

Review

Nano-Biochar as a Sustainable Catalyst for Anaerobic Digestion: A Synergetic Closed-Loop Approach

Lalit Goswami ^{1,†} , Anamika Kushwaha ^{1,†}, Anju Singh ², Pathikrit Saha ¹, Yoseok Choi ¹, Mrutyunjay Maharana ³ , Satish V. Patil ⁴ and Beom Soo Kim ^{1,*} 

¹ Department of Chemical Engineering, Chungbuk National University, Cheongju 28644, Korea; lalitgoswami660323@gmail.com (L.G.); kushwaha.anamika@gmail.com (A.K.); pathikritsaha89@gmail.com (P.S.); y.choi@chungbuk.ac.kr (Y.C.)

² Department of Chemical Engineering, Babu Banarsi Das National Institute of Technology and Management, Lucknow 227105, India; anjusinghch1711@gmail.com

³ School of Electrical Engineering, Xi'an Jiaotong University, Xi'an 710049, China; maharana@xjtu.edu.cn

⁴ School of Life Sciences, Kavayitri Bahinabai Chaudhari North Maharashtra University, Jalgaon 425001, India; satish.patil7@gmail.com

* Correspondence: bskim@chungbuk.ac.kr; Tel.: +82-43-261-2372

† These authors contributed equally to this work.

Abstract: Nowadays, the valorization of organic wastes using various carbon-capturing technologies is a prime research area. The anaerobic digestion (AD) technology is gaining much consideration in this regard that simultaneously deals with waste valorization and bioenergy production sustainably. Biochar, a well-recognized carbonaceous pyrogenic material and possessing a broad range of inherent physical and chemical properties, has diverse applications in the fields of agriculture, health-care, sensing, catalysis, carbon capture, the environment and energy. The nano-biochar-amended anaerobic digestion approach has intensively been explored for the past few years. However, an inclusive study of multi-functional roles of biochar and the mechanism involved for enhancing the biogas production via the AD process still need to be evaluated. The present review inspects the significant role of biochar addition and the kinetics involved, further focusing on the limitations, perspectives, and challenges of the technology. Additionally, the techno-economic analysis and life-cycle assessment of biochar-aided AD process for the closed-loop integration of biochar and AD and possible improvement practices are discussed.

Keywords: biochar-amended process; mechanism involved; kinetics; techno-economic analysis; zero-waste approach



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1. Introduction

Presently, the human population has crossed 7.2 billion and is expected to reach between 9.6–12.3 billion by 2100 [1]. This tremendous population growth is further accompanied by enormous industrial development and unprecedented consumption of energy, enhancing the stress on natural resources at a startling level [2,3]. To meet this rising demand, over-exploitation of fossil-based energy is occurring, with deleterious environmental and societal impacts [4–8]. Renewable energy is recognized as a sustainable option to overcome all these challenging issues. Sources such as wind, hydro, geothermal, solar energy, biogas, microbial fuel cells, bioethanol, biodiesel, biohydrogen, etc. have been explored to find a viable solution [9]. Amidst these available options, some utilize silver, titanium, platinum, ruthenium, nickel, and other metal oxides as catalysts on a huge scale [10,11]. Though these metals are very efficient, there is a hunt for sustainable catalyst materials that are cost-effective, efficient, eco-friendly, and widely available.

Biomass is currently the most sustainable option available, and has been widely explored for synthesizing various sustainable materials such as carbon fibers, biochar, activated carbon, graphene, etc. that show tremendous applicability in the energy sector [12,13].

Biochar is a carbonaceous material that is produced via the thermochemical decomposition of organic materials [14]. It is a highly porous, amorphous material with a good surface area containing various functional groups, while displaying stable physicochemical properties and biocompatibility, and easy to further modify in accordance with the particular need [15,16]. The properties of biochar for various application such as bioremediation, energy storage, catalysis, agriculture, carbon capture, wastewater treatment, pharmaceutical, electrodes, cosmetics, etc. rely on the production process, kind of feedstock and operating parameters used [17–21].

During the past decade, biochar has also been utilized in the anaerobic digestion (AD) process. The AD process has ability to use organic biomass and wastes for the production of biogas (containing ~60% methane) and high quality of bio-fertilizers [22,23]. This conversion is purely dependent on to the synergistic metabolic activities of the prevailing microbial consortia within the digester and has to be further maintained under steady state conditions for the best performance. Various electron transfers amongst the similar partners are required to avoid the longer acclimatization period along with the high substrate consumption rate [24]. The direct interspecies electron transfer (DIET) is recognized as more rapid and stable pathway where the transfer of electrons takes place between the syntrophic bacteria to the methanogenic archaea [25].

Recently, researchers have started focusing on non-biological conductive materials such as magnetite, biochar, granular activated carbon, etc. to enhance the DIET performance. Biochar has the ability to enhance the DIET via a conduction-based mechanism that channels the electron flow between the electron-donor and electron-acceptor ends [22]. In addition, biochar supplementation leads to a simple and efficient microbial community possessing the enriched and equilibrated DIET. Biochar-aided anaerobic digestion mediates the formation and degradation of intermittent acids and leads to the enrichment of methanogenic archaea, shortening the lag phase, and enhancing the methane yield [26].

Henceforth, the present review aims to summarize the recent advancements regarding the utilization of nano-biochar in anaerobic digestion processes. This review's focus is on the application of nano-biochar as a sustainable nano-catalyst for the production of renewable energy, particularly by anaerobic digestion. Here, we have considered the biochar according to its particle size, i.e., macro-biochar (>1 μm), colloidal biochar (1 μm –100 nm), and nano-biochar (<100 nm). The role, kinetics, mechanism(s) involved, and possible improvements along with the closed-loop integration of nano-biochar and AD have also been discussed. The review also covers the involvement of techno-economic and environmental life-cycle assessments for moving forward with the least limitations. A network visualization of terms associated with anaerobic digestion and biochar with at least 10 occurrences of the associated keywords is represented in Figure 1. It depicts the present trends in research and development regarding the application of biochar in association with the anaerobic digestion in the Web of Science. Here, the various colors of the nodes represent the different clusters whereas the size of each bubble depicts its frequency of occurrence.

of physical and chemical properties. During the upscaling of MFCs, low current output and high cost are the major limitations [30]. The electrodes represent 20–50% of the overall cost of a MFC as they are usually made of non-renewable materials, viz., stainless steel, Ni, Cu, etc. These materials further require surface modifications for biofilm formation and electron transfer [31]. Table 1(a) summarizes the utilization of nano-biochar for MFCs. Further, researchers are utilizing sediment MFCs, also known as benthic MFCs (in some cases), applied in the natural systems such as constructed wetland [32]. The energy output from such MFCs is generally very low (e.g., 10–50 mW cm⁻²). Coconut shell-derived biochar-amended sediment MFC improved the power generation 2–10 times along with the increased total organic carbon (TOC) removal [33]. Also, soil-based MFCs have good performance in low-power continuous energy sources along with the soil remediation application [34]. Li et al. [35] utilized a chicken manure, wheat straw and wood sawdust-derived biochar-amended soil MFC for the biodegradation of petroleum hydrocarbons.

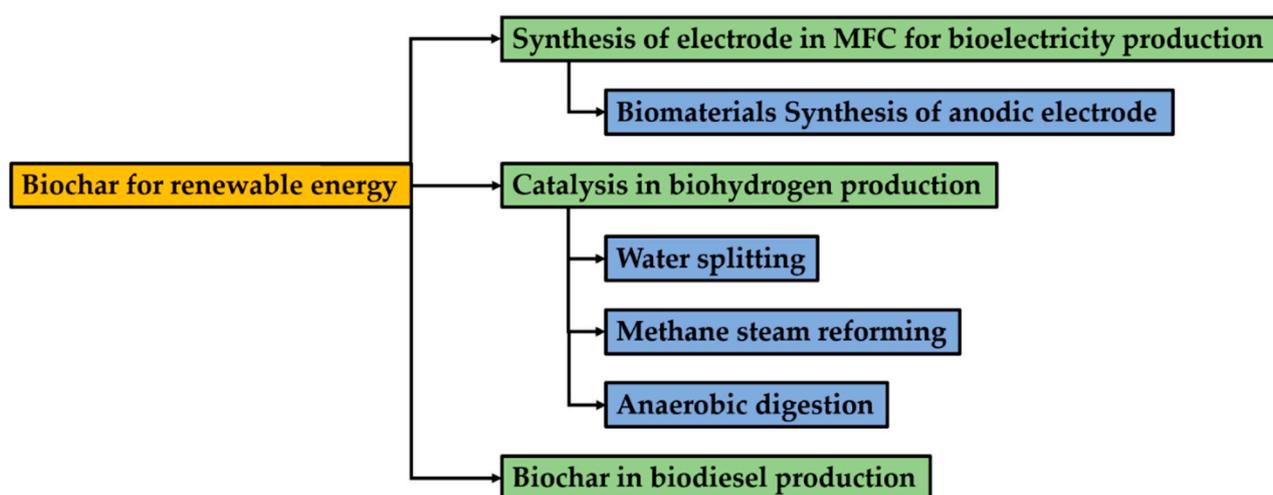


Figure 2. Utilization of biochar for renewable energy production.

Table 1. Application of nano-biochar as catalysts for the production of different renewable energy. (a) Nano-biochar for MFC for bioelectricity production; (b) Nano-biochar for anaerobic digestion for hydrogen production; (c) Nano-biochar for biodiesel production.

(a)				
As Anode				
Biomass	Preparation	Comments	Power Density	References
Chestnut shell	900 °C, 2 h	Activation with KOH modified microporous structure with reduced O and N content that is beneficial for charge transfer and microbial adhesion	23.6 Wm ⁻³	[36]
Microalgal sludge (MSB)	800 °C, 2 h	Cobalt and chitosan were used as a mediator for electron transfer by immobilization on MSB (MSB/Co/chitosan).	3.1 mWcm ⁻²	[37]
Microalgal	900 °C, 1 h	Contains intrinsic N and P	12.8 Wm ⁻³	[38]
Deoiled <i>Azolla</i> biomass	600 °C, 3 h	Nano-biochar was activated with KOH at 1:4 ratio at 600 °C for 2 h. Bio-electrode was prepared by using 5% polyvinylidene fluoride (PVDF).	-	[39]

Table 1. Cont.

(a)				
As Anode				
Biomass	Preparation	Comments	Power Density	References
As Cathode				
Bamboo charcoal	Carbonization at 900 °C under N ₂ atmosphere followed by heating at 350 °C under air atmosphere for 2 h	Porous structure of the bamboo derived cathode provides possible channels for oxygen supply and proton transport.	40.4 Wm ⁻³	[40]
Corn cob	650 °C for 2 h	Higher contents of graphitic and pyridinic nitrogen accelerate electron transfer.	458.8 mWm ⁻³	[41]
Balsa wood biochar	800 °C for 1 h	Biochar can be used directly without using the binders and catalysts.	72 mWm ⁻²	[42]
Water hyacinth	900 °C for 2 h	Capable of transferring electrons	24.7 mWm ⁻²	[43]
Eggplant	Pre-treated with K ₃ [Fe(C ₂ O ₄) ₃] and pyrolyzed at 800 °C for 1 h	Possesses hierarchical porous structure with a large specific surface area and high graphitization degree	667 mWm ⁻²	[44]
(b)				
Biomass	Synthesis	Comment	Productivity	References
Corncob	Corncob particles mixed with melamine heated at 121 °C for 2 h. Material soaked with ZnCl ₂ and pyrolyzed at 700 °C for 3 h	Fabricated biochar promoted the growth of dominant bacteria and the electron transfer rate.	230 mL g ⁻¹	[45]
Cornstalk	Pyrolyzed at 600 °C for 2 h	Biochar promotes cellulolytic enzymes activity and leads to increased substrate conversion into hydrogen.	286.1 mL g ⁻¹	[46]
Sewage sludge	Pyrolyzed at 600 °C for 3 h	Phosphate-laden biochar used with Ca- and Mg-saturated resin. Both facilitated substrate degradation and reduces the lag phase.	197 mL g ⁻¹	[47]
Timber sawdust	Calcinised at 500 °C for 2 h	Biochar along with Fe acts synergistically and results in enhancing the growth and activity of microbes and the utilization of substrate.	50.6 mL g ⁻¹	[48]
Woody biomass	Pyrolysis at 400–500 °C	Co-culture of <i>Enterobacter aerogenes</i> and <i>E. coli</i> was used. Biochar mitigates ammonia inhibitory effect and facilitates biofilm formation for efficient colonization and reduces the lag phase.	96.6 mL g ⁻¹	[49]

Table 1. Cont.

(a)				
As Anode				
Biomass	Preparation	Comments	Power Density	References
(c)				
Biomass	Oil	Catalyst Preparation	Yield (%)	References
Peanut shell	Algal oil	400 °C for 1 h followed by H ₂ SO ₄ treatment	94.9	[50]
Brown algae	Waste cooking oil	900 °C for 4 h, calcified with CaO and K ₂ CO ₃ at 500 °C for 3 h	98.8	[51]
Sludge biochar	Palm oil	800 °C for 30 min calcined with CaO at 700 °C	93.7	[52]
Sugarcane bagasse	Palm oil	400 °C for 2 h, sulfonated with ClSO ₃ H at 300 °C for 5 h	98.6	[53]
Cork biochar	Waste cooking oil	600 °C for 2 h and sulphonated with H ₂ SO ₄ at 100 °C for 10 h	98	[54]

In recent times, bioinspired carbonaceous materials, viz. graphene, biochar, carbon fibers, carbon nanotubes, etc., are gaining much consideration owing to their biocompatible nature for biofilm formation and microbial growth along with high surface area and conductivity. Here, nano-biochar is the renewable carbon-based material produced even by waste-organic materials for electrode production. Various biomass sources have been examined for anode/cathode preparation for efficient biofilm formation, and the properties are further dependent on several factors, i.e., pore size, available surface area, and surface properties. The pyrolyzed carbonaceous heteroatoms function as a natural dopant, delivering admirable electrical conductivity. In addition to the generation of bio-electricity, MFC is also utilized for wastewater treatment and produces low amounts of sludge compared to the traditional anaerobic digestion techniques [31]. For the cathodic performance of the carbonaceous materials, the surface area alone is a weak indicator as the existence of increased acidic functional groups regulates the oxygen reduction capability of the cathode [1].

2.2. Nano-Biochar for Hydrogen Production

Nano-biochar has also been utilized for biohydrogen production via three different processes, namely water splitting, methane steam reforming and anaerobic digestion. A brief discussion regarding all the mentioned technologies is presented in the following section. Table 1(b) summarizes the utilization of nano-biochar for hydrogen generation.

2.2.1. Nano-Biochar for Water Splitting

Water splitting using numerous electro-catalysts of the noble metals and their oxides, e.g., RuO₂ and IrO₂, is the cleanest way of hydrogen production, however, the process is still inefficient owing to the high catalyst cost, instability in the alkaline environment, and overpotential of the H₂ evolution reaction (HER) and O₂ evolution reaction (OER) at the cathode and anode, respectively [55,56]. Therefore, bio-inspired carbonaceous materials are nowadays being explored as electrocatalysts due to their cost-efficient electrical conductivity [1]. Further, to reduce the overpotential and enhance the hydrogen generation ability, transition metals can be doped on carbonaceous materials to create more active sites for rapid electron transference [57]. In addition, the presence of alkali and alkaline earth metals assists in the carbon and porosity activation through the ionic migration effect at the high temperature. Recently, biochar-derived molybdenum carbide (Mo₂C) has gained consideration owing to its Pt-similar stability and structure. Still, the HER efficacy of Mo₂C

electro-catalysts is less because it lacks exposed catalytic sites along with strong Mo-H bonding [1,56].

2.2.2. Nano-Biochar for Methane Steam Reforming

Methane can be generated via the anaerobic digestion of the organic wastes that present the maximum hydrogen to carbon ratio (4:1). Further, the thermo-catalytic decomposition of methane leads to the generation of pure hydrogen at a very high temperature (1200 °C) for the conversion reaction initialization. Thus, metallic catalysts (Ni, Fe, Cu, etc.) are involved in enhancing the methane conversion at a lower temperature. However, these metallic catalysts lose their activity very fast. In addition, the presence of sulphur in the natural atmosphere is further harmful to the catalysts [1]. Carbon materials have greater stability and are resilient to sulphur content. Carbonaceous materials doped with metals in trace amount present enhanced activity owing to the generation of high energy active sites that attract the methane, further helping in the enhanced methane conversion to hydrogen. Nowadays, the nano-biochar prepared from bio-solids recovered from wastewater treatment plants is utilized for the methane steam reforming process resulting in 65% conversion [58].

2.2.3. Nano-Biochar for Biogas Production

Organic bio-waste management using an AD process leads to bioenergy generation. It was stated that the nano-biochar addition during the AD enhances the hydrogen yield with a minimal lag phase. It is predicted that the nano-biochar enables biofilm formation and pH stabilization, and enhances the generation of volatile fatty acids (VFAs) [59]. Further, the minerals existing in the nano-biochar are responsible for providing supplements for microbial metabolism and enzyme synthesis and activity. Biochar-derived from pine dust during the two-phase AD of aqueous carbohydrates resulted in enhanced methane and hydrogen yield by 10% and 31%, respectively [60]. Furthermore, microbes may acclimatize to numerous inhibitors, but that might be time-consuming and affect cellular productivity. The nano-biochar aided AD process tends to remove the inhibitors and reduce the toxicity, thus improving in hydrogen production [1].

2.3. Nano-Biochar for Biodiesel Production

The occurrence of long carbon chain (C_{14} – C_{20}) fatty acids has gained the attention for biodiesel production for the present engines owing to their high energy densities. The transesterified oils from various renewable resources produce biodiesel [61]. During the transesterification process, catalysts playing a major role are further categorized into two types, i.e., homogenous and heterogeneous catalysts. Heterogeneous catalysts can simultaneously perform transesterification and esterification reactions. Table 1(c) lists examples of the utilization of nano-biochar as catalyst for biodiesel production.

Biochar, defined as a heterogeneous catalyst, has clearly shown its potential for biodiesel production. Transesterification reactions were carried out in the presence of nano-biochar that was altered via either acid/alkali as the catalyst. The porosity of the nano-biochar permits the reactants easy access to active sites to enable the transesterification reaction [1]. In addition, the hydrophobic surface of nano-biochar assists in the water elimination during the conversion reaction. The biochar acid-modified via the sulfonation process contains $-SO_3H$ groups on the biochar surface and further acts as the catalyst, while the alkali-modified biochar has basic sites primarily consisting of calcium, potassium, or sodium oxides that are produced during the calcination of the minerals present in the organic substrate [51–53]. During the transesterification reaction, the alcohols and lipids utilize the porous structure to accelerate the reactants' collision frequency at ambient pressure.

3. Nano-Biochar for Anaerobic Digestion

Depending on the conditions, the nano-biochar characteristics can be enhanced for application. Nano-biochar characteristics such as porosity, specific surface area (SSA), cation exchange capacity, electrical conductivity, redox potential, pH, and functional groups play an essential role during the AD process [62].

3.1. Porosity

Nano-biochar porosity is a crucial factor in recognizing the probable association with microbes during AD. The biochar pore size acts as microhabitats for microbes to flourish [63]. The typical microbial size in AD is 0.3–13 μm for bacteria/archaea, 2–80 μm for fungus, and 7–30 μm for protozoa [56]. In addition, the porosity of biochar enables the formation of biofilm, acting as a protection for the amelioration of selective and effective microbes participating in the AD system in an acidic environment [64]. The addition of nano-biochar selectively enhances the numerous bacterial species in the AD system. Most research has documented *Methanolinea*, *Methanobacterium*, and *Methanosarcina* sp. in anaerobic digester supplemented with biochar. Numerous studies reported the spatial dispersion of archaea and bacteria by separating the sludge into several portions [65]. The spatial dispersal of methanogens in the biochar pores is due to their diverse size and morphology [66].

3.2. Specific Surface Area

The SSA of nano-biochar is one of the crucial parameters for environmental pollutants adsorption [63]. The nano-biochar capacity to remove CO_2 , H_2S , etc. in a biogas fermenter was studied by Sethupathi et al. [67]. They observed values of 0.208 mmol g^{-1} and 0.126 mmol g^{-1} for CO_2 and H_2S , respectively. The adsorption of CO_2 by biochar (hickory wood and bagasse), the involvement of high SSA and N_2 group of biochar for removal was reported by Creamer et al. [68]. The pore size of biochar (0.5–0.8 nm) and enhanced SSA were reported for sequestration of CO_2 [69], whereas the group I-II A metals and primary functional groups present on the surface play an essential role [70].

3.3. Cation Exchange Capacity

The concentration of ammonium (NH_4^+) and NH_3 are sustained under an optimized threshold for an AD process; it helps in buffer capacity for improved growth of bacteria, whereas the excess amount of total NH_3 /free $\text{NH}_3\text{-N}$ (TAN/FAN) can cause AD catastrophe [71]. It was observed that TAN content (1.7 and 14 g L^{-1}) decreased the generation of CH_4 by 50% and free ammonium nitrogen (FAN) (150 and 1200 mg L^{-1}) content significantly influences the growth of methanogens [71,72]. Biochar could significantly improve the inhibition of NH_3 and increase CH_4 generation by decreasing the microbial lag phase owing to its strong cation exchange capacity (CEC). Shen et al. [73] reported the positive role of biochar in AD of sewage sludge. Su et al. [74] stated that biochar alleviated the $\text{NH}_3\text{-N}$ ($\sim 1500 \text{ mg L}^{-1}$) in food waste AD. Likewise, Lü et al. [66] stated that enhanced NH_4^+ content (up to 7 g-N L^{-1}) could be repressed by biochar supplementation during AD. The mechanisms include microbial immobilization, physicochemical adsorption capacity, CEC, surface functional groups (SFG), and DIET advancement [73–75].

3.4. Electrical Conductivity

The microbial syntrophic interaction depends on the electrical conductivity (EC) [63]. However, the EC of nano-biochar is insignificant in contrast to the EC of digestate, which is based on the microbes' metabolism and composition [76]. Nano-biochars' ability to enhance DIET is equal to that of granular activated carbon, despite the lower biochar EC [77] although some nano-biochar has high EC (e.g., basswood nano-biochar) [78]. Barua and Dhar [79] reported increased EC (0.2–36.7 $\mu\text{S cm}^{-1}$) in numerous microbes due to DIET. Martins et al. [76] proposed that humic substances could act as electron transport media to accelerate DIET.

3.5. pH

The pH influences the conductivity of nano-biochar and associated microbes in AD [80]. Due to the ash concentration and acidic functional groups volatilization, the pH values of nano-biochar are alkaline. The rise in biochar's pyrolysis temperature and pH value frequently surges [81]. In addition, the nano-biochar has redox ability, i.e., it can accept or donate the electrons. Further, the presence of aromatics and phenolic groups also aids in the electron transfer [3,82]. Nano-biochar increases the AD alkalinity (minimum pH ≥ 6), enhancing the microbial activity for fast CH₄ generation and adaptability to initial the loading shock [83]. Nano-biochar significantly facilitates the methanogenesis stage under acidic conditions (pH 5.3), improving the operating conditions with increased organic loading and total solids [81]. Hence, with the addition of nano-biochar, a continuous AD process can function with a shorter hydraulic retention time and operate under an extra organic loading rate.

3.6. Surface Functional Groups

The nano-biochar surface consists of various functional groups such as -OH, C-O, -COOH, CO, -NH_x, etc. which assist in nutrient retaining and pollutant removal [84]. Nano-biochar displayed significant outcomes in the adsorption of NH₃ from wastewater and digestate. The nano-biochar's porosity and high SSA aid in the physisorption [85]. However, in some studies, it is not a predominant parameter in adsorption of NH₄⁺ [86,87]. For instance, amid NH₄⁺ and nano-biochar acidic functional groups, ion exchange occurs [85], and CEC plays a significant role in enhancing the adsorption capacity of biochar's towards NH₄⁺ [88]. Sahota et al. [89] employed biochar to remove H₂S from biogas and attained 84.2% elimination efficacy. Likewise, Kanjanarong et al. [90] accomplished 98% H₂S elimination efficacy via biochar and concluded that COOH and OH groups are responsible for the observed H₂S adsorption.

3.7. Redox Potential

The nano-biochar redox properties are critical during AD. The biochar redox properties are due to its SFG, free radicals, and metals (M) and metal oxides (MO) [91]. For example, the electron-donating capacity is due to the presence of phenolic C-OH fractions, while electron-accepting ability is due to quinoid C=O fractions [92]. An oxidation process can enhance nano-biochar SFG [93]. Hitherto, the oxidation process should be appropriate to familiarize with novel functioning, but not too robust to trigger the alteration to the COOH group (redox-inactive) or even to eliminate CO₂ [91]. Free radicals influence the nano-biochar redox propensity, such as aryl radicals or as semi-quinoid radicals [94]. Concerning the nano-biochar's inorganic constituent, Fe and Mn oxides (redox-active metals) usually exist in the biomass and diverse oxidation states act as electron acceptors and donors [95].

4. Roles and Mechanisms of Nano-Biochar in Anaerobic Digestion

The intrinsic characteristic of nano-biochar boosts biofilm microbial development (methanogens colonization) and adsorption of NH₃ and acetate (inhibitors) [96]. AD process aids in the development of a defensive layer for microbes that enhances CH₄ generation. Nano-biochar also stabilizes the microbe's nutrient access and eliminates volatile fatty acids and NH₃ [97]. Figure 3 presents a brief schematic of the anaerobic digestion system aided with the nano-biochar for enhanced biogas production.

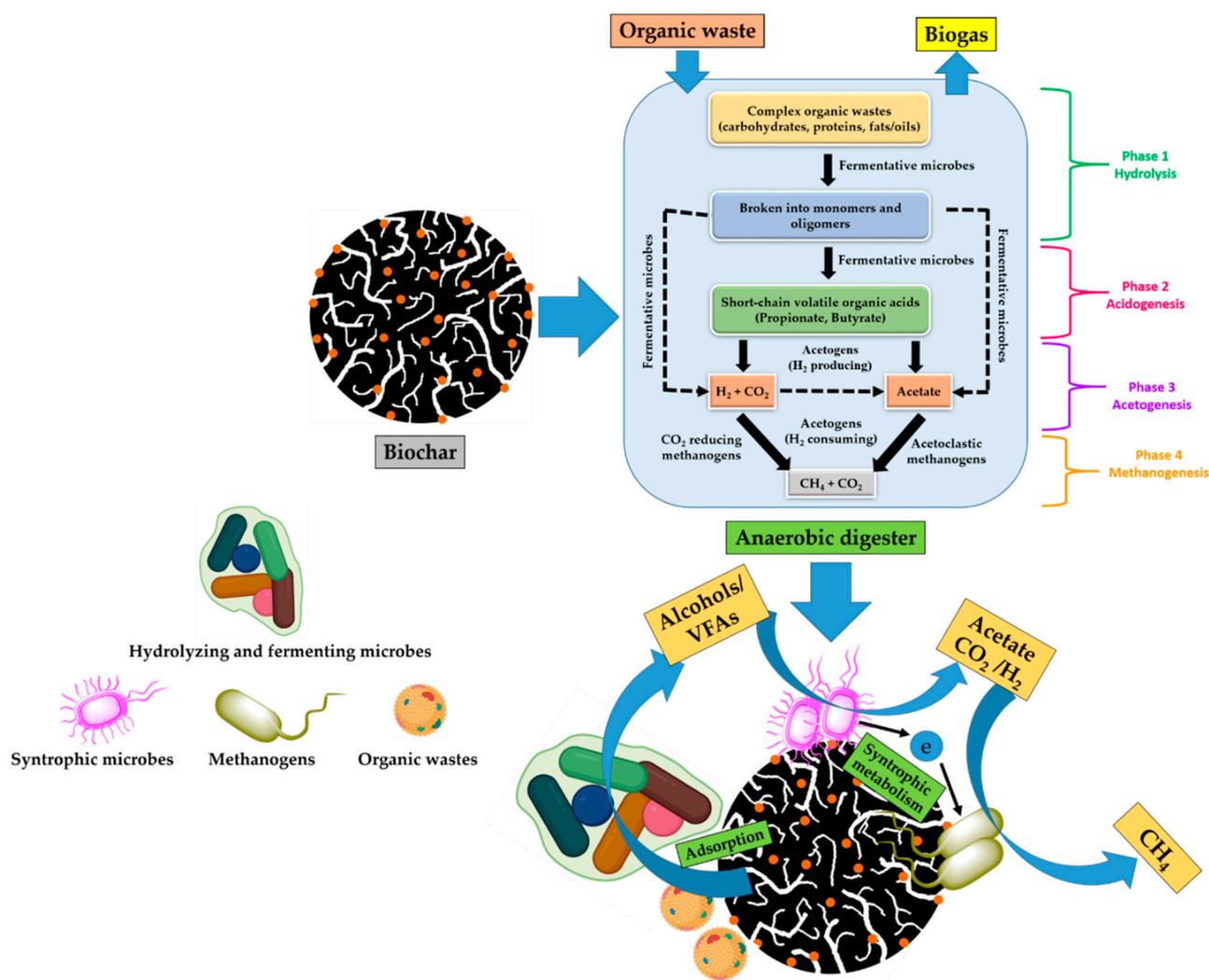


Figure 3. Anaerobic digestion system aided with the nano-biochar for enhanced biogas production.

4.1. Improving the Process Stability

AD stability is crucial for a continuous conversion of biowaste, which can be enhanced by nano-biochar usage via $\text{NH}_3\text{-N}$ improvement [75]. Nano-biochar improves the methanogenic microbes in the presence of acid and NH_3 impediment, which ultimately helps in nitrogen-rich substrate degradation and reduces NH_3 inhibition, thereby improving AD performance [97]. The nano-biochar addition decreases the AD major inhibitor (free NH_3) by 10.5% and encourages the methanogenesis process under an acidic environment [98]. Nano-biochar significantly increases the AD alkalinity ($\text{pH} \geq 6$), therefore supporting the acclimatization of microbes and enriching their activity in the presence of organic loading for more substantial production of CH_4 [99,100]. However, studies reported the toxic effects of the high biochar concentration (~ 4.5 g biochar/g of dry sludge), such as decreased microbial activity [98]. Therefore, optimizing the nano-biochar amount and incessant monitoring are crucial to curtailing the adverse effects on the metabolism of microbes and the intermediate metabolite generation.

4.2. Accelerating the Process Rate

AD system process rates can be efficiently enhanced with the addition of nano-biochar. Shanmugam et al. [101] observed a decrease (24 h) in the methanogenic microbe lag phase when algal-derived biochar was used for wastewater AD. Earlier results supported this outcome that the microbial lag phase duration was inversely proportional to the

biochar to substrate ratio. The 7.5 days lag phase was the optimized ratio [102]. Likewise, Sunyoto et al. [60] reported 21.4–35.7% and 41–45% decreases in the lag phase of H₂ and CH₄ reactors on biochar, respectively. The magnetic biochar addition during methanogenesis entirely avoided the lag phase or decreased it by 0.9–1.83 days [103,104]. Furthermore, Wang et al. [105] reported a reduction of lag phase from 4.7 to 1.8–3.9 days during co-digestion of food waste and sewage sludge on biochar application. The daily production of CH₄ was improved by 136% after the amendment of biochar (wood-pellet-derived) during the AD process [97].

4.3. Buffering Potency and Alkalinity

The efficiency of AD systems mainly relies on the pH value, where a slight decline in the pH of the solution remarkably hinders microbial growth and functioning [106]. Food wastes with low C:N ratio and enhanced biodegradability result in a rapid acidification rate during AD. During the acidogenesis phase, the fast growth of acidogenic bacteria will affect the activity of methanogen's and result in the VFAs accumulation [107]. Fotidis et al. [108] established that the aforementioned state might arise during high organic load with easily biodegradable biomass. As the AD system has an extended recovery period from gathered VFAs, amendment of nano-biochar can aid in a fast and simple process to hasten the recovery of acidified anaerobic reactors [81]. The buffering capacity and availability of nutrients are significantly influenced by nano-biochar during the co-digestion system [105,109]. However, there are a few opposing results regarding the biochar application in the AD process. Luo et al. [64] proposed that before CH₄ generation, acid inhibition might happen during synthetic wastewater AD, and nano-biochar cannot significantly upsurge the pH buffering capacity. A decrease in pH value (5.0 to 3.0) owing to VFAs accretion even after nano-biochar addition during AD was observed by Sunyoto et al. [60]. Thus, there is no inference about the nano-biochar pH buffering capacity during the AD, which is based on the nano-biochar physicochemical properties and flexible operational parameters.

4.4. Inhibitors Adsorption

One of the key advantages that nano-biochar offers to raise AD effectiveness is the adsorption of inhibitors. During the adsorption process, the biochar aromatic structures enable π - π interaction due to OH and COOH groups [90]. The adsorption of VFAs by nano-biochar and alleviation of acid surges the CH₄ yield [101]. The study showed direct proportionality amid NH₄⁺-N adsorption and hydrochar SSA [105]. Linville et al. [110] assessed biochar derived from the walnut shell and found significant removal of CO₂ by coarser (51%) and smaller biochar (61%) in the food waste AD. In the two-stage waste-activated sludge AD by pine wood and corn stover biochar, CH₄ contents of 81–88.6% in corn stover and 72.1–76.6% in pinewood biochar were observed, respectively [73]. The CO₂ was sequestered into carbonate/bicarbonate by base cations released by biochar [96,111].

4.5. Enriched Microbial Functionality

Nano-biochar encourages the extracellular polymeric substance (EPS) secretion from microbes during the formation of biofilm, thereby increasing the adhesion of microbes on the surface of nano-biochar [112]. It is a cost-effective and easy method to evade fast sludge granulation and decrease the methanogens loss during AD. Sun et al. [113] observed the microbial richness in the incidence of biochar carriers. Dang et al. [114] found that *Enterococcus* and *Sporanaerobacter* capacity was improved during biochar addition, which aids in fermentable substrates breakdown for electron transfer to *Methanosarcina*. In addition, the biological interaction between *Methanosaetaceae* and *Methanosarcinales* and biochar efficiently decreases the lag time [66]. Wang et al. [115] found that the hydrochar content is directly proportional to the attachment of methanogenic bacteria. Similarly, in the presence of hydrochar, *Methanosaeta* (acetoclastic methanogen) enrichment was observed [81]. Henceforth, CH₄ generation from VFAs is enhanced by immobilization

of methanogens by hydrochar amendment [116]. Furthermore, biochar increases biofilm formation and functional microbial enrichment, thus, improving the AD process [80].

4.6. Electron Transfer Mechanism

The earlier investigations reported the importance of nano-biochar and its electron transfer amid archaea and anaerobic bacteria. AD system efficacy mainly depends upon the syntrophic interactions amid bacteria and methanogens, which help electrons fulfill their energy requirements [76]. Figure 4 gives an overview of proposed electron transfer mechanisms between oxidizing bacteria and methanogens. It is carried out in various ways: DIET via a conductive medium (e.g., granular activated carbon, magnetite, carbon cloth, nano-biochar) [117], membrane-bound transporter proteins [76], electric conductive pili [79], and indirect interspecies electron transfer (IIET) through insoluble (humic compounds) [118] and soluble (acetate, formate) substances [119,120]. In IIET, formate and hydrogen act as electron transport between methanogens and syntrophic-generating bacteria [76]. The microbial metabolite exchange is governed by Fick's Law, occurring via diffusion. Thus, after the cell accumulation is attained, the interspecies hydrogen transfer rate is raised by anaerobic bacteria and methanogenic archaea form the compressed structures [121].

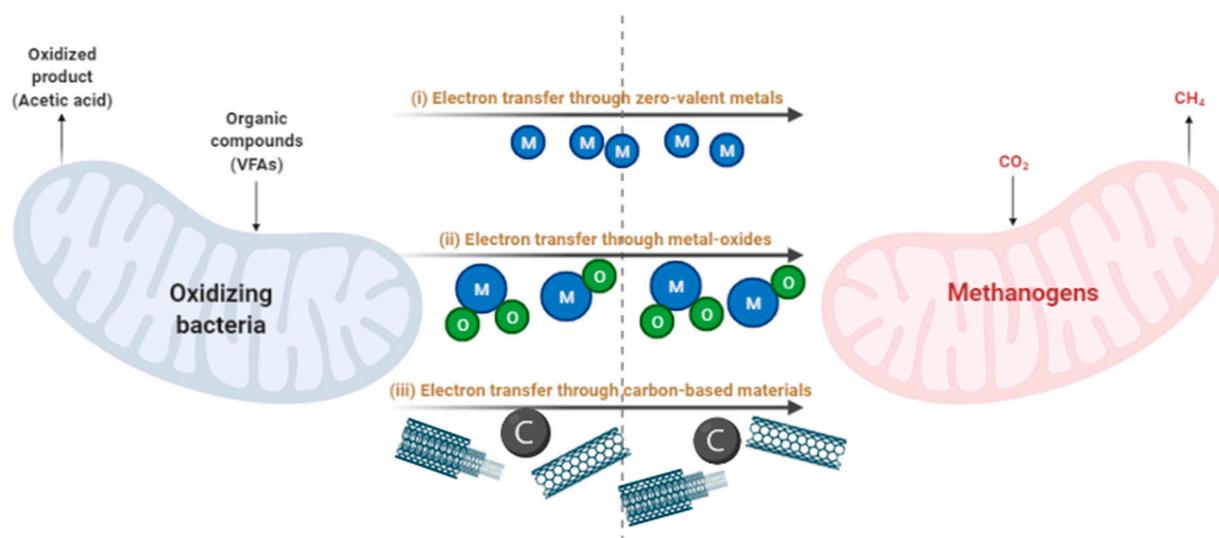


Figure 4. Application of conductive nanoparticles for electron transfer between oxidizing bacteria and methanogens via (i) zero-valent metals; (ii) metal oxides, and (iii) carbon-based materials.

During CH_4 production, IIET and diffusion of soluble metabolites are bottlenecked by decelerating the electron transference and energy transfer rate [77,122]. DIET does not entail the electron transport intercession for generating an electric current amid electron-accepting and donating microbes [76]. DIET was more precise and rapid than IIET [122]. Martínez et al. [123] reported that co-culture enhances CH_4 generation, for instance, enrichment of homoacetogenic bacteria such as *Eubacterium*, *Clostridium*, and *Syntrophomonas*. In synthetic wastewater AD, *Methanosaeta* and *Geobacter* enrichment on biochar in the presence of propionate and butyrate were reported [65]. During conductive biochar amendment, DIET was able to eliminate butyrate and propionate and establish interspecific electron shuttle by *Smithella* and *Syntrophomonas* richness.

5. Kinetics Involved during the AD Process

The kinetic study of AD system is the most important way to evaluate the performance of the reactor for biogas production, mechanism of metabolic pathways, biomass degradation, and the monitoring of the growth rate of microorganisms [124,125]. Based on increasing CH_4 production after the biochemical CH_4 production (BMP assay), the

bio-kinetics parameters such as CH₄ generation potential, maximum rate, and its period of lag phase are evaluated to utilize the three diverse kinetics models. In general, the first-order kinetic model such as Chen and Hashimoto model [126], Cone model, and modified Gompertz model [124,127] were applied to mimic the kinetic patterns of biogas production in different condition. The first-order kinetic model and modified Gompertz model are used for biomass degradation rate and biomethane production rate in batch and continuous reactors [128,129]. The obtained cumulative biomethane productivity results through the modified Gompertz kinetic model (fitting error 0.7–13.7%) were more authentic than first-order kinetic (fitting error 9.2–37.1%) for organic waste material [129]. In addition, the quality of products depends on the type of substrates responsible for acidogenesis, acetoclastic, and methanogenesis by microorganisms in the digestion system. Here, the modified Gompertz and logistic function obey the sigmoidal process that correlates the methanogenic archaea growth with the CH₄ generation in an anaerobic reactor. In contrast, the transference function follows the first-order curve to correlate the CH₄ generation with the microbial activity [130].

$$\text{Modified Gompertz Model; } y = M \cdot \exp \left\{ - \exp \left[\frac{R_m e}{M} (\lambda - t) + 1 \right] \right\} \quad (1)$$

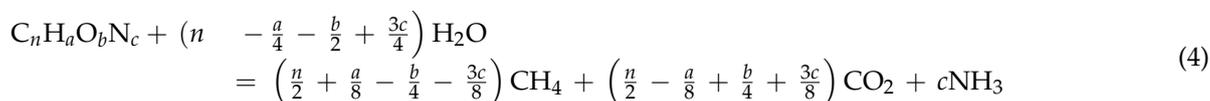
$$\text{Logistic Function Model; } y = \frac{M}{1 + \exp \left(\frac{4 R_m (\lambda - t)}{M} + 2 \right)} \quad (2)$$

$$\text{Transference Function Model; } y = M \left\{ 1 - \exp \left(- \frac{R_m (t - \lambda)}{M} \right) \right\} \quad (3)$$

where y is the accumulated CH₄ (mL) at time t (h), M , R_m , λ , and e are the potential CH₄ generation (mL CH₄ g⁻¹), maximum rate of CH₄ production (mL CH₄ g⁻¹ h⁻¹), lag phase time (h), and base and constant of the natural logarithms, respectively.

Kinetic models can be divided into structured (complex degradation and fermentation mechanism analysis) and unstructured (substrate consumption, growth rate along with production evaluation) models. The structured models are used for unsteady-state balance, while the unstructured models are used to assess steady-state balance conditions during the anaerobic process [127,129]. Some researchers have reported that the maximum growth rate value in the exponential phase is minimum at low substrate concentration. In the case of acetate inhibition at a higher substrate concentration, Andrew's kinetic models for AD (Equations (2) and (3)) that express the acetolactic methanogenesis stage can be used [124,131].

To examine the theoretical CH₄ yield (TMY) from the organic wastes on the basis of the elemental contents of the substrates, the following equations are given (Buswell formula [132]):



$$TMY \left(\frac{\text{mLCH}_4}{\text{gVS}} \right) = \frac{(22.4)(1000) \left(\frac{n}{2} + \frac{a}{8} - \frac{b}{4} - \frac{3c}{8} \right)}{12n + a + 16b + 14c} \quad (5)$$

In addition, the anaerobic biodegradability of the organic feedstocks can be evaluated by dividing the experimental CH₄ yield by theoretical CH₄ yield. Furthermore, the surface-related models (Contois kinetics) for anaerobic digestion have not been much developed. Several researchers reported hydrolysis as a first-order kinetic model reaction that depends on various substrates and particle size. These limitations of pertinent simulation in the biogas generation mainly rely on the data availability and accuracy of the process. The methanogenesis effect with the kinetic limitation of the substrate is used in diverse kinds of inhibition models in the AD system. AD process is considered as H₂ and H₂S inhibition with

the ionic balance and pH level in the biogas process system. The standard CH₄ formation rate is based on the un-dissociated hydrogen and sulphur concentration. Furthermore, the occurrence of oxygen is very sensitive; it breaks the degradation process in the AD system [133].

6. Closed-Loop Integration of Biochar and Anaerobic Digestion

The inherent complication in AD process is related to the different groups of microbes. The conventional ways such as pre-treatments (reducing the retardation rate) and co-substrates (the balance of nutrients, very low accumulation of toxicity), do not perform well to deal with such challenges [62,134]. In this respect, several new approaches and productive concepts are required, some of which are enumerated below:

- (i) a synergetic integration of different technologies and proceed in methodical ways
- (ii) development of the zero liquid discharge (ZLD) through cascade system
- (iii) processing biomasses in concurrence with the closed-loop integrated system

These methodical routes of advanced blueprinted bio-energetic system offer several advantages, viz. supporting maximum recycling of biomass through managing material and energy which needed from the same feedstock (low energy consumption) [135], promoting the new income of source. Therefore, it also favors the ecological environment [136,137]. This integrated system uses the solid biomass residue for pyrolysis, which produces nano-biochar and is used as an additive in the AD reactor to enhance bio-methane production. Further, nano-biochar can be used as an adsorbent to enrich the nutrients in the slurry, or can also be used for agriculture as a fertilizer and soil conditioner. In this process, methane gas is produced, and it can further be used to generate power and heat. Hence, this integrated closed-loop system promotes crucial techniques for producing biomass during AD [138].

Deng et al. [139] achieved 17% yield increase of CH₄ and 10% bio-oil yield increase through the integrated system of AD and pyrolysis, and obtained 26% reduction in digestate biomass from seaweed. Similarly, Sen et al. [140] reported that in a study of a closed-loop system using the additive nano-biochar, the biomethane yield could be enhanced by 7%, the bio-methanation rate constant by 8.1%, and the maximum methane production rate by 27.6%, as well as increased alkalinity and mitigated NH₃ inhibition for AD. AD with pyrolysis favored both pyrolysis of liquor and pyrolysis of solid digestate, where nano-biochar acts as a catalyst for AD by supporting the mitigated NH₃, buffering, and alkalinity. Therefore, an integrated system of AD with pyrolysis is a promising way for the amalgamation of biological (AD) and thermochemical processes (pyrolysis) [141].

To improve circular economics and the sustainability effect of the AD effluent, alternative methods (converting digestate to pyrogenic carbon) are required, which may be considered as a feasible pathway because nowadays nano-biochar is considered as a carbon reservoir/carbon-negative technology, that is, contributing to greenhouse gases (GHG) emission [142], due to its properties such as having a high amount of highly stable carbon, and long-term carbon segregation capacity especially in an integrated system with AD [135,137]. Monlau et al. [135] revealed that solid-digestate (containing about 30–50% of organic carbon, on dry basis) was treated close to the pyrolysis in terms of excess amount of energy, similar to the pyrolysis nano-biochar. It was evident that the integrated system (AD & pyrolysis) anticipated a net 42% increase in electricity production. The AD system has various limitations such as inhibition of NH₃, quality of digestate, and low quality of biogas. However, by using this vigorous closed-loop integration (AD-pyrogenic carbon), more green and clean energy can be produced.

Further, the accomplishment of nano-biochar on anaerobic reactors such as acidogenesis, acetogenesis, hydrolysis, and methanogenesis is to be carried out for improving the buffering capacity and increasing acid pressure [62]. Nano-biochar is a vital way to aid in bio-shielding of archaea under acidic pressure and its reactive mechanism in AD reactors. Nano-biochar has proven its role as a stabilizer to enhance the syntrophic metabolism of VFAs and alcohol, enabling one to shorten retention times in AD [143].

The productivity for CH₄ during bio-methanation can be improved by improving anaerobic methanogens, which are promoted through a consortium of methanosarcina and syntrophic bacteria. Selective colonization is observed and had an ammonium adsorption capacity up to 17.6 mg g⁻¹ by biochar [144]. DIET has been recognized as an alternative pathway for hydrogen interspecies transfer of syntrophic electrons between *Geobacter* and *Methanosarcina* to accelerate the syntrophic metabolism of ethanol by incorporating nano viruses. After which, methanogenic electron movement can be increased due to acetic acid formation [143], amplifying methanogenesis, directing to acidogenesis-acetogenesis, supporting the minimal corrosion and eccentric colonization of methanogenesis for improvement in selective productivity.

The most interesting factor for nano-biochar use as an AD additive is its minimal complexity, low cost, and very low risk of formation of second-hand pollutants. Meanwhile, porous material biochar contains a specific molecular structure [66], which stimulates AD at advanced levels. Many researchers have reported the performance of biochar such as hydrothermal carbonization and pyrolytic biochar for their low effects on ammonia inhibition and microbial growth [63]. Some issues related to using biochar in AD are still unsolved. Thus, there is a need to model the operational procedure, evaluation via advanced techniques with references at an earlier stage. Hence, nano-biochar may be a suitable replacement for conventional approaches.

7. Techno-Economic and Environmental Life Cycle Assessment

The techno-economic and environmental assessment of nano-biochar application in AD is imperative according to the production cost, vending cost, operating cost, profits, low carbon emissions, reduced secondary pollution, and less global warming potential at the commercial level [62]. These evaluations were also performed to raise the economic feasibility of nano-biochar application in full-scale along with the long-term operation of the AD process. In addition, the characteristic properties of the nano-biochar, feed type, production conditions, etc. all play a vital role in the AD performance that is mentioned in the current section.

7.1. Techno-Economic Analysis

Various researchers have performed the economic assessment of nano-biochar production to determine the investment that might be further balanced via the biochar trade price (470 € t⁻¹) [145]. Nano-biochar yield is mostly affected via oxygen to carbon (O/C), molecular ratio during pyrolysis and the ash content. A high O/C ratio in the feed substrate reduces the nano-biochar selectivity and enhances the formation of bio-oil, while a low ash content leads to an increase in the nano-biochar yield and decreases the bio-oil yield [62]. Adding biological and inorganic elements within the nano-biochar as additives in AD is usually carried out to increase methane production. These additions further lead to an increase in the overall production of the biochar; for instance, nutrients and enzymes add in 13–16 and 3.6–4.1 € L⁻¹, respectively [146].

The trending circular economy model was also applied for managing the digestate produced via the AD process of the organics [147]. The researchers have followed the “back to Earth” concept to deal with the digestate produced via AD of food and municipal solid wastes. The simultaneous integrated utilization of the biochar-aided AD and further recycling the digestate for the nano-biochar synthesis is consistent with the “zero-waste” concept approach. The digestate can also be used for fuel, energy, fertilizer, and chemical production for the industries [148]. In addition, the installation cost, pre-treatment cost (covering 43%), and hydrogen purification cost (22%) is chiefly involved in the overall cost. The average operating cost for nano-biochar derived from woody and straw biomasses are 0.68 and 0.86 € L⁻¹, respectively, in comparison to the additives, viz., nutrients (13–16 € L⁻¹) and enzymes (4.10 € L⁻¹) [121]. Traditional biochar (5–25 g L⁻¹) can be utilized as an additive in the AD process and is reused many times, making the process more economically feasible and the additional gain of by-products [149]. González et al. [150]

reported a case study of the economic feasibility of an integrated system and *NPV* could be calculated using the following equation:

$$\text{Net present value (NPV)} = -TCC + \sum_{t=1}^n \frac{CF_t}{(1+r)^t} \quad (6)$$

where *TCC* is the total capital cost of the investment for the digestion and pyrolysis plant, CF_t is the cash flow expected at time t , and r is the discount rate.

Nevertheless, this analysis for the cost evaluation of nano-biochar aided AD process on a large scale is still at its embryonic stage. Henceforth, many researchers have further approached the life-cycle assessment (LCA) to analyze the total input energy required for CH_4 production [151].

7.2. Life-Cycle Assessment

An optimistic energy balance should be attained for the addition of nano-biochar for the anaerobic digestion process in the LCA. This “cradle to grave approach” must also be beneficial from the environmental and economic perspective [152]. LCA of the biochar produced via the lignocellulosic wastes showed the GHG emission in between 20–50 g CO_2 -eq MJ^{-1} ; whereas for pit/shell/husk, it ranges amid 120–250 g CO_2 -eq MJ^{-1} [62]. The feedstocks for biochar possessing an ash content in the range of 0–2% and having a high O/C ratio are mainly related to the enhanced GHG emissions [62,84]. In addition, compared to the petro-derived fuels, the utilization of biofuels leads to >85% reduction in GHG release, equivalent to 93 g CO_2 -eq MJ^{-1} . The biochar-aided AD process offers encouraging effects in contrast with AD alone. However, further LCA studies are needed to associate and integrate the waste conversion and resource recovery processes [153]. The methodical outcomes primarily depend on the type of biomass, compositions, reaction condition, and reactor, but lack the LCA for biofuels production [154–158].

Moreover, landfills, carbon sources, and other ambiguous factors (infrastructure, transportation, and waste management) should also be considered in the LCA [5]. ReCiPe and Tool for Reduction and Assessment of Chemicals and other environmental Impacts (TRACI) is a method for the life-cycle impact analysis (LCIA) and environmental impact assessment, respectively [5]. Hence, more studies of LCA are needed to assist the optimization of methodical, financial, and environmental performances of the additive nano-biochar and its integration in AD processes.

8. Conclusions and Prospects for Future Research

The properties of nano-biochar are primarily dependent on the organic feedstock used and its processing. Further, it is extensively being used as a catalyst for enhancing renewable energy production. Our comprehensive evaluation of the recent literature available on biochar-amended anaerobic processes concluded the credible importance of nano-biochar from the economical, simple processing, and enhanced biogas yield. Further, the metal-doped/impregnated nano-biochar composites show more magnetization properties and recycling ability, which can reduce the costs of biochar addition. The recycling of nano-biochar composites during the AD process further leads to the loss of the methanogen population due to the digestate disposal. In addition, Fe_2O_3 and Fe_3O_4 impregnated biochar perform as electron channels for promoting the interspecies electron transfer. The enhancement in the stability and reliability of anaerobic digestion via nano-biochar addition is much significant and depicts a novel paradigm for the generation of renewable energy, resource recovery, and waste management. The biochar-aided AD process mitigates the acidification impact caused via VFAs accumulation, encouraging the electron species and microbial growth. Further, in comparison to the traditional AD process, the nano-biochar addition helps reduce the environmental impacts and cost-involved. In addition, the following are some proposals that can further improve this feature:

- (i) Numerous references report on the fed-batch operation of nano-biochar-amended AD processes. Further efforts should be made to develop continuous or semi-continuous operational modes, nano-biochar recycling, and reusability.
- (ii) Prudent procedures should be developed and followed to determine the quantitative inhibition exhibited via the nano-biochar for the AD process.
- (iii) Effective microbial metabolic pathways should be tracked along with the prime attention to the nano-biochar-microbe interactions, and mechanistic insights.
- (iv) Techno-economic and the socio-economic analyses of the pilot- and industrial-scale plants, including the mass and energy balance assessments, are essential for the nano-biochar-amended AD process. The life-cycle and supply chain management further needs to be monitored for the overall impact of the integrated process.
- (v) Exploration of DIET/IIET is highly encouraged for electron-based elucidation to enhance biogas production and further establish a pioneer avenue of research in renewable energy research.
- (vi) Nano-biochar-amended co-digestion approaches need to be explored for the reduction in the reactor volume, zero-waste approach, carbon capturing, and encouraging the circular bioeconomy concept.

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