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Review

# Production of biochar from crop residues and its application for anaerobic digestion

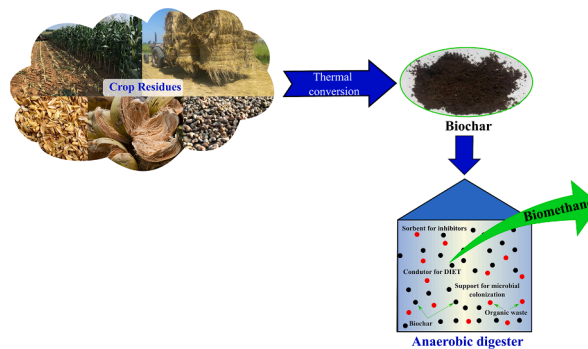
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HIGHLIGHT

- Crop residues are renewable biomass for biochar production.
- Effects of biochar on anaerobic digestion (AD) efficiency are reviewed.
- The role and mechanism of biochar in anaerobic digestion system are scrutinized.
- Limits and prospects for biochar application in the real world are highlighted.
- AD is found to be cost-effective to convert organic waste into renewable energy.

GRAPHICAL ABSTRACT



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ABSTRACT

Anaerobic digestion (AD) is a viable and cost-effective method for converting organic waste into usable renewable energy. The efficiency of organic waste digestion, nonetheless, is limited due to inhibition and

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instability. Accordingly, biochar is an effective method for improving the efficiency of AD by adsorbing inhibitors, promoting biogas generation and methane concentration, maintaining process stability, colonizing microorganisms selectively, and mitigating the inhibition of volatile fatty acids and ammonia. This paper reviews the features of crop waste-derived biochar and its application in AD systems. Four critical roles of biochar in AD systems were identified: maintaining pH stability, promoting hydrolysis, enhancing the direct interspecies electron transfer pathway, and supporting microbial development. This work also highlights that the interaction between biochar dose, amount of organic component in the substrate, and inoculum-to-substrate ratio should be the focus of future research before deploying commercial applications.

## 1. Introduction

Recent increases in the consumption of fossil fuels have had a negative impact on the sustainable development of society and the economy, as a result of the energy crisis. Anthropogenic activities also produce large volumes of bio-waste, which pose severe threats to the environment. In order to address these issues, scientists are currently investigating technologies that convert massive bio-based wastes into renewable energy which can replace fossil fuels (Varbanov et al., 2022). Among alternatives, anaerobic digestion (AD) is not only considered a potential approach to recover energy released from bio-wastes but is also widely used to treat municipal solid waste, domestic wastewater, agricultural residues, and industrial wastewater (G. Wang et al., 2020c). AD is a cost-effective way to manage biodegradable waste because it produces biogas and digestate (Yuan et al., 2022). Biogas derived from AD can be utilized to replace fossil fuels straight away (Bui et al., 2022), but it also can be converted into bio-methane for fueling vehicles or be used in the gas grid (Shinde et al., 2021), while digestate may be used as soil amendment (Panuccio et al., 2019). Compared to alternative organic waste treatment methods, AD has additional benefits like removing pathogens, limiting odor and greenhouse gas emissions, as well as adaptability to various substrates (Jin et al., 2021). Due to these benefits, the AD process is one of the most beneficial waste management strategies and it has been widely implemented on both a small scale, especially in developing countries and rural regions, and on a large scale in industrial zones (Chiappero et al., 2020).

AD process is a natural approach that is carried out in an anoxic environment by numerous archaea and microscopic organisms. Importantly, in the anaerobic digester, four consecutive stages, including methanogenesis, acetogenesis, hydrolysis, and acetogenesis must be completed along with the division of the macromolecular into monomers effectively broken at the phase of hydrolysis (Xiao et al., 2021a), in order for organic matter to be converted into biogas, which is mainly composed of carbon dioxide (CO<sub>2</sub>) and methane (CH<sub>4</sub>) (Amin et al., 2021). The anaerobic consortia in the AD system undergo biological degradation concurrently in order to share vitality via the exchange of electrons or hydrogen amongst relevant species (Khalid et al., 2021). Even though the digestion of different kinds of waste does not affect the environment, it has a low methane production, which may lead to several instabilities during the process (Ryue et al., 2020). Furthermore, several issues such as the dynamic nature of micro-organisms and the biodegradability of food waste could even restrict the efficiency of the process and the methanogenesis reactions (Yu et al., 2021). Alternatively, microbial activity is always disrupted by unfavorable factors in the AD process, resulting in inefficient energy recovery (Cardona et al., 2020). Therefore, to support metabolic practice, it is necessary to upgrade anaerobic bacteria as an alternative approach by incorporating them into the biochemical process of anaerobic digestion (Van Steendam et al., 2019). Indeed, the porous surface of supporting materials such as biochar provides an ideal substrate to which microorganisms can adhere, increasing biowaste digestibility as well as minimising the startup time for digestion (Wu et al., 2022). As a result, carbonaceous additives have been employed to improve AD stages and address the aforementioned issues (Xiao et al., 2021b). Based on the ability to increase CH<sub>4</sub> production by promoting methanogenesis, acidogenesis, and

hydrolysis along with the compatibility with the ecosystem (Kumar et al., 2021) (Xiao et al., 2019), conductive carbonaceous substances including biochar, carbon cloth, and granular activated carbon are preferred over non-conductive carbonaceous substances (Gahlot et al., 2020). Biochar is advantageous, as compared to other additives, in view of its diverse physicochemical properties which are controlled by several factors like methods of modification or activation, synthesis temperature, and types of feedstock (Hassan et al., 2020). According to recent studies, biochar had specific features including plentiful oxygen-containing functional groups (M. Kumar et al., 2020b), good capability of conducting electricity (Ambaye et al., 2020), low density and high porosity, relatively high specific surface area (M. Kumar et al., 2020c), and high capacity of exchanging cation (Chen et al., 2022). It was revealed that biochar possesses the unique capacity to stimulate the activity of live microorganisms (Khalid et al., 2021). Biochar also possesses solid carbonaceous features since it is the predecessor of activated carbon, produced during the thermochemical conversion of organic matter in an inert (oxygen-free) environment (Yücedağ and Durak, 2022). Beyond applications in AD, carbon sequestration and a wide range of other useful properties make biochar a popular choice for environmental remediation, soil amendment, waste management, and functional material preparation (Wan et al., 2020).

The fact shows that biochar can be generated from a variety of biomass materials such as municipal solid wastes, sewage, energy crops, and agricultural residues. As reported, the annual production of crop residues in China is 600–800 Tg, with rice straw, corn straw, wheat straw, and rapeseed straw accounting for a significant proportion (J. Chen et al., 2019). In India, crop wastes are produced in excess of 500 million tons (Mt) each year, in which surplus crop residues are between 84 and 141 Mt/year, with fiber and cereal crops accounting for around 23 % and 58 % of total crop residues respectively (Pawar and Panwar, 2020). In 2020, the EU-27, except the United Kingdom, was reported to generate 127 million dry tons of crop waste (Scarlat et al., 2019). Based on six kinds of crops including corn rice, wheat, sunflower, barley, rapeseed, and oats, it was predicted that the annual global crop residue production would be roughly 3700 million dry tons (Scarlat et al., 2019). Burning a large quantity of crop residue has detrimental effects on humans, notably on young children and pregnant women who are susceptible to cardiovascular and respiratory diseases (Pawar and Panwar, 2020). Therefore, turning leftover crop residues into biochar and other carbon materials is a potential method to reduce CO<sub>2</sub> emissions released into the environment while simultaneously enhancing other advantages (Yetri et al., 2020; Kumar et al., 2022). Indeed, biochar is a cost-effective product, so it could be employed as an additive to improve the AD system's performance as mentioned above. In addition to using biochar in conventional AD systems to handle decomposable organic waste, there is a growing interest in utilizing biochar in advanced AD systems to treat refractory organics. However, understanding of the biochar production process from crop residues and its application to the AD systems, as well as the critical mechanisms and core interactions between biochar and components in the AD systems are limited. On this basis, this current work presents unique insights into biochar production from crop residues, as well as its application in the AD system, with the objective of identifying significant difficulties pertaining to the mechanisms of biochar in regulating and affecting the performance of the AD

system and proposing effective solutions for overcoming those difficulties.

## 2. Biochar production techniques and characteristics

### 2.1. Biochar production techniques

Biomass produced from agricultural activities is abundant, implying a high potential for the development of bio-based materials. For example, every kilogram of grain that is harvested creates 1–1.5 kg of straw (Bheel et al., 2021), representing one of the most plentiful agricultural wastes in the world. Lignocellulosic biomass, the main component of crop residues, generally contains lignin from 15 to 25 %, hemicellulose from 20 to 40 %, and cellulose from 30 to 50 %. Such a high lignin in crop residues could promote the production of biochar with high content of fixed carbon and high yields (Lee et al., 2020).

A variety of traditional and modern methods were used in the last several decades to convert crop residues into biochar. Apart from batch processes, the continuous process was identified as one of the potential thermochemical biomass processes for energy conversion due to its greater flexibility towards biomass feedstock and higher biochar production of 25–35 % (Pawar and Panwar, 2020). The use of an auger-type reactor can increase the biochar yield and its quality, and improve the maximum efficiency of conversion (Jalalifar et al., 2020). There are multiple techniques for generating biochar such as gasification, pyrolysis, hydrothermal carbonization, and torrefaction, as shown in Fig. 1 (Zhang et al., 2019b).

The process to produce biochar has considerable impact on both the yield and final characteristics of the biochar. During the conversion process, the biomass devolatilizes semi-volatile and volatile elements in the form of gas and liquid products, leaving a solid biochar residue (James et al., 2022). Due to devolatilized vapors re-condensing on the primary char surface, heterogeneous reactions can result in the creation of additional char, which increase the biochar output, depending on the residence duration and temperature. One of the oldest and most popular methods to generate biochar is pyrolysis, heating in an environment of low or non-oxygen. In addition to biochar production, gas and liquid can be used as energy sources to power various applications (Escalante et al.,

2022). Chemically, the breaking of weaker connections such as C-OH linkages and hydrogen bonds causes lignin decomposition during pyrolysis, and as the temperature increases, stronger links, like the  $\beta$ -O-4 bonds, are broken (Yang et al., 2021). During the first low-temperature stage of pyrolysis, hydroxyls, aldehydes, guaiacyl, styrenes, and toluols are often produced (Ong et al., 2021a). The second phase of pyrolysis produces P-hydroxy-phenols, cresols and catechols at a higher temperature. Once the  $\beta$ -O-4 bonds are broken, free radicals are released, initiating lignin depolymerization (Gul et al., 2021). These radicals can combine to generate chemicals such as 2-methoxy-4-methylphenol and vanillin. A chain propagation is also initiated by the creation of a large number of important radicals. It was shown that biochar can be generated over 350 °C via radicals' random repolymerization, as shown in Fig. 2 (Fang et al., 2021). In addition, Ahmad et al. (2021) showed that intermediate pyrolysis, slow pyrolysis, and rapid pyrolysis are based on residence duration, heating rate, pressure, temperature, and other factors for biochar production from crop residues. The yield of biochar produced by rapid pyrolysis is typically low; for example, at a reaction temperature of 480 °C, only a 17 % yield of wood biochar was obtained (James et al., 2022). Slow pyrolysis requires a longer residence time up to a few hours or days and a slower heating rate (ranging from 0.1 to 10 °C/min). The high solid yield from slow pyrolysis is one of the reasons for its widespread use in biochar generation. Fast pyrolysis, on the other hand, generates more liquid and gas, including syngas components such as H<sub>2</sub>, and CO, as well as pyrolysis bio-oil, at higher temperatures and faster heating rates (Yaashikaa et al., 2020). Bio-oil yields from intermediate pyrolysis are higher as compared to those from fast pyrolysis, however, this process is rarely used to make biochar because of the higher yields of gas and liquid products.

Torrefaction is a thermochemical method with operating temperatures between 200 °C and 300 °C, a long residence period (>1 h), a lower heating rate less than 50 °C/min, with a small amount of oxygen or no oxygen supply at atmospheric pressure (Haris et al., 2021). Torrefaction is also known as mild pyrolysis; for lignocellulosic biomass it also entails devolatilizing hemicelluloses, lignin and cellulose as a function of temperature. At first, biomass degrades between 150 and 200 °C by devolatilization of surface moisture, bound water and light volatiles often associated with cellulose (Chen et al., 2021a). After that, hemicelluloses

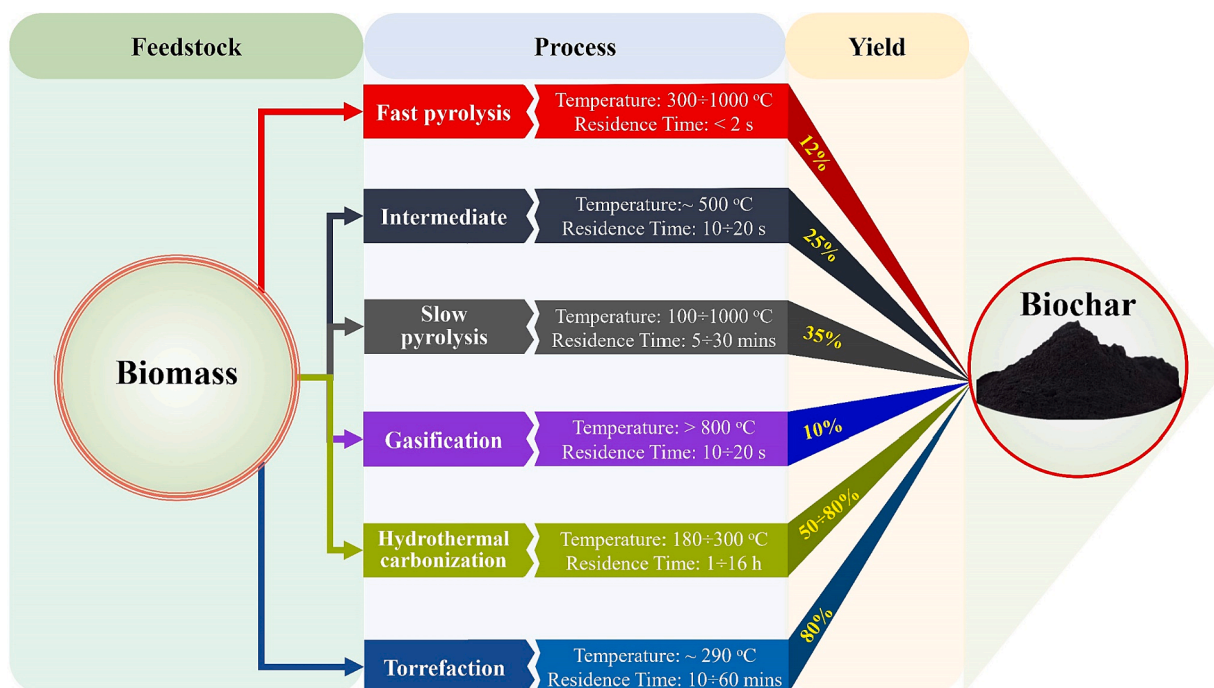


Fig. 1. Techniques for biochar production from biomass residue.



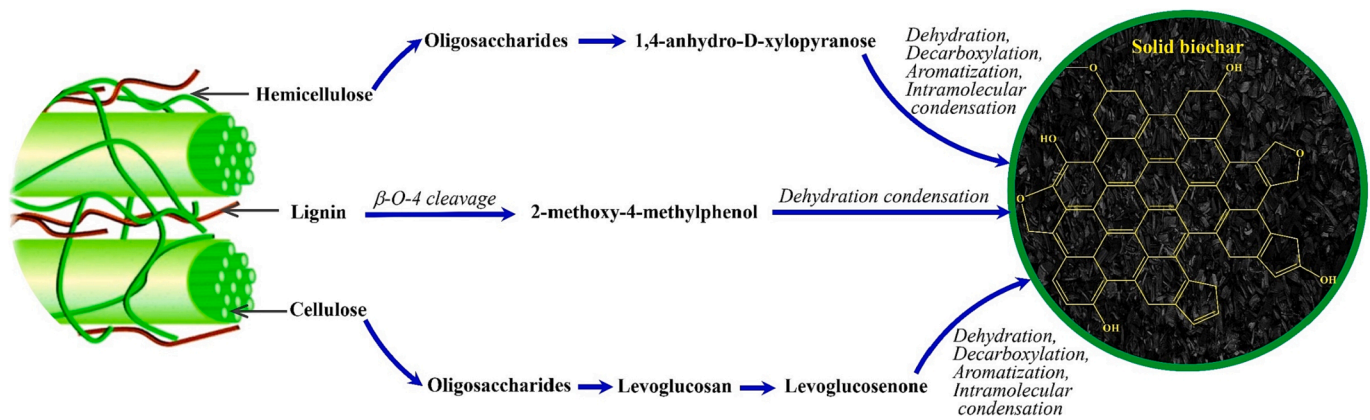


Fig. 2. Mechanism of biochar formation from cellulosic biomass.

begin to pyrolyze around 200 °C, with depolymerization and deacetylation processes occurring (Adeleke et al., 2019). Deacetylation leads to the formation of acetic acid, which could catalyze the low-order carbohydrates' depolymerization as well as the degradation and condensation of lignin (Ivanovski et al., 2022). During biomass torrefaction, the softening of lignin begins between 160 and 190 °C, in which the division of  $\alpha$ - and  $\beta$ -aryl-alkyl ether bonds occurs between 150 and 300 °C, while the splitting of aliphatic side chains occurs at approximately 300 °C. Finally, the elimination of methoxyl groups, also known as demethoxylation, is caused by linkage cleavage at higher temperatures. When the reaction temperature exceeds 300 °C, substantial depolymerization occurs, which signifies a shift to pyrolysis (Ong et al., 2021b; Chen et al., 2021a). Accordingly, torrefaction products have a high potential energy recovery, ranging from 80 to 90 %, and a mass yield in the range between 70 and 80 %; thus, the energy density might be enhanced by 30 % (Haris et al., 2021).

Thermal gasification is believed to be a viable technique to integrate the generation of bioenergy with biochar from various biomass wastes (Hoang et al., 2022). Biochar produced by gasification often contains a significant quantity of carbon and refractory minerals, the latter of which depends on the mineral content of the raw biomass (Haris et al., 2021). The yield of charcoal obtained through gasification is sometimes assumed to be lower, about 200 g/kg, than that obtained through pyrolysis of 200–500 g/kg because during gasification some of the volatile matter and fixed carbon present oxidizes, leading to lower mass yields. However, the presence of alkaline earth metals and alkali species (Ca, K, Mg, Na) in the feedstock often catalytically enhances the gasification process and produces a biochar of potentially higher value than a biochar made via pyrolysis at the same temperature (Lee et al., 2020). Recent advances in gasification processes release less CO<sub>2</sub> and equipment setups are more compact and thermally efficient. Nevertheless, gasification has less biochar output and greater emissions of hazardous gases including NO<sub>x</sub> and SO<sub>x</sub> than pyrolysis. This leads some to favor pyrolysis over gasification for biochar production (Elkhalifa et al., 2019).

Hydrothermal carbonization (HTC) of biomass is a thermal technique that occurs in subcritical liquid water under high pressure, above the water saturation pressure, and moderate temperature from 180 °C to 220 °C (Gul et al., 2021). In comparison with slow pyrolysis, hydrothermal carbonization produces biochars that are acidic, contain higher carbon content, have a higher surface charge, and more oxygen-containing functional groups than biochars from the same biomass (Haris et al., 2021). During hydrothermal treatment, the division of C—O—C and C—C linkages, condensation, alkylation and demethoxylation are considered to be the most prevalent reactions. Initially, during HTC, the  $\beta$ -O-4 bonds and  $\alpha$ C- $\beta$ C connections are broken, but aromatic bonds are not substantially affected. Volpe et al. (2020) demonstrated how the char structure of lignin changes during

HTC, when the temperature increases, lignin degradation intensified. At higher temperatures, it was observed that HTC char had a stronger crystalline structure. Also, functional groups began to disappear, leaving just —OH groups when the temperature exceeded 350 °C. Lignin HTC produced more charcoal than lignin pyrolysis; however, the product formed was less stable due to higher volatile matter content (Gul et al., 2021). The fundamental advantage of hydrothermal carbonization in comparison to other thermochemical procedures is its ability to process wet biomass without expensive drying steps beforehand. Some other benefits of this method could be the effectiveness of cost, high biochar yields, simple operation, and quality of the product (Zhuang et al., 2022).

Compared to other types of methods for generating biochar, pyrolysis is often touted as the most environmentally favorable and requires the smallest infrastructure. Pyrolysis is versatile in handling different types of feedstock under diverse working circumstances, which allows for the development of the desired final product qualities (Parascanu et al., 2019). Therefore, pyrolysis receives the greatest attention among the numerous thermal approaches, and is regarded as the best technique for producing biochar from dry feedstocks that have a moisture content of less than 10 % (Chiappero et al., 2020). Meanwhile, HTC is gaining popularity for its ability to process wet biomass (A. Kumar et al., 2020a).

## 2.2. Biochar characteristics

### 2.2.1. Physical properties

Biochar is a viable additive to improve AD because it can work as a sorbent for hydrophobic inhibitors, support for microbial colonization, a reactant to enhance *in situ* biogas, as well as a conductor to directly transfer electrons among species (Lü et al., 2020). Furthermore, based on the ash composition in biochar, putting it in an anaerobic digester can enhance the concentration of trace metals and alkalis, resulting in improved performance of the process (Pan et al., 2019b). Biochar's porous structure and surface area serves as a living environment for microorganisms (Wang et al., 2022). However, heating rate, reaction temperature, and feedstock all affect biochar characteristics, including the fixed carbon content, nutrient content and availability, cation exchange capabilities and pH (Ghodake et al., 2021). The characteristics of biochar are closely linked with its potential to sequester inhibitors present in the AD system (Günel et al., 2019).

Biochar may enhance AD by acting as an absorbent substance to inhibit hydrophobicity, a provider for bacterial colonization, reactant for producing biogas and a bridge for promoting interspecies electron transfer (Zhao et al., 2020). The efficacy of biochar to improve AD is determined by biochar features like surface functional groups, ash content, specific surface area and porous structure. The interplay between these physical–chemical characteristics and the specific microbial community are key considerations. For example, *Pseudomonas sp* was

found to adapt better to biochars that enhance alkalinity, and those with Ca- and Mg-based buffering capacities (Zhao et al., 2020).

The specific surface area of a biochar influences the ability of microbes to establish residency on the biochar's surface and within its pore spaces (Gao et al., 2019). Depending on the feedstock and pyrolysis temperature, the observed specific surface area values of biochar can vary widely from below 100 to over 1000 m<sup>2</sup>/g (Leng et al., 2021). Specific surface area was also demonstrated to be a critical feature in enhancing biochar's adsorption ability as specific surface area is relevant to the distribution of biochar pore size (Kumar et al., 2021). In turn, specific surface area is roughly correlated with microbial activity; Zhao et al. (2020) concluded that microbes can attach to both biochar surface and internal pores by electrostatic interactions, promoting reproduction. The specific surface area of biochar from crop residues can be increased by modifying the surface, particularly with chemical treatments such as acid, ionic liquids, and alkaline, along with physical operations like ultrasound and milling (Tu et al., 2020). For instance, Cao et al. (2019) showed that when pyrolysis temperature reached 600 °C, the surface area of biochar produced from ball-milled wheat straw was 130.14 m<sup>2</sup>/g, which was larger than that of biochar from raw wheat-straw of 6.89 m<sup>2</sup>/g.

Along with specific surface area, porosity and pore size may impact biochar's AD performance. As AD could provide living environments for microorganisms in both anoxic and oxic settings, the ability to access the biochar's surface is a function of the pore size and tortuosity (Zhao et al., 2021b). In an effort to understand the potential interactions between organisms and biochar, Wang et al. (2020d) explored how the distribution of biochar pore size impacts AD environments. The authors found that microorganisms were able to locate a suitable environment to grow based on pore dispersion. In addition, biochar's mechanical strength is partly governed by its density; a biochar with high compressive strength required raw feedstocks with high density concentration and high lignin content. Physical properties of biochar from crop residues could also be provided in a study of Chen et al. (2022).

### 2.2.2. Chemical properties

Cation exchange capacity (CEC) refers to the ability of biochar to exchange cations with organic or inorganic substances. Having a high CEC value showed a high level of the surface negative charge, which permitted the removal of a significant number of cations (Lago et al., 2021). Thus, CEC appears to be proportional to surface oxidized functional groups (Zhu et al., 2020). The existence of surface functional groups including hydroxyl, amino, and carboxylic, often expressed as atomic proportions of H/C, N/C and O/C, primarily depends on the feedstock and tends to decrease as pyrolysis temperature increases (Das et al., 2021). The H/C ratio is believed to measure the degree of biochar aromatization, whereas the O/C is an indicator of functional groups, which contributed to biochar hydrophilicity and high values of CEC (Venkatesh et al., 2022). In addition, a rise in pyrolysis temperature was found to have a detrimental impact on the amount of acidic functional groups as well as the CEC (Chiappero et al., 2020). A high CEC may enhance NH<sub>3</sub> inhibition and promote CH<sub>4</sub> production by shortening the microbial lag stage. Goswami et al. (2022) revealed that biochar played a beneficial role in the AD system of sewage sludge while Su et al. (2019) reported that biochar reduced NH<sub>3</sub>-N (by about 1500 mg/L) in the AD of food waste. Similarly, Chen et al. (2021b) indicated that biochar supplementation may prevent the accumulation of NH<sub>4</sub><sup>+</sup> during AD. In addition, some have suggested that electrical conductivity could be used to evaluate the conductivity capabilities of biochar, which are known to be critical for microbial syntrophic activities (Gabhi et al., 2020). However, others have shown that the electrical conductivity of biochar was as insignificant as the electrical conductivity of digestate, depending on the microbial strains' composition and metabolism (Kumar et al., 2021). Moreover, conductive compounds like humic chemicals can act as electron transporters that donate and receive electrons in an effort to accelerate direct electron transfer across species (Xu et al., 2020). The

role of electrical conductivity in the syntrophic oxidation of volatile fatty acids contained in sewage sludge and sawdust-derived biochar was further assessed by Wang et al. (2019). Because of the presence of redox-active structures, biochar was observed to enhance volatile fatty acid degradation and microbial activity through direct interspecies electron transfer (DIET).

Biochar possesses a high capacity for electron transfer due to the arrangement of electrochemical functional groups along with conjugated  $\pi$  electrons on its condensed aromatic surface (W. Zhao et al., 2021c). Biochar was considered an electron conduit to promote DIET and enhance the electron exchanging process between methanogens accepting electrons and bacteria donating electrons (J. Wang et al., 2021c). Even though electron transfer could be enhanced by the biochar aromatic structure produced at higher pyrolysis temperatures (He et al., 2019), it might be decreased due to the degradation of oxygen-containing functional groups into H<sub>2</sub>O, CO, and CO<sub>2</sub> (Zhang et al., 2019a). The optimized transfer of electrons in biochar is ultimately governed by both the graphitized structures and functional groups. Prior work shows that higher pyrolysis temperatures may benefit straw-derived biochar properties, but the impact on increasing pyrolysis temperature for sawdust-based biochar was not as important (Nzediegwu et al., 2021).

Biochar's redox characteristics were identified as a critical parameter in the AD process (G. Wang et al., 2019a). According to Chacon et al. (2020), some factors like the presence of metal oxides, metals and free radicals as well as biochar surface functional groups could govern its redox features. For example, phenolic C-OH fractions were found as the essential functional groups accountable for their electron-donating capacity, whilst quinoid C=O fractions were recognized as the major functional groups responsible for their electron-accepting capacity (Kumar et al., 2021). These fractions determined the biochar's overall electron exchange capacity. In terms of the inorganic elements present in biochar, redox-active metals commonly exist in biomass feedstocks, and in a variety of oxidation states, functioning as electron acceptors and donors (Dieguez-Alonso et al., 2019). The level of engagement in the electron exchange capacity was determined by types of metal, oxidation state changes, coordination as organo-mineral complexes and metal oxide dispersion on the surface of biochar (Ren et al., 2020). Furthermore, an oxidation technique could increase the relevant biochar surface functional groups (M. Kumar et al. (2020d)); however, the oxidation approach should preserve additional key functionalities without causing conversion into the redox-inactive -COOH functional groups as well as removal as carbon dioxide (Chacon et al., 2020).

Biochar conductivity and related microorganisms in the AD process were affected by the pH (Yin et al., 2019). In this instance, the pH of biochar should be alkaline because the ash content and the volatilization of functional groups were acidic. It was found that the pH of biochar made from crop residues not only varied widely depending on the source of feedstock, ranging from 6 to 11.4, but was also significantly affected by pyrolysis temperature. Biochar made from rice husk at 300 °C, for example, had a lower pH of 6.5; but as the temperature rose to 500 °C and 600 °C, its pH increased from 9.5 to 9.8 (Shi et al., 2019). Maize and straw-derived biochar had an alkaline pH of 9.8 at 300 °C, 10.5 at 450 °C and 11.4 at 600 °C (Haris et al., 2021). Biochar raised the alkalinity of the AD to a pH of at least 6, increasing microbial activity for rapid CH<sub>4</sub> production and adaptation to the initial loading shock (Goswami et al., 2022). Under acidic circumstances (with pH = 5.3), biochar considerably improved the methanogenesis phase, accordingly enhancing the operating conditions with higher total solids and organic loading (Ren et al., 2020). Moreover, biochar also possesses redox capacity, which allowed to accept or release electrons.

From the above analysis, it can be concluded that biochar properties are heavily influenced by the biomass origin, pretreatment, biochar production conditions and post-treatment or activation steps. Additional effort is required to manage the combined effects of these important factors in order to increase and maximize the target response's biochar

characteristics. In terms of physical application, the biochar surface area and porosity enhance the exposure to vapor, CO<sub>2</sub> gas agents, and mixtures at temperatures above 700 °C (Anto et al., 2021). Biochar also enhances water-holding ability, cation exchange capability and carbon content (Jeyasubramanian et al., 2021). Thus, biochar addition can improve a continuous AD process with an increased organic loading speed as well as a shorter hydraulic retention time.

### 3. Biochar application in anaerobic digestion

Although instability in the AD system can be controlled by optimizing technical and operating settings, such stability can be compromised if the metabolic intermediates of a substrate limit the activity of microorganisms in the digester. AD is a robust approach for treating organic waste using bacterial and archaea species. Generally, size and volume of pore, surface microstructure, hydrophobicity and ion-exchange capacity are the most common biochar properties to tune when utilizing biochar during the AD process. These properties impact biochar's potential for immobilizing microorganisms, improving cation exchange, increasing alkalinity of AD, stimulating biofilm formation, and enhancing electrical conductivity, which can support the DIET phenomena.

#### 3.1. Improving biogas production

Hydrolysis is the breakdown of large compounds, such as macromolecules, into smaller compounds, under alkaline (OH<sup>-</sup>) or acidic (H<sup>+</sup>) conditions, and is the first step in the AD process. The addition of biochar could be used to improve the hydrolysis of low biodegradable substrates (Khalid et al., 2021). Due to the high amounts of protein, nitrogen, and organic matter in the feedstock, fatty acids and ammonia can accumulate during AD (Latifi et al., 2019), such that biogas yield can vary with inoculum/substrate ratios. Indeed, the use of a suboptimal inoculum/substrate ratio could make methanogen bacteria act sub-optimally, leading to a reduction in biogas and methane performance (Owamah et al., 2021). Thus, it is necessary to determine the optimum inoculum quantity to maximize biogas yield. Anaerobic co-digestion of other wastes is considered as a method to address the above-mentioned problems (Kumar et al., 2021), because the optimal inoculum/substrate ratio could provide a balance about feedstock needed by anaerobic microorganisms, dilute toxic and inhibitory substances, and increase the digestion rate (Latifi et al., 2019). In addition, biochar could alleviate natural difficulties by suppressing microbial growth and improving cell density through finely accessible substances in high electrical conductivity blends. During the AD process, there is a significant increase in digestate chemical oxygen demand (COD) in biochar, indicating the biodegradation of natural materials (Tayibi et al., 2021b). The rate of organic matter hydrolysis in the presence of biochar increased during AD. The higher carbon concentration due to biochar may degrade via solitary inorganic carbon digest hydrolases activating the hydrolysis process, which were found to increase macromolecular biological accessibility and power generation (Yang and Wang, 2019). The activity of hydrolytic germs can be improved by adding biochar. However the actual efficacy of biochar's impact on hydrolysis is associated with various factors including technology and implementation.

Moving beyond hydrolysis and further into the AD process, acetogenesis converts germicidal acid hydrolysates like sugars, amino acids, and fatty acids into alcohol, NH<sub>3</sub>, volatile fatty acids (VFA). Acetogenesis converts CH<sub>3</sub>OH, propionate, and lactate into easily convertible molecules, which are then transformed into CH<sub>4</sub> (Amin et al., 2021). VFAs generated as intermediates during the AD process appear to lower the pH (Wainaina et al., 2019). Syntrophic acetogens and methanogens, which transform VFAs into methane and CO<sub>2</sub>, often mitigate this impact (Qiu et al., 2019). Nevertheless, when the organic content of easily biodegradable wastes is high, meaning the VFAs generation rate exceeds the consumption speed, VFA accumulation may occur, resulting in a

decrease in pH and perhaps the failure of AD (Xiao et al., 2020a). AD systems can easily enter an unstable state owing to VFA accumulation or organic overload. The excess of VFA in the AD process, for example, would slow down methanogenesis and even damage the anaerobic process (G. Wang et al., 2021b). Thus, biochar can be effectively employed as an additive to foster VFA degradation in the AD process to alleviate the issue of VFA inhibition (Fig. 3a) (W. Zhao et al., 2021c). The literature revealed that the biochar addition alleviates methanogenesis inhibition and efficiently restores biogas generation, as well as decreases the lag time and increases the yield of CH<sub>4</sub> with the superior electron transfer capability of biochar playing a vital part. Electroactive bacteria would be enhanced by the continual addition of biochar, and prospective VFA metabolism may change from a thermodynamically disadvantageous interspecies hydrogen transfer approach to a DIET (C. Wang et al., 2021a). As a result, the matrix pH could be quickly recovered to 7 in the AD system by the use of biochar following a large organic loading shock, whereas the pH in the AD system without biochar fell to below 6 because of fast acidification (C. Wang et al., 2021a). Indeed, by adding sawdust derived from biochar, Wang et al. (2021) accomplished methanogenic recovery of a strongly acidified AD process with high VFA accumulation (58 g COD/L). This research also revealed that biochar addition may improve the pH level from 6.7 to 7.2 during the methanogenic lag time before increasing CH<sub>4</sub> synthesis. Therefore, the biochar addition to the AD process could significantly enhance the balance between methane and acid generation rates, resulting in a 38.0 % reduction in the lag stage of methanogenesis and a 70.6 % increase in the production of methane (C. Qi et al., 2021a) (Fig. 3b).

Aside from the biochemical reasons, the strong buffering ability of biochar played an important role in the VFA inhibition release occurring in AD systems, particularly when the organic loading was high (Ma et al., 2020). The abundant presence of basic functional groups, alkaline-earth metals such as Ca, Mg, and alkali metals such as Na, K in the biochar was the key to maintaining the buffering capacity, resulting in a significant increase in system alkalinity and a near-neutral pH level (Altamirano-Corona et al., 2021). Wei et al. (2020) observed that adding maize stover-based biochar which was rich in alkaline earth metals into primary sludge AD improved the generation of methane and removal of solids. Consequently, increased total alkalinity ranging from 3500 to 4700 mg/L CaCO<sub>3</sub> and pH were detected in biochar-adjusted reactors, implying that biochar possessed a considerable buffering capability. Recent research conducted by Giwa et al. (2019) investigated how biochar addition had an effect on alkalinity throughout the continuous steady operation. Both the control reactor and the commercial biochar-amended reactor maintained sufficient total alkalinity at an organic loading rate of 2.02 gVS/L/d. Nonetheless, due to significant VFA accumulation, the control reactor experienced a rapid drop in CH<sub>4</sub> generation. Two biochar-supplemented reactors, on the other hand, obtained stable performance at below 6.0 gVS/L/d without any increase in alkalinity. The effect of biochar on the anaerobic digestion of fruit waste was also investigated, which revealed that the addition of biochar increased methane generation and the breakdown of VFAs (Ambaye et al., 2020). A lack of certain nutrients or trace minerals in the substrate could also promote a rise in VFAs, which inhibited microbial activity in the AD process (Chiappero et al., 2020). Thus, employing biochar as a source of trace metals, was presumed to stabilize the AD system. Meng et al. (2020) determined that a biochar dosage of 10 % to 20 % improved CH<sub>4</sub> generation as effectively as the inoculum addition method during the batch solid-state anaerobic digestion system. In the presence of a high concentration of accumulated acetate, it was also shown how the buffering capacity of biochar enhanced methanogenesis.

A number of studies on the application of biochar in the AD process were conducted with the aim of reducing methanogenesis inhibitions caused by acid and NH<sub>3</sub> accumulation (Christou et al., 2021). Recently, it was reported that DIET between *Geobacter metallireducens* and *Methanosarcina barkeri* was enhanced with biochar (Abbas et al., 2021). The electron recovery of CH<sub>4</sub> generated from ethanol was improved by 86 %



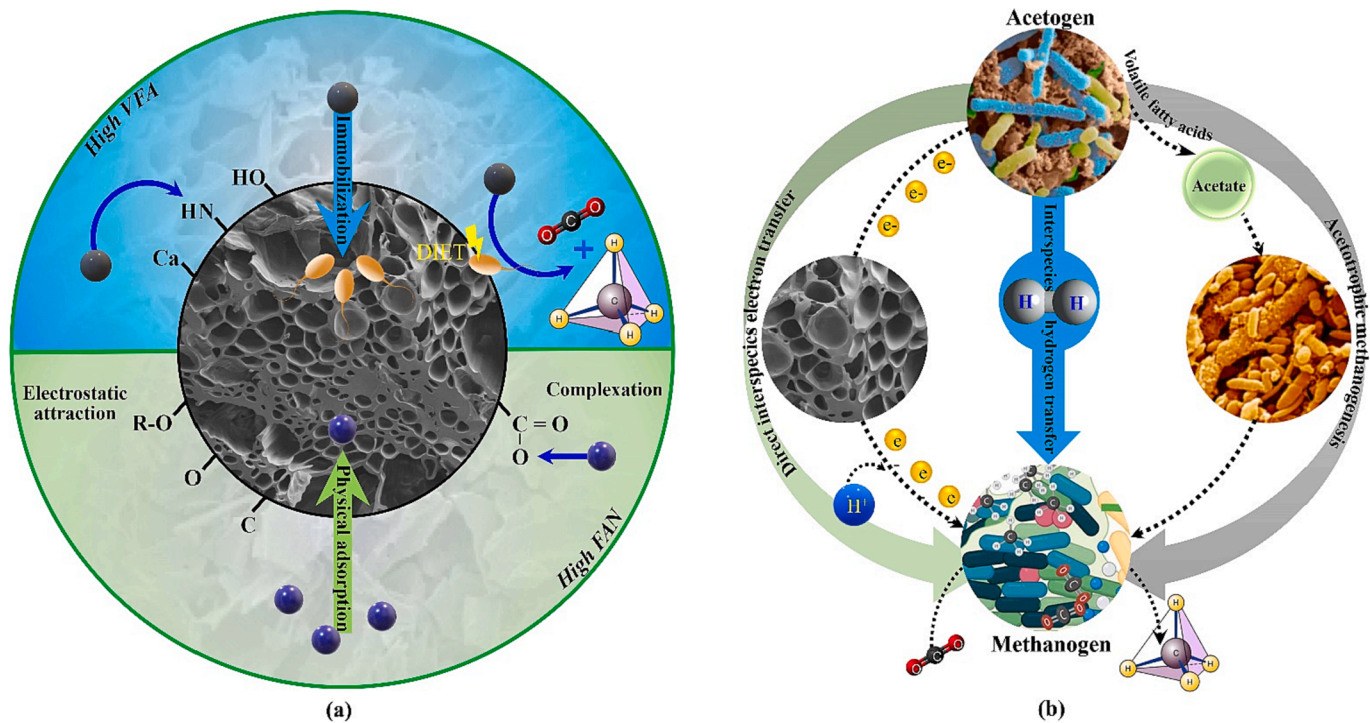


Fig. 3. (a) - Chemical and physical mechanism in using biochar for improving the stability of anaerobic digestion system; (b) - Methanogenesis pathway of anaerobic digestion process with the support of biochar through direct interspecies electron transfer mechanism (Z. Wang et al., 2019; Yu et al., 2022) (VFA for short of volatile fatty acids; FAN for short of free ammonia) (W. Zhao et al., 2021c).

when biochar was used, compared to the 77 % when using activated carbon (Abbas et al., 2021). In addition, the impact of bio-derived carbons on the co-digestion system was assessed and a biochar-based DIET method was proposed by Wang et al. (2019) (as illustrated in Fig. 3b). In the acetogens metabolism, the electrons from the disintegrated VFAs might be immediately transported to specific methanogenic archaea through the conductive bio-originated carbon substances. Developing an improved biological interspecies electrical link in AD with the addition of bio-derived carbons accelerants might successfully increase the VFAs consumption, hence relieving acid accumulation inhibition as well as generating a favorable habitat for methanogenesis (Z. Wang et al., 2019b). In an investigation by Pan et al. (2019a), the influence of several biochar varieties on the AD of chicken manure was examined at a temperature of  $35 \pm 1$  °C. Fruitwood, wheat straw, were pyrolyzed with up to 5 wt% dried chicken manure at varying temperatures. Compared to AD reactors without biochar, the reactors outfitted with nine different forms of biochar all generated more CH<sub>4</sub>, especially using biochar pyrolyzed at 550 °C, the average total output of CH<sub>4</sub> was 294 mL/g VS, which was 69 % higher than that without biochar.

In conclusion, VFA inhibition can be mitigated by adding biochar in the presence of a high number of easily degradable wastes. The considerable fluctuation in the microbial diversity of biochar-adjusted AD reactors has a crucial role in enhancing the AD system's efficiency without inhibiting VFA or free ammonia. The alkaline nature of biochar, which imparts its pH buffering ability, can help to avert VFA inhibition. Under acid stress, porous biochar is able to support the development of biofilm as well as protect selectively enriched functional microorganisms which are tightly associated with it (Chiappero et al., 2020). Furthermore, the addition of biochar can accelerate the syntrophic oxidation of VFA, mitigating the effects of acidogenic product inhibition (D. Zhao et al., 2021a). The porous characteristic and large specific surface area of biochar could promote the bacteria and archaea colonization, leading to an improvement in AD performance (Kumar et al., 2021). Beyond these advantages, biochar addition enhances methanogenesis enzyme activity, which in turn can increase the production of

methane (Q. Qi et al., 2021b). According to the authors' knowledge, crop straw-based biochar shows better performance in improving methane generation in thermophilic AD, whereas better performance is observed using woody biochar in mesophilic AD. Under the same conditions, biochar particles with a smaller size produce more methane than larger particles. However, excessive biochar use can result in a decrease in methane generation, as discussed in the following section.

### 3.2. As absorbent

Biogas is a mixture of hydrogen sulfide (H<sub>2</sub>S) (0.1–4 % v/v), CO<sub>2</sub> (36–50 % v/v), CH<sub>4</sub> (45–70 % v/v), as well as other gases according to the chemical elements of the feedstocks (Kapoor et al., 2020). However, the abundance of CO<sub>2</sub> along with other impurity gases can lower biogas' calorific value and limit its economic viability. Furthermore, high H<sub>2</sub>S levels can oxidize steel pipelines and pose a risk to human health and the environment if emissions are improperly managed. Because of its large specific surface area, high porosity, polar and hydrophilic nature, biochar has a high immobilization and adsorption capacity (Dissanayake et al., 2020). Biochar is also an efficient *in situ* adsorbent of CO<sub>2</sub> and obtaining partially upgraded biogas (W. Zhao et al., 2021c). The addition of biochar to AD could enhance the CH<sub>4</sub> concentration to over 90 %, which can be explained from two perspectives and absorption mechanism of CO<sub>2</sub> by using biochar (Wei et al., 2020). First, CO<sub>2</sub> adsorbed directly by hydrophobic sites on biochar raises the relative CH<sub>4</sub> concentration (W. Zhao et al., 2021c). Second, biochar could foster the syntrophic growth of CO<sub>2</sub>, decreasing organic acid oxidizing bacteria and methanogens present in biochar (Pan et al., 2019b). Furthermore, CO<sub>2</sub> could be isolated as carbonate or bicarbonate due to the base cations that were released by biochar. Indeed, the CO<sub>2</sub> adsorption capacity of biochar can reach dozens to hundreds of milligrams per gram odd as-used biochar (W. Zhao et al., 2021c). However, the difference in the CO<sub>2</sub> adsorption capacity of biochar is found to have much dependence on the biochar physicochemical properties, including the content of functional groups, and aromaticity (Lee et al., 2021). Thus, various modifications



on the surface, such as functional group grafting, element impregnation and chemical activation were suggested to improve biochar's adsorption capability to remove CO<sub>2</sub>. The CO<sub>2</sub> removal effectiveness of amine-activated biochar which was treated by ultrasound, for example, was nearly 7 to 9 times that of raw biochar (Dissanayake et al., 2020). Moreover, the biochar modification by other methods aiming to increase the functional group content and surface basicity of the biochar due to the diffusion of chemical elements into the internal structure of the biochar matrix, resulting in the increase in the pore width and generation of new pores, and improvement of the CO<sub>2</sub> adsorption (Dissanayake et al., 2020).

Aside from volatile fatty acids, ammonia, particularly free ammonia (FAN), was also identified as a key factor adversely affecting AD operation. Owing to the high ammonia concentration originating from nitrogen-rich components, the inefficient digesting performance of high protein wastewater was shown to be related to the imbalance of protons transmission induced by the fast FAN diffusing via cell membrane (Cai et al., 2022). When the C/N rate of the substrate was less than 15 such as cattle manure, microalgae and food waste, sludge, the digestion system was frequently threatened by ammonia inhibition (Cai et al., 2021). Besides, NH<sub>3</sub> could enter the cell structure, inducing a proton imbalance, whereas high NH<sub>4</sub><sup>+</sup> content might cause harm to the structure of enzymes. Moreover, a high quantity of FAN hindered methanogenesis, leading to volatile fatty acids accumulation and poor CH<sub>4</sub> production (Ambaye et al., 2021). Therefore, the high buffering ability of biochar could result in good resistance against FAN (Wei et al., 2020). Biochar has an outstanding adsorption ability in terms of removing heavy metals, ammonia, and other toxins that could considerably hinder methanogenesis (W. Zhao et al., 2021c), and it also provides resistance to toxicity damage in the AD system (Antonangelo et al., 2021). From a theoretical perspective, toxins might be absorbed by the surface of biochar (Ambaye et al., 2021). In general, there are four adsorption mechanisms for ammonia nitrogen, including physical adsorption, electrostatic attraction, complexation, and ion exchange (Masebinu et al., 2019). All these adsorption processes were influenced by biochar parameters (specific surface area, types of functional groups and quantity, and porosity) and digesting conditions (pH and cation concentration) (T. Wang et al., 2021d).

Physical adsorption is favorably associated with specific surface area and porosity. Based on the findings of Wei et al. (2020), biochar's porosity and conductivity were observed to improve DIET as well as aid in transferring electrons. Remarkably, the average ammonia nitrogen adsorption capacity of biochar without modification was around 50 mg/g. Because oxygen-containing functional groups (including chromene, lactol, carboxyl, pyrone, lactone, ether, quinone, carbonyl, anhydride and phenol) existed and dissociated, the surface of biochar was often negatively charged (Cai et al., 2022). The negative surface charge was found to be positively associated with biochar's surface polarity, affecting its capacity for adsorbing chemicals. In addition, it was reported that there is a strong relationship between negative surface charge and pH (Tan et al., 2020). Indeed, the pH of the digestive system affected biochar adsorption by influencing the biochar's surface charge and NH<sub>4</sub><sup>+</sup>-N formation. The pH of the system could be increased by the addition of biochar. However, according to Chen et al. (2021c), when the biochar addition is above a particular threshold, the volumetric biogas generation rate will decrease (Indren et al., 2020). Excessive biochar addition may harm the digestive system in two ways. Firstly, the pH of biochar used in this work was high – ranging from 6.8 to 11.3. Based on the NH<sub>4</sub><sup>+</sup>-N chemical equilibrium, the high pH of biochar might increase the conversion of NH<sub>4</sub><sup>+</sup> to NH<sub>3</sub>. This would be detrimental to the AD system since NH<sub>3</sub> is more toxic compared to NH<sub>4</sub><sup>+</sup> (Wei et al., 2020). Secondly, when NH<sub>4</sub><sup>+</sup>-N content was low, adding a considerable amount of biochar would result in a nitrogen supply shortfall. The reason is that NH<sub>4</sub><sup>+</sup>-N is a nitrogen source for microbes, so it could limit the growth and metabolism of microorganisms (Cai et al., 2022). In a study by Yan et al. (2021), it was found that woodchip-derived biochar with a higher

specific surface area and maximum NH<sub>4</sub><sup>+</sup>-N adsorption at the liquid stage increased CH<sub>4</sub> generation by 35 %. Also, biochar demonstrated an exceptional capability of adsorbing toxicants such as nonylphenols, phenols and heavy metals (Kumar et al., 2022; Ambaye et al., 2021). According to Wang et al. (2020a), adding 15 g/L biochar to an AD system containing phenol shortened the methanogenic lag time (from 15 d to 1.1–3.2 d), allowing the maximum rate of methane generation to increase by 1.6–2.5 times. Current research has focused on chemical modification as well as biochar activation in terms of adsorbing various inorganic/organic pollutants; however more investigation is needed to determine how biochar affected the adsorption of the toxicants in the environment.

To summarize, absorbing ammonia through using biochar in the AD process considerably increases biogas production because of its high specific surface area and acidity. As a result, in the AD system, a high specific surface area of biochar leads to a significant decline in ammonia content (Cai et al., 2022). Furthermore, the microporous structure of biochar is also an important factor in providing a good living environment for microorganisms, such as methanogens, and building colonies that can help FAN inhibition recovery. The acidities of biochar can also be raised by the acid functional groups, which are required to remove FAN adsorption and maintain the system buffering ability (Pan et al., 2019a). Given the ongoing operation, biochar may adsorb the metabolites that are accumulated or produced, releasing the inhibitory effect and enhancing the stability of the system.

### 3.3. Enhancing microorganism metabolism

Immobilizing microorganism is critical to balance the optimum nutrition as well as to sustain the activity of the biocatalyst during the AD process. In addition to providing active sites for the adsorption of ammonium, hazardous contaminants, and gaseous wastes, the eco-compatibility and porous structures that form on the surface of biochar provide a refuge for microbial adhesion. The adsorption occurring on the pore surface of biochar along with entrapment can both naturally immobilize microbes. Biochar is advantageous at the bacteriological level during AD in stabilizing cell and bacterial growth. The high specific surface area and porosity of biochar increase the immobilization of microorganisms and aid in the attachment of functional microorganisms, which accounted for the significant difference in microbial diversity between biochar-amended AD reactors (Miao Chen et al., 2021a). Additionally, a considerable specific surface area along with porous structures of biochar encourage methanogenic archaea and syntrophic acetogenic bacteria to colonize, allowing for total organic carbon removal and an increase in the rate of AD reaction. By the use of scanning electron microscopy, microorganisms including hydrophobic microbiota and methanogenic archaea were reported to easily thrive in the biochar pore (Pytlak et al., 2020). Porous biochar showed a greater abundance in methanogenesis archaea (including *Methanosarcina*, *Methanosaeta*, *Methanobacterium*, *Methanosarcina*, *Methanolinea*) than in the bacterial population (Kumar et al., 2021). Sequencing analysis revealed that the addition of biochar significantly increased the variety and number of microbial groups in reactors compared to non-biochar-added reactors (Miao Chen et al., 2021a). The AD process of food waste could be enhanced by using biochar against process inhibitors, forming a surface area for methanogenic microorganism colonization, fostering the digestate quality via retaining nutrients, reducing the microbial lag stage to its optimal value, and helping the system's buffering capacity. Furthermore, minerals such as Mg, Na, K, P, and N leached from biochar enhanced syntrophic metabolic processes among various bacteria, which could be another explanation for the improved digestive performance (Ambaye et al., 2021). Complementary work suggested that biochar was able to selectively enhance the bacteria involved in the AD system (Qin et al., 2020). Adding biochar to AD in another study boosted methanogenesis enzyme activity such as dehydrogenase enzyme and coenzyme F420, hence improving methane generation (Q.

Qi et al., 2021b).

In terms of supporting DIET cycles in order to activate the AD system, biochar's electrochemical characteristics allow to act as a mediator in syntrophic metabolism by promoting interspecies electron transfer (G. Wang et al., 2020c). As an additive, biochar facilitates the exchange of cations, enhances the stability of biochar bacteria, enhances electrical conduction, improves biofilm adhesion and area, and increases AD alkalinity. DIET could further be improved between the AD system's methanogen group and the syntrophic acetogen by the expansion of biochar. When the same microorganism structure and distinct AD performance were considered, it was determined that the impacts of microorganism spatial dispersion could cause the various AD performances (Qin et al., 2020). Biochar promoted microbe extracellular polymeric substance production in the biofilm formation, which boosted the microbe's adherence to the biochar surface (Goswami et al., 2022). This technique is not only inexpensive but also simple for reducing methanogen loss and preventing rapid sludge granulation in the AD process. Indeed, affixing microbes to biochar could considerably reduce microbial contact distance; however, it might increase DIET between methanogens and electricigens. Li et al. (2021c) reported that biochar increased the capacity of *Sporanaerobacter* and *Enterococcus*, which supported the breakdown of fermentable substrates to transfer electrons to *Methanosarcina*. Furthermore, lag period was remarkably reduced by the biological interaction of *Methanosarcinales* and *Methanosetaeaceae* with biochar (Yee and Rotaru, 2020).

Further fundamental evidence for biochar's ability to improve AD systems lays within microbial electrochemical cell studies. Based on the result by Yin et al. (Yin et al., 2019), adding biochar might contribute to DIET by replacing *Thermincola* spp. on the anode while increasing *Methanothermobacter* spp. on the cathode. The addition of conductive elements, such as biochar, supplied habitat for microflora as well as worked as electrical conduits. Acting as the conductive material, biochar could increase the generation and consumption of the organic intermediate (e.g. butyric acid and propionic acid) in order to produce methane by fostering DIET between syntrophic microbes via electroactive microorganisms' selective colonization and the formation of abiotic conductive networks (Cui et al., 2021). For example, Wang et al. (2020a) demonstrated that the variety of the electroactive microbe *Geobacter* was significantly increased from 3.8 to 7.7 % up to 11.1–23.1 % by adding biochar for promoting DIET and hence methane generation. Wang et al. (2021) also reported the same findings when observing that the abundance of electroactive bacteria, e.g. *Geobacter*, *Desulfovibrio* and *Smithella*, increased by 6 to 22 times by using modified biochar. Biochar had the potential to boost interspecies electron transfer in specific co-cultures as well as enrich syntrophic partners capable of DIET (L. Li et al., 2021a). Moreover, DIET could transport electron 106 times faster compared to indirect interspecies' electron transfers (Qiu et al., 2019), leading to faster degradation of the substrate. To summarize, biochar can be employed as a medium for the growth, metabolism and breeding of microorganisms; nevertheless, it is not clear which strains engage in the DIET process in a biochar-mediated anaerobic environment, due to the lack of micromechanism understanding and electron intake by methanogens archaea, which are supplied by non-living creatures and extracellular microorganisms. The effects of biochar on AD performance are tabulated in Table 1.

For some industrial-scale and commercial applications of AD system in CH<sub>4</sub> production, Le Pera et al. (2021) reported that an industrial AD plant in Italy could provide 860 m<sup>3</sup> of biogas per tonne of total volatile solids in the case of using organic municipal solid waste. Moreover, the average percentage of CH<sub>4</sub> in produced biogas was around 59.09 %. In another industrial application, Ronga et al. (2020) conducted experiments using pine wood chips-originated biochar for the AD system. As a result, liquid digestate and residue biochar after the AD process were used to fertilize tomato plants, showing a maximum yield of 72 tons/ha compared to the unfertilized case with liquid digestate and residue biochar (47 tons/ha). A similar application in France was also reported

**Table 1**

The application of biochar in AD process.

Biochar type	Operating conditions	Obtained results after adding biochar	Reference
Wood pellet	30 days for the entire AD with added biochar of 7.5–15 g/L at 55 °C of thermophilic temperature	CH <sub>4</sub> concentration is sharply increased, and biochar dosage and size, methanogenic pathways, and AD scale-up are the most affected factors on CH <sub>4</sub> concentration.	(Zhang et al., 2020b)
Wheat straw/ Soft wood	30 days for the entire AD with added biochar of 10 g/L at 35 °C of mesophilic temperature	Wheat straw produces higher CH <sub>4</sub> concentration and better vS removal compared to softwood	(Kaur et al., 2020)
Corn stover	23 days for the entire AD with added biochar (66.6 g/L) at 37 °C	Max CH <sub>4</sub> yield = 342.1 mL/gVS with enriched <i>M. harundinacea</i>	(Zhou et al., 2020)
Wood chips	14 days for the entire AD with added biochar of 0–10 g/L at 55 °C of thermophilic temperature	Lower volatile fatty acids, enhanced stability of the AD process, and higher CH <sub>4</sub> concentration could be achieved after adding biochar	(Lim et al., 2020)
Wood chips	55 days for the entire AD with added biochar of 15 g/L at 55 °C of thermophilic temperature	CH <sub>4</sub> concentration is increased by 54 % at the optimal condition, and CH <sub>4</sub> production depends much on biochar dosage.	(Zhang et al., 2020a)
Waste forest	49 days for the entire AD with added biochar at 55 °C	Max CH <sub>4</sub> yield = 328 mL/g COD, CH <sub>4</sub> production rate increased 269 % in the first 16 days and finer particle size of biochar produces more CH <sub>4</sub>	(Zhang et al., 2020b)
Saw dust	Entire AD with added biochar at 35 °C	Max CH <sub>4</sub> yield = 452 mL/g vS CH <sub>4</sub> production gets the maximal rate with biochar pyrolyzed at 500 °C.	(G. Wang et al., 2020b)
Corn straws	34 days for the entire AD with added biochar at 35 °C	Max CH <sub>4</sub> yield = 118.29 mL/gVS with enriched <i>Methanobacter</i>	(J. Li et al., 2019)
Pomelo peel	Entire AD with added biochar at 22 °C and load of 0.5 g/L	Increase in the removal ability of sulfamethazine by more than 30 %, and CH <sub>4</sub> yield ≈ 0.2 L/g COD	(Cheng et al., 2021)
Rice straw	Entire AD with added biochar at 55 °C	CH <sub>4</sub> yield increased by 133.7 %	(Yue et al., 2019)
Sawdust	Entire AD with added biochar at 35 °C and load of 15 g/L	Decrease in lag times by 10.6 days, increase in CH <sub>4</sub> production by 1.78 mL/d.	(Q. Li et al., 2021b)
Rice husk	Entire AD with added biochar at mesophilic temperature and load of 10 g/L	CH <sub>4</sub> yield increased from 27.8 to 96.4 %	(Yu et al., 2021)

by Tayibi et al. (2021a), in which they land-applied liquid digestate with residue biochar after the AD process on a wheat field. They found that the simultaneous use of liquid digestate with residue biochar could enhance wheat growth up to 67.8 % compared to soil alone. Although the industrial and commercial applications of biogas and digestate produced from the biochar-assisted AD system have considerable potential, the barriers relating to policy, market, shortage of competent, and technologies should be addressed so that this technology can be deployed more widely to reduce net CO<sub>2</sub> emissions, green our energy sources, and protect the environment.

#### 4. Limitations and prospect

Recently, there has been an increase in studies concentrating on the combination of biochar and AD aiming to alleviate difficulties connected with the AD process. Nonetheless, there are challenges preventing the advancement of this method.

The advantages of applying biochar as buffering agents in AD systems in order to mitigate pH reduction are apparent. The majority of current investigations examining the effects of biochar buffering ability on AD systems use batch tests carried out under methanogenic inhibition settings and with a high accumulation of VFA. Methanogenesis was also considered a process of producing alkalinity in a stable long-run operating AD system; thus, it might somewhat counteract the pH reduction potential induced by VFA accumulation. As a result, assessing how the biochar improves buffering capability under stable methanogenic activity are important for AD systems with the long-term operation. DIET's long-term operation is another question that requires attention. DIET's role and performance during real, year-long anaerobic digestion should be investigated, as the impacts of DIET in continuous-operational systems are unknown. Additionally, to further comprehend the mechanism and existence of DIET during anaerobic digestion, it is necessary to conduct more research on bacteria and archaea relevant to DIET in co-cultures as well as pure cultures of pure microorganisms (Xiao et al., 2020b).

Selecting raw materials is a critical first step in influencing the synthesis of biochar and subsequent production of methane. Every year, numerous varieties and enormous amounts of biomass waste are created, so it is vital to specify the sorts of biochar that are compatible with various AD substrates. Moreover, in order to ensure the successful incorporation of biochar into AD systems, it is necessary to understand biochar's role and mechanism, as well as the reactions associated with the addition of biochar in improving the operating efficiency of the AD process. Previous research, nevertheless, tended to concentrate on examining certain features of biochar while overlooking the relationships between the processes. Notably, there is still a need for clarification on the interplay between biochar's chemical properties, microbial communities, and efficiency of the overall AD system operation. As a result, more research is necessary to analyze the roles of different biochar reactions and processes in enhancing AD performance. When the quantity of biochar ranged from 2 to 40 g/L, the addition of biochar was advantageous for the ammonia-nitrogen-rich digestion system. Apart from that favorable impact, there may also be adverse effects on digestion performance that are yet unknown. However, an extensive amount of biochar could raise the pH of the AD system, which would harm the microbes.

When incorporating biochar as an additive into the digestion system in an effort to increase biogas generation and reduce ammonia nitrogen, the proportion of biochar addition has to be optimized on varying TAN contents. More investigations should be conducted to analyze the trade-off between AD performance and biochar adsorption behavior in order to understand the electron transfer mechanism between syntrophic partners as a function of biochar properties. Although there have been a large number of reports on the use of biochar to improve AD performance in treating organic solid wastes, especially in terms of system stability, biogas production, and the removal of pollutants, more research in this area is also needed to better understand the fundamental mechanisms of biochar in order to further remove such contaminants. The AD performance of treating organic solid waste should therefore be improved by making more attempts at creating modified biochar.

The impact of biochar at pilot and industrial scales, as well as energy and material balance assessments for the biochar-adjusted AD system, should be critically evaluated. The importance of a comprehensive assessment in the areas of optimizing energy recovery by AD, life cycle assessments, and the use of digestate as biofertilizer is important for boosting the real-world applicability of this concept. It was reported on the basis of life cycle assessments that most of the biochar applications in AD systems could bring positive impacts compared to other practices, indicating that CO<sub>2</sub>-eq emission could be reduced to 2.74 kg/kg biochar by using forestry waste-originated biochar (Kumar et al., 2021). More importantly, the integration of other thermal processing for biochar production from crop residues into AD and digestate could enhance the net energy generation with added environmental and economic

advantages (Antoniou et al., 2019). As per life cycle assessments of biochar production and application, it is demonstrated that AD systems amended by crop residues-originated biochar could provide environmental benefits compared to non-integrated processes (Kumar et al., 2021). Another major concern is the low-carbon and sustainable treatment of the liquid and solid digestate generated by the AD process. Therefore, the optimal AD process, the biochar generation for application, related energy consumption and biogas creation, and so on, should be analyzed and demonstrated from the perspective of the complete life cycle and supply chain management.

## 5. Conclusions

Biochar may significantly enhance the performance of anaerobic digestion (AD) systems by increasing methane production, stabilizing system pH, supporting microbial communities, and sequestering pollutants. These improvements are attributed to biochar's inherent properties, including its high porosity and surface area, surface functionality, alkalinity, and favorable interactions with anaerobic bacteria that promote biodegradation. Widespread commercialization requires further investigation to answer several key questions including: (1) Which fundamental biochar properties mediate system performance, and by what mechanisms? (2) Is there an optimal biomass-to-substrate ratio that enhances AD, or one that inhibits it? (3) What are the technoeconomic opportunities and limitations of this approach?

## 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.

## Data availability

Data will be made available on request.

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