrement in cytotoxicity of sludge by

TABLE 5 Reported nano-scale transition metal carbides their influence on biogas generation

NPs type	NPs size (nm)	NPs concentration	Feedstock	Temperature (°C)	HRT	Result	References
HfC	300	0.025 wt%	CM	37 ± 1	35 days	63.9%increase in cumulative biogas production	Li et al. (2018)
SiC	40	0.025 wt%	CM	37 ± 1	35 days	69.7% increase in cumulative biogas production	Li et al. (2018)
TiC	70	0.025 wt%	CM	37 ± 1	35 days	57.5% increase in cumulative biogas production	Li et al. (2018)
WC	400	0.025 wt%	CM	37 ± 1	35 days	69% increase in cumulative biogas production	Li et al. (2018)

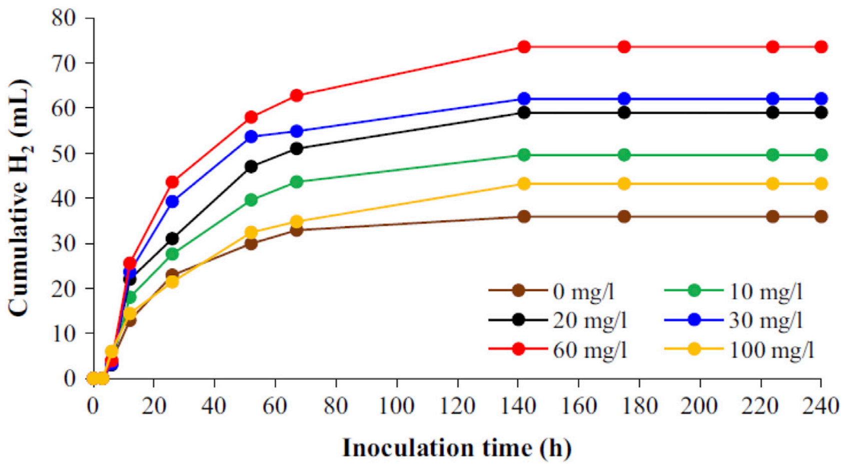

FIGURE 12
Cumulative hydrogen production at different concentrations of Ni-Gr NC (Elreedy et al., 2017).

nanotubes. The addition of SWCNTs in the AD system produced a more Extracellular Polymeric Substance (EPS) which prevented SWCNTs from reaching cells and hence resulted in limited to no effect on biogas yield.

Impact of Multi-Walled Carbon Nanotubes (MWCNTs) with the length of 1–10 μm, outer and inner diameters of 5–20 nm and 2–6 nm, respectively, were investigated on UASB microflora by Yadav et al. (Yadav et al., 2016). It was observed from SEM and fluorescent microscopy images that MWCNTs damaged acidogenic and acetogenic microbial cells, which caused an increase in EPS proteins, DNA, and carbohydrates. According to the authors, this microbial cell damage is the possible reason for low VFAs generation and biogas yield. The 1 mg/L and 100 mg/L concentration of MWCNTs caused 21% and 54% inhibition in biogas as compared to control.

In contrast, Zhang and Lu (2016) found an enhancement in biogas production with conductive MWCNTs (diameter: 10–20 nm, length: 10–30 mm) by syntrophic oxidation of butyrate in two different lake sediments. The CH_4 production rate in the presence of MWCNTs was almost 50% greater than the control. The results showed that the electric conductivity of the added MWCNTs facilitated the syntrophic oxidation of butyrate and had a stimulatory effect on microorganisms. Microscopic observation showed that abundant aggregates formed in lake enrichments under the presence of MWCNTs. The microbial aggregates in control were in close physical proximity whereas, in MWCNTs samples, dark areas within aggregates filled with nanotubes. This showed that greater intercellular distances existed on average, which form cell-nanotube-cell networks and facilitate DIET, which contributed to an increase in methane yield.

In another study, Ambuchi et al. (2017) investigated the response of MWCNTs (10–20 nm outer diameter) on AGS during AD of beet sugar industrial wastewater. An increase in biogas (1.09 times than control) and methane production (12.6% more ml/g-VSS CH_4 gas than control) was observed.

TABLE 6 Reported carbon nanotubes and their influence on biogas generation.

NPs type	NPs size	NPs concentration	Feedstock	Temperature (°C)	HRT	Result	References
SWCNT	Diameter 1–2 nm, length 5–20 nm	1000 mg/L	AGS	35	8 days	No effect	Li et al. (2015)
	1–2 nm diameter, 5–30 μm length	10000 mg/L	Glucose	55	20 days	CH4 production rate increased by 92%	Yan et al. (2017)
MWCNT	length 1–10 μm, outer diameter 5–20 nm and inner diameter 2–6 nm	1 and 100 mg/L	UASB Reactor Sludge	37 ± 1	15 days	21% reduction in the test sample with 1 mg/L MWCNTs and 54% in the test sample with 100 mg/L as compared to control	Yadav et al. (2016)
—	2–20 μm length, 20–30 nm diameter	50 mg/kg, 500 mg/kg	Sheep manure	35	45	presence of 500 mg/kg multiwall carbon nanotubes increased the daily and accumulative production of methane by 46.8 and 33.6%	Hao et al. (2019)
—	10–20 nm in diameter and 10–30 mm in length	0.5% (w/v)	lake sediments	—	40 days	CH4 generation rate was almost 50% larger	Zhang and Lu, (2016)
	10–20 nm outer diameter	1500 mg/L	BSIWW	36 ± 1	74 days	1.09 times increase in biogas. 12.6% more ml/g-VSS CH4 gas	Ambuchi et al. (2017)
	-	1500 mg/L	Granular sludge	36	96 h	Increase 43% of methane production	Ambuchi et al. (2016)
Graphene	4–20 nm	0.5–2 g/L	Ethanol	35	—	Increase 25% in methane yield and 19.5% in biogas production rate	Lin et al. (2017)
—	—	30–120 mg/L	Glucose	35	55 days	Up to 51.4% increase in methane production rate	Tian et al. (2017)
Fullerene (C_{60})	—	50,000 ng/kg of biomass	Waste water sludge	Ambient Temp	89, 154 days	No effect observed	Nyberg et al. (2008)
—	40–60 nm	50 mg/kg, 500 mg/kg	Livestock Sheep manure	35	45	The highest value of daily methane yield was 3.269 ml/g VS., is evident in the 500 mg/kg C_{60} treatment	Hao et al. (2019)
—	129.5 nm	100 mg/kg DW	Sludge	35 ± 2°C	20	No significant change in methane yield, hence failed to alter	Lin Zhao et al. (2018)

Summarized results reported that carbon nanotubes influence on biogas generation is shown in Table 6.

Nanowires, nano composites and nano-ash augmentation for biogas

Nanowires

The Octahedral Molecular Sieve (OMS-2) is a form of manganese dioxide that holds distinctive features like mixed-valence of manganese, acidic sites and has wide applications. The effect of synthesized OMS-2 NPs (diameter of nanofibers of about 10–20 nm and lengths of about 100–500 nm) on Sludge from the sewage treatment plant at concentrations of 0.025, 0.25, and 2.50 g/L was investigated by Pan et al. (2015). The addition of 0.025 g/L OMS-2 NPs resulted in an 11% enhancement in biogas production. The investigation of microbial metabolism revealed an increase in microbial metabolic level and enhanced microbial diversity. OMS-2 NPs also increased the quantities of acetogenic bacteria and Archaea and promoted acetogenesis and methanogenesis.

Lupitskyy et al. (2018) studied the influence of zinc oxide nanowires at a concentration of 1 g/L on the AD of AGS. According to the author, the use of ZnO nanowires as inorganic reactive absorbents can help in reducing the sulfur-containing compounds in wastewater and improve biogas production. The experiment was carried out for three feeding cycles. Sulfates were added at the beginning of each feeding cycle. Results showed that nanowires reduced the sulfide toxicity during AD as no methanogenic activity and biogas inhibition were observed (Lupitskyy et al., 2018). The summary of the reported nanowire and its influence on biogas generation is shown in Table 7.

Nano-composites

The effect of Ni-graphene nano-composite (Ni-Gr-NC) as a supplement to an AD of industrial wastewater containing MEG to enhance biohydrogen production was studied by Elreedy et al. (2017). The authors used the unique properties of Ni-based NPs as Ni ion suppliers and graphene as support materials.

TABLE 7 The reported nanowire, nano-composite, nano-ash, and their influence on biogas generation.

NPs type	NPs size	NPs concentration	Feedstock	Temperature (°C)	HRT	Result	References
OMS-2	Dia of nanofibers is about 10–20 nm, lengths are about 100–500 nm	0.025, 0.25, and 2.50 g/L	WWTPS	35	189 days	11%increase in biogas production	Pan et al. (2015)
ZnO Nanowire	-	1 g/L	AGS	35	60 h	No argumentative effect on the methanogenic activity was found	Lupitskyy et al. (2018)
Ni-Gr Nano -composite	23 nm	10, 20, 30, 60 and 100 mg/L	industrial wastewater containing mono-ethylene glycol (MEG)	55	240 h	60 mg/L dosage caused 105% increase in hydrogen production	Elreedy et al. (2017)
Micro Nano Fly Ash	0.4–10,000 nm	3 g/g VS.	MSW	35	90 days	Biogas enhancement by 2.9 times	Lo et al. (2012)
Micro Nano Bottom Ash	0.4–10,000 nm	36 g/g VS.	MSW	35	90 days	Biogas enhancement by 3.5 times	Lo et al. (2012)
Ni-Co-Ferrite	—	0–140 mg/L	Cow Manure	38	35 days	32.8% increase in biogas production	Mansour et al. (2020)
Zinc ferrite	6.22 nm	500 mg/L	Cattle manure	40	50 days	185.3% increase in biogas production	Hassaneen et al. (2020)

This is the first study with Ni-Gr-NC addition to the AD process. The results showed that 60 mg/L dosages caused a 105% increase in hydrogen production from other concentrations. The maximum specific hydrogen production obtained by Ni-Gr-NC (60 mg/L dose) was 294.24 ± 12.06 ml/L, see Figure 12. The hydrogenase enzyme activity affected by Ni ions in the presence of graphene resulted in an enhanced hydrogen yield. The summary of the reported nano-composites and their influence on biogas generation is shown in Table 7.

Mansour et al. (2020) studied the effect of Ni-Co-Ferrite on biogas production and reported that these nano additives increase biogas production by about 30%. In another study, Hassaneen et al. (2020) proposed the use of a novel nanocomposite (based on metal enzyme cofactors, highly conductive carbon materials, and DIET activators) and tested different formulations for the enhancement of biogas production. Methane production was observed to boost by 185.3% using Zn ferrite.

Nano-ash

The influences of micro-nano fly and bottom ash attained from MSW incinerator on the AD of MSW were investigated by Lo et al. (2012) at mesophilic conditions (35°C) for 90 days. The concentrations used for micro-nano fly ash was 0.12, 3, 6, 18, and 30 g/g VS. whereas micro-nano bottom ash was used at the concentration of 0.6, 12, 36, 60, and 120 g/g VS Results indicated that micro-nano fly and bottom ash produced a significant enhancement in biogas generation. The inoculation of 36 g/g VS. bottom ash produced the highest amount of biogas production among all dosages, as shown in Figure 12. The authors mentioned that the presence of various compounds (Al_2O_3, ZnS, $CaCO_3$, $CaMg(CO_3)_2$, Ca_3SiO_5, $Ca(OH)_2$, PbO, SiO_2, and Ca_2SiO_4) inside fly and bottom ash increased biogas production. The compounds present in the form of nano-substances supplied additional habitats for the microorganism. The summary of the reported nanoash and its influence on biogas generation is shown in Table 7.

Key challenges and way forward to nanomaterials augmentation in biogas production

Nanomaterials as additives to biomass were widely studied for biogas production enhancement, especially in the last decade. Unfortunately, their use may not always enhance biogas production, depending on many factors such as the size of nanomaterials, their concentration, and the type of substrate used. However, it is observed that nanomaterials used in the mixture tend to produce a much better effect on biogas production than separately used. Using different nanomaterials as a mixture and studying their interactions with different substrates could be a leading field research area in the years to come.

Furthermore, the environmental impact of NMs application with biomass for biogas production has not been discussed thoroughly, and climate concerns remain high for spent biomass with NMs. One of the significant challenges that need to be addressed urgently is that after utilizing NMs in AD, how to track them, and what would be the best methodology for dumping the waste and biomass that contains NMs? There is a possibility that spent biomass with a high concentration of NMs

TABLE 8 Reported nanomaterials and their influence on biogas generation.

Category	Nanomaterials	Effect on biogas production
Metal Nanoparticles	NZVI, Co., Ni	Increase biogas production rate
	Ag, Au, Cu	Decrease or no change biogas production rate
Metal Oxide Nanoparticles	Fe_2O_3, Fe_3O_4, Co_3O_4, NiO, MoO_3	Increase biogas production rate
	CeO_2	Mixed-effect on biogas production depending upon size and concentration of NPs
	ZnO, CuO, TiO_2, MgO, MnO_2	Decrease or no change biogas production rate
Nano-scale Nb-based compounds	NbO_2, $Nb_{3.49}N_{4.56}O_{0.44}$, and NbN	Increase biogas production rate
Nano-scale transition metal carbides	HfC, SiC, TiC, WC	Increase biogas production rate
Carbon Nanotubes	SWCNTs	No change biogas production rate
	MWCNTs	Mixed-effect on biogas production depending upon size and concentration of NPs
Nanowires	Octahedral molecular sieve (OMS-2)	Increase biogas production rate
	ZnO Nanowire	No change biogas production rate
Nano-composite	Ni-Gr Nano -composite	Increase biogas production rate
Nano Ash	MNFA, MNBA	Increase biogas production rate

may prove beneficial for soil and help maintain a nutrient level in the soil. On the other hand, these nanomaterials can increase the toxicity of the area and can also mix with underground water. These aspects have to be answered in future studies. Moreover, multiple studies can be found on the feasibility and financial aspect of NMs application in biogas production throughout the literature. However, studies related to NMs in biomass applications' environmental analysis and life cycle assessment are quite rare, which needs attention in future studies. The review and analysis of the available literature conducted in this study, the future direction, research area, and themes are depicted in Figure 3B. Currently, the most active countries working on nanotechnology-based biogas production as per citation record (minimum 100 documents and 100 citations) are presented in Figure 4. In addition, future guidelines may comprise the following:

1. In order to avoid the toxicity of the presently spent nanomaterials, causing an inhibitory effect on anaerobic bacteria, bioactive nanomaterials can be used for process improvement.
2. Recollecting spent nanomaterials at the end of the process remained a significant drawback for the environment and sustainability of their utilization in biogas or related applications. Avoiding the leak of nanomaterials in the natural resources and designing processes that limit this to happen should be the top priority for the implementation for large-scale production.
3. Optimization of nanomaterials for a wide range of sizes, doses, and shapes can be carried out to get the maximum advantage of nanotechnology for biogas and methane production.
4. Microalgae and lignocellulose biomass are potential feedstock for bioenergy production. However, the effect of NPs on these substrates can be carried out for improvement in biogas production.
5. Other commonly applied methods for biogas escalation, including pretreatment of substrate or inoculum and supplementation biological and inorganic additives, can be used in combination nanomaterials to get an overall energy gain.

Conclusion

By method of quantitative literature review, the impact of NMs on biogas production and methane yield is stated in this study. Several kinds of NMs have been investigated as additives in the AD process for biogas augmentation for various kinds of biodegradable wastes. For brevity, the eventual effect of nanomaterials and their positive or negative impacts on biogas generation are summarised in Table 8, which is concluded from the exhaustive literature review and presented from the materials' point of view. Additionally, the following conclusions have been drawn from the reviewed literature.

- Metal NPs such as NZVI, Co., and Ni showed a positive effect on biogas yield. However, Ag NPs showed no inhibitory effect.
- Metal oxide NPs such as iron oxide (Fe2O3 and Fe3O4), Co3O4, NiO, MoO3 NPs showed an increase in biogas and methane production, whereas ZnO, TiO2, CeO2, and CuO NPs showed an inhibitory effect. In contrast, the literature showed MgO NPs showed a mixed effect.
- Nb-based compounds (NbO2, Nb3.49N4.56O0.44, and NbN) and nano-scale transition metal carbides (HfC, SiC, TiC, and WC) showed an enhancement in biogas yield.

- Carbon nanotubes showed a mixed effect. Single-walled CNTs showed no effect, whereas multiwall CNTs showed an increase in biogas production.

Author contributions

SK, AZ, and HA contributed to the conception and data collection of the study. SK and AZ wrote the first initial draft of the manuscript. MN performed a bibliometric technique for the data sets. All authors contributed to manuscript revision, read, and approved the submitted version.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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Comparative appraisal of nutrient recovery, bio-crude, and bio-hydrogen production using *Coelestrella* sp. in a closed-loop biorefinery

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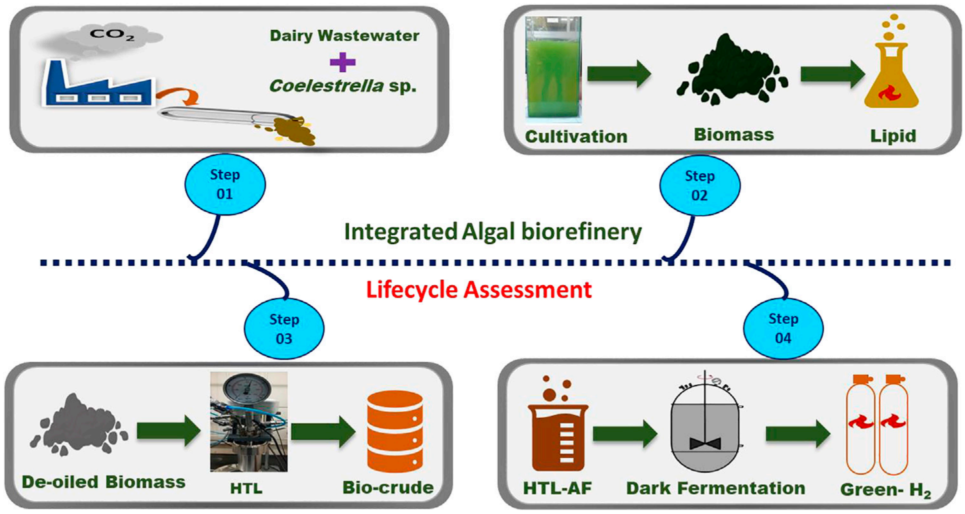
A closed loop algal-biorefinery was designed based on a three-stage integration of dairy wastewater (DWW) treatment, hydrothermal liquefaction (HTL) of defatted algal biomass, and acidogenic process in a semi-synthetic framework. Initially, *Coelestrella sp* SVMIICT5 was grown in a 5 L photo-bioreactor and scaled up to a 50 L flat-panel photo-bioreactor using DWW. The microalgal growth showed higher photosynthetic efficiency, resulting in a biomass growth of 3.2 g/L of DCW with 87% treatment efficiency. The biomolecular composition showed 26% lipids with a good fatty acid profile (C_{12}-C_{21}) as well as carbohydrate (24.9%) and protein (31.8%) content. In the second stage, the de-oiled algal biomass was valorized via HTL at various temperatures (150°C, 200°, and 250°C) and reaction atmospheres (N_2 and H_2). Among these, the 250°C (H_2) condition showed a 52% bio-crude fraction and an HHV of ~29.47 MJ/kg (bio-oil) with a saturated hydrocarbon content of 64.3% that could be further upgraded to jet fuels. The energy recovery (73.01%) and elemental enrichment (carbon; 65.67%) were relatively greater in H_2 compared to N_2 conditions. Finally, dark fermentation of the complex-structured HTL-AF stream resulted in a total bio-H_2 production of 231 ml/g of TOC with a 63% treatment efficiency. Life cycle analysis (LCA) was also performed for the mid-point and damage categories to assess the sustainability of the integrated process. Thus, the results of this study demonstrated comprehensive wastewater treatment and valorization of de-oiled algal biomass for chemical/fuel intermediates in the biorefinery context by low-carbon processes.

KEYWORDS

nutrient recovery, aliphatic/aromatic hydrocarbons, flat-panel photo-bioreactor, circular chemistry, acidogenesis/dark-fermentation, decarbonization, semi-synthesis



Graphical Abstract

Highlights

- *Coelestrella* sp. SVMIICT5 was used for dairy wastewater treatment and nutrient recovery
- Photosynthetic transition and biomolecular yields during microalgae cultivation were studied
- Bio-crude, aqueous fraction, and energy profiles during HTL were studied
- A higher bio-crude fraction (52%) was observed in H-HTL at 250°C
- The bioprocess (HTL-AF) resulted in 231 ml/g of bio-H_2 with 63% TOC removal
- Microalgae with a semi-synthesis approach allowed closed-loop biorefinery

1 Introduction

Biomass-based biorefineries have recently been considered as a potential strategy to mitigate environmental pollution and climate change by ensuring sustainable waste management (Venkata Mohan et al., 2020; Hao et al., 2021; Wahab et al., 2022). Bio-based energy production is one sustainable alternative (Amulya et al., 2020; Kokkinos et al., 2021; Kopperi et al., 2021), accounting for 9–10% of the global energy supply (Bagchi et al., 2021). Using nature-inspired processes to design an efficient biorefinery system to produce environmentally-friendly biofuels and chemicals can help to build sustainable bio-refineries and carbon-neutral bioeconomies (Katakojwala and Venkata Mohan, 2021). Microalgae is emerging as a third-generation feedstock for the production of biofuels with high energy density (Galadima, and Muraza, 2018; Mutanda et al., 2020; Bagchi et al., 2021) with in-built bio-sequester (CO_2) capability and the accumulation of significant lipids and other value-added products (Chew et al., 2017; Kokkinos et al., 2021; Kuravi and Mohan, 2021). Algal biorefinery is a potential platform that has been studied extensively for the production of a variety of products in a sequential and integrated pathway (Venkata Mohan et al., 2020). Following wastewater treatment, bio-oil extraction from microalgae, targeting biogas production by utilizing biomass, defatted biomass for improving soil fertility, etc. has been explored (Prajapati et al., 2014; Venkata Mohan et al., 2020; Arora et al., 2021). Phycoremediation uses nutrients as a growth medium to provide biomass production (Venkata Mohan et al., 2020). Nutrient recovery using algae followed by integration with an aerobic digester for the production of biofuels in closed-loop approaches has been reported (Prajapati et al., 2014; Al-Jabri et al., 2020). The bioremediation of various wastewaters (marine, brackish water, etc.), as well as CO_2 fixation from CO_2-rich flue gas emissions from stationary using algae, have also been evaluated (Hemalatha et al., 2019; Molazadeh et al., 2019; Watson et al., 2020).

Thermo-chemical processes such as gasification, pyrolysis, and hydrothermal liquefaction (HTL) are being considered as efficient routes to rapidly convert biomass to fuels or chemicals (Wang et al., 2018; Kokkinos et al., 2021). HTL has emerged as an economically feasible and environmentally friendly method for biomass conversion. HTL uses water as a catalyst to convert algae biomass to bio-crude and other by-products in an inert or reducing system (oxygen-free) at elevated temperatures and high pressures of 5–28 MPa (Katakojwala et al., 2020; Hao et al., 2021; Kopperi et al., 2022). Process conditions such as solid-to-liquid ratio, feedstock composition, temperature, solvent, pressure, and catalyst impact the efficiency and

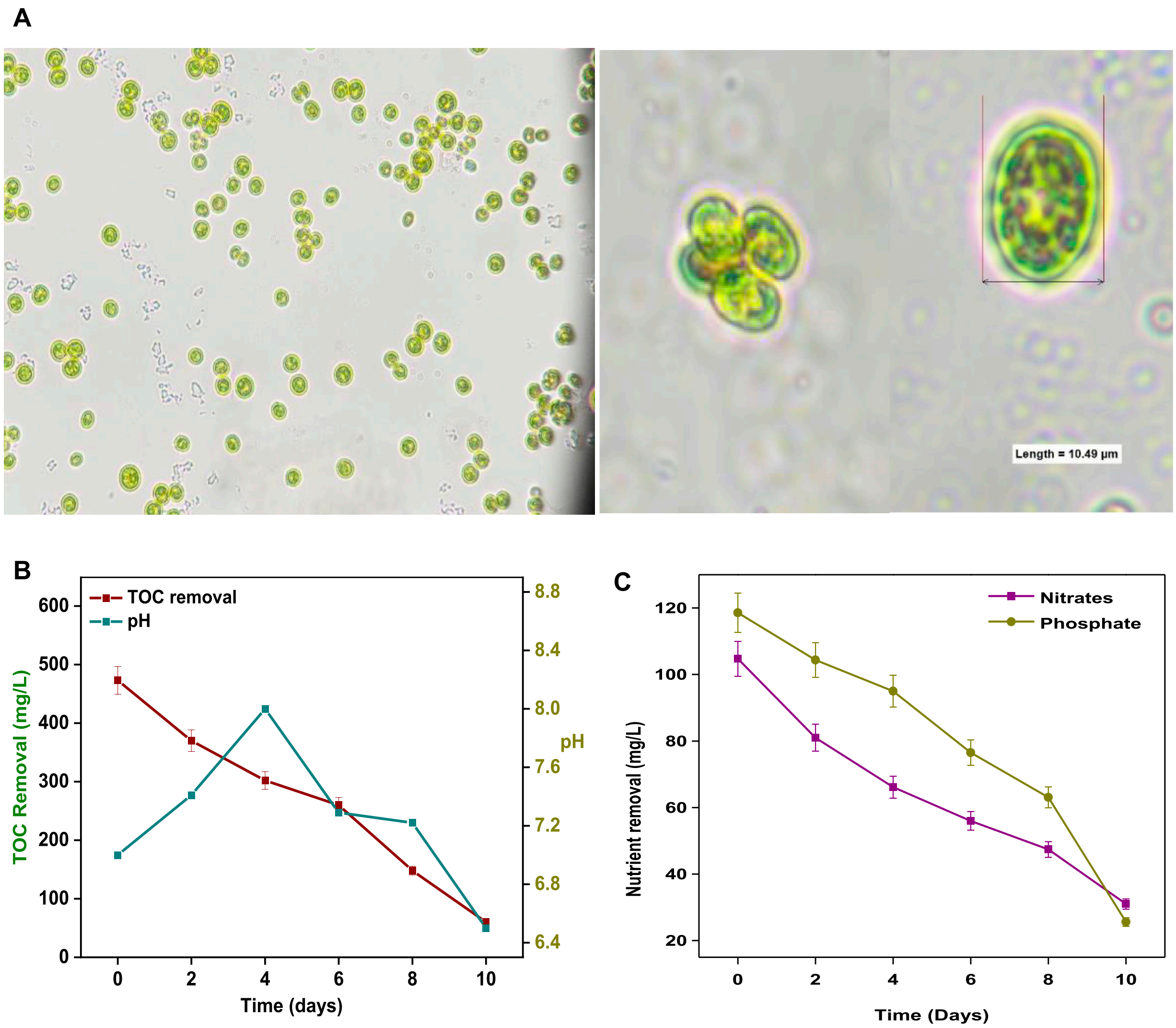


FIGURE 1
(A) Microscopic images and **(B)** size and shape of *Coelestrella* sp. **(B)** TOC removal and pH change and **(C)** nutrient removal with respect to time during SDWW treatment.

specificity of the reaction products (Carpio et al., 2021). The practical application of HTL for converting organic feedstock into biofuels and further upgradation resulting in aviation/jet fuels with zero waste is of increasing interest in the global community (Hao et al., 2021; Kopperi et al., 2022). However, HTL results in an aqueous organic fraction of 20–50% (HTL-AF) from feedstock and its recovery from AF is an important step for nutrient and energy recovery (Si et al., 2019; Watson et al., 2020). The HTL-AF contains complex molecules including furans, phenols, volatile fatty acids (VFAs), N-heterocyclic compounds, etc. Moreover, the integration of dark fermentation (DF) is a potential pathway for bio-energy production due to its higher tolerance for HTL-AF. It is also a potentially cost-effective biological process with reduced environmental impacts (Watson et al., 2020; Chen et al., 2021; Kopperi et al., 2022).

The chemical industry is currently reorienting itself towards semi-synthesis employing biobased materials or combining chemicals with renewable feedstocks (Venkata Mohan and Katakojwala, 2021). In this context, the integrated biorefinery process is a semi-synthetic route for the conversion of biological feedstock to valuable energy/fuel and chemical components. Additionally, the utilization of the byproducts could ensure the overall sustainability of the process, ensuring the circular chemistry paradigm shifting from conventional linear flow practices to low-carbon closed-loop approaches (Katakojwala and Venkata Mohan, 2021; Kopperi et al., 2022). Therefore, the present study mixotrophically cultivated *Coelestrella* sp. using dairy wastewater with an integrated strategy in the “waste to wealth” framework. Initially,

TABLE 1 Chemical composition of the synthetic dairy wastewater (SDWW).

Ingredient	Amount (gL^{-1})
Skim milk powder	0.8
Urea	0.27
CH_3COONa	0.21
K_3PO_4	0.15
$(NH_4)_2SO_4$	0.06
$MgSO_4{\cdot}7H_2O$	0.05
NH_4Cl	0.54
$Na_2HPO_4{\cdot}2H_2O$	0.9
$NaHCO_3$	1.56
KCl	0.6
$CaCl_2{\cdot}H_2O$	0.036
TOC	0.473
NO_3^-	0.104
PO_4^{3-}	0.118

this study explored wastewater treatment, nutrient recovery, and biomass growth with photosynthetic response. Bio-molecules (carbohydrates, proteins, and lipids) accumulation was also studied in detail. Additionally, HTL was applied to produce bio-crude from the defatted biomass under different temperatures and atmospheric conditions. The biomass conversion ratios, bio-crude yields, and energy recovery ratios were explored. Furthermore, HTL-AF carbon and nutrient recovery were studied by DF to determine the bio-H_2 for all HTL experiments using pretreated mixed microbial consortiums. Furthermore, a life cycle assessment of the integrated algal biorefinery was performed based on the "cradle to gate" system boundary including the sub-process steps of algal cultivation in dairy wastewater, biomass de-oiling (lipid extraction), bio-oil recovery, and bio-H_2 production. Based on the above descriptions, the waste valorization and resource recovery using microalgae were evaluated in a circular biorefinery approach.

2 Materials and methods

2.1 Microalgae strain

Indigenous *Coelastrella* sp. SVMIICT5 microalgae were isolated from water body at CSIR-IICT, Hyderabad (17.4301° N, 78.5416° E) by quadrant streaking. Microscopic observations showed *Coelastrella* sp. cells arranged in tetraploid and hexaploid (four and six cells) structures. Each cell was oval in shape and >10 μm in size (Figure 1A). The isolate was deposited at the National Collection of Industrial Microorganisms (NCIM) in Pune (accession number NCIM-5793 (05-04-2021)).

2.2 Flat-panel photo-bioreactor-mixotrophic cultivation

Initially, *Coelastrella* sp was pre-cultured in a 50 ml tube in 30 ml modified sterile 3 N-Basel Bold Medium (BBM) (Kona et al., 2021) at 25 ± 1°C for 7 days. Later growth was continued in 250 ml flasks and optimized. The culture was further scaled in 5 L Erlenmeyer flasks in 3.5 L of 3N-BBM for 7 days with a pH of 7.0. Continuous air bubbling was provided to avoid cell aggregation After 7 days, the cells were harvested for further experiments. Mixotrophic (axenic) outdoor cultivation was performed in 50 L (working volume) flat panel photo-bioreactors (FP-PBR; 45 cm (length) x 15 cm (width) x 90 cm (height); 8 mm (thick) transparent glass) exposed to natural sunlight (ambient temperature, 29 ± 6°C). The reactor was fixed with fine bubbling air spargers at the bottom. Continuous air was supplied using an air pump (Hailea-Aco-208) at a flow rate of 35 L/min to provide CO_2 and to mix the culture. The composition of the synthetic dairy wastewater (SDWW) was as described elsewhere, with minor modifications (Kiran and Mohan, 2022) (Table 1). FP-PBR fed with 40 L of SDWW was inoculated with 10% *Coelestrella* sp SVMIICT5 (OD, 0.1) and cultured for 10 days. The reactor was monitored by microscope to observe the cell purity and size. During microalgal growth, samples were collected on alternate days and centrifuged (7000 RPM; 5 min) to determine the pH; biomass concentration; carbon, nitrogen, and phosphate removal; and bio-molecular composition.

2.3 Hydrothermal liquefaction-de-oiled biomass

The de-oiled algal biomass (DAB; lipid extracted) was dried and used as a feed for the HTL reaction using deionized (DI) water as the solvent. A 15% (w/v) of DAB was mixed in 200 ml of DI water and transferred to a customized 300 ml high-pressure stirred reactor (KLB Instrument Ltd., India). Initially, the reactor headspace was purged with inert gas (N_2) to replace the air and further pressurized to 100 bar with N_2 (N-HTL) or H_2 (H-HTL) to create inert and reduced atmospheres, respectively. The reactions were performed at various (150, 200, and 250°C) for inert (N-HTL) and reduced (H-HTL) conditions for 60 min with vigorous mixing (500 rpm). After 60 min of reaction, ice-cold water was passed through the cooling coil to stop further reactions. The gases from the headspaces were collected into Tedlar gas bags and analyzed. The solid and liquid fractions were filtered and the solid residue was washed with acetone/chloroform to remove organic soluble mater and dried at 105°C for 12 h. The conversion yields were calculated as the weight losses during the experiments. Liquid-liquid separation methods were used using an organic solvent (chloroform) to separate the aqueous and organic fractions of the bio-crude.

2.4 Dark fermentation-bio-H_2 production

The HTL-AF from all experiments was used as feedstock for bio-H_2 production using the pre-treated inoculums (Santhosh et al., 2021) taken from the semi-pilot scale bio-hydrogen reactor at CSIR-IICT. The experiments were performed in 500 ml bioreactors with 400 ml working volume and 100 ml of headspace with a retention time of 72 h at 35 ± 2°C. The carbon content of HTL-AF was adjusted to 4 g/L of TOC and a pH of 6.5 Gas production was monitored in a continuously stirred bioreactor (Bioprocess Control-AMPTS II, Sweden). The gas outlets from the bioreactors were connected to a flow meter through fixed gas lines that continuously measured biogas in an online system. The gas production and substrate conversions were evaluated by sampling liquid and gas at 12-h intervals and analyzed further.

2.5 Analysis

2.5.1 Microalgae growth

Algal growth was quantified by UV-VIS spectrophotometer (JASCO V-750) at a wavelength of 720 nm to measure biomass growth. The dry cell weight (DCW) was obtained by passing culture through filter paper and drying it in an oven at 60°C until the biomass was invariant. The specific algal growth rate (mg d^{-1}) was calculated using Eq. 1, where ln X was the n-log of the final DCW and X_0 was the natural logarithm for the initial DCW at a given interval "t" (Kiran and Mohan, 2021).

$$\text{Specific growth rate}\,(\mu) = \text{In}\,X - \text{In}X_0/t \tag{1}$$

2.5.2 Bio-molecule estimation

The samples were measured for pH variation (Adwa, AD-8000). The nitrate and phosphates (mg L^{-1}) removal was measured by standard protocols (American Public Health Association and American Water Works Association, 1998). The chlorophyll a, b and carotenoid contents of the algal biomass were estimated by cell disruption (40 kHz; 5 min) with 90% acetone and the supernatant was separated (7000 xg). The chlorophyll (a, *b*) and carotenoid concentrations in the supernatant were measured based on their ODs at 661.6, 644.8, and 470 nm, respectively, and further calculated using Eqs 2–4 (Jeffrey and Humphrey, 1975).

$$\text{Chl a}\,(\mu g/ml) = 11.24{\times}A_{661.6} - 2.04{\times}A_{644.8} \tag{2}$$

$$\text{Chl b}\,(\mu g/ml) = 20.15{\times}A_{664.8} - 4.19{\times}A_{661.6} \tag{3}$$

$$\text{Carotenoids}\,(\mu g/ml) = (1000 \times A_{470} - 1.90 \times \text{Chl a} - 63.14 \times \text{Chl b})/214 \tag{4}$$

The total carbohydrate content was measured using the hydrolysis (phenol-sulphuric acid) method, (Yirgu et al., 2020) while the protein content was estimated using a bicinchoninic acid (BCA) protein assay kit (Takara-T9300A) with bovine serum albumin (BSA) as the standard. The total organic carbon (TOC) content of the SDWW was analyzed on a TOC analyzer (TOC-L CPH, Shimadzu; 4 μg/L to 30,000 mg/L detection limit). The fatty acid methyl ester (FAME) profiles were analyzed using 100 mg of dried biomass (transesterified) to which acidified (2%) methanol was added in a parallel synthesis reactor (Radleys, UK) and kept at 70°C for 5 h (close-refluxing). The mixture was fractionalized using a 2: 1 ratio of ethyl acetate and water. The lipid product was dissolved in anhydrous chloroform for gas chromatography (GC; (Agilent- 7890B) analysis (Kuravi and Mohan, 2021).

2.5.3 Photosynthetic fluorometry measurements

The Fv/Fm (PS I) parameters were measured by fluorescence using a PAM fluorometer (Aqua pen, AP-C 100) on whole algal cells adapted to the dark for 10 min (Kona et al., 2021). The photosynthetic regulatory reactions of *Coelastrella* sp were studied based on the PSII (P680-specific *Chl a* fluorescence) and PSI (P700-specific light absorption) signals using a DUAL-pulse amplitude modulator (DUAL-PAM; Walz, Germany). For these measurements, 1 ml of thick algae culture was dropped in a cuvette (quartz-10 mm) under continuous stirring with a micro stirrer and adapted in the dark for 15 min to open the reaction centers (RCs) of the photosystems (PSII and PSI) before measuring (White et al., 2011). The rapid light curve (RLC) triggers were measured every 10 s, escalating actinic irradiance from 10–832 μmol photons $m^{-2}s^{-1}$. The RLCs provided a snapshot of electron transport chain (ETR) saturation and the overall photosynthetic performance of the *Coelastrella* sp. The dual PAM was operated with v-1.9 software to record the data and generate RLCs (White et al., 2011; Jokel et al., 2018; Kiran and Mohan, 2021).

2.5.4 HTL and bioprocess analysis

The off-gas composition was assessed by GC (Agilent-7890B). The elemental (C, N, S, H, and O) compositions of solid and liquid (biochar, bio-oil) samples were analyzed (ElementarVario Microcube-63505). The bio-oil profiles were identified by GC-MS. The chromatogram peaks were analyzed using the NIST-Database (Katakojwala et al., 2020). The aqueous fraction composition was analyzed by high-resolution quadrupole time-of-flight mass spectrometry (HRMS; Waters

AcquityXevo G2-XS) (Katakojwala et al., 2020). The DF samples were analyzed three times using TOC. The average results were presented. The VFA composition was estimated by high-performance liquid chromatography (HPLC; Shimadzu LC20A) (Kopperi et al., 2022).

2.5.4.1 Yield calculations

The DABs for various constituent conversions such as bio-crude yields (%), HTL conversion (%), and higher heat value (HHV, $MJ.kg^{-1}$) were calculated using Eqs 5–8 (Villaver et al., 2018; Wang et al., 2018). Elements (E) (C, H, N, S, and O) and HHV of DAB and bio-crude were calculated based on Eq. 6. The bio-crude yields and HTL conversions were calculated according to Eqs 5 and 7. From the equations, m_B, m_A, m_M, m_{SR}, and m_C, are the mass of the bio-crude, ash of algae, microalgae, solid residue, and catalyst, respectively. The energy recoveries (ER) were the HHV ratios of the bio-crude to DAB-HTL and are calculated using Eq. 8, where HHV_M and HHV_B are the HHVs of microalgae and bio-crude, respectively.

$$\text{BiocrudeYield}\,(\%) = \frac{m_B}{m_M} \times 100\% \tag{5}$$

$$\text{HHV}\,(\text{MJKg}^{-1}) = 0.3404C_B + 1.2432H_B + 0.0628N_B + 0.1909S_B - 0.0984O_B \tag{6}$$

$$\text{HTLConversion}\,(\%) = \left\{1 - \frac{m_{SR} - m_A - m_C}{m_C}\right\} \times 100\% \tag{7}$$

$$\text{EnergyRecovery}\,(\%) = \frac{HHV_B \times \text{BiocrudeYield}}{HHV_M} \tag{8}$$

2.6 Life cycle analysis

The environmental sustainability of integrated algal biorefinery with a defined system boundary was analyzed using LCA software (SimaPro v.9.1.1) as per ISO 14040:2006 guidelines. The inventory for energy and chemical inputs to the biorefinery system are detailed in Figure 6A. A cradle-to-gate system boundary approach was applied, with a functional unit of a 100 L biorefinery system, including dairy wastewater treatment, biomass processing (lipid extraction/de-oiling), HTL, and acidogenesis. (Supplementary Table S2). All the primary inputs, as well as secondary data, were provided according to the LCA framework (Katakojwala and Venkata Mohan, 2021). The best experimental conditions (H-HTL-250°C) were considered in the LCA study. The sustainability of the integrated biorefinery process was studied with respect to fifteen mid-point and four end-point (damage) categories using the Impact 2002 + lifecycle impact assessment (LCIA) method. The damage impact categories included health, ecosystem, quality, climate change, and resource depletion (Sarkar et al., 2021).

3 Results and discussion

3.1 Cultivation and metabolites

3.1.1 Wastewater treatment

During cultivation, changes in nutrients (N and P), pH, and carbon were monitored (Figure 1). The pH increased from 7.1 (day 1) to 8.02 (day 4) and then gradually decreased to 6.59 (day 10) (Figure 1B). The pH influences microalgae cultivation by affecting nutrient uptake. The nitrate and phosphate concentrations decreased from 104 mg/L and 118 mg/L, respectively, to 31 mg/L and 25 mg/L with removal efficiencies of 70.39 and 80.1% by the end of day 10 (Figure 1C). The nutrient (N and P) uptake by microalgae occurred through interconnected biochemical pathways for storage/assimilation into nucleic acids and proteins for cell growth (Taziki et al., 2015). Nitrates were assimilated into amino acids and processed for protein formation (Taziki et al., 2015). Phosphorus (as orthophosphate) entered the cell membranes and was assimilated into nucleotides for ribosomal RNA synthesis (Mao et al., 2021). The levels of organic carbon (TOC) decreased from 473 mg/L to 60 mg/L by the 10th day of cultivation, with 87% treatment efficiency (Figure 1B).

3.1.2 Biomass and pigments

During the experimental period, the growth characteristics of *Coelestrella* sp were monitored every two days. The SDWW was inoculated with 0.15 g/L (DCW) (day 0) of microalgae culture. The concentration increased to 3.2 g/L (DCW) by the end of the growth period (day 10). The microalgae growth with organic carbon under mixotrophic conditions increased the growth rate by improving biomass yield and lipid accumulation, simultaneously consuming CO_2 and producing oxygen through photosynthesis (Lv et al., 2019). SDWW treatment (carbon removal) was well correlated with the biomass growth rate. A specific growth rate of 581.57 mg/L/d was observed on the 10th day of cultivation (Figure 2A). Similar growth and carbon removals fractions were previously performed with *Tetradesmus* sp. and *Scenedesmus* sp. cultures using different wastewater (Alvarez-Diaz et al., 2015; Kiran and Mohan, 2022). Elemental analysis of the harvested biomass showed 48.1% C, 6.3% H, 9.5% N, 0.5% S, and 35.6% O. No growth inhibition was observed in the SDWW during the cultivation period. The tolerance of diverse wastewaters for the cultivation of microalgae has been reported (Al-Jabri et al., 2020). Kothari and co-workers (Kothari et al., 2013) reported no toxic or inhibitory effects on microalgae growth when dairy wastewater (maximum 6 g/L) was used as cultivation medium. However, the algal growth rates were lower in industrial wastewaters due to the presence of toxic metal ions such as

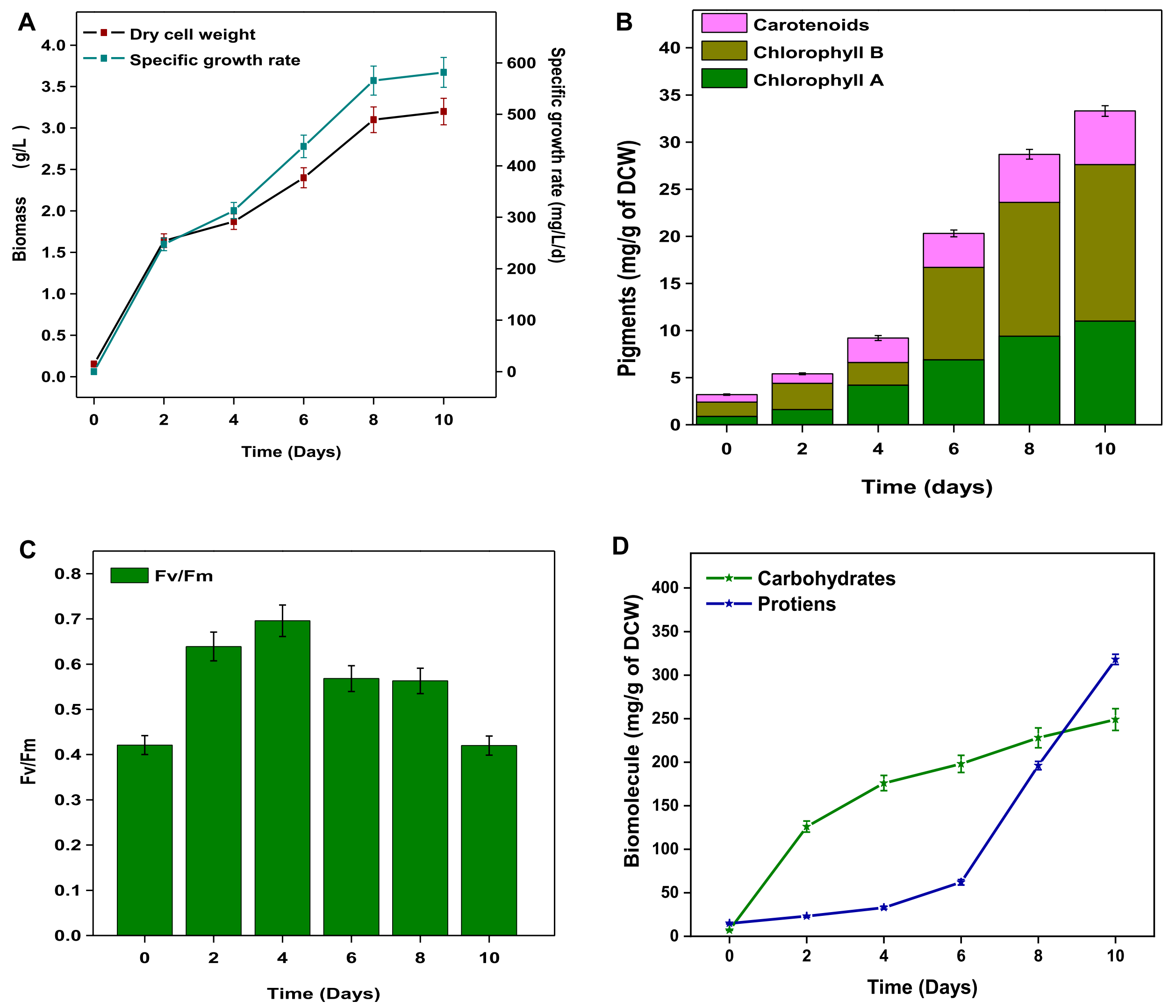


FIGURE 2
(A) Maximal photosynthetic yield (Fv/Fm). **(B)** Biomass and specific growth rate. **(C)** Chlorophyll a, b, and carotenoids and **(D)** total carbohydrate and protein contents.

Cd, Cr, etc. and organic toxins (hydrocarbons, surfactants, biocides, etc.) (Molazadeh et al., 2019).

The pigment fractions (chlorophyll (*Chl*) a and b and carotenoids) as a function of cultivation time are shown in Figure 2B. Gradual increases in *chl* a and *chl* b concentrations were observed from day 4 to 10 and reached maximum concentrations of 11 mg/g (*chl* 1) and 16.6 mg/g (*chl* 2) by the end of the cycle (day 10). The concentrations of secondary metabolite (carotenoids) increased significantly from 0.8 mg/g (day 0) to a maximum value of 5.7 mg/g on day 10. The chlorophyll content is directly proportional to biomass growth (Masojídek et al., 2010) with the conversion of 5-aminolevulinic acid to porphobilinogen (Huang et al., 2019). Intracellular free nitrogen (nitrates, amino acids) directs the controlling metabolism toward carotenoid synthesis (Huang et al., 2019). The changes in the photosynthetic activity of *Coelestrella* sp. were also analyzed. The Fv/Fm ratios indicate the PSII (photosystem) photochemical efficiency in the dark-adapted state with fully open reaction centers of the PSII system (Kona et al., 2021). Initially, the Fv/Fm value was 0.42 (day 0) and later reached a maximum value (0.69) on day 4, indicating a maximum photosynthetic activity. The ratio then gradually decreased to 0.42 by the end of cultivation (Figure 2C). The lower Fv/Fm ratios might result in carotenoid synthesis (Masojídek et al., 2010).

TABLE 2 Composition analysis of *Coelestrella* sp. SVMIICT5 after cultivation.

Component	Unit fraction
Biomass yields (DCW)	3.2 ± 0.16 (g/L)
Specific growth rate	0.43 ± 0.02 (g/L/d)
Carbohydrate	24.9 ± 1.24%
Protein	31.8 ± 1.5%
Total Lipid	26 ± 1.3%
Neutral Lipid	10 ± 0.5%
Fatty acids Composition	Fatty acid (%)
Undecanoic acid (C11:0)	2.2 ± 0.1
Lauric acid (C12:0)	4.6 ± 0.2
Tridecanoic acid (C13:0)	5.9 ± 0.3
Myristic acid (C14:0)	7.3 ± 0.35
Pentadecanoic acid (C15:0)	6.2 ± 0.3
Heptadecanoic acid (C17:0)	11.5 ± 0.5
Arachidic acid (C20:0)	4.3 ± 0.21
Myristoleicc acid (C14:0)	8.6 ± 0.4
Pentadecanoic acid (C15:1)	14.1 ± 0.7
Heptadecanoic acid (C17:1)	16.9 ± 0.8
Oleic acid (C18:1)	8.6 ± 0.43
Linolenic acid (C18:2 ω-6)	3.5 ± 0.17
Eicosapentanoic acid (C20:5ω-3)	6.3 ± 0.3
SFA	**50.6** ± 2.5
MUFA	**39.6** ± 1.9
PUFA	**9.8** ± 0.49

3.1.3 Bio-molecules

Analysis of the biomolecule composition of *Coelestrella* sp. showed 24.9% carbohydrates, 31.8% proteins, and 26% total lipids (10% neutral lipids) (Table 2; Figure 2D). A maximum concentration of 249 mg/g of carbohydrate was observed on day 10. The protein fraction resulted in 318 mg/g of biomass at the end of the cycle. Algae synthesize carbohydrates by photosynthesis-mediated carbon absorption of cells by an inducible (hexose/H^+) symport mechanism (Alvarez-Díaz et al., 2015). Carbon-rich SDWW results in an easy uptake of carbon compared to other sources for carbohydrate synthesis. The nutrients (N and P) and carbon sources direct metabolism toward protein synthesis and cell growth acceleration. In the presence of adequate carbon source and light energy, proteins are further utilized and converted to carbohydrates or lipids (Hemalatha et al., 2019). The photosynthetic carbon internalization mechanism shifts from the production of molecules such as proteins and carbohydrates to the storage of lipids (Alvarez-Díaz et al., 2015). A C/N imbalance in the cell caused due to nitrogen deprivation affects metabolism, promoting the storage of lipids/triglycerides (Kuravi and Mohan, 2021).

When assessing the commercial viability of microalgae, lipid productivity is one key product. The *Coelestrella* sp. dried biomass resulted in 26% of total lipids per gram of DCW, with 10% neutral lipids. The GC-FAME analysis showed a wide range of saturated (SFA) and unsaturated (USFA) fatty acids. The fatty acid profiles of *Coelestrella* sp. SVMIICT5 showed a relatively higher fraction of SFA (50.6%) followed by USFA (49.4%) (Table 1). In SFA, heptadecanoic acid (C17:0) was a major fraction (11.5%), followed by myristic acid (C14:0, 7.3%) and pentadecanoic acid (C15:0, 6.2%). The USFA contained monounsaturated fatty acids (MUFAs) such as pentadecanoic acid (C15:1, 14.1%), heptadecanoic acid (C17:1, 16.9%), and oleic acid (C18:1, 8.6%). The polyunsaturated fatty acids (PUFAs) included 3.5% linolenic acid (C18:2 ω-6) and 6.3% eicosapentaenoic acid (C20:5ω-3). By the end of the treatment, the nutrient deficiency and high irradiance favored higher MUFA assimilation (Kuravi and Mohan, 2021). The above-mentioned fatty acids have medicinal and biotechnological applications in fuels, nutrition, fodder, pharmaceuticals, and skin care products (Kiran and Mohan, 2022). Linolenic acid in PUFA is most useful in the synthesis of eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA), which reduce the risk of immunological, neurological, and degenerative diseases (arthritis, heart, and skin) (Kuravi and Mohan, 2021). SFA and USFA are commonly used as emulsifiers in skin care, antioxidant, antibacterial agent, and lubricant preparations (Hemalatha et al., 2019; Kuravi and Mohan, 2021). The mixotrophic growth of *Coelestrella* sp. SVMIICT5 showed significant biomass production and lipid productivity, with fatty acid composition associated with nutraceutical functions and lubricant preparations.

3.2 Photosynthetic transients

On every other day from day 0 to 8 during the growth period, photosynthetic parameters (PSII and PSI) of *Coelestrella* sp. SVMIICT5 were measured immediately after 10 min of dark adaptation (Figure 3). Dark adaptation relaxes the thermal dissipation mechanism and oxidizes photosynthetic reaction centers, resulting in maximum photochemical efficiency (Fm). Upon activation of actinic light (AL) on chlorophyll pigments, chlorophyll a fluorescence and P700 transients aid in the measurement of photosynthetic performance (Kiran and Mohan, 2022). PS II is explained by Fo, Fm, F′, and Fm' (fluorescence variables), whereas the energetic state (PSI) is defined according to the Po, Pm, and Pm' fluorescence variables (Kona et al., 2021). While PSII and PSI have different light absorption maxima, activating their light-harvesting centers enhances their respective photosystems. YPSII determines both electron excitation to drive PSII and PSI re-opening after photochemical activity (Bonnanfant et al., 2019). By induced saturation pulse, the maximal PSII quantum yield in the present study increased from 0.518 (day 0) to 0.715 (day 6), indicating improved photosynthetic performance, before gradually decreasing to 0.504 (day 8) (Figure 3A). The splitting of water molecules in PSII is facilitated by the light energy captured by reaction centers (RCs), with the released

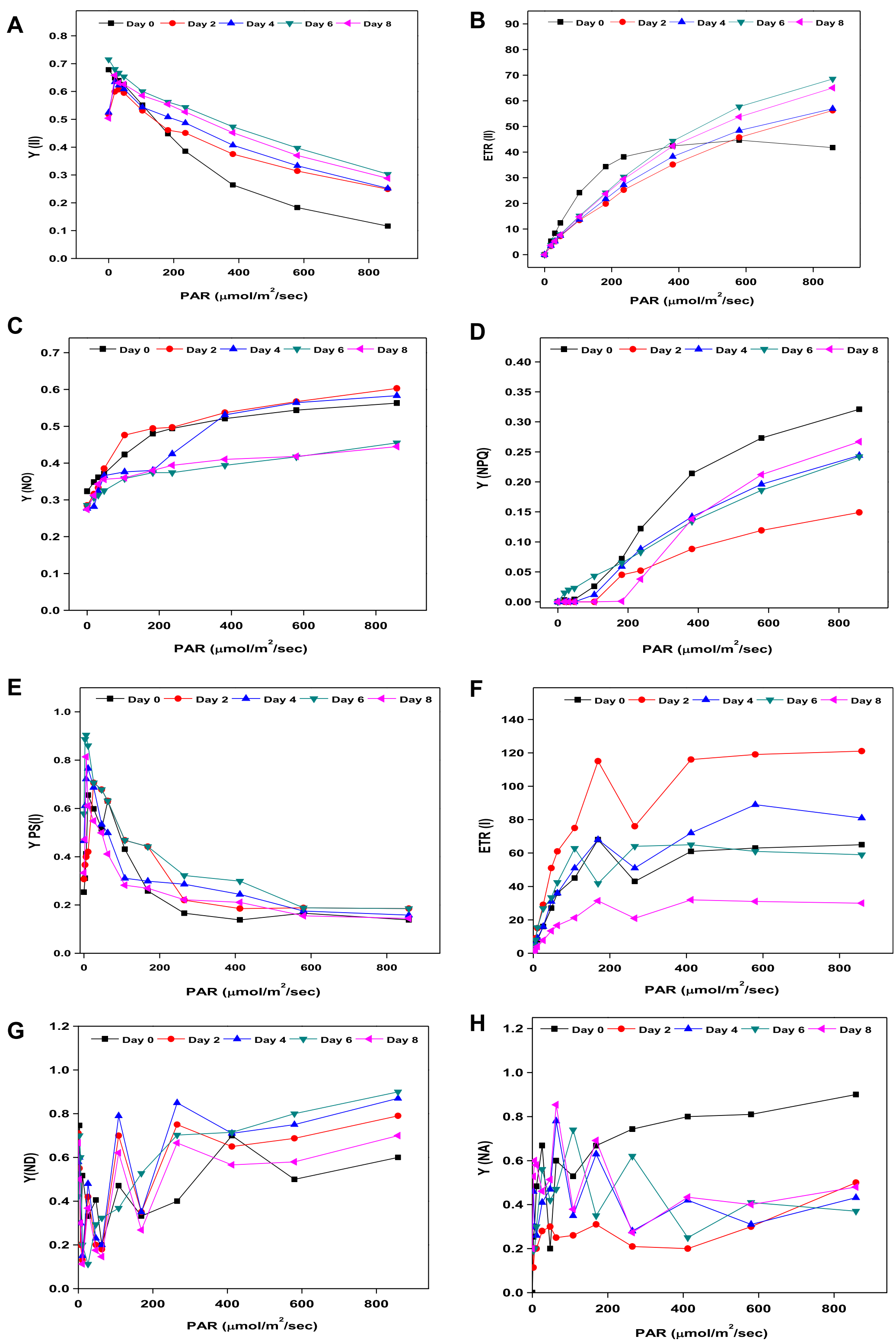


FIGURE 3
(A–D) Chlorophyll a fluorescence. **(E–H)** P700 transients of *Coelestrella* sp.

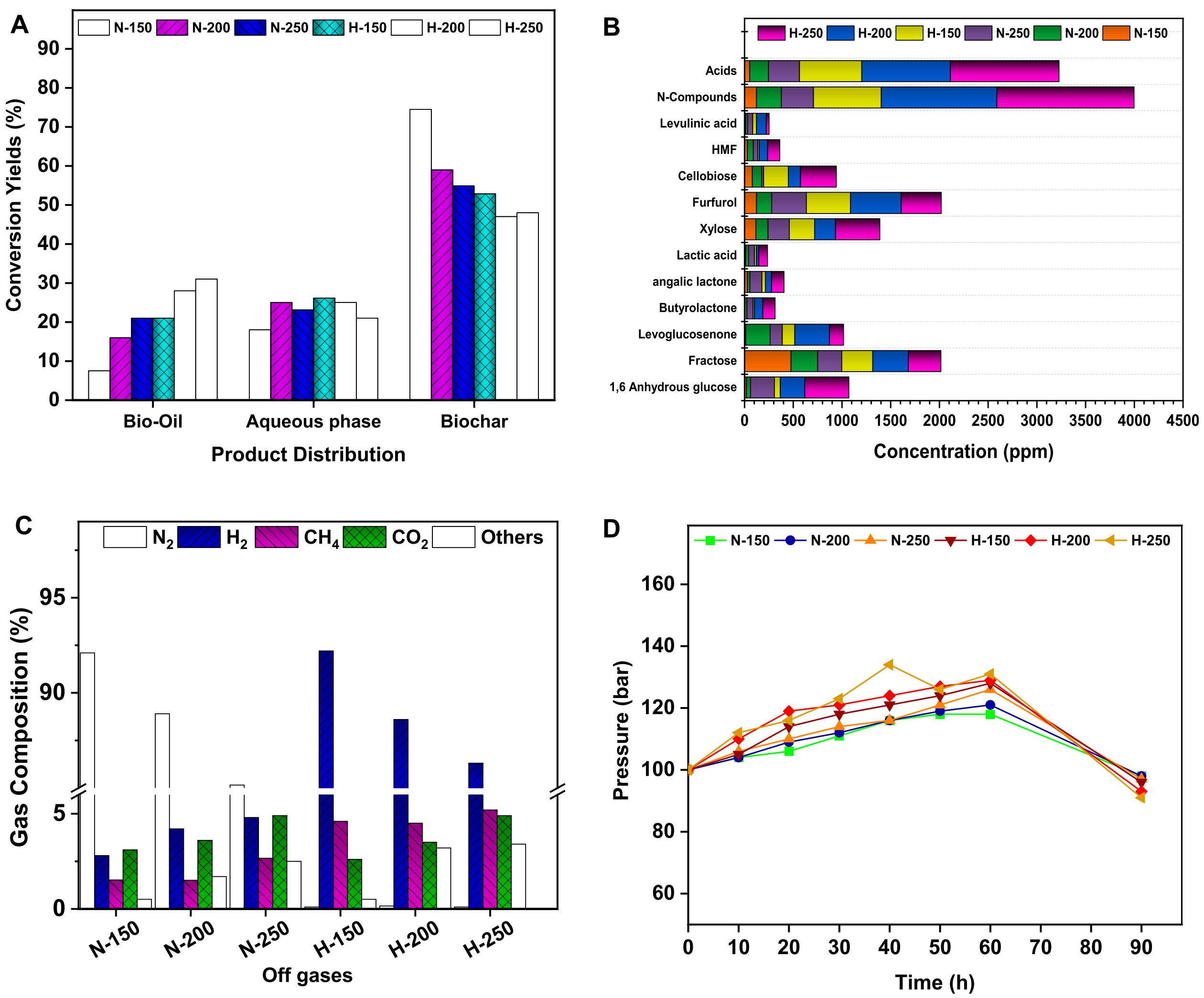


FIGURE 4
(A) Product distribution profile. **(B)** Aqueous fraction product profile. **(C)** Off-gas composition. **(D)** Pressure variation with respect to temperature.

protons driving PSI to reduce ATP and NADPH (Bonnanfant et al., 2019). The increased YPSII ratios indicated efficient electron donors at the initial and final electron acceptors, implying faster cell growth until day 6 in SDWW (Kiran and Mohan, 2021). The ETRII is a measure of electron transport in the photosynthetic cycle, which is also aligned with oxygen liberation and CO_2 fixation. The electron transfer rate of *Coelestrella* sp. cells increased steadily from day 0 (41.7) to day 6 (68.5) and decreased slightly to 65 at end of day 8 of the cycle upon induction with actinic light (Figure 3B). This decrease might be caused by excessive exposure to light or nutritional depletion during the growth process (Bonnanfant et al., 2019). A higher Fv/Fm ratio implies the efficiency of water splitting and carbon fixation at PSII, allowing for higher photosynthetic electron transport (Wimalasekera, 2019).

Non-photochemical quenching drives microalgae to lose surplus light energy as heat and fluorescence from light-harvesting complexes, which is inversely proportional to quantum yield [Y(NPQ) - regulated energy dissipation and Y(NO) - non-regulated energy dissipation] (Tikkanen et al., 2015). Y(NO) (inversely proportional to YPSII) decreased from 0.563 (day 0) to 0.445 (day 8) (Figure 3C). As the cell growth increases, Y(NO) remains steady and defective in inducing thermal dissipation (Wimalasekera, 2019). The change in Fm and Fm' indicates photochemical quenching (NPQ). An increase from 0.149 (day 2) to 0.267 (day 8) was observed (Figure 3D). The PSI photosynthetic metrics included Y(I), ETR(I), Y(ND), and Y(NO). The photochemical quantum yield of PSI increased from 0.253 (day 0) to 0.578 (day 6) and decreased slightly from day 8 (Figure 3E). The electron transport rate ETR(I) of PSI showed a maximum rise from 2.2 to 61 on day 6 and further decreased to 31 by the end of the treatment period (Figure 3F). Y(ND) was inversely proportional to Y(I). By the end of the growth period, there was a study decrease in Y(ND) from day 0 (1.0) to day 8 (0.66) (Figure 3G). The redox potential of the intersystem electron transport chain controls the PSI acceptor side limitation, Y (NA). In the present study, NA decreased with increases in PAR, from 0.81 (day 0) to 0.4 (day 8) (Figure 3H). As a result, sufficient electron and proton transport, which is required for ATP and NADPH generation under limited conditions, restricted the photosynthetic assimilation, which further affected biomass and biomolecules (Bonnanfant et al., 2019).

3.3 HTL conversion and yields

3.3.1 Conversion profiles

The liquefaction of de-oiled biomass resulted in bio-crude i.e., aqueous and bio-oil fractions, along with the co-products. The yield and composition of the respective products were measured for the quantitative carbon flux in the HTL process with reference to temperature and micro-atmosphere. Figure 4A presents the substrate-to-product selectivity (%) on a weight basis towards bio-oil, aqueous fraction, and char at 150°C, 200°C, and 250°C for the N-HTL and H-HTL reactions. With increasing temperature, the yields of bio-crude fraction increased from 12.75 to 44.1% in N-HTL and from 47 to 52% in H-HTL. Comparatively higher bio-oil yields were obtained in H-HTL (150°C: 21%; 200°C: 28%; 250°C: 31%) compared to N-HTL conditions, while the aqueous fractions were higher in N-HTL. The inverse trends were observed for aqueous to bio-oil fractions with increasing temperature. Increasing temperature favors cleavage and recombination reactions between polar organic (water soluble) compounds, resulting in the elimination of polar functional groups, which leads to the formation of bio-crude (water-insoluble) molecules (Xu and Savage, 2017. The char fractions of N-HTL conditions decreased with increasing temperature (150°C: 74.5%, 200°C: 59%, 250°C: 54.9%. The H-HTL conditions showed relatively lower char fractions (150°C: 52.8%, 200°C: 48%; 250°C: 47%). Thus, the char formed in HTL reactions acted as co-products and can be used for trace metal removal, soil fertilizer, etc. (Katakojwala et al., 2020). Among all the experimental conditions, H-HTL at 250°C showed a cracking effect towards the formation of bio-crude with reduced char formation.

3.3.2 Bio-crude

3.3.2.1 Bio-oil

The major contents of bio-oil constitute combinations of hydrocarbons, alcohols, phenols, acids, esters, ketones, and other chemicals (Li et al., 2022). The bio-oil composition was analyzed by GC-MS and the relative components were calculated according to the peak areas (Table 2). The bio-oil

TABLE 3 Conversion effects of HTL process variation with respect to element and relative yields.

Composition		Elemental ratio (%)				HHV (MJ kg-1)	Bio-crude (%)	Energy recovery (%)	H/C atom ratio	O/C atom ratio	N/C atom ratio	
		Carbon	Hydrogen	Nitrogen	Sulphur							Oxygen
Initial DAB		**48.1**	**6.3**	**9.5**	**0.5**	**35.6**	**21.39**	-	-	**1.56**	**0.55**	**0.17**
150°C	N_2	53.5	8.5	7.8	0.69	29.45	26.50	25.5	31.58	1.89	0.41	0.12
	H_2	53.2	8.6	8.1	0.61	30.1	26.46	47.1	58.26	1.92	0.42	0.13
200°C	N_2	56.4	8.9	7.9	0.74	26.5	28.29	41	54.22	1.88	0.35	0.12
	H_2	57.6	8.6	6.8	0.4	27	28.14	52	68.4	1.77	0.35	0.1
250°C	N_2	58.5	8.6	7.3	0.5	25.1	28.68	44.1	59.13	1.75	0.32	0.1
	H_2	59.6	8.9	6.1	0.61	24.1	29.47	53	73.01	1.77	0.30	0.08

TABLE 4 HTL effects on elemental enrichment (%).

Composition		Element enrichment, %			
Initial DAB		Carbon	Hydrogen	Nitrogen	Oxygen
At 150°C	N_2	28.36	34.4	20.9	21.0
	H_2	52.09	64.3	40.1	39.8
At 200°C	N_2	48.0	57.9	34.1	30.5
	H_2	62.27	70.9	37.2	39.4
At 250°C	N_2	53.63	60.2	33.8	31.0
	H_2	65.67	74.8	33.4	35.8

composition predominantly showed aliphatic/aromatic hydrocarbons, carboxylic acids, furan, ketones, and indanone derivatives. N-HTL resulted in lower bio-oil fractions of 7.5% (150°C), 16% (200°C), and 21% (250°C). Although the inert gas (N_2) did not participate in the reactions, it increased the starting pressure to accelerate the HTL reaction rate by promoting DAB solubility and lowering diffusion resistance, thus decreasing the water viscosity. The total bio-oil fractions in the H-HTL conditions were relatively higher (21% (150°C), 28% (200°C), and 31% (250°C). The higher yields of bio-oil were noticed in H-HTL compared to those in N-HTL indicated that H_2 acted as a promoter for the hydrogenation reactions. Thus, the hydrodeoxygenation and hydro-denitrogenation reactions can be attributed to the HTL process. H_2 substitution at a higher temperature (250°C) decreased the levels of unsaturated hydrocarbon and aromatic fractions in the bio-oil by increasing the levels of saturated hydrocarbons. H_2 in the reactor increases the rate of hydrogenation of unsaturated compounds and the selectivity for aliphatic hydrocarbons by reducing aromatization and polymerization (Hao et al., 2021). Table 3 summarizes the elemental compositions (C, H, N, S, and O), HHV ratios, bio-crude percentages, energy recovery, atom ratios (H/C; O/C; N/C), and elemental enrichment (%) of bio-crude derived at various reaction temperatures and atmospheres. The carbon ratio of bio-oil increased with temperature and atmosphere and oxygen content was significantly reduced, likely due to the deoxygenation reactions under reduced conditions. The HHV of bio-oil increased with temperature and pressure, from 26.5 to 29.4 MJ/kg, which was relatively lower compared to those of fossil-based crude (HHV 42.7 MJ/kg) (Carpio et al., 2021). The energy recovery ranged between 31.58 and 73.01%, with the bio-crude percentages ranging from 25.5 to 53% and the elemental enrichment maximizing (C-65.67%; H-74.8%; N-33.4%; O-35.8%) in H-HTL at 250°C (Table 4). These findings were consistent with those of other studies reporting that increased temperatures under reactive atmospheres lead to deamination reactions during HTL (Maddi et al., 2016; Hao et al., 2021). The elemental ratios of H/C, O/C, and N/C are shown in Table 4. During deoxygenation, the oxygen from the biomass could be eliminated as H_2O molecules through dehydration or CO_2/CO via decarboxylation reactions, while nitrogen was eliminated as NH_4^+ via deamination (Carpio et al., 2021). At higher temperatures, denitrogenation predominantly occurred with an increased O/C ratio, possibly due to repolymerization, condensation, and cyclization reactions between intermediate compounds that formed at elevated temperatures (Carpio et al., 2021). Overall, deoxygenation tended to occur with increased reaction temperatures, while an H_2 reaction atmosphere promoted the repolymerization of fragments and resulted in bio-oil fractions. The resulting HTL bio-oil can be converted to aviation fuels (AF) by hydrotreatment/upgradation methods. Upgradation by hydrogenation for bio-oil under H_2 pressure results in saturated/hydrogenated bio-oils, while hydrocracking yields higher-chain alkanes to desired C_6-C_{15} hydrocarbons (Basar et al., 2021). These fuels can also be used to replace or blend bio-oil with AF/jet fuel fractions to reduce dependency on THE fossils (Basar et al., 2021).

3.3.2.2 Aqueous fraction (HTL-AF)

The aqueous soluble fraction of bio-crude accounted for 18–26% of the total feedstock. The compositional spectrum was analyzed by HR-MS. Figure 4B presents the detailed components and relative composition of HTL-AF. During HTL, N-HTL resulted in organic soluble fractions in the range of 1088 ppm (150°C), 1555 ppm (200°C), and 2204 ppm (250°C). H-HTL resulted in 2989 ppm (150°C), 4287 ppm (200°C), and 5190 ppm (250°C). Unlike the bio-oil fraction, aqueous-soluble hetero compounds were observed in the HTL-AF fractions due to their higher solubility. The N-hetero atom compounds in the ranges of 123 ppm (150°C), 256 ppm (200°C), and 329 ppm (250°C) were observed in the N-HTL conditions. In contrast, H-HTL resulted in 695 ppm (150°C), 1187 ppm (200°C), and 1408 ppm (250°C). The N-hetero atom compounds might be generated due to deamination and dehydrogenation mechanisms that degrade proteins and amino acid components (Maddi et al., 2016; Hau et al., 2021). The aqueous stream also contained organic oxygenates such as xylose, butyrolactone, angelica lactone, furfurals, cellobiose, levulinic acid, fructose, levoglucosenone, etc. and carboxylic acids like formic acid, acetic acid, glycol acid, etc. as larger fractions (Figure 4B). These were produced by the degradation of carbohydrate and hemicellulose fraction of biomass. Additionally, increased reduction reactions occurred in presence of the H_2 atmosphere, monosaccharides, and other derivatives, which might result in the formation of xylose, furfurals, levoglucosenone, and butyrolactone. The short-chain carboxylic acids were formed due to the isomerization and hydrolysis reactions of monomers (Reddy et al., 2016; Kopperi et al., 2022). Since HTL-AF contains considerable fractions of organic matter, it can be integrated with energy/nutrient recovery models for resource recovery.

3.3.3 Gaseous fraction

After the HTL reaction, gases from the reactor headspace were collected and analyzed. Gaseous products such as H_2, CH_4, CO_2, and others at lower fractions (possibly ammonia, C_2H_6, CO, and C_3H_8) were observed. The reactive temperature and atmosphere might have shown a greater influence on the gas profiles (Figure 4C). Under nitrogen atmospheric (N-HTL) conditions, N-HTL at 150°C produced 2.8% H_2, 1.52% CH_4, 3.1% CO_2, and 0.5% others. N-HTL at 200°C produced 4.2% H_2, 1.5% CH_4, 3.6% CO_2, and 1.7% others. N-HTL at 250°C yielded 4.8% H_2, 2.66% CH_4, 4.9% CO_2, and 2.5% others. The variations in HTL temperature implied that water acted as a catalyst that aided in the formation of CO_2, CH_4, and H_2 as the major gases, mainly by promoting decarbonization and water-gas shift reactions (Hao et al., 2021). The other gases from the reaction could be produced from the cracking effect of longer-chain alkanes (Hao et al., 2021). Similarly, H-HTL at 150°C produced 92.2% H_2, 1.52% CH_4, 3.1% CO_2, and 0.5% others. H-HTL at 200°C produced 88.6% H_2, 4.5% CH_4, 3.5% CO_2, and 3.2% others. H-HTL at 250°C yielded 86.3% H_2, 5.2% CH_4, 4.9% CO_2, and 3.4% others. In the present study, H_2 acted as a reducing atmosphere to initiate faster reactions and also reacted with DAB during deoxygenation. The significant reduction of pressure indicated higher H_2 consumption that aided in the removal of heteroatoms in different forms (H_2O, NH_3, and CH_4) (Barreiro et al., 2013; Antonetti et al., 2016). The H_2 consumption in H-HTL suggested that the reducing atmosphere facilitated the formation of higher hydrocarbon fractions compared to the N-HTL of bio-oil (Table 3).

3.3.4 Influences of temperature and pressure

The yield and selectivity of bio-crude fractions are predominantly influenced by reaction conditions such as reaction temperature, atmosphere, and solvent medium. The rates of re-polymerization, hydrolysis, fragmentation, and other reactions direct the final product formation (Reddy et al., 2016; Katakojwala et al., 2020). During N-HTL, the N_2 pressure reached maximums of 116 bar (150°C), 121 bar (200°C), and 126 bar (250°C) at the reaction end (60 min), with slight decreases (1–3 bar) upon cooling (90 min) (Figure 4D). Although N_2 (inert) gas is involved during the chain reaction, the increase in initial pressure accelerated the HTL rates. The H_2 (H-HTL) atmosphere resulted in maximum values of 127 bar (150°C), 129 bar (200°C), and 131 bar (250°C) by the end of 60 min, with drops of 4–9 bar upon cooling. H_2 gas acts as a reducing atmosphere, promoting the reaction rate and product selectivity towards hydrocarbons. The bio-crude yields were higher in H-HTL than in N-HTL, indicating the role of H_2 as a catalytic promoter of hydrogenation. Pressure is also a critical factor in lowering the reaction time and energy consumption for bio-crude formation. The pressurized inert gas and temperature reduce the viscosity and dielectric constant of water by lowering the diffusion resistance (aids in acid-catalyzed reactions by H^+ concentration) and increase DAB solubility (Duan, and Savage, 2011). Temperatures not only affect the deoxygenation rate of feedstock to bio-crude yield but also prevent byproduct formation by a cracking mechanism. The C and N recovery during HTL bio-crude yields was significantly influenced by the reaction temperature. High temperatures also increase the kinetic energy and collision frequency, which hasten the cracking process by converting longer-chain alkanes to short-chain alkanes and CH_4 (Reddy et al., 2016; Basar et al., 2021). As the temperature increases, the bio-crude yields increased in both N-HTL (12.75–44.1%) and H-HTL (47–52%) conditions. Further temperature increases might result in gas formation. Similarly, the trends of char formation showed inverse relationships to bio-crude yields in N-HTL (74.5–54.9%) and H-HTL (52.8- 47%). Water acts as a solvent and has advantages for easy bio-oil separation, promotes lipid hydrolysis, shifts the deoxygenation reaction pathway, and inhibits secondary reactions such as ketonization and esterification (Kopperi et al., 2022). The reaction temperature also affects bio-crude formation by varying the polarity of water. A change in temperature increases the ionic production of water (Kw = [H+] [OH]), which liberates more H+ and OH ions to drive the hydrothermal cleavage of DAB biomolecules to bio-crude (Reddy et al., 2016).

3.4 Dark fermentation of HTL-AF

The TOCs of the water-soluble aqueous fractions in both N-HTL and H-HTL were characterized and were tightly related to the HTL conditions. The TOC of N-HTL resulted in 4125 mg/L (N-150), 5510 mg/L (N-200), and 5637 mg/L (N-250), while the TOC of H-HTL resulted in 4637 mg/L (H-150), 5966 mg/L (H-200), and 6216 mg/L (H-250) (Figure 5A). In both conditions, H-HTL resulted in higher carbon flux due to the formation of more polar compounds as they dissolve efficiently in water, leading to the formation of HTL-AF, which showed a significant difference in the composition, as detailed in Section 3.3.2.2. Compared to the lower temperature (150°C), higher total nitrogen and aromatic compounds concentrations were observed at higher temperatures, which were attributed to increased degradation reactions and protein content in the feedstock. The presence of these chemicals could be challenging for the disposal of the water stream due to their toxicity (Si et al., 2019). Thus, nutrient recycling by DF might be a feasible route for detoxification as well as valorization of HTL-AF in the context of biorefinery.

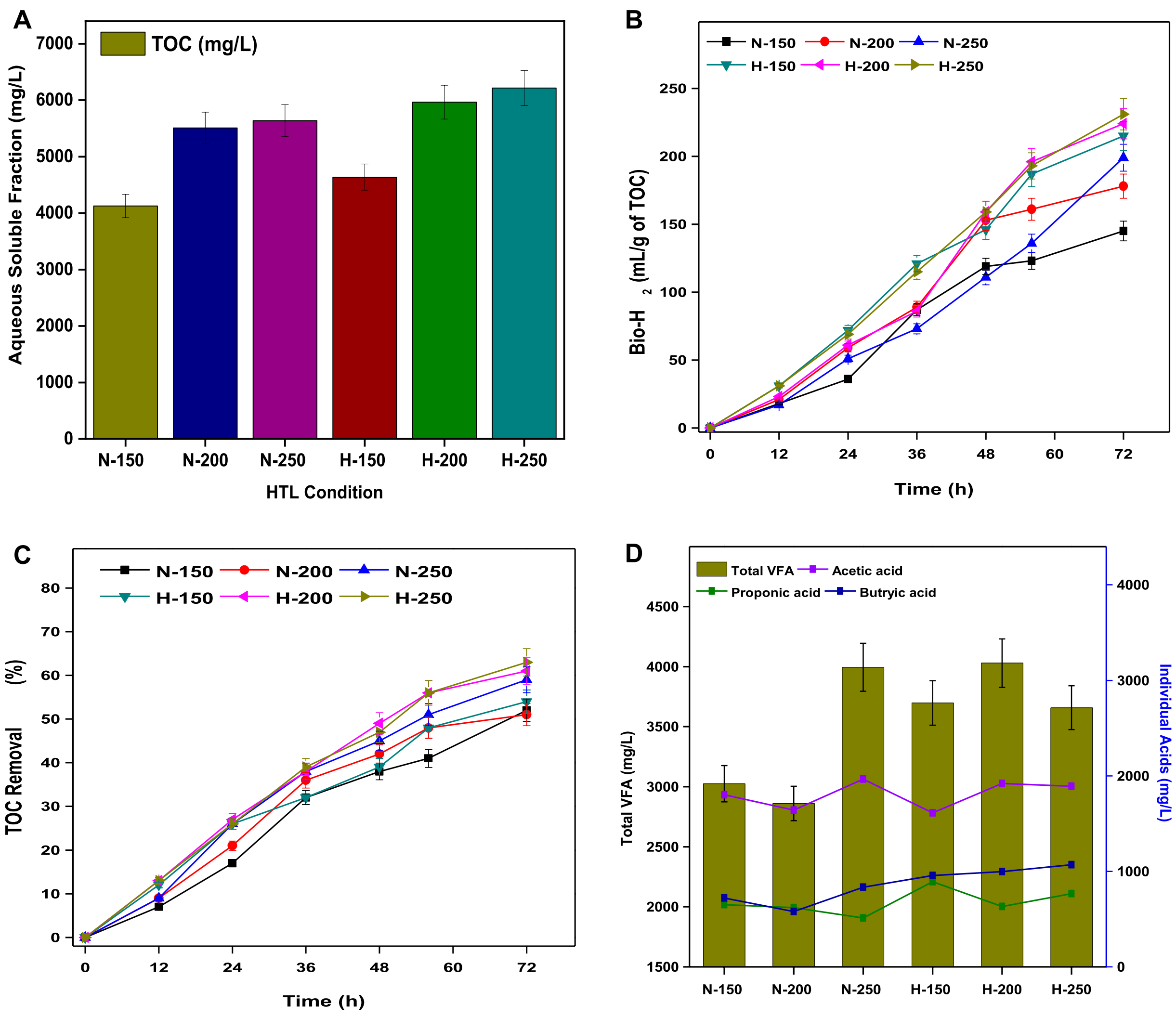


FIGURE 5
(A) Aqueous soluble fraction from the TOC analysis. **(B)** Total bio-H_2 production. **(C)** Total VFA and individual acid profiles. **(D)** Percentages of TOC removal.

3.4.1 Bio-H_2 and substrate removal

The enriched biocatalyst dominated the acidogenesis process by proceeding towards acetogenesis and methanogenesis; thus, DF of HTL-AF resulted in bio-H_2 and VFA production. Figure 5B shows the bio-H_2 production from HTL-AF of all HTL experimental conditions. The maximum bio-H_2 yield of TOC conversion (231 ml/g) was observed by the end of 72 h for H-HTL (250°C), with a composition of 55% ± 3 H_2 and 35% ± 5 CO_2. Similar performances were observed in all treatment conditions, ranging from 215–231 ml/g of TOC in H-HTL conditions and 178–215 ml/g of TOC in N-HTL conditions. In general, the acidogenesis of 1 mol of glucose produced 4 mol of H_2 by the acetic acid pathway and 2 mol of H_2 from the butyrate pathway (Eqs 9, 10).

$$C_6H_{12}O_6 + 4H_2O \rightarrow 2CH_3COO^- + 2HCO_3^- + 4H_2 + 4H^+ \Delta G^0 = -48kJmol^{-1} \tag{9}$$

$$C_6H_{12}O_6 + 4H_2O \rightarrow CH_3CH_2CH_2COO^- + 2HCO_3^- + 2H_2 + 3H^+ \Delta G^0 = -137kJmol^{-1} \tag{10}$$

Initially (until 12 h), due to hydrolysis, the bio-H_2 generation was limited, and then increased rapidly until 48 h before stabilizing by end of 72 h. This might be attributed due to a pH drop (4.5) caused by VFA accumulation, which caused *in-situ*

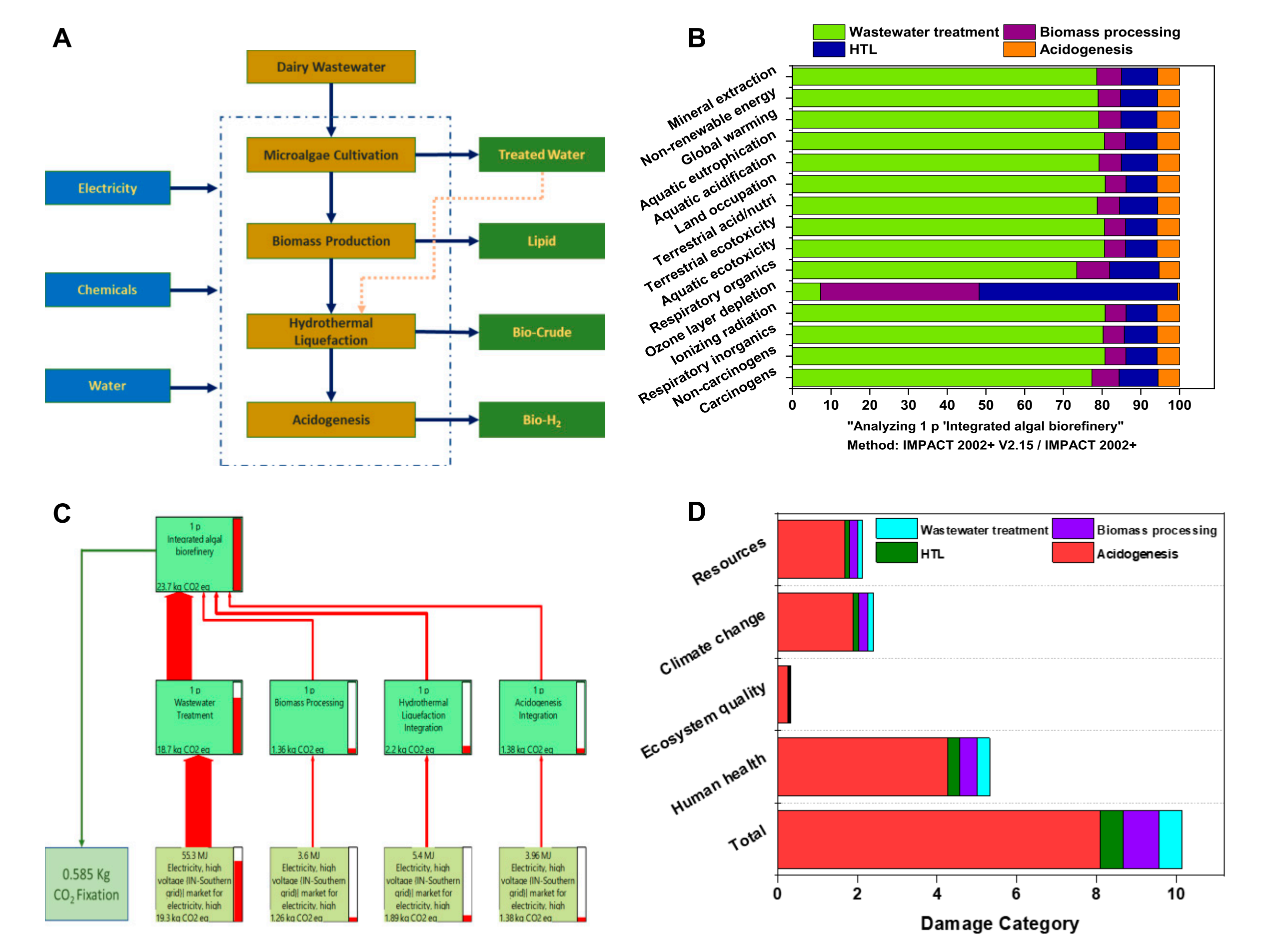


FIGURE 6
(A) System boundary of the integrated algal biorefinery considered in the LCA analysis. **(B)** Lifecycle analysis results of the biorefinery scenarios. **(C)** Sankey diagram representation of the global warming potential. **(D)** Endpoint/damage categories.

acid shock to the biocatalyst, resulting in decreased H_2 yields. The increased H_2 yields could be attributed to an acidophilic environment that aided the proton (H+) rich reactions, thus accelerating substrate conversion (Santhosh et al., 2021; Sarkar et al., 2021). The levels of aqueous soluble organic compounds decreased over time through catabolic reactions, resulting in a maximum TOC removal of 63% in H-HTL (250°C) and the overall substrate degradation trend demonstrated in all treatment conditions, ranging from 54–63% in H-HTL and 51–59% in N-HTL (Figure 5C). Although the reaction conditions and substrate concentrations were the same in all experiments, the difference in the HTL-AF product spectrum in each case might be influenced by substrate removal and fermentation products. The acidic pH condition favored acidogenesis and yielded higher VFA production. Analysis of total VFA and its relative composition (acetic acid (AA), butyric acid (BA), and propionic acid (PA)) produced in all experiments showed a maximum total VFA production of 4.03 g/L with a relative composition of 1.92 g/L AA, 0.63 g/L BA, and 0.99 g/L PA in H-HTL (250°C) by the end of 72 h. This and all other experimental VFA profiles are shown in Figure 5D. The total VFA and composition trends were satisfactorily correlated with substrate consumption and bio-H_2 yields.

3.5 Lifecycle assessment of the biorefinery processes

The quantified impact categories were derived from the inventory data (Supplementary Table S2). The LCA assessments of the feasibility, system engineering, and environmental impacts of microalgae on biofuels according to various thermochemical pathways showed that the standalone process was energy-intensive and the suggested need for process integration for sustainability (Bennion et al., 2015). The integration process in this study led to the production of lipids, bio-oil, and bio-H_2. The individual inputs of the processes showed their specific contributions with respect to each mid-point and end-point category. From all inputs, energy in the form of electricity showed its high impact on most of the mid-point categories. Among all unit operations, algal cultivation with the wastewater step showed its higher impact on mid-point categories and its significant share of global warming, land occupation, terrestrial/aquatic ecotoxicity, ionizing radiation, and non-renewable energy. However, during the algal cultivation process, the resulting biomass fixed approximately 0.58 kg of CO_2 eq by the photosynthetic process, indicating a reduced burden on the environment (Figure 6B). Other steps, such as biomass processing, HTL, and acidogenesis involving various chemicals (solvents), also exhibited lower impacts. The global warming potential (climate change) (IPCC GWP 100a LCIA method) was represented in the Sankey diagram, with the direction of the arrows with specific width proportional to the matter structure and distribution (energy/material) within the integrated system (Figure 6C; Supplementary Table S3). The integration process resulted in the production of 23.7 kg of CO_2 eq per 100 L, in which >90% (18.74 kg CO_2 eq) of carbon emissions were released through electricity, which was used during the algal cultivation step, followed by the HTL process (2.1 kg of CO_2 eq), and the acidogenesis (1.38 kg CO_2 eq) and de-oiling (1.3 kg CO_2 eq) steps. The electricity used was predominantly derived from fossil fuels (Coal), resulting in the highest CO_2 gas emissions. In the analysis of damage categories, algal cultivation operation showed more effects on human health, followed by climate change, resources, and ecosystem quality (Figure 6D). Furthermore, energy from renewable resources may aid in the overall sustainability, with low carbon emissions.

4 Conclusion

The results of the present study demonstrated the integrated biorefinery process for nutrient recovery from dairy wastewater using *Coelestrella* sp. and the production of an energy-dense biomass. The removal efficiencies of phosphate and nitrate were 70.39 and 80.1% respectively. The lipid analysis resulted in a higher SFA fraction (50.6%), mostly heptadecanoic acid (C17:0, 11.5%) and a MUFA fraction of 39.6%. The liquefaction of de-oiled biomass resulted in higher bio-oil yields in H-HTL (31%; 250°C) compared to those in N-HTL (21%; 250°C), suggesting the role of H_2 for hydrogenation. This study also explored the organic oxygenate/acid composition of the aqueous streams of N-HTL and H-HTL in detail. The gas profiles showed 5.2% CH_4 and 4.9% CO_2 in H-HTL at 250°C and a decline in pressure at the end of all H-HTL reactions, indicating H_2 consumption for the formation of higher hydrocarbons. However, further up-gradation to remove oxygen content is recommended to bio-crude to provide an aviation fuel with a higher HHV (42.7 MJ/kg). The HTL-AF valorization suggested that nutrient recycling and bio-H_2 production by DF could act as a wastewater detoxification process. The LCA of integrated biorefinery demonstrated the specific impact of electricity on the mid-point category. Overall, the results suggested the usefulness of a semi-synthesis approach by integrating biological and HTL conversion processes will accelerate the implementation of circular practices.

Data availability statement

The raw data supporting the conclusion of this article will be made available by the authors, without undue reservation.

Author contributions

HK: conceptualization, experimentation, investigation, writing—original draft. SM: conceptualization, methodology, writing—review and editing, supervision, funding acquisition. The authors have discussed the results and contributed to the final manuscript.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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Supplementary material

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fbioe.2022.964070/full#supplementary-material

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Current challenges and future prospect of biomass cooking and heating stoves in Asian Countries

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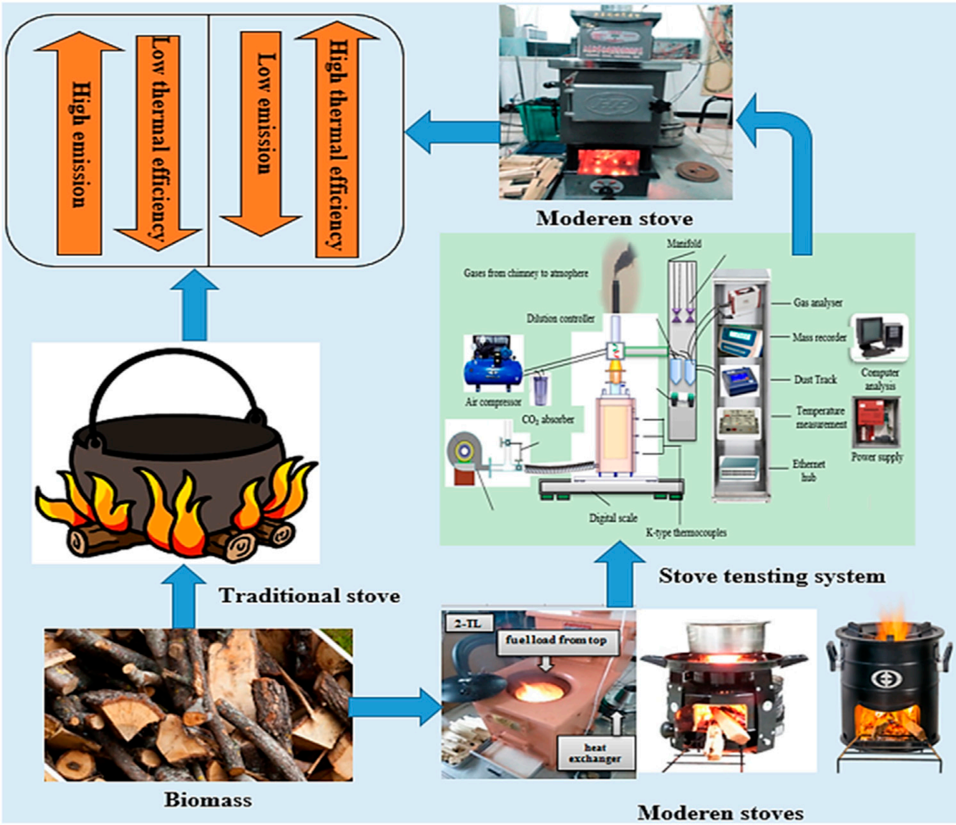
The utilization of biomass for cooking and heating is old, occurring from the early stages of human evolution because of its wide and easy availability. In Asia, a majority of the population is dependent on solid biomass for cooking and heating applications. Biomass cookstove produces emissions like carbon monoxide (CO), and particulate matter with aerodynamic diameter ≤2.5 μm ($PM_{2.5}$) which are dependent on the classifications and characteristics of fuel used in stoves. These emissions trigger many health risks because of the utilization of traditional cookstoves (TCS) which have less thermal efficiency. The literature contains a considerable amount of information on biomass cookstoves; however, it is dispersed particularly in Asian countries. In this principle, this paper gives an overview of available literature on biomass cookstoves for cooking and heating in Asian countries which are involving Bangladesh, China, India, Mongolia, Nepal, Pakistan, Sri Lanka, and Laos. This paper covers a detailed discussion on various aspects of biomass cookstoves: history, classification, fuel characteristics, health risks, design criteria, the scenario in selected Asian countries, thermal efficiency and emission comparison, and barriers to dissemination of improved biomass cookstoves (ICS). Learning from the review and comparison made conclude that the ICS has better thermal efficiency, and lesser emissions, as well as health risks but, have some potential barriers to dissemination.

KEYWORDS

biomass cookstoves, improved biomass cookstoves, health risks, thermal efficiency, emissions performance, asia

Abbreviations: CDM, Clean Development Mechanism; CNISP, Chinese National Improved Stoves Programme; CO, carbon monoxide (mg/MJ_{NET}).;CPURE, Clean Production and Utilization of Renewable Energy; GERES, Group for the Environment, Renewable Energy, and Solidarity; IAP, indoor air pollution; ICS, improved biomass cookstoves; KIDP, Kalam Integrated Development Project; LPG, liquid petroleum gas; NBCI, National Biomass Cookstove Initiative; NGOs, Non-Governmental Organizations; NPIC, National Programme on Improved Chulhas; PDR, People's Democratic Republic; $PM_{2.5,}$ particulate matter with aerodynamic diameter ≤2.5 μm (mg/MJ_{NET}); TCS, traditional cookstove; TSF, three stone fire.



Graphical Abstract

Background

In the era of computers and technological gadgets, approximately 2.6 billion people do not have clean cooking facilities, and if forecasts are correct this figure will remain roughly the same into 2030 (IEA, 2012). In Asia, about 1,460 million people rely on the traditional use of biomass for cooking with approximately 57% having access to clean cooking by 2018 (IEA, 2020). Figure 1 shows the percentage of the population with access to clean cooking throughout the world. The use of conventional biomass for cooking causes indoor air pollution (IAP) and human health issues, especially in poorly ventilated facilities (Das et al., 2017; Yip et al., 2017; Goldemberg et al., 2018). The IAP, caused by traditional solid fuel cooking, causes the premature deaths of over 2.6 million people each year in low- and middle-income countries (Haines et al., 2009; Arku et al., 2018). Traditional solid fuel cooking contributes significantly to global greenhouse gas and black carbon emissions, accounting for 1–3% of all human-generated global warming (Smith, 1994). The use of household solid biomass for cooking and heating accounts for around a quarter of all annual anthropogenic black carbon emissions worldwide (Bond et al., 2013). It is expected that 3 billion people in the world are directly dependent on the combustion of biomass that causes IAP in terms of smoke and other hazardous materials (Assad et al., 2015). These most common hazardous materials which contain smoke are CO (carbon monoxide), $PM_{2.5}$, (fine particular matter with aerodynamic diameter ≤2.5 μm), and CO_2 (carbon dioxide) which causes health problems.

As a solution to the aforementioned global problems, improved biomass cookstoves (ICS) are introduced worldwide to improve cooking efficiency. The motivation behind the development and design of the ICS is to acquire clean burning and reduce negative health effects, emissions, and the quantity of fuel needed. As a result, the expert panel on cookstove technologies set new benchmarks for the ICS at the "Bio-Mass Cookstoves Technical Meeting" in January 2011: "at least 90% emissions reductions and 50% fuel savings over baseline technology (three-stone fire)" (U.S. Department of Energy, 2011). More than 160 cookstove programs are currently active across the world (Ruiz-Mercado et al., 2011).

The major portion of the population in Asian countries is dependent on biomass for cooking and heating purposes. The TCS utilized by these countries has several limitations which are

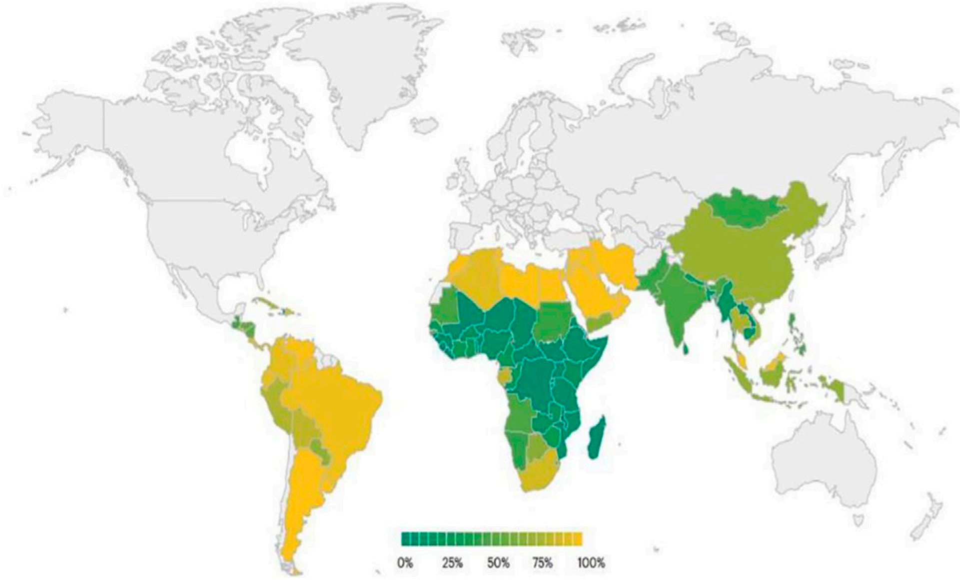


FIGURE 1
Percentage of population access to clean cooking throughout the world (IEA, 2020).

involving, including emissions of CO_2, $PM_{2.5}$, low thermal efficiency, and more fuel consumption. The IAP due to the emissions causes several health risks. The ICS thermal efficiency, emissions performance, and dissemination barriers for the Asian countries are available in the literature, however, these are dispersed. In this regard, this paper is an effort to overview the biomass stoves for cooking and heating scenario in various Asian countries including Bangladesh, China, India, Mongolia, Nepal, Pakistan, Sri Lanka, and Laos. In addition, the study included a comparison of thermal efficiency, CO and $PM_{2.5}$ emissions of the TCS and ICS, and barriers to dissemination of these ICS in Asian countries. After going through various research conducted on ICS in Asia, we found that the ICS has better thermal efficiency, and emissions performance, thereby fewer health risks. However, we found different barriers to the dissemination of the ICS among the Asian countries such as financial, infrastructure, awareness, market, stove size, and socioeconomic factors. Therefore, these barriers should be the focus of the research community.

Biomass cookstoves

The term "biomass cookstove" refers to a physical structure that incorporates air-fuel combustion for heat release and then transfers that heat to a cooking target. Besides cooking, stoves can be used for space/water heating, in-house lighting, fish/meat smoking, and grain/flour roasting, in addition to cooking. In many cultures, the same device is used for several purposes. Modern cookstoves offer characteristics such as high efficiency, low emissions, and greater user safety than traditional fire stoves. There are a variety of cookstove designs around the world, whether traditional or improved, based on a wide range of food patterns, socio-cultural factors, and fuel types accessible.

History and development

Cookstoves are as old as human history. They have evolved in numerous shapes and sizes, made up of varied materials, and adapted to different cultures and cuisines, with the advent of time. Table 1 shows the history and development of biomass cookstoves with objectives, benefits, and limitations.

Classifications and available technologies of biomass cookstoves

Biomass cookstoves can be classified in a variety of ways. Traditional and improved cookstoves are the two broad categories. The traditional cookstoves have been established for thousands of years in response to community culture and eating habits. These stoves are most affordable, and consumers are acquainted with how to use them, therefore they are broadly accepted in society. The Improved Cookstove is a cook stove that uses scientific concepts to aid better combustion and heat

TABLE 1 History and development of cookstoves with objectives, benefits, and limitations.

History of Cookstoves		Objectives	Benefits	Limitations	References
Time immemorial-1950	• "Archetypal" stove, which is today's "traditional stove" or "three stone fire (TSF)," has remained unchanged for over 12,000 years. • The TSF dominated for thousands of years, up to the 18th century in Europe and Asian countries	• Render food into a more digestible form	• Protection against large animals and insects. • Food preservation and providing heat during the cold seasons	• Dispersion of the flames and heat during windy conditions. • A lack of proper control over the fire, exposure to heat and smoke as well as fire hazards	(Bronowski, 1973; Regional Wood Energy Development, 1993; Westhoff and Germann, 1995)
The Recent Past (1950–2000)	• The initial phase of the ICS in India began in the early 1950s with technological initiatives. • The oil crisis of the 1970s induced the second phase of the ICS development. • The Indian National Programme on Improved Chulhas (NPIC) began as a demonstration initiative in 1983 and was expanded to a full-fledged program in 1985. • The "World's biggest publicly financed project to improve stoves," the Chinese National Improved Stoves Programme (CNISP) between 1982 and 1992. • The 3rd phase of the ICS began at the start of the 1990s	• To improve design of biomass fired cookstoves in many Indian kitchens. • To achieve fuel reserves, increasing efficiencies, and reducing smoke exposure. • The development of more than 60 stove designs and distribution of over 35 million stoves. • To provide more efficient biomass burners and, eventually, improved coal stoves for cooking and heating in rural communities. • To contemplate the customers regarded factors like cooking comfort, smoke-free kitchens, stove safety, and fuel savings	Q	• In the early 1980s, scientific research and development of the ICS was zero. • Socioeconomic as well as cultural aspects of the cooking were missing because of lack of long-term development aims, and appropriate local manpower development. • The NPIC has not been practical or successful in pushing a fundamental switch to improved stoves in India over the long term. • Between the 1980s and the early 1990s, stove programs were not much successful. • Apart from Karnataka, all states have been unable to launch programs due to a lack of central government support and money	(Samuel, 1987; Smith, 1989; Smith et al., 1993; Hanbar and Karve, 2002; Kishore and Ramana, 2002; Smith and Francisco, 2005)
The New Millennium (2000-to date)	•; In 2002, the "US Environmental Protection Agency" launched the "Partnership for Clean Indoor Air" at the "World Summit on Sustainable Development" in Johannesburg •; In February 2008, the "Clean Development Mechanism" (CDM) revised the programmatic guidelines to include cookstove programs in their agenda under "smaller decentralized projects.". •; In December 2009, the Government of India launched the "National Biomass Cookstove Initiative" (NBCI) for the ICS. •; In September 2010, the US Department of State, and the Environmental Protection Agency assisted in the launch of "The Global Alliance for Clean Cookstoves" in New York. •; In May 2013, Bangladesh's Infrastructure Development Company Limited in partnership with the world bank was began. •; Between 2015 and 2020, Efficient, Clean Cooking and Heating program contribute to the clean cooking agenda	• To address the environmental health risk posed by people using traditional biomass fuels indoors. • To provide clean cooking and fuel savings. •"To achieve the quality of energy services from cookstoves comparable to that from other clean energy sources such as LPG". • To create a worldwide market for energy and carbon-efficient cookstoves in order to address a variety of concerns related to their use. • To distribute ICS. • To distribute ICS particularly in the developing countries	• Reduction in health hazards and pollutants emissions • Significant reduction in fuel usage by the cookstoves. • About 14 cookstove projects have been registered with CDM as "Programs of Activities" as of May 2013. • 100 million families adopt clean and efficient stoves and fuels by 2020. • One million ICS was distributed throughout the country. • 20% reduction in $PM_{2.5}$. • 90% reduction in CO. • About 44 million people gain access to the ICS. • 90% reduction in $PM_{2.5}$	• N/A. • Despite all attempts to enhance access to cooking energy more than half of the world's population continues to cook with solid fuels and traditional biomass. • Lack of information on real field performance, usage rates, fuel sensitivity, fuel processing requirements, or lifetimes. • Limited access to modern fuels for cooking in developing countries. • Limited access to ICS in rural areas. • Less adoption of new technology	Bailis et al., 2009; Blunck et al., 2011; Greenglass and Smith, 2007; Kishore and Ramana, 2002; Legros et al., 2009; Smith and Francisco, 2005; Venkataraman et al., 2010; World Bank, 2020, 2018

transfer, as well as modern construction to improve emissions and efficiency performance (Kshirsagar and Kalamkar, 2014). In addition, classifications of biomass cookstoves depend on the use of technology, combustion type, construction material, chimney, and portability as represented in Table 2.

The different types of stoves available on the market can be classified differently. The technology of the stove can be classified by the material of construction and whether it is a fixed or portable stove. Additionally, the amount of fuel burned can be determined by how many chimneys the stove has and if it has grates inside the firebox to increase combustion. There are a variety of stoves in use, depending on the location and the type of fuel available. Some stoves are specially designed for burning one fuel; others burn a variety of fuels. A traditional biomass cookstove consists of an air intake and transport system, a bed of fuel, a gas phase combustion zone, and a cooking pot. There are three primary types of traditional household biomass cookstoves based on the treatment of the combustion chamber shown in Figure 2.

Stove testing standards and protocol

A proper design of stoves enhances the efficiency of combustion ultimately helping to reduce deforestation. The testing of stoves in a standard laboratory leads to improved future designs and also to the adoption of standard terminology. The Global Alliance for Clean Cookstoves (GACC) and International Standards Organization (ISO) have identified a clear need for a common standard for Improved Cookstoves and are working in an attempt to standardize test procedures for all cookstoves. Major stove testing protocol categories include 1) Water Boiling Test (WBT), 2) Heterogeneous Testing Protocol (HTP), which are lab-based tests. The procedure is repeated for any pot/fuel/stove combination tested. The Controlled Cooking Test (CCT) Kitchen Performance Test (KPT) and Uncontrolled Field Test (UFT) are field based tests. The WBT, CCT, and KPT are the most accepted testing protocols for cookstoves.

The WBT is a lab-based test using the laboratory emissions monitoring system (LEMS). The test measures and analyses thermal efficiency, emissions (CO_2, CO, and PM), fuel to boil 5 L of water, energy to boil 5 L of water, and time to boil 5 L of water. Thermal efficiency and emissions are measured in Tiers with Tier 4 being the highest performance and Tier 0 being the lowest. The minimum accepted rating by the Global Alliance for Clean Cookstoves is Tier 2 for these 2 parameters. The CCT is designed to assess the performance of the improved stove relative to the common or traditional stoves that the improved model is meant to replace. Stoves are compared on how they perform a standard cooking task that is closer to the actual cooking that local people do every day. However, the tests are designed in a way that minimizes the influence of other factors and allows for the test conditions to be reproduced.

The KPT is the principal field–based procedure to demonstrate the effect of stove interventions on household fuel consumption. It includes 1) an assessment of the qualitative aspects of stove performance through household surveys and 2) comparison of the impact of improved stove(s) on fuel consumption in the kitchens of real households. An important parameter assessed in KPT is the safety of the stove. The following are evaluated: sharp edges/points, cookstove and pot tipping, containment of fuel, obstruction near cooking surface, surface temperature, heat transfer to surroundings, cookstove handle temperature, chimney shielding, flames surrounding the pot, and flames exiting the fuel chamber.

Characteristics of fuel used in biomass cookstove

The majority of solid biomass is woody biomass (some of which is turned into charcoal) obtained directly from forests and it is the most commonly used cooking fuel in developing countries. Solid biomass fuels, which go beyond firewood and charcoal, can be made from agricultural waste and forest wastes, and are becoming significantly more popular. For example, agriculture produces an estimated 140 billion tonnes of biomass residues per year, which is comparable to 50 billion tonnes of oil (UNEP, 2009). Cookstoves can burn a variety of solid biomass fuels like crop waste, dung, wood, charcoal, briquettes, pellets, coal, and woodchips (Sweeney, 2017). Figure 3 shows households in millions (m) or billions 2) relying on solid fuel use for cooking and heating throughout the world. The most common methods for obtaining energy from solid biomass are gasification, direct burning, pyrolysis, liquefaction, anaerobic absorption, alcoholic fermentation, and transesterification (Ahmad et al., 2019). Between the middle of the 1980s and the early 1990s, China designed several coal- and briquette-burning stoves (Gujral, 1992). Although some cookstove manufacturers claim that their stoves can burn a variety of fuels, however mostly cookstoves are built to burn only one type of fuel. Densified biomass pellets as a source of energy have a great influence on low-income populations due to their ease of accessibility, low price, and sustainability. Furthermore, biomass briquettes as a source of energy are carbon neutral and have no impact on the environment (Abbas et al., 2022). In terms of innovation, aside from the energy savings over wood, charcoal may have minimal respiratory health risks to consumers compared to a variety of other traditional fuels (Santín et al., 2015; Sundberg et al., 2020).

Coal is also an important source of energy for domestic cooking and heating in Asian countries. Coal is a type of carbon that contains a solid, black substance (Ahmad et al., 2022), that is found underground and is one of the most popular fossil fuels (Rahimi et al., 2020). Agricultural residues are non-edible components of plants that are left in rural areas, such as

TABLE 2 Classification of stoves with their advantages and disadvantages.

Classification of Stoves		Popular Types of Stoves	Advantages	Disadvantages	Pictorial view	References
Classification based on the use of technology	Three stone fire	Not available	•Simple design, •No special material, tools, and skills are required for construction, •No cost	•High fuel consumption, •High CO and $PM_{2.5}$ emissions, •Low thermal efficiency of about 20%	 Chagunda et al., 2017	Chagunda et al., 2017; Jetter and Kariher, 2009
	Built-in stove	•Chullah, •Angithi, •Haroo	•Simple and easy design, •Less radiation loss due to enclosed fire, •Less fuel consumption	•Incomplete combustion, •High CO and $PM_{2.5}$ emissions, •Low thermal efficiency of about 29%	 Bruce et al., 2013	Bruce et al., 2013; MacCarty et al., 2010; Mukhopadhyay et al., 2012
Classification based on combustion type	Direct combustion or Rocket stove	•StoveTec, •Side Feed Fan Stove, •Gusto Wood Flame Stove	•Better thermal efficiency, •Less CO emissions of about 86% as compared to traditional stoves, •Less fuel consumption	•Wood must be extremely dry and thin, •Requires much maintenance	 Teshome et al., 2020	MacCarty et al., 2008; MacCarty 2010; Oliver, 2014; Teshome et al., 2020
	Gasifier/forced draft stove	•Turbo Stove, •Phillips Stove, •Oorja Stove, •Champion Stove, •Vesto Stove, •Karve Stove, •Sampada	•Quickly heated, •Lighter weight, •High thermal efficiency of about 84% as compared to traditional stoves, •Low CO emissions	•Economically unaffordable, •Slow to ignite, •Fuel specific	 Coulson and Ferrari, 2019	Coulson and Ferrari, 2019; Jetter et al., 2012; Reed et al., 2008
Classification based on construction materials	Mud stove	•Anagi, •Improved clay stove, •Rocket mud stove,	•Inexpensive, •Less fuel consumption	•Prone to insects and weather damage,		Barnes et al., 2012; Kishore and Ramana, 2002; Ochieng et al., 2013; Rahman, 2015

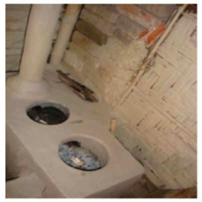
(Continued on following page)

TABLE 2 (*Continued*) Classification of stoves with their advantages and disadvantages.

Classification of Stoves	Popular Types of Stoves	Advantages	Disadvantages	Pictorial view	References
	•Mud stove by Escorts Foundation, •Parvati		•Need high maintenance, •Less life span of about 2 years only	 Ochieng et al., 2013	
Ceramic stove	•Mogogo. •Maendaleo. •Lakech charcoal stove. •Gyapa. •New Lao stove. •Uhai. •Ceramic Jiko	•Burn at high temperature. •Better durability. •Better insulation.	•Costly and more difficult to construct than a mud stove. •Need high maintenance. •Limited flexibility for different pot sizes	 Chan et al., 2015	Beyene and Koch, 2013; Chan et al., 2015; Clough, 2012
Metallic stove	•Bukhari. •Vesto. •Philips Natural Draft Stove HD4008. •Vikram. •Harsha. •Magh	•Quick heating. •Lighter weight. •Portable. •Needs little maintenance	•Prone to corrosion. •Risk of burns. •High cost	 Tryner et al., 2014	Jetter and Kariher, 2009; Lambe, and Atteridge, 2012; Tryner et al., 2014
Cement stove	•Laxmi. •Astra. •Priya. •Mirt. •Roi-et	•Easy installation. •Simple design. •Low Cost	•High fuel consumption. •High CO and $PM_{2.5}$ emissions. •Low thermal efficiency of about 11%	 Bhattacharya et al., 2002	Beyene and Koch, 2013; Bhattacharya et al., 2002
Hybrid stove	•Philips Power Stove HD4012. •Oorja. •Side Feed Fan Stove	•Durable. •Provide cleaner burn. •Less smoke emission	•High cost. •Prone to corrosion	 (Mukunda et al., 2010)	(Jetter and Kariher, 2009; MacCarty N, 2010; Mukunda et al., 2010)

(Continued on following page)

TABLE 2 (*Continued*) Classification of stoves with their advantages and disadvantages.

Classification of Stoves		Popular Types of Stoves	Advantages	Disadvantages	Pictorial view	References
Classification based on chimney	Chimney stove	•Astra. •Uganda 2-pot. •Patsari. •Justa. •Ecostove. •Onil	•Better combustion. •Reduced IAP. •Greater emissions from the kitchen of about 99%	•High cost. •Blockage of chimney. •High fuel consumption	 Jetter and Kariher, 2009	Jetter and Kariher, 2009; Shastri et al., 2002
Classification based on portability	Portable stove	•Uthaao challah. •Gasifier stove. •Rocket stove	•Quickly heated. •Lighter weight	•Not efficient in harsh weather. •Could not use in fire ban areas. •High emissions	 Urmee and Gyamfi, 2014	Mukhopadhyay et al., 2012; Urmee and Gyamfi, 2014
	Fixed stove	•Abhinav. •Akash. •Alok. •Uganda 2-pot. •Patsari. •Grihlaxmi. •Onil	•Reduce IAP about 67%. •Less fuel consumption. •Better combustion	•Low thermal efficiency of about 20%. •Need high maintenance. •Take more time to cook	 Urmee and Gyamfi, 2014	Jetter and Kariher, 2009; Regional Wood Energy Development, 1993; Urmee and Gyamfi, 2014

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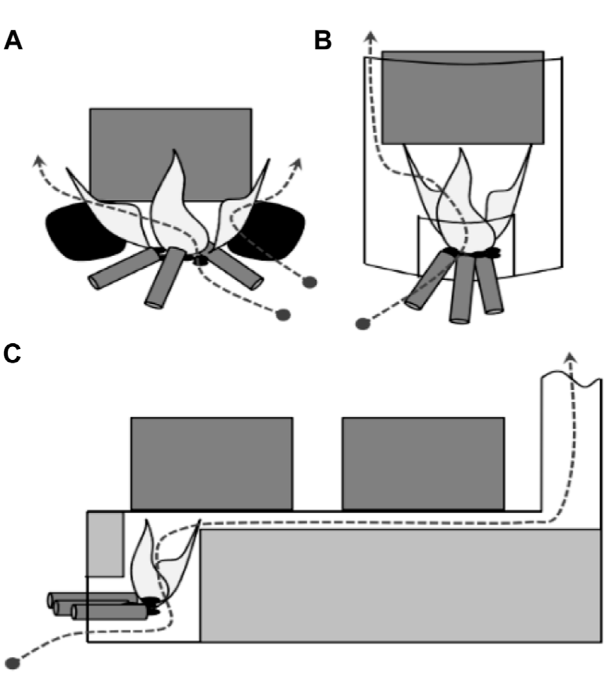

FIGURE 2
Types of cookstoves: **(A)** Open cooking fire, **(B)** Shielded cooking fire, **(C)** Enclosed fire with chimney (MacCarty et al., 2010).

leaves, stalks, straws, husks, shells, peels, and so on. Wood fuels and agricultural residues differ in that they have higher ash, and volatile matter content, low density, and lower energy content. Densifying the crop residues enhances their properties for cooking. Briquettes, also known as cakes, rods, or pellets, are biomass materials made (or densified/extruded) in a variety of sizes and produced using crop wastes, recycled materials, or other materials such as sawdust. In developing countries, pellets or briquettes/cakes can usually be used with a variety of improving biomass stoves (Ahmad et al., 2021a). The types and characteristics of solid fuel for cooking and heating are represented in Figure 4. In rural areas of developing countries, the technique of fuel stacking is very common. Fuel stacking occurs when a home uses multiple fuel types regularly. The fuel stacking depends on the meal to be cooked, the availability of various kinds of fuels, and the family's present financial situation (Johnson and Bryden, 2012).

Health risks of biomass cookstoves emissions

Approximately three billion people worldwide are exposed to indoor air pollution (IAP) because of solid fuel (wood, charcoal, coal, dung, and crop residues) cookstove

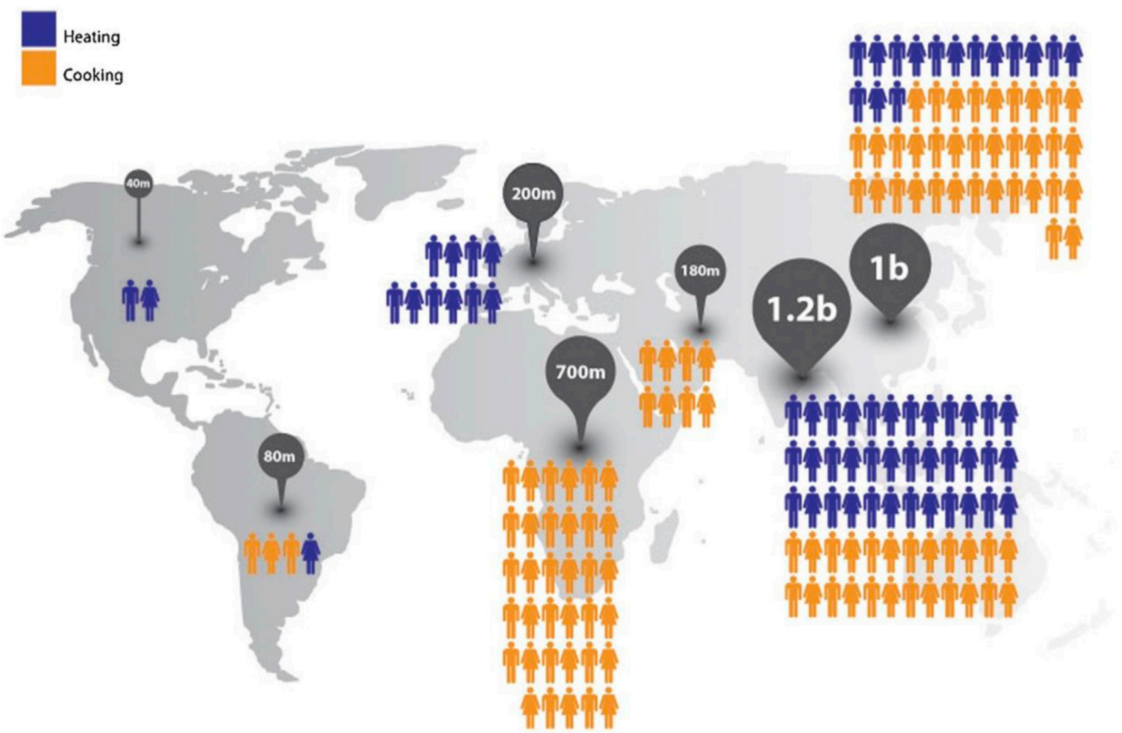

FIGURE 3
Million (m), billion (b) of households rely on solid fuels for cooking and heating throughout the world (Carvalho et al., 2016).

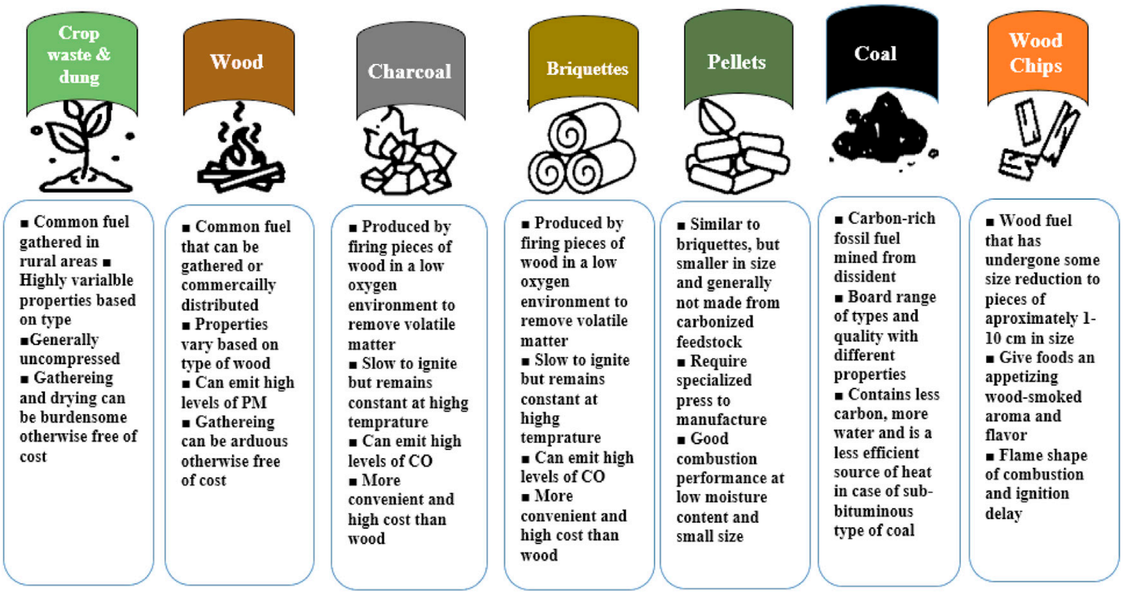

FIGURE 4
Types and characteristics of solid fuel for cooking and heating, data are obtained from (Sweeney, 2017).

emissions (Bonjour et al., 2013). The IAP is generated by inefficient solid fuel combustion, which has several immediate negative effects on human health, particularly among small children and their mothers. According to the 2013 Global Burden of Disease Study (GBD), the IAP accounts for between 3 and 5% of the GBD in terms of disability-adjusted life years, with roughly one-third of those affected being children under the age of five and the rest being adults (Steenland et al., 2018). Carbon monoxide (CO), and $PM_{2.5}$ (fine particular matter with aerodynamic diameter ≤2.5 μm) are major emissions associated with the IAP and have significant health risks. Respiratory (cough, and dyspnea), and childhood pneumonia are acute health effects while longer-term exposure has been linked to an increased prevalence of chronic diseases such as blood pressure or hypertension, low birth weight, cardiovascular diseases, lung cancer, mutagenicity, and other kinds of neoplasia. Figure 5 shows possible health risks of solid fuel cookstoves emissions. The ICS can be served as an intervention to lessen the health risks by lowering emissions from cookstoves. A recent study has reported the ICS as an intervention to minimize health risks (Pratiti et al., 2020). The authors concluded that the ICS is effective in reducing the effect of air pollution on blood pressure in women over the age of 40 and women who use ICS have a higher health-related quality of life. The use of ICS to tackle childhood pneumonia, birthweight, and cardiovascular diseases is not beneficial, thereby still needs to improve.

Design criteria used for biomass cookstoves

Numerous designs of biomass cookstoves have been developed which can be classified according to the materials used in their construction, the number of pots used, the types of fuel used, and so on (Mehetre et al., 2017). However, there are three major aspects while designing of cookstoves which are involving social, technical, and economical aspects. Social aspects are based on current cultural and local demands and limits and are a prerequisite for the society's long-term adoption of a cookstove. The present research and development operations in cookstove design are centered on technical aspects such as high efficiency, low emissions, material durability, and user safety (Kshirsagar and Kalamkar, 2014). Finally, the economic factor dictates the investment's return period, and is thus critical for effective cookstove adoption. Most of the major and sub-criteria listed in Figure 5 are interdependent, despite being classed in distinct categories. For example, technological and economic issues, are inextricably linked, as the cost effectiveness of a stove is usually determined by its technical capabilities.

The ICS reduces the load of fuel collection on women as well as children and saves time due to less firewood consumption. The biomass cooking and heating stoves should be manufactured in such an approach that is appropriate to end-users. While designing the ICS, some general steps should be considered. Firstly, the ICS design must be low-cost and energy efficient as

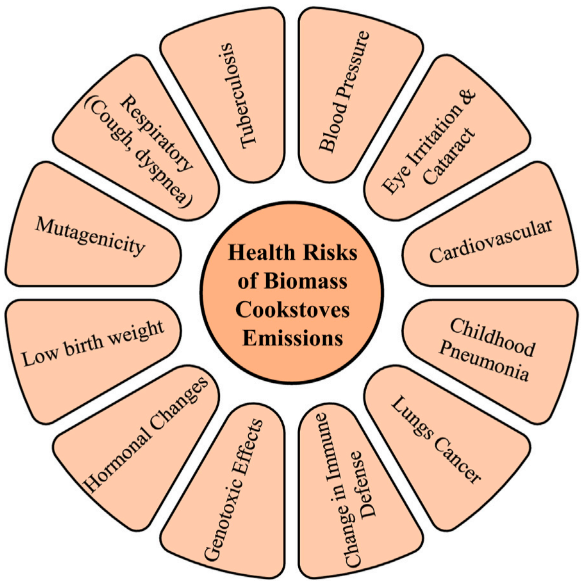

FIGURE5
Possible health risks of solid fuel cookstoves emissions.

compared to open fire. Second, the ICS design must have the potential to combat heavy use for at least 1 year. Thirdly, the ICS design must be able to be constructed using locally available resources and apparatus. In addition, the scientific understanding, engineering principles, and concepts including are significant for cookstove designing. The steps toward products for household use indicate that one who is going to design the stove should have a better scientific understanding and knowledge about engineering principles as shown in Figure 6.

Safety protocol and modern tool usage

A safety evaluation should be part of the design process for stoves. Humanitarian and private sector organizations have made a commitment to increase the adoption of improved cookstoves (ICS) in low- and middle-income countries in order to mitigate pollution, deforestation, and injuries caused by their use. A timeline of the evolution of laboratory-based protocols is shown in Figure 7. (Kshirsagar and Kalamkar, 2014). provided detailed information regarding testing protocol and modern technology usage in his study.

As part of the International Workshop Agreement (IWA), cookstoves are rated against a series of performance indicators, including Fuel Use (Efficiency), Emissions (Carbon Monoxide and Particulate Matter 2.5), Indoor Emissions (Carbon Monoxide and Particulate Matter 2.5), and Safety. Rather than select a single laboratory protocol to determine cookstove performance, this International Workshop Agreement will enable stove testers to utilize laboratory protocols most appropriate for the stove and performance indicator being tested. The following minimum equipment or methodology is required for certified testing of emissions, performance, and indoor emissions:

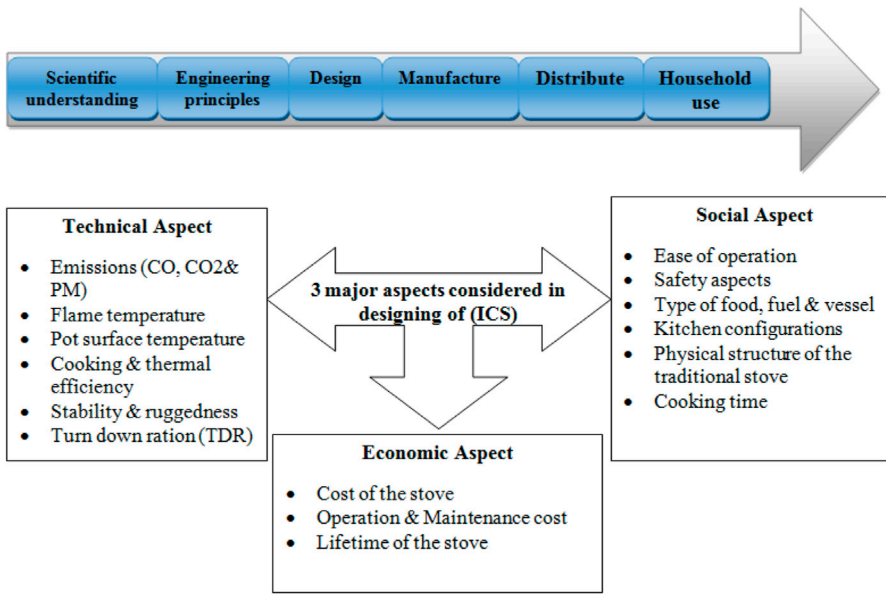

FIGURE 6
Important aspects that should be considered for cookstove design.

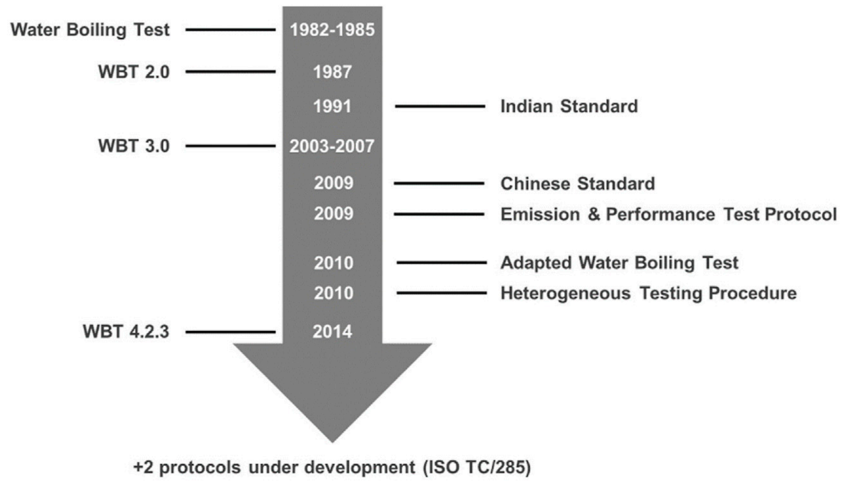

FIGURE 7
Summary of protocols evolution over time (Lombardi et al., 2017).

1) For carbon monoxide emissions or room measurement: non-dispersive infrared (with calibration consistent with U.S. EPA 40 CFR Part 60,) or electrochemical cell (with pre/post calibration method).

2) For particulate matter emission or indoor air quality measurement: 1) real-time measurement of a particulate matter proxy via light scattering, and 2) $PM_{2.5}$ gravimetric measurement such as U.S. EPA 40 CFR Part 60, Appendix A, Method 5.

3) For emissions exhaust gas flow: constant volume pump or flow grid both with real-time temperature and pressure correction consistent with U.S. EPA 40 CFR Part 60, Appendix A, Method 1 or 2d, or equivalent.

4) For temperature measurement: Type K thermocouple or equivalent.

5) Computer data logging of all measurements with a minimum time resolution of one measurement per 10 seconds.

6) For measuring fuel and water masses, a calibrated digital scale with 1-g resolution or better.

Computational fluid dynamics and modeling of household biomass cookstoves

The use of computational fluid dynamics (CFD) and modeling in conceptual design can improve the speed, accuracy, and efficiency of cookstoves. Regarding stove design, it provides details of assumptions, theory, results, and validation. CFD provides an accurate means of analyzing the stove's thermal and emission characteristics. Once it has been experimentally validated, CFD can be used as a standalone tool, in addition to preliminary experimentation (Pande et al., 2020). A CFD-assisted optimization biomass cookstove was developed and tested, incorporating geometric design modifications to achieve uniform air-fuel distribution. As shown in Figure 8, in a recent study, optimal power output and temperatures were obtained when the grate was placed at a height of 25 mm, and the 15-hole plate was located at a height of 105 mm from the bottom of the cookstove.

The three main zones of the stove system, namely the fuel bed, the flame zone, and the heat transfer zone, play a crucial role in stove design. Correlations between heat transfer and fluid flow can be compiled, as can various methods for radiation heat transfer and combustion heat release. Several recent models include steady-state simplified analytic models of packed bed combustion, generalized correlations for convection and radiation, and Computational Fluid Dynamics (CFD) based heat transfer models. Additionally, there are more than a few factors to take into account in stove modeling, including transient processes; models for combustion of various shapes, sizes, and arrangements of fuel; and pollutant formation. A schematic of a small biomass cookstove of the type that is used in virtually all numerical models of cookstoves is shown in Figure 9.

The purpose of cooking stove modeling is to improve the efficiency of heat transfer by exploring the relationship between the combustion rate, excess air, geometry, and heat transfer. All three major zones of the cookstove system have been described and coupled with zonal models: the reacting fuel bed zone, the gas phase combustion zone, and the heat transfer zone around the cooking pot. Table 3 provides a summary of traditional and improved cookstove modeling efforts.

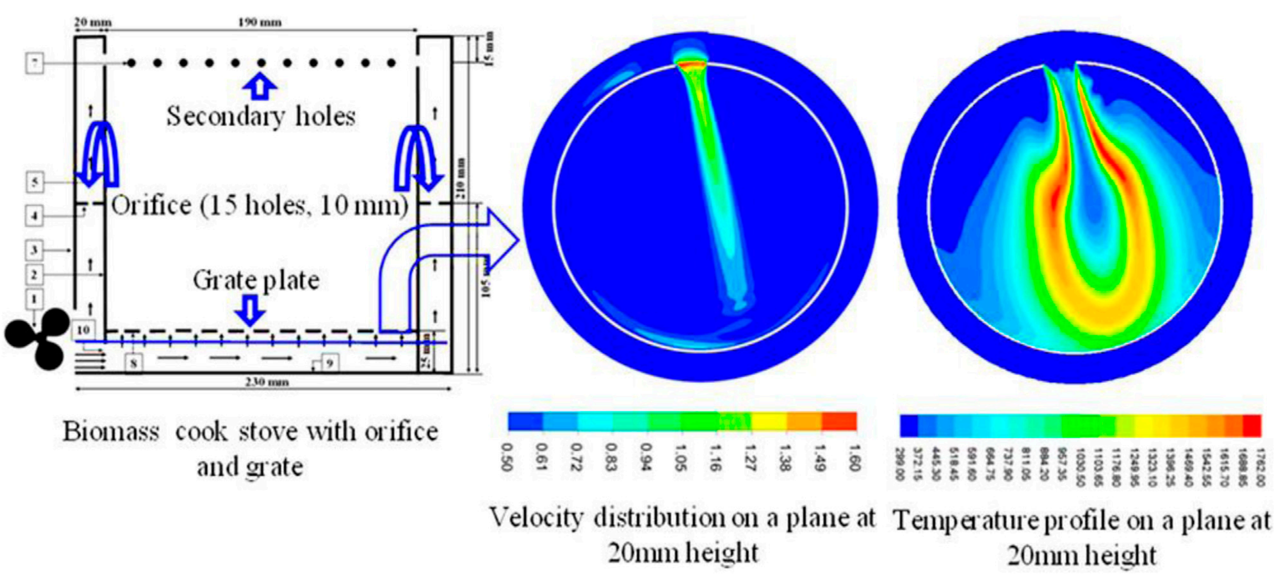

FIGURE 8
A CFD assisted optimized biomass cookstove designed with geometric design modification (Husain et al., 2019).

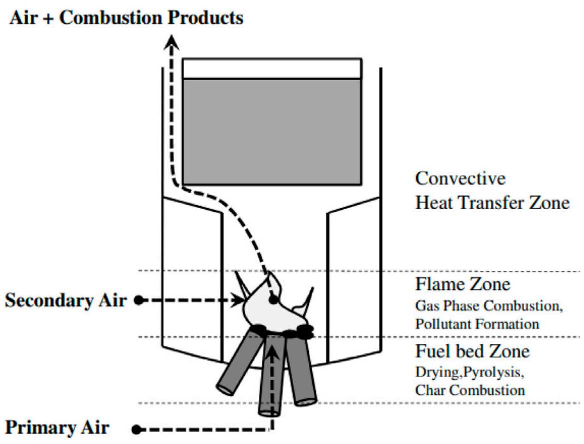

FIGURE 9
Processes within a cookstove (MacCarty et al., 2010).

Application of computational fluid dynamics for combustion modeling of biomass cook stoves

The thermochemical conversion of biomass has attracted a lot of attention over the past 2 decades. Developing reliable designs and scaling up procedures has been the objective. A balanced approach combining experiments and mathematical modeling was effective in achieving the objectives. In addition, there have been significant improvements in the development of efficient and reliable numerical models for simulating hydrodynamics, mixing, combustion, and related phenomena over the past decade (Ngo and Lim, 2020). This has allowed for the detailed analysis of thermochemical reactors such as combustors, pyrolyzers, incinerators, gasifiers, etc. In order to analyze and optimize the above-mentioned thermochemical reactors, CFD simulations have been conducted continuously (Sedighi and Salarian, 2017).

A computational model for the conceptual design of biomass cookstoves would enable a more accurate, faster, and more adaptive understanding of heat transfer and flow within the stove (Commeh et al., 2022). Experimental data sets with thermal performance characteristics in terms of design characteristics are required for model validation. Numerical models of stoves can be divided into two types. Zone models combine processes into zones and calculate efficiency, excess airflow, and average temperatures throughout a system, and may also indicate emissions. Within the prescribed design space, zonal models are fast and flexible, with various measurements available for validation. For the development of a zonal model, design variables include 1) geometry, 2) materials composing the flow path, as well as 3) operational variables such as fuel supply and the power of the flame. Thermal efficiency can be determined by dividing the energy transfer into the pot measured by water temperature rise and evaporation by the energy released by the fuel measured by lower heating value and mass of fuel used during the test. Based on this, the following data are needed for input into the model: 1) Operational variables, including experimental firepower, fuel moisture content, and lower heating value, 2) Geometrical variables providing a full description of the flow path, stove body, and cooking pot

TABLE 3 Summary of traditional and improved cookstove modeling efforts.

Stove type	Model characteristics	Validation	References
Flat bottom institutional cookstove	Description: analyze the performance of a Flat bottom Institutional Cookstove, water boiling test experiment used to test the stove power and efficiency followed with CFD using ANSYS Fluent simulations	Quantitative and qualitative experimental	Commeh et al. (2022)
	Statistical model: model is used to analyze the power, efficiency, and water temperatures. reduced computational cost without compromising the accuracy of the numerical solution		
Gasifier stove combined with heat exchanger	Description: formulated model volume is a combination of cylindrical gasifier and heat exchanger tube	Experimental	Nega et al. (2022)
	Combustion model: CFD analysis was performed using an n-premixed combustion model		
Rocket stove	Description: A two-dimensional (2-D) FLUENT model is used to save the computational time	Experimental	Pande et al. (2020)
	Combustion model: there is no premixing of fuel and air in the combustion chamber, a non-premixed combustion model was used in FLUENT		
	Algebraic heat and mass transfer model: CFD analysis of firepower with indoor air pollution variation		
Mud stove with chimney	Description: heat source is simulated in the flame zone of the CFD model	Experimental	Sowgath et al. (2015)
	Heat transfer efficiency: CFD analysis of different zones in the stove and optimize heat transfer efficiency of the stove		
Shielded Fire	Description: CFD analysis of flow and temperature in pot shield to determine the optimal gap	Experimental	Joshi et al. (2012)
	Packed bed model: no separate packed bed model		
	Gas phase combustion model: no separate gas phase combustion model		
	Heat transfer model: CFD analysis of heat transfer within pot shield with inputs determined experimentally from an LPG burner		
Enclosed Stove	Description: Modeled flow conditions from a given heat source to optimize the angle of baffle under the pot	None	Bryden et al. (2003)
	Packed bed model: no separate packed bed model		
	Gas phase combustion model: no separate gas phase combustion model Heat transfer model: CFD to optimize baffle angle		
Open Fire	Description: A coupled zonal model to predict temperature, plume width, and velocity for varying firepower, excess air, and volatile fraction	Quantitative and qualitative experimental	Bussmann et al. (1983)
	Packed Bed Model: Conservation of energy for a control volume with given firepower and volatile fraction		
	Gas phase combustion model: Differential conservation equations including reacting flow with air entrainment		
	Heat transfer model: Local convective heat transfer correlations for bottom and sides of the pot, blackbody radiation with nonparticipating media		

dimensions (Figure 10) subject to the constraints of the model, 3) Material variables such that the thermal conductivity of the stove body components can be determined, 4) Thermal efficiency as measured.

User-centric design, experimental and optimization techniques

Globally, biomass cookstoves have been implemented in a variety of ways, and many more are being developed. The adoption rates and effects of new cooking technologies in developing countries have been explained with different models (Ruiz-Mercado et al., 2011). Traditional "energy ladder" models were defined originally (Van Der Kroon et al., 2013). It holds that traditional devices are completely replaced by modern alternatives as a family's income increases. Transitions are not unidirectional, and people evolve to a "multiple fuel" model as they move up the energy ladder, while maintaining their traditional sources. Researchers have made many new designs and changes to cooking stoves, but users have not adapted to them (Bosque et al., 2021). In order to facilitate the adoption of improved cookstoves and ensure their success, theoretical analyses and user experiences are vital.

There is a distinct cooking situation for every cuisine. The range of cooking power and shape and size of utensils required are almost rigid at the user's end (Kshirsagar and Kalamkar, 2016). Researchers are focusing on the development of biomass

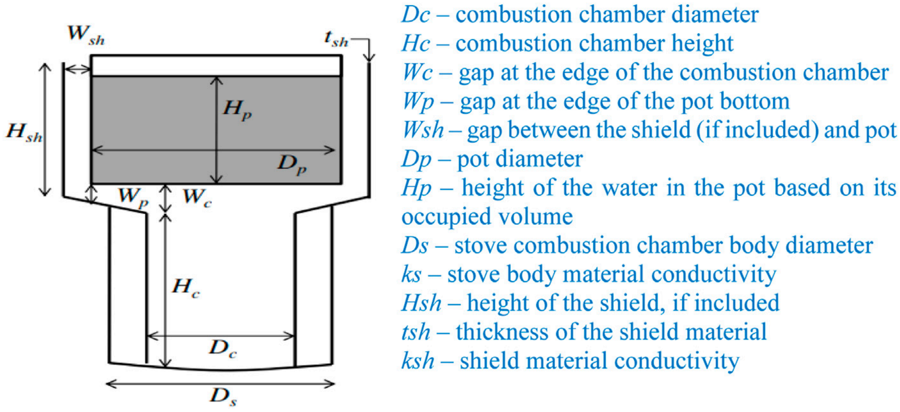

FIGURE 10
Geometrical variables (Maccarty et al., 2013).

cookstoves that can burn biomass more efficiently, which requires an understanding of pollution emissions caused by different parameters. Using the multi-factor parameters Inlet area ratio, Primary air ratio, Pot gap, Fuel surface to volume ratio, and Pot diameter, ((Kshirsagar et al., 2020) improved the combustion performance of biomass cookstoves. A central composite design combined with Response Surface Methodology and desirability function was found to be an effective way to optimize a natural draft biomass cookstove's performance. Detailed information on user-centric sizing of biomass cookstoves subjected to different constraints is presented with a mathematical equation (Kshirsagar and Kalamkar, 2016; Kshirsagar et al., 2020).

Use of forced draft or hybrid draft in modern-day stoves

Technology-based cookstove designs have been introduced to the markets of developing countries for domestic and institutional use. Most developing countries face challenges with the sustainability of biomass cookstove designs that have been churned out over the years (Gill-Wiehl et al., 2021). Nowadays, forced drafts and hybrid drafts are very popular. An effective method of increasing air-fuel mixing and combustion is to create turbulence using forced draft. Several factors contributed to the high capital costs, including fan design, manufacturing technique, and the complexity of the fan. Due to the availability of computer-based fans at a relatively low cost, the problem of high-cost fans has been overcome. For eliminating the running cost of fans, researchers used the thermoelectric generator (TEG) to harness a small fraction of the stove's thermal energy to provide power on demand for fans and surplus power for providing electricity to remote places (Raman et al., 2014; Najjar and Kseibi, 2017). A hybrid draft stove is a small-capacity combustion device that combines natural drafts and forced drafts. Hybrid draft biomass cookstoves designed with the help of the Central Composite Design and Response Surface methodology can achieve low emissions and be efficient in terms of energy and emissions (Kshirsagar and Kalamkar, 2020). A biomass cook stove with affordable fan power was tested using a hybrid draft to reduce CO and PM2.5 emissions. Based on a mathematical model for a hybrid graft stove, a spreadsheet was used to determine the dimensions of the prototype using Visual Basic for Applications. Figure 11 shows a hybrid draft prototype that has 30% higher efficiency than seven other models (Vicente and Alves, 2018; Zhang et al., 2019).

Biomass stoves scenario in Asia

Around the world, many cookstove programs have been implemented. Those programs aim to reduce fuel consumption in order to reduce deforestation, and to improve health conditions by reducing emissions and therefore environmental pollution. Other objectives include improving social conditions in developing countries and reducing global warming. Improvements to Cookstove programs have reported mixed results. Many of the programs have failed to achieve their target objectives. The improved biomass cookstoves (ICS) have become an important topic of research for more than 40 years, but still 2.6 billion population cook over traditional open fire stoves (Kshirsagar and Kalamkar, 2014). The ICS are biomass cooking stoves that are designed to maximize thermal and fuel efficiency, operate safely, and emit low levels of pollutants that are damaging to human health (Mehetre et al., 2017). Evidence suggests that extensive implementation of cookstoves technology with improvements in energy and combustion efficiencies could

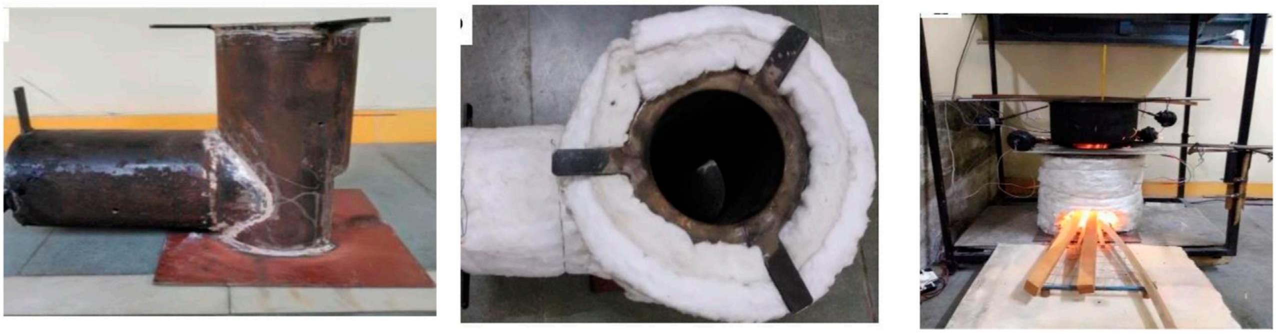

FIGURE 11
The high-efficiency hybrid draft stove prototype (Kshirsagar and Kalamkar, 2022).

significantly help to mitigate adverse human health, energy, and environmental effects (Smith, 1994; Pratiti et al., 2020). According to the International Energy Agency, about half of developing countries' populations rely on biomass in the form of fuelwood, agricultural residues, animal dung, and biofuel charcoal to meet their cooking and heating needs (International Energy Agency, 2006). Improved cooking stove projects have been launched in most Asian countries in the field of biomass utilization. The programs have been commenced in China, where 129 million stoves had been placed by early 1992, and in India, where 35.2 million stoves had been installed by March 2003 (Rofiqul Islam et al., 2008). Figure 12 represents the percentage of household distribution of improved cookstoves in rural and urban areas of some selected Asian countries.

Biomass stoves in Bangladesh

In Bangladesh, about 74% of the rural population cooks predominantly with biomass fuels such as straw/leaf (28.6%), husk/bran (4.0%), and jute stick/wood/bamboo (41.2%) (Finance, 2020). The TCS typically consists of a mud-built cylinder with three slightly raised platforms on which utensils are placed. The efficiency of biomass cookstoves is between 5% and 10%, producing greenhouse gases, and creating a health threat in the kitchen. According to the World Health Organization, more than 70,000 people die in Bangladesh each year because of diseases caused by the IAP from the TCS. Despite these health concerns, families have been diffident in moving to cleaner, more efficient cookstoves in

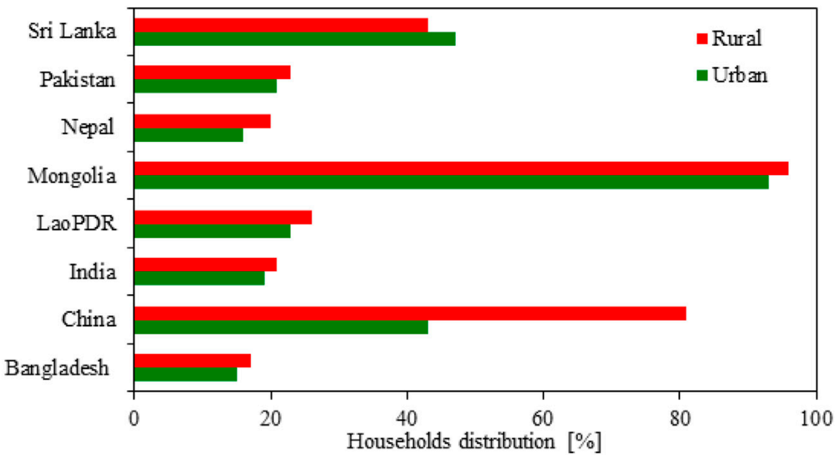

FIGURE 12
Distribution of improved cookstoves (ICS) in rural and urban areas of Asian countries in recent decades (ESCAP, 2018; World Bank, 2014).

the past owing to a lack of understanding and a fear that their meals will lose quality and taste. However, in May 2013, the ICS program began addressing the problem comprehensively by concentrating on the gender and health factors of clean cooking. Furthermore, the ICS program has started assisting women as part of the supply chain for cleaner cookstoves, allowing them to earn money and, as a result, reducing poverty in rural households (World Bank, 2018). By January 2017, this program has distributed one million improved cookstoves, about 2 years ahead of plan. All the program's direct beneficiaries were women, and the program's second phase of execution seeks to reach an estimated five million users by 2021 (World Bank, 2018).

Ahmed and Iqbal studied the benefits of improved cookstoves considering Bondhu Chula in rural Bangladesh (Ahmed and Iqbal, 2018). The 2018 household survey data of the Bangladesh Institute of Development Studies, which collected information from 600 users of Bondhu Chula and 396 users of traditional cookstoves, was used to use Propensity Score Matching, a quasi-experiment econometric method. According to the results, homes utilizing Bondhu Chula save roughly 50 kg of biomass fuel per month, or 30–37% of biomass fuel use, when compared to households using the TCS. Bondhu Chula was also proven to improve health outcomes by lowering indoor air pollution and decreasing household cooking time (Ahmed and Iqbal, 2018). Uddin et al. studied thermal performance and emission analysis of metallic, and nonmetallic (cement) improved cookstoves. The authors concluded that metallic improved cookstove has a better thermal performance of about 35–40% as compared to nonmetallic at 20–30%. However, the nonmetallic improved cookstove emits fewer pollutants when a chimney is connected to the exhaust (Uddin et al., 2020).

In Bangladesh, the ICS are available in a variety of fuel (pellets, briquettes, ethanol, and solar) and form/material (cement/clay/concrete, fixed/portable, and locally manufactured/imported) options. Despite its tremendous fuel-saving potential and a three- to 4-month low-cost recovery period, uptake has been slow, with barely 10% countrywide adoption (Finance, 2020). The organizations involved in biomass cookstove-related activities and trying to improve the cookstoves are Bangladesh Energy Research Council, Bangladesh University of Engineering and Technology, Grameen Shakti, German Development Cooperation, Village Education Resource Centre, Bangladesh Council for Scientific and Industrial Research, Building Resources Across Communities, and Bright Green Foundry.

Biomass stoves in China

Most people living in rural areas of China depend on biomass for cooking and space heating. The widespread use of inefficient biomass stoves for cooking and heating in China's rural areas generates natural and ecological problems; as a result, the Chinese government encouraged the spread of the ICS in 1982. From 1982 to 1994, those ICS were utilized by 144 million household units or around 90% of every improved stove introduced in total which was 62% of the Chinese market (Qiu et al., 1996). However, about 95% of the rural population in China uses wood, coal, and other biomass for cooking and heating resulting in a huge amount of $PM_{2.5}$ emissions (Bruce et al., 2015; Qu et al., 2015). In this principle, China is focusing on improving biomass stoves for cooking, heating, and low-pressure boilers, thereby constricting high-quality stove

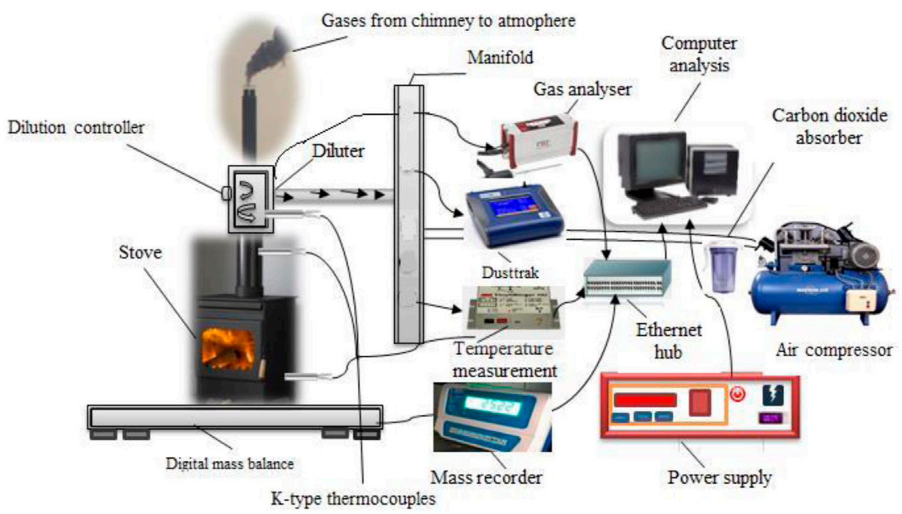

FIGURE 13
Testing system by the laboratory of Clean Production and Utilization of Renewable Energy (CPURE).

testing laboratories (Ahmad et al., 2019). The Key Laboratory of Clean Production and Utilization of Renewable Energy (CPURE), China Agricultural University, Beijing, has constructed a well-designed and modern stove testing lab. The testing system by the laboratory of the CPURE for stoves is shown in Figure 13. Ahmed et al. conducted an experimental study to investigate the performance of the ICS for cooking and heating compared with the TCS by using the testing system for the laboratory of CPURE from viewpoints of thermal and emission efficiency. The authors concluded that the ICS achieved thermal efficiency of 69.6 ± 0.8%, and the lowest emissions of $PM_{2.5}$ 2.9 ± 1.0 mg/MJ_{NET} and CO 2.4 ± 0.3 g/MJ_{NET} (Ahmad et al., 2021b). Results of the study concluded that utilization of the ICS could result in significant reductions of $PM_{2.5}$ and CO emissions for a household. The information regarding stove testing and modern lab instruments would be beneficial to other Asian developing countries.

Biomass stoves in India

In India, biomass fuels such as wood, crop residues, and animal dung remain the most common source of cooking energy. About 90% of rural households utilized biomass fuel for cooking purposes (Venkataraman et al., 2010). In rural areas, access to modern cooking fuels ranged from 0% for the lowest-income households to 43% for highest-income households (Sinha, 2002). Despite ICS programs like NPIC, and NBCI in the country, a significant portion is still relying on the TCS. Women are the primary users of stoves, but they are frequently excluded from household purchasing decisions, among other decision-making. Improved cookstoves can significantly raise the value of life and the possibilities for women's future life. Mukhopadhyay et al. did an exploratory study to investigate the improved cookstoves (Phillips and Oorja) performance in Haryana as compared to the TCS in perspective of cooking practice, $PM_{2.5}$, and CO emissions. The authors considered thirty-two participating households, and they concluded that the participants were satisfied with Phillips cookstove as it meets the local criteria for usability and emission (Mukhopadhyay et al., 2012). Gupta et al. utilized a practical evaluation approach to compare the performance of TCS and ICS which involve Greenway, Envirofit, and Onil with newly designed natural draft ICS from perceptions of multifuel usage, user-friendliness, emissions, and thermal efficiency. The authors found that using solid fuels with a larger energy content in ICS may result in higher efficiency, but it would also result in much higher emissions. The newly designed natural draft ICS attained better performance than TCS and other commercial ICS with a 75% decline in $PM_{2.5}$ and 63% drop in CO concentrations, respectively. The thermal efficiency of newly designed natural draft ICS achieved a significant increase of 106% from TCS (Gupta et al., 2020). Similarly, Suresh et al., did an experimental study to investigate the performance of two natural draft, and one forced draft ICS as compared to TCS in the preparation of a specific meal using a variety of solid biomass fuels (e.g., fuel wood, dung cake, and crop residue). The study was conducted in Indian rural kitchen, and performance was explored based on emissions and thermal efficiency. The authors found that force draft ICS concentration of $PM_{2.5}$ and CO were reduced by 21–57%, and 30–74%, respectively as compared to TCS. The thermal efficiency of force draft ICS of 30–35% was found as compared to TCS of 15–17%.

Despite such improvement, the industry is still facing difficulty and government policy has yet to concentrate on market-based solutions in the stove area. The organizations involved in cookstove-related research activities are the Center for Rural Development and Technology, Indian Institute of Technology, The Energy and Resources Institute, Maharana Pratap University of Agriculture and Technology, and Tamil Nadu Agricultural University.

Biomass stoves in Mongolia

Ulaanbaatar is one of the coldest capital cities in the world, with an average low temperature of −20°C. Heating is essential in these conditions, and heat in Ulaanbaatar is generated mostly by coal burning. The ger districts, located on the outer edge of Ulaanbaatar, include between 80,000 and 100,000 additional families that use individual coal stoves for heating and cooking (World Bank, 2014). Because of insufficient coal burning in low-efficiency metal stoves, polluting gases and dust are released, affecting both the interiors of the tents and the overall air quality of the city (Pemberton-pigott, 2006). Mongolia's largest market, Ulaanbaatar, obtained a very high penetration of improved stoves in a very short period of time. Mongolia's clean stove endeavor, with its unique problems and near-term success story, has the potential to greatly contribute to the international body of knowledge in the development of cleaner cookstoves. The Mongolian Government and Ulaanbaatar Municipality have developed a multi-year, multi-sector strategy to enhance the air quality in Ulaanbaatar, which includes reducing emissions from heating and cooking (World Bank, 2014).

Pemberton-Pigott et al. developed a low-smoke Mongolian coal stove, and experimentally investigated the performance of the developed natural draft chimney improved stove. The author found about a 99% reduction in $PM_{2.5}$, and a 90% reduction in CO by utilizing a natural draft chimney improved stove (Pemberton-pigott, 2006). Mongolian households must be persuaded to move permanently to the ICS which will necessitate a multi-year, coordinated set of policies and programs. In Mongolia, cookstove research is being carried out by the Desert Research Institute Reno, and the National University of Mongolia.

Biomass stoves in Nepal

In Nepal, 69% of the country's population relies on solid biomass (wood, cattle manure, agricultural waste) and 75% of people rely on TCS for cooking and heating (Paudel et al., 2021). In rural areas, high amounts of indoor smoke have been reported in kitchens utilizing (TCS). These emissions are responsible for >18,000 deaths in Nepal (Davidson et al., 1986; Reid et al., 1986; Rupakheti et al., 2019). The ICS are more energy-efficient than previous kitchen ranges and do not pollute the air within the home. In Nepal, efforts to improve the efficiency of stoves are not new. Early initiatives, from the 1950s–1980s, and new initiatives, which began in the 1990s with new stove models that could be built with inexpensive, readily available materials and appropriate methodology from the top-down, were scattered until 1998. The ICS program on a national basis has been started in mid-1999 with the help of the Energy Sector Assistance Program. The point was to set up a reasonable structure and system for making ICS technologically accessible and socially suitable for rural people in the light of the limits of the local societies, and income production (Robinson et al., 2021). The rural energy policy of 2006 attempted to address the ICS to implement economic activities that would help overcome the aforementioned issues and to alleviate poverty. Similarly, the 3-year provisional plan has established a goal of installing 3,00,000 ICS throughout the country's mid-hill and high-hilly regions, to reduce deforestation and the negative impact on the environment (Bhattarai, 2009).

The mud stove is the most well-known ICS, as it is simple, inexpensive, and can be built with locally available materials. In Nepal, several mud ICS designs have been created (Nienhuys, 2005). The Nepal Alliance for Clean Cookstoves is a collaboration of groups working on renewable clean cooking technology, such as improved cookstoves. Alternative Energy Promotion Center, Agricultural Engineering Division-Nepal Agricultural Research Council, Rural Energy Development Program, Biogas Support Program/Nepal (BSP/N) BSP Nepal, Center for Rural Technology/Nepal, Center for Energy Studies, and the National Academy of Science and Technology are the organizations involved in biomass cookstoves-related activities.

Biomass stoves in Pakistan

In Pakistan, about 63% of the population live in rural areas and cook using TCS. About 72% of the population relies on solid biomass for cooking and heating in the country (Irfan et al., 2020). Solid biomass comprises 63% wood, 21% animal dung, and 16% crop residue and has been used by most of nearly 20 million rural households in Pakistan for cooking and heating through inefficient stoves resulting in 115,000 premature deaths (Mahmood, 2007; Saghir et al., 2019; Tareen et al., 2020). Some NGOs working in different regions of Pakistan have begun interventions to disseminate improved cookstoves in their project areas in order to decrease the social, economic, environmental, and health concerns connected with the use of TCS. A Pak–Swiss collaboration called Kalam Integrated Development Project (KIDP) started one such program in Swat in the early 1990s. However, the operations of KIDP terminated in Swat in 1998 due to a variety of socio-political, financial, and institutional factors. Nonetheless, a few local manufacturers continue to make upgraded cookstoves known as project stoves in the area. In this regard, scientific approaches have been used to improve the performance of cookstoves in the last several decades, and various varieties of ICS have been introduced and disseminated in rural parts of Pakistan (Qaseem et al., 2005). Harijan and Uqaili reported that the ICS has fuel (biomass) saving of 14.5 million tonnes. The ICS has efficiencies of 20–40% and can save roughly 40–50% of the fuel used by the TCS. The ICS has several advantages, including the conservation of biomass fuel, the reduction/removal of indoor air pollutants from kitchens, the reduction of deforestation and environmental degradation, the reduction of the drudgery of tasks performed by women and girls, and the reduction of health risks associated with IAP exposure (Harijan and Uqaili, 2013).

The institutes such as the Pakistan Council of Renewable Energy Technology, and the Alternative Energy Development Board are involved in cookstove research in Pakistan. A few NGOs working in different parts of Pakistan have been forced to intercessions to disseminate improved cookstoves in their target areas (January 2012). The Aga Khan Development Network in Pakistan aims to improve human satisfaction in all provinces of Pakistan. Regardless of the Building and Construction Improvement Initiative program, its cost away at water supply, sanitation, minimal effort lodging, and disaster hazard decreasing US$1 = PKR 165.53 (Pakistan rupees, in October 2020). Typically installed prices for products which are involving efficient stove PKR 4,303 (US$26), efficient stove + water-warming facility PKR 8,275 (US$50), roof hatch window PKR 7,778 (US$47), floor insulation PKR 215 (US$1.3) per square meter, wall insulation is PKR 4940 (US$7.6) per square meter (Nienhuys, 2000).

Biomass stoves in Sri Lanka

About 78% of Sri Lankan households utilize biomass fuel for cooking, and the country's strong reliance on wood-burning stoves is the largest source of (IAP) (Elledge et al., 2012). About 84% of these households are in rural areas of the country. Even in urban areas, over 34% of the population uses wood as their main fuel source. However, while more than 80% of Sri Lankan households have electricity, it is used primarily for lighting, and wood is used for cooking (Elledge et al., 2012). According to a recent analysis by the Energy Conservation Fund, there are three types of stoves are used in the rural areas of the country, these stove types include TSF, partial-confined, and ICS having the contribution of 47%, 32%, and 21% respectively. Similarly in rural areas, the contribution of three types of stoves is about 56%, 31%, and 13%, respectively (Perera and Sugathapala, 2002).

Since 1972, various institutes in Sri Lanka have contributed to the design, promotion, and commercialization of improved cookstoves. The Sri Lanka Standard Institute distributed two-pot biomass clay cookstoves, which are for improved cook stoves resulting in a reduction of smoke (Sirikumara, 2018). The National Engineering Research & Development Centre of Sri Lanka introduced two types of more efficient wood gasifier stoves: one is a forced draft stove with a small electrically operated blower connected to it, and the other is a natural draft stove with a combustion efficiency of around 35%, compared to the TCS (Joseph, 2011; Musafer, 2013). The institutes like the Sri Lanka Sustainable Energy Authority and the National Institutes of Fundamental Studies are involved in cookstove research in Sri Lanka.

Biomass stoves in Laos

In Laos, about 91% of people continue to cook and heat using solid biomass and TCS, with fuelwood at 67% and charcoal at 24% being the most common sources of fuel. On average, a family in Laos consumes 5 kg of fuelwood each day for cooking, which amounts to almost 2 million tonnes per year. Families that use charcoal consume approximately 1.86 kg per day in rural regions and 2.33 kg per day in urban areas; however, it takes up to 6–10 kg of wood to make 1 kg of charcoal, making it a much larger contributor to emissions and health risks (World Bank, 2013). The use of sophisticated cooking energy sources such as liquefied petroleum gas and electricity is quite limited in Laos, therefore dependent on solid biomass (Dave and Balasundaram, 2016). Since 2012, the Lao Institute for Renewable Energy is working to promote more efficient means of biomass use through skilled design programs (efficient cookstoves), policy and marketing research, and development of solid renewable fuel. The Group for the Environment, Renewable Energy, and Solidarity (GERES) developed a new cookstove, the New Lao Stove (NLS), that uses 22% less wood and charcoal than the TCS. In the country, there are 36 NLS production centers that produce 30,000 stoves per month for local markets. The GERES′ support program, as well as its collaboration with producers and distributors, enable capacity building, monitoring, and quality control of the products. By December 2011, sales of the New Lao Stove had surpassed expectations, with 1,607,283 units sold (Dave and Balasundaram, 2016; Baltruschat, 2019). The institutes involved in cookstoves are the research institute of Laos, the Lao Institute for Renewable Energy, and the National Institute of Public Health.

Stove efficiency and emissions comparison between Asian Countries

Stove efficiency is measuring the heat transfer to the cooking pot as a fraction of the calorific value of input biomass. The TCS have low thermal efficiency of less than 10%, and emissions are different according to the operation of the stoves. The principle of analyzing emissions from the combustion process is used to compute emission factors. By multiplying the amount of a specific biomass fuel utilized in the energy system by the comparable emission factors, the total amount of different pollutants emitted by the system may be computed. Different aspects of the combustion process, such as the kind and design of the stove, the type of fuel used, and the operating conditions, all have a significant impact on the emission factors (Arora et al., 2014). According to a different analysis of the research, China is performing better from viewpoint of the ICS than other Asian countries. Many organizations and institutes are working on improving and testing stoves. In China, producers must obtain a certificate from a recognized stove testing facility to certify their new stove design. The stove testing labs examine new stove designs according to their standards; if the stove passes the lab testing requirements, the institute issues a certificate, and the manufacturers then enable the stove to be sold on the market. If a stove fails to pass the lab testing criteria, the manufacturer will not sell it. Many ministries and organizations in India are working on the ICS, and they are doing a better job than those in other Asian countries. In Pakistan, the thermal efficiency of the ICS is about 20–40% and particulate matter (PM) levels in the kitchen ranged from 4,000 to 8,555 g/m^3 but utilizing the ICS with improved solid fuel contributed a range of 200 g/m^3 to 5,000 g/m^3 (Fatmi et al., 2010; Harijan and Uqaili, 2013). Table 4 shows the types of fuel and stoves used with their thermal efficiencies and emission rate for selected Asian countries.

Barriers to dissemination of improved biomass cookstoves

The ICSs are broadly advertised as a technology that improves the environment and health, however, there remains a huge space among their presumed profit and vague effect of most contributions largely fail to achieve their stated aims. Furthermore, the lack of adequate awareness of customer needs such as convenient operation, purchasing capability, unpredictable earnings in rural areas, and the limited facility development of marketplaces and stove designers generate the distribution agreement (Pampallona and Bollini, 2014). Most of the ICS projects in developing countries appear to be heavily focused on excellent designs from a production and design perspective, as well as improving industrial manufacturing procedures (Brown et al., 2017). Initially, the stoves were distributed, and their contribution was hardly measured after the operators in the model characteristic. As a result, they were either not used by customers or were unfit for genuine cooking (Lindgren, 2020). According to the research of several projects, the most common mutual complaint among stove operators is “stove size too small and not suited for all vessels."

TABLE 4 Thermal efficiency and emissions comparison of TCS and ICS between some Asian countries.

Country	Type of Fuel	Types of Stoves	Thermal Efficiency (%)	Emission		References
				$PM_{2.5}$ (mg/ MJ_{NET})	CO (mg/ MJ_{NET})	
China	Solid fuels	TCS/Traditional Chinese stove with chimney	<10	0.265	0.033	Shen et al., 2015; Zhang et al., 2015
		ICS/combined with cooking and heating	27–35	1.2–4.3	0.1	
Mongolia	Coal	TCS/traditional Baseline Mongolian stove with chimney	63	0.388	8.16	Pemberton-pigott, 2006
		ICS/combined with cooking and heating	72	0.4	0.53	
Bangladesh	Wood	TCS/three stone fire	<10	0.792	0.0128	Alam et al., 2006
		ICS/cooking	23.2	0.683	0.005	
India	Wood	TCS/three stone fire	<10	2.99	0.7	Mohan and Kumar, 2011
		ICS/cooking	24–26	1.17–3.47	1.9–4.43	
Nepal	Wood	TCS/three stone fire	10.5	1.3–1.4	10.5–11.3	Arora et al., 2014
		ICS/cooking	15	-	1.31	
Pakistan	Wood	TCS/three stone fire	<10	-	-	Nienhuys, 2000
		ICS/cooking	15–22	-	-	
Sri Lanka	Wood	TCS/three stone fire	>10	1.2	-	Perera and Sugathapala, 2002
		ICS/cooking	30	-	-	
Laos	Wood	TCS/three stone fire	8	-	1.36	Bhattacharya et al., 2000
		ICS/cooking	27	-	3.01	

In a typical case of fuel gathering, numerous Indian families associated with the LPG primarily employ wood-based cookstoves, mainly for bread baking, the alleged good flavor of the meal, and, to some extent, economic concerns. LPG is only used carefully for quick cooking, such as making tea (Palit and Bhattacharyya, 2014). Furthermore, wood savings appear to have low application in rural areas, owing to their easy supply from farmsteads, agricultural lands, or forests. The additional key barrier is the lack of statistics and information about cookstove acceptability. If progress is to be stopped in changing trends, a significant study is required to support evidence-based action/policy. To overcome these barriers, the ICS distribution could be attractive, and the market potential for clean cooking fuels and skills will not be understated. However, the marketplaces should be separated according to revenue, as there are numerous misstatements in both traditional and modern fuels (Vahlne and Ahlgren, 2014).

Conclusion

The present review was conducted to evaluate the current scenario of biomass cooking and heating stoves in Asian countries including Bangladesh, China, India, Mongolia, Nepal, Pakistan, Sri Lanka, and Laos. The major portion of the population in Asian countries is dependent on biomass for cooking and heating purposes. The TCS utilized by these countries has several limitations which involve emissions of CO_2, $PM_{2.5}$, low thermal efficiency, and greater fuel consumption. Due to these emissions, the IAP causes several health risks. After going through various research conducted on ICS in Asia, we found that the ICS has better thermal efficiency and emissions performance, and thereby fewer health risks. China's status regarding ICS was found better as compared to other Asian countries. However, we found different barriers in the dissemination of the ICS among the Asian countries such as financial, infrastructure, awareness, market, stove size, and socioeconomic. Therefore, these barriers should be the focus of the research community. In addition, the following guidelines have been suggested for future research focus:

- It is necessary to manufacture high-quality, well-designed, standardized, and cost-effective stoves that are easy to sell and service.
- The cookstoves should be constructed considering the needs of consumers as well as their purchasing power.
- Workshops, schemes, and training programs should be used to encourage the adoption of improved cookstoves.
- For the successful promotion of cookstoves, collaboration between research institutes and support groups should be encouraged.

- The government should support the development of new cookstove designs by providing financing services to stove makers and establishing specialized criteria.
- Before the introduction and after installation in the fields, proper procedures should be created for the frequent evaluation of various cookstove types.
- All stove manufacturers should have an authentic stove testing department to confirm its design, quality, heating, and emission performance.

Author contributions

RA: overall conceptualization and drafting. HI: conceptualization. BL: sources, funding, and review. MS: review, drafting. MA: Review. AA proofread. MI drafting. FR: Review, Editing. All authors read and approved the final manuscript.

Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

The reviewer (JH) declared a shared affiliation with the author(s) (AA) to the handling editor at the time of review.

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Enabling the complete valorization of hybrid *Pennisetum*: Directly using alkaline black liquor for preparing UV-shielding biodegradable films

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The conversion of lignocellulosic biomass into various high-value chemicals has been a rapid expanding research topic in industry and agriculture. Among them, alkaline removal and utilization of lignin are important for the accelerated degradation of biomass. Modern biorefinery has been focusing the vision on the advancement of economical, green, and environmentally friendly processes. Therefore, it is indispensable to develop cost-effective and simple biomass conversion technologies to obtain high-value products. In this study, the black liquor (BL) obtained from the alkaline pretreatment of biomass was added to polyvinyl alcohol (PVA) solution and used to prepare degradable ultraviolet (UV) shielding films, achieving direct and efficient utilization of the aqueous phase from alkaline pretreatment. This method avoids the extraction step of lignin fraction from black liquor, which can be directly utilized as the raw materials of films preparation. In addition, the direct use of alkaline BL results in films with similar UV-shielding properties, higher physical strength, and similar thermal stability compared with films made by commercial alkaline lignin. Therefore, this strategy is proposed for alkaline-pretreated biorefineries as a simple way to convert waste BL into valuable products and partially recover unconsumed sodium hydroxide to achieve as much integration of biomass and near zero-waste biorefineries as possible.

KEYWORDS

energy grass, hybrid *Pennisetum*, alkaline black liquor, film, UV-shielding, lignin, biorefinery

Highlights

- Prepare anti-ultraviolet film by directly using alkaline pretreatment black liquor.

- Adding black liquor to polyvinyl alcohol enhanced the performance of composite film.
- Black liquor alkaline pretreatment can be directly utilized to the maximum extent.
- Combine with current technology, zero waste liquid biorefinery can be realized.

1 Introduction

Lignocellulosic biomass is widely considered as a sustainable source of biofuels and biochemicals (Usmani et al., 2021; Kumar et al., 2022; Saravanan et al., 2022) *via* various techniques such as thermochemical, biological, and mechanical treatments (Periyasamy et al., 2022; Sidana and Yadav, 2022; Zhou and Tian, 2022). In the area of biological valorization, most efforts are focused on valorizing the saccharides (mainly hemicellulose and cellulose) into targeted products such as biogas, bioethanol, and other valuable chemicals (Ghimire et al., 2021; Devi et al., 2022; Raj et al., 2022), while the presence of lignin significantly suppresses the biodegradation activities and needs to be removed (Areepak et al., 2022; Mikulski and Klosowski, 2022; Nordin et al., 2022). Alkaline pretreatment is effective for biomass delignification, and normally, ideal lignin removal performance can be achieved when grass biomass is alkaline pretreated under mild conditions. Recent studies on alkaline pretreatment on hybrid *Pennisetum* achieved 68.6% lignin removal at 35°C for 24 h (Kang et al., 2018), and the obtained cellulose-rich residue was used for bioethanol and biogas production *via* singular and co-production scenarios. It achieves conversion of biomass for biofuel production, but the aqueous phase after pretreatment (mainly including lignin and a fraction of hemicellulose) still remains unused components and is considered waste. The conversion of alkaline lignin to various products (e.g., biochar and biochemicals) has been extensively studied (Jin et al., 2022; Kim et al., 2022; Paul et al., 2022; Xiu et al., 2022), whereas the direct utilization of lignin-rich alkaline black liquor (BL) for valuable products has been seldomly reported.

Recently, the usage of lignin as an additive for preparing polyvinyl alcohol (PVA)-based films has emerged as a method of using lignin in the material context. By simply adding lignin to PVA gels, the obtained films can exhibit higher mechanical strength and UV-shielding properties (Posoknistakul et al., 2020; Zhang et al., 2020; Ma et al., 2022). However, in identical practice, commercial lignin needs to be obtained as another co-ingradient. Obtaining lignin from alkaline BL requires a cost-addition process for lignin extraction and purification. Thus, if alkaline BL can be straightly and sufficiently used as an additive for PVA films, the process cost can be reduced. In addition, the successful direct utilization of alkaline BL as a valuable raw material for UV-shielding films will enable the development of integrated techniques for near-complete valorization of lignocellulosic biomass. However, no studies have reported the direct usage of BL as an additive for biodegradable plastic materials.

Thus, this study was conducted to (1) directly use alkaline BL as an additive for preparing UV-shielding biodegradable films, (2) characterize and analyze the properties of the obtained PVA/BL films compared with those of PVA/alkaline lignin (PVA/AL) films, and (3) analyze the composite film formation mechanisms. In addition, a brief discussion has been provided on the feasibility of the co-production of UV-shielding films and biofuels for the complete valorization of lignocellulosic biomass.

2 Materials and methods

2.1 Materials

Hybrid *Pennisetum* was collected from the Zengcheng District, Guangzhou, China, in November 2021. To collect 60–100 mesh particles for further use, the raw biomass was dried, ground and sieved. The total solid (TS) and volatile solid (VS.) contents were 96.71 ± 0.06 and 85.30 ± 0.14%, respectively. The cellulose, hemicellulose, and lignin contents of the samples were 35.33 ± 2.74, 19.08 ± 2.58, and 18.61 ± 0.47%, respectively. Sodium hydroxide (NaOH, 95%) and polyvinyl alcohol (1799-PVA) were purchased from Shanghai McLean Biochemical Co., Ltd. Glucose, xylose, and arabinose standards were obtained from Aladdin Biochemical Technology Co. Ltd. (Shanghai, China). Commercial alkaline lignin was purchased from Shanhu Chemical Co. Ltd. (Nanjing, China). All the chemicals were used without further purification.

2.2 Preparation of black liquor and polyvinyl alcohol glue

The alkaline BL was the liquid fraction collected from alkaline pretreatment on hybrid *Pennisetum* with 6 wt% NaOH aqueous solution at 37°C for 24 h, as described in a previous study (Kang et al., 2018) from our group, which is the optimized condition for alkaline pretreatment on Hybrid *Pennisetum*. The obtained BL was used directly without addtional treatment. PVA glue (10 wt%) was prepared using a method introduced in recent studies (Zhang et al., 2020; Yang et al., 2021).

2.3 Preparation of the composite films

The preparation of PVA/BL and PVA/AL films was an upgraded method based on previous studies (Xiong et al., 2018; Huang et al., 2021; Yang et al., 2021). First, 50 g of PVA glue (10 wt%) was added to a conical flask (volume

TABLE 1 Preparation parameters of PVA/BL films.

Sample	Proportion (wt%)	Lignin mass (g)	Black liquor (ml)
PVA-0.5%BL	0.5	0.025	1.65
PVA-1.0%BL	1.0	0.050	3.29
PVA-3.0%BL	3.0	0.150	9.88
PVA-5.0%BL	5.0	0.250	16.47
PVA-10.0%BL	10.0	0.500	32.93

TABLE 2 Preparation parameters of PVA/AL films.

Sample	Proportion (wt%)	Alkali lignin (g)	NaOH solution (ml)
PVA-0.5%AL	0.5	0.025	1.65
PVA-1.0%AL	1.0	0.050	3.29
PVA-3.0%AL	3.0	0.150	9.88
PVA-5.0%AL	5.0	0.250	16.47
PVA-10.0%AL	10.0	0.500	32.93

100 ml). Next, alkaline lignin/NaOH or alkaline BL was added to the PVA glue, as detailed in Tables 1, 2, respectively. Different volumes of the solution were selected to achieve a composition of lignin in the film from 0 to 10%. Subsequently, the mixtures were stirred constantly (250 rpm) for 3 h at 60°C, followed by cooling to room temperature (25 ± 10°C). Finally, each film required 2 g of mixed glue solution to be added to a polytetrafluoroethylene (PTFE) column mold (Φ = 5 cm) and evaporated at 35°C for 48 h to form the films, which were then rinsed with deionized water and dried. The samples were labeled according to the type and concentration of additives. It should be noted that the percentages on the labels represent the mass ratio of the lignin content in the BL/AL additives and PVA.

2.4 Properties of composite films

2.4.1 Ultraviolet and visual light absorption

The UV absorption properties of the films were measured using a UV-Visible-NIR-Spectrophotometer (Lambda PerkinElmer, United States). Each film was cut into squares of 3 cm × 3 cm and fixed to a mold for analysis. Each sample was scanned at 260 nm/min within the range of 200 nm–760 nm. Each test was repeated six times.

2.4.2 Mechanical strength

The mechanical properties of the films were tested using a universal mechanical testing machine (INSTRON 5982) according to the ISO 179-1993 standard. In each test, the dumbbell-shaped specimen (7.50 cm × 5.00 mm) was mechanically stretched, a load cell sensor of 200–250 N was used, the crosshead moving speed was 5 mm/min, the initial fixture spacing was 4.00 cm, and the experiment was conducted at 25°C and relative humidity of 46%. A minimum of five tensile tests were conducted for each sample.

2.4.3 Water uptake and swelling properties

The water absorption and swelling properties of the films were tested by soaking them in deionized water for 48 h at room temperature. After soaking, the samples were wiped with filter paper (Φ = 90 mm) to remove surface water. The weight and thickness before and after soaking were measured, and the equilibrium swelling rate (ESR) and water retention (WR) rate were calculated as per Eqs 1, 2, respectively. Each test was performed in triplicate, and the average value is presented as the relative standard deviation as the error bar.

$$WR = \mathrm{Ws} / \mathrm{Wd} \tag{1}$$

$$ESR = (\mathrm{Ws} - \mathrm{Wd}) / \mathrm{Wd} \tag{2}$$

Where W_d represents the dry weight and W_s represents the weight after swelling (Pan et al., 2006; Tong et al., 2007; Wu et al., 2019).

2.4.4 Surface roughness

The surface roughness of the films was characterized using atomic force microscopy (AFM; Multimode 8 Bruker, United States). For each sample, a square area of 5 μm × 5 μm was scanned at a rate of 0.996 Hz and consisted of 256 lines. The probe model used was RFESPA-75 (f_0 = 75 kHz, k = 3 N/m, Bruker, United States). Air-soft tapping was applied as the test mode, and the data were analyzed

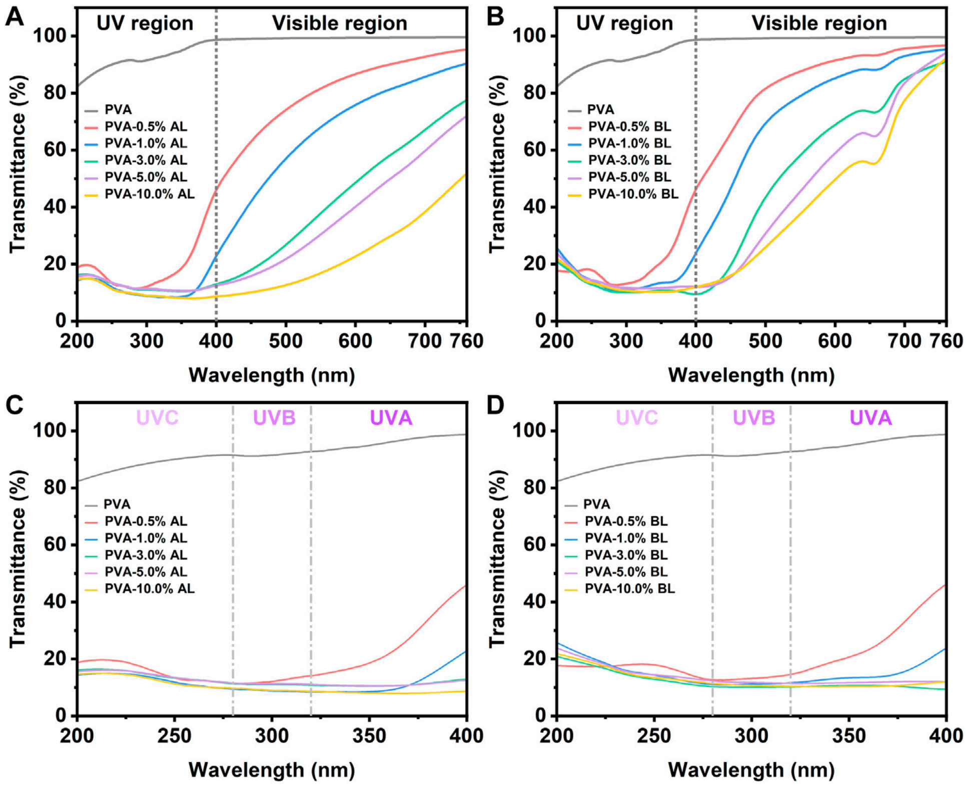

FIGURE 1
Light transmittance of PVA, PVA/AL, and PVA/BL films. **(A)** 200–760 nm AL; **(B)** 200–760 nm BL; **(C)** 200–400 nm AL; **(D)** 200–400 nm BL.

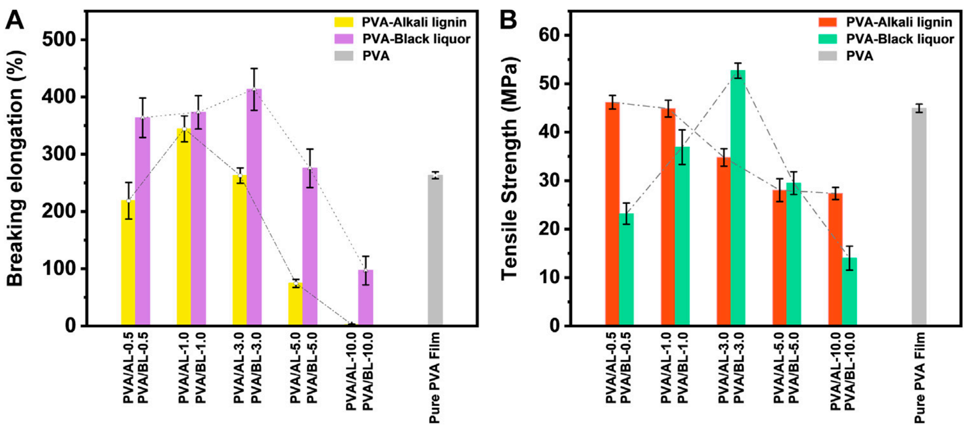

FIGURE 2
Mechanical Properties of various films. **(A)** breaking elongation of various composite films; **(B)** tensile strength of various composite films.

using NanoScope Analysis 1.5. The roughness of the composite film is specified by the magnitude of the values of Rq and Ra, where Rq represents the root mean square value and Ra represents the average value of the relative datum plane.

2.4.5 Thermal stability

The thermal stability of the films was tested by thermogravimetric analysis (TGA; SDT650 TA, United States) in the range of 25–700°C at a heating rate of

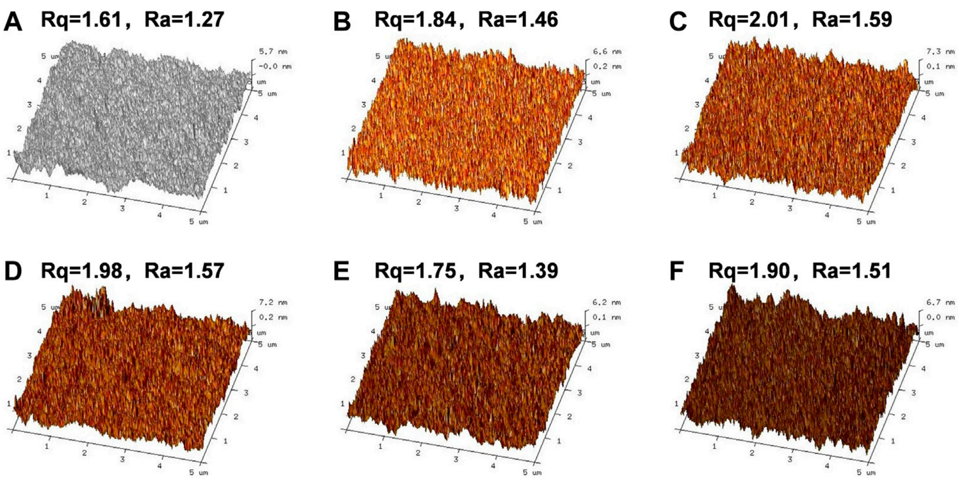

FIGURE 3
Atomic Force Microscope (AFM) of PVA and PVA/AL films. **(A)** PVA; **(B)** PVA-0.5%AL; **(C)** PVA-1.0%AL; **(D)** PVA-3.0%AL; **(E)** PVA-5.0%AL; **(F)** PVA-10.0%AL.

10°C/min, with nitrogen (feeding rate: 40 ml/min) as the protection gas.

2.4.6 Differential scanning calorimetry

The thermophysical properties of materials were analyzed by low differential scanning calorimetry (DSC6000, PerkiElmer, Netherlands). The samples were heated from 25°C to 230°C at 10°C/min under argon for 3 min to remove the volatile components and thermal history. Then the samples were cooled to 25°C at the same rate and heated to 230°C after 3 min, during which the glass transition temperature of (Tg) the samples were recorded.

2.5 Functional groups of film materials

The surface functional groups of the samples were analyzed using a Fourier transform infrared spectrometer (FTIR, Nicolet Is 50, Thermo Fisher Scientific) in the attenuated total reflection mode (IS5O ATR). Each scan was conducted in the range of 4,000–800 cm^{-1} with automatic gain on.

2.6 NMR characterisation of lignin

The black liquor was adjusted to acidity, the solids were precipitated and extracted, and two-dimensional heteronuclear single-quantum coherent NMR spectroscopy (2D-HSQC-NMR) was performed on lignin samples using a Bruker AVANCE III 400 MHz NMR spectrometer equipped with a PABBO probe. A 50 mg solid sample was dissolved in 0.6 ml of DMSO-d_6 and HSQC spectroscopy was performed at a relaxation delay of 2 s. The percentages of G, H and S units and the S/G ratio were according to the calculations presented in a previous study (Wen et al., 2013).

2.7 Concentration of NaOH in rinsed water

The concentration of NaOH in the solution collected from the rinsing films was quantified by testing the alkalinity using an automatic potentiometric titrator (APT; YLB-Titron Line Easy, Julabo, Germany). In this test, the endpoint pH was set to 7, and the endpoint determination was delayed for 1 s. The standard curve is provided in the supplementary material. Alkalinities of various NaOH/water mixtures is shown in Supplementary Figure S1 in the supporting materials.

3 Results and discussion

3.1 Properties of polyvinyl alcohol films with the addition of alkaline lignin and alkaline black liquor

As mentioned above, the exact properties of PVA/BL films remain unknown. In this study, the diverse properties of PVA/BL films based on multiple characterizations were analyzed and compared based on the properties of PVA/BL and PVA/AL.

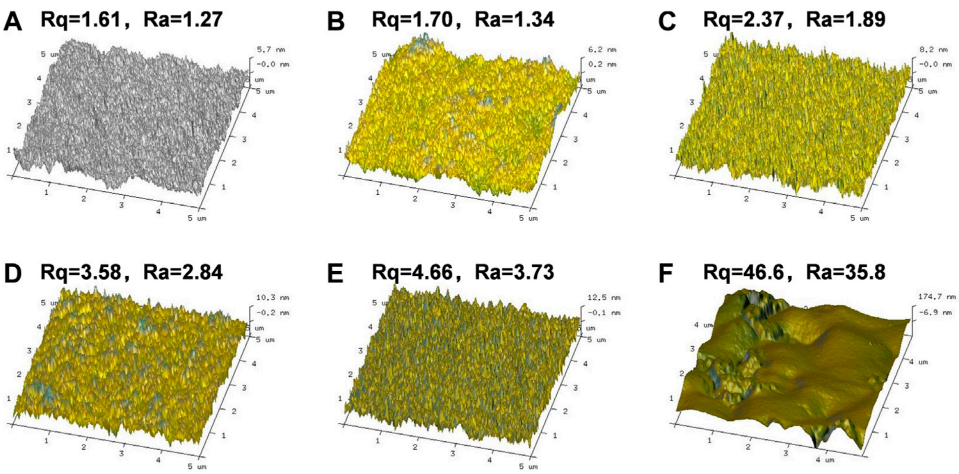

FIGURE 4
Atomic Force Microscope (AFM) of PVA and PVA/BL films. **(A)** PVA; **(B)** PVA-0.5%BL; **(C)** PVA-1.0%BL; **(D)** PVA-3.0%BL; **(E)** PVA-5.0%BL; **(F)** PVA-10.0%BL.

3.1.1 Light transmission properties of various composite films

Figures 1A,B show the full-band (wavelength at 200–760 nm) light transmittance of the PVA/AL and PVA/BL films, respectively. The PVA films had light transmittances of 81–100% in the UV region (200–400 nm) and 100% in the visible region (400–760 nm), which is compatible with previous studies on the optical properties of PVA (Wang Y. et al., 2017b; Huang et al., 2021; Van Nguyen and Lee, 2022). Notably, with the addition of only 0.5% AL, the transmittance of UV light in the UV region significantly declined, which range from 12 to 42%. The amount of AL was further increased to more than 1.0% and the light transmittance was less than 25%. Therefore, the use of lignin as an additive can significantly enhance the UV-shielding performance of PVA films.

However, the addition of AL also resulted in the absorption of visible light. Figure 1A reveals that the transmittance of visible light gradually decreased with increasing AL. Specifically, the transmittance of visible light for the PVA/AL film with 0.5% AL ranged from 45 to 90%, whereas when 10.0% AL was added, it reached 10–50%. Interestingly, adding BL directly into PVA achieved similar UV-shielding performance; meanwhile, the transmittance of visible light also declined with increasing BL content, as shown in Figures 1C,D. Interestingly all the PVA/BL films observed slight fluctuations at wavelengths near 660 nm, a particular phenomenon that deserves further investigation.

Collectively, the appropriate amount of alkaline pretreatment-derived black liquor can be used directly as an additive to improve the optical properties of PVA-derived biodegradable films, whose high transparency and strong UV absorption properties are of great value for packaging materials and have many potential applications (Akhramez et al., 2022; Liu et al., 2022; Zhang et al., 2022).

3.1.2 Mechanical properties of various composite films

The breaking elongation and tensile strength are critical indices for film materials. The former represents the soft and elastic properties of the materials, whereas the latter represents the resistance of the materials to the material to the maximum uniform plastic deformation. Figure 2A illustrates the breaking elongations of the films. The elongation of the PVA film was 263.32%. As for the breaking elongation of the two kinds of composite films, both showed a similar tendency with the addition of AL and BL. Specifically, the breaking elongation displayed an obvious increase with the addition of AL and BL; afterwards, it reached a peak of 344.28% and 413.32%, where the addition of AL and BL were 1.0% and 3.0%, respectively. When successive additions of AL and BL were made, there was an obvious decrease, but the elongation at break of the PVA/AL film was relatively low, which could be attributed to the enhanced intermolecular forces of the polymer due to the hydrolysis products of cellulose and hemicellulose in the black liquid (Gao et al., 2014). Figure 2B shows the tensile strengths of the films. It is clear that the maximum value of PVA/BL (52.70 Mpa) is higher than that of PVA/AL (46.19 Mpa) with the same variation in AL and BL addition, which in combination with the relevant literature can be explained by the high efficiency of hydrogen bonds entangled between various compounds such as lignin, hemicellulose derivatives and PVA in the black liquor. In addition, the variation in tensile strength of the composite film in the range

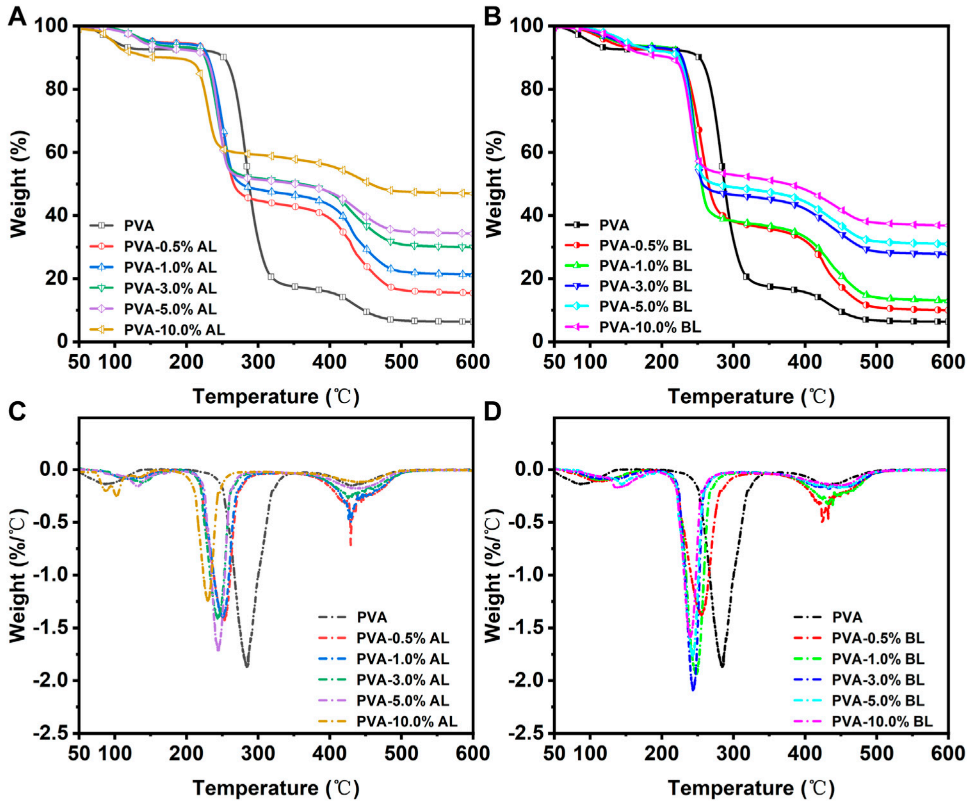

FIGURE 5
Thermal Stability of various composite films. **(A,C)** present the TG and DTG spectra of PVA and PVA/AL films; **(B,D)** present the TG and DTG spectra of PVA and PVA/BL films.

0.5–10.0% BL may be due to the dispersion state of the additive in the matrix (Guan et al., 2014; Xiong et al., 2018). In view of the higher breaking elongation and tensile strength of PVA/BL films, it is evident that PVA/BL showed superior mechanical durability with a BL of 3.0% compared with other films.

3.1.3 Surface roughness of various composite films

Figures 3, 4 present the AFM images of various films. It is plausible to conclude that adding AL or BL to PVA caused a slight increase in the surface roughness of the obtained films. Specifically, when the BL content reached 10.0%, the root means square value (Rq) and average value of the relative datum plate (Ra) increased to 46.6 and 35.8, respectively. Compared with the PVA/AL films, both the Rq and Ra of PVA/BL were substantially higher, indicating that using BL as the additive drastically increased the surface roughness.

3.1.4 Characterization of composite films based on other basic properties

Data for the PVA films were not obtainable because PVA dissolved in deionized water during soaking (Supplementary Figure S2) which presents the water absorption and swelling ratios of the films. Both the PVA/AL and PVA/BL films showed a similar trend in ESR and WR, with an increasing trend from 0.5 to 3.0%, followed by a decrease. Thus, the PVA/BL films exhibited water uptake and swelling properties similar to those of the PVA/AL films.

Figures 5A,C show the weight loss (%) and weight-loss rates (%/°C) of the PVA and PVA/AL films at 50–600°C. The weight loss of the PVA film can be divided into three stages: (Stage 1) water evaporation (50–140°C), (Stage 2) decomposition and degradation of PVA (234–350°C), and (Stage 3) chain scission and cyclization reactions (395–500°C). A similar description has been provided in previous studies and has not been discussed further (Zhao et al., 1998; Alexy et al., 2001; Dong et al., 2014; Dong et al., 2016). The addition of AL caused differences in the thermostability of Stages 2 and 3. Specifically, the decomposition of compounds advanced to 200°C, which is related to the decomposition/evaporation of some light compounds (e.g., lignin monomers and oligomers). Less weight loss was achieved, likely due to interactions such as the hydrogen bond crosslinking between lignin and PVA, which formed compounds that were difficult to decompose. Further, the addition of AL resulted in less weight loss at Stage 3 and gradually decreased with the increase in AL content. As shown in

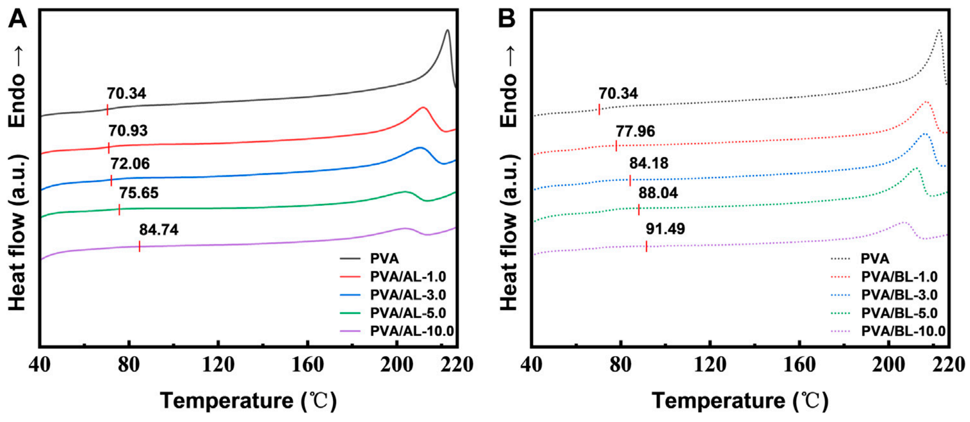

FIGURE 6
Differential scanning calorimetry (DSC) of various composite films. **(A)** PVA-AL; **(B)** PVA-BL.

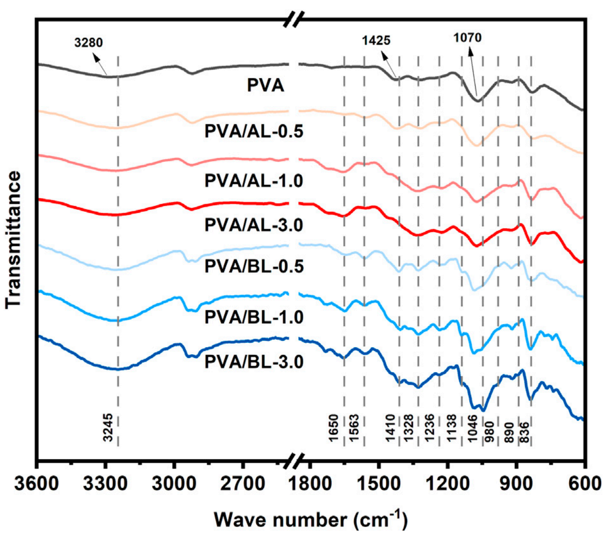

FIGURE 7
FT-IR spectra of PVA, PVA/AL, and PVA/BL composites.

Figures 4B,D, the addition of BL suppressed the thermal decomposition of the obtained films and exhibited a trend similar to that of the PVA/AL films. However, the addition of BL resulted in slightly more weight loss at both Stages 2 and 3 compared with the addition of AL. This is likely due to the decomposition of carbohydrates in the BL as carbohydrates have lower pyrolytic temperatures than lignin (Sousa et al., 2016; Rao et al., 2021).

Figures 6A,B show the warming transition of two polymeric materials respectively. It was observed that the glass transition temperatures (Tg) of the composite films were both higher than those of the pure PVA films (70.23°C). The values for Tg increased from 70.93 to 83.5°C when increasing the AL content from 1.0 to 10.0%. This should be attributed to the hydrogen bonding between the alkali lignin and PVA molecules, limiting the degree of free movement of the PVA molecular chains, which is consistent with relevant lignin-based materials reported in the literature (Xiong et al., 2018; Zhang et al., 2020). As the BL content increased from 1.0 to 10.0%, the Tg value increased from 77.96 to 88.60°C. In contrast, the glass transition temperature of the black liquor composite films showed a similar shift and had a higher glass transition temperature (Tg), because both the carbohydrate derivatives and lignin in the black liquor cross-linked with the PVA, increasing the rigidity of the molecular chains, and reducing the intermolecular mobility, thus increasing the glass transition temperature (Tg) of the polymer.

3.2 Discussion on the formation mechanisms of composite films

As shown in Figure 7 and Supplementary Table S1, the FT-IR spectra of various films exhibited five main peaks at 3,280, 2,915, 1,425, 1,070, and 836 cm^{-1}, corresponding to the intermolecular interaction of the alcohol hydroxyl group, CH_2 group asymmetric stretching bands from the methyl group, deformation of O–H and C–H bonds in the plane, C–O bond out-of-plane vibration, and the appearance of the PVA skeleton band, respectively (Mahmud et al., 2006; Abdelrazek et al., 2010; Franca et al., 2022). Several changes were observed with the addition of alkaline lignin. The bands

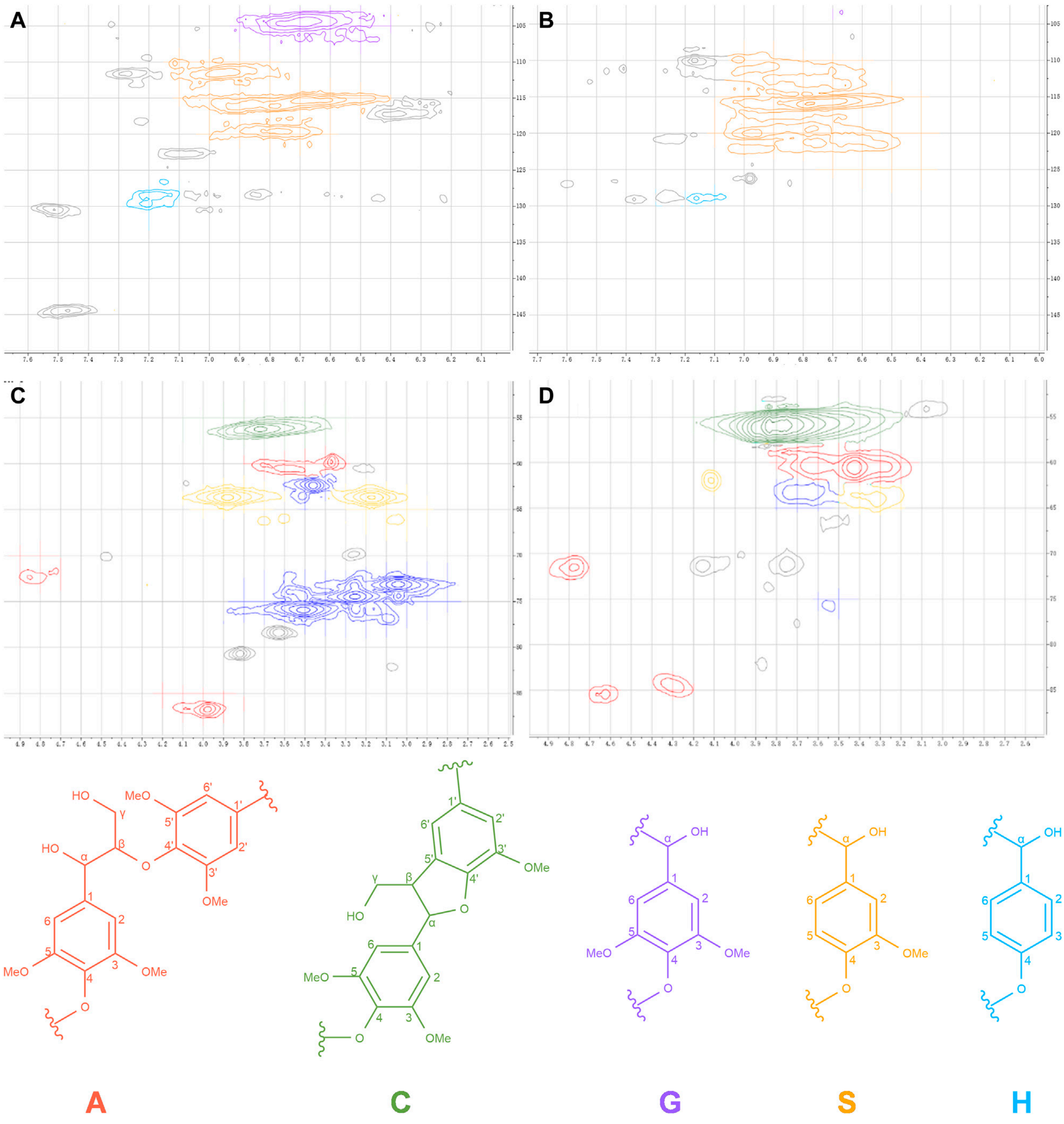

FIGURE 8
2D-NMR spectra for lignin. **(A,C)** represent the aliphatic-oxygenated ^{1}H–^{13}C correlations (δH/δC 2.5–6.0/50–90 ppm region) giving information on lignin side-chain interunit linkages; **(C,D)** represent the aromatic/olefinic ^{1}H–^{13}C correlations (δH/δC 6.0–8.0/100–150 ppm region) giving information on lignin aromatic units.

at 1,650, 1,563, 1,328, and 836 cm^{-1} are typical lignin characteristic peaks (Serrano et al., 2010; Wu et al., 2016; Jin et al., 2022). Further, the peak positions of some of the functional groups changed. The association vibration of the C–H bonds on the lignin S and H units and the CH_2 groups of PVA occurred at 836 cm^{-1}. In addition, the hydroxyl peak at 3,280 cm^{-1} shifted to 3,264 cm^{-1}, and a similar shift from 1,070 cm^{-1} to 1,078 cm^{-1} was observed, which confirmed

TABLE 3 Aromatic unit structures of lignin.

Aromatic unit strutures	Lignin extracted from BL (%)	Akalin lignin (%)
S	44.97	2.96
G	48.28	87.18
H	6.75	9.86
S/G	0.931	0.034

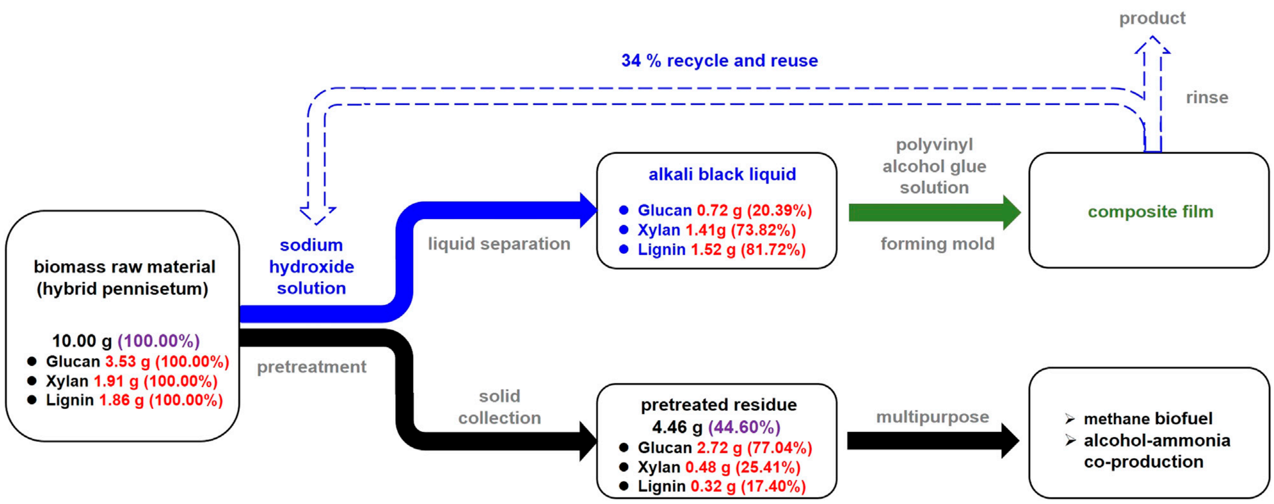

FIGURE 9
A proposed schematic of the integrated valorization of hybrid *Pennisetum* by co-producing biodegradable UV-shielding films and biofuels with mass flow.

the strong crosslinking phenomenon between alkaline lignin and PVA, as found in previous studies (Kubo and Kadla, 2003; Huang et al., 2021).

With the addition of BL, additional peaks were observed. The bands at 1,650, 1,563, 1,328, and 836 cm^{-1} were assigned to lignin, whereas those at 1,236, 1,138, 1,046, 980, and 890 cm^{-1} were assigned to carbohydrates (e.g, glucan, xylan) (Peng et al., 2014; Sun et al., 2014; Wang F. L. et al., 2017a; Liu X. W. et al., 2019a; Boukir et al., 2019). The addition of BL also caused changes in the characteristic PVA peaks. Compared with the PVA film, there was a red shift at 3,280 cm^{-1}. Unlike the blend of alkaline lignin, the BL composite films had a more obvious shift from 3,280 cm^{-1} to 3,245 cm^{-1} and showed a strong broad peak, combined with the characterization results of DSC and previous reports, which confirmed that hydrogen bonding between carbohydrates in BL and PVA formed (Liu X. X. et al., 2019b). Additionally, there is a double peak absorption in the range of 3,000–2,880 cm^{-1}, which is attributed to the mixture of methyl, methylene, and asymmetric stretching vibrations owing to the complicated compositions of BL (Posoknistakul et al., 2020; Zhang et al., 2020).

3.3 HSQC NMR spectra of lignin in samples

For the lignin-rich black liquor fraction, lignin was collected, characterized with 2D-NMR, and compared with alkaline lignin. NMR spectra for the δ_H/δ_C 2.6–6.0/50–90 and 6.0–8.0/100–150 (aromatic and fatty) ppm regions are given in Figure 8, and the assignment of the main signals is shown in Supplementary Table S2 in the Supporting Information (Fan et al., 2021; Huang et al., 2021).

At anomeric regions (Figures 8A,B), significant differences were observed at δ_H/δ_C 3.04–3.51/62.3–75.90 ppm. In brief, the correlation of δ_H/δ_C 3.3–3.6/59–64 ppm was mainly manifested by the signal of C_γ-H_γ in β-O-4′ substructure (A) overlapped with the signal of C_5-H_5 in β-D-xylopyranoside (X) and the signal of C_γ-H_γ in phenylcoumaran substructures (C). The δ_H/δ_C 73.23/3.04, 74.50/3.26, 75.90/3.51 ppm were attributed to the C_2-H_2, C_3-H_3, and C_4-H_4 units of β-D-xylopyranoside (X), respectively, which coincided with the FTIR detection of xylose-related outgoing peaks. No obvious signals were found for the X_2, X_3, X_4, and X_5 units in alkaline lignin, indicating that the release of xylan and the removal of lignin occurred simultaneously during the pretreatment and that some of the structures were connected.

The aromatic region corresponds to the vibration of the aromatic ring skeleton detected by FTIR and lignin fractions of both samples were quantified according to the results. As presented in Table 3, the pretreatment produced a higher content of lignin eugenol (S), which was significantly higher than the S/G of alkali lignin, further and indicating a difference in the distribution of lignin and alkali lignin in the black liquor, a result that may be one of the reasons for some of the performance differences between the two composite films.

3.3 Discussion on biomass valorization by integrated film synthesis and biofuel production

As mentioned above, using BL as the PVA additive is feasible for improving the UV-shielding performance of the obtained film and can achieve similar durability under various test conditions. Particularly, when 3.0% BL was added to the PVA glue, the PVA/BL films showed good ultraviolet absorption performance, mechanical strength, and thermostability, which were not worse or better than those of PVA/AL films. However, it must be noted that using BL directly caused higher roughness and could uptake more moisture content, which needs to be addressed in future studies. In view of these results, it is plausible to conclude that producing PVA/BL UV-shielding films directly is a suitable alternative means for valorizing alkaline BL.

Combined with the valorization of the delignified biomass, Figure 9 briefly shows the integrated production of UV-shielding biodegradable films and biofuels. In brief, alkaline pretreatment of 10 g biomass with NaOH (6 wt%) under 37°C for 24 h could produce a BL containing 1.52 g lignin, 0.72 g glucan, 1.41 g xylan, and some content of unconsumed NaOH. This BL can be added to a PVA solution, producing a UV-shielding film *via* the process proposed in this study. In addition, after film formation, the rinsing process could recycle 34% NaOH. The solid content, containing 2.72 g glucan, 0.48 g xylan, and 0.32 g lignin, was more suitable as a feedstock for its further application (e.g., producing biofuels *via* anaerobic digestion or fermentation). As investigated by Kang et al. (2018), alkaline- pretreated hybrid *Pennisetum* with 9.9% lignin is capable of producing methane at 257.6 ml/g VS In another study by Hosgun et al. (2017), this pretreated biomass achieved a glucose yield of 48.32%, which can be fermented for bioethanol production.

4 Conclusion

This study provides a simple and feasible approach for valorizing alkaline BL produced by biomass pretreatment. By mixing the BL with PVA solutions, the formed PVA/BL films exhibited excellent UV-shielding performance and physical durability. Specifically, adding 3.0% of alkaline BL achieved a film that suppresses the UV transmittance to less than 20%, with breaking elongation at higher than 400% and tensile strength higher than 50 MPa, which were better than the films prepared by commercial alkaline lignin. This simple approach can drastically reduce the cost of preparing PVA/lignin films by extracting lignin from biomass delignification waste streams. It is recommended as a means to achieve near-complete valorization of lignocellulosic biomass. In addition, by recycling the unconsumed NaOH *via* a simple rinsing process, lower pollutant emissions were achieved as far as possible. Further efforts are suggested to improve the properties of PVA/BL films, especially the surface smoothness and hydrophobicity.

Data availability statement

The original contributions presented in the study are included in the article/Supplementary Material; further inquiries can be directed to the corresponding author.

Author contributions

HQ: Writing—original draft, Investigation, Methodology, Conceptualization. YS: Writing—review and editing, Funding acquisition. YF: Writing—review and editing, Data curation. LH: Writing—review and editing, Data curation. JC: Writing—review and editing. LL: Writing—review and editing, Funding acquisition, Conceptualization.

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Conflict of interest

LL, HQ, and YS are inventors on patent application held/ submitted by GIEC that covers the current utilizing method of alkaline black liquor.

The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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Supplementary material

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fbioe.2022.1027511/full#supplementary-material

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Sustainable economic growth potential of biomass-enriched countries through bioenergy production: State-of-the-art assessment using product space model

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The current study aims to examine the economically viable biomass feedstocks for bioenergy generation and their export potential. The Product Space Model (PSM) is the primary tool used to achieve the aim by accomplishing certain objectives. The study's findings show that Pakistan has abundant biomass resources for energy production. Canola oil, leather flesh wastes, and poultry fattening show the highest PRODY values, 46,735, 44,438, and 41,791, respectively. These have high-income potential and are considered feasible for export after meeting local energy demand. While goat manure, cashew nutshell, and cotton stalk show lower income potential having values of 3,641, 4,225, and 4,421, respectively. The biowastes having low-income potential are more beneficial to utilize in energy generation plants within the country. The United States is observed to make the most sophisticated products, indicated by an EXPY value of 36296.89. While the minimum level of sophistication is observed for Indonesia, as revealed by its EXPY value of 22235.41 among all considered countries. The PSM policy map analysis of the current study shows that Pakistan and Argentina are located in the Parsimonious Policy quadrant, suggesting shifting toward unexploited products closely related to the existing export baskets. Although the United States, China, India, Indonesia, and Brazil are found in the most desired Let-it-be Policy quadrant. They have more room to diversify their industries and enhance their

Abbreviations: HIP, High-Income Potential; HS, Harmonized System; LIP, Low-Income Potential; MIP, Medium-Income Potential; OEC, Observatory of Economic Complexity; OECD, The Organization for Economic Co-operation and Development; PSM, Product Space Model; RCA, Revealed Comparative Advantage; UN, United Nations.

export potential. The study has practical applications in economic, social, and environmental perspectives, focusing on economic, clean, and sufficient energy. Furthermore, exportable biomass feedstocks are identified to strengthen the economy. Further research must be conducted to evaluate other indicators of the PSM to explore the proximity aspect of PSM, as it would provide a clearer picture of bioenergy and biomass export prospects.

KEYWORDS

biomass, bioenergy, product space model, sustainability, circular economy

1 Introduction

The environmental factors and exhaustion of conservative fuels indicate a dire need for renewable energy sources to harness sufficient and clean energy using feasible technologies. Global energy requirements will rise by 48% from 2012 to 2040 (Conti et al., 2016). Conversely, non-renewable energy sources will be reduced to 84% in 2040 compared to 91% in 1990. Therefore, the demand for renewable energy sources is predicted to increase from 9% to 16% to meet global energy needs. The increasing energy demand also indicates that renewable energy share in electricity production will decline from 78% to 71% in 2040. Many renewable energy sources can be utilized to extract energy, such as solar, wind, hydro, and biomass. These sources are abundantly available both in developing and developed countries. Furthermore, renewable resources emit almost negligible amounts of carbon compared to hazardous emissions from conventional fuels. Hence, renewable sources are eco-friendly and valuable in combating climate change (Thapar et al., 2016). There are various conversion technologies for biomass bioenergy production, and biochemical conversion has been one of the most effective. With the help of the biochemical conversion method, any organic waste can be converted into biogas. This biogas can be used for cooking, power generation, and many other purposes (Roopnarain & Adeleke, 2017).

Numerous countries have intended to produce biomass in terms of fuel sources. The energy from fuel extracted from biomass considers bioenergy. As biomass is considered a renewable energy resource, it can be utilized as an alternative feedstock for sustainable and green energy production. In ancient times, biomass was eventually used as an energy source in firewood through combustion. Various feedstocks are currently available in industrialized countries for biofuel manufacturing, including forestry residues, agricultural residues, industrial waste, and municipal solid waste (MSW). The biofuels generated by utilizing the feedstock are classified as second-generation biofuels. While the biofuels produced using edible food crops, including sugarcane, corn, wheat, coconut, sunflower, and soya bean, belong to first-generation biofuels. Lignocellulosic materials, including wood, jatropha, straw, and biomass residues, produce these biofuels (Naik et al., 2010; Sims et al., 2010). Therefore, biofuel production can tackle the waste disposal issue from biomass residue.

Biomass residues can be classified into primary, secondary, and tertiary groups. The leftovers of main food crops and forest products are primary residues (corn stalks, stems, leaves, and straw). In contrast, the biomass waste produced during the processing of food crops for other valuable products is secondary biomass residues (woodchips, coffee husk, rice hulls, and sugarcane bagasse). Municipal solid waste can be described as tertiary biomass residue produced when humans or animals consume the biomass-derived product (Chen et al., 2015). Waste cooking oil is also an efficient example of tertiary biomass residue. Therefore, agricultural residues and waste cooking oil seem promising for bioenergy production among all biomass residues.

Livestock is considered an essential source of biomass residue in animal manure, which could be used for biogas synthesis through anaerobic digestion. This biogas may be employed to produce electricity for the farm. Therefore, this practice is both economically and ecologically viable. Various studies in the United States revealed that around 60 million tons of manure could be adapted to generate bioenergy in 2030. Additionally, China is a chief producer of wheat, rice, and corn. Hence, China is one of those countries that can produce bioenergy by utilizing an enormous amount of available resources. It can significantly reduce the use of coal for energy generation (Mohammed et al., 2018). There are different conversion technologies present to convert biowaste into bioenergy. Some are biochemical processes, while others are thermochemical, such as gasification, pyrolysis, and combustion. Transesterification and anaerobic digestion are biochemical processes.

The bioenergy economic potential is mainly assessed by technology and fuel expenditures. Moreover, it includes the financial issues that a particular region faces (Portugal-Pereira et al., 2015). Limited technologies are available in underdeveloped countries, and electricity is comparatively expensive because of the lack of modern technologies. Conversely, the feedstock cost is lower for agricultural countries with abundant biomass, reducing overall cost. Hence, bioenergy is more feasible for agricultural economies than fossil fuels (Paolotti et al., 2017). Brazil is also one of those countries having advantageous conditions and large amounts of biomass resources to increase biofuel production. Brazil has been characterized as a global giant due to the great potential for biofuel feedstocks that can enhance its production levels further. The country is significant in bioenergy generation as it has the potential to synthesize plantation crops such as sugarcane, the primary feedstock for bioethanol (Welfle, 2017). In addition, Brazil can enhance biomass residue production by utilizing vast areas of arable savannas for crop cultivation without compromising forest deterioration (Welfle, 2016).

Forest biomass can generate bioenergy, which is abundantly present in Indonesia. This forest biomass resource can economically benefit bioenergy production through various conversion technologies. In 2013, Indonesia was found to have 132 PJ of potential biomass resources available to convert into bioenergy.

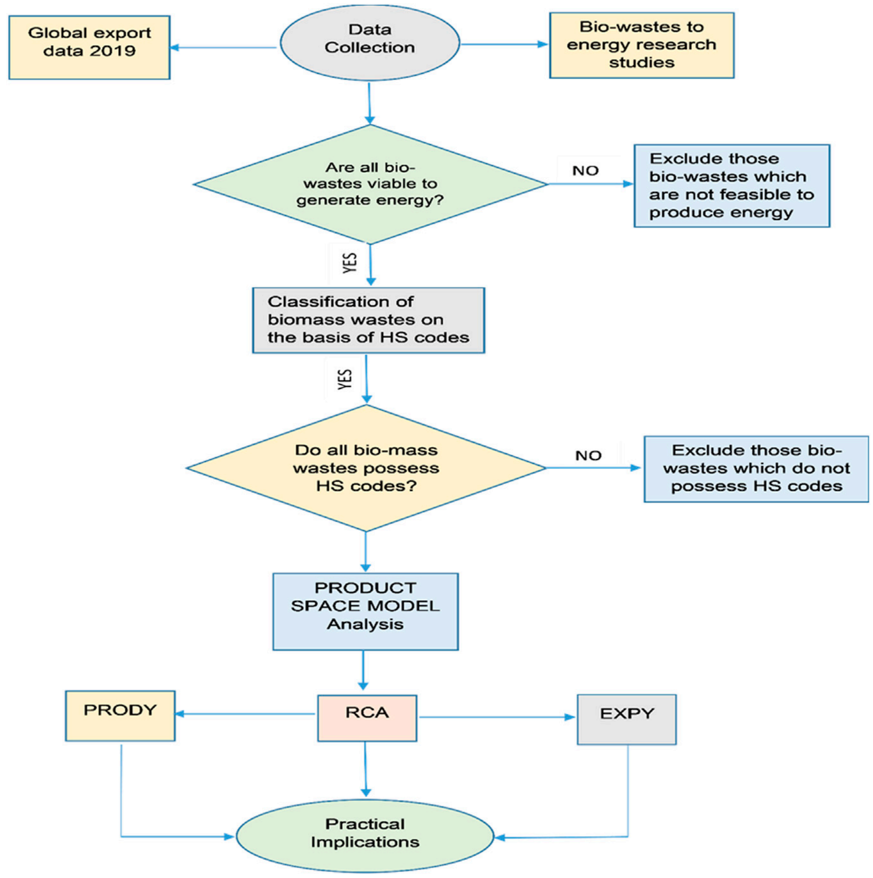

FIGURE 1
Flow pattern for product sophistication and economic growth analysis utilizing PSM.

Approximately 50.4% and 49.6% could be generated from harvesting residues and wood processing residual materials, respectively. Using forest biomass for bioenergy would generate revenue for the country. It would also aid in poverty alleviation through a noticeable reduction in import bills (Simangunsong et al., 2017). This study aims to evaluate economically feasible biomass feedstocks in all considered biomass-enriched countries using the Product Space Model (PSM). The potent feedstocks for bioenergy production are analyzed and identified by PSM, illustrating a global network of exportable products depending on their resemblances. In addition, it identifies the relation among different products produced by a country. This analysis also indicates the income potential associated with specific products. Furthermore, it describes the sophistication level of a country's export basket and associated economic benefits.

2 Methodology

The PSM is a novel economic model with a strong explanatory power that can appraise the income potential and sophistication at the country and product levels. Initially, PSM measures the product level sophistication of the globally exportable products and then measures a country's total sophistication level by assessing its export basket. In other words, it assesses a country's production capacity or total capability set. Once a country-level sophistication is calculated, it identifies and prioritizes the unexploited feasible products and sectors within the country's reach. This study employs the PSM approach to assessing the biowaste convergence potential of the selected countries into bioenergy. Figure 1 represents the flow pattern for product sophistication and economic growth analysis using PSM.

2.1 Data collection

A detailed literature review was done initially to find the maximum possible biowaste for bioenergy-based research studies. Later, different biomass feedstocks were considered for the proposed study from the collected studies. The 25 biowastes and seven biomass-enriched countries were selected. The countries were nominated depending on their biowaste export share. In the next phase, these biomass feedstocks were assigned Harmonized System (HS) codes from the HS-6 digit code list in 2019. Only those biowastes considered for this study which have HS codes. The HS-code list was downloaded from the UN-Comtrade website, the United Nations international trade database for all the member countries. There are different categories of trade data, and HS is one of those categories. This database recorded global export as well as import data per annum. The Observatory of Economic Complexity (OEC) extracted global export data in 2019 comprising all exportable products. This data was used as input to calculate PSM indicators.

2.2 Data processing tool

The PSM was employed to assess the feasibility of economically efficient feedstocks for bioenergy production. Significantly, PSM was used as a tool for data processing. PSM is a network of global exportable products that describes the relatedness among various exportable products. It facilitates the formation of a network of related products to encourage industrialization, leading to economic growth. PSM consists of two regions: a core region and the other is known as a peripheral region. The products lying in core region are considered more sophisticated, with technical skills and high-value additions. The products present in the peripheral region are less sophisticated with low-value addition.

Furthermore, the PSM method outlines the paths and relatedness between products. To exemplify, if any country synthesizes product A, its existing production infrastructure facilitates the prediction of whether the country can manufacture product B or not by showing the extent of relatedness between them. It also depends if the products share similar inputs related to productive data in producing those particular products (Hidalgo et al., 2007). Therefore, a product space map of the country reflects future export diversification and economic growth. In addition, numerous international organizations, including World Bank, United Nations, and the OECD (The Organization for Economic Co-operation and Development), have used the PSM technique to evaluate the capability of diverse nations and assist them in exploring new unexploited exports for upcoming feasible industrialization and economic development authenticating its application elsewhere (Hausmann and Klinger, 2008b; Qyyum et al., 2021).

The PSM technique has several indicators: EXPY, path, PRODY, proximity, distance, density, open forest, and strategic value. Calculating the indicators can predict the potential of a country's predicted export diversification. Each of the indicators provides information regarding different aspects of likely product diversification. The PSM approach revolves around two basic traits: sophistication and distance or proximity. The sophistication can be described as incorporating advanced technical skills and value addition. It was calculated by the PRODY and EXPY using Eqs 1, 2. PRODY measures the sophistication level of a required product, while EXPY refers to the overall sophistication level of the country's export basket. On the contrary, proximity assesses the distance of the provided product to the existing production capacity and between other products. The present investigation focuses on the sophistication aspect of the PSM approach. This study has used PRODY, EXPY, and Revealed Comparative Advantage (RCA) to appraise the economically efficient biomass feedstocks for bioenergy production.

2.2.1 PRODY

It refers to a product-based indicator that measures the income potential of exportable goods and associates the *per capita* income of all nations exporting that product. Moreover, it reflects the income potential of a given product by analyzing its sophistication level. The more sophisticated products have high-income potential because of high-value addition (Hausmann and Klinger, 2008a). Generally, developed countries export more sophisticated products and multifaceted attributes, while developing countries export less sophisticated and low-value-added products. It is calculated using the formula given below, where Xc,p is the export of product p by country c, $\sum$ p Xc,p indicates the total exports of country c, and Yc is the *per capita* income of country c (Hausmann and Klinger, 2010).

$$\mathbf{PRODY_P} = \sum c \frac{Xc, p/\sum p\, Xc, p}{\sum c(Xc, p/\sum p\, Xc, p)} \times Y_c \tag{1}$$

2.2.2 EXPY

It can be described as a country-specific indicator, which depicts the total sophistication level of the export basket in a country. It reveals the extent of value addition in the goods that the country exports. In addition, it denotes the average PRODY value of the country's exports and the average income linked to it. Therefore, the EXPY is a substantial determinant of predicted economic development (Grancay et al., 2015).

$$\mathbf{EXPY_c} = \sum\nolimits_c \left(\frac{Xc, p}{\sum p\, Xc, p}\right) \times \mathrm{PRODY_P} \tag{2}$$

2.2.3 Revealed comparative advantage

It is an index representing a country's relative merits and demerits in a specific category of goods. It is a ratio between the domestic share of a product and the global share of that product. This index indicates whether a country is an effective exporter of that product or not. It is calculated by the given formula, where the numerator denotes the product p's share in the country c's overall exports, while the denominator symbolizes the product p's share in the worldwide exports (Balassa, 1965). A higher domestic share depicts that the country is a viable product exporter.

$$\mathbf{RCA_{c,p}} = \frac{Xc, p/\sum p\, Xc, p}{\sum c\, Xc, p/\sum c \sum p\, Xc, p} \tag{3}$$

3 Results and discussion

This study analyzed biomass-enriched countries and assessed their economic development and exporting diversification prospects using PSM indicators. Figure 1 validates the flow pattern of analysis using the PSM method. Three PSM indicators were calculated in this study, including RCA, PRODY, and EXPY, by using Eqs 1–3, respectively.

3.1 Product sophistication analysis

PRODY is an indicator that determines the potential income generation of different products. Biomass-enriched countries are supposed to produce extensive biowastes, which can benefit their growing economy, particularly for a developing country. The

TABLE 1 Low-Income Potential (LIP).

HS ID	Biowaste	PRODY
010420	Animal manure (goat)	3641.65
080130	Cashew nutshell	4225.91
230610	Cotton stalk	4421.27
010410	Animal manure (sheep)	4910.55
120799	Non-edible seed oil of *prunus cerasoides*, Seed oil of *raphnus raphaniserum* L.	6256.53
	Martynia annua seed, Neem seeds,	
	Ceper (*capparis spinose* L.) seed oil	
230690	Jatropha oil cake, Olive residue	6808.89
230210	Corn cob	8751.31
230650	Coconut oil cake	11284.2

TABLE 2 Medium-Income Potential (MIP).

HS ID	Biowaste	PRODY
230400	Soya bean oil cake	17047.7
150710	Soya bean oil	18279.8
121300	Rice straw, wheat straw, wheat husk, rice husk	18412.7
151219	Sunflower waste cooking oil	20917.8
440121	Long wood sticks	22048.8
230320	Sugar cane	22104.2
050210	Porcine	27015.8

TABLE 3 High-Income Potential (HIP).

HS ID	Biowaste	PRODY
151800	Vegetable oils	32950.4
440130	Pine sawdust	34042.7
230800	Food waste, vegetable waste	36276.8
010229	Animal manure,	36276.8
	Cattle manure slurry, livestock manure	
060490	Grass waste, lawn grass	36276.8
300212	Animal waste (Manure, Blood, and Rumen content)	36276.8
391290	Cellulose	41098
150100	Poultry fattening, chicken fat	41791.9
151600	Fat fraction from MSW, Leather fleshing waste, duck tallow	44438.1
151490	Canola oil	46735.9

TABLE 4 Biowastes PRODY categorization.

Categories of PRODY	PRODY value	Number of biowastes
High-income potential (HIP)	≥30,000	10
Medium-income potential (MIP)	15,000–30,000	7
Low-income potential (LIP)	≤15,000	8

25 biowastes were considered for this study. The PRODY of all biowastes was calculated to appraise their income potential biowaste. According to the findings, some biowastes have higher PRODY values than others. Therefore, all the considered biowastes are categorized into three groups according to their PRODY values as Low-Income Potential (LIP), Medium-Income Potential (MIP), and High-Income Potential (HIP) in Tables 1–3, respectively. biowaste.

The biowastes showing minimum values of PRODY are placed in (Table 1). The biowastes categorized as Group 1 have PRODY values ranging between 3641.65–11284.2. Therefore, they have lower income potential as well as are the least beneficial in terms of export. The second category consists of the biowastes (Table 2) with PRODY values ranging from 17047.7 to 27015.8, indicating their moderate-income potential. They can be perceived as more advantageous than the previous category due to their higher PRODY values. Finally, the biowastes having the highest income potential among all considered biowastes are placed in Group 3. Their PRODY values range between 32950.4–46735.9 (Table 3). The criteria for categorizing biowastes with low, medium, and high-income potential is presented in Table 4. Among the studied biomass feedstocks, 40% belong to the high-income potential group, while medium and low-income potential groups include 28% and 32%, respectively.

The higher values of HIP products show they can be economically beneficial if exported. Therefore, moderate-income potential biomasses are beneficial both for export and energy generation. Furthermore, low-income potential biomass products are more suitable for energy production within the country. In this way, they can save non-renewable energy costs. This study revealed

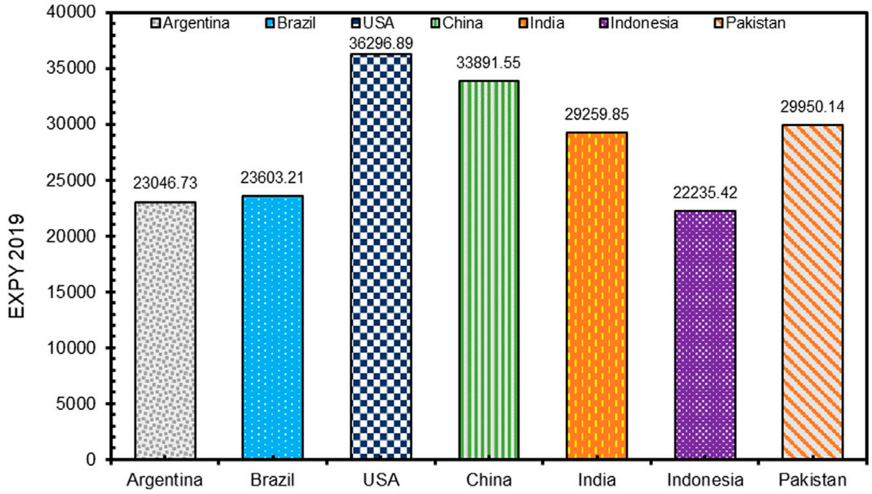

FIGURE 2
EXPY of all the investigated countries in 2019.

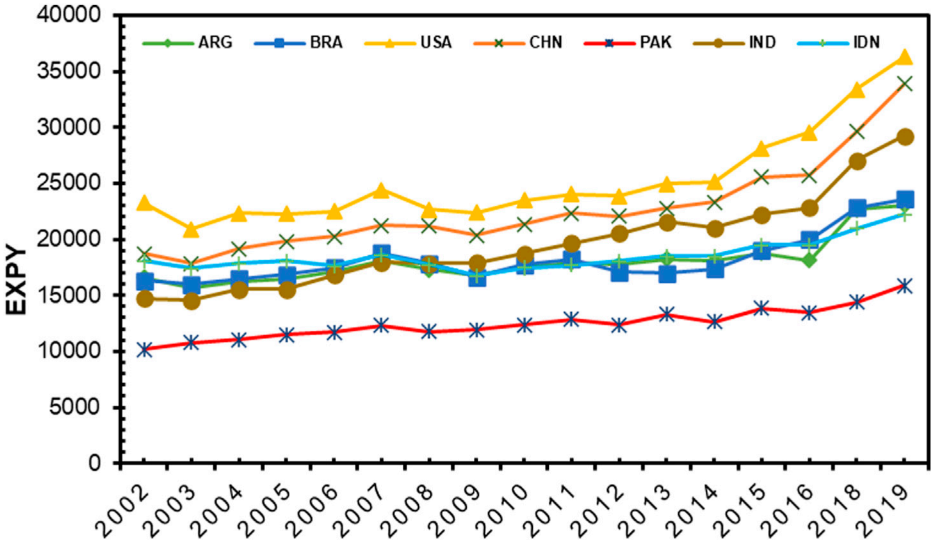

FIGURE 3
EXPY trend of considered countries from 2002 to 2019.

that the maximum PRODY value was found for canola oil 46,735, and the minimum value of 3,641 was observed for animal manure (goat), as presented in Table 3 and Table 1, respectively. The higher PRODY value of canola oil suggests it has high-income potential and can be exported. While goat manure having the lowest value indicates its low-income potential. Therefore, using it for energy production rather than exporting it can be more beneficial.

3.2 Country-level sophistication

The EXPY value depicts how sophisticated products a country can produce. In addition, it informs the level of incorporation of advanced technologies and skills into the products made by the country. In this study, seven countries were considered, and their EXPY values were calculated using (Eq. (2)) as mentioned in the methodology for 2019. Figure 2 represents the different levels of sophistication for products of different countries.

Figure 2 shows that USA made the most sophisticated products, indicated by EXPY value 36296.89. While the minimum level of sophistication was observed for Indonesia, as shown by its EXPY value of 22235.41 among all considered countries. A country with higher EXPY value is considered rich in complex productive knowledge and strong economically. Therefore, EXPY was calculated to determine the sophistication level of biomass-enriched countries from 2002 to 2019. The EXPY trends of

TABLE 5 RCA values of Biowastes for studied countries.

HS ID	Biomass	Argentina	Brazil	USA	China	Pakistan	India	Indonesia
120799	Non-edible seed oil of prunus cerasoides, Seed oil of *raphnus raphaniserum* L. Martynia annua seed, Neem seeds,	2.46	0.13	0.69	1.32	0.45	1.02	0.06
	Ceper (*capparis spinose* L.) seed oil							
230320	Sugarcane	0.02	0.22	1.56	0.00	0.02	0.04	0.10
50210	Porcine	0.06	0.00	0.14	5.88	0	0.17	0
150100	Poultry fattening, chicken fat	0.38	0.55	2.98	0.02	0.06	0.00	0.04
391290	Cellulose	0.012	1.40	3.73	0.49	0.05	2.47	0.09
121300	Rice straw, wheat straw, wheat husk, rice husk	0.00	0.01	0.86	0.06	73.04	0.96	0.00
150600	Fat fraction from MSW,	0.04	0.00	1.28	0.13	0.00	0.07	0.00
	Leather fleshing waste,							
	Fleshing Cattle fat waste, Duck tallow							
230690	Jatropha oil cake, olive residue	35.27	0.08	0.49	0.39	0.74	17.35	6.74
230650	Coconut oil cake	0.00	0.00	0.01	0.00	0.01	0.12	33.90
151219	Sunflower Cooking oil	9.26	0.01	0.19	0.01	0.00	0.07	0.12
151490	Canola oil	0.00	0.016	0.23	0.02	0.02	0.11	0.19
230610	Cotton stalk	10.76	0.03	2.97	0.01	0	3.12	0.43
80130	Cashew nutshell	0.01	1.28	0.03	0.00	0.01	4.83	2.32
230400	Soya bean oil cake	99.23	18.48	1.71	0.13	0.11	1.73	0.00
150710	Soya bean oil	130.82	6.68	0.92	0.01	0	0.01	0.00
440130	pine sawdust	0.06	0.59	2.67	0.01	0.02	0.00	0.60
440121	Long wood sticks	0.00	0.00	2.82	0.00	0.00	0.00	0.00
151800	Vegetable oils	4.41	0.40	0.71	1.13	0.012	0.34	5.91
10410	Sheep manure	0.01	0.00	0.01	0.00	0.03	0.11	0.00
10420	Goat manure	0	0.00	0.21	0.02	0.17	5.13	0.06
230210	Corn cob	14.04	0.99	3.23	0.24	2.78	0.09	0.59

considered countries are illustrated in Figure 3, it illustrates the progress in sophistication level of a country's export basket over the years.

In Figure 3, India's EXPY experienced extreme growth at 49.76%, followed by China, Pakistan, the United States, Brazil, Argentina, and Indonesia, with a growth rate of 44.78%, 36.03%, 35.86%, 30.86%, 27.94%, and 18.66%, respectively during 2002–2019. Surprisingly, China witnessed a low EXPY growth rate despite being a continuously growing economy. Moreover, despite being a solid economy, the United States has a low EXPY growth rate compared to India, China, and Pakistan, indicating a less accumulation of newer productive knowledge because of the saturation of their unexploited products. On the other hand, the continuous development in a country's EXPY value is considered a positive signal for economic growth. This issue is because it indicates the constant addition of more advanced skills and technologies in all products a country export. Furthermore, this continuous increase in EXPY's growth has positive implications for a country's economy by earning more monetary benefits from more sophisticated products.

3.3 Revealed comparative advantage analysis

The revealed comparative advantage (RCA) value of a product depicts whether a country is a feasible exporter of the given product or not. Having the RCA value for a particular product shows that the country considers an essential exporter. Countries with RCA values greater than 1 are considered efficient product exporters and *vice versa*. Table 5 presents the RCA values of the studied countries to appraise biowaste's potential in bioenergy production.

In Table 5, Argentina, China, and India have RCA values of 2.45, 1.32, and 1.02, respectively, for seed, whereas Brazil, the United States, Pakistan, and Indonesia have RCA values of less than 1. Therefore, Argentina, China, and India export non-edible seeds efficiently. The United States is observed as a viable exporter of bagasse due to an RCA of 1.56, while the rest of the studied countries have an RCA of less than 1 for bagasse. Despite the production of large amounts of food waste, it is not exported; therefore, it would be useful to generate energy from it. The United States is also a proactive cellulose exporter, followed by India and Brazil. Interestingly, Pakistan has the highest value of RCA 73.04 for cereal crop waste, including wheat and rice waste. Therefore, cereal waste export is highly beneficial for Pakistan compared to other agricultural countries considered for this study. Furthermore, animal fat, including leather fleshing waste, duck tallow, and cattle fat waste, is also effectively exported by the United States, having a value of 1.28. In contrast, the remaining countries can use their animal fat wastes for energy production to add value.

It is clear from Table 5 that Argentina is the biggest exporter of olive residues among other countries in the present study, followed by India and Indonesia. The reported value of RCA for Argentina is 35.27, whereas the highest value of RCA (33.90) was reported for coconut oil cake in Indonesia. The rest countries have RCA values of less than 1 for coconut oil cake. Waste cooking oil is produced significantly regularly but has no RCA value greater than 1, except for Argentina. The RCA value of waste cooking oil for Argentina is 9.26. Cotton is an essential crop for its use in the textile industry. Therefore, much cotton stalk is produced as biowaste during cotton harvesting. This cotton stalk has the highest value of RCA for Argentina, followed by India and the United States at 10.76, 3.11, and 2.97, respectively, exhibiting their efficiency in exporting cotton stalk.

Soya bean oil and soya bean oil cake can contribute significantly to energy production and a country's economy by export. The highest RCA (99.23) value was observed for soya bean oil cake in Argentina, followed by Brazil and the United States of America. In the case of soya bean oil, the highest value has been noticed for Argentina, 130.8. Therefore, Argentina is an efficient exporter of soya bean oil and soya bean oil cake. All other countries considered for this study can utilize this waste to aid their energy sector. Argentina and Indonesia are also feasible exporters of vegetable oils indicated by their RCA values. Corn cob, which is also produced in large amounts, is efficiently exported by Argentina owing to the RCA value of 14. Pakistan has an RCA value of 2.77 for corn cob; hence it has great potential to export corn cob.

Agricultural countries are not exporting animal waste and manure, despite their existence in significant quantities. Although many other biowastes mentioned in Table 5 have negligible RCA values, they can be used for energy production to strengthen the economy of countries having these wastes. They can also export energy manufactured by utilization of biowastes.

3.4 Global export value linkage with PRODY

The PRODY value of a product illustrates the total income associated with the export of that product by all countries. Table 6 represents the worldwide export values (million USD) and the biowastes' PRODY values. Comparing global export values in Table 6 identifies major exportable biowastes among all considered biowastes. For example, soya bean oil cake is the most exportable biowaste. Its global export value is 24,649 million USD, followed by cashew nutshell, soya bean oil, and pine sawdust 7,289, 7,055, and 5,006, respectively. Conversely, the minimum export value is noticed for grass waste at 0.0028, followed by animal manure and food waste at 0.0225 and 0.08, respectively. The biowastes providing higher global income values are more suitable for export than energy production. In contrast, the products with low-income potential value are more suitable for clean energy production.

3.5 Policy recommendations for industrialization in the selected countries

Successful industrialization and export diversification need prudent industrial policy geared with the government's utmost commitment. In this regard, the PSM approach provides an incredibly instrumental tool named "Policy Map Analysis", which identifies appropriate industrial policy for successful future industrialization considering a country's current production capacity (Qyyum et al., 2022). For example, in Figure 4, the policy map diagram illustrates the four quadrants with different industrial policies.

In Figure 4, the Policy Map Diagram provides four different industry-level policies for various countries, considering the orientation in the product space. Moreover, the "Strategic-Bets" quadrant presents that the country's current export is at a low sophistication level in the peripheral region of product space; therefore, the country has limited prospects for future industrialization. The "Competitiveness-policy" quadrant indicates fair opportunities for the countries in this quadrant, where they must focus on improving existing exportable products. While the "Parsimonious-industrial-policy" quadrant shows higher prospects for future industrialization. Countries in this quadrant need to move to unexploited products closely related to current exported products. Finally, the "Let-it-be" quadrant shows the highest prospects for industrialization. Countries in this quadrant are advantageous because of their strong positioning in the product space. Therefore, these countries can move to produce the remaining unexploited products.

The Policy Map diagram depends on the results of two regression models; i) In the first regression model, the EXPY values of selected countries are run on GDP *per capita* data of the same countries. The obtained residual from the regression is used as the "X-axis" of the Policy Map. ii). In the second regression model, the Open Forest values of the selected countries are run on GDP *per capita*. The obtained residual from the second regression is used in a "Y-axis" of the policy map. The values used in both regression models are in logs of the 30 selected countries.

In Figure 5, this study's PSM Policy Map results revealed that the studied countries are located mainly in two quadrants. Pakistan and Argentina are in the Parsimonious Policy quadrant, where they are suggested to start moving to exportable products with higher relevance and proximity to existing products. Therefore, they have a moderate and decent level of opportunities for their future export diversification and industrialization. While the United States, China, India, Indonesia, and Brazil are based in the most desired Let-it-be Policy quadrant. These countries can move to the remaining unexploited products with much ease. These countries must opt for the PSM-suggested industrial policies to scale their industrialization.

TABLE 6 Global export share of biomass wastes and their PRODY values.

HS code	Biomass	PRODY 2019	Global exports (million USD)
120799	Non-edible seed oil of prunus cerasoides, seed oil of *raphnus raphaniserum* L. Martynia annua seed, Neem seeds, Ceper (*Capparis spinose* L.) seed oil	6256.53	1,244
230320	Sugarcane	22104.2	690
050210	Porcine	27015.8	64
150100	Poultry fattening, chicken fat	41791.9	399
230800	Food waste, vegetable waste	36276.8	0.08
010229	Animal manure, cattle manure slurry, livestock manure	36276.8	0.0225
391290	Cellulose	41098	1,121
121300	Rice straw, wheat straw, wheat husk, rice husk	18412.7	315
150600	Fat fraction from MSW, leather fleshing waste, duck tallow	44438.1	376
230690	Jatropha oil cake, olive residue	6808.89	424
060490	LawnGrass waste	36276.8	0.0028
230650	Coconut oil cake	11284.2	125
151219	Sunflower Cooking oil	20917.8	3156
151490	Canola cooking oil	46735.9	3044
230610	Cotton stalk	4421.27	114
080130	Cashew nutshell	4225.91	7,289
230400	Soya bean oil cake	17047.7	24649
150710	Soya bean oil	18279.8	7,055
440130	pine sawdust	34042.7	5,006
440121	Long wood sticks	22048.8	925
151800	Vegetable oils	32950.4	3253
300212	Animal waste blood and rumen	36276.8	138
010410	Sheep manure	4910.55	1,510
010420	Goat manure	3641.5	182
230210	Corn cob	8751.31	257.6

3.6 Proximity and sophistication analysis in similar studies

The PSM tool is highly effective for various kinds of analysis, including product value, export expansion, determining the existing capability set of a country, and appropriate directions for future growth. It also has useful applications for assessing different research aspects, such as bioenergy, waste reduction, and economic strength.

PSM was used to estimate the potential of different polymers to produce polymeric membranes, which have beneficial applications in industrial processes and environmental remediation. The study outcomes showed the favorable industrialization prospects for United Kingdom, Italy, Poland, and India revealed by proximity and policy analysis. Canada and Indonesia have intermediary opportunities for progress in their polymer membrane industry, whereas Russia and Saudi Arabia face challenges in utilizing unexploited polymers for membrane production (Khan et al., 2022).

A study conducted by Qyyum et al. (2021) used thePSM to evaluate feasible feedstocks and technologies for hydrogen production, a clean energy source. The availability of feedstocks was analyzed on a global level. The results showed that Natural gas is the most exportable hydrogen feedstock with a high global export value. Natural gas, coal, electrical energy, and nuts are exportable. The products with low-income potential are more suitable for energy production than export. This study evaluated exportable feedstocks only for hydrogen production, while the current study assessed the exportable and feasible feedstocks for the different bioenergy forms, including biogas, biodiesel, and bio-oil. Qyyum et al. (2021) evaluated production sophistication and proximity, while the current study focused on product sophistication. The

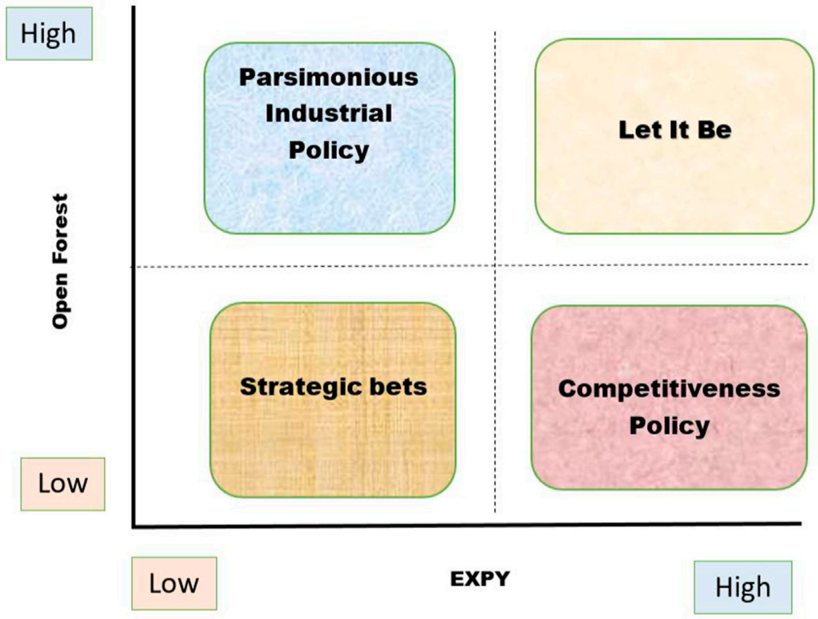

FIGURE 4
Policy Map Diagram for Future Industrialization and export diversification.

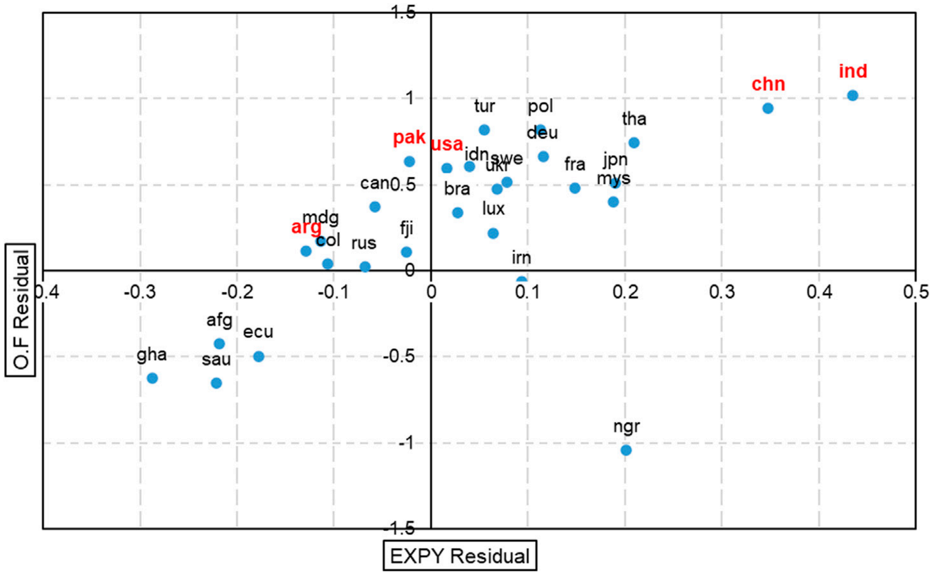

FIGURE 5
PSM, industrial policy map.

current study has evaluated the product sophistication of the country's export basket.

Another study determined the bioenergy production potential of developing countries using the PSM approach. Both sophistication and proximity were measured for considered biowastes, and the study findings showed that Argentina had the most exports (9.59 billion USD) while all the considered biowastes had low-income potential. Thailand was revealed to produce the most sophisticated products, followed by India, Brazil, Ukraine, and Argentina. Adopting bioenergy in Thailand and Ukraine can gain significant monetary benefits (Qyyum et al., 2021). The reported study analyzed the model's relatedness and value-addition aspects, while the current study focused on sophistication. This study emphasizes the conduction of such research works in the future, which will help the economies achieve their economic growth targets and energy efficiency. The current study is significant in economic analysis because of the ecocentric approach. The studies illustrate the validity of the findings of this study and the dynamic role in policy development.

4 Conclusion

This study used the PSM to show biomass-enriched countries an organized and concise pathway to feasible, viable, and sustainable economic development by exporting biowastes and utilizing them to generate energy. The PSM technology is an excellent tool for assessing exportable products based on sophistication and relatedness. Therefore, this study analyzed the level of sophistication of biomass waste products and their major producer countries. The conclusions of the current study are summarized as follows:

- The United States produced the most sophisticated products, followed by China and India in 2019, while India experienced the highest EXPY growth from 2002 to 2019, followed by China, Pakistan, the United States, Brazil, Argentina, and Indonesia. EXPY growth defines the direction for further progress in the industrial sector of any economy. Producing more sophisticated products and utilizing biowastes can strengthen studied countries' economies and reduce the cost of fuel importation for energy needs.
- Product level sophistication analysis illustrated that canola oil has the highest income potential among all selected biowastes, and the considered biomass-enriched countries are inefficient exporters of canola oil, indicating the need to explore their growth opportunities. Canola oil was also found to have a fair share of global export income, indicating the potential monetary benefits of its export. Therefore, all the investigated countries must export canola oil to boost their economy owing to its high-income prospect.
- RCA findings showed that the United States is an efficient exporter of bagasse because of an RCA of 1.56, while the rest of the studied countries have an RCA of less than 1 for bagasse, presented in the results section. Therefore, bagasse can be a valuable feedstock for bioenergy production in these countries because of the large amounts produced there.
- Soya bean oil cake is the most exportable biomass feedstock indicated by the global export value. Therefore, it predicts a substantial benefit for countries having higher production of soya bean oil cake.
- Agricultural countries are not exporting animal waste and manure, despite their existence in significant quantities. Although many other biowastes considered in this research have non-significant RCA values, they can be used for energy production to strengthen the economy of countries having these wastes. They can also export energy manufactured by biowaste utilization.
- PSM policy map analysis revealed that of the studied countries, Pakistan and Argentina are in the Parsimonious quadrant of the Policy Map, with moderate opportunities for future industrialization. However, they must move towards unexploited products closely connected to the current exports.
- The United States of America, China, India, Indonesia, and Brazil are in the most desired Let-It-be quadrant of the policy map, where they can be moved in every direction to explore unexploited materials for industrial growth. They have ample space to diversify their export basket and product line.

4.1 Future directions/recommendations

This research assessed the bioenergy and biomass export potential for selected countries. Other countries with weak economies and energy crises must be analyzed using the PSM tool. It would provide suitable industrial growth directions to resolve the issues mentioned. Non-exportable biomass feedstocks were not included in the analysis, and therefore suitable methodologies must explore their local energy potential. Moreover, proximity analysis must be carried out in further research works.

Author contributions

AA: Data curation, Writing—original draft, Conceptualization, Investigation. SA: Formal Analysis, Validation. MQ: Validation, Visualization, Review and Editing Resources, Conceptualization. D-e-YH: Formal Analysis, Visualization. MM: Formal Analysis, Visualization. MR: Review and Editing Resources. MT: Formal Analysis, Validation. MA: Formal Analysis, Validation. MW: Writing-review and editing. A-SN: Supervision, Formal Analysis, Writing-review and editing, Conceptualization.

Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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Lactic acid production from food waste at an anaerobic digestion biorefinery: effect of digestate recirculation and sucrose supplementation

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Low lactic acid (LA) yields from direct food waste (FW) fermentation restrict this production pathway. However, nitrogen and other nutrients within FW digestate, in combination with sucrose supplementation, may enhance LA production and improve feasibility of fermentation. Therefore, this work aimed to improve LA fermentation from FWs by supplementing nitrogen (0–400 mgN·L^{-1}) as NH_4Cl or digestate and dosing sucrose (0–150 g·L^{-1}) as a low-cost carbohydrate. Overall, NH_4Cl and digestate led to similar improvements in the rate of LA formation (0.03 ± 0.02 and 0.04 ± 0.02 h^{-1} for NH_4Cl and digestate, respectively), but NH_4Cl also improved the final concentration, though effects varied between treatments (5.2 ± 4.6 g·L^{-1}). While digestate altered the community composition and increased diversity, sucrose minimised community diversion from LA, promoted *Lactobacillus* growth at all dosages, and enhanced the final LA concentration from 25 to 30 g·L^{-1} to 59–68 g·L^{-1}, depending on nitrogen dosage and source. Overall, the results highlighted the value of digestate as a nutrient source and sucrose as both community controller and means to enhance the LA concentration in future LA biorefinery concepts.

KEYWORDS

fermentation, lactic acid, food waste, nitrogen, digestate, mixed culture, organic acid

1 Introduction

Food waste (FW) is edible food lost along the supply and consumption chain which is produced in large quantities, and continues to increase with a growing global population (Wolka and Melaku, 2015). Recent estimates have suggested 1.6 billion tonnes of FW is produced globally each year, costing the global economy USD 2.6 trillion per annum (WBA, 2018). Consequently, there is a pressing need to develop closed-loop technologies that beneficially utilise and reduce FW to mitigate associated adverse impacts. Anaerobic digestion (AD) is a technology now widely used to process FWs into renewable biogas energy, and digestate as a fertilizer nutrient source. However, the economic feasibility of FW AD heavily relies on gate-fees, which are subject to government policy or subsidy support

(Bastidas-Oyanedel and Schmidt, 2018). To address this, recent research has proposed and demonstrated pairing AD with lactic acid (LA) production and recovery, aimed at generating additional revenue via a LA-AD biorefinery concept to make FW AD facilities more economically feasible (Kim et al., 2016; Demichelis et al., 2018; Bühlmann et al., 2022). LA, which is generally produced from expensive first-generation feedstocks (e.g., corn and beet) (Malacara-Becerra et al., 2022), is a valuable commodity chemical with uses in various industries including the food, pharmaceutical, and textile industries or as a raw material for the production of biodegradable bioplastics (Kim et al., 2016). To reduce dependency on traditional feedstocks and on food resources, literature has explored LA production from FW and identified production is technically feasible at both lab (Kim et al., 2016; Pleissner et al., 2017) and commercial scale (Bühlmann et al., 2021). However, barriers which limit LA production from FWs still exist including 1) the slow hydrolysis rate of FW (Zhang et al., 2020b), 2) formation of competitor metabolite by-products, and 3) the low LA yield (Yousuf et al., 2018). Arguably, the last listed is currently one of the most significant constraints on the development of commercial LA biorefineries, as it directly limits the final LA concentration achieved, therefore elevating recovery costs (Alves de Oliveira et al., 2018).

FW fermentation to LA is thought to be limited by the inability of LA bacteria to fully utilise the FW substrate. While higher substrate concentrations promote LA production (to a point) (Pleissner et al., 2017; Yousuf et al., 2018; Pu et al., 2019) and the growth of LA bacteria (Pu et al., 2019), overall yields generally reduce with higher substrate concentrations, lowering process efficiency. Pre-treated can enhance LA production (Kwan et al., 2016; Pleissner et al., 2016), likely by increasing substrate bioavailability, but is generally costly to operate (Surendra et al., 2015). Alternatively, FWs may be supplemented with simple carbohydrates, such as sucrose (commonly used LA production Olszewska-Widdrat et al., 2020), to increase the concentration of bioavailable substrate, and hence, elevate the final LA concentration. As the FW context is highly variable (Bühlmann et al., 2021), this approach would be realistic in a FW biorefinery where it would aid in reducing process variability related to the final LA concentration while minimising downstream processing costs.

Nitrogen (N) is essential for synthesising carrier proteins, with ammonium being the preferred N source for all bacteria, including LA bacteria (Zhang et al., 2020b). Recent literature has shown NH_4Cl can be an effective N supplement to enhance FW fermentation to LA, yielding a 2.0–2.4 fold increase in LA concentration following supplementation with 300–400 $mgN \cdot L^{-1}$ (Zhang et al., 2020a; Zhang et al., 2020b). However, FW AD digestate naturally contains elevated ammonium concentrations (3,280–5,000 ppm N (Serna-Maza et al., 2015; Buhlmann et al., 2018)), and so may be a promising low-cost N source for LA fermentation. Limited available research has indeed shown the benefits of digestate on FW fermentation, improving pH stability, increasing microbial diversity, maintaining a low oxidation reduction potential (Wang et al., 2021), or simply being a process water source for LA fermentation following pre-treatment (Zhang et al., 2019). While these reports are promising, they seeded LA fermentation with waste activated sludge (Wang et al., 2021) or a specific strain of LA bacteria (Zhang et al., 2019). However, these inoculum sources either provide resilience in terms of a diverse microbial community (i.e., waste activated sludge), or the targeted performance of a pure culture, but not both. Instead, an adapted inoculum would more likely be used in future FW biorefinery concepts that can reliably produce high LA concentrations, as well as having adequate microbial diversity to accommodate imminent process changes. For this reason, it would be vital to understand the impact of digestate for an adapted mixed culture inoculum.

To address the above knowledge gaps, this study assessed the effect of sucrose and N addition (as digestate or NH_4Cl) on FW LA fermentation, for an acclimatised inoculum, sourced from the first-stage of a commercial two-stage FW AD facility. The study aimed to resolve individual and combined effects of substrate availability (via sucrose addition) and N supplementation, and the distinct effects of N source as digestate or NH_4Cl. The impact on microbial community and fermentation pathways were also explored. The aim was to improve LA fermentation from FWs to enable future LA-AD biorefinery concepts.

2 Methods

2.1 Substrate and inoculum

A synthetic mixed FW feedstock was used in this study and prepared following the recipe of Capson-Tojo et al. (2017) (Supplementary Table S1). Preparation of the FW included maceration, blending, and screening as described by Bühlmann et al. (2022). The synthetic substrate was stored overnight at 1–4°C before use. As per Bühlmann et al. (2021), the inoculum was obtained from the acidic fermentation stage (first-stage) of a commercial-scale two-stage AD facility treating FW. Anaerobic digestate was sourced from an anaerobic digester at the same facility. The inoculum and digestate were stored at 1–4°C before use. Compositional analysis of the prepared synthetic FW, inoculum, and digestate was conducted at the Analytical Reference Laboratory (Perth, Australia) using standard methods (Supplementary Table S2). Reagent grade sucrose (Chem-Supply, Australia; SA030) and analytical reagent grade ammonium chloride (Chem-Supply, Australia; AA049) were used as carbohydrate and model N source in the experiments, respectively.

2.2 Batch fermentation tests

Batch fermentation tests were performed in glass serum vials (250 mL). Vials were filled with 20 mL inoculum and 180 mL synthetic FW, and digestate (see below) or tap water up to a total working volume of 234 mL. Sucrose crystals were added at dosages of 0, 43, 107, or 150 $g_{sucrose} \cdot L_{mixture}^{-1}$ to align with similar conditions of relevant past studies (Reddy et al., 2015). In line with Zhang et al. (2020b) (Section 1), fermentation vessels were supplemented with N at 0, 300, or 400 $mgN \cdot L_{mixture}^{-1}$ (excluding background), added as NH_4Cl powder (Chem-Supply; AA049) or digestate. Levels in each test vial was set by a bi-factorial experimental design, assessing the effects of sucrose and N addition. The tests were conducted in four blocks (Supplementary Table S3), which did introduce an additional time factor, due to progressive aging of the inoculum from block 1 to 4, and this was added as a separate variable in the subsequent analysis. Following reagent addition (as relevant), the test vessels were sealed with a screw top cap plugged with a butyl rubber septum and the headspace was purged with high purity nitrogen, and the fermentation mixtures were adjusted to pH 6.0 and maintained at this pH by the method previously reported elsewhere (Bühlmann et al., 2022). The vessels were then incubated at 50°C for 5 days. A previous study by the authors identified this test pH and temperature as being preferred for LA fermentation by the same adapted inoculum (Bühlmann et al., 2022). pH was measured using a calibrated pH meter (Rowe Scientific, Australia; IP1400 and IP1163). Liquid samples were periodically collected for measurements of LA and other volatile fatty acids (VFAs) (Section 2.3). For this, the vessel was inverted, and a 5 mL sample was extracted and stored in 15 mL centrifuge vials for a maximum of 2 days at 1–4°C prior to analysis (Section 2.3). At the end of fermentation (5 days), an additional 10 mL sample was taken and immediately stored at −20°C for DNA sequencing (Section 2.4).

2.3 Analytical methods

Total solids (TS) and volatile solids (VS) were measured according to Standard Methods (APHA, 1995). Prior to organic acid analysis, each liquid sample was centrifuged at 10,000 g for 10 min and the pellet discarded while the supernatant from the centrifuged sample was collected for analysis. To ensure the organic acid concentrations were within measurement range, predetermined quantities of deionised water were used to dilute the liquid sample. The diluted mixture was then filtered through a 0.45 mm PES Millipore® filter before measurement by HPLC (Bühlmann et al., 2021). LA selectivity was calculated using Eq. 1 after first converting acid concentrations from g·L^{-1} to gCOD·L^{-1} using theoretical COD to mass ratios.

$$LA(\%) = \frac{C_{LA}}{C_{LA} + C_{SA} + C_{AA} + C_{PA} + C_{BA}} \quad (1)$$

where C_{LA}, C_{SA}, C_{AA}, C_{PA}, and C_{BA} denote the LA, succinic acid, acetic acid, propionic acid, and butyric acid concentration (gCOD·L^{-1}), respectively.

2.4 DNA extraction and amplification

Prior to DNA extraction, the frozen whole liquid samples collected on fifth day of fermentation were thawed and vortexed for 15 s. Detailed methods describing DNA extraction, amplification, and screening can be found elsewhere (Bühlmann et al., 2022). The extracted DNA was sequenced at the Australian Centre for Ecogenomics (ACE), The University of Queensland (Brisbane, Australia), on the Illumina® Mi-seq platform.

2.5 Bioinformatics

2.5.1 Taxonomy analysis

Taxonomic assignment used Mothur v1.46.1 (Schloss et al., 2009) using a slightly modified operating procedure. The Silva database (Release v132) was used to assign operational taxonomic units to the processed sequences based on 97% similarity. Detailed description of the methods undertaken for the taxonomy analysis can be found elsewhere (Bühlmann et al., 2022).

2.5.2 Phylogenic investigation of communities by reconstruction of unobserved states (PICRUSt)

For PICRUSt, sequences were again processed using Mothur 1.46.1 (as above) and were assigned GreenGene (gg_13_5) operational taxonomic units based on 97% similarity. For this study, NSTI values ranged from 0.06 ± 0.003 to 0.12 ± 0.019 with an average of 0.099 ± 0.019 s d which is lower than the threshold (0.15) used to indicate similarity with the reference genome database and similar to those for environmental communities (Langille et al., 2013; Louvado et al., 2020). The KEGG database was used to identify all genes (KEGG, 2022).

2.6 Data analysis and statistics

As the inoculum naturally contained LA and other organic acids, all acid yields and concentrations presented below are displayed as net values (i.e. measured values minus the initial concentration at time $t = 0$). All measured data is presented as the mean ± 95% confidence interval (calculated using a two-tailed student t-test) unless otherwise stated. Acid yields were normalized with respect to the initial VS of FW and sucrose added (not including VS from added inoculum or digestate). The rate of LA formation and maximum LA yield were estimated using a first-order plus lag model (Eq. 2).

$$P(t) = P_{max}\left(1 - \exp\left(-k(t - \theta)\right)\right) \quad (2)$$

where $P(t)$ is LA yield ($g_{LA} \cdot g_{VS}^{-1}$) at time t (h), P_{max} is the maximum LA yield ($g_{LA} \cdot g_{VS}^{-1}$), k is the first-order rate constant (h^{-1}), and θ is an initial time lag (h). This analysis was conducted in AQUASIM 2D (Reichert, 1994) and included all data up to the visually identified maximum measured LA yield. Parameter uncertainty was estimated at the 95% confidence limit based on a two-tailed t-test on parameter standard error around the optimum, as determined by AQUASIM 2D. The coefficient of determination (R^2) of the model fits were calculated in Microsoft Excel. Response surface methodology (RSM) was used to identify single and interactive effects of N supplementation and sucrose addition on the maximum LA concentration and rate of LA formation (k values from Eq. 2). Independent variables were sucrose (X_S), N_dosage (X_N), and the N_source (X_{NS}). The raw triplicate data of measured LA concentration (individual observations) and the model estimates of k, were the response variables in separate analyses. For the statistical analysis, the numerical independent variables were normalised linearly (Supplementary Table S3), to ensure each predictor had an equal weighting. N source was included as a categorical variable (X_{NS}; N_Source) in the model (0 = NH_4Cl, 1 = Digestate). As the tests were conducted in runs in time sequence (4 blocks in total), a block factor (R_B) was included within the regression analysis as a continuous factor (1–4) to test

TABLE 1 Kinetic parameters for the first-order model. Errors (±) represent 95% confidence intervals.

Block	Sucrose ($g{\cdot}L^{-1}$)	N ($mgN{\cdot}L^{-1}$)[a]	Max. Time (h)[b]	Max. LA ($g_{LA}{\cdot}L^{-1}$)	Net. Yield ($g_{LA}{\cdot}g_{VS}^{-1}$)[c]	k (h^{-1})	Lag phase (h)
1	0	0	60	25.7 (±2.2)	0.63 (±0.06)	0.08 (±0.03)	9.4 (±2.0)
1	107	0	120	61.7 (±3.2)	0.45 (±0.01)	0.04 (±0.01)	4.3 (±0.8)
1	43	300	72	51.7 (±4.6)	0.62 (±0.03)	0.08 (±0.02)	7.4 (±1.4)
1	150	300	120	60.9 (±5.7)	0.35 (±0.01)	0.04 (±0.01)	6.4 (±1.4)
1	0	400	48	26.1 (±0.6)	0.64 (±0.02)	0.13 (±0.02)	4.1 (±0.7)
1	107	400	120	66.5 (±9.7)	0.50 (±0.01)	0.03 (±0.01)	7.6 (±1.0)
2	43	0	72	44.7 (±3.7)	0.60 (±0.08)	0.04 (±0.02)	10.6 (±2.2)
2	150	0	120	56.2 (±6.7)	0.33 (±0.01)	0.03 (±0.01)	8.9 (±0.9)
2	0	300	84	29.7 (±0.6)	0.69 (±0.03)	0.08 (±0.02)	6.3 (±2.1)
2	107	300	120	66.9 (±5.2)	0.49 (±0.01)	0.04 (±0.01)	7.2 (±0.9)
2	43	400	72	52.8 (±4.9)	0.66 (±0.03)	0.05 (±0.01)	8.5 (±1.3)
2	150	400	96	59.9 (±9.7)	0.35 (±0.01)	0.04 (±0.01)	7.7 (±1.0)
3	0	300_D	48	28.5 (±2.4)	0.69 (±0.05)	0.11 (±0.04)	9.0 (±1.2)
3	43	300_D	60	51.3 (±7.0)	0.62 (±0.03)	0.09 (±0.02)	8.1 (±1.2)
3	107	300_D	72	63.7 (±15.9)	0.49 (±0.03)	0.05 (±0.01)	7.3 (±2.1)
3	0	400_D	60	29.9 (±0.5)	0.72 (±0.05)	0.13 (±0.05)	5.3 (±1.2)
3	43	400_D	60	52.1 (±8.6)	0.64 (±0.02)	0.09 (±0.02)	8.9 (±1.0)
3	150	400_D	84	68.2 (±8.1)	0.40 (±0.02)	0.05 (±0.01)	7.4 (±1.4)
4	150	300_D	96	47.2 (±2.9)	0.29 (±0.01)	0.04 (±0.01)	17.1 (±1.1)
4	107	400_D	72	51.3 (±15.6)	0.38 (±0.02)	0.07 (±0.02)	15.2 (±1.5)

[a]N source is indicated as either NH_4Cl (no subscript) or digestate (subscript D).
[b]Corresponds to the time at which the LA concentration was at its maximum value.
[c]Yield on FW and sucrose.

for aging of the inoculum (Table 1). The standard scores were fitted to a second order regression model (Eq. 3) via least squares regression analysis, as follows:

$$Y = \beta_0 + R_B X_B + (\beta_S X_S) + (\beta_N X_N) + (\beta_{NS} X_{NS}) + (\beta_{S\_N} X_S X_N) + (\beta_{S\_NS} X_S X_{NS}) + (\beta_{N\_NS} X_N X_{NS}) + (\beta_{S^2} X_S^2) + (\beta_{N^2} X_N^2) \quad (3)$$

where β_0 is an intercept, β_S, β_N, and β_{NS} are linear terms, β_{S_N}, β_{S_NS}, and β_{N_NS} are two-way interaction terms, and β_{S2} and β_{N2} are squared effects. Model parameters were determined using the RSM function in R (R Development Core Team, 2022). To avoid overfitting and ensure the most significant parameters remained within the model, the step() function was applied to sequentially remove parameters from the model as previously described (Bühlmann et al., 2021). The 95% confidence intervals for each parameter estimate were determined using confint() in R, and 95% confidence intervals for the model predictions were determined using the predict() function in R. To assess the effects of N supplementation and sucrose addition on other measured organic acids, microbial community composition, and putative metabolic pathways, the RSM described above was further applied to individual VFA concentrations achieved at the visually selected maximum LA concentration, the relative abundance of genera (>1%), and select genes related to LA formation, as respective response variables in separate analyses. The relative abundance of all genes included in the analysis was arbitrarily multiplied by a factor of 1,000 to improve the sensitivity of the model fit. Predictor variables remained unchanged from that described above. To further explore the effects of sucrose, ammonium, and digestate on the product spectrum, a principal component analysis (PCA) was conducted on the VFA concentrations at the peak LA concentration using the prcomp() function in R with scale = T.

3 Results and discussion

3.1 Effect of sucrose and nitrogen addition on lactic acid production

All test conditions showed similar LA production profiles, with the LA concentration initially rising rapidly to an asymptotic final value, with minimal to no subsequent LA depletion observed over the 120 h test period (Figure 1) confirming the test conditions outlined by Bühlmann et al. (2022) promoted LA accumulation. Consequently, all tests were appropriately described by 1st order kinetics with an initial time lag (Table 1). With no sucrose or N

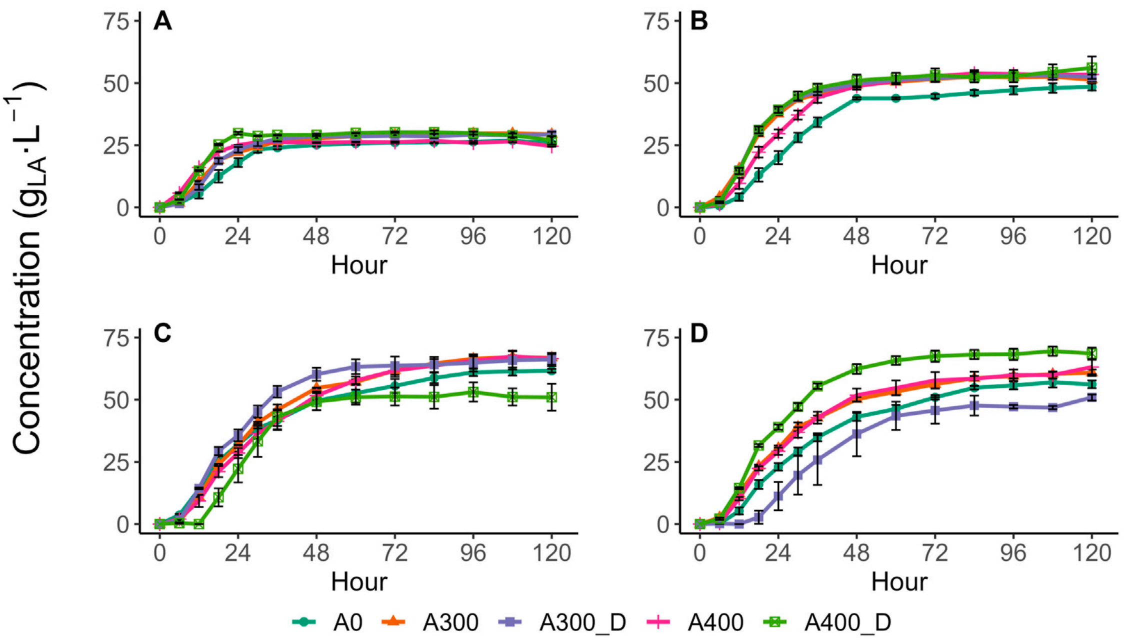

FIGURE 1
Lactic acid production profiles with sucrose amendments of **(A)** 0, **(B)** 43, **(C)** 107, and **(D)** 150 g·L^{-1}. Values are presented as the mean of triplicates ± the standard error.

TABLE 2 Simplified RSM model parameters with associated 95% confidence intervals.

Variable	Symbol	LA concentration model	k (Rate) model
Intercept	$β_0$	32.32 (±4.88)***	0.09 (±0.02)***
Block	R_B	−4.97 (±2.69)***	−0.01 (±0.01)
Sucrose	$β_S$	95.52 (±12.47)***	−0.12 (±0.06)***
N_Amount	$β_N$	5.21 (±3.62)**	0.03 (±0.02)*
N_Source	$β_{NS}$	5.99 (±5.43)*	0.03 (±0.02)*
Sucrose^2	$β_{S2}$	−63.91 (±12.02)***	0.08 (±0.05)**
N_Amount^2	$β_{N2}$	—[a]	—[a]
TWI(Sucrose:Ammonia)	$β_{S\_N}$	—[a]	−0.03 (±0.04)
TWI(Sucrose:N_Source)	$β_{S\_NS}$	—[a]	—[a]
TWI(Ammonia:N_Source)	$β_{N\_NS}$	—[a]	—[a]
Adj.R^2	—	0.89	0.88

[a]Removed by step () function (Section 2.6.1).
***=(p < 0.001), **=(p < 0.01), *=(p < 0.05).

addition, LA accumulated rapidly within the first 24 h, and then slowed significantly, reaching a maximum yield of 0.63 $g_{LA}·g_{VS}^{-1}$ by 60 h (Table 1). This yield was similar to those reported by studies conducted at similar conditions e.g., 0.57 $g_{LA}·g_{VS}^{-1}$ (Yang et al., 2022), 0.58 $g_{LA}·g_{VS}^{-1}$ (Akao et al., 2007), and 0.55 $g_{LA}·g_{VS}^{-1}$ (Bühlmann et al., 2022).

The final simplified RSM models (Supplementary Figures S1, S2) described the observed data well, having an adjusted R^2 of 0.89 and 0.88 (Table 2). No two-way interactions were retained by the step() function, except for a single interaction term within the rate model, albeit that its coefficient estimate was not found to be significant (i.e., not significantly different from zero) (Table 2).

Sucrose displayed a strong positive linear effect and a strong negative second-order effect on LA concentration (Table 2), indicating that LA concentration was increased by sucrose addition up to a certain dosage (Table 1), but higher dosages led to a reduction in

LA concentration, likely due to substrate inhibition. In contrast, sucrose displayed a strong negative linear effect on LA formation rate (k), indicating rate inhibition at all levels. Sucrose also had a minor positive second-order effect on k (Table 2). *N_Amount* retained a positive linear effect on both LA concentration (and yield) and k, with the model estimating an incremental concentration increase of 5.2 ± 4.6 g·L^{-1} LA at the highest level (400 mgN·L^{-1}) compared to a modelled base case with no sucrose or N addition (i.e., 27.3 ± 3.4 gLA·L^{-1}). Similar studies by Zhang et al. (2020b); Zhang et al. (2020a) outlined a 2–2.4 fold increase in LA concentration resulting from N supplementation using NH_4Cl, much higher than that observed in the current study (max 1.2-fold). This difference may be, at least partially, due to different inoculum sources and FW utilised. The seed material has been suggested to be a crucial in the development of relevant metabolic pathways, production of LA, and evolution of competing biological processes (Wang et al., 2014; Tang et al., 2017; Arras et al., 2019). Both Zhang et al. (2020b) and Zhang et al. (2020a) utilised waste activated sludge for inoculation and reported NH_4Cl significantly increasing the relative abundance of LA producers. However, the adapted mixed inoculum utilised in the current study had LA bacteria naturally dominant (Section 3.3), even in the 0 N test (Section 3.3). The use of an adapted inoculum could have promoted LA production, leading to a lower overall response from N addition as NH_4Cl. A lower background N concentration (more limited N conditions) could also have caused the larger response to N observed by Zhang et al. (2020b); Zhang et al. (2020a) but they did not report compositional data for their FW, so background N levels in their study could not be estimated. The RSM model showed that digestate led to a 1.3 ± 4.5 g L^{-1} change in the LA concentration, compared to the modelled base case, and at the highest digestate level resulted in an increased k of 0.13 ± 0.01 h^{-1}, compared to the base case of 0.08 ± 0.02 h^{-1}. Similar to the current study; Wang et al. (2021) outlined that industrial digestate improved LA fermentation when utilised at a ratio of 0.2 $L_{digestate}$·$L_{feedstock}^{-1}$ (current study used a ratio of 0.19 $L_{digestate}$·$L_{feedstock}^{-1}$, at 400 mgN·L^{-1}). While digestate contains high concentrations of NH_4^+-N, its complex matrix also contains various other nutrients (Supplementary Table S2) and additional fermentative bacteria which may further aide LA fermentation or increase substrate utilisation for alternative organic acids. The second-order effect for N was not significant in either of the RSM models (Table 2), suggesting that, unlike for sucrose, inhibitory concentrations for NH_4Cl and digestate were not reached in the current study. Previous research by Zhang et al. (2020b) outlined a reduction in LA production with NH_4^+-N supplementation above 500 mgN·L^{-1}, which is higher than the maximum added dose in the current study (400 mgN·L^{-1}). Limited research is available exploring LA fermentation with added digestate, however, it has been suggested that excessive ammonia-N, zinc, iron, sulphur, and manganese within digestate could inhibit *Lactobacillus casei* during batch LA fermentation from starch, when the digestate is used as a process water source (Zhang et al., 2019). Comparably, Wang et al. (2021) suggested that excessively high dosages of digestate would alter fermentation pathways, lowering LA selectively; however, these same authors did not report any inhibition of fermentation, possibly because of relatively lower digestate dosages and a mixed culture utilised for fermentation in their study.

Overall, the net LA yield was highest at the lowest sucrose level but was generally improved, albeit by small increments, by N supplementation at all N dosage rates (Table 1). The N effect is supported by RSM results in Table 2. With NH_4Cl, at the lowest sucrose level, the net LA yield was at its maximum for the FW sucrose mixture, regardless of N dosage. With digestate, similar net yields were achieved at the lowest sucrose level, albeit higher variability in the measured max LA concentration were noted (Table 1). At the higher sucrose dosage of 107 g L^{-1}, the net LA yield reduced, possibly due to the previously mentioned substrate inhibition, however, all yields were similar regardless of N dosage or source, apart from 400 mgN·L^{-1} with digestate, which saw a 24% reduction in net LA yield, as compared to 400 mgN·L^{-1} with NH_4Cl. At the highest sucrose level, net yields were similar across treatments (Table 1), apart from 300 mgN·L^{-1} with digestate, which saw a 17% reduction in net yield, as compared to 300 mgN·L^{-1} as NH_4Cl.

3.2 Product spectrum

Due to the complex composition of FW and presence of a mixed microbial community (Section 3.3), fermentation of mixed FW for LA will also lead to the production of competitor organic acids through the competitive uptake of available substrate or by the consumption of LA as the substrate, resulting in a lower LA yield/selectivity (Arras et al., 2019). To minimise downstream processing costs and increase LA output, it is important to tune LA fermentation to minimise the production of competitor acids wherever possible.

The observed production of various competitor VFAs varied dynamically with sucrose, NH_4Cl, and digestate addition. Acetic acid and propionic acid production profiles differed the most between treatments, displaying variations in both apparent production rate and maximum concentration achieved (Figures 2A, C). In contrast, succinic and butyric acid production generally followed similar production profiles with different treatments with production peaking in select treatments (Figures 2B, D).

As LA would likely be recovered at an LA-AD facility at its peak concentration (Table 1), it was appropriate to carry out an analysis of variable effects on VFA concentrations measured for samples of each experiment for which LA concentration was at its maximum. The resulting RSM model (Table 3) interestingly showed that while *N_Source* was retained within all models by the step() function, its effect was not significant in the acetic and propionic acid models. However, acetic acid was generally observed to be higher in the digestate treatments (Figure 2A; Supplementary Table S4), indicating digestate played some role in promoting acetic acid production. Therefore, a PCA was conducted on the same data set (Figure 3) to further explore the variable impacts on the product spectrum.

The PCA displayed a strong relationship between sucrose addition and acetic acid production, which is in agreement with the RSM model (Table 3). However, while *N_Source* was non-significant within the model, a clear relationship between NH_4Cl and digestate was observed, with digestate increasing acetic acid production.

The highest competitor VFA levels (22.1 gCOD·L^{-1}) were observed at 150 g·L^{-1} sucrose and 400 mgN·L^{-1} as digestate. In contrast only 3.9 $gCOD_{VFA}$·L^{-1} of VFAs were produced with 43 g L^{-1} sucrose and no N added, increasing to only 5.5 gCOD·L^{-1} with 400 mgN·L^{-1} as NH_4Cl. Compared to the modelled base case (i.e., no sucrose, no added N), LA selectivity improved at these conditions, achieving 91–92% LA as

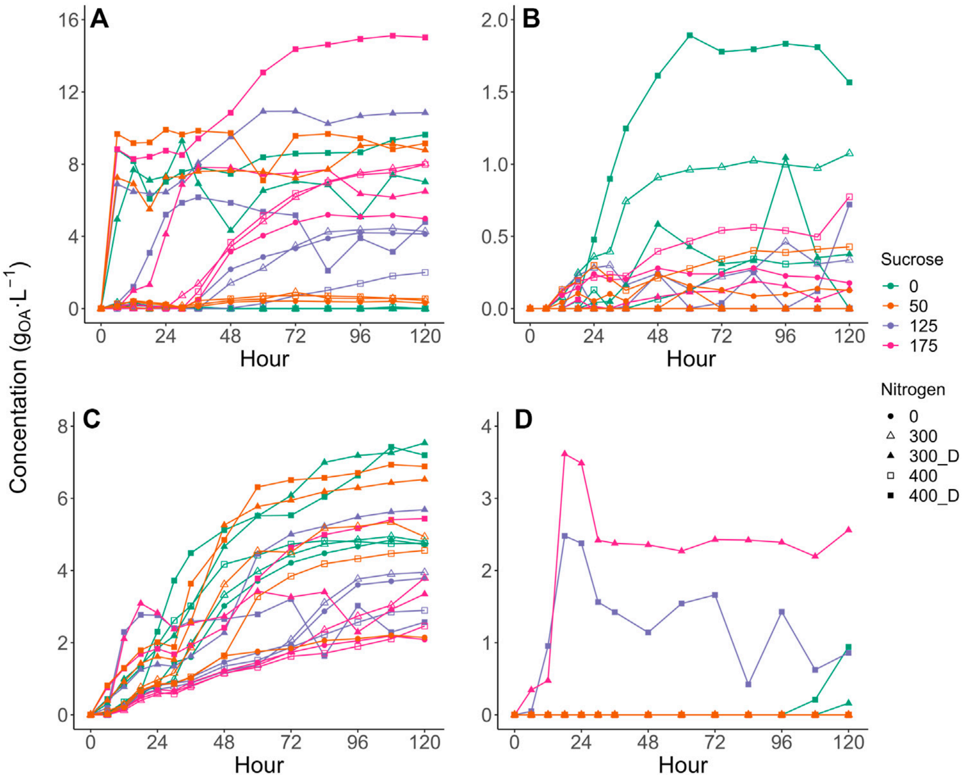

FIGURE 2
Production curves of **(A)** Acetic acid, **(B)** Succinic Acid, **(C)** Propionic Acid, and **(D)** Butyric Acid. Values are presented as the mean of triplicates. Error bars were removed to improve readability. Please see Supplementary Figure S9 in the Supplementary Material for expanded plot with error bars.

TABLE 3 Simplified RSM model parameters for competitor VFAs given with ±95% confidence intervals.

Variable	Succinic	Acetic	Propionic	Butyric
Intercept	−0.19 (±0.37)	3.18 (±2.47)*	4.49 (±1.1)***	−0.74 (±0.61)*
Block	0.37 (±0.19)***	−2.10 (±1.40)**	−1.13 (±0.52)***	0.52 (±0.36)**
Sucrose	−1.87 (±0.88)***	—[a]	1.39 (±2.66)	−0.08 (±0.54)
N_Amount	0.20 (±0.26)	0.40 (±1.95)	7.05 (±3.54)***	—[a]
N_Source	−1.03 (±1.03)*	3.90 (±7.7)	−2.69 (±3.82)	−0.95 (±0.76)*
$Sucrose^2$	1.69 (±0.83)***	6.21 (±1.67)***	−1.60 (±2.30)	—[a]
N_Amount^2	—[a]	—[a]	−6.02 (±3.57)**	—[a]
TWI(Sucrose:Ammonia)	—[a]	—[a]	−1.37 (±1.66)	—[a]
TWI(Sucrose:N_Source)	−1.04 (±0.46)***	—[a]	—[a]	1.08 (±0.86)*
TWI(Ammonia:N_Source)	1.12 (±1.1)*	5.68 (±8.33)	6.47 (±4.2)**	—[a]
Adj.R^2	0.54	0.67	0.6	0.34

[a]Removed by step () function (Section 2.6.1).
***=($p < 0.001$), **=($p < 0.01$), *=($p < 0.05$).

compared to 83% at base case. All digestate treatments produced more competitor VFAs than those without added N or with NH_4Cl (Supplementary Table S4). However, like NH_4Cl, higher sucrose dosages increased the production of LA (Figure 3) and, while competitor VFA production also increased, sucrose generally increased LA production to a larger extent than that of competitor acids (Tables 2, 3), increasing the overall LA selectivity. Previous work by Zhang et al. (2020b) suggested proteins present within waste

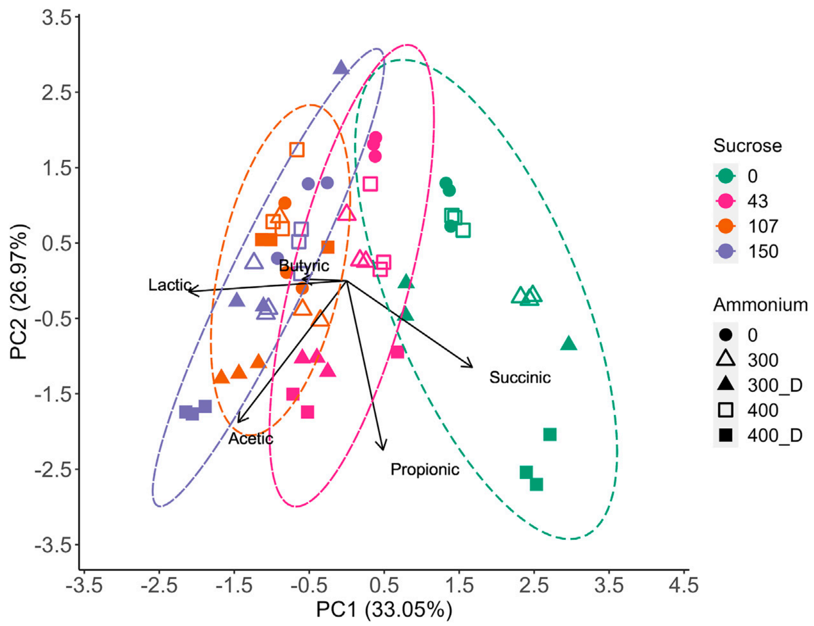

FIGURE 3
Principal Component Analysis (PCA) showing the influence of sucrose, NH_4Cl, and digestate on the product spectrum at the peak LA concentration for each treatment level. Ellipses represent the 95% confidence interval for the sucrose impact on the product spectrum.

activated sludge can be a substrate for VFA production, elevating undesired metabolite levels, which may have occurred in this study. However, as the digestate was not sterilised in the current study, alternative fermentative bacteria introduced with the digestate likely competed with LA bacteria for substrate and contributed to the observed increase in VFA production (Section 3.3). Butyric acid production generally remained low for all treatments, except for some digestate containing vessels with sucrose at 107–150 g·L $^{-1}$ (Supplementary Figure S7). At 400 mgN·L^{-1} without sucrose, butyric acid production appeared to be accompanied by a slight reduction in the LA yield at the end of fermentation (Supplementary Figure S3E), suggesting the initiation of LA consumption for butyric acid, which as been previously observed for this inoculum (Bühlmann et al., 2022). Previous research has suggested that the formation of butyric acid from LA may be related to substrate availability (Detman et al., 2019; Hoelzle et al., 2021), with the addition of substrate shown to prevent the conversion of LA to butyric acid (Hoelzle et al., 2021). While it cannot be confirmed that butyrate production was prevented through sucrose addition in the current study, butyric acid was not detected with sucrose and NH_4Cl addition and was only observed in some digestate containing treatments (Figure 2D), which could be related to changes in microbial community composition (Section 3.3).

3.3 Microbial community analysis

The most abundant phyla across all treatments were Firmicutes (66–99%), with other minor phyla including Actinobacteria (0.2–29%), Bacteroidetes (0.0–2.4%), Euryarchaeota (0–2.0%), Chloroflexi (0.0–1.4%), and Thermotogae (0–0.8%) (Supplementary Figure S7). While all phyla were detected in nearly all treatments, digestate likely acted as a secondary inoculum. For example, Bacteroidetes, Thermotogae, Actinobacteria, Euryarchaeota, and Chloroflexi were primarily enriched in the digestate treatments (Supplementary Figure S7). Chloroflexi, and Bacteroidetes are commonly found within FW AD systems (St-Pierre and Wright, 2014; Buhlmann et al., 2018), and were likely inoculated when digestate was added to test vessels. Thermotogae have been reported to form a syntrophic relationship with hydrogenotrophic methanogens for the oxidation of acetate during methanogenesis at high total ammoniacal N concentrations (Li et al., 2016). The digesters from which digestate was sourced in the current study, have been reported to operate at elevated total ammoniacal N concentrations (Buhlmann et al., 2018), which could have caused an increased relative abundance of Thermotogae in the digestate treatments.

Lactobacillus was the dominant genus within all treatments but showed a reduced relative abundance in the RSM model when digestate was added without sucrose (Supplementary Table S5), down to 50% and 30% with digestate dosages of 300 and 400 mgN·L^{-1}, respectively (Figure 4). *Clostridium Sensu Stricto 15* (*CSS_15*) proliferated with the addition of 400 mgN·L^{-1} as NH_4Cl, while *Bifidobacterium*, *CSS_18*, and *Proteiniphilum*, primarily grew in digestate containing environments without sucrose (Sucrose and N_Source effects, Supplementary Table S5). Research detailing the metabolic process of *CSS_15* are limited, however, *Clostridium* include a variety of bacteria which are specialised in utilising multiple sugars to generate methanogenic precursors, such as acetate, butyrate, carbon dioxide, and hydrogen (Song et al., 2021). *Bifidobacterium* form short chain fatty acids (e.g., LA and acetate) from carbohydrates and may form a syntrophy with *Clostridium* for butyrate formation (Xiong et al., 2019), which

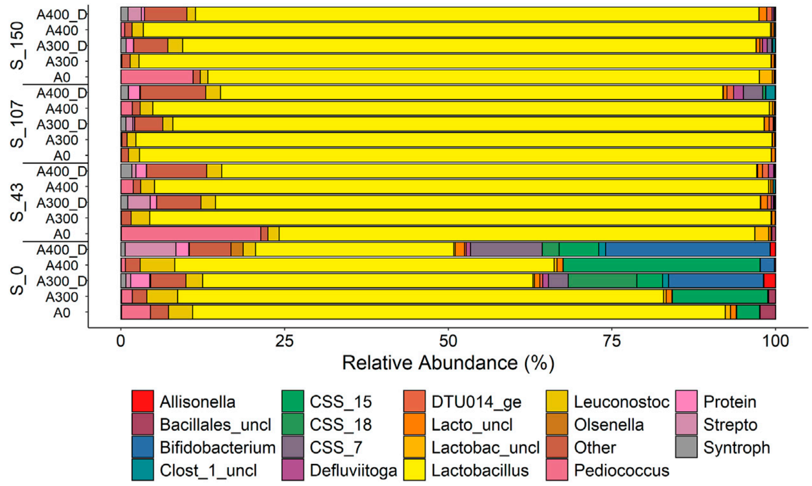

FIGURE 4
Relative abundance of microbial genera (>1%) following 5-days of FW fermentation supplemented with sucrose and N (NH_4Cl or digestate). Sucrose level is denoted by an "S" followed by the initial supplement concentration, while supplemented N is denoted by an "A" and N added as digestate is denoted by "D". The names of various genera have been shorted to fit them within the legend. Full names are as follows: Bifid (Bifidobacteriaceae), Clost_1 (Clostridiaceae_1), CSS (Clostridium sensu stricto), Lacto (Lactobacillales), Lactobac (Lactobacillaceae), Protein (Proteiniphilum), Strepto (Streptococcus), and Syntroph (Syntrophaceticus). All genera containing "uncl" were unclassified.

may have occurred in this study (Section 3.2). *Proteiniphilum* plays an important role in protein degradation and has been isolated from biogas plants, particularly those treating FW, brewery waste, and wheat straw (Orellana et al., 2022), such as the plant from where the digestate was sourced (Bühlmann et al., 2021).

For both NH_4Cl and digestate treatments, sugar addition at any level significantly suppressed the growth of the flanking community and promoted the growth of *Lactobacillus* (Supplementary Table S5; Figure 4). While research exploring sugar supplementation during FW fermentation could not be found, previous studies have reported that higher substrate concentrations promote LA production and the growth of LA bacteria during FW fermentation (Pu et al., 2019; Simonetti et al., 2021).

3.4 Functional gene analysis

To better understand the impact of sucrose and N supplementation on metabolic pathways for LA production, a conceptual pathway diagram was constructed based on various relevant metabolic pathways (Supplementary Figure S8). The resulting predicted genes from the PICRUSt analysis were then utilised to explore the effect of sucrose and N addition on relevant microbial degradation pathways. The *in-silco* prediction suggested LA production likely occurred through multiple pathways working in tandem. The abundance of Lactate dehydrogenase (*LDH*) tended to increase with the addition of digestate ($p < 0.001$; Supplementary Table S6) which aligns with the increased LA concentration associated with those treatments (Section 3.1). Genes utilised within the glycine, serine and threonine metabolism associated with the production of methylglyoxal, namely *AOC3* and *MAO*, fluctuated with the addition of sucrose and N (Supplementary Table S6). *AOC3* was primarily enriched with NH_4Cl addition, though the combined addition of digestate and sucrose increased the relative abundance of this gene ($p < 0.001$). In contrast, the combination of sucrose and digestate tended to reduce the relative abundance of *MAO* ($p = 0.04$; Supplementary Table S6). Methylglyoxal is a toxic compound produced from glycolysis when glucose consumption surpasses the rate of phosphate uptake during the conversion of dihydroxyacetone-P (Hoelzle et al., 2021). *Lactobacillus* strains generally carry out methylglyoxal detoxification through the production of either acetol (Hydroxyacetone) or 1,2-propanediol (Gandhi et al., 2018), of which a gene related to acetol formation (*yqhD*) was predicted to be present, but tended to reduce in relative abundance with sucrose ($p < 0.001$) or N addition ($p = 0.03$), and this effect was exacerbated with digestate ($p < 0.001$). Detoxification can also occur through the glyoxalase pathway which consists of two enzymes, *GLO1* and *gloB*, which convert the toxic methylglyoxal to D-LA (Jain et al., 2018). The high relative abundance of *gloB* in this study, as compared to alternate LA producing genes (accounting for 81–95% of all identified LA producing genes, i.e., *gloB*, *ldhA*, *dld*, *pct*, *ldh*, and *aldA*), suggests methylglyoxal detoxification could have been a major pathway for LA production at the test conditions. However, the relative abundance of *GLO1* primarily reduced with higher sucrose dosages ($p < 0.001$; Supplementary Table S6). Reduced abundance of this gene may have reduced the capacity of the fermentation system to reduce methylglyoxal, possibly leading to its accumulation to toxic levels at higher sucrose dosages. Such accumulation may have contributed to the reduced LA yields observed at higher sucrose dosages (Section 3.1).

3.5 The integrated LA-AD biorefinery

Overall, digestate effectively improved the production of LA from FWs but introduced process variability (increased error bar size; Supplementary Figures S3–S6), increased microbial diversity, and increased the production of alternate organic acids. However, in combination with sucrose, digestate was an effective nutrient source which improved the rate and production of LA (Table 2), while having minimal impact on the microbial community (Figure 4). Furthermore, in an industrial context, digestate could form a valuable process water source to reduce the demand on valuable fresh-water resources, reducing operational costs and environmental impacts from FW processing. Moreover, digestate is commonly considered a liability to many AD facilities, generally requiring pre-treatment (primarily solid-liquid separation) before agricultural land application and tends to be expensive to transport and apply to land because of its moisture content (Turnley et al., 2016; Lu and Xu, 2021). However, the results from the current study have shown that, in combination with sucrose supplementation, digestate recirculation can boost LA fermentation from LA-AD biorefineries for negligible cost (i.e., installation of piping).

In contrast, while sucrose increased the LA concentration and steered fermentation towards LA in the presence of digestate, it is important to explore additional costs associated with its use. Utilising the RSM developed in Section 3.1, the cost to implement sucrose supplementation was estimated at 0.54, 0.85, and 1.33 $AUD{\cdot}kg_{LA}^{-1}$ (based on additional LA produced) for scaled sucrose levels of 0.29, 0.71, and 1, respectively, and assuming a sucrose price of 0.28 $AUD{\cdot}kg^{-1}$ (0.21 $USD{\cdot}kg^{-1}$ (Efe et al., 2013)). With the price of LA previously estimated at 2.18 $AUD{\cdot}kg_{60wt\%\ LA}^{-1}$ (1.36 $Euro{\cdot}kg_{60wt\%\ LA}^{-1}$ (Demichelis et al., 2018)) and assuming a recovery efficiency of 51% (Demichelis et al., 2018), the additional cost of sucrose would be easily justified by the value of additional LA product, at all sucrose dosages applied in the current study. Adaptation of the fermentation inoculum to higher sucrose dosages may also improve LA yield on sucrose, thereby increasing the associated economic benefits. However, it is important to note that while fermentation efficiency may have been improved, a fraction of the added sucrose will remain in the fermentation broth. Downstream AD of solid and liquid extraction residues would likely utilise this residual sucrose for methane generation, which can further offset energy requirements of LA separation and recovery, reducing the demand for grid-based fossil-fuel power. This can be important because recovery of LA is known to be energy intensive (Din et al., 2021).

4 Conclusion

Overall, the complex FW mixture was effectively fermented for LA production, which was aided by addition of digestate as a relatively low-value N source and supplementing with sucrose as a readily bioavailable substrate. Digestate addition improved both the rate and yield of LA production. However, digestate also increased the microbial diversity which promoted the production of competitor organic acids. Sucrose effectively improved the LA concentration, steered the product spectrum towards LA, and selectively promoted the growth of the desired *Lactobacillus,* while suppressing the flanking community when either NH_4Cl or digestate were added. A simple evaluation indicated that the value of additional LA produced with sucrose addition outweighed the costs of the sucrose. Overall, the results indicated that an integrated LA-AD biorefinery can effectively implement digestate recirculation without prior pre-treatment or sterilisation, and benefit from sucrose supplementation as a relatively low-value carbon source. This could increase the viability of future LA-AD biorefinery concepts. Future studies should explore the detailed economic impacts of sucrose supplementation and digestate recirculation LA-Ad biorefineries.

Data availability statement

The original contributions presented in the study are publicly available. This data can be found here: [https://www.ncbi.nlm.nih.gov/bioproject/945514].

Author contributions

All authors contributed to the conception and design of the study, CB organise the database, CB and DB performed the statistical analysis, CB wrote the first draft of the manuscript, all authors contributed to the revision, reading, writing of the subsequent drafts of the manuscript, and approval of the final manuscript version. All authors contributed to the article and approved the submitted version.

Conflict of interest

Author BM was employed by Richgro Garden Products.

The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Publisher's note

Supplementary material

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fbioe.2023.1177739/full#supplementary-material

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