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Review

Biochar and Its Potential Application for the Improvement of the Anaerobic Digestion Process: A Critical Review

Musa Manga [1,*], Christian Aragón-Briceño [2], Panagiotis Boutikos [3], Swaib Semiyaga [4], Omotunde Olabinjo [5] and Chimdi C. Muoghalu [1]

[1] Department of Environmental Sciences and Engineering, University of North Carolina at Chapel Hill, 166 Rosenau Hall, 135 Dauer Drive, Campus Box # 7431, Chapel Hill, NC 27599, USA
[2] Department of Industry and Energy, CIRCE-Research Centre for Energy Resources and Consumption, 50018 Zaragoza, Spain
[3] Center for Research and Technology—Hellas, 57001 Thessaloniki, Greece
[4] Department of Civil and Environmental Engineering, College of Engineering, Design, Art and Technology (CEDAT), Makerere University, Kampala P.O. Box 7062, Uganda
[5] Department of Mechanical Engineering, Obafemi Awolowo University, Ile-Ife A234, Nigeria
* Correspondence: mmanga@email.unc.edu

Abstract: Poor management of organic waste is a key environmental and public health issue as it contributes to environmental contamination and the spread of diseases. Anaerobic digestion (AD) presents an efficient method for organic waste management while generating energy and nutrient-rich digestate. However, the AD process is limited by key factors, which include process inefficiencies from substrate-induced instability, poor quality digestate, and poor management of effluent and emissions. Lately, there has been more interest in the use of biochar for improving anaerobic digestion. Biochar can improve methane production by speeding up the methanogenesis stage, protecting microorganisms from toxic shocks, and reducing inhibition from ammonia and volatile fatty acids. It can be applied for in situ cleanup of biogas to remove carbon dioxide. Applying biochar in AD is undergoing intensive research and development; however, there are still unresolved factors and challenges, such as the influence of feedstock source and pyrolysis on the performance of biochar when it is added to the AD process. In light of these considerations, this review sheds more light on various potential uses of biochar to complement or improve the AD process. This review also considers the mechanisms through which biochar enhances methane production rate, biochar's influence on the resulting digestate, and areas for future research.

Keywords: biochar; biomass; greywater; contaminant removal; adsorption; pyrolysis

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1. Introduction

Climate change, the energy crisis, scarcity of resources, and environmental contamination are the main issues that will plague humankind in the coming decade [1,2]. One major contributor to the above-mentioned issues is waste, which is generated in extensive quantities. World Bank estimates show that in 2020, 2.24 billion tons of solid waste were generated globally, and it is envisaged that this number will rise by 73% to 3.88 billion tons in 2050 [3]. The management and disposal of large quantities of waste is usually a source of environmental concern [4–6]. When not properly disposed of, solid waste, particularly the organic fraction, is of environmental concern as its decomposition leads to the release of methane, a powerful greenhouse gas that contributes substantially to global warming and climate change [7,8]. This is worsened by the fact that a large percentage (~75%) of the waste generated worldwide is usually landfilled, where its decomposition leads to the generation of leachate [9]. Landfill leachate contains contaminants (nutrients, heavy metals, and emerging contaminants) that pollute the environment. Poorly managed waste can also lead to flooding conditions [10]. Apart from being a source of environmental concern, poorly managed waste negatively affects public health as uncontained pathogens lead to the spread of infectious diseases, and fumes from the waste can lead to respiratory infections [6,11,12].

Another contributor is the overreliance on fossil fuels, whose combustion leads to greenhouse gas emissions into the environment and, in turn, climate change [13]. Due to the bad effects of fossil fuels, there is a great deal of research on alternative energy sources that are clean, carbon neutral, and effective in reducing overdependence on fossil fuels. Techniques for producing energy from waste like anaerobic digestion (AD), pyrolysis, gasification, and incineration provide a double-barreled approach for effectively managing waste while reducing dependence on fossil fuels [14].

Among the aforesaid waste-to-energy technologies, the bio-based process of anaerobic digestion (AD) has the lowest negative environmental impact [15]. Anaerobic digestion is a well-known technique for effectively managing a wide variety of organic substrates as it involves simultaneous organic degradation and energy recovery (produces biogas) [16]. In AD, the breakdown of organic substrates is carried out by a consortium of bacteria and archaea to create biogas—that can be further reformed to biomethane—and nutrient-rich digestate [17]. However, AD in practice is usually hindered by the accretion of volatile fatty acids (VFA), ammonia, or heavy metals, leading to an unstable process and a low biogas production rate, most of which are substrate induced [18]. To prevent inhibition, expedite the AD process, and obtain higher biogas production rates, a lot of methods have been applied to the process. For example, bases are usually applied to control serious acidification and keep the pH in the neutral range [19]. However, this is not sustainable, as acidic conditions may build up again when the bases are completely used up. Additionally, to make the AD process more stable, two-phase AD is usually applied, in which one digester is used for acidification and the other is used for methanogenesis [20]. However, this technique usually leads to inhibition of the substrate at some point in time. Further, co-digestion is considered another effective way of increasing buffering capacity, reducing inhibition from VFA accumulation, and increasing methane yield [21]. However, it is difficult to find substrates that can be a perfect match within the same temporal and spatial scale [22].

Lately, there has been increased interest in using biochar as an affordable accelerant that can be used to increase the tolerance and resistance of anaerobic digestion to inhibition. Biochar refers to the solid product from pyrolysis, which is the thermochemical conversion of biomass without oxygen [23]. It can be produced from various kinds of feedstock, which can be plant-based (i.e., wood), manure-based (sewage sludge, fecal sludge, poultry litter), or agricultural/food processing residual (spent coffee grounds, orange peels, walnut shells) [24]. Biochar has several applications, including flue gas cleaning, metallurgy, agriculture, animal rearing, construction material, heat generation, and electricity generation [25]. Biochar is a highly porous carbonaceous material that has a large specific surface area (SSA), high porosity, and abundant surface functional groups [26]. Thus, through adsorption and ion exchange, it can remove free ammonia and ions, thereby curbing their deleterious effect on the AD process [27]. Additionally, due to its conductivity, biochar can be used as a conductor and to enable the electrical connection of syntrophic metabolism [28]. Though biochar helps to enhance the AD process, there is a limited understanding of how the pyrolysis conditions, the type of feedstock, and the dosage of biochar affect its performance in anaerobic digestion. Additionally, the various mechanisms through which biochar enhances the performance of anaerobic digestion are not well understood. Against this backdrop, this paper is a review on: (i) AD and challenges encountered in the process; (ii) synergistic relationship between pyrolysis and AD; (iii) effect of pyrolysis conditions, biochar dosage, and feedstock type on performance of biochar in the AD process; (iv) mechanisms underlying the improvement effect of biochar in the AD process with regards to microbial communities, reduction of VFA, and ammonia inhibition; and (v) areas for further research in applying biochar for anaerobic digestion.

2. Description of the Anaerobic Digestion Process and Challenges Faced in the Process

Anaerobic digestion (AD) is a complex process involving biochemical reactions that lead to the decomposition of biomaterials by a consortium of bacteria and archaea in an anaerobic environment to produce biogas [29,30]. The conversion of biomaterials to biogas (principally methane and carbon dioxide) typically occurs through hydrolysis, acidogenesis, acetogenesis, and methanogenesis [29,31] (Figure 1). The first is the hydrolysis process, where macromolecular organics—carbohydrates (polysaccharides), proteins, and lipids—are monomerized to simpler molecules, that is, sugars, amino acids, and fatty acids, respectively, by enzymes [32,33]. In acidogenesis, the hydrolysis products are changed into volatile fatty acids (VFAs), lactic acid, hydrogen, carbon dioxide, and alcohol by acidogenic bacteria. Then, during the acetogenic stage, acetogens convert VFAs into acetate, more hydrogen gas (H_2), and carbon dioxide (CO_2). The last methanogenic step is carried out by acetotrophic methanogens that change acetate into methane (CH_4) and hydrogenotrophic methanogens that convert hydrogen and carbon dioxide into methane [34]. How effectively the AD process occurs is based on the balance of the four stages [27]. From a microbiological perspective, the formation of methane depends on the AD process, which is basically based on the syntropy between bacteria and Archaea [27]. Fermentative bacteria breakdown complex organic compounds and generate intermediate metabolites (mainly VFAs), which are then degraded by the acetogens acetate, hydrogen (H_2), and carbon dioxide (CO_2). The initiation and completion of anaerobic digestion depend on the reduction of hydrogen partial pressure by hydrogenotrophic methanogens. The consortium of bacteria and archaea involved in methanogenesis has a syntrophic relationship [35].

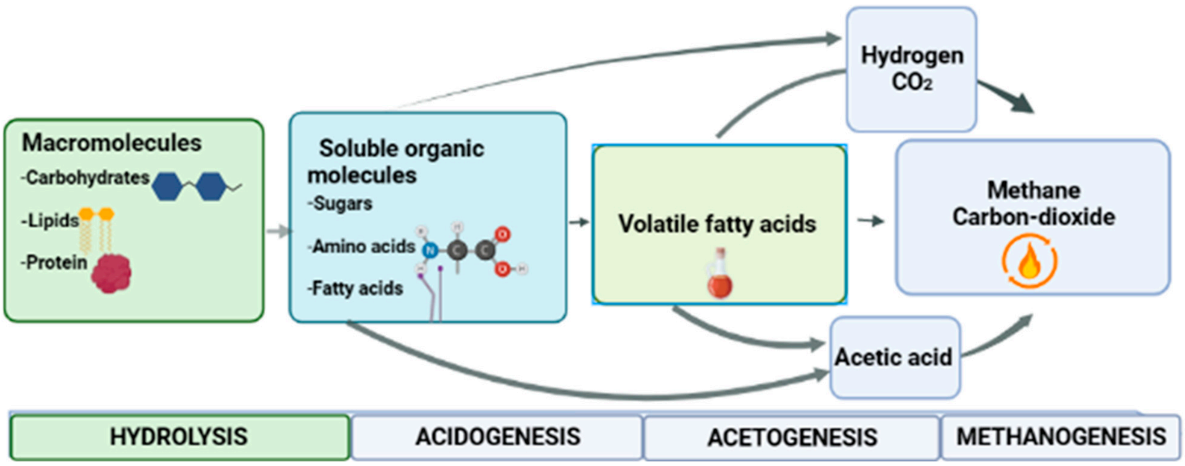

Figure 1. Description of the anaerobic digestion process.

The balance of anaerobic digestion is typically impacted by the buildup of intermediate products such as VFAs, which can prohibit methanogenic activities [36–38]. Imbalance in the AD process results in ponderous breakdown of fermentative intermediates (alcohol and VFAs) and, in turn, excessive accumulation. Accretion of the intermediates hinders methanogenesis, leads to pH decline and increased ammonia (NH_3) concentration [16,39], and in turn causes failure of anaerobic digestion [40]. The imbalance of anaerobic digestion is mainly due to feedstock type [41], and several techniques have been applied to counteract this. One technique that has been used is two-phase anaerobic digestion (TPAD), where hydrolysis, acidogenesis, and acetogenesis occur in a bioreactor/digester as the first step and the methanogenic step, which occurs in another reactor as the second step [42]. In TPAD, inhibitory metabolites and VFAs that are generated in the first stage are provided in regulated amounts to methanogens to increase the amount of biomethane in the second stage [43]. Using this approach makes the system less erratic as there is improved pH self-adjusting capacity, reduced VFA accumulation, and higher resistance to organic loading shock. Co-digesting different substrates is another technique that is used to enhance the tolerability of the AD process [17,20]. This technique brings about a balance of the C/N ratio, helps in supplementing nutrient deficiencies, curtails inhibitory effects, and helps to enhance the energy production kinetics.

Physical (mechanical and ultrasound), thermal, chemical (addition of alkalis), and biological pre-treatments have also been applied to reduce tendencies toward instability when digesting organic waste [44]. Another technique that has been applied is the adjustment of inoculum, temperature, pH, and replacement of the supernatant liquid at different stages of the digestion process [45]. This technique helps to relieve inhibition and improve biogas production. VFA inhibition can also be controlled by bioaugmentation with photosynthetic bacteria (PSB), which can survive within pH ranges of 5.5–9.4 making them tolerant to extreme acidity and alkalinity [46]. The addition of PSB can relieve excessive accumulation of acids and improve methane production, particularly under light conditions [47]. The aforementioned conventional techniques for managing the instability of the AD process have their own limitations. TPAD is usually more expensive than one-stage anaerobic digestion, and disturbances in the syntropic relationship of microorganisms between the two stages can occur. In using co-digestion, it is pertinent that all the required substrates are always available. Additionally, the mixture must be properly proportioned [48,49]. Depletion of neutralizing alkali chemicals leads to increased acidity while excessive application inhibits the AD process [50]. Controlling the pH, temperature, and inoculum at various stages of the AD process prolongs the lag phase and digestion period, thus raising the total cost of the process [45]. Another substrate-induced problem in the AD process is ammonia inhibition. Ammonia emanates from the decomposition of nitrogenous matter during AD. Techniques that have been employed for curtailing ammonia inhibition in anaerobic digestion include struvite precipitation [41], the application of zeolite, and carbon fiber textiles [51]. Though they significantly reduce ammonia inhibition, implementing them on a large scale is usually costly. Additionally, physical covers and fillers have been incorporated into the bioreactors to reduce ammonia inhibition. However, selecting fillers for waste treatment is difficult, and fillers can hinder high solid mass transfer [52].

Asides from substrate-induced instability, another problem with anaerobic digestion is the quality of the biogas produced. The generated biogas contains CO_2, which is non-combustible and reduces the heating value of the biogas. In addition, transporting CO_2-concentrated biogas is expensive [53]. The aforesaid challenges affect biogas sustainability, and there is a need to reform the biogas into biomethane, which is fungible with natural gas. Techniques usually applied for upgrading biogas include pressure swing adsorption, absorption, membrane separation, and cryogenic cooling [54]. The abovementioned techniques are expensive.

In sum, all the aforementioned conventional techniques for solving the problems associated with AD do not fully address the challenges. Hence, there is a need for other alternatives like biochar to enhance the applicability of AD in waste management.

3. Synergistic Relationship between Anaerobic Digestion and Pyrolysis

Biochar is the stable, carbon-based solid residue from the pyrolysis of organic matter. Pyrolysis is the thermochemical breakdown of biomaterials under conditions without oxygen [24,55]. Distinctive attributes of biochar like its high specific surface area [45], porosity [56], oxygen-rich functional groups [57], high cation exchange capacity (CEC) [58], and good electrical conductivity (EC) [59] make it more advantageous than other additives in the AD process. These properties are usually a function of the substrate used in the AD process, synthesis temperature, and modification/activation methods [41,58]. When biochar is added to the AD process, it enhances methane generation by expediting methanogenesis, protecting microorganisms from process disturbance as it acts as support for microbial colonization [18], and reduces inhibitory substances [27]. Biochar has also been noted to be a better conductor for promoting direct interspecies electron transfer (DIET) [28].

Apart from using biochar directly in the AD process, there are other techniques involved in the symbiotic relationship between AD and pyrolysis [60–62]. Wang et al. [62]

investigated the influence of anaerobic digestion pretreatment on Sargassum pyrolysis and noted that the lignin content of Sargassum increased from 10.0 wt% to 14.7 wt% after anaerobic digestion, which in turn helped to increase the char yield. Additionally, pretreated sargassum was thermally stable as most of the organic materials had been removed after anaerobic digestion. The pyrolysis process can be used to convert lignin-rich biomass and digestate to biochar, thereby increasing the digestibility of recalcitrant biomass while reducing digestate volume and GHG mitigation resulting from the use of such digesters (Figure 2). Wang et al. [63] pyrolyzed sewage sludge and food waste digestate to increase the quality of sewage sludge biochar and immobilize heavy metals from sewage sludge. They noted that pyrolyzing sewage sludge with food waste made the blended biochar more basic—the pH increased by 13.2–26.6% while considerably decreasing the heavy metal contents.

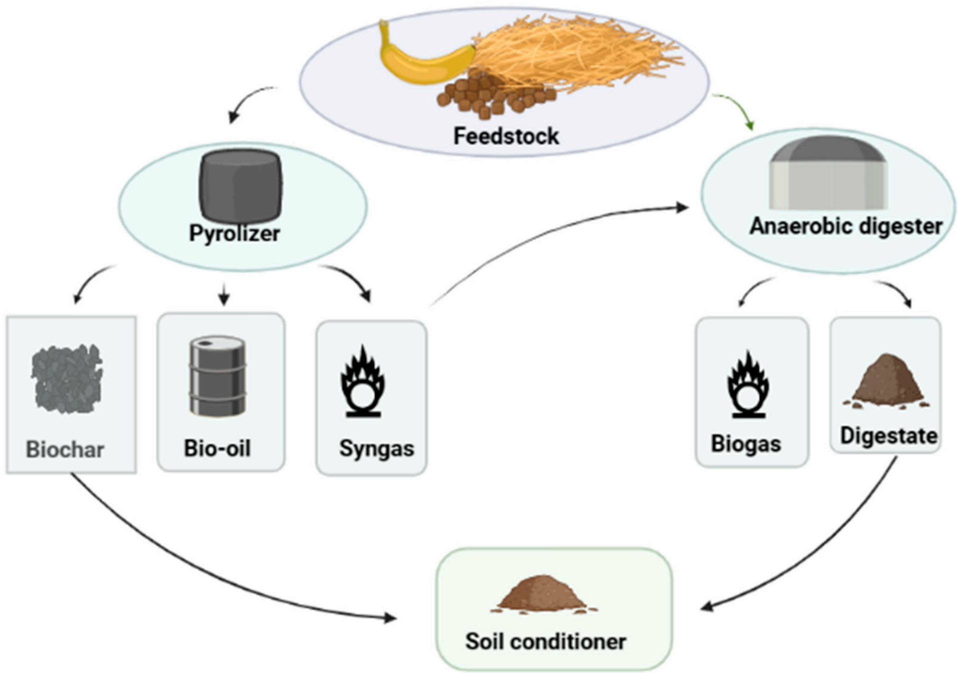

Figure 2. Synergistic relationship between pyrolysis and anaerobic digestion.

Biochar produced can be used back in the AD process or can be used to enhance the quality and quantity of soil nutrients, water-holding capacity, and carbon sequestration [64–66]. Additionally, biochar doped with catalyst can be applied to change tar, the liquid product of pyrolysis, to syngas [51]. The syngas can be used directly in the AD process, where it can be converted to methane via bio-methanation [67]. Increased methane production is due to the consumption of hydrogen gas (H_2) and carbon dioxide (CO_2) from syngas by hydrogenotrophic methanogens, resulting in the production of methane (CH_4) as the main product [68].

4. Factors Affecting the Efficiency of Biochar in the Anaerobic Digestion Process

4.1. Pyrolysis Temperature

One of the key factors that influences biochar composition and, in turn, its performance in the AD process is the pyrolysis conditions under which it was prepared [64]. Pyrolysis conditions that affect the properties of biochar include heating rate, temperature, and residence time [69]. Of all the aforementioned factors, the pyrolysis temperature is the most relevant [70]. Pyrolysis temperature influences the yield, SSA, pH, type, and amount of surface functional groups in biochar [70]. Various experiments have been carried out to investigate the impact of temperature on the composition of biochar, and it has been noted that high temperature brings about high SSA, low cation exchange capacity (CEC), high pH, reduced yield, and high carbon fractions [71] (Figure 3). For instance, Hossain et al. [72] pyrolyzed dried sewage sludge using different temperature ranges (from 300 to 700 °C) at a heating rate of 10 °C/min using nitrogen gas to provide an inert environment. They noted that the quantity of biochar produced reduced from 72.3 to 63.7, 57.9, and 52.4% with an increase in temperature from 300 to 400, 500, and then 700 °C, respectively. The decrease in the quantity of biochar can be attributed to heating at high temperatures, which leads to faster breakdown of organic matter, and in turn, some parts of the raw biomass are volatilized [73]. Konczak et al. [71] noted an increase in the SSA of biochar from 69.7 to 75.5 and then 89.2 m^2/g, with pyrolysis temperatures increasing from 500 to 600 and then 700 °C, respectively. They attributed the increase in SSA to volatilization of organic matter and, in turn, enlargement of the pores at high pyrolysis temperatures.

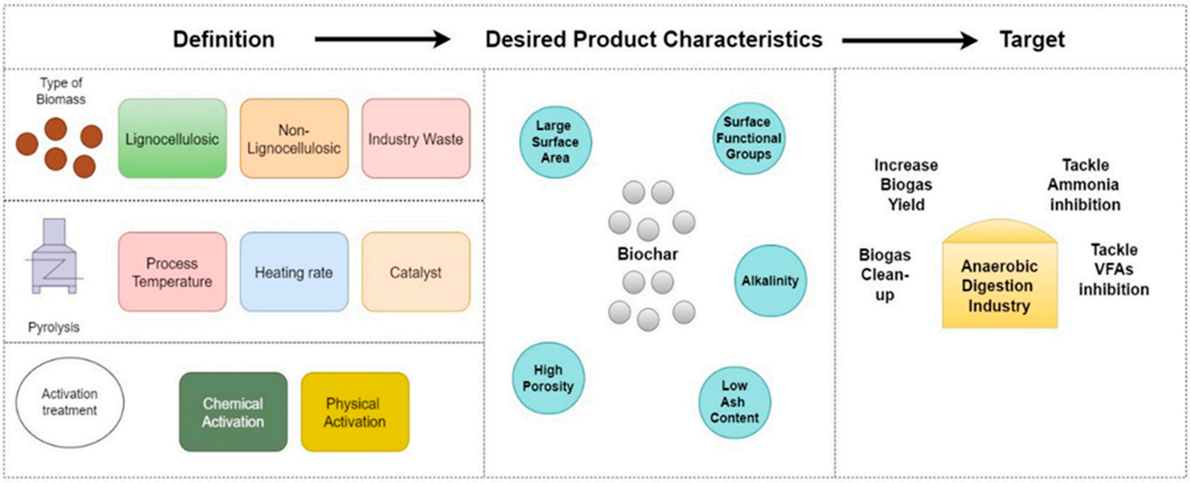

Figure 3. Factors affecting the performance of biochar in anaerobic digestion.

Further, biochar synthesized at high temperatures usually has a very high pH due to the loss of volatile matter and acidic surface functional groups [74]. This was noted by Pan et al. [18], who studied the biochar effect on anaerobic digestion of chicken manure and observed that biochars produced at a higher temperature (550 °C) were more alkaline than those made at a lower temperature (350 °C). In addition, the temperature at which pyrolysis is conducted has an influence on the elemental composition of biochar. Higher temperatures increase the carbon percentage [41]. The substantial differences in hydrogen (H) and oxygen (O) contents after pyrolysis have been ascribed to the cleaving of heterocyclic compounds and nitrile groups at high temperatures [71]. From the aforementioned, it can be seen that conducting pyrolysis at high temperatures can either be beneficial or detrimental to biochar yield. Thus, in pyrolyzing biomass for the AD process, the choice of temperature should be based on the intended purpose of biochar in anaerobic digestion [57]. However, Tripathi et al. [75] stated that to make the process economical, temperatures between 450 and 600 °C are the most suitable based on the type of substrate that suits the purpose of biochar production.

4.2. Biochar Dosage

Several authors have noted that increasing the quantity of biochar used in anaerobic digestion increases the efficiency of the process, but extremely high doses have detrimental effects on the efficiency of the process [76,77]. A decrease in digestion performance has been attributed to inhibition from increased concentrations of alkali based metals beyond acceptable limits and destruction of the diversity of microbial networks [51]. For example, Paritosh et al. [76] assessed the use of hardwood biochar (HBC) (5, 10, 15, 20, 25, and 30 g/L) in the digestion of wheat straw. They observed that in comparison with the methane yield in the control group without HBC (110 L/kg VS), the optimum biochar dosage of 10 g/L doubled the methane yield (223 L/kg VS). But dosing the digester with biochar beyond 10 g/L reduced the amount of methane produced with 15, 20, 25, and 30 g/L HBC, resulting in methane yields of 179.6, 160.0, 148.8, and 149.8 L/kg VS, respectively. In an experiment by Linville et al. [78], walnut shell biochar (with concentrations of 0.96, 1.91, and 3.83 g biochar/g VS added) was used for converting CO_2 into methane in the digester during the anaerobic digestion of food waste. It was noted that the digester to which biochar was added increased the methane (77.5–98.1% CH_4) yield more than the control digester. However, very high dosages (3.83 g biochar/g VS added) resulted in digester cation toxicity. Li et al. [79] studied the anaerobic digestion of mono-cardboard with biochar (at concentrations of 0.23, 0.62, 0.77, 1.16, 2.32, and 3.86 g/g TS sludge). They noted that in comparison with the control group, applying biochar considerably increased methane production, with a biochar dose of 0.77 g/g TS sludge having the highest methane yield (89.28 mL/g VS). However, they observed that surplus quantities of biochar (beyond 0.77 g/g TS) severely disrupted the diversity of microorganisms and reduced the methane yield from the process. In a study by Sun et al. [80], where beer lees were digested with cow manure biochar (at concentrations of 2, 6, 10, and 14 g/L), it was observed that biochar addition increased the AD performance, with a biochar dose of 10 g/L having the maximum methane yield. The authors noted that dosing the digester beyond 10 g/L brought about a substantial decrease in the methane yield.

4.3. Feedstock Type

Various types of biomass can be pyrolyzed to produce biochar; these range from plant materials, manure, and sludge to agricultural/food processing residual-based biomass [64] (Figure 3). The feedstock used for biochar affects the yield, chemical composition, and physical composition of biochar, which in turn affects its efficiency in the AD process. Generally, plant/wood-based feedstocks that are lignin-rich and have high fixed carbon content result in biochar with high SSA, a fine aromatic structure, and low ash content [27]. Unlike plant/wood-based materials, animal manure and sludge have high mineral content, and a high amount of ash is produced when pyrolyzed, resulting in reduced surface structure and a decline in the surface functional groups of the resulting biochar [81]. Since large SSA stimulates interspecies electron transfer and speeds up the AD process, wood-based biochar with a larger specific surface area is more efficient in DIET than animal manure or sewage biochar. In addition, plant-based biochar maintains its cell structure and contains interconnected pores (5–10 µm in diameter) [82]. The abundant pores provide habitat for the entrapment and immobilization of microorganisms, leading to digestion improvement [83]. All these properties give plant/wood-based biochar an edge over manure or sludge biochar, and this has been reported by several researchers. Indren et al. [77] studied the digestion of poultry manure with wood pellet biochar and sheep manure biochar. The authors noted that compared to control digesters without biochar, the addition of wood pellet biochar enhanced the methane yield by 32%, whereas the addition of sheep manure biochar was detrimental to the digester's performance.

Though plant/wood-based biochar has a large SSA and high porosity, its ash content is low, and the concentration of alkaline metals—calcium (Ca), magnesium (Mg), sodium (Na), and potassium (K)—in it is low, leading to less alkalinity and a lower ability to prevent acidification in the AD process (from the buildup of volatile fatty acids) [77]. Thus, compared to plant/wood-based biochar, the use of manure or sewage biochar will make the biochar more basic, thereby mitigating ammonia inhibition and increasing the tolerance of the microbial community to acidity. Another important factor to take into consideration with regards to the composition of the parent material is the presence of surface functional groups, thereby enabling direct interspecies electron transfer. Biochar's EC and abundant surface functional groups increase the methane production rate through direct or indirect electron transfer mechanisms by anaerobes [83,84]. In general, livestock manure and sewage sludge biochar have higher nitrogen (N) and sulfur (S) contents than biochar derived from plants, which are richer in carbon.

From the aforementioned, it can be inferred that in choosing feedstock for the production of biochar (that will be used in the anaerobic digester), the availability of the feedstock as well as the aim of the digestion process should be given due consideration. Table 1 shows the feedstock type and biochar properties that facilitate specific outcomes when biochar is applied in the AD process.

Table 1. Feedstock types and biochar properties that influence the performance of biochar in the anaerobic digestion process.

Aim	Feedstock Type	Biochar Property	Reference
Mitigation of ammonia through adsorption	Plant/wood-based biochar	Large specific surface area (SSA)	[85,86]
Reduction of VFA accumulation	Sewage or manure biochar	High ash content/high pH	[77]
DIET	Plant/wood-based biochar	Surface functional groups (redox-active moieties)	[41]
Habitat for the immobilization (trapping, binding, and immobilization) of microorganisms	Plant/wood-based biochar	Relatively interconnected pores (5–10 µm diameter)	[82]
In situ cleanup of biogas (removal of CO_2 and H_2S	Plant/wood-based biochar	Large surface area and porosity	[35]
	Sewage or manure biochar	Alkali and alkaline earth metals	[41]

5. Mechanisms Underlying the Improvement of the AD Process by Biochar

5.1. Mitigation of Ammonia Inhibition

The breakdown of nitrogenous matter during AD brings about the accretion of ammonia and long-chain fatty acids (LCFA) [87]. Though ammonia nitrogen produced in the AD process serves as a nutrient supplement and provides partial alkalinity, high levels of ammonia production inhibit the AD process [88]. Excess ammonia can infiltrate the bacterial cell membrane, interrupt proton balances and intracellular pH, and inhibit enzymatic activities, making anaerobic digestion ineffective. Adding biochar to the AD process can help increase its resistance to high concentrations of ammonia and nitrogen [18]. Aside from serving as a catalyst to speed up anaerobic digestion, biochar provides a platform on which microorganisms can grow and form biofilms, which curbs ammonia inhibition better than suspended microorganisms [89] (Figure 4). Additionally, the functional groups on the surface of biochar react with ammonia on the surface and can make it unreactive [90] (Table 2). Studies have shown that black carbon, of which biochar is a type, can chemically react with nitrogen compounds and convert them [90,91]. The oxygen groups on the surface of biochar can react with adsorbed ammonia and convert it to amines and amides under ambient conditions [92]. These amines and amides are usually undegradable, which makes them stable.

Quite a lot of research has been done to assess the influence of biochar on ammonia inhibition during anaerobic digestion. Mumme et al. [86] revealed that paper sludge and wheat husk biochar can mitigate small ammonia inhibitions. Su et al. [93] posited that using biochar in the food waste AD process can prevent ammonia inhibition in a range of less than 1500 mg L^{-1} ammonia-N [94]. Lü et al. [95] documented that biochar can increase the tolerance of the AD process to high ammonia toxicity (up to 7 g-N/L). Giwa et al. [61] noted that applying biochar to the AD process significantly reduced ammonia nitrogen concentrations (>2450 mg/L). Lü et al. [95] studied the AD of glucose solution and noted that employing biochar attenuated ammonia inhibition.

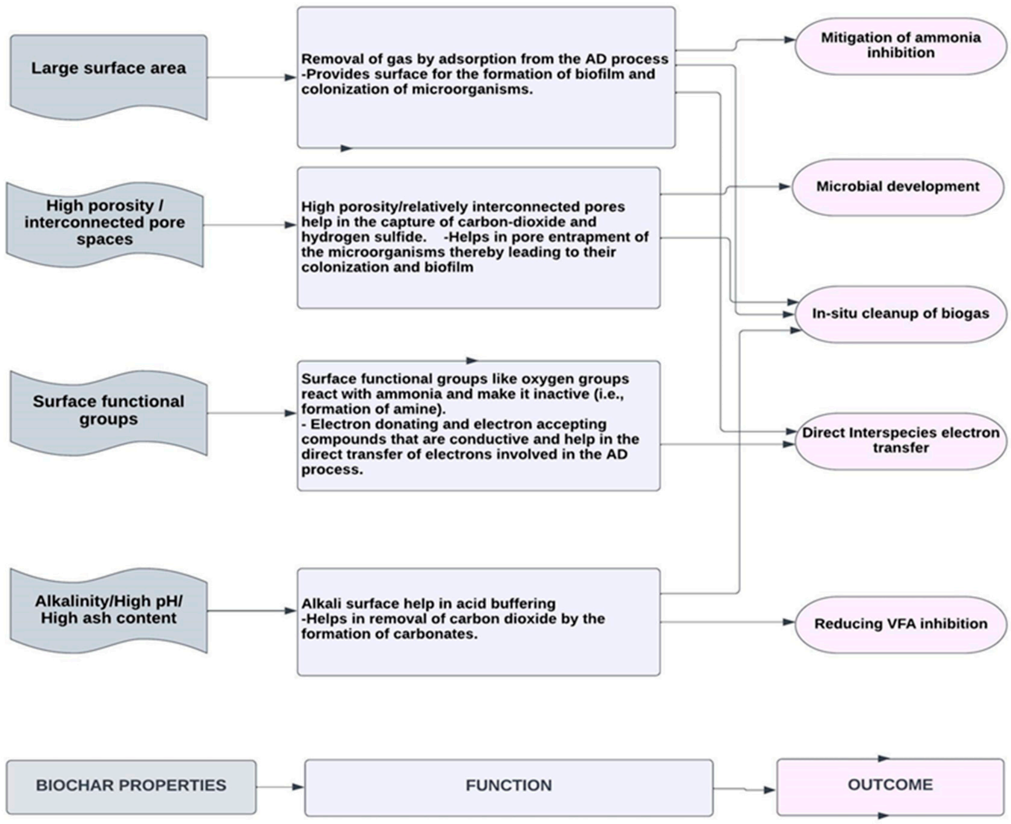

Figure 4. Role of biochar in the AD process.

Table 2. Sources, pyrolysis conditions, properties, and mechanisms that influence biochar in an anaerobic digestion process.

Biochar Feedstock	Pyrolysis Conditions	Biochar Properties	AD Substrate	AD Conditions	Properties of Biochar Highlighted	Study Results	Reference
Pine sawdust	Temp: 650 °C, Retention time: 20 min	Particle size: 3.5–25.9 µm SSA: 130.0 m^2/g PV: 0.0138 cm^3/g	Food waste	Two phase AD process—First stage for hydrogen: temperature of 35 °C and pH 5 and second stage for methane production: temperature of 35 °C; pH 7	Large SSA of biochar that enabled the formation of biofilm	The application of biochar enhanced hydrogen and methane production rates by 32.5% and 41.6%, respectively. It also reduced the AD lag phase.	[66]

Table 2. *Cont.*

Biochar Feedstock	Pyrolysis Conditions	Biochar Properties	AD Substrate	AD Conditions	Properties of Biochar Highlighted	Study Results	Reference
Whiskey "draff"	Pyrolysis temperature: 500–900 °C	BET surface area: 94.12–368 m^2/g	Whiskey Draff	Mesophilic AD at 37 °C at 30 days	DIET	Increasing the pyrolysis temperature from 500 to 700 °C brought about a significant increase in surface functional groups and helped promote interspecies electron transfer. However, the quantity of surface functional groups on biochar reduces with pyrolysis temperatures above 700 °C, limiting its ability to promote. interspecies electron transfer.	[96]
Corn stover biochar (CSBC) Pine biochar (PBC)	Temp: >450 °C	CSBC Particle size: 6.50 nm BET surface area: 315.2 m^2/g PBC Particle size: 5.07 nm BET surface area: 353.1 m^2/g	Sewage sludge	The thermophilic temperature was 55 °C and the pH was maintained at 5.3–6.0	DIET	Methane production was 37% higher in the digester with corn stover biochar than without corn stover biochar.	[52]
Chicken manure	Temp: 350, 450, and 550 °C	Particle size: 0.3–0.45 mm SSA: 209 m^2/g	Chicken manure	Mesophilic AD at 35 °C	Biochar addition enhanced the resistance of the system through the rapid conversion of macromolecular substances to dissolved substrates.	There was a considerable increase in methane production for the nine kinds of biochar tested.	[27]

Table 2. *Cont.*

Biochar Feedstock	Pyrolysis Conditions	Biochar Properties	AD Substrate	AD Conditions	Properties of Biochar Highlighted	Study Results	Reference
White oak Pine wood	Temp: 600–900 °C	Pine wood: Particle size: 177–1707 µm BET surface area: 310.19 m^2/g Pore volume: 0.19 cm^3/g White oak biochar: Particle size: 250–354 µm BET surface area: 296.81 m^2/g Pore volume: 0.15 cm^3/g	Wood biochar and sewage sludge	Mesophilic and thermophilic operated AD at 37 °C and 55 °C, respectively.	High aromaticity; cation exchange; alkalinity	Average methane contents of 92.3% and 79.0% in mesophilic and thermophilic AD, respectively, were observed in the biogas of the biochar-amended bioreactors.	[51]
Wood biochar	-	-	Ice cream waste	Thermophilic temperature at 50 °C for 50 days	Alkalinity to reduce ammonia inhibition	Application of biochar brought about a very high methane production rate of 17.3 mL/g COD/day.	[87]
Corn stover biochar	Temp: 600–700 °C	SSA: 315.3 m^2/g.	Sewage sludge	Thermophilic AD at 55 ± 1 °C	Alkalinity to reduce ammonia inhibition; large surface area for in situ CO_2 removal.	Application of biochar brought about 7.0%, 8.1%, and 27.6% increases in the methane yield, a constant biomethanation rate, and the highest methane production rate.	[97]
Orchard wood waste	Temp: 550 ± 50 °C	-	Chicken manure	Mesophilic AD operated at 35 °C and had a hydraulic retention time of 20 days			[27]
Hardwood, corncob, and mixed sawdust pellets	Temp: 600 °C at 10 °C/min Residence time: 8 h	Hardwood –SSA: 147 m^2/g; PV: 0.176 cm^3/g Corncob—SSA: 23 m^2/g PV: 0.098 cm^3/g Sawdust pellets BET SSA: 6.80 m^2/g PV: 0.038 cm^3/g	Pig manure digestate	Mesophilic AD	High SSA and large pore volume	High sorption capacity of ammonium with biochar was observed.	[98]

Table 2. *Cont.*

Biochar Feedstock	Pyrolysis Conditions	Biochar Properties	AD Substrate	AD Conditions	Properties of Biochar Highlighted	Study Results	Reference
Wood straw, wood pellets, and sheep manure	Temp: 680–770 °C Residence time: 2.5 h		Poultry manure	Mesophilic AD at 37 °C	Large surface area and pores, which enabled the entrapment and colonization of microbes for the degradation of intermediates like propionate and isovalerate	The average methane yield in the wood biochar amended digester was 32% (66 mL CH_4/g-VS) higher than that of the controls (50 mL CH_4/g-VS). Adding wheat straw or sheep manure biochar negatively affected the performance of the digester when compared with the controls.	[77]
Vermicompost	Temp: 500 °C Residence time: 2 h	Particle size: 5.3 nm BET surface area: 56.6 m^2/g	Kitchen waste and chicken manure	Mesophilic batch-operated AD was operated at 35 °C	Alkaline nature of biochar and surface functional groups	Increased methane yield and enhanced buffering capability.	[17]
Waste sludge and dairy manure	Temp: 400–800 °C Residence time: 90 min		Waste activated sludge	Mesophilic AD operated at 37 °C	Electrostatic attraction, precipitation, surface complexation, and ion exchange	Biochar removed the lead present in sewage sludge through adsorption. The mechanism of adsorption was also studied.	[99]
Sawdust	Temp: 500 °C at 10 °C/min, Residence time: 1.5 h	-	Activated sludge and food waste	Batch mesophilic AD at 35 °C	DIET: increased buffering capacity from increased alkalinity.	The application of biochar brought about a 27.5–64.4% reduction in the lag time, thereby increasing the methane production rate by 22.4–40.3%.	[100]
Hardwood			Wheat straw			Maximum methane yield (223 L/kg VS, a 2-fold increment in comparison with the control) was obtained with the application of 10 g/L of hardwood biochar.	

Table 2. *Cont.*

Biochar Feedstock	Pyrolysis Conditions	Biochar Properties	AD Substrate	AD Conditions	Properties of Biochar Highlighted	Study Results	Reference
Wood chips and anaerobic digester residue	Temp: 600 °C	pH of 7.98 ± 0.03	Cattle manure	Mesophilic operated AD at 35 °C	Alkalinity; surface area; and surface functional groups	Biochar-amended digester achieved 98% removal of hydrogen sulfide (H_2S).	[101]

Abbreviations: SSA—specific surface area; PV—pore volume.

5.2. Volatile Fatty Acid Reduction

The digestion process may come to a halt if the syntrophic relationship between acetogenic and methanogenic organisms is not maintained [76,83]. The hydrolysis process leads to the formation of numerous organic acids. The accumulation of these acids (especially VFAs) lowers the pH of the digestion process and inhibits methanogens, especially at high organic loadings [102]. In addition, the high concentration of the acids can cause their penetration into the cell membrane and subsequent damage to macromolecules [103]. For an improved syntrophic relationship, the pH of the digester must be kept in the neutral range [104]. Due to its highly basic nature, biochar can relieve the acid inhibition brought about by hydrolytic acidification (Figure 4). Wang et al. [104] assessed how vermicompost biochar (VCBC) aids in acid buffering when digesting kitchen waste and chicken manure. They noted that, in comparison with the control digester without VCBC, the bioreactor with VCBC had better buffering capacity as the reduction in pH was milder. The high buffering capability of VCBC can be attributed to the high concentration of alkali-based metals (Na, K, Ca, and Mg), which are 8.47 g/kg, 2.53 g/kg, 15.82 g/kg, and 0.44 g/kg, respectively, in VCBC [105]. Paritosh et al. [76] examined the influence of hardwood biochar (HBC) on the AD of wastewater sludge using doses of 5, 10, 15, 20, 25, and 30 g/L. They found that higher doses of HBC increased the alkalinity of the process, with a dosage of 10 g/L HBC showing the highest alkalinity at 3.2 g/L of $CaCO_3$ and a pH of 7.6. However, adding biochar beyond this level increased the alkalinity of the process and disrupted the pH of the process. It should, however, be noted that for AD reactors in which the accretion of acid has taken place, adding biochar cannot increase the pH value. This was shown in a study by Luo et al. [18], where they noted that the buffering capability of AD reactors did not considerably increase when biochar was added after acid accretion had occurred.

5.3. Effect of Biochar on Microorganisms

Anaerobic digestion entails the decomposition of organic materials by a complex consortium of microorganisms. Hydrolysis, acidogenesis, and acetogenesis are usually carried out by bacteria, whereas a particular branch of archaea conducts methanogenesis [106]. Thus, the performance of the AD relies on the synergistic activities of microbial communities belonging to diverse functional groups [107]. Applying biochar to the AD process provides a platform for trapping microorganisms, binding and colonization of microbial communities, formation of biofilms, and acclimatization of microbes, thereby facilitating interspecies electron transfer and preventing the removal of microorganisms [108] (Figure 4). In addition, biochar helps enrich microbial communities found in the AD process by catalyzing the generation and operation of different groups of beneficial microorganisms. The positive effect of biochar on microbial communities in the AD process has been documented by several authors. For instance, Pan et al. [27] carried out an experiment in AD of chicken manure with wheat straw, discarded fruitwood, and air-dried chicken manure biochar. They observed that the addition of biochar (irrespective of feedstock) garnered more Bacteroidetes in the anaerobic digester than the control group: the relative abundance for the digester with biochar is 38.2–50.4% in the digester with biochar and 36.42–46.49% in the control digester. Bacteroidetes are important as they produce sufficient VFAs for methane generation, thereby helping in anaerobic hydrolysis and acidification [27]. They also observed that adding biochar supplement helped to stimulate denitrification (the conversion of nitrate to dinitrogen) as they noted the presence of Epsilon proteobacteria, which acts as a terminal electron acceptor and reduces nitrate [109]. Zhao and Zhang [110] assessed the effect the direct addition of biochar will have on the DIET process in a continuous up-flow anaerobic sludge blanket reactor. They found out that, in comparison to the control reactor, there was a 16–25% improvement in methane production rate in the bioreactor to which biochar was added. They attributed the increased yield in the biochar-amended reactor to an increase in genes closely related to Geobacter and Methanosaeta, which are used in facilitating the formation of CH_4 [41]. Luo et al. [18], who investigated the digestion of glucose and biochar, showed that applying biochar reduced acidity and facilitated an increase in Archaea production and, in turn, methane generation. Shen and Forrester [52], in their study on AD of sewage sludge with corn stover and pinewood biochar, concluded that biochar addition brought about a notable change in the bacterial community, which facilitated syntrophic bacterial growth.

Apart from enriching the microbial communities present in the AD process, adding biochar can transform the microbial community structure of the AD process and enhance methane production. This has been observed by quite a number of researchers. Wang et al. [100] investigated the anaerobic digestion of food waste and dewatered activated sludge with sawdust biochar. When the 16S rRNA gene sequences were analyzed, it was revealed that the application of biochar restructured the bacterial community, as it was observed that only the biochar-amended digesters had Anaerolineaceae and Methanosaeta, which are typical microorganisms involved in direct interspecies electron transfer. Sawayama and Tada [111] examined the adsorption of ammonium by microbial species attached to the surface of carbon felt by motile microbial communities in batch AD processes. In their study, they observed that the main methanogenic species of the colonized cells had changed compared to those of the motile cells: Methanosaeta spp. were transmuted to Methanobacterium and Methanosarcina spp. They posited that the colonization of microbial cells brings about alteration in the principal methanogenic species, thus increasing their resistance to ammonia inhibition.

Though directly applying biochar to anaerobic digestion improves the functionality of microorganisms, it has some limitations. One such limitation is that there is usually an alteration in the number of methane-generating microorganisms attached to biochar [108,112]. Additionally, it takes several days for the complex microbial communities to form on a solid support [113]. One technique that can be applied to improve this is using biochar, which is already loaded with microorganisms. To reduce costs associated with continuous production of biochar, the pre-loaded biochar can be biochar recycled from high-solids digesters or effluent from low-solids digesters [77]. Inden et al. [77] assessed the impact preloading of wood pellet biochar would have on the AD of poultry litter. It was observed that, in comparison to the control digester, the addition of pre-loaded biochar brought about a rise in the cumulative methane yield to about 16% and 46% of the original material.

5.4. Direct Interspecies Electron Transfer

During the methanogenic stage of anaerobic digestion, hydrogenotrophic methanogens [106] reduce CO_2 to carbonates (to facilitate the formation of methane). The reduction of CO_2 to carbonates is largely dependent on the syntropy organic acid-oxidizing acetogenic bacteria establish with CO_2-reducing methanogenic Archaea [114]. Interspecies electron transfer is vital for syntrophic relationships in the AD process. This usually occurs through indirect interspecies electron transfer (IIET), where hydrogen and formate help transferring electrons between syntrophic-producing bacteria and consuming methanogens [114]. The exchange of metabolites between the microorganisms is regulated by diffusion [84]. However, the transfer of soluble metabolites by diffusion is generally slow [115], and hydrogen IET is considered a major problem in methane production [116].

To speed up the digestion process, direct interspecies electron transfer (DIET) can be engineered with conductive materials like graphene, activated carbon, magnetite, and biochar [28,117]. This is because these materials have electron-donating and electron-accepting capacities related to the surface chemical properties of biochar, thereby speeding up the conversion process [118]. DIET has been noted by several authors to be more effective than IIET as it does not make use of diffusion and is not slowed down by the diffusion rate of electron carriers such as hydrogen and formate [38] (Table 2). DIET has been noted to speed up the conversion of different reduced organic compounds to methane [119]. For instance, Cruz Viggi et al. [120], in their study on the AD of organic waste, investigated the role of micrometer-sized magnetite (Fe_3O_4) (a conductive material) in methane formation. It was observed in their study that the use of the conductive material increased the methane production rate. They posited that the increase was mainly due to DIET, as there was direct conversion of 33% propionate (an intermediate of the AD process) to methane, and this electron transfer was mainly influenced by the direct exchange of metabolic electrons. Zhao et al. [121] studied the role of two conductive materials—magnetite and granular activated carbon (GAC)—in expediting and stabilizing the digestion of organic waste. It was noted that magnetite increased the breakdown of complex organics to simple organics, whereas a GAC enhanced the syntrophic conversion of fermentation products to methane by DIET. All these show that the application of activated carbon can help improve the speed at which methane is produced in the AD process. Compared to activated carbon, biochar has certain properties, such as the presence of redox-active group of metals on its surface that make it more advantageous than other conductive materials. For instance, when Shanmugam et al. [122] studied the anaerobic digestion of glucose and aqueous phase bio-oil with biochar and GAC, it was observed that both biochar and GAC promoted DIET and increased the yield of methane. However, biochar improved the methane yield by 72%, whereas GAC increased the yield by 40%. They posited that having redox-active compounds on the surface of the biochar brought about the speedy movement of electrons between the fermentative bacteria and methanogens (Figure 4).

5.5. In Situ Cleanup of Biogas

Asides from increasing production of methane, biochar can be put in the AD process for in situ removal of carbon dioxide (CO_2) [123]. Practically implementing the application of biochar for in situ cleanup of biogas will lead to significant reductions in the cost of upgrading biogas to meet fuel specifications [96]. Biochar's physical properties, like its large SSA and high porosity, provide favorable conditions for the capture of CO_2 and H_2S [97] (Table 2). Apart from its physical properties, chemical properties like having alkali-based metals (high concentrations of potassium (K), magnesium (Mg), and sodium (Na)) facilitate in situ CO_2 removal in the bioreactor. Normally, the removal of CO_2 from a medium usually involves its dissolution in water to form carbonates and then reaction with alkali-based metals (i.e., Ca, Mg, and K) to, respectively, form calcium magnesium and potassium carbonates [124]. Owing to the fact that biochar has very high monovalent and divalent cation concentrations, it can be used to catalyze the carbonation process during AD [41] (Figure 4). This is because the use of alkaline metals brings about the conversion of CO_2 to carbonate/bicarbonate. Thus, in preparing biochar for use in the AD process, it is important that pyrolysis conditions favor the formation of an alkaline surface to help in the in situ removal of CO_2. Another way to ensure alkaline conditions in the digester is to carry out the AD process at thermophilic temperatures (50–60 °C). Digesting at elevated temperatures enhances the release of alkali-based metals from biochar and their subsequent dissolution, thereby enhancing the in situ removal of CO_2 and H_2S [125,126]. In addition, compared to mesophilic conditions, thermophilic conditions result in lower toxicity levels due to enhanced hydrolysis and a rapid microbial reaction rate prior to releasing cations [52,78]. Shen et al. [97] assessed the capability of corn stover biochar to adsorb CO_2 and H_2S during batch thermophilic AD of sewage sludge. They stated that the application of biochar brought 54.9–86.3% CO_2 removal efficiency. They attributed the in situ CO_2 removal to the pores on biochar's surface, the large SSA, the hydrophobicity of biochar, the electrostatic interaction, and the polarity attraction. In a study by Shen and Forrester [52], corn-stover biochar and pine biochar were used in the thermophilic AD of sewage sludge. They noted that though biochar-amended bioreactors produced less biogas than the control bioreactors, they had higher methane contents in the biogas, implying that CO_2 was removed from the biogas. They posited that the base cations leached from the biochar at high temperatures and sequestered CO_2 by chemical reaction to produce bicarbonates. Aside from digesting at high temperatures, another way through which alkali and alkaline earth metals can be made available is to make use of small-size biochar particles, as this will favor the dissolution of biochar and in turn promote CO_2 adsorption on biochar [41].

6. Effect of Biochar on the Quality of Digestate

One major concern in the digestion process is the quality of the digestate. Digestate is an end product of anaerobic digestion and is made of recalcitrant raw materials not digested in the bioreactor, bacterial biomass and metabolites, and inert organics [127]. Digestate from anaerobic digestion can be applied to enhance soil quality and facilitate plant growth. When organics in the bioreactor are not completely degraded due to process instabilities, over 45% of recalcitrant organics may remain in the digestate [128]. This produces digestate with inherent methane and ammonia that can easily be emitted into the environment. In addition, exposure of the digestate to aerobic conditions when it is applied to the soil leads to slow microbial decomposition and plausible nutrient loss through leaching or alterations in soil conditions [129]. Applying biochar in the AD process speeds up the decomposition process and transforms the organic materials present in the AD process into dissolved organic carbon (in digestate) which is vital for plant growth and helps to enhance the water holding capacity of the soil. Another major concern is that digestate from the AD process usually has a high moisture content (70–80%) [130], and when applied to land in such a state, high nutrient and metal losses will occur via leaching to surrounding watercourses. Applying biochar to the digester increases the solid content of the digestate as a result of the added solid matter of biochar, which does not degrade in the digestion process [87]. This in turn helps to enhance the capability of the soil to retain water.

Another major concern with the digestate is the amount of volatile organic acids, emerging contaminants, and heavy metals retained in it from the digestion process. Biochar, which remains in the digestate after AD, helps to improve its nutrient retention capacity and mitigate the leaching of heavy metals and pollutants through adsorption [131]. The enhanced quality of the digestate is due to the properties of biochar, such as its large SSA, multiple surface functional groups, ash content, and presence of metals [84].

Apart from the aforementioned advantages of using biochar in anaerobic digestion, biochar can help increase the amount of micro- and macronutrients present in the digestate, the soil's cation exchange capacity, and enable carbon capture and storage when applied to the soil (56). An increase in the quality of digestate from the addition of biochar has been noted by several authors. For instance, Shen et al. [97] revealed that the digestate from a bioreactor treated with biochar had about three times the concentration of total calcium (Ca), iron (Fe), magnesium (Mg), and potassium (K) in comparison to a control digester. Fagbohungbe et al. [132] posited that the presence of biochar in digestate can help curtail nutrient leaching after applying the digestate on land [41].

7. Implications of the Study and Areas of Future Research

This is a review on the application of biochar in the AD process, taking into consideration factors that affect its performance as well as mechanisms through which biochar can enhance process performance. The review points towards the fact that carrying out digestion under thermophilic (temperatures between 50 and 60 °C) conditions will prevent VFA and ammonia inhibition, thereby bringing about an increase in the yield and quantity of biomethane. Though thermophilic conditions enhance the performance of the

AD process, very high temperatures (>60 °C) can lead to reduced methane yield due to the fact that acetoclastic methanogens are inhibited at high temperatures. Thus, intensive research is required to determine optimum levels for other parameters that can be used with thermophilic temperatures to attenuate the effect of high temperatures during the digestion of organic waste with biochar.

Apart from using thermophilic temperature to curtail ammonia and volatile fatty acid inhibition, various studies have reported other mechanisms, such as the adsorption of ammonia on biochar surfaces. However, these studies have investigated only one mechanism for ammonia inhibition in isolation. Thus, there is a need to further clarify the particular role different mechanisms play in the AD systems while other phenomena are occurring, for instance, the interaction between inhibition by ammonia and VFA. This is because, in certain scenarios, removal by dissolution might not be the principal reason for mitigation of ammonia inhibition by biochar.

Further, with regards to microbial community structure in the AD process with biochar, the review revealed some limitations, such as changes in the population of methanogenic microorganisms attached to biochar [77,112], long periods for the formation of complex microbial communities on biochar support, and fluctuations of microbial communities in the digester. Thus, further research into the use of bacteria immobilized on biochar bacteria or preloaded biochar is urgent. Using immobilized bacteria will speed up the acclimatization process in the digester and, in turn, hasten the AD process.

Finally, there is a need to research more on the interactions between biochar, digestate, and the soil to effectively use the mixture of digestate and biochar as soil conditioners. Additionally, future studies on adding biochar in the AD process should take into consideration the agronomic value of the resulting digestate (i.e., nutrients, germination, and phytotoxicity index, amongst others).

8. Conclusions

Biochar's addition to the AD process presents an efficient technique for simultaneously tackling multiple problems associated with the biological process but still presents some challenges to be addressed. The challenges imply that the choice of feedstock, pyrolysis conditions, or even the activation of the biochar should be made with the aim of obtaining the desired product for targeted use in the anaerobic digestion industry. In addition, its efficiency also depends on the dosage applied in the AD process. Therefore, when preparing biochar for use in the AD process, it is important that whole-process conditions favor the creation of a large SSA, a large pore structure, a high pH, and surface functional groups. This review points to the fact that pyrolyzing at high temperatures (>450 °C) will lead to the formation of the aforementioned relevant properties. However, one negative effect of high-temperature pyrolysis is that it removes oxygen (O) and hydrogen (H) functional groups from the biochar surface. Thus, in pyrolyzing biomass for the AD process, the choice of temperature should be based on the intended purpose of the biochar in the AD process. Apart from factors related to the pyrolysis of biomass, operating conditions applied in the AD process also affect the methane yield and quality of biogas produced. Hence, it is necessary to enhance the design and stabilize the operational parameters of anaerobic digesters.

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