Environmental Technology & Innovation 30 (2023) 103100

Contents lists available at ScienceDirect

Environmental Technology & Innovation

journal homepage: www.elsevier.com/locate/eti

Emerging trends in role and significance of biochar in gaseous biofuels production

Ranjna Sirohi [a,1], V. Vivekanand [b,1], Ashutosh Kumar Pandey [c,1], Ayon Tarafdar [d], Mukesh Kumar Awasthi [e], Amita Shakya [f], Sang Hyoun Kim [c,*], Sang Jun Sim [g,*], Hoang A. Tuan [h], Ashok Pandey [i,j,**]

[a] School of Health Sciences and Technology, University of Petroleum and Energy Studies, Dehradun 248 007, Uttarakhand, India
[b] Center for Energy & Environment, Malaviya National Institute of Technology, Jaipur 302 017, Rajasthan, India
[c] Department of Civil and Environmental Engineering, Yonsei University, Seoul, Republic of Korea
[d] Livestock Production and Management Section, ICAR-Indian Veterinary Research Institute, Bareilly 243 122, Uttar Pradesh, India
[e] College of Natural Resources and Environment, Northwest A&F University, Yangling 712100, Shaanxi Province, China
[f] Amity Institute of Biotechnology, Amity University Chhattisgarh, Raipur, India
[g] Department of Chemical and Biological Engineering, Korea University, Seoul, Republic of Korea
[h] Institute of Engineering, HUTECH, University, Ho Chi Minh 72300, Viet Nam
[i] Centre for Innovation and Translational Research, CSIR-Indian Institute of Toxicology Research, Lucknow 226 001, Uttar Pradesh, India
[j] Sustainability Cluster, School of Engineering, University of Petroleum and Energy Studies, Dehradun 248 007, Uttarakhand, India

ARTICLE INFO

Article history:
Received 27 January 2023
Received in revised form 5 March 2023
Accepted 6 March 2023
Available online 9 March 2023

Keywords:
Anaerobic digestion
Biochar
Biogas
Biohydrogen
Photo and dark fermentation

ABSTRACT

Transition from fossil fuels to non-conventional sources is needed to tackle the global energy crisis and environment related issues. Thus, the use of organic waste generated from various industrial sectors can help to produce gaseous fuels through anaerobic digestion, photo and dark fermentation, and other biochemical strategies. Current biogas and biohydrogen production practices are less efficient and require additional interventions for biofuel yield improvement. In this regard, adding biochar has shown to enhancing gaseous fuel yield by about 5%–400%, adsorbing inhibitors such as ammonia, pathogens, hydrogen sulfide, and activating gas-producing mesophilic and thermophilic microorganisms. This review provides recent updates and future perspectives associated with the effect of biochar on gaseous biofuel production and its underlying mechanism. Further, there is a need for establishing a circular bioeconomy approach for biochar production and utilization through a 'waste-chain', for which a techno-economic analysis and life-cycle assessment are required.
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1. Introduction

Exponential growth of the global population has become the primary concern which is one of the reasons for environmental issues, mainly global warming, wastewater, food, and energy crisis, generation of wastes, and exploitation

* Corresponding authors.
** Corresponding author at: Centre for Innovation and Translational Research, CSIR-Indian Institute of Toxicology Research, Lucknow 226 001, Uttar Pradesh, India.
E-mail addresses: sanghkim@yonsei.ac.kr (S.H. Kim), simsj@korea.ac.kr (S.J. Sim), ashok.pandey1@iitr.res.in, ashokpandey1956@gmail.com (A. Pandey).

[1] Contributed equally and share first authorship.

https://doi.org/10.1016/j.eti.2023.103100
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of biodiversity (Elsayed et al., 2020; Yang et al., 2019). Additionally, ∼75%–80% of increased energy demands are being achieved by using fossil fuels which lead to emissions like carbon dioxide (CO_2), particulates, smoke, oxide of nitrogen (NO_x), etc. Thus, there is a requirement to implement renewable energy technologies such as bioenergy, solar energy, wind energy, and geothermal, which can mitigate adverse effects on the environment (Kongto et al., 2022; Singh and Kumar, 2022). To come over with these issues, anaerobic digestion (Singh et al., 2022); photo and dark fermentation (Mahmoodi-Eshkaftaki and Mockaitis, 2022); direct and indirect photolysis is the biochemical methods can be used to treat food waste (Pan et al., 2021), animal waste and municipal sewage waste (MSW). Anaerobic digestion (AD) is a promising process used for biogas production by utilizing biodegradable feedstocks in an oxygen-free environment (Awasthi et al., 2018).

Similarly, photo and dark fermentation (PDF) can be employed to generate biohydrogen (bio-H_2) from different types of feedstocks in the absence of oxygen (Toledo-Cervantes et al., 2020). Biogas and bio-H_2 are renewable gaseous fuels that can substitute for fossil fuels. Moreover, bio-H_2 is a high calorific value (∼120 MJ/kg) fuel means it is higher than other hydrocarbon fuels like ethanol (29.9 MJ/kg), natural gas (50 MJ/kg), and biodiesel (37 MJ/kg). Biogas contains significant constituent methane (CH_4), which can compete with and reduce the dependence on natural gas for power plants. Numerous advantages of AD and PDF, are such as reduction in carbon footprints, utilization of nutrients present in the waste, fewer emissions than fossil fuels, sustainable processes, etc. (Muri et al., 2018). However, the methods used to produce bio-H_2 are still not economical and are under-developing. On the other side, biogas has numerous applications, used as cooking gas, vehicular fuel, and in combined heat and power plants. However, the AD process has encountered some issues in treating different feedstocks, such as ammonia inhibition from chicken manure due to protein and urea content (Kizito et al., 2022), poor buffer capacity, accumulation of high volatile fatty acid (VFA) and variable process stability (Chen et al., 2021). These issues affect the yield and quality of biogas.

Additionally, bio-H_2 production from different feedstocks by anaerobic fermentation has numerous problematic issues, such as required controlled conditions, low yield, and process efficiency (Bu et al., 2021). In this regard, various additives such as nanomaterials, metal monomers, metal oxides, and biochar have been supplemented to improve AD and PDF processes (Kaushal and Baitha, 2021; Yang and Wang, 2018a,b). Among all additives, biochar is a promising and cost-effective additive that has numerous advantages, such as being used as an absorbent for contamination from antibiotics residues (Mitchell et al., 2015), oleaginous compound (Sohaimi et al., 2017), phosphate, ammonium and metal ions dispersed in wastewater (Jin et al., 2016). Also, biochar has higher porosity which provides the surface for accumulating microorganisms.

Biochar is a carbon-rich material with a high surface area, porous structure, and excellent surface functionalities obtained by the thermochemical treatment of biomass under an oxygen-limited environment. Biochar presents a great potential to manage the organic bio-waste of plant and animal origin by using them as raw materials for biochar production (Shakya and Ahmad, 2020; Raj et al., 2021a). By means of biochar production, CO_2 and CH_4 that could be released to the environment due to biomass decay in landfill sites are captured in the form of solid biochar, which helps in climate change mitigation. This practice could reduce the extra burden of bio-waste and associated pollution factors such as GHG emission, disposal, and landfill issues. Reusing different waste biomass for biochar production could be a conscious environmental management strategy to manage the residual waste and reduce the associated health and environmental risks (Zhang et al., 2019). Biochar research has discovered that high organic carbon-containing biochar-type substances help sustain fertility in ''Amazonian Dark Earths'', locally known as Terra Preta de Indio (Lehmann, 2007; Lehmann and Joseph, 2015). Since carbon content in biochar is highly stable (half-life >100–1000 years), it was primarily used as a tool for carbon sequestration in soil (Spokas, 2010). A decade earlier, biochar application was majorly focused on carbon sequestration, waste management, soil amendment and as adsorbent for various pollutant remediation/immobilization from soil and water (Ahmad et al., 2013; Raj et al., 2021b). However, recent research has shifted to explore more non-conventional usage of biochar beyond carbon storage, soil, and adsorptive applications (Bolan et al., 2022; Qian et al., 2015).

The composition of biochar is not entirely carbon content; its a rational combination of carbon (C), hydrogen (H), oxygen (O), and nitrogen (N) with elements like S, P, K, Ca, Mg, Na, and Si in the ash fraction of biochar (Chen et al., 2019). The physicochemical properties of the biochar that govern the application diversity of biochar significantly depend on the type of thermal treatment, processing conditions (heating temperature, retention time, heating rate, pressure), and feedstock (Enders et al., 2012). An extensive range of lignocellulosic biomasses, including agro-food processing waste, aquaculture waste, invasive plants, forestry residues, paper, and pulp processing waste, as well as non-conventional organic wastes such as municipal sewage sludge, animal cascade, bird/animal manure, was used to prepare biochars and utilized it in various applications (Behnam and Firouzi, 2022). Interestingly, each biochar acts/reacts differently towards the end application due to variations in the lignocellulosic content of the biomass and preparation conditions, which ultimately influence the characteristics of the biochar (Shakya et al., 2022).

The high treatment temperature increases the structural complexity of biochar, resulting in the creation of more complex fused ring organic carbon structures through lignocellulosic biomass breakdown and microstructural rearrangement (Lehmann and Joseph, 2015). Besides biochar (solid), non-condensable gases (syngas) and combustible liquids as bio-oil are also produced during the thermal processing of biomass. During the biomass to the biochar conversion process, many transition phases occur, resulting in the development of transition char (dehydrogenated, depolymerized), amorphous char (condensed hetero intermediate), composite char (stable organics), and turbostratic char (graphene like) (Keiluweit et al., 2010). The carbon content is the most sought property of biochar, and IBI categorized biochar based on their carbon content as class 1: C content ≥60%; class 2: C content ≥30% to ≤60%, and class 3: ≥10% to ≤30% (IBI, 2012). Biochar is produced using thermochemical processes like dry pyrolysis, gasification, torrefaction, and hydrothermal carbonization (wet pyrolysis). During thermal processing, biochar has a much higher specific surface area, porosity, stability, and functionality (cation exchange capacity, ash content, alkalinity, hydrophobicity, pore size distribution, functional groups) than biomass (Qin et al., 2022).

Biochar has several other advantages, such as soil conditioner, carbon sequestration, and storage source, which also alleviate environmental degradation (Salman et al., 2019). Several researchers have investigated the dosing of biochar to enhance biogas and bio-H_2 yield. However, further research is required to optimize biochar dose in AD and PDF. To simulate the underlying processes, novel research methodologies are to be developed.

This review aims to explore biochar's usage to enhance biogas and bio-H_2 yield. The significant properties of biochar and biochar-doped catalysts and their impact on the AD and PDF processes along with associated mechanisms such as the buffer capacity, process stability, electron transfer etc. have also been discussed in detail. Moreover, literature on biochar supplementation in the AD and PDF processes has been conferred for evaluating the knowledge gaps for further research and highlighting the available scientific opportunities for research in this area.

2. Synthesis and characteristics of biochar and biochar catalysts

Charcoal production from biomass is an ancient practice, and 'pit kilns' and 'trenches' were employed for this purpose; however, specialized functional small as well as commercial and industrial reactors and furnaces are now preferred for biochar production in controlled conditions. This study compiled a brief overview of the thermochemical processes involved in biochar production. For example, pyrolysis, gasification, hydrothermal carbonization, and torrefaction are popular methods for biochar production, for which a brief overview has been provided here.

2.1. Pyrolysis, gasification and torrefaction

The thermochemical decomposition of biomass in a deoxygenated environment at 300–900 °C is known as pyrolysis. Based on the heating rate (HR) and residence time (RT), it can further be categorized as slow pyrolysis (HR: 0.1–10 °C/S RT: >5 min to several hours), fast pyrolysis (HR: 10–200 °C/S; RT: 10–25 min), and flash pyrolysis (HR: >1000 °C/S; RT: <1 min) with expected biochar yields of 25%–50% (slow pyrolysis) >15%–25% (fast pyrolysis) >5%–15% (flash pyrolysis) (Ahmad et al., 2013; Bolan et al., 2022). Moreover, slow pyrolysis favors high biochar yield, while fast/flash pyrolysis produces more bio-oil. Pyrolysis is a complex process that consists of various steps of reactions and interactions: (i) Elimination of moisture; (ii) formation and release of various other low molecular weight volatiles, gases, and bound moisture, decomposition, and fragmentation of lignocellulosic components and primary char formation; (iii) The last step is fast followed by slow reactions which include chemical rearrangements in biochar. At this step, char decomposes at a prolonged rate, and carbon-rich secondary residue (biochar) forms (Demirbas, 2004; Shakya and Agarwal, 2019).

Gasification is the process in which the biomass is treated at high temperature (700–900 °C) in the presence of gaseous media like CO_2, N_2, steam, or the combination of these gases as an oxidizing agent for the production of gaseous fuel (Mohan et al., 2014). This process involves partial oxidation of biomass and converts it into gaseous product syngas (85%): a combination of H_2, N_2, CO, and CO_2. Biochar with 10%–15% of the total weight yield of the biomass is generated as the by-product of the gasification process. In order to accomplish synergistic effects and produce gaseous fuel of higher quality than that produced by traditional gasification, the waste derive fuel can be co-gasified with various feedstock and biochar (Yang et al., 2021).

Torrefaction is another thermal method often used for biomass processing in an inert environment at low temperatures (200–300 °C) with a high heating rate of <50 °C/min. However, the solid product from torrefaction is not technically biochar (low C-content) but can be referred to as pyrogenic material.

Among all the above methods, slow pyrolysis has been accepted as a highly efficient method for biochar preparation with a high biochar yield compared to liquid and gas components.

2.2. Hydrothermal carbonization (HTC)

HTC is often known as wet pyrolysis, where high moisture (70%–90%) organic biomass is converted to "bio-crude" under high pressures (2 to 10 MPa) through thermal depolymerization at moderate temperatures (180 °C to 350 °C). The critical factors distinguishing HTC from pyrolysis are aqueous media and high pressure (Jang et al., 2022). During HTC., liquid water acts as a reactive agent and reaction medium. It stimulates various chemical processes like hydrolysis, dehydration, decarboxylation, aromatization, and polymerization, which break down and rearrange the hydrocarbons into a lignite-like final product (Seo et al., 2022). In an investigation, high-moisture palm waste was converted into hydrochar over a variety of process temperatures from 150 to 300 °C using a single-mode microwave HTC method that included steam purging. In addition to recording a reduced process time (10 min), microwave HTC also avoided the development of hot areas inside the reactor. This method also resulted in higher hydrochar yield of 94.3% at 150–200 °C (Yek et al., 2022).

2.3. Advanced pyrolysis methods

A recent trend in the literature suggested using more energy-efficient, cost-effective, and advanced pyrolysis methods to obtain a high yield and tailored physicochemical and morphological properties of the biochar. Microwave-assisted pyrolysis, co-pyrolysis, catalytic pyrolysis, and steam-assisted pyrolysis are the few modified pyrolytic techniques used for biochar preparation. For instance, due to consistent and selective heating with a high heating rate, microwave-assisted pyrolysis reduces the pyrolysis reaction time and increases the porous architecture of biochar despite the feedstock used (Hadiya et al., 2022; Motasemi and Afzal, 2013; Zhang et al., 2022). Similarly, wet/hydrothermal pyrolysis handles the wet/high moisture-biomass such as municipal sludge, providing an advantage over conventional pyrolysis by overcoming the pre-drying of biomass under moderate conditions and above-saturated pressure (Lachos-Perez et al., 2022; Zhuang et al., 2022). However, it is always recommended to select pyrolysis parameters reasonably to obtain biochar with desired functionalities according to the specific objectives. Nevertheless, pre/during/post surface modifications at the time of biochar synthesis through physical treatment (ball milling, crushing), chemical treatment (acid, base), gas activation (CO_2, plasma, N_2), biochar conjugation (clay, ash) and pre/post metal impregnation (Zn, P, Mg) would provide a chance to enhance its adsorptive and, catalytic properties.

3. Biochar modification

Pyrolytic temperature significantly affects biochar's chemical and morphological properties. High pyrolysis temperature promotes volatilization of organic matter during thermal treatment, resulting in deep channels with high pore density on biochar surface (Shakya et al., 2022; Waqas et al., 2018). However, literature also observed structural destruction, suggesting the importance of carefully selecting pyrolysis parameters.

The plethora of physicochemical properties of biochar includes high surface area, pore size, pore volume and pore density, acid density, oxygenated surface functional groups, and intrinsic heteroatoms (N, O, S, H, etc.), metal dispersion and speciation that provided biochar a recent recognition as catalyst (Lee et al., 2017; Xiong et al., 2017). Pre- and post-modifications in biochar have the advantages of surface modifications and catalytic site tailoring for maximum efficiency. They present it as the cost-effective, efficient replacement of activated carbon. Recent literature showed the use of biochar (nano, metal impregnated)/biochar-based catalysts for bio-diesel and biofuel production (Cheng and Li, 2018), bio-refinery process (Ramos et al., 2022; Song et al., 2022), syngas production amplification Wang et al. (2022a,b), tar reduction in bio-oil and syngas (Chen et al., 2022), de-NO_x reactions, fuel cell (Cai et al., 2022) and microbial fuel cell electrodes (Jiang et al., 2022).

4. Application of biochar for the production of gaseous biofuels

Biochar has significant and numerous applications in different fields, such as agriculture, wastewater treatment, and thermal power plants. It is sustainable, cost-effective, and has good properties, making it a valuable pyrolysis product. It can be used as a soil conditioner and absorbs heavy metals from wastewater. On the other hand, biochar can be utilized as a catalyst for enhancing the production of gaseous fuels such as biogas and biohydrogen. Several studies have been undertaken to examine the effect of biochar with various feedstocks for the generation of gaseous biofuels like biogas and biohydrogen; these studies are covered in the following sections.

4.1. Bibliographic research biochar in biogas production

Relevant publications using keywords like biochar, anaerobic digestion, pyrolysis, methane, digester, energy, and biomass were explored. From the Scopus database, 384 publications were hand selected from 570 articles depending on direct relevance to the theme. The collected articles were data mined, mapped, and grouped using VOSviewer (version 1.6.10) (Fig. 1). Therefore, the impact and importance of each keyword determined the size/diameter of the circle, which became more extensive as the object's impact increased.

A total of 327 articles that were published between 2017 and 2023 were extracted from the Scopus database and analyzed using the VOSviewer analytic tool with the most recent 5-year restriction. Along with it, the number of publications on this topic has increased. The network visualization of the phrases connected to biochar's use in biogas generation via anaerobic digestion was examined using the program's network analysis tool for co-occurrences. In this investigation, two keyword repeats were the absolute minimum. Only 10,182 keywords satisfied the criterion, and 60% of the most relevant phrases were chosen as standard practice. The minimal relevance level for the verification was set at 0.7, and words with relevance values below this threshold were explicitly deselected from consideration for plotting the graph. The network visualization image was plotted using the association strength normalization approach. "Anaerobic digestion", "Biochar addition", "biomass", "pyrolysis", and "energy" were the most often used keywords throughout the data retrieval procedure, and they kept the top rank. These keywords had total link strengths of 709, 239, 464, 574, and 379, respectively (Fig. 1). It is evident from the figure ad data that the number of articles published with keywords like biochar, anaerobic digestion, pyrolysis, methane, digester, and biomass, has significantly increased in last five years but not much explored. It indicates the importance of the field in the upcoming future of the use of biochar in anaerobic digestion for enhanced biogas production and carbon-enriched digestate (Liu et al., 2022a,b,c; Shao et al., 2022a,b; Sharma and Suthar, 2021a,b; Tratzi et al., 2021).

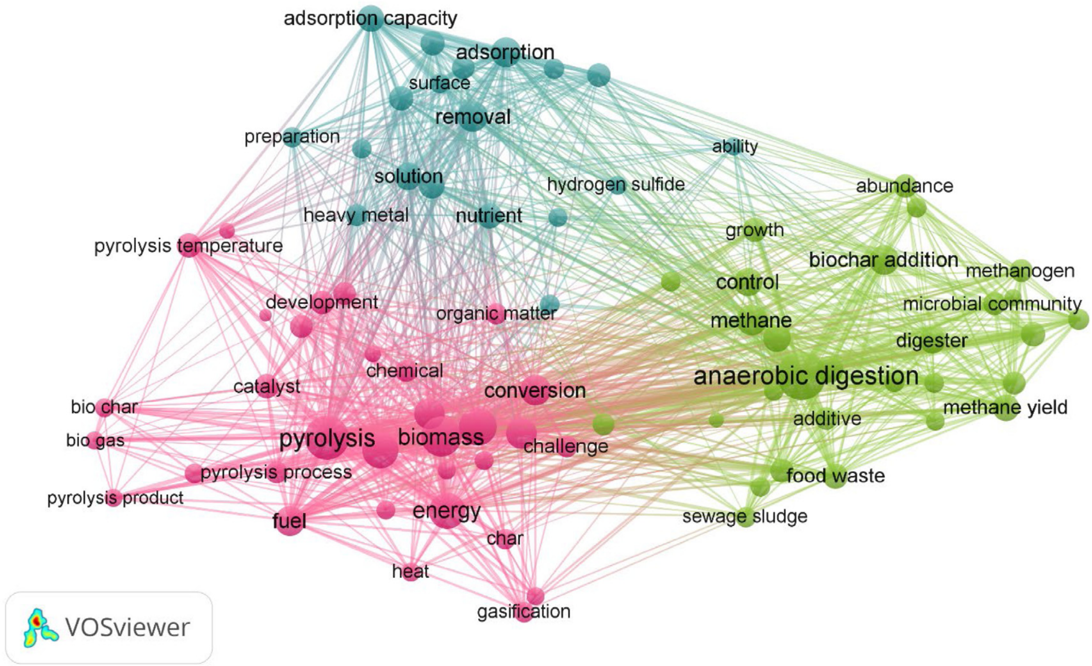

Fig. 1. Bibliographic analysis of the current scenario of biochar application in biogas fuel.

4.2. *Impact of biochar utilization in anaerobic digestion (AD) for biogas production*

In this section, various studies related to addition of biochar in AD of different substrates have discussed. Researchers have utilized biochar as an additive in the AD process for examining the effect of biochar dose on biogas yield and stability of the process which have been tabulated in Table 1. AD process is the biochemical process in which biodegradable substrates containing carbohydrates, proteins, lipids, and fats undergo decomposition by microorganisms in an enclosed container under anaerobic conditions (Agarwal et al., 2022). After the process, biogas is produced as the main product and slurry as a by-product. Biogas contains a mixture of "CH_4 (40%–65% v/v), CO_2 (35%–55% v/v), sulfides of hydrogen (H_2S) (0.1%–3% v/v), moisture and other trace gases", which needs to be further purified to get 90%–95% pure methane. Hence biomethane could be supplied for several valuable applications in industries (Gao et al., 2019). However, some barriers related to the AD process include low methane yield, a decrease in buffer capacity, and low process stability due to different feedstocks and generation of inhibitors, mainly ammonia, pathogens, hydrogen sulfide (H_2S), etc. These inhibitors may reduce the action of microorganisms and increase the pH, affecting the buffer capacity in the AD process. Besides, other factors such as "temperature, type of feedstock, C/N ratio, hydraulic retention time (HRT) and organic loading rate (OLR)" (Kapoor et al., 2020; Pan et al., 2021). Zhao et al. (2021a,b) have examined the influence of pH on AD process stages and investigated that pH between 6–8 is appropriate for AD, on which it works efficiently. The low C/N feedstocks, such as food waste, decrease the pH value, disturbing the AD process's stability. Biochar has significantly boosted the biogas yield and stabilized the AD process due to its better properties. Huang et al. (2023a,b) have conducted a study on semi-continuous co-digestion of pig-manure and corn-straw for the biogas production along with effect of biochar on biogas yield was analyzed. It was reported that W higher biomethane was obtained as 812.8 ± 28.0 mL/(L d) in which approx. 63% methane and remaining CO_2 was achieved. In another research study, Liu et al. (2022a,b,c) have investigated the impact of biochar produced from digestate residue, coconut and corn waste on the AD of sewage sludge and food waste for biogas production. Daily biomethane production was obtained as 432.2 mL/g VS with addition of digestate biochar which was higher than other biochar addition (coconut and corn waste). From the discussed studies, the addition of biochar in AD efficiently stabilizes the fatty acids and increase the breakdown of substrate. Also it maintains the ammonia nitrogen (NH_4N) concentration at minimum level as well as relieve the free ammonia collection. Another benefit of biochar addition, it enriches the bacteria activity which lead the methanogenesis in predetermined environment which help to increase biogas yield (Liu et al., 2022a,b,c). AD system with the addition of biochar and its benefits has been illustrated in Fig. 2. The literature related to the effect of biochar on AD process parameters is discussed below.

4.2.1. *Process stability and biogas enhancement*

Process stability is primarily affected by the generation of ammonia (NH_3) and organic acids owing to nitrogen-rich waste or substrate, inhibiting microorganisms' action. This phenomenon reduces the methane yield and erupts the

Table 1
The effect of biochar dose for biomethane production.

References	Primary feedstock of AD	Feed-inoculum ratio	Environment conditions	Biochar induction	Biomethane yield enhancement
Chen et al. (2021)	Potato pulp waste and dairy manure	2:1, 1:1	Mesophilic (37 °C) 50 days	6.3 g biochar from apple tree branches	87.5% at biochar dose
Pan et al. (2019)	Chicken manure (CM)	TS of 2%, 8% and 17% (CM, inoculum and biochar)	Mesophilic (35 °C), 115 days at OLR (0.625 3.125, 6.25 g VS/L.d)	4.97% biochar from orchard waste wood	33%, 36%, and 32% at different biochar doses
Zhang et al. (2020b)	Food waste and seed sludge	3.13:1	Thermophilic (55 °C)	7.5–15 g/L wood pellets biochar	46% at 6 g of biochar addition
Suthar et al. (2022)	Water hyacinth	1.5:1	Mesophilic (35 °C).	0.5, 1.0, and 1.5% v/v cow manure biochar	54.7–68.5% at different biochar doses
Zhang et al. (2020a)	Food waste and algal biomass	OLR (at 1.60, 3.21, and 4.81 gVS/Ld)	Mesophilic and thermophilic 43 days	15 g/L of biochar from Algal biomass	12%–54%
Zhang et al. (2020a)	wastewater sludge	1 g COD/L of inoculum	25 °C, 37 °C and 55 °C 30 days	10 g/L of biochar from douglas fir	11%, 48.3% and 98% at 37 °C, 55 C and 25 °C
Gao et al. (2021)	Food waste	(1:4.6)	Mesophilic (35 °C).	2, 4, 6, 8 g of raw and HNO3-modified corn stover biochar	36% and 90% for raw biochar and HNO_3 treated biochar
Wei et al. (2020)	Primary Sludge	1:1.33	Thermophilic (55 °C)	1.82, 2.55 and 3.06 g/g TS corn stover biochar	67.5%, 81.3%, 87.3% for biochar dose
Wei et al. (2020)	Sewage sludge	1.82, 2.55, 3.06 and 3.64 g/g TS of sludge, (1:2)	Thermophilic (55 °C)	10 g/L corn stover biochar	7.0%, 8.1% and 27.6%
Quintana-Najera et al. (2022)	Chlorella vulgaris and cellulose	0.5, 0.8 and 0.9 ratios	Mesophilic (37 °C) 30 days	1.5g/L and 3g/L Oak wood biochar	1.8–4.6 times than control
Deng et al. (2021)	Whiskey by-products	9.77 g feedstock and 247.32 g of inoculum	Mesophilic (37 °C) 30 days	0.75 g/L of biochar	5% increased
Tsui et al. (2021)	MSW leachate	4:1	Mesophilic (36 °C) 30 days	6 g/L of biochar from wood chips	27.9% increased
Liu et al. (2022a,b,c)	Sewage sludge and food waste	67.8 g/L TS and 49.6 g/L VS, (1:1)	Thermophilic (55 °C) 35 days	8.0 g/L biochar from biogas residue, coconut shells and corn stalks	46.16%, 30.6% and 27.7% with each biochar
Li et al. (2022)	Kitchen waste	1:1	Mesophilic (37 °C) 30 days	6 g/L biochar from biogas residue	10.5% higher than that of control
Sugiarto et al. (2021a,b)	Food waste	5:1	Mesophilic (35 °C)	15g/L Pinewood biochar	47% higher than that of control

process stability. Pan et al. (2019) examined the AD of chicken manure under different OLRs (0.625, 3.125, and 6.25 g VS/L.d) at mesophilic conditions (35 °C). Biochar was also added to analyze the effect on biomethane yield and process stability. It was reported that biomethane yield was enhanced by 33%, 36%, and 32% at different OLRs with biochar dosing. Additionally, biochar promotes the electron transfer in-between bacteria and electrotrophic methanogens; it also stimulated the denitrification process for NH_3–N concentration by *Epsilonproteobacteria*, which stabilized the process. Similarly, Suthar et al. (2022) have explored the impact of biochar on dilute acid-thermal pretreated water hyacinth in the AD process under mesophilic conditions. Results showed that compared to the control, 73.4–98.7% of biogas yield was enhanced by pretreated and biochar dosing (1% v/v) samples. Wang et al. (2020) reported the effect of Douglas fir biochar on biogas yield and microbial community during AD of sludge. The results analyzed that it enhanced the biogas production level by 11% and 98% compared to samples without biochar at 37 °C and 25 °C.

4.2.2. Buffer capacity and alkaline nature

The pH is another parameter that influences the stability of the AD process. The efficacy of the AD system principally depends on pH value. As pH drops down, it significantly lessens microbial activation. High digestibility and low C/N ratio of the substrate also increase the acidification rate during the AD process. This accumulation of drastically degrades the

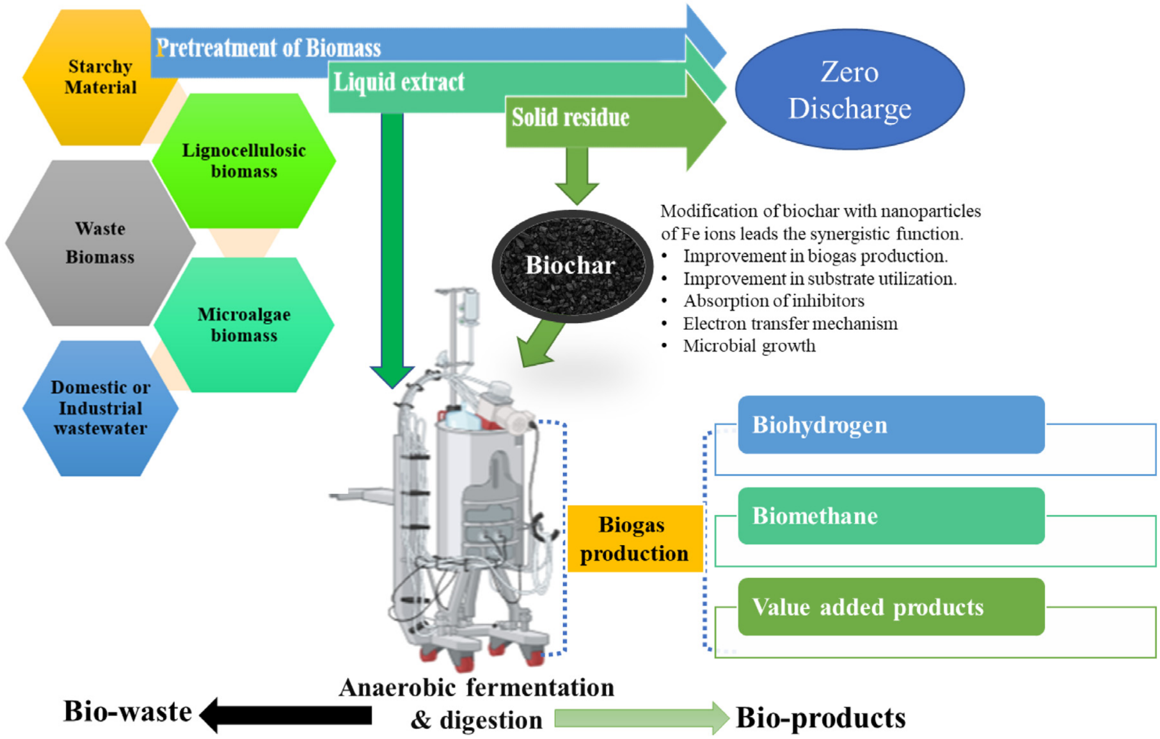

Fig. 2. Schematic of anaerobic digestion with biochar dosing.

AD system, decreasing the biogas yield (Ren et al., 2018; Zhang et al., 2020b). Adding biochar with feedstock in AD also controls the pH of the mixture. This is attributed to the alkaline nature of biochar owing to ash content and volatilization of acidic compounds in pyrolysis reactors (Suthar et al., 2022). Wang et al. (2020) and Zhang et al. (2020b) have explored the addition of biochar to the digestion of food waste in the AD process for biogas production. Researchers investigated that the pH value of control and substrate without biochar decreased to 5–6 with day by day. However, the biochar dosing samples maintained a pH value of 8.7. Also, the biochar samples provided a high yield of biogas compared to positive control and samples without biochar. Biochar has performed well in stabilizing the pH value of the mixture in the AD system due to the alkaline nature of biochar (Wei et al., 2020; Zhang et al., 2020a). However, some opposing results have been obtained in a research study that contradicts all positive results (Sunyoto et al., 2016a,b). Due to this, there is a need to explore more in-depth research studies on the usage of biochar in AD systems.

4.2.3. Inhibitor adsorption and effect on microbial activation

Inhibitors biochar adsorption property also enhances the biogas yield and stability of AD. The biochar's chemical structure helps improve the adsorption process due to the presence of –OH and –COOH groups (Kanjanarong et al., 2017). Pan et al. (2019) showed the effect of biochar which adsorbed the inhibitors such as ammonia and organic acids produced during co-digestion of potato pulp waste and dairy manure. Sugiarto et al. (2021a,b) have also examined the dosing of biochar in the digestion of food waste which enhanced the biogas yield and microbial activation. Additionally, the presence of iron (Fe) in biochar has helped to promote the degradation of VFAs and proliferated the count of *Clostridia* sp and *Methanosaeta* sp as *Clostridia* bacteria help to reproduce the methanogens that improve the metabolism of VFAs. Numerous researchers analyzed biochar's impact on microbial reproduction, promoted biofilm formation, and enriched the microbes counts for AD improvement (Liu et al., 2022a,b,c; Tsui et al., 2021). Quintana-Najera et al. (2022) have investigated the effect of biochar on co-digestion of microalgae and cellulose for analyzing the biogas enhancement, inhibitor adsorption and kinetic modeling by using optimization conditions. It is reported from study that microbial activation is increased as biochar was added owing to higher surface area which provides a platform for reactions. As per the literature, biochar induction in the AD process improved the process stability, inhibitors adsorption, enrichment in microorganisms, and biogas enhancement (Kizito et al., 2022; Ovi et al., 2022). Also, biochar is a promising additive, sustainable, carbon capture fuel, and cost-effective, which can be used in AD systems.

4.2.4. Electron-transfer mechanism

Many studies have emphasized the role of biochar induction in the electron-transfer process between "archaea and anaerobic bacteria". The effectiveness of AD plants is mainly reliant on syntrophic action in-between methanogens and

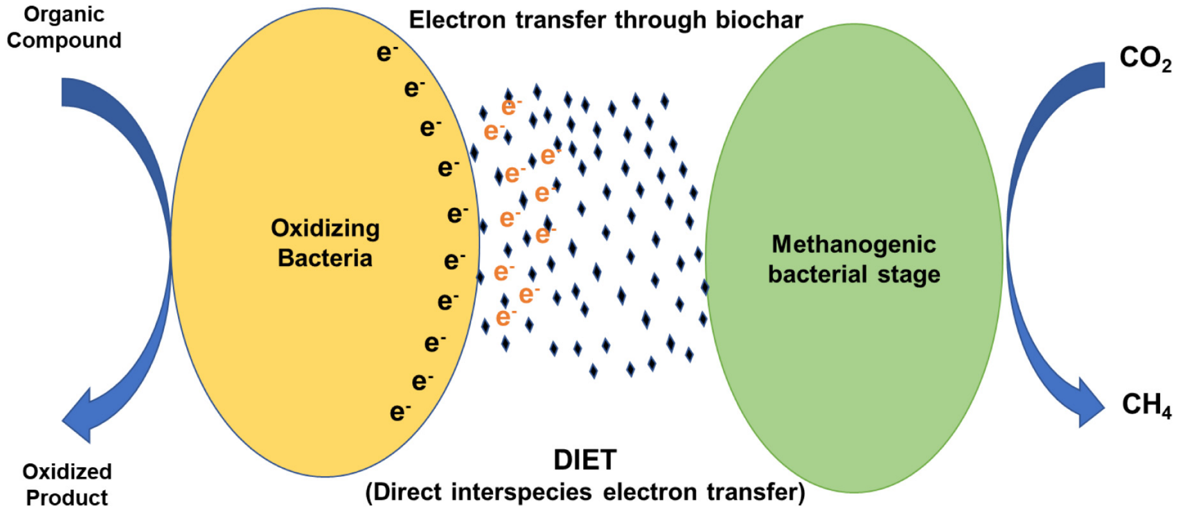

Fig. 3. 3 Electron transfer mechanism as biochar usage in AD.

bacteria, which provide electrons for complying with energy requirements (Deng et al., 2021). It occurs through numerous pathways, such as direct interspecies electron transfer (DIET) with biochar and many others. Additionally, the electron transfer mechanism is shown in Fig. 3 in which electrons from oxidizing bacteria (Donater) to methogenesis bacteria (acceptor) in AD process through biochar media (Jadhav et al., 2021). Martins et al. (2018) have reported that homo-acetogenic bacterial growth, which includes ''*Eubacterium*, *Clostridium*, *Syntrophomonas,* and H_2 with methanogens'', have enhanced the biogas yield. Zhao et al. (2016) examined the growth of ''Methanosaeta and Geobacter'' on the biochar surface during the AD of wastewater. DIET (conductive biochar) has degraded the production of propionate and butyrate. It was reported that *Smithella and Syntrophomonas* found the interspecies electron transfer (IET) mechanism. Wang et al. (2018) investigated microbial enrichment in a biochar-dosed reactor where AD of wastewater occurred. It was reported the enhancement of DIET acquaintances like ''*Bacteroidetes, Geobacter, Methanosarcina and Methanosaeta*''; also accelerated the removal of COD and biogas yield with the addition of biochar. As per previous studies, the research on the electron transfer mechanism with biochar in AD is in the developing stage. More detailed research studies are required to optimize biochar use and focus on DIET.

5. Biochar for argumentation in biohydrogen application

In recent years, it has been established that adding fermentation additives to improve the hydrogen production of dark fermentation is a successful strategy (Sun et al., 2020; Yang and Wang, 2018a,b; Yin and Wang, 2019). Among the different additives metal additives, immobilization carriers, boosting microbes, reducing agents, and enzymes. These additive categories are continually growing, and new practical additions, such as biochar, are being developed. Their characteristics depend on several factors (Morya et al., 2022; Tripathi et al., 2016), including (a) the temperature (Ippolito et al., 2020), (b) the residence period (Te et al., 2021), (c) the thermal treatment method used (Ippolito et al., 2020), (d) the heating rate (Te et al., 2021), (e) the biomass (Ippolito et al., 2020) and its mineral content (Zhao et al., 2019), and (f) the atmosphere (air, H_2, Ar, N_2 their combination, etc.). Because of the wide range of biomass characteristics, adjustable catalysts are required to guide reactions toward producing desired molecules. Cleavage of C–C and C–O bonds requires acid sites on catalysts. While zeolite has been the traditional catalyst for these processes, scientists are becoming more interested in alternatives such silica and biomass-derived activated carbon (Norouzi et al., 2021).

Recently, a hydrogen fermentation system has gained acceleration using biochar as additive to enhance the production, a carbon-rich substance created by the thermal pyrolysis of biomass (Sharma and Melkania, 2017; Zhang et al., 2017). Biochar has a large specific surface area and microporosity, making it an excellent carrier for microbial adhesion and biofilm development. Meanwhile, biochar can supply transitory nutrients (such as heavy hydrocarbons) to boost microbial growth and cell survival. Furthermore, biochar can diminish the inhibition of fermentative bacteria by soluble metabolic products (e.g., organic acids and NH_4^+). Several studies found that adding biochar to the hydrogen fermentation process increased its efficiency (Yang and Wang, 2019). According to Sunyoto et al. (2016a,b), adding biochar to anaerobic fermentation increased hydrogen yield and production rate by 31.0 and 32.5% in hydrogen production applications. In a study by (Deheri and Acharya, 2020) they reported the effect of biochar on the growth phase the lag phase was observed to be up to 36.0% shorter in mesophilic anaerobic digestion of food waste.

Furthermore, from the study of Huang et al. (2022) the incorporation of biochar facilitated substrate breakdown, enhanced hydrogenase and electron transfer system activities, and promoted microbial growth and metabolism (Fig. 4).

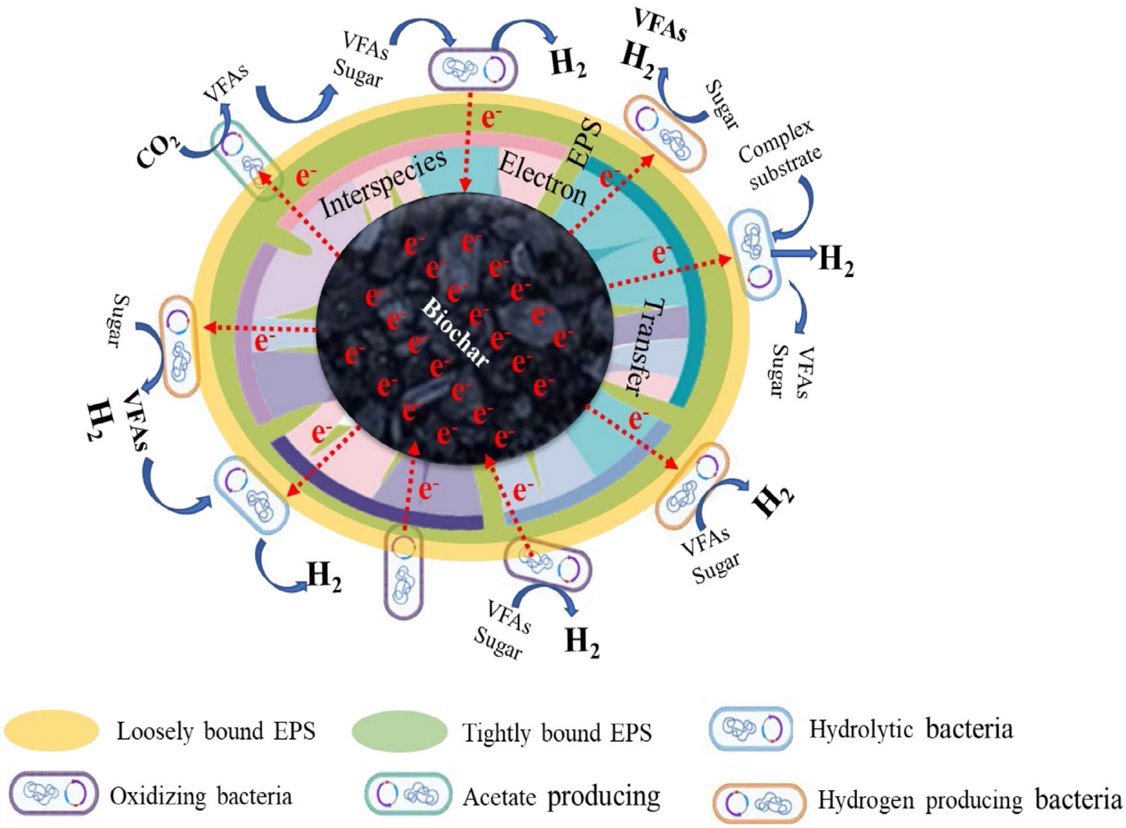

Fig. 4. Electron transfer mechanism in between the microorganisms to improve H_2 production rate.

At higher temperatures bacterial strain *thermosaccharolyticum*, a *thermoanaerobic bacterium* Using MJ2 and biochar, we increased sugarcane bagasse's potential as a thermophilic hydrogen source. Using biochar greatly enhanced hydrogen production by 158.10%, on top of the 95.31% increase achieved with MJ2 bioaugmentation alone (Huang et al., 2022). Table 2 represents the current research development of biohydrogen production with bioaugmentation of the biochar with different substrate and inoculum.

There may be several limitations of application of biochar for production of gaseous fuels. The major limitation of usage of biochar is its availability and production. As different feedstocks have different composition, physical and chemical properties which needs to identify the biochar dosing for a particular feedstock. There is another limitation related to properties of biochar which depends on biomass from which biochar is prepared. It means, in-depth studies are required to analyze the effect and optimal proportion of biochar dosing for better results in terms of higher gaseous fuels yield.

6. Scope, future perspectives and limitations

The physicochemical properties and functions of biochar have been recognized as a value-added product that significantly improved the AD process. Much research on AD of different feedstocks such as food waste, animal manure, municipal sewage sludge, and algae with the induction of biochar has been conducted (Saif et al., 2022; Shen et al., 2020). However, biochar induction in the AD process is in the developing stage. There is a lot of scope for exploring the effect of biochar dosing (g/L) and its particle size range (μm) with different feedstocks. Additionally, biochar can be produced from other feedstocks using the pyrolysis process, affecting properties such as porosity, surface area, electrical conductivity, cation exchange capacity, buffer capacity, and surface functional groups. The comprehensive assessment of literature on the carbon-induced AD process reported that biochar has better results and advantages than other additives like "carbon cloth, graphene, magnetite carbons, and other nanomaterials" in terms of cost, a simple process of synthesis and the enhanced yield of biogas. Apart from these biochar have some demerits. The quality of the biochar is primarily responsible for its limitations in applications for biogas production. For the pyrolysis of solid biomass treatment process, the viability of the environmental, energy requirements, carbon emission, and energy recovery are extremely significant aspects to generate low value and high-quality additive for biogas production. Despite its many advantages, pyrolysis frequently results in low-quality products and high levels of heavy metal contamination, which have an inhibiting influence on the

Table 2
Comparative biohydrogen production from the biochar bioaugmentation.

Inoculum	Substrate	Biochar	H_2 production	References
Secondary sedimentation tank sludge	Mix sugar (Glucose 5 g/l and Xylose 5 g/l)	Rice straw (500 °C)	1330.41 ml/L	Wu et al. (2022)
Clostridium sp. YD09	Xylose (10 g/L)	Algal feedstock (600 °C)	1.62 mol H_2/mol xylose and 1.98 mL H_2/mL	Kim et al. (2022)
Anaerobic Sludge Heat Treated (8 g VS.l^{-1})	Food Waste	Pine Sawdust Biochar 10 g/L (650 °C)	820.6 ± 81/mL Day	Sunyoto et al. (2017)
Heat treated Sewage sludge (85 °C, 30 min)	Glucose	Corn-bran residue biochar (600 °C, 600 mg/L)	204.0 mL/g	Zhang et al. (2017)
		Fe_2^+ (600 °C, 200 mg/L)	217.4 mL/g	
		Biochar + Fe_2^+ (600 °C, 3:1)	234.4 mL/g	
Brewery Waste Anaerobic Sludge (Heat treated)	Dewatered activated sludge and food waste (4:1, VS: 7.91%)	Sawdust Biochar 10 g/L (700 °C)	81 ± 3 mL/g VS	Wang et al. (2018)
		Wheat Bran Biochar 10 g/L (700 °C)	81 ± 2 mL/g VS	
		Peanut Shell Biochar 10 g/L (300 °C)	68 ± 4 mL/g VS	
		Sewage sludge Biochar 10 g/L (700 °C)	73 ± 3 mL/g VS	
		Without biochar	72 ± 3 mL/g VS	
R. sphaeroides and *C. acetobutylicum* (Co-culture)	Synthetic food waste	Sewage sludge biochar (500 °C, 0.5 g/L) and resin rich in calcium and magnesium (5 g/L)	197.15 mL/g VS	Rezaeitavabe et al. (2020)
		Without Biochar	102.00 mL/g VS	
T. thermosaccharolyticum M18	Pretreated Cornstalk	RCA-biochar (15 g/L) (500 °C, residue cornstalk left after anaerobic (RCA)	5.7 mL/g substrate/h	(Zhao et al. 2021)
Ethanoligenens harbinense Yuan-3	Glucose	Rice straw biochar (3 g/L) (700 °C for 4 h)	2.36 mol/mol	Li et al. (2020)
		Without Biochar	1.11 mol/mol	
Anaerobic Sludge (Heat treated)	Grass biomass (Lolium perenne L.)	Without Biochar	26.6 mL/g dry	Yang and Wang (2019)
		Sawdust Biochar (500 °C for 2 h, 600 mg/L)	30.9 mL/g dry grass	
		Zero-valent iron nanoparticles (Feo NP's: 400 mg/L)	40.9 mL/g dry grass	
		Without Biochar	26.6 mL/g dry grass	
Enterobacter aerogenes and *E.Coli* (Co-culture)	Organic fraction of municipal solid waste	Woody biomass biochar (500 °C, 12.5 g/L)	2.58 L/L substrate	Sharma and Melkania (2017)
		Without Biochar	0.60 L/L substrate	
Anaerobic sludge-heat treated (80 °C, 60 min)	Sucrose	Granular activated carbon (mesh size of 1060pt16 VS 45)	5.6 mol/mol sucrose	Lutpi et al. (2015)
Sewage sludge Heat-treated (95 °C, 30 min)	Food waste	Pinewood Biochar (650 °C, 15 g/L)	957 mL/L	Sugiarto et al. (2021a,b)
		Pinewood Biochar (900 °C, 15 g/L)	1154 mL/L	
		Without Biochar	610 mL/L	

(*continued on next page*)

Table 2 (*continued*).

Inoculum	Substrate	Biochar	H_2 production	References
Clostridium sp. T2	Cornstalk hydrolyzate (13.8 ± 1.3 g/L Glucose and 5.7 ± 0.2 g/L xylose)	Residue cornstalk left after pretreatment (300 °C, RCPH-biochar: 5 g/L)	2530 mL/L	Zhao et al. (2020)
		RCPH-biochar (10 g/L)	3215 mL/L	
		RCPH-biochar (15 g/L	3990 mL/L	
		RCPH-biochar: 20 g/L	3688 mL/L	
		Without Biochar	2364 mL/L	
Ethanoligenens harbinense Yuan-3.	Biomass waste	Sugarcane bagasse-based biochar (300 °C, 3g/L)	84.58 mL/L	Li et al. (2021)
Phanerochaete chrysosporium	feedstock–cornstalk,	Residue cornstalk left after pretreatment		Wang et al. (2022a,b)
Thermoanaerobacterium thermosaccha-rolyticum MJ2	Sugarcane bagasse	Left bagasse after pretreatment	391.66 mL/g substrate	Huang et al. (2022)
		Without biochar	395.1 mL/g substrate	
Clostridium butyricum	Glucose	Nitrogen-doped biochar	230 mL/g	Zhang et al. (2021)
		Corncob-derived biochar	159/g glucose	

generation of biogas and heavy metal contamination to environment (Huang et al., 2023a,b). Previous studies also noted the need for surface treatment, which was seen as a restriction on the use of biochar in biogas applications (Gil et al., 2013). In contrary to these, high-quality biochar with a wide surface area and heavy metal free is regarded as a useful supplement for the synthesis of biohydrogen because of its conductivity and function as an electron exchange matrix (Abbas et al., 2021). The usage of biochar in the AD process can promote the concept of circular bioeconomy (Singh et al., 2022). However, there are several challenges related to techno-economic and life cycle analysis (LCA) which are required to be addressed. Techno-economic analysis (TEA) and LCA will provide the feasibility of the biochar amended system. Further mass and energy balance analysis will give a platform to investigate the system so that the modified system can be implemented at pilot and industrial scales.

7. Conclusions

The production and application of biochar using different waste sources and their respective properties positively impact AD and PDF. Adding biochar leads to a significant positive change in biogas and biohydrogen yield primarily due to its buffering action and enhanced process stability. This concludes that large scale production of gaseous fuels can be made more sustainable with biochar addition as the yield can be enhanced up to 4.6 times with suitable biochar doses. Moreover, pre- and post-modification of biochar can increase the efficiency of biochars through enhanced ion exchange mechanisms. Further, for sustainable biochar production a waste supply chain could be established supported by techno-economic analysis and life-cycle assessment for a circular bioeconomy.

CRediT authorship contribution statement

Ranjna Sirohi: Writing – original draft, Literature survey, Data collection. **V. Vivekanand:** Writing – original draft, Literature survey, Data collection. **Ashutosh Kumar Pandey:** Writing – original draft, Literature survey, Data collection. **Ayon Tarafdar:** Reviewing, writing and editing. **Mukesh Kumar Awasthi:** Reviewing, writing and editing. **Amita Shakya:** Reviewing, writing and editing. **Sang Hyoun Kim:** Resources and reviewing. **Sang Jun Sim:** Resources and reviewing. **Hoang A. Tuan:** Reviewing and editing. **Ashok Pandey:** Conceptualization, Supervision, Resources.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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