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Review

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The Role of Biochar to Enhance Anaerobic Digestion: A Review

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Abstract: Biochar, one of the products of thermochemical conversion of biomass, possesses specific physiochemical properties such as conductivity, pore adsorption, surface functional groups, and cation exchange capacity. Anaerobic digestion (AD) as a classical bio-wastes conversion technology, suffers from inhibitions, process instability, and methanogenic inefficiency which limit its efficiency. With the advantages of pH buffering, functional microbes enrichment, inhibitors alleviating, and direct interspecies electron transfer (DIET) accelerating, biochar suggests a promising application as additives for AD. Herein, this paper reviewed the noting physicochemical properties of biochar, and discussed its roles and related mechanisms in AD. Further, this paper highlighted the advantages and drawbacks, and pointed out the corresponding challenges and prospects for future research and application of biochar amending AD.

Keywords: Biochar; physiochemical properties; anaerobic digestion; methane production; mechanisms

1 Introduction

Biochar is a carbonaceous solid product produced via restructuring or incomplete oxidation during thermochemical conversion processes [1], and it could be produced from a variety of biomass such as wood [2], mixture of straw and livestock manure [3], and digestate [4]. The existing studies suggested that biochar exhibited some specific properties, such as high porosity, large specific surface area (SA), good electrical conductivity (EC), excellent ion exchange capacity, and abundant surface functional groups [5], all of which indicate its promising applications. The physiochemical properties of biochar highly depend on the characteristics of feedstocks, fabrication methods (gasification [6], pyrolysis [7], hydrothermal carbonization and liquefaction [8,9]) and the corresponding operation conditions (heating rate [10], maximum temperature [11], residence time [12], and carrier gas [13]). Given these physiochemical characteristics, preceding studies confirmed that biochar could increase and fix nutrients in the soil, improve soil fertility and shock resistance. It can also remove organic or inorganic toxins from sewage to reduce environmental pollutions [14]. Hence biochar has been widely used in the field of soil remediation [15] and wastewater treatment [16,17]. Moreover, biochar was used as a platform to investigate or produce carbon based functional materials, which were widely introduced for energy storage and conversion [1,18], as well as environmental contaminants removal [15,19].

Biochar attracted increasing attentions as an additive for enhancing the performance of anaerobic digestion (AD) [20–23]. AD, based on the syntrophic metabolisms of microbes, is one of the most successful technologies worldwide for converting waste biomass to biofuel [24]. AD process is usually divided into three stages, namely hydrolysis, acidogenesis and methanogenesis, and each stage involves different microbial communities [25]. AD performance was directly affected by temperature, pH, substrates concentration, inocula, additives, etc., and the balance between the above-mentioned three stages was always realized by regulating these factors [26]. Previous studies demonstrated that AD could be applied to a variety of feedstocks, such as kitchen waste, livestock manure and waste activated sludge (WAS) [6,27]. Although widely studied, AD faces a multitude of challenges including instability and inefficiency due to pH shock, high organic loading, and various inhibitions induced by accumulated ammonia, volatile fatty acids (VFAs), inherent toxic substances and heavy metals in feedstocks [28]. It was reported that the eco-compatible biochar could serve as an effective additive for AD [29]. The lag phase of methanogenesis was shortened and chemical oxygen demand (COD) removal capacity was enhanced with the addition of biochar [30]. Lü et al. [31] found that the coarse- and medium-sized biochar was helpful for the lag phase reduction for methanization, and fine biochar had a better promotion on hydrolysis and acetogenesis. Besides, sludge in AD reactor with biochar addition showed an excellent settling property, high biomass retention, and great degradation ability [32]. Biochar addition also enhanced valorization of AD via increasing the content of metallic elements in digestate, such as potassium (K) (by up to 33 times) [23], which improved the fertilizer value of digestate. Different mechanisms were proposed for enhanced AD with biochar addition. The great adsorption capacity and abundant redox active moieties of biochar were reported to be beneficial to methane production [22]. The adsorption alleviated inhibitions caused by toxicants, while the redox active moieties may favor the electron transfer among anaerobic microorganisms. The occurrence of direct interspecies electron transfer (DIET) induced by biochar provided a microcosmic (electron level) explanation for the mechanism of biochar enhancing AD [33], and opened up a new research direction for further AD optimization and biochar utilization.

Although the subject of biochar amended AD has been extensively investigated, there is still a lack of comprehensive review and analysis on the mechanisms of specific biochar physiochemical properties affecting AD. In this review, the physiochemical properties of biochar are firstly summarized. And then, based on the biochar improved AD performance, relevant mechanisms are discussed. Lastly, this review presented the challenges and prospects of biochar integration with AD, aiming to provide inspirations for future research and application of biochar in AD.

2 Biochar Physiochemical Properties and Its Related Factors

2.1 Production and Physiochemical Properties of Biochar

Biochar is produced via thermochemical approaches under a wide range of temperature (180–1500°C) in anoxic conditions (Fig. 1) [1,18]. Thermochemical treatment of biomass includes pyrolysis [12], gasification [6], hydrothermal carbonization [8], and hydrothermal liquefaction [9]. Livestock manures and agricultural residues [3,13], forest residues [2], WAS [34], digestate [7] and algal biomass [35], have been used as raw materials for biochar production (Tab. 1). Different thermochemical approaches are selected depending on specific feedstock characteristics. For example, pre-dry biomass is suitable for pyrolysis while wet biomass (moisture $>$ 80 wt.%) favors the hydrothermal process [36].

The physiochemical properties of biochar, including density, pore volume and size, SA, pH, elemental composition, functional groups (e.g., C−O, C=O, COOH, OH, and $-NH_x$), EC, and cation exchange capacity (CEC), are primary interests since they are tightly related to its functionality and applications (Fig. 2) [10,18,37]. The pore structure of biochar contributed to its large SA. Though the SA of biochar (152 m^2/g) was reported much lower than that of granule activated carbon (GAC) (895 m^2/g), the

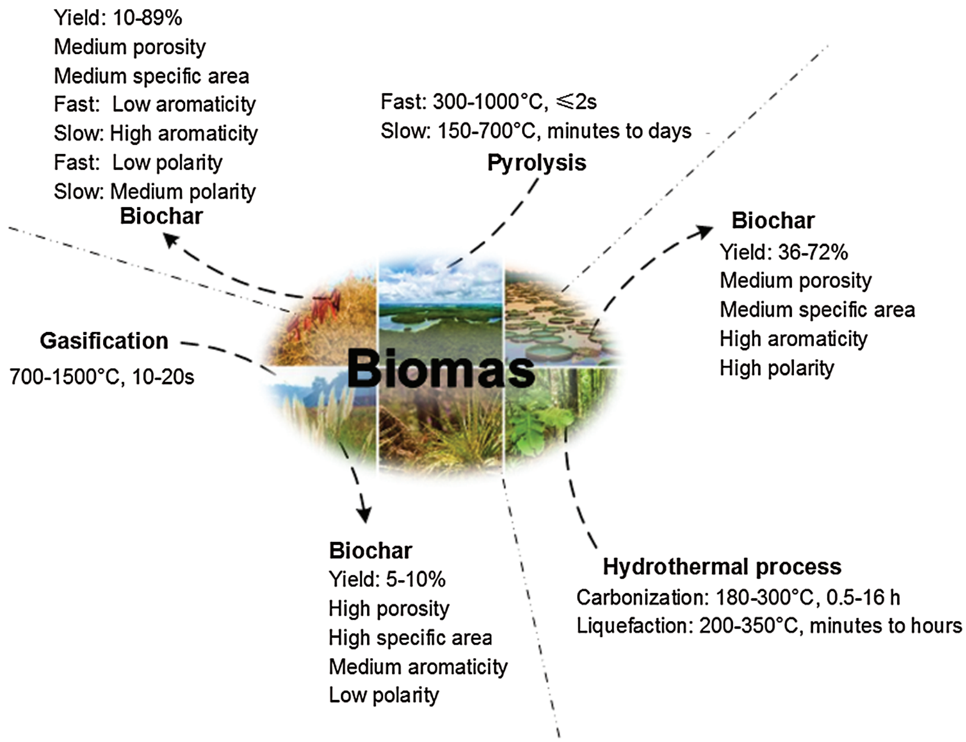

Figure 1: The main thermochemical conversion processes of biochar and its characteristics. Adapted from [9,18,19]

distribution of macropores size in biochar was larger and extensive (1–40 μm) than that of GAC (1 μm) [38]. The larger macropores in biochar provided a better environment for microbial growth, which may be advantageous compared with GAC in AD for microbial enrichment and sewage treatment. Additionally, biochar was alkaline in most cases (Tab. 1) although it was reported a wide range of pH between 3 and 12 [18]. Generally, biochar contains bulk elements including carbon (C), hydrogen (H), and oxygen (O). Heteroatoms (N, S, and P) and metal elements (K, Na, Mg, Ca, etc.) also exist in almost all biochars [39]. These elements correlated directly with the functional groups. The ratios of H/C, O/C, and N/C decided the quantity of oxygen-containing and nitrogen-containing functional groups in biochar [9,14]. Moreover, biochar has both negatively and positively charged functional groups, and the CEC of biochar increased due to the attraction of the negatively charged functional groups [14]. It was demonstrated that the EC, ranged from 0.002 to 23.8 dS/m (Tab. 1) even higher than that of GAC (3 ± 0.327 dS/m) under certain conditions, is also a vital property for further study and application of biochar [3,40]. In summary, these specific physiochemical properties, the high porosity, large SA, good EC, excellent ion exchange capacity, and abundant surface functional groups, allow biochar to serve as a catalyst, adsorbent, microbial carrier, buffer, or electron conduit additive for soil and aqueous pollutants remediation, as well as AD enhancement [14,20,41]. However, a comprehensive evaluation of these physiochemical properties of biochar and the corresponding activation methods need to be further investigated.

2.2 Factors Influencing Biochar Physiochemical Properties

Present studies suggested that the physiochemical properties of biochar depend on feedstocks characteristics, thermochemical methods and related process parameters (temperature, heating rate, residence time, and carrier gas) (Tab. 1) [14,35]. In order to purposefully prepare and utilize certain properties of biochar for specific conditions, it is necessary to be familiar with biochar physiochemical properties, and the relationship between these properties and its influencing factors. First of all, the properties of biochar are tightly related to the feedstock composition [7]. The composition of feedstock decides the elemental distribution of biochar. For example, cow manure derived hydrochar had a lower C content but a higher N and ash content than corn stock derived hydrochar, which was corresponding to the lower-carbon (43.18 ± 0.18 wt%) and higher-nitrogen (1.08 ± 0.03 wt%) contents in cow manure compared with corn stock (carbon: 44.96 ± 0.03 wt%; nitrogen: 0.49 ± 0.03 wt%) [11]. Feedstocks with high lignin and fixed carbon contents were conducive to the production of biochar with high SA and aromatic structures [26]. This was consistent with the results of previous study that the cow manure (lignin content 12.7 ± 0.89 wt.%) derived hydrochar had more surface functional groups and a higher SA in comparison with corn stalk (lignin content 9.78 ± 0.1 wt.%) derived hydrochar [11]. Fagbohungbe et al. found that the rice husk-derived biochar had a higher CEC (43.28 ± 1.49 meq/100 g) than that of the coconut biochar (31.17 ± 0.35 meq/100 g) and wood biochar (21.47 ± 0.65 meq/100 g) [43]. This could also be attributed to the difference in lignin content among these raw materials. It is noteworthy that there was a dramatic improvement in CEC (from 43.28 to 321 meq/100 g), C content (from 55.8 to 57.0–58.1%), SA (from 16.4 to 16.6–27.5 m^2/g), and pH (from 9.12 to 10.4–11.4) of biochar produced via co-pyrolysis of polymers and rice straw at 550°C [44]. These results demonstrated that the mixture of specific feedstocks with specific ratio has a great potential to modify biochar physiochemical properties.

The temperature, heating rate, and residence time of thermochemical conversion processes had significant influences on the physiochemical properties of biochar [45]. Igalavithanaa et al. summarized that (Fig. 3) the biochar had a relatively higher O content (10–40%) at a low temperature (200–400°C), and the content of C, H, and O decreased at higher temperature (600–1000°C) which can be attributed to the increased crack of volatile organics when temperature increased from 200 to 1000°C [18]. This was consistent with the results reported by Stefaniuk and Oleszczuk that the increased temperature from 400–800°C led to a reduction of H and O content, and an increase of C content [7]. Stefaniuk and Oleszczuk demonstrated that the temperature increased from 400 to 800°C resulted in the increase of pH (10.42–12.76), EC (2.91–23.8 dS/m), aromaticity, and ash content (14.12–43.56%) [7]. However, the biochar yield (45.27–27.16%), polarity, and bulk elements including H (3.22–0.71%), N (2.55–1.40%) and O (16.73–8.07%) decreased with the increase of temperature. It was evidenced that the high temperatures (800°C) led to a high SA [7], which was coherent with the results reported by Brown et al. [46] that the higher temperature (≥750°C) resulted in a sharp increase in SA and widening of micropores. Thermochemical processes of biochar fabrication also presented significant effects on its physiochemical properties. Mumme et al. confirmed that the physiochemical properties of biochar (pH = 9.3, content of dry matter 54.7%, and ash 39.2%) produced via pyrolysis (500°C) were significantly different from hydrochar (pH = 4.8, dry matter 99.8%, and ash 7.8%) produced via hydrothermal carbonization at 230°C [12]. In general, the pH values of the pyrochar were higher than that of hydrochar (Tab. 1). This was also confirmed by Ren et al. and Yin et al. [9,34]. To sum up, the thermochemical methods and process parameters for biochar production should be chosen based on a comprehensive consideration of the feedstock property and economic feasibility. Typically, the temperature from 450 to 600°C was recommended for biochar production [42].

As for heating rate of thermochemical processes, it was demonstrated that the O/C and H/C ratios increased as heating rate increased from 2 to 20 °C/min at the temperature between 250 and 350°C [35]. Further, the surface functional groups of biochar were changed accompanied by the ratio of C, H, and O transformation. While it was also reported that the higher heating rate was not conducive to biochar formation, and the biochar yield was found decreased from 22–23% to 8–9% with the heating rate increased from 5 to 140 °C/min [47]. The residence time of thermochemical approaches also significantly affected biochar physiochemical properties. At a residence time of 0.5–1 hours, increased residence time could not only promote the biochar generation but also favor the improvement in pore volume and SA of biochar [48]. However, further increase of residence time (2 h and 4 h) led to the decline of porosity due to the gasification of volatile organic carbon. One previous study demonstrated that the carrier gas contents in pyrolysis process also had a significant impact on the physiochemical properties of biochar [13]. In particular, the SA of biochar produced with CO_2 (109.15 m^2/g) was higher than that of biochar generated in N_2 (32.46), and biochar generated from pyrolysis in CO_2 was more recalcitrant than that in N_2. However, the high content of CO_2 significantly reduced biochar yield, which can be explained by that the CO_2 served both as an expediting agent to accelerate the decomposition of volatile organic carbon and a reacting agent to react with substrates simultaneously.

From the above discussion, it is clear that biochar formation and its composition can be complicated. There is a compounded impacts among thermochemical process temperature, heating rate, residence time and carrier gases during biochar fabrication [35,49]. Their respective roles in determining the physiochemical properties of biochar need to be further investigated.

Table 1: Physiochemical properties of biochar

Feedstock	Method	Temp (°C)	Heating rate (°C/min)	Physical properties				Chemical properties						Reference
				EC (dS m^{-1})	SA (m^2/g)	D (nm)	PV (cm^3 g^{-1})	pH	C/N	O/C	H/C	Ash (%)	DM (%)	
Corn residue	Slow pyrolysis	350	3	4.2	NA	NA	NA	7.4	22	NA	0.07	NA	NA	[3]
Corn residue	Slow pyrolysis	650	3	5.9	NA	NA	NA	10.6	34.5	NA	0.02	NA	NA	[3]
Poultry manure	Slow pyrolysis	350	3	4.7	NA	NA	NA	9.9	9.9	NA	0.06	NA	NA	[3]
Poultry manure	Slow pyrolysis	650	3	2.91	NA	NA	NA	12.2	16.2	NA	0.02	NA	NA	[3]
Digestate	Pyrolysis	400	25	4.52	4	10.1	0.009	10.6	23.5	0.23	0.68	28.7	NA	[7]
Digestate	Pyrolysis	600	25	7.02	3.3	18.1	0.013	11.9	24.9	0.23	0.32	31.6	NA	[7]
Digestate	Pyrolysis	800	25	23.8	7.1	11	0.016	11.6	28.5	0.24	0.24	31.1	NA	[7]
Pepper stalk	Pyrolysis	600	NA	0.16	71.3	3.2	0.06	10.8	32.9	0.09	0.32	10.6	94.2	[13]
Paper sludge and wheat husks	Pyrolysis	500	NA	NA	NA	NA	NA	9.3	33.2	NA	0.02	39.2	54.7	[12]
Straw digestate	Hydrothermal carbonization	230	NA	NA	NA	NA	NA	4.8	45.3	NA	0.05	7.8	99.8	[12]
Pinewood	Slow pyrolysis	600	NA	NA	112.9	NA	NA	7.2	345	NA	NA	NA	NA	[2]
Pine sawdust	Pyrolysis	650	NA	NA	130	NA	0.0138	9.6	260	NA	0.05	NA	NA	[50]
Sewage sludge	Hydrothermal liquefaction	300	NA	NA	57.66	NA	NA	6.5	8	0.19	0.12	NA	NA	[9]
Wood and digestate	Pyrolysis	600	Continuous	NA	NA	24–25	NA	7.98	408	NA	0.02	13.6	NA	[4]
Bamboo	Hydrothermal carbonization	200	3	NA	9.32	14.75	0.136	5.18	133	0.67	0.11	0.95	99.04	[8]
Bamboo	Hydrothermal carbonization	240	3	NA	7.63	11.36	0.067	5.31	98.5	0.34	0.08	1.08	98.65	[8]
Bamboo	Hydrothermal carbonization	280	3	NA	5.18	11.3	0.021	5.32	92.1	0.26	0.07	0.71	98.9	[8]
WAS	Pyrolysis	500	10	0.466	41.8	NA	NA	8.01	5.49	NA	0.07	66.5	NA	[34]
Bamboo	Pyrolysis	800–900	NA	NA	NA	NA	NA	9.17	208	0.1	0.44	1.32	NA	[51]
Rice husk	Pyrolysis	500–600	NA	NA	NA	NA	NA	9.45	77.4	0.26	0.61	27.6	NA	[51]
Fruitwood	Pyrolysis	800–900	NA	NA	NA	NA	NA	8.63	208	0.07	0.47	5.49	NA	[31]

NA: Not Available; SA: Specific Surface Area; WAS: Waste Activated Sludge; D: Pore Size; PV: Pore Volume; DM: Dry Matter

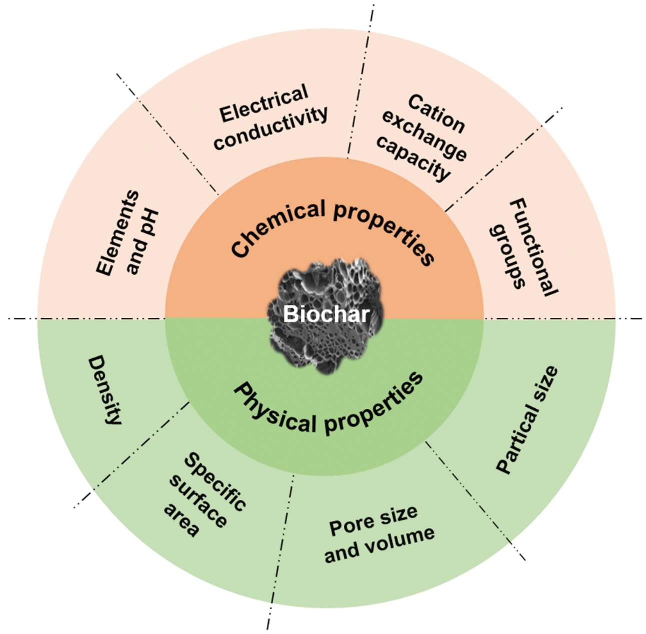

Figure 2: The principle physiochemical properties of biochar [1,18,42]

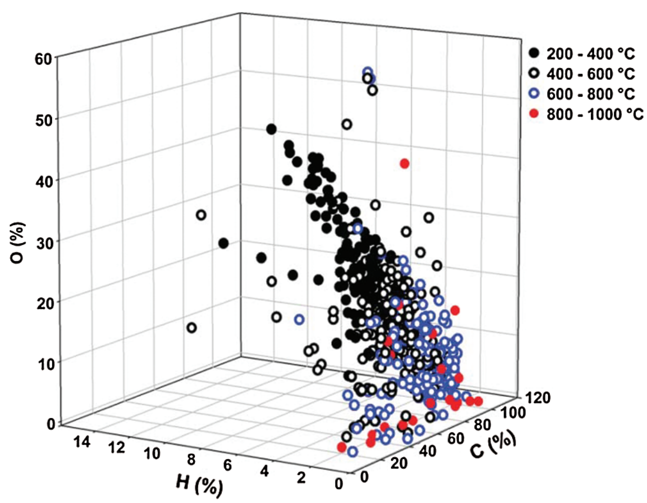

Figure 3: Changes of organic carbon (C), hydrogen (H), and oxygen (O) (percentages) in biochar as a function of pyrolysis temperature [18]

3 Role of Biochar in AD

AD is a well-documented biochemical process that converts biodegradable biomass into biofuel under O_2-limiting situations [29,52]. Main metabolic processes includes hydrolysis, acidogenesis, and methanogenesis (Fig. 4). With porous structure, good electrical conductivity, several functional groups, and a remarkable buffering capacity [17,53,54], biochar could effectively accelerate the start-up, improve the methane production, and promote the process stability during AD (Tab. 2). Precisely, the enhanced and balanced hydrolysis, acidogenesis, and methanogenesis of AD could be achieved via biochar addition (Fig. 4) [12,29,43], and the detailed enhancements and related mechanisms were reviewed and discussed in Sections 3 and 4, respectively.

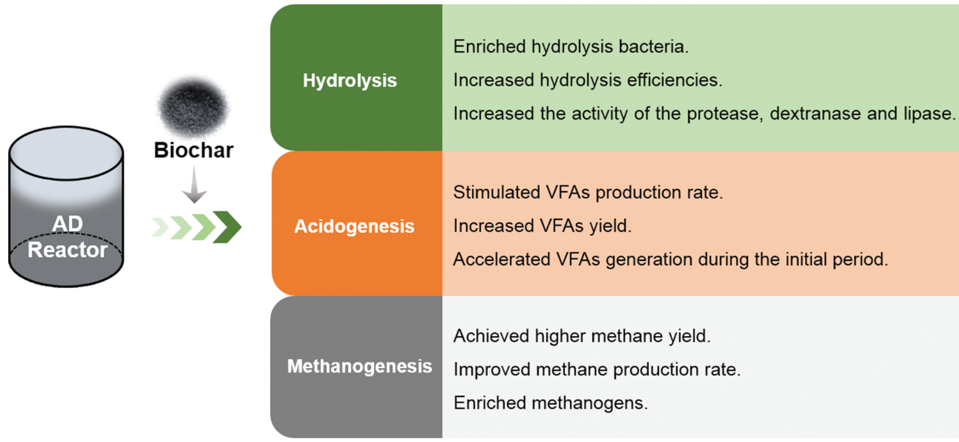

Figure 4: Impacts of biochar on hydrolysis, acidogenesis, and methanogenesis. Summarized from [26]

3.1 Accelerate Start-up of AD

Biochar has a great potential of accelerating the start-up of AD. Shanmugam et al. documented that the lag phase of methanogenic microbial colonization in AD of complex organic waste (wastewater of algae hydrothermal liquefaction) could be reduced by 24 hours with biochar addition [22]. This was in line with the results that the microbial lag phase decreased with the increased biochar to citrus peel ratio, and the shortest lag phase of 7.5 days was achieved with the optimum citrus to biochar ratio of 1:3 [43]. Likewise, Sunyoto et al. observed a similar phenomenon that biochar addition shortened the lag phase of H_2 reactor and CH_4 reactor by 21.4–35.7%, 41–45% respectively in a two-phase AD of food waste [50]. It is noteworthy that the addition of biochar during AD of food waste almost eliminated the lag phase for methane production [55]. The effects of four different types of magnetic biochars on methanogenesis have been systematically studied by Shen et al., and the results suggested that all biochar treatments shortened the lag phase by 0.9–1.83 days [56]. Similarly, Wang et al. [57] found that the lag time of co-digestion of food waste and dewatered sewage sludge decreased from 4.7 to 1.8–3.9 days in all trails with biochar application.

Overall, biochar addition accelerated the start-up of methanization, even under ammonium and acids stressed conditions. Nevertheless, the alleviation of ammonium inhibition with biochar addition was not observed during the AD of agricultural waste digestates [12]. This may be attributed to the relatively stable substrate, the low VFAs level (80 mg/L), and low dosage of biochar (6.67%). In addition, although biochar addition shortened lag phase of the AD of dairy manure, Jang et al. [58] observed a decrease in total VFAs, which may result in the decrease of accumulative methane yield. Therefore, the balance among AD conditions (substrates, pH, temperature, and reactor configurations and so on), biochar dosage, and intermediate and final products performance should be considered reasonably in further studies and applications. These can be referred to the parameters summarized in Tab. 2.

3.2 Enhance Methane Production

Previous studies (Tab. 2) suggested that biochar addition has a promising potential to improve the methane production rate, yield, and content. For example, Lu et al. found that biochar addition resulted in a substantial increase of the methane production rate (23.5–47.1%) during AD even under an ammonium and acids stressed condition [31]. Indren et al. [6] reported a significant increase of daily methane yield by 136% with the addition of wood-pellet biochar in AD of poultry litter. Likewise, Li et al. [27] observed a significant improvement (1.6 times) of the maximum methane production rate with biochar supplementation in the co-digestion of food waste and WAS along with high feedstock to seed sludge ratio of 2.5–3. Similar trends were also reported by Cruz Viggi et al. [55] that a 3.9–5.0 folds enhancement of the initial methane production rate was achieved with biochar addition, but methane production performance varies with the particle size of biochar. Furthermore, Shen et al. [23] reported that biochar also increased methane content by up to 25%, in addition to a 37% increase in methane production rate in a yearlong semi-continuous AD. It is worth noting that with biochar (pinewood biochar and white oak biochar) introduced in AD of WAS, the average methane content reached up to 79–92.3% during the initial stage (day 1) [59]. The methane content was found increased to 57.5–69.8% after hydrochar addition in co-digestion of rice straw and digestate of solid products from animal carcass [60]. Jang et al. [58] found that the cumulative methane yield increased by 27.65–35.71% in biochar (10 g/L) amended AD at different temperatures (20, 35, and 55°C). Significant improvement of methane production was confirmed in a solid-state fermentation of municipal solid waste, in which a 3–5% increase in methane yield was achieved [21]. Sunyoto et al. [50] introduced biochar into a two-phase AD system, and the maximum production rate and potential of CH_4 in the methane reactor increased by 23.0–41.6%, and 1.9–9.6% respectively.

Although the positive effects of biochar addition on methane production were reported extensively in presented studies, adverse effects of biochar dosage and specific physiochemical properties were also found in several studies (Tab. 2). For instance, Xu et al. [35] discovered that methane yield decreased with the increase of hydrochar dosage (4–8 g/L). Similarly, Dudek et al. [45] confirmed that the high amount of biochar addition (20–50%) decreased the methane production during AD of brewers' spent grain. The study conducted by Cheng et al. [61] showed a substantial decrease of methane production with the increased dosage of powdered and granular biochar. The inconsistent results could be explained by that VFAs were adsorbed by biochar rather than used for methane production. In addition, Aragón-Briceño et al. and Danso-Boateng et al. [62,63] speculated that the decreased methane production with biochar addition may be resulted from the formation of indigestible macromolecular organic compounds or other compounds that could delay methane production during hydrothermal conversion process. But specific information about these compounds and their functions was not specifically clarified. This suggested that the impact of biochar on methane production depends both on biochar physiochemical properties and loadings. Further studies should be conducted to reveal the mechanisms of the negative effects of biochar on methane production of AD for further application of biochar and AD.

3.3 Improve Process Stability

The stability of AD is critical for long-term continuous conversion of bio-waste, and biochar addition has a potential to improve the stability of AD. It was reported that biochar has the superior potential to promote the AD process stability in terms of ammonia-N alleviation [31]. The addition of biochar could enrich methanogenic microbes under ammonia and acid inhibition [6]. Hence, biochar could alleviate the ammonia inhibition and the limitation of anaerobic degradation of nitrogen-rich substrates, then lead to a stable and efficient AD. Lü et al. [31] observed that the inhibition of ammonia was obviously alleviated during AD of synthetic wastewater, which was consistent with that biochar could facilitate the methanization under high ammonium stress conditions (7 g total ammonia/L). Similarly, Shen et al. [59] found that free ammonia, which is one of the main inhibitors of AD, could be reduced by up to 10.5% with biochar addition. In addition, biochar was also reported to improve the ability of methanogenesis under acid (pH = 5.9) inhibition. Biochar effectively increased AD alkalinity (minimum pH $\geq$ 6), which facilitated the adaption of microbes to loading shock in the initial stage and enhanced the microbial activity for rapid methane production under high organic loading shock [27]. Lü et al. [31] demonstrated that biochar could also facilitate the stable methanogenesis under acid stressed environment (pH = 5.3). Therefore, biochar increased the operating capacity with high total solids content and organic loadings [9]. This indicated that a shorter hydraulic retention time and higher organic loading rate can be applied in the continuous AD with biochar addition.

Table 2: Impacts of biochar on AD

Biochar				Substrates of AD	AD process parameters	Volume of AD reactor (mL)	Conclusions	References
Feedstock	Method	Conditions	Dosage (g/L)					
Sawdust	Pyrolysis 20 °C/min	500°C for 1 h	10	Food waste; WAS	Batch; 55°C	120	Shortened the lag phases from 2.05 to 18.6 d.	[27]
Wood-pellets mixed with timber waste	Gasification	800°C for 2.5 h	25.2	Poultry litter; wood-shavings	Batch; 37°C	500	Lag time reduced by 17−41%. Methane production rate increased by 136%	[6]
Dairy manure	Pyrolysis 10 °C/min	350°C for 3 h	1, 10	Dairy manure	Batch; 20, 35, and 55°C	280	Shortened the lag phases 0.21–1.55 d. Enhanced methane yield to 26.47% in 20°C, 24.90% in 35°C, and 24.69% in 55°C. Enhanced maximum production rate by 20.41%–50.45%.	[58]
Bamboo	Pyrolysis	600°C	5, 20, 50	Cattle manure wastewater	Batch; 35°C	250	Reduced the risk of antibiotic resistance genes spreading.	[64]
Sewage sludge	Hydrothermal liquefaction	300°C for 1 h	10	Synthetic wastewater	Batch; 37°C	118	Enhanced the methane production rate by 37 %.	[9]
Pine sawdust	Pyrolysis	650°C for 20 min	8.3, 16.6, 25.1, 33.3	Food waste	Batch; 35°C	100	Improved hydrogen yield by 31.0% and methane by 10.0%. Shortened the lag phases by 36.0% in H_2 reactor and 41.0% in methane reactor.	[50]
Fruitwoods	Pyrolysis	800–900°C	10	Synthetic wastewater	Batch; 35°C	500	Reduced the lag phase by 5.9–23.9%. Increased the methane production rate by 23.5−47.1%.	[31]
Corn cob	Flash carbonization 25 °C/min	350°C for 1.4 min	5.5, 25	Grease trap waste	Continuous; 37°C	5000	COD reductions up to 95%. Resulted a methane content between 60%–80%.	[65]
Wood residue	Pyrolysis	650°C	2.6, 5.2	Municipal solid waste	Batch; 40°C	18000	Methane yield increased around 3–5%.	[21]
Wheat bran pellets, coppiced woodlands, and orchard pruning	Fast pyrolysis	800°C for 3 h	25	Food waste fermentate	Batch; 20 ± 2°C	120	Biochar-amended made the lag phase of methane production almost eliminated. Conversion of VFAs proceeding at a rate that was up to 5 times higher than control.	[55]
WAS	Hydrothermal carbonization	Below 240°C	7.2	Synthetic wastewater	Batch; 35 ± 1°C	500	Hydrochar enhanced the acidification but inhibited the activity of methanogenic bacteria.	[66]
Rice straw	Hydrothermal carbonization	260°C for 1 h	2, 4, 6, 8, 10	Dead pig carcass	Batch; 37 ± 1°C	500	Hydrochar improved biogas production by 60.7–90.8%. Methane content increased from 57.5% to 61.8–76.7%.	[60]
Pine sawdust	Pyrolysis	650°C	10	Carbohydrates food waste	Batch; 35°C	100	Improved the efficiency of the first phase of two-phase AD (hydrogen production rate improved by up to 26%, hydrogen yields increased by up to 41%).	[67]

On the other hand, Shen et al. [59] reported the negative effects of high biochar dosage (4.4–4.97 gram of biochar per gram of dry matter of sludge), including the inhibition of microbial activity and kinetics. The inhibition of methanogenic metabolisms was also reported with VFAs accumulation induced by hydrochar (generated from WAS) addition [66]. Consequently, above-mentioned results demonstrated that the dosage of biochar (1–33.3 g/L) should be carefully controlled (Tab. 2), and the inhibition of the excess dosage of biochar on microbial metabolisms and the accumulation of intermediates need to be minimized.

4 The Mechanisms of Biochar Enhancing AD

Biochar is believed functioning as a buffer for pH appropriation, a carrier for microbial colonization, an adsorbent for inhibitors alleviating, and an electron tubule for DIET to promote AD performance (Fig. 5) [12,26,68]. The mechanisms of biochar to improve AD performance were mainly to overcome toxicants inhibitions, improve microbial metabolism, and promote interspecies electron transfer efficiency [20,26,27]. However, the performance of AD with biochar addition was also influenced by the type of substrates and the ratio of inoculum to substrates [54]. This suggested that the mechanisms of biochar affecting AD have not been fully understood. Further investigation concerning the mechanisms and their internal relationships of biochar affecting AD should be considered.

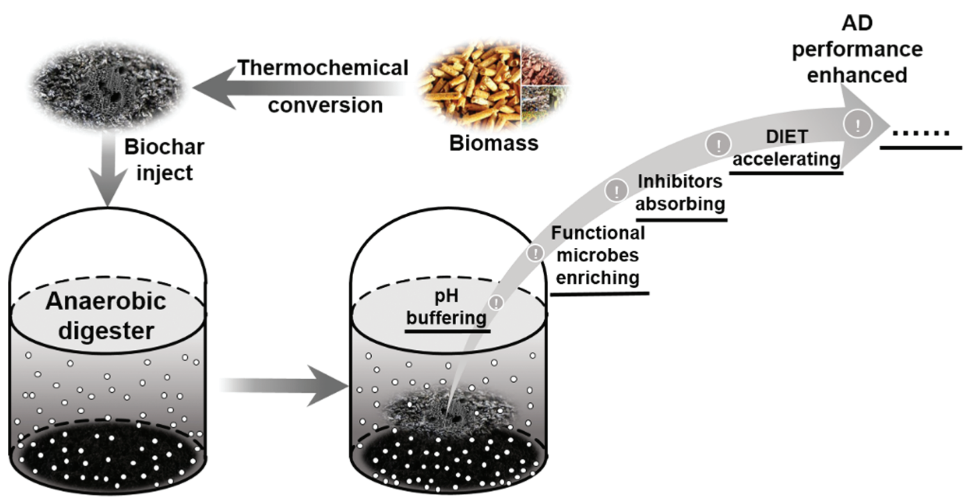

Figure 5: Concept diagram of the mechanisms of biochar enhancing AD. Adapted from [26]

4.1 pH Buffering

Low pH is one of the primary factors limiting the efficiency of AD process, which could inhibit the activity of methanogenic microbes [20]. Previous studies demonstrated that VFAs as inhibitors may have significant effects on metabolic pathways of AD systems, particularly during methanogenesis [69,70]. And the low pH was induced by rapid accumulation of VFAs, particularly at high organic loading rate with easy-acidification substrates. It generally takes a long time for AD reactor to recover from high concentrations of VFAs [9]. The addition of biochar could be a simple and effective solution to accelerate the recovery of acidified anaerobic reactors. With ash-inorganic alkalis and organic alkalis functional groups, biochar showed a great buffer capacity that could effectively neutralize the generated VFAs and prevent the fast pH dropping [27]. Specifically, Shen et al. [71] found that the functional groups existing on the surface of hydrochar and its alkaline nature helped maintain the optimal pH (7.5–8) for AD. This means that biochar addition facilitated a suitable environment for methanogens to transform VFAs to methane. Consequently, the methane content will be increased. Likewise, Wang et al. [57] confirmed that a strong pH buffering capacity of biochar was critical to keep pH stable during the stage of VFAs accumulation in a co-digestion system of food waste and dewatered sewage sludge. Sunyoto et al. deliberated that biochar may provide temporary nutrients that were helpful for pH stabilization in a two phase AD of carbohydrate food waste [50,67]. Similarly, another study found that the high nutrients and alkalinity potential of biochar played significant roles in enhancing methane production during the AD of dairy manure [58]. In summary, biochar possesses a great potential to alleviate the effects of acidification caused by VFAs accumulation, then favors microbial growth and adaption in AD with high organic loading and easy acidification substrates.

Nevertheless, the main pathways and vital factors that affected by the excessive accumulation of VFAs were not fully understood. Luo et al. [29] reported that the pH buffering ability during AD of synthetic wastewater was not significantly increased by biochar, and there is a possibility that the acid inhibition occurred before methane production. This was consistent with a previous result that biochar significantly promoted the production of VFAs during the initial stage of AD with high organic loading [31], which led to a sharp decrease of pH and even reactor failure. Also, Sunyoto et al. observed that there was an obvious pH drop, from 5.0 to 3.0, accompanied by the accumulation of VFAs at the beginning of the biochar amended AD [50], which may inhibit the metabolic activities of methanogens. Furthermore, hydrochar contains more organic matters such as humic acids that helped to enhance sludge solubilization, while both humic acid and fulvic acid in hydrochar promoted acidification [66]. Consequently, there was no conclusive conclusion concerning the pH buffering of biochar in AD. The most likely reason for these differences is that the physiochemical properties of biochar varied with the raw materials and the parameters of thermochemical conversion processes, as well as the various AD conditions used in different studies.

4.2 Functional Microbes Enrichment

Preceding studies demonstrated that biochar effectively enhanced the microbial activity for methane production through the enrichment of functional bacteria and methanogens participating in AD [27,56]. Zhang et al. [32] observed that biochar stimulated extracellular polymeric substance secretion, which was regarded as important mediators for the adhesion of microorganisms to carrier surface when the biofilm was formed [72]. Hence, the addition of biochar facilitated the growth of attached microbes, leading to a rapid sludge granulation, then offered a potential solution for the methanogens loss in anaerobic digesters. Likewise, Sun et al. [2] confirmed that biochar functioned as an effective carrier that significantly increased the microbial abundance in AD. Specifically, Dang et al. [73] found that biochar enriched the abundance of *Sporanaerobacter* and *Enterococcus*, which could metabolize fermentable substrates and transfer electrons to *Methanosarcina* species that were also enriched with biochar addition. Indren et al. [6] reported that the *Methanosaetaceae* preferentially attached to biochar and formed a biological-based interaction, and this kind of interaction could lead to a reduced lag time. These results were consistent with the study that found biochar assisted bioaugmentation of methanogens via enriching *Methanosarcinales* [31]. Wang et al. [35] reported that as the dosage of hydrochar increased, it is more advantageous for the attachment of methanogenic bacteria. This was in line with the result that hydrochar enriched the strict acetoclastic methanogen *Methanosaeta* [9]. Therefore, hydrochar addition could promote the conversion of VFAs to methane by the immobilization of methanogens [60]. In addition, biochar also enhanced the yield of VFAs via facilitating biofilm formation during the initial stage of AD [34]. This phenomenon further confirmed that biochar has the potential of enhancing AD with functional microbial enrichment. On the other hand, there was an inhibitory effect of the hydrochar which might inhibit methanogenic metabolisms also reported by a preceding study [62].

The various effects of biochar on microbial community enrichment are highly dependent on its morphological characteristics. Biochar offered a high SA (>300 m^2/g) that could be used as ideal carriers for microbial enrichment and colonization [32]. The enrichment of microorganisms on biochar led to an enhanced anaerobic conversion of bio-waste [55]. It was reported that biochar had a pore size ranged from 1 to 40 μm [38]. This indicated that the micro-/macropores of biochar could accommodate 2–10 methanogenic cells [31]. Hence it was supposed that the suitable pore size of biochar was critical for biofilm formation and granulation [32]. *Methanosaeta* could be enriched by biochar and served as a pioneer during the initiation of methanogenesis [31]. Then *Methanosaeta*, which were affinitive to biochar-associated regions, could utilize the acids that diffused in the biochar pores and continue the acid degradation process after *Methanosarcina* [74]. Also, the accessibility of methanogens to biochar pores was related to the morphology of microbes [31]. Biochar promoted the colonization of *Methanosaeta* and *Methanosarcina* to the superficial layer, while the colonization of minor *Methanoculleus* to the inner porous region of the biochar matrix.

The conductive property of biochar may also contribute to the selective enrichment of microbes. Yu et al. [75] found that biochar was functioned as an electron acceptor for microbial extracellular respiration and growth, suggesting that biochar act as electron acceptors for a diversity of electroactive microorganisms may be a general feature. Biochar was supposed to enrich the electro-active microbial consortia and promote an enhanced syntrophic metabolism interaction between bacterial and archaeal populations, which resulted in an improvement in AD performance [76]. This kind of enrichment on syntrophic microbes (*Anaerolineaceae* and *Methanosaeta*) with biochar addition was also reported by Wang et al. [53], and that also improved VFAs degradation and methane production from the AD of complex organic waste (mixture of dewatered activated sludge and food waste). Li et al. [27] demonstrated that this was possibly due to the selective succession of bacteria and methanogens which were evidenced participating in DIET. Hence the addition of biochar allowed the formation of biofilm that improved the production of methane. These phenomena further indicated the advantage of biochar in improving AD. However, it is important to recognize that it is difficult to draw the conclusion regarding the influences of biochar conductivity on microbial enrichment during AD. Cheng et al. [61] found that conductivity of biochar was poorly correlated to methane production during swine wastewater AD. Sunyoto et al. [67] proposed that biochar may support microbial metabolism and growth with carbonaceous biodegradable contents, and then to promote the methanogenic biofilm formation during AD of food waste. These results demonstrated that other properties (nutrient contents, adsorption, pH, surface properties) rather than conductivity of biochar largely explained its influences on microbial enrichment in short-term batch AD under certain conditions.

4.3 Inhibitors Adsorption

Sophia et al. [15] confirmed that the π-π interaction resulted in the adsorption of biochar. In addition, Kanjanarong et al. [4] demonstrated that the presence of carboxylic and hydroxide radical groups may also be responsible for adsorption. Nevertheless, Bagreev et al. [77] proved that the pores of biochar were responsible for absorbing chemical compounds such as phosphate, nitrate, nitrite, ammonium, pesticides, heavy metals, and CO_2. But Tan et al. [19] found that the presence of functional groups played a larger role than the pore structure in determining the adsorption capacity of hydrochar. Unfortunately, there is a lack of comprehensive comparison of these physiochemical or other properties that resulted in the contradictory results for adsorption ability of biochar. The adsorption is one of the main mechanisms by which biochar enhancing AD. Shanmugam et al. [22] attributed the improvement of methane yield in AD to the adsorption capacity of biochar, which alleviated acids inhibition via adsorption of VFAs. A similar result was confirmed by Cheng et al. [61] that VFAs inhibition was alleviated by biochar adsorption, as a consequence, strongly enhanced short-term AD performance. On the other hand, Wang et al. [35] reported that the adsorption of NH_4-N increased with the increase of SA of hydrochar. Consistent with that, Reza et al. [78] found that NH_4-N removal was increased by 27–35% and the removed quantity was related to the SA of hydrochar. Xu et al. [60] found that 1 g hydrochar from rice straw could adsorb 25 mg of ammonium and 50 mg of VFAs during the AD of dead pig carcass. However, Lü et al. [31]

reported a different result that the removal of NH_4^+-N was merely 2–3 mg with 1 g biochar, indicating biochar had no significant influence on VFAs concentration. This demonstrated that the adsorption capacity of biochar had limited influence on ammonia and VFAs inhibition. And the results from Lü et al. [31] also demonstrated that acids and ammonia adsorption were not the reasons for the enhancement of AD. However, only a single raw material and production condition of the biochar was studied in their research. The biochar adsorption properties varies with biochar feedstock, particle sizes, as well as the thermochemical process parameters.

Except for the ammonia and acid inhibition, there are many other organic and inorganic toxins that may inhibit AD [28]. Biochar also showed an excellent ability in adsorbing these toxicants, including heavy metals [79,80], phenols [81] and nonylphenol [17]. Present studies focused on the chemical modification or activation of biochar for the adsorption of various inorganic/organic contaminants [1,82]. More studies are needed to evaluate the effects of biochar on the adsorption of these toxicants during an inhibited AD.

4.4 DIET Acceleration

DIET between microorganisms has been evidenced via conductive pili, cytochromes, or conductive minerals [83]. DIET is considered as a more thermodynamically favorable electron transfer route than interspecies hydrogen or formate electron transfer during anaerobic biodegradation process [84,85]. Barua et al. [86] documented that biochar improved DIET kinetics between methanogen and their syntrophic partners, *Geobacter metallireducens* and *Methanosarcina barkeri*, and the addition of biochar resulted in a higher electron recovery (86%) than that with GAC (77%) addition. Based on electron stoichiometry analysis, Yu et al. [75] found that 58.7% of the electrons released from acetate oxidation could be recovered by biochar due to the enrichment of typical microbes (*Anaerolineaceae* and *Methanosaeta*) for DIET.

Low-cost biochar with abundant functional groups (-OH, C=O, and -NH_x) was a promising conductive additive to benefit the establishment of DIET and improve AD performance [37]. Ren et al. [9] demonstrated that hydrochar facilitated the AD of glucose by surface oxygen-containing functional groups-mediated DIET. The redox active moieties such as quinones and phenazines in biochar were responsible for electron transport, which ultimately enhanced methane production through DIET acceleration [22]. There was a study found that biochar improved the conductivity and electron transport system by 1.9 times and 80.2% respectively in the AD of coal gasification wastewater [87]. Biochar [53] was verified to promote the syntrophic degradation of VFAs via DIET during AD of butyrate. Li et al. [27] found that biochar effectively enhanced electron exchange between bacteria and methanogens attached to biochar via the syntrophic oxidation of butyrate and acetate in a manner that was believed to be DIET.

Furthermore, biochar could promote DIET both by substituting exoelectrogen and enriching hydrogenotrophic methanogens [34]. It has been suggested that conductive materials (activated carbon, biochar, and iron oxides) could promote the DIET between VFAs-degraders and methanogens in AD [33]. Specifically, Rotaru et al. [88] found that carbon based materials could substitute pili and/or outer surface cytochromes as the electrical conduit between the electron-donating *Geobacter metallireducens* and the electron-accepting *Methanosarcina barkeri*. Due to its wide range of electrical conductivity (0.002–23.8 dS/m) (Tab. 1), biochar was verified to strengthen AD via accelerating DIET formation between *Geobacter metallireducens* and *Methanosarcina barkeri* [40]. Even *Methanosarcinales* is far away from acetate, they can accept electrons to produce methane via the conductive surface of biochar [31]. This suggested that biochar induced DIET strengthened the affinity of *Methanosarcinales* to biochar, and improved the ability of *Methanosarcinales* to counteract inhibitions. Additionally, DIET between *Methanosaeta* and its syntrophic microbes stood out. *Methanosaeta* has been proved to be able to directly exchange electrons with bioelectricity generating bacteria with the addition of biochar [89]. Wang et al. [30] reported that biochar enhanced DIET by facilitating the enrichment of potential syntrophic metabolic partners, *Methanosaeta* and *Geobacter* sp., during AD of synthetic wastewater. These results comprehensively suggested that, based on DIET, there is a great potential of biochar to strengthen AD by changing the main microbial metabolic pathways.

5 Conclusions and Prospects

Biochar has a great potential to be used as an AD additive to improve the efficiency, which could enhance AD by overcoming toxicants inhibitions, enriching robust microbes, and promoting interspecies electron transfer. Additionally, from a perspective of biorefinery, a system integrating AD and thermochemical conversion of biochar could be an effective strategy for waste management and biofuels production [90–92]. Here, biochar is used as a bond to combine thermochemical and biochemical transformations (Fig. 6).

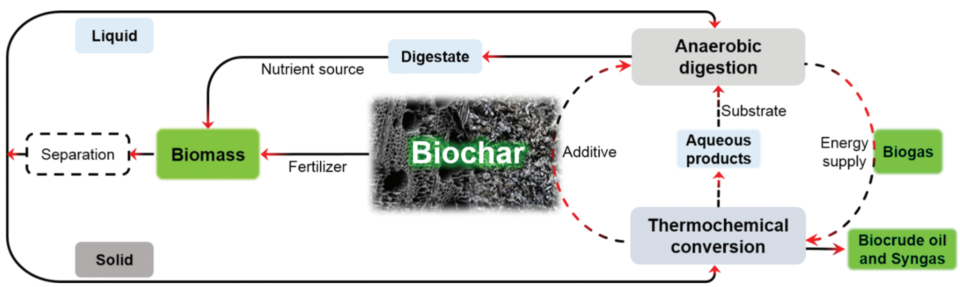

Figure 6: Diagram of a system integrating thermochemical conversion and AD for biomass treatment and biofuel production. Adapted from [5,45,59,91–95]

However, there are some persistent barriers for biochar amended AD processes and its commercial scaling up.

1. The current studies of biochar amending AD mainly focus on lab scale batch experiments, and reactor volumes were generally small (0.1–18 L) (Tab. 2).
2. Excessive dosage of biochar or biochar produced under certain production conditions may inhibit AD.
3. Production of biochar with desired physiochemical properties is feedstock and processing condition specific, thus it is difficult to maintain biochar product consistency;
4. The relationships between biochar physiochemical properties and AD performance are not fully understood;
5. The mechanisms of efficient microbial metabolic pathway in AD, such as DIET, with biochar addition are not fully grasped;
6. The performance of AD reactors with biochar addition needs to be further investigated, and the economic feasibility needs to be evaluated at pilot- and commercial scale.

The future work, therefore, may focus on the design and production of biochar with desirable properties by activation technologies and synergistic enhancement with other additives. Equally, the study of microbial metabolic mechanisms with biochar addition, and the optimization and scaling-up of biochar amended AD reactor for large-scale continuous conditions are necessary. It is also indispensable to attach great importance to the technical and economic analysis, the life cycle assessment, the pilot- and commercial-scale study, and related energy balance analysis of the thermochemical and AD processes hyphenated by biochar.

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