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Review of biochar role as additive in anaerobic digestion processes

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Abstract

Anaerobic digestion (AD) could be considered as a mature technology and nowadays it can still play a pivot role because of the urgent need to provide renewable energy sources and efficiently manage the continuously growing amount of organic waste. Biochar (BC) is an extremely versatile material, which could be produced by carbonization of organic materials, including biomass and wastes, consistently with Circular Economy principles, and "tailor-made" for specific applications. The potential BC role as additive in the control of the many well-known critical issues of AD processes has been increasingly explored over the past few years. However, a clear and comprehensive understanding of the connections between BC and AD is still missing. This review paper analyses and discusses significant references (review articles, research papers and international databases and reports), mostly published in the last 10 years. This review is aimed at addressing three key issues related to the better understanding of the BC role in AD processes: 1. Investigation of the influence of BC properties on AD performances and of their ability to counteract its main challenges; 2. Assessment of the optimal BC production chain (i.e. feedstock-pyrolysis-activation) to achieve the desired features; 3. Evaluation of the economic and environmental advantages connected to BC use in AD processes, compared to conventional solutions applied to address AD challenges.

Highlights

- Biochar key properties were specific surface, pores and surface functional groups
- Lignocellulosic biomass, slow pyrolysis and physical activation made the best biochar
- Biochar addition exhibited economic and environmental advantages
- Biochar improved methane production (in average 25 %) and digestate quality

Keywords: anaerobic digestion; biochar; bioenergy; biomass; circular economy; waste

Abbreviations

AD: anaerobic digestion; BC: biochar; BET: Brunauer–Emmett–Teller; CE: circular economy; CEC: cationic exchange capacity; CIC: controlling internal circulation; CLSM: confocal laser scanning microscopy; COD: chemical oxygen demand; DIET: direct interspecies electron transfer; EAC: electron accepting capacity; EDC: electron donating capacity; EU: European union; FAN: free ammonia nitrogen; FISH: Fluorescence in situ hybridization; FW: food waste; GAC: granular activated carbon; GHG: green-house gas; HRT: hydraulic retention time; IET: interspecies electron transfer; LCA: life cycle analysis; MSW: municipal solid waste; OFMSW: organic fraction of municipal solid waste; OLR: organic loading rate; PAH: polyaromatic hydrocarbons; PCBs: polychlorinated biphenyls; S/I: substrate to inoculum ratio; SMP: specific methane potential; SS: suspended solids; SSA: specific surface area; TAN: total ammonia nitrogen; TPAD: two phased anaerobic digestion; TSS: total suspended solids; UASB: up-flow anaerobic sludge blanket; VFA: volatile fatty acids; WAS: waste activated sludge; WWTP: wastewater treatment plant; WV: working volume; V: volume.

Contents

1. Introduction

The global energy consumption increased from around 8,800 million tonnes of oil equivalents (Mtoe, including coal, gas, oil, electricity, heat and biomass) in 1990 to 14,400 Mtoe in 2018 [1]. In 2016 renewable energy sources met this demand for about 14 % of primary energy supply, while fossil fuels accounted for 81% of greenhouse gas (GHG) emissions [2]. The need to decrease fossil fuel dependency and GHG emissions and to generate economic benefits is stimulating initiatives to produce energy as well as high-value chemicals and products from sustainable non-food biomass, residues, co-products and wastes.

Anaerobic digestion (AD) is a well-established technology for the treatment of wastewater and organic waste, e.g. the organic fraction of the municipal solid waste (OFMSW), waste activated sludge (WAS), animal manure, etc. Biogas can directly replace fossil fuels in heat and power generation or be upgraded to bio-methane as vehicle fuel or injected in the gas grid [3], while digestate can be employed as soil amendment [4,5]. Other benefits of AD, compared to alternative treatment options applied to organic waste, include control of odor and GHG emissions, removal of pathogens and adaptability to many substrates [6]. AD has been extensively implemented, from small-scale applications, particularly in rural areas and developing countries, to large-scale industrial plants [7]. Despite the rapidly growing number of biogas installations in Europe (from about 6,200 to 18,202 between 2009 and 2018) [8], many challenges regarding AD processes still persist. Different options have been explored to address these challenges: optimization of working parameters and bio-reactor configuration, co-digestion and nutrients control [9]; adoption of pre-treatments to enhance the degradability of various substrates [10,11]; use of inorganic and biological additives to support biomass immobilization, supplement nutrients, mitigate inhibitors and improve process stability [12–14].

Among the additives, conductive carbonaceous materials, as granular activated carbon (GAC) and biochar (BC), gained interest because of their ability of enhancing methane production [15,16]. BC may present several advantages over other additives; it can be produced with a wide variety of physico-chemical properties by controlling feedstock, pyrolysis operating conditions and the activation process [17,18], resulting “tailor-made” for specific applications. In recent years, several authors confirmed the possibility of increasing methane production through BC addition (Table 1), suggesting different potential mechanisms: (1) increase of the buffering capacity of the AD system; (2) mitigation of inhibition phenomena or agents; (3) support media for biomass immobilization; (4) promotion of syntrophic metabolisms; (5) enhancement of digestate quality; (6) biogas cleaning and upgrading. The most significant and updated scientific literature investigating the BC role within AD processes can be classified as follows (Table 1):

- Studies considering the advantages of coupling AD with thermal processes (gasification, pyrolysis and hydrothermal carbonization) from a general point of view;
- Studies exploring the positive influence of BC on AD, based on methane and/or biogas production enhancement and/or improvement of digestate quality;
- Studies analysing in detail the BC features that may influence one or more of the above-mentioned mechanisms.

Considering the digestate, BC has been reported to enhance its quality in terms of nutrient retention, increase of the carbon-to-nitrogen ratio and reduction of nutrient leaching [19].

Consequently, BC doesn’t need to be separated from digestate at the end of its utilization in AD.

Table 1. Overview of literature studies exploring the connections between BC and AD

Studies considering the general advantages of coupling AD with thermal processes	Studies exploring the positive influence of BC on AD, based on a general analysis of methane and/or biogas production enhancement	Studies exploring the positive influence of BC on AD, based on a general analysis of the improvement of digestate quality	Studies analysing in details the biochar features that may influence one or more of the six above-mentioned mechanisms
Pecchi and Baratieri, 2019 [20] Fabbri and Torri, 2016 [21] Hübner and Mumme, 2015 [22] Salman et al., 2017 [23]	Linville et al., 2017 [24] Torri and Fabbri, 2014 [25] Sunyoto et al., 2016 [26] Jang et al., 2018 [27] Sun et al., 2019 [28] Zhao et al., 2015 [29] Inthapanya et al., 2012 [30] Inthapanya and Preston, 2013 [31]	Bruun et al., 2011 [32] Shen et al., 2016 [33] Shen et al., 2017 [34]	Fagbohungbe et al., 2017 [19] Ye et al., 2018 [13] González et al., 2018 [15] Zhang et al., 2018 [16] Codignole Luz et al., 2018 [35] Masebinu et al., 2019 [36] Pelaez-Samaniego et al., 2018 [37] G. Wang et al., 2018b [38] D. Wang et al., 2017 [39] Fagbohungbe et al., 2016 [40] Mumme et al., 2014 [41] Shanmugam et al., 2018 [42] Su et al., 2019 [43] Lü et al., 2016 [44] Cruz Viggi et al., 2017 [45] Li et al., 2018 [46] Martínez et al., 2018 [47] Luo et al., 2015 [48] Wang et al., 2019 [49] C. Wang et al., 2018 [50] Zhao et al., 2016 [51] Yu et al., 1999 [52] Cooney et al., 2016 [53] Dang et al., 2017 [54] Sasaki et al., 2010 [55] Martins et al., 2018 [56] S. Chen et al., 2014 [57] Pan et al., 2019b [58] Qiu et al., 2019 [59]

To the best of our knowledge, despite the growing number of studies investigating the connections between BC and AD, three main issues still need to be explored: a clear comprehension of the above-mentioned six mechanisms; a correlation between BC features and their effects on AD processes; environmental and economic outcomes related to BC use. The present review is therefore aimed at addressing the following issues: 1) investigation of the influence of BC properties on AD performance and of their ability to counteract its main challenges; 2) assessment of the optimal BC production chain (i.e. feedstock-pyrolysis-activation) to achieve the desired features; 3) evaluation of the economic and environmental advantages connected to BC use in AD processes, compared to conventional solutions applied to address AD challenges.

2. Review methodology

The selection of scientific literature was made considering the following criteria:

a) *Relevant international databases and information sources*. Bibliometric sources as Web of Science, Science Direct and Scopus were used to retrieve articles, book-chapters and proceedings of indexed conferences. Official international databases (Eurostat, International Energy Agency, European Biogas Association, etc.) were searched for the selection of technical reports and statistics;

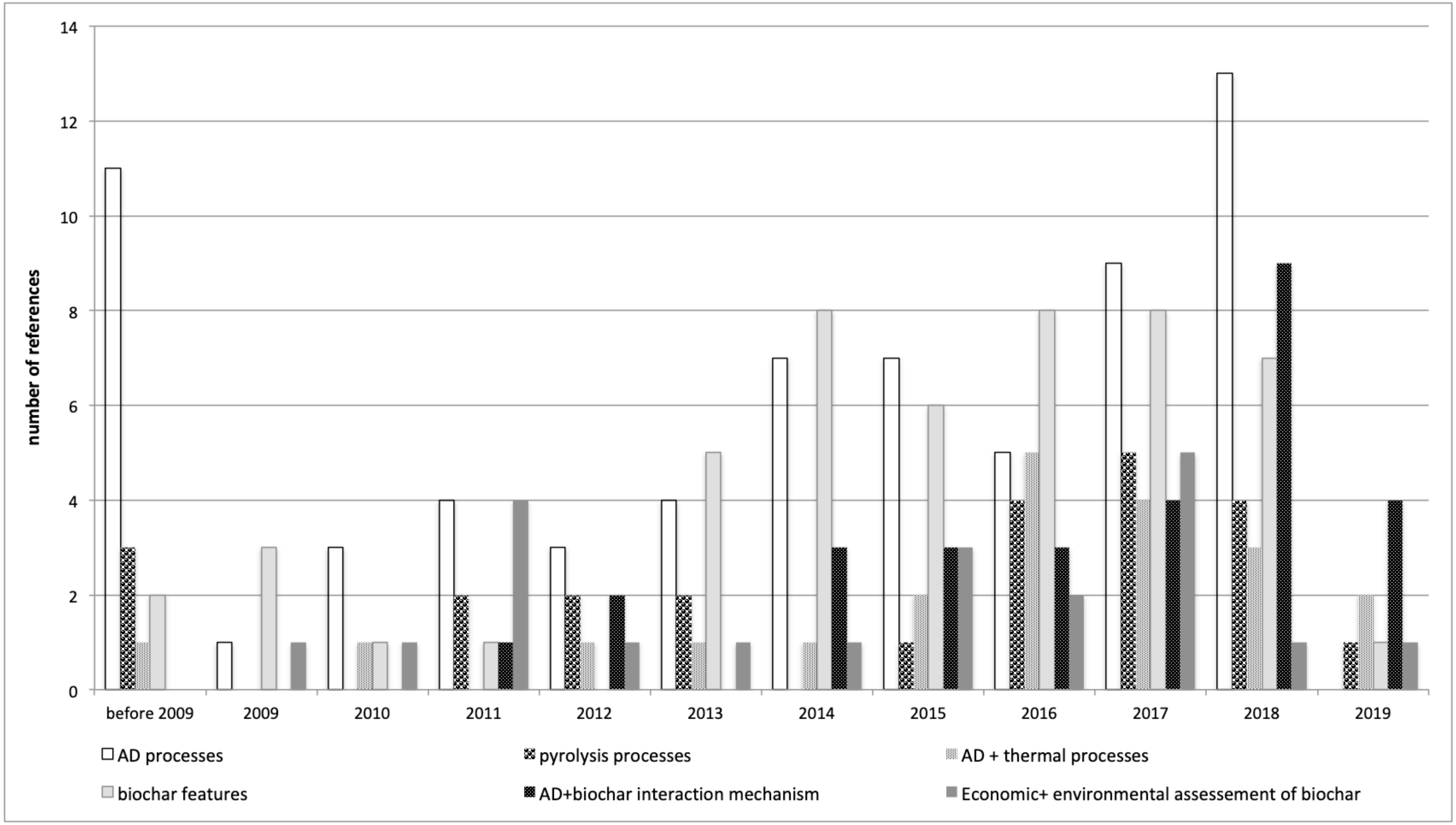
b) *Chronological order*. The majority of the references in this review are from 2015 to 2019 (67 %) and from 2009 to 2014 (26 %), with the balance before 2009 (7 %);

c) *Relevant keywords for the topics of interest*. A first survey adopted the following keywords in different combinations: “biochar, anaerobic digestion, methane, pyrolysis, economic assessment, environmental assessment, life cycle analysis, LCA”. Based on this preliminary selection, the review questions have been identified. Thereby, additional keywords have been adopted to face specific issues, as: “biochar, buffer capacity, anaerobic digestion, volatile fatty acids”, “biochar, ammonia inhibition, ammonia removal, anaerobic digestion”, “syntrophic metabolisms, biomass immobilization, biochar, anaerobic digestion, DIET, electron transfer”.

d) *Selection of the references based on content analysis.* After a first screening considering the abstracts of all identified reference sources, 259 relevant references were analyzed as full content and included in this review. The relevant scientific content was sourced from scientific articles (240 research papers and reviews – 93 %), book chapters and indexed conference proceedings (11 documents – 4 %), and international databases and reports (8 documents – 3 %). Considering only the scientific research papers and the reviews, they were related to (Figure 1): AD (31 %) and pyrolysis (10 %); coupling AD and thermal processes (10 %); BC features (25 %); BC and AD interaction mechanisms (14 %); economic and environmental aspects related to BC use (10 %). The distribution of the relative contributes of the scientific literature to the different topics concerning the investigation of BC role in AD in 2009 – 2019 exhibits a clear increasing trend due to a growing interest, particularly in the last five years, for the topics covered by the present work and consequently strengthens the need to address the above mentioned review questions.

This review is structured according to the contents outline. At the end of each section, the last paragraph summarizes the main findings and research gaps of the specific topic explored, which are finally condensed in the conclusions.

Figure 1. Relative contributions of the scientific literature selected for this work



3. Biochar

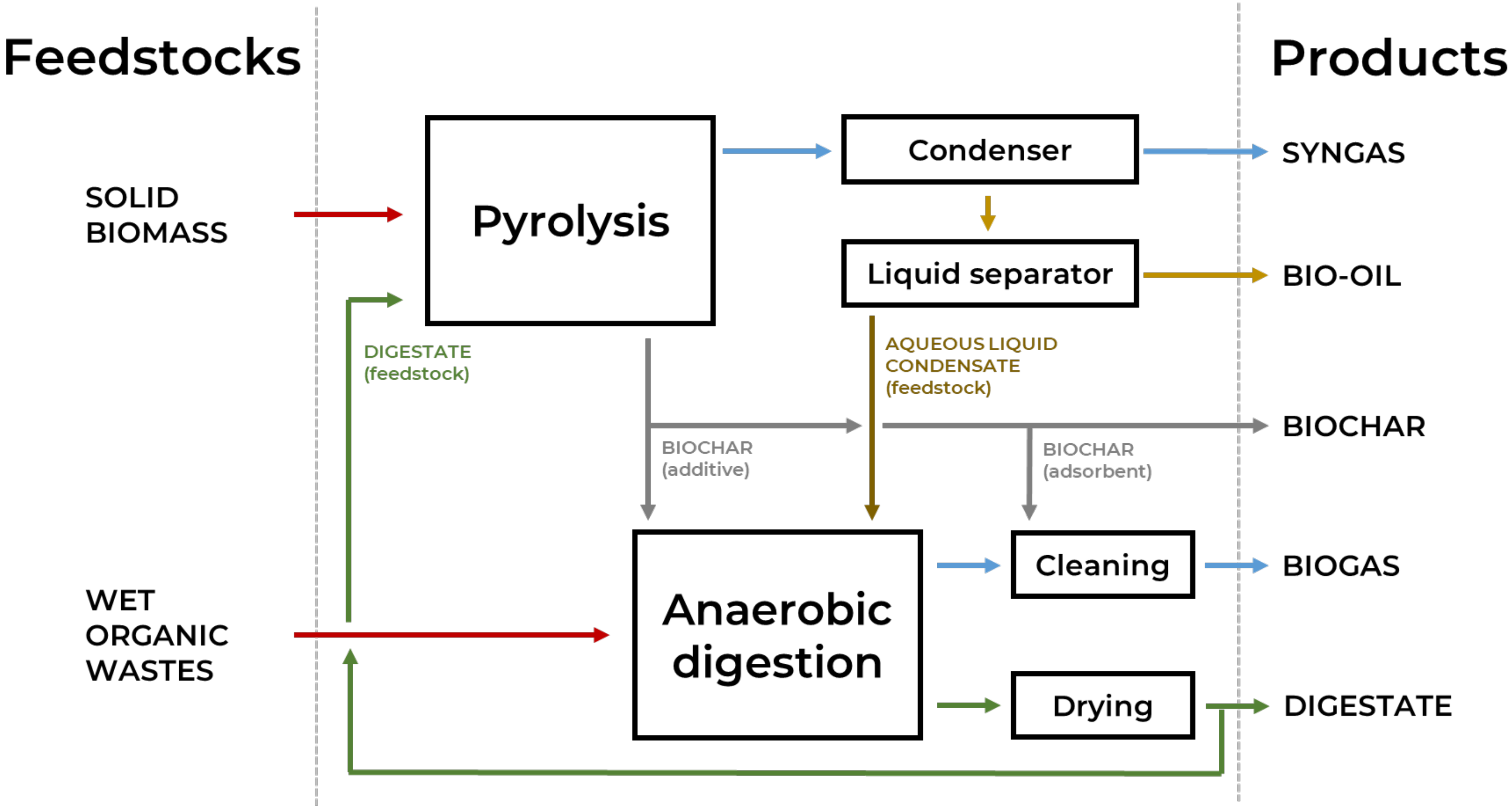
BC is the porous carbonaceous solid residue of the complex physical and chemical phenomena simultaneously occurring during the thermochemical treatment of raw biomass [60–63]. While AD is particularly suitable to produce biogas and digestate from wet organic waste (Figure 2), pyrolysis is a thermochemical process able to convert solid dry biomass in an oxygen-limited environment into valuable liquid chemicals (bio-oil), as well as gaseous biofuels and charcoal (biochar, BC) [64–67]. Although pyrolysis was conventionally mostly focusing on the production of liquid biofuels from woods and purpose-grown energy crops, the most recent studies found that it is not cost effective unless the feedstock is inexpensive, dry and readily available, and there are valuable chemical co-products (liquid bio-oil and solid BC) or favorable government policies [68]. Both AD and pyrolysis can contribute to fulfill Circular Economy targets, but research on biological and thermochemical processes traditionally progressed along parallel and separate pathways, often in competition.

In recent years, improved understanding of the characteristics of bio-oil and BC has helped to develop key quality requirements to expand their potential value [69]. High value liquid bio-oil products can be obtained from the pyrolysis of biomass residues, such as phenolic substitutes for adhesives or antioxidants [70,71]. However, there are limitations: the most valuable chemicals are usually mixed with impurities that impair their properties. Similarly, there are many promising applications for BC, such as soil improver [18], composite materials [72], activated carbon [73], electrodes for batteries or electrolysis cells [74], metallurgical coke substitute [75], catalyst for tars [76], and could be eligible for carbon credits [77]. The efficiency of BC in most applications significantly depends on its physico-chemical properties and elemental composition, which are subject to variations depending on feedstock, pyrolysis conditions, pre- and post-processing treatments.

The characteristics of AD and pyrolysis processes and products may offer interesting opportunities for the integration of such technologies (Figure 2), with the objective of contributing to the Circular Economy. For example, pyrolysis could be utilized to convert dewatered digestate into BC, which could then be used for a variety of applications [17,78,79], including its potential use to improve the quality of biogas and digestate [37], or to reduce instabilities and inhibition in digestors [16,24]. On the other hand, the acetic acid-rich aqueous pyrolysis condensate could be utilized as a feedstock for AD, possibly with the addition of BC for the selective adsorption of toxic inhibitors [21–23,25,80–88].

In conclusion, BC represents the key link between pyrolysis and AD and, consequently, in this section we wish to review its characteristics, including suitable feedstocks, production technologies, activation processes and characterization techniques.

Figure 2. Outline of potential integrations between anaerobic digestion and pyrolysis (derived from [20,21]).



3.1. Feedstocks

During thermal processing under oxygen free or oxygen-limited conditions (as pyrolysis), as the temperature increases, the polymeric components of lignocellulosic biomass crack and liquid intermediate phases are formed with different visco-elastic behaviors [89,90]; under slow progressive heating, cellulose remains hard and elastic up to 400 °C, whereas hemicellulose softens within a relatively narrow temperature range (230 to 280 °C) and remains viscous, while lignin softens and bubbles over a broader temperature range (150 to 350 °C) and remains mainly elastic. The overall process cannot be simply designed based on the linear combination of the behaviors of the individual components, but it is the result of their interactions at different temperatures and it is catalyzed by the mineral matter present in the ashes. As the temperature increases over these ranges, the depolymerized liquid undergoes two competitive processes, oligomer evaporation and crosslinking reactions, with the former favored at high heating rates, and the latter under slow pyrolysis. These findings explain why, under slow pyrolysis, the char yield is greater, and the particles globally keep the same macro-structure of the original biomass, although forming an intermediate soft material. Montoya et al. (2017) [91] confirmed the presence of molten liquid intermediates formed from cellulose, xylan and lignin and showed that the presence of minerals prevents the complete liquefaction of the xylan, therefore contributing to the preservation of the general shape and structure of the solid material during pyrolysis.

Therefore, BC can be produced from a wide range of lignocellulosic materials, containing cellulose, hemicellulose (xylan), lignin, small quantities of other organic compounds (phenols, phytosterols and fats) and inorganics (P, N, S, Si, alkali and alkaline earth metals and traces of other minerals). Such materials include wood, agricultural and forest residues, food waste, sugars, industrial organics, sewage sludge and manure. BC can be mesoporous or microporous depending on the operating conditions employed for its production and on the feedstock.

3.2. Thermochemical production

Recent reviews illustrated the different technologies and processes used experimentally and industrially to produce BC [17,92]. These include torrefaction, pyrolysis, gasification, combustion and hydrothermal carbonization [93]. Scale and potential mobility are important considerations in relation to the feedstock supply, logistics, seasonality, further refining, of products quantities, characteristics and value, and potential markets [17,60].

Torrefaction involves biomass treatment at atmospheric pressure and within a temperature range of 200–300 °C, without oxygen or with limited oxygen supplies [94]. As discussed earlier, partial depolymerization and liquefaction of the biomass components take place reducing the biomass tenacity and improving grindability. Torrefaction produces char with less moisture, higher energy density, lower weight, lower O/C and H/C ratio, increased hydrophobic nature and resistance to biological degradation with respect to the original feedstock. Typical yields of torrefied biomass range between 50 and 80 % [95].

Gasification is a thermochemical process carried out at temperatures higher than 750 °C in the presence of a gasifying agent (air, oxygen, or steam) at atmospheric or at high pressures. Under these conditions, biochar yields are not sufficiently significant to consider gasification an appropriate BC production process. Similarly, combustion is not a suitable BC production process, since, under good combustion conditions, BC yield should be negligible.

The various modes of *pyrolysis* include slow, intermediate, fast, flash, and ultra-pyrolysis, carried out under vacuum, atmospheric pressure or under pressure [65,69]. As a result of the balance between primary, secondary cracking and recombination reactions, bio-oil yields are typically maximized (up to 70 %) at intermediate temperatures (450-550 °C), faster heating rates (100-500 °C/s) and short vapor residence times (< 1~2 s), which are characteristic of fast and flash pyrolysis. Under these conditions, BC yields are typically of the order of 15~20 %. On the other hand, higher BC yields (25~40 %) are achieved at moderate temperatures (300-450 °C), slower heating rates (~ 1 °C/s) and longer vapor residence times (> 5~10 s), representative of slow or intermediate pyrolysis, when bio-oil yields vary between 40 and 50 % with the balance being gas.

Hydrothermal carbonization (HTC) is performed on wet biomass (moisture > 10 %) as feedstock, making the process highly energy-intensive [96]. HTC happens under water in a sealed confined system and heated at the temperature range of 175–300 °C for up to 16 h under saturated pressure under subcritical conditions producing tar-free BC (hydrochar) with large number of functional groups [97–99]. Hydrochars are usually obtained at yields of 20-25 % [96], and they contain mainly aliphatic compounds and more oxygen functional groups and higher cation exchange capacity than conventional BC. On the other hand, they have lower surface area, microporosity and carbon stability [96,100].

Among the various thermal technologies, pyrolysis has been the most investigated technique and it is considered the best technology for the production of BC [101] from relatively dry feedstock (moisture content below 10 %). However, also HTC is gaining interest to produce hydrochar, particularly from wet biomass [96]. In a comparison between the chars, it should be noticed that BC yields are higher, as well as porous structure and aromatics and ash contents, while hydrochar exhibits a non-porous structure, lower fixed and total carbon contents and higher amounts of alkyl functional groups [96].

3.3. Activation

BC with different properties can be produced from a wide range of feedstock and by adjusting processing conditions. Further modification of BC chemical and physical properties can be achieved through a process defined “activation”, aimed at increasing BC porosity and modifying its pore size distribution (Figure 3), as well as to some extent surface chemistry. Activation can be carried out in a number of ways, depending on type of activation agents (e.g. physical and chemical activation) or mode of operation into single-stage or multi-stage activation.

Chemical activation utilizes chemical agents, e.g., H_3PO_4, HNO_3, KOH, NaOH, H_2SO_4, and $ZnCl_2$ [102,103]. It typically involves two steps; in the first the feedstock is impregnated with a selected chemical agent, and then thermally treated in the second step. Another option is the activation of already produced BC by soaking it in a chemical agent, followed by a thermal treatment. Depending on the agent selected and thermal treatment conditions used, different degrees of activation can be achieved. The activated BC needs to be thoroughly washed with deionized water to neutralize its pH and to remove any remaining chemicals [104], and this procedure can contribute to a negative environmental impact of the technology. Oxidative activation that uses acidic or alkaline agents is among the most common activation methods. Besides enhancing porosity and surface area, it also creates oxygen-containing functional groups on the surface of BC (e.g. carboxyl, hydroxyl, lactone, phenol, carbonyl, and peroxide groups). These functional groups play an essential role in different applications of BC, such as for contaminant removal or nutrient sorption.

Physical activation does not utilize chemicals, thus avoiding some of the negative environmental impacts that can be associated with chemical activation. Instead, BC is exposed to physical oxidizing agents, such as steam, CO_2, ozone or air/O_2, typically at temperatures above 700 °C. These gaseous agents penetrate the internal structure of BC gasifying the carbon atoms, which results in opening and widening of pores [105]. Similarly to chemical activation, physical activation not only enhances BC porosity, but also modifies its surface functional groups, increasing the abundance of oxygen functional groups [105].

In conclusion, both chemical and physical agents can be used effectively to activate BC and obtain high porosity, surface areas over 1000 m^2/g, and modified surface functional groups, tuned to specific applications. The key challenges of BC activation are without any doubt related to their potential negative environmental impacts, mainly for chemical activations, and high-energy intensity need.

3.4. Physico-chemical characteristics

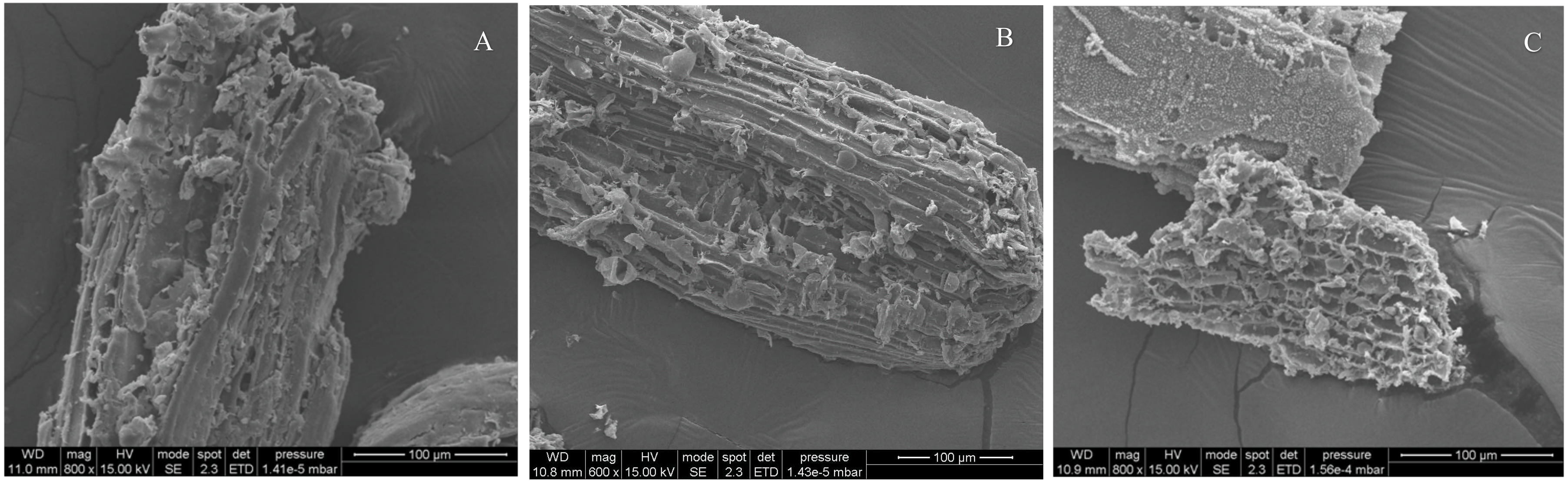
The variability of BC physico-chemical properties resulting from the proper selection of feedstock, pyrolysis and activation can be adapted to a wide range of applications.

S*pecific surface area* (SSA), expressed as m^2g^{-1}, is the ratio between the total surface area and the total particle mass of BC [106], commonly determined by Brunauer–Emmett–Teller (BET) analysis. The reported SSA values of BC can vary significantly, in the range 10^0 - 10^2 m^2g^{-1} [107,108] depending on pyrolysis temperature and feedstock, and up to over 10^3 m^2g^{-1} after activation. SSA is a key parameter enhancing the adsorption capacity of BC, even if the chemical composition of its surface is determinant in the interactions with other species [109]. SSA is related to BC pore size distribution [18].

P*orosity* can be described by the pore volume (m^3g^{-1}) and by the pore size distribution, including micro-, meso-, and macro-pores (respectively < 2nm, 2-50 nm, >50 nm) [110], based on their internal diameters. The relative abundance of these pores produces different BC structures (Figure 3), since micro-pores have the major contribute to BC surface area, micro- and meso-pores are essential for its adsorption capacity, while macro-pores can provide an appropriate habitat for microorganisms [18,111]. Yin et al. (2017) [112] stated that within a proper range, a high temperature results in a large surface area and pore formations. Trigo et al. (2016) [113] found that SSA increased between 350°C and 700 °C for different hardwood biochars, while Chen et al. (2014) [114] revealed an enhanced porous structure of BC from sewer sludge varying the temperature from 500 °C to 900 °C.

Specifically considering the effect of the feedstock on BC characteristics [101], yields and aromatic functional groups are much higher from lignin (48.8 %) than from hemicellulose (21.1 %), while no differences were found in the elemental composition of resulting BCs. High lignin and mineral content in the feedstock result in higher yields of BC [115,116]. Woody and grassy biomasses generate a more carbon-rich BC when compared to sewage sludge and manure [32,117,118]. Specifically considering the effect of pyrolysis process on BC characteristics [119], increasing pyrolysis temperature decreased concentrations of aliphatic carbons, oxygenated functional groups, nitrogen, oxygen and hydrogen. However, carbon mass fraction, micropore volume, ash content, fixed carbon and carbon stability increase with higher pyrolysis temperatures.

Figure 3. SEM micrographs of (A) raw biomass (eucalyptus) and of derived (B) biochar and (C) physically activated biochar (Courtesy of the authors. The samples were produced at ICFAR and analysed at Politecnico di Torino).



BC *composition* is mainly of C, H, O, N, and S, along with mineral trace components, such as K, Ca and Mg, varying according to pyrolysis conditions and feedstock [110]. The mineral content can be enhanced by increasing the temperature of pyrolysis [107]. The *cationic exchange capacity* (CEC) of BC can be defined as its ability of absorbing and attracting cations (nutrients and heavy metals) decreasing with higher pyrolysis temperature [18]. A high CEC value is due to a negative surface charge of BC. The presence of *surface functional groups* such as hydroxyl, carboxylic, and amino, expressed respectively as atomic ratio of H/C, O/C, and N/C (generally studied by Fourier transform infrared (FTIR) spectroscopy), mostly depends on the feedstock and it is reduced with a higher temperature of pyrolysis [107]. Further, the H/C ratio is considered as a measure of the degree of aromatization of BC and the O/C ratio as an indication of more oxygenated functional groups, contributing to high CEC values and hydrophilicity of BC [120,121]. An increase in pyrolysis temperature has been reported to negatively affect the amount of acidic functional groups and the CEC [112,122].

pH values are generally basic and increase as the pyrolysis temperature grows, due to the volatilization of acidic functional groups and to the higher ash content [18]. Moreover, BC can present redox characteristics, being able to donate and accept electrons, and these tendencies are quantified respectively by the *electron donating* and *accepting capacities* [110]. Phenolic groups may be the electron donating species, while quinones and polycondensed aromatic structures the electron accepting compounds [110,123]. In addition, the *electrical conductivity*, expressed as S m^{-1}, decrease as consequence of the increase of the pyrolysis temperature [17].

A full characterization of BC involves several analytical methods [124]. Scanning electron microscopy (SEM) is employed to investigate the superficial structure of BC, as well as its chemical composition if coupled with energy dispersive X-ray spectroscopy (SEM-EDX); transmission electron microscopy (TEM) allows to observe BC bulk structure; X-ray diffraction (XRD) analysis detects the crystalline phases; nuclear magnetic resonance (NMR) spectroscopy investigates BC composition, specifically the aromatic structure; X-ray photoelectron spectroscopy (XPS) quantitatively analyses the superficial composition.

4. Application of biochar as additive in anaerobic digestion

4.1. Buffer capacity and alkalinity

The volatile fatty acids (VFAs) produced as intermediates during AD tend to lower the pH [125]. This effect is generally counteracted by syntrophic acetogens and methanogens microorganisms, which convert VFAs to methane and carbon dioxide [126]. However, in case of high organic loads of easily biodegradable wastes (i.e. when the VFAs production rate exceeds the consumption rate), the accumulation of VFAs can occur, resulting in pH drop and even in the failure of AD [126,127]. The buffer capacity in a digestor is linked to the ability to neutralize VFAs, and it is considered a rate-limiting step in AD processes [38,39,128]. The buffer capacity is determined by the alkalinity of the AD system, mainly in the form of carbon dioxide and bicarbonate [6,125]. So it is technologically challenging to build a bioreactor aimed at digesting easily biodegradable feedstock with high pH buffer capacity [16]. Even if several methods have been proposed (Table 2) so far, the most diffused solution to improve buffer capacity implemented both at lab [129] and full scale [130] is co-digestion. In particular, manure or sewage sludge showed high buffer capacity, mainly due to the quite high ammonia content, which is able to counteract the pH drop due to VFAs production. Therefore, manure or sewage sludge are often co-digested with OFMSW and/or agricultural waste biomass.

Table 2. Advantages and disadvantages of conventional methods for creating buffering capacity in bioreactors

Methods	Advantages	Disadvantages
Alkaline pretreatment [131]	Cellulose more available to the enzymes	Expensive and considered as the technological bottleneck
Commercial alkaline materials (e.g. NaOH and $CaCO_3$) [132,133]	Easy pH adjustment	pH continually should be analyzed Temporary Lower biogas output at higher organic loads
Co-digestion [16]	Increasing methane yield Low cost and green	Hard to achieve an appropriate mixture of feedstocks to limit VFAs production
Geopolymer (Composite and monolith) [132,133]	Controllable alkali leaching Prevent the need for continuous pH adjustment	25 g L^{-1} costs around 0.10 $

However, it still remains a great challenge to develop simple, permanent and cost-effective methods to improve buffer capacity of AD systems. Nowadays, BC is considered as an attractive alternative to the aforementioned methods for two important reasons. Firstly, it can be produced via cost-effective and environmentally friendly approaches. Secondly, its physical and chemical properties can be matched with the operational conditions [19,40,41].

BC's buffer capacity mainly depends on two factors:

I. *Functional groups*: Rapid accumulation of VFAs during AD process results in a medium with low pH value in which some functional groups of BC like amine adsorbs H^+ and accepts electron. This phenomenon could mitigate the sudden pH drop.

II. *Inorganic materials*: Ash portion of biochar contains inorganic materials such as Ca, K, Mg, Na, Al, Fe, Si and S. Among them, alkali and alkaline earth metals (AAEMs) are responsible for alkalinity of biochar via reaction 1 (Ca and CxHxCOOH are selected as representative of AAEMs and VFAs, respectively) [16]:

$$CaCO_3 + 2C_xH_xCOOH \rightarrow [C_xH_xCOO]2Ca + H_2O + CO_2 \qquad (1)$$

Table 3 shows the literature data related to BC buffering capacity and its effects on bio-methane production, showing total alkalinity, pH values and the increase in CH_4 production (%), ranging from 8 % up to about 26 %. Some studies suggest that the alkalinity of BC due to AAEMs in ash fraction could effectively contribute to the buffering capacity of AD against VFAs inhibition. Jang et al. (2018) [27] investigated the effects of BC from dairy manure on AD of dry dairy manure at 20°C, 35°C, and 55°C. In each case they observed a lower total VFAs concentration and increased methane production. They suggested the role of high nutrients (9.1% Ca, 3.6% Mg, 1.3% N, 0.14% P) and alkalinity potential of BC in enhancing methane production. Wang et al. (2017) [39] investigated the role of BC from vermicompost on the buffering capacity of AD of high organic loads of kitchen waste and chicken manure. The authors proved the high buffer capacity of vermicompost BC to different short-chain VFAs (700-3800 mg L^{-1}), probably due to the presence of AAEMs and superficial functional groups. Linville et al. (2017) [24] studied the effects of BC from walnut shell during the AD of FW in mesophilic and thermophilic conditions. They observed that BC improved process stability by enhancing the total alkalinity from 2800 to 4800-6800 mg L^{-1} $CaCO_3$ and pH (initial pH >8) in BC amended digesters. Wei et al. (2020) [134] found enhanced methane production and solids removal by adding BC from corn stover (rich of alkaline earth metals) to AD of primary sludge. The authors observed higher total alkalinity (3500-4700 mg L^{-1} $CaCO_3$) and pH in BC amended reactors, suggesting that BC provided a strong buffering capacity. Ambaye et al. (2020) [135] investigated the role of BC from sewage sludge on the AD of fruit waste. They observed that the BC addition enhanced methane production and VFAs degradation. Further, the deficiency of some nutrients or trace elements in the substrate may cause an increase of VFAs inducing inhibition of microbial activity during AD [33,135]. Extra doses of trace metals may be required for an effective activity of methanogens without VFAs accumulation [136]. Thereby, it could be speculated that BC could provide adequate concentrations of trace metals for the stability of the AD system [135].

In summary, BC addition can counteract VFAs inhibition in case of high loads of easy degradable wastes such as FW, OFMSW, primary sludge. The alkaline nature of BC determining its pH buffering capacity may contribute to prevent VFAs inhibition. The ash fraction of BC contains AAEMs possibly contributing to its acid-buffering capacity and important trace elements for microorganisms. However, further investigations are required to confirm the effectiveness of these mechanisms and to identify the optimal dose of BC related to these properties. Higher doses can be toxic for AD [24,134], perhaps due to inhibitory concentrations of alkali metals [137]. Besides, other mechanisms could be responsible of BC role in alleviating VFAs inhibition. Porous BC could provide support for biofilm growth and protection to selectively enriched functional microbes closely attached to it under acid stress [48]. Secondly, BC could promote the activity of microbial partners enhancing the syntrophic VFAs degradation and methane production under high organic loads [38,138]. The latter microbial mechanisms will be fully adressed in section 4.3.

Table 3. Results of pH drop and CH_4 production/yield of AD processes in the presence of various types of BCs

Pyrolysis Operational condition				**AD Operational conditions**				**Results of buffering effect**					**Ref**
Temp (C°)	Time (min)	Reactor	Feedstock	Temp (C°)	HRTor duration (d)	Substrate	inoculum	Total alkalinity (g L^{-1} $CaCO_3$)		pH		Increase in CH_4 (%)	
								Control	BC	Control	BC		
350	180	Muffle furnace	dairy manure	20	35	dairy manure	Anaerobic sludge	1.8-4.8	5.3-7.3	7.18	7.71	26.47[a]	[27]
350	180	Muffle furnace	dairy manure	35	35	dairy manure	Anaerobic sludge	1.8-4.8	5.3-7.3	7.09	7.68	24.90[a]	[27]
350	180	Muffle furnace	dairy manure	55	35	dairy manure	Anaerobic sludge	1.8-4.8	5.3-7.3	7.12	7.55	24.69[a]	[27]
500	120	Tube furnace	vermicompost	35	50	chicken manure	Anaerobic sludge	6.0	7.3	7.0-7.1	7.8-8.0	N.P.	[39]
500	120	Tube furnace	vermicompost	35	50	kitchen waste	Anaerobic sludge	0.0	2.3	3.5-3.7	4.7-4.9	N.P.	[39]
600	120	Kiln	corn stover	55	15	primary sludge	Anaerobic sludge	2.8	3.5-4.7	7.2	7.6-8.0	8.6-17.8[a]	[134]
350	15		sewage sludge digestate	37		fruit waste	Anerobic sludge	N.P.	N.P.	4.5-5	7-8	13-27[a]	[135]
550	15		sewage sludge digestate	37		fruit waste	Anerobic sludge	N.P.	N.P.	4.5-5.5	7-8.6	12-22[a]	[135]
500	120	Slow pyrolysis	rice straw	35	25	Municipal solid waste	Anaerobic sludge			7.8	7.5	11.69[a]	[139]

a) CH_4 Yield; N.P: Not provided.

4.2. Adsorption of inhibitors

Inhibition is often defined as the predominant cause of reduction of bio-methane yields and instability of AD processes. A substance can be identified as “inhibitor” when it determines an adverse shift in the microbial population or arrests of the bacterial growth [137]. There are direct inhibitors, such as metals (Cu^{2+}, Zn^{2+}, Cr^{3+}, Cd, Ni, Pb^{4+}, Hg^{2+}, Na^+, K^+, Mg^{2+}, Ca^{2+}, Al^{3+}), organic compounds (chlorophenols, halogenated aliphatics, pesticides, antibiotics, lignocellulose hydrolysate); and indirect inhibitors, such as VFAs, long-chain fatty acids, hydrogen, ammonium and sulphides [19]. Among the inhibitors, ammonia (NH_3 or free ammonia nitrogen, FAN) and ammonium (NH_4^+) concentrations are considered crucial (ammonia and ammonium are together considered as total ammonia nitrogen, TAN). The optimal control of ammonia and ammonium may ensure stable bacterial growth and significantly contribute to the buffer capacity of the AD system. However, excess FAN/TAN concentrations are major causes of AD failure [140,141]. Chen et al. (2008) [137] reported a wide range of TAN concentrations (between 1.7 and 14 g L^{-1}) causing a 50 % reduction in methane production. FAN concentration is considered the main cause of inhibitions for methanogens [140,142] and it was reported to have a toxic effect to anaerobes ranging from 150 to 1200 mg L^{-1} [143,144]. Various mitigation strategies have been investigated to effectively counteract TAN/FAN inhibitory effects on AD. Some were based on the removal and immobilization of the inhibitor, as: dilution, co-digestion and microbial adaptation [145–147]; struvite precipitation [148]; use of a microbial desalinisation cell [149]; ammonia stripping [150]. An alternative approach is based on the use of adsorbents, inorganic as zeolites [142] and organic as GAC [143] and BC [41].

Based on several studies focusing on BC impacts on AD and ammonia inhibition (Table 4), it seems that BC could effectively mitigate ammonia inhibition, resulting in reduced lag phase and enhanced methane production respect to control reactors. Some authors [33,34,151] promoted BC use in AD of sewer sludge. Mumme et al. (2014) [41] revealed that BC from pyrolysis of paper sludge and wheat husks could limit mild ammonia inhibition (2.1 g TAN kg-1). Su et al. (2019) [43] stated that the addition of BC may alleviate inhibition in case of up to 1500 mg L^{-1} ammonia-N in food waste AD [152]. Lü et al. (2016) [44] revealed that BC can support AD under high ammonium stress (up to 7 g-N L^{-1}). The above-mentioned studies suggest a positive effect of BC towards ammonia inhibition, however, there isn't full agreement on the mitigation mechanisms hypothesized: cation exchange capacity [34,151]; chemical and/or physical adsorption capacity and surface functional groups [33,34,151]; promotion of direct interspecies electron transfer (DIET) [44,153]; immobilization of microorganisms [43,44].

Therefore, BC may contribute to ammonia mitigation by direct (cation exchange capacity, adsorption, surface functionality) and/or indirect factors (DIET and immobilization of microorganisms), depending on the characteristics of both BC and digested substrate, along with the operating conditions of the AD process (e.g. pH and temperature). Focusing on direct factors, a better understanding of the interactions between BC and FAN/TAN is a key step to identify its physico-chemical properties able to maximise the ammonia removal. The mechanisms for ammonia adsorption on BC from wastewater and digestate have been studied in literature (Table 5), resulting in promising values of ammonium adsorption capacity (up to hundreds of mg NH_4-N g^{-1} BC). Yin et al. (2017) [112] reported that physical sorption could be supported by high SSA and large porous structure. However, various studies suggested that porosity and SSA may not be the predominant factors in ammonium adsorption [154,155]. For instance, ion exchange may occur between acidic functional groups on BC surface and ammonium [112,156,157], and CEC could have a major role in enhancing the ammonium adsorption capacity of BC [157]. Zhang et al. (2014) [158] found that BC derived from pyrolysis of corn cob at 400 °C exhibited higher ammonium adsorption capacity than those produced at 600 °C due to the presence of functional groups with higher acidity. Thus, the definition of the proper pyrolysis temperature and the other control parameters is crucial for enhancing the adsorption capacity of BC.

In conclusion, various studies reported the potential of BC in alleviating ammonia inhibition (Tables 4 and 5) through different mechanisms. The direct adsorption of ammonia on BC may contribute to the mitigation of ammonia inhibition. However, further studies are required to clarify the effective role of direct mechanisms in complex AD systems in presence of other phenomena, i.e. the close bond between ammonia and

VFAs inhibition. In some cases the direct removal of ammonium may not be the main contribution to the mitigation of ammonia inhibition by BC [44,82,153]. Instead, other indirect mechanisms (immobilization and faster acclimation of biomass, DIET) have been suggested in literature and will be discussed in the next sections.

Table 4. A summary of selected works focusing on ammonia/ammonium inhibition mitigation by BC in AD processes (FAN: free ammonia nitrogen; TAN: total ammonia nitrogen).

Biochar			Anaerobic digestion									Reference
Feedstock	Process: temperature [°C]	Dose of biochar	Substrate	Inoculum	Inoculum to substrate ratio (VS basis)	Temperature [°C]	pH	Critical TAN conc. or as specified [mg L^{-1}]	Critical FAN conc. or as specified [mg L^{-1}]	Ammonia removal by biochar	Results and comments	
Fruitwood	Pyrolysis: 800-900°C	10 g L^{-1}	Glucose solution (6 g L^{-1})	Granular sludge from AD of paper mill wastewater	1:6	35	7	260 3500 7000	- - -		• ↑ Specified CH_4 prod. rates increased by 18.6%, 10.1% and 23.5% respectively • ↓ Lag phase by 30.4%, 12.7% and 23.8% respectively	[44]
1:2 (v/v) mix: - paper sludge - wheat husks	Pyrolysis: 500°C	6.67% w/w (2 g BC per 30 g inoculum)	-	Meso. AD (TS = 4.05%) + Ammonium carbonate	Only 30 g of inoculum	42	7.66	1626	-	2.4 mg TAN g^{-1} BC	• No clear effect on biogas production was observed	[41]
							7.73	2126	-	2.0 mg TAN g^{-1} BC		
							7.93	3126	-	4.2 mg TAN g^{-1} BC		
							7.84	4126	-	4.5 mg TAN g^{-1} BC		
							8.07	6626	-	6.8 mg TAN g^{-1} BC		
Macadamia nut shells	Pyrolysis: 350°C	33.3 g L^{-1}	Food waste (+ water + $NaHCO_3$)	AD from UASB (SS =34 g	-	Room temperature		1500	-		• ↑ COD removal from 78% without BC to 90% with BC	[43]
Corn stover	Gasification	1.82, 2.55, 3.06, 3.64 g BC g^{-1} TS sludge	WWTP sludge	Thermo WWTP AD	2:1	55	7.5	1100 (total N)	600 (NH_3-N)		• CH_4 yield, biomethanation rate constant and ↑ max CH_4 prod. rate up to 7.0%, 8.1% and 27.6% respectively • ↑ NH_3-N concentration by 41.5% after AD without BC, while by 0.2-18.1% with BC	[151]
Pine pellets White oak pellets	Gasification	2.49, 4.97 g BC g^{-1} TS sludge 2.20, 4.40 g BC g^{-1} TS sludge	WWTP primary sludge TS = 1.25% (inoc +subs)	Meso. and thermo. WWTP AD TS = 1.25% (inoc +subs)	2:1	37, 55	7.2-7.3	750 (total N)	400-450 (NH_3-N)		• ↑ CH_4 yield by 3.9-9.5% • ↑ NH_3-N concentration by 67.0% after AD without BC, while by -7.2 to 4.7% with BC • ↑ CH_4 yield by 5.7-9.6% • ↑ NH_3-N concentration by 67.0% after AD without BC, while by -7.2 to 4.7% with BC	[33]

Corn stover	Gasification: 850°C	0.25, 0.375, 0.5, 1.0 g d^{-1}	Primary sludge + WAS (TS = 7.01%)	WWTP AD from TPAD: 1 stage (TS = 6.14%) 2 stage (TS = 3.77%)	2:1	55	7.4 (stage 1); 5.3-6.0 (stage II)	-	-	6.2-13.2%	• ↑ CH_4 content by 13.7-25.3% • ↑ CH_4 prod. rate by 5.5-36.9%	[34]
Pine								-	-	3.6-11.2%	• ↑ CH_4 content by 0.7-9.1% • ↑ CH_4 prod. rate by -2.3-16.6%	
Wheat bran pellets	Pyrolysis: 800°C	25 g L^{-1}	Food waste fermentate	Anaerobic methanogenic culture (from WAS AD)	-	20	7.5		200–250 (NH_3-N)		• After acclimation: ↑ rate of VFAs degradation and ↓ lag-phase; • No adsorption of ammonia by BC	[45]
Coppiced woodlands	Pyrolysis: 500°C											
Orchard pruning	Pyrolysis: 500°C											
Wheat straw	Pyrolysis: 350, 450, 550°C	5% w/w (chicken manure)	Chicken manure (+ water)	Chicken manure meso. AD	Inoculum: 20% of WV of AD reactor	35	Initial: 6.7-7.6	3450-3540 (average)	472-600 (max)		• ↑ Cum. CH_4 yield • ↓ TAN compared to control	[82]
Fruit wood	Pyrolysis: 350, 450, 550°C						Initial: 6.7-7.0	3440-3650 (average)	421-634 (max)	up to 25% TAN	• ↑ Cum. CH_4 yield up to 69% • ↓ TAN compared to control • ↓ FAN up to 58% compared to control	
Air-dried chicken manure	Pyrolysis: 350, 450, 550°C						Initial: 6.9-7.3	3880-3960 (average)	496-701 (max)		• ↑ Cum. CH_4 yield • ↓ TAN compared to control	

Table 5. Ammonium adsorption capacity of different BCs (NA: not available)

Biochar production		Biochar properties				Adsorption			Reference
Feedstock	Pyrolysis temperature [°C]	BET-SA [m^2g^{-1}]	pH	CEC [$cmol_c$ kg^{-1}]	Total pore volume [mL g^{-1}]	Source of NH_4^+-N	Initial NH_4^+-N [mg L^{-1}]	NH_4^+ adsorption capacity [mg NH_4^+-N g^{-1} biochar]	
Oak wood	400-450	NA	9.9	59.4 ± 8.1	NA	Ammonium solution	1000	100.9 ± 3.4	[154]
Oak wood	-	NA	9.7	105.8 ± 12.1	NA		-	129.4 ± 34.8	
Greenhouse waste	-	NA	10.6	109.5 ± 21.8	NA	-	-	118.2 ± 26.9	
Municipal waste	-	NA	9.5	65.7 ± 16.2	NA	-	-	137.3 ± 0.6	
Presscake from AD	-	NA	10.3	51.0 ± 5.5	NA	-	-	105.8 ± 11.5	
Oak wood	600-650	NA	10.3	76.6 ± 0.7	NA	-	-	114.4 ± 3.4	
Oak wood	-	NA	8.6	65.2 ± 20.2	NA	-	-	123.5 ± 28.7	
Greenhouse waste	-	NA	11.0	146.2 ± 32.3	NA	-	-	99.3 ± 28.5	
Municipal waste	-	NA	10.2	67.9 ± 12.5	NA	-	-	128.3 ± 6.7	
Presscake from AD	-	NA	10.1	52.6 ± 11.5	NA	-	-	136.2 ± 18.1	
Hardwood	600	147.0	9.80	NA	0.176	AD slurry	500–580	114.2	[159]
Corncobs	-	23.0	8.92	NA	0.098	-	-	108.9	
Mixed sawdust	-	6.80	8.60	NA	0.038	-	-	24.7	

Mixed wood	600	273.623	9.80	NA	0.176	Swine manure AD slurry	1400 mg N L^{-1}	44.64 ± 0.602	
Rice husk	/	10.995	7.80	NA	0.038	-	-	39.8 ± 0.54	[155]
1:2 (v/v) mix: - paper sludge - wheat husks	500	NA	NA	NA	NA	During anaerobic digestion	1626 mg TAN kg^{-1}	2.4 mg TAN g^{-1}	
		-	-	-	-	-	2126 mg TAN kg^{-1}	2.0 mg TAN g^{-1}	
		-	-	-	-	-	3126 mg TAN kg^{-1}	4.2 mg TAN g^{-1}	[41]
		-	-	-	-	-	4126 mg TAN kg^{-1}	4.5 mg TAN g^{-1}	
		-	-	-	-	-	6626 mg TAN kg^{-1}	6.8 mg TAN g^{-1}	
Fruitwood	800-900	NA	NA	NA	NA	NH_4Cl solution	NA	2-3 mg N g^{-1}	[44]

4.3. Effects on microbial populations

Many authors reported the positive effects of BC on microbial populations in AD (Table 6). In semi-continuous and continuous AD experiments, BC addition improved methane production [34] keeping it stable even with rising OLRs [29,49] and resulted in higher COD removal rates [43,50,51].

Although there is a good agreement among the studies in terms of enhancement of AD process performances (11-30 % reduction of lag phases and 11-50 % increments of methane production rates) (Table 6), there is not a common hypothesis to explain BC influence on microbial populations, and different possible mechanisms are proposed as follows.

4.3.1. Microbial attachment and acclimation

Immobilization and acclimation of balanced microbial consortia on various support media are commonly adopted for counteracting various drawbacks of AD processes [160], thanks to the intensification of syntrophic conversion relationships, along with a major resistance to inhibition effects [161]. Wang et al. (2018) [50] found that BC acted as an inert core for microbial aggregation, resulting in a higher microbial growth rate and accelerating sludge granulation. Cooney et al. 2016 [53] investigated the possibility of accelerating biofilm formation by adding BC during the start-up of a packed bed anaerobic digester at pilot scale. In a relatively short time, the AD system reached stable and good performances, suggesting the rapid development of biofilms rich in active methanogens.

High SSA, proper porosity structure and particle size, superficial hydrophobicity seemed to be important properties favouring microbial immobilization [12,52]. Further, conductive materials may act as ideal support media due to their surface hydrophobicity and porous structure [54,55]. In particular, macropores can help the attachments of bacterial cells [19,162,163]. Lü et al. (2016) [44] explored the influence of different particle sizes of BC (2-5 mm, 0.5-1 mm, 75-150 μm) on the microbial distribution during the AD of glucose under ammonium stress. They stated that bacteria could access more easily fine particles than coarse particles. As a consequence, the attachment and colonization of microbial populations on BC can limit the risks of wash-out, accelerate the acclimation of microbes during substrate-induced inhibition, reduce the distance between syntrophic bacteria and methanogens, facilitate interspecies electron transfer and exchanges of VFAs or other metabolites [16,36,137]. Li et al. (2018) [46] found that methanogens survived under acidic stress in presence of BC during co-digestion of FW and WAS. Further, the immobilization of microbes could significantly attenuate ammonia inhibition [43,44]. The colonization of porous materials by microbes can alter the dominant species, making them more resistant and more rapidly acclimatized to substrate-induced inhibition [29,36,164]. Magnetic BC favoured the enrichment of acido/acetogens and methanogens absorbed on its surface shortening the microbial contact distance, thus VFAs produced by acido/acetogen bacteria could be more quickly transported to methanogens than in control digesters during AD of OFMSW in batch tests [16,139]. The distance of less than 1 μm has been reported to be essential for the oxidation of VFAs and hydrogen production [19,165].

4.3.2. Selective colonization of functional microbes

The effect of BC addition on microbial communities was investigated with the aim of identifying the most abundant bacterial and archaeal populations and, indirectly, the main interspecies interactions (Table 6). In detail, most studies focused on: biofilm formation [26,48,53]; shifts of microbial populations [28,34,46,47]; selective enrichment of microbial -DIET partners [38,44,49,50]; promotion of DIET [38,44–46,49,51,139]. The relevant anaerobic bacteria and archaea enriched in BC amended digesters are reported in Table 7, together with BC properties, substrate and inoculum used in AD tests. Many bacterial species were found in reactors supplemented with BCs, none of them identified as more recurrent. Among archaeae, most studies identified *methanosaeta*, *methanosarcina*, *methanobacterium*, and *methanolinea* species in BC amended reactors. Different studies [44,48,51] investigated the spatial distribution of bacteria and archaea by dividing sludge samples into different fractions, from suspended to attached to BC. Lü et al. (2016) [44] postulated an explanation for the spatial distribution of methanogens into BC pores by their cell morphology and dimension. The short fibrous form of Methanosaeta (0.8-7 μm in size) could explain its attachment into internal and external pores, while the long fibrous form of Methanobacterium (1.2-120 μm in length) could limit its penetration into BC pores [44,166].

4.3.3. Promotion of syntrophic metabolisms

Many studies (Table 7) suggested that BC addition may improve electron transfer mechanisms between anaerobic bacteria and archaea closely attached to BC surface. The overall AD efficiency depends on effective syntrophic interactions between bacteria and methanogens exchanging electrons to satisfy their energy requirements [56], happening through various routes:

- Indirect interspecies electron transfer (IIET) via soluble (i.e. hydrogen, formate, acetate) [167,168] and insoluble (humic substances) [169,170] compounds;
- Direct interspecies electron transfer (DIET) via electrical conductive pili, membrane-bound electron transport proteins, and conductive materials (i.e. magnetite, biochar, granular activated carbon, carbon cloth) [171–173].

In IIET hydrogen and formate operate as electron shuttles between syntrophic-producing bacteria and consuming-methanogens [56]. Diffusion regulates the transfer of a metabolite between microorganisms, as defined by Fick's Law [174]: the shorter the distance, the higher the flux of metabolites between microbes. Thereby, when cells aggregate the rate of interspecies hydrogen transfer is enhanced by the moment anaerobic bacteria and methanogenic archaea form compact structures acting as an organ [174,175]. However, the diffusion of soluble metabolites is considered a relatively slow mechanism of energy and information transfer [173] and hydrogen IET is regarded as a bottleneck in methane production [171]. On the contrary, DIET consists in the formation of an electric current between electron-donating and electron-acceptor microorganisms without the mediation of electron shuttles [56]. DIET could be faster and more specific compared to IIET [173,176]. Park et al. (2018) [171] reported that direct exchange of electrons via conductive pili was observed in co-cultures between *geobacter metalliriducens* and *geobacter sulfurreducens* [176], *methanosaeta harundinacea* [177], or *methanosarcina barkeri* [178]. Conductive materials such as magnetite [179], GAC [180], and BC [57] were shown to effectively mediate DIET between syntrophic partners.

Based on changes in the microbial community composition, many studies justified the enhancement of AD activity by means of the improvement of hydrogen and formate interspecies transfer mechanisms or, more frequently, by DIET via conductive biochar (Table 7). These findings are usually based on indirect observations, i.e. the enrichment of bacterial and archaeal species able to participate to DIET function as potential partners. Martinez et al. (2018) [47] found an enrichment of homoacetogenic bacteria, as *Clostridium, Eubacterium* and *Syntrophomonas*, and H_2 using methanogens through the analysis of microbial communities in digesting WAS and orange peels with BC, suggesting the formation of co-cultures enhancing methane production. Zhao et al. (2016) [51] observed the selective enrichment on BC of *Geobacter* and *Methanosaeta* during AD of synthetic wastewater with butyrate and propionate in UASB reactors. They suggested that butyrate and propionate could be degraded via DIET in the presence of a conductive material, and they found abundance of *Syntrophomonas* and *Smithella*, concluding that the metabolism via interspecies H_2 transfer for butyrate and propionate degradation was probably present. Wang et al. (2018) [50] showed that the microbial community analysis in a BC amended reactor during AD of synthetic wastewater resulted in the selective enrichment of potential DIET-partners, as *Geobacter* and *Bacteroidetes,* as well as archaea *Methanosaeta* and *Methanosarcina*. They suggested that BC could enhance DIET among electrogenic microbes and archaea, improving the electron transfer characteristics of granular sludge, as well as COD removal and methane yield. Wang et al. (2018) [38] found that the addition of different BC doses increased methane production rate and shortened the lag phase during mesophilic AD of dewatered WAS and FW. According to the authors, BC counteracted the pH decrease due to VFAs accumulation through its buffering capacity, and it seemed to promote DIET.

Aside from physical properties as SSA and porosity, favouring microbial colonization, other chemical and conductive characteristics of BC may be crucial in the promotion of electrons transfer. The role of electrical conductivity (EC) of BC in AD has been investigated in literature[59]. EC of digestate has been reported to increase in presence of BC [50,151]. However, the EC of digestate seemed unrelated to the conductivity of BC, which varies depending on the metabolism and composition of microbial species [56]. The capability of BC in promoting DIET appeared to be comparable to that of GAC, even if the EC of BC was roughly 1000 times lower [57,171]. Barua and Dhar (2017) [181] reported that multi-species aggregates from anaerobic digesters exhibited conductivity ranging 0.2-36.7 μS cm^{-1}, suggesting its relation with DIET via conductive pili . Martins et al. (2018) [56] stated that conductive materials could have a similar role of humic substances in DIET, acting as electron shuttles by receiving and donating electrons. Wang et al. (2019) [49] suggested that BC from sawdust may act as a temporary electron acceptor for VFAs oxidation during thermophilic AD. They found a significantly higher and more stable methane yield at higher OLR values during anaerobic co-digestion in semi-continuous mode with the addition of BC from sawdust, while they did not show any enhancement of AD with the addition of BC from sewage sludge. The main effects of sawdust BC seemed to be the enhancements of microbial activities and syntrophic oxidation of VFAs. The EC of both BCs was similar, suggesting it was not a determinant factor in the promotion of syntrophic oxidation of VFAs. Instead, the authors speculated that the presence of redox-active phenazine structures in the BC from sawdust could promote VFAs degradation via DIET. Thereby, for better investigating whether BC from sawdust could substitute hydrogen as electron acceptor in syntrophic oxidation of VFAs, they conducted a series of batch experiments with butyrate or propionate as substrates in which methanogenesis was inhibited. The control reactors did not show degradation of butyrate and propionate, while the addition of BC stimulated their oxidation as well as the production of acetate, supporting the hypothesis of the electron-accepting capacity of BC in the syntrophic process.

The adoption of a further control in AD tests amended with a non-conductive material can be crucial to investigate whether the stimulatory effects of BC on methane production can be more closely linked to its physical properties (i.e. SSA and porosity) rather than its electrical properties [56]. This was evident in the study of Cruz Viggi et al. (2017)

[45], where they introduced two controls without BC and with non-conductive silica sand for AD of FW. They found that VFAs degradation and methane production were faster in the case of BC amended reactors than both the control reactors, suggesting the predominant influence of the electrical properties of BCs.

Table 6. A summary of selected works focusing on positive effects of BC on microbial populations in AD processes

Biochar		Anaerobic digestion							References
Feedstock	Production	Dose of biochar	Substrate	Inoculum	Temperature [°C]	Experimental mode	Results	Possible mechanisms	
Sawdust	Pyrolysis: • 500°C • 1 h • 20°C min^{-1}	10 g L^{-1}	Food waste (TS = 94.2 g L^{-1})	WAS (TS = 89.1 g L^{-1})	55°C	Batch V = 120 mL S/I (VS) = 0.25 - 3	By ↑ OLR: • ↓ lag time • ↑ CH_4 prod. rate	• ↑ buffer capacity • Microbial attachment and acclimation on BC • Promotion of DIET • Selective succession of microbes	[46]
Pine sawdust	Pyrolysis: • 650°C • 20 min	8.3 - 33.3 g L^{-1}	Food waste (bread) (TS = 61.2%)	WWTP-sludge (heated at 95°C)	35°C	Batch V = 100 mL TPAD	1st phase: • ↓ lag phase • Faster VFAs generation • ↑ H_2 prod. rate • ↑ Cum. H_2 prod. 2nd phase: • ↓ lag phase (41-45%) • Faster VFA degradation • ↑ CH_4 prod. rate	1st phase: • Promotion biofilm formation • Providing temporary nutrients • Buffering pH by BC 2nd phase: • Promotion methanogenic biofilm formation • No buffering pH by BC	[26]
Macadamia nut shells	Pyrolysis: • 350°C • 2 h	33.3 g L^{-1}	Food waste + water + (↑ N-NH_4 conc.)	AD from	Room temperature	CIC reactor V = 4.6 L HRT=16 h	• ↑ COD removal by 15%	• ↓ NH_3 inhibition by BC • ↑ Alkalinity by BC • ↓ VFAs accumulation	[43]

Biochar		Anaerobic digestion							References
Feedstock	Production	Dose of biochar	Substrate	Inoculum	Temperature [°C]	Experimental mode	Results	Possible mechanisms	
	• 10°C min^{-1}			(SS = 34 g L^{-1})				• ↑ Selective enrichment of functional microbes • Microbial attachment and acclimation on BC	
Sawdust	Pyrolysis: • 500°C • 1.5 h • 10°C min^{-1}	2 - 15 g L^{-1}	Dewatered WAS + Food waste (TS = 8.8%) + water	Meso. AD from brewery factory (TS = 6.8%)	35°C	Batch Serum bottles WV = 90 mL S/I = 0.75 - 3 (VS)	• ↓ lag phase by 27.5–64.4% • ↑ Max CH_4 prod. rate by 22.4%–40.3%	• Buffer capacity by BC (alleviate ↓ pH due to ↑ VFAs) • ↑ DIET by BC (temporary electron acceptor, due to the richness of surface functional groups) • Selective enrichment of microbial DIET-partners by BC	[38]
Sawdust	Pyrolysis: • 500°C	15 g L^{-1}	Food waste + Sewage sludge (TS = 9.2%) FW/Sludge = 4:1 (TS)	Brewery Meso. AD (TS = 5.2%)	55°C	Semi-continuous Serum bottles WV = 150 mL ↓ HRT, ↑ OLR	• ↑ CH_4 yield by 16.0%−55.2% • Stable CH_4 prod. at ↑ OLRs	• ↑ VFAs syntrophic oxidation by BC • High SA of BC → microbial attachment (?), closer association of syntrophic partners • Electroactive functional groups of BC → stimulation of DIET (?)	[49]
Corn stover	Gasification: • 850°C	0.25 - 1.0 g d^{-1} (2nd phase)	Primary sludge + WAS (TS = 7.01%)	WWTP AD	55°C	Semi-continuous V = 500 mL TPAD:	• ↑ % CH_4 by 13.7-25.3% • ↑ CH_4 prod. rate by 5.5-36.9%	• Adsorption and precipitation of CO_2 by BC • ↓ TAN • ↑ Alkalinity • ↑ Macro-/micro-nutrients in digestate • Shift in bacterial community	[34,182]

Biochar		Anaerobic digestion							References
Feedstock	Production	Dose of biochar	Substrate	Inoculum	Temperature [°C]	Experimental mode	Results	Possible mechanisms	
				TPAD: 1 ph. (TS = 6.14%) 2 ph. (TS = 3.77%)		1) HRT = 5, 15 d 2) HRT = 13 - 30 d		• Inhibition at high BC doses	
Pine	-	-	-	-	-	-	• ↑ % CH_4 by 0.7-9.1% • ↑ CH_4 prod. rate by 2.3-16.6%		
Corn stover	Gasification	1.82 -3.64 g BC g^{-1} TS sludge	WWTP sludge	Thermo. WWTP AD	55°C	Batch V = 600 mL 26 days	• ↑ % CH_4 (88.5-96.7%) • ↑ CH_4 yield	• ↑ buffer capacity • ↑ electrical conductivity in digester (+37%) → ? ↑ extracellular electron transfer • ↓ NH_3 inhibition • CO_2 sequestration by BC • ↑ macro-/micro-nutrients in digestate	[151]
Rice husks	Gasification: • 900-1000°C	1%, 3% w/w	Cattle manure + water (TS = 5%)	-	35°C	Batch V = 1400 mL	• ↑ Biogas prod. by 31% by 1% BC • ↓ % CH_4 by 7% by 1% BC • No benefits by 3% BC	• ? Microbial biofilm formation on BC	[30]

Biochar		Anaerobic digestion							References
Feedstock	Production	Dose of biochar	Substrate	Inoculum	Temperature [°C]	Experimental mode	Results	Possible mechanisms	
Rice husks	Gasification: • 900-1000°C	1%, 3% w/w	Cattle manure + water (Mix: TS = 5%)	-	25-30°C	Semi-continuous WV = 12 L HRT = 20 days	• ↑ Biogas prod. by 4-5% by BC • ↓ % CH_4	• ? Not enough time for biofilm formation	[31]
Dry dairy manure	Pyrolysis: • 350°C • 3 h • 10°C min^{-1}	0, 1, 10 g L^{-1}	Dry dairy manure	Inoculum from lagoon, fed with dried manure (TS = 115.85 g L^{-1})	20°C	Batch: Serum bottles V = 280 mL S/I = 1 (VS)	• ↑ CH_4 yield up to 26.5% • ↓ lag phase • ↓ total VFAs	• No biofilm formation on BC (?) • No effects on DIET by BC (?) • ↑ Alkalinity and ↑ pH (buffer capacity)	[27]
-	-	-	-	-	35°C	-	• ↑ CH_4 yield up to 24.9% • ↓ lag phase • ↓ total VFAs	• ↑ Alkalinity and ↑ pH (buffer capacity)	
-	-	-	-	-	55°C	-	• ↑ CH_4 yield up to 24.7% • ↓ lag phase • ↓ total VFAs	• ↑ Alkalinity and ↑ pH (buffer capacity)	
Vineyard prunings	Pyrolysis: • 550°C	10, 30 g L^{-1}	Co-digestion:	WWTP AD	37°C	Batch: • V = 250 mL	Batch: • ↓ lag phase	• Promotion of synthrophic metabolism by BC • Adsorption of inhibitors	[47,183]

Biochar		Anaerobic digestion							References
Feedstock	Production	Dose of biochar	Substrate	Inoculum	Temperature [°C]	Experimental mode	Results	Possible mechanisms	
			• Orange peels (TS = 311g kg^{-1}) • Sewage sludge (TS = 28.7g kg^{-1})	(TS = 35.5 g kg^{-1})		Semi-continuous • V = 3 L • HRT = 10-30 days	• ↑ CH_4 prod. Semi-continuous: • ↑ CH_4 prod.	• Adhesion and growth of microorganisms by BC SA	
Coconut shell	Pyrolysis: • 450°C	1:1 (TS)	Citrus peel (TS = 16.6%)	WWTP AD (TS = 11.0 %)	35°C	Batch V=500 mL S/I = 0.31 - 0.33 (VS)	• ↓ lag phase • ↑ Cum. CH_4 prod.	• Limonene adsorption by BC	[40]
Rice husk	-	1:1 (TS)	-	-	-	-	• ↓ lag phase • ↑ Cum. CH_4 prod.	• Limonene adsorption by BC • Adhesion and growth of microbes on BC	
Wood	-	1:1; 1:2; 1:3; 2:1 (TS)	-	-	-	-	• ↓ lag phase • ↑ Cum. CH_4 prod.	• Limonene adsorption by BC • Adhesion and growth of microbes on BC	

Biochar		Anaerobic digestion							References
Feedstock	Production	Dose of biochar	Substrate	Inoculum	Temperature [°C]	Experimental mode	Results	Possible mechanisms	
Rice straw + FeCl$_3$ (3.2 g FeCl$_3$:100 g rice-straw)	In FeCl$_3$ solution: • 2h Carbonization: • 500°C • 2h	0.5% w/w	OFMSW + water (TS = 1.64%)	OFMSW thermo. AD + water (TS = 2.19%)	35°C	Batch Serum bottles V = 500 mL, S/I = 1 (VS)	• ↓ lag phase • ↑ CH$_4$ prod. by 11.69%	• No effects on NH$_3$ by BC • No effects on pH by BC • ↑ syntrophic associations of bacteria on BC • (?) DIET by high conductivity of BC	[139]
Rice straw	Carbonization: • 500°C • 2h	-	-	-	-	-	• ↓ lag phase • ↓ CH$_4$ prod.	• No effects on NH$_3$ by BC • No effects on pH by BC	
Cow manure	Pyrolysis: • 500°C • 4 h • 100°C h^{-1}	2 – 14 g L^{-1}	Dry beer lees (TS = 62.5%)	Meso. WWTP AD (TS = 36.7%)	35°C	Batch WV = 150 mL TS = 25% S/I = 3 (TS)	• ↓ lag phase • ↑ Max cum. CH$_4$ prod. up to 82.9%	• Promotion of DIET by BC conductive properties (?) • Microbial colonisation and biofilm formation on BC (?) • ↑ Alkalinity and ↑ pH (buffer capacity) • Selective enrichment of methanogens by BC	[28]
-	-	-	-	Thermo. WWTP AD (TS = 38.5%)	55°C	-	• ↓ lag phase • ↑ Max cum. CH$_4$ prod. up to 47.2%	-	
Rice straw	Pyrolysis: • 500°C	4 g L^{-1}	Synthetic wastewater	WWTP sludge	35°C	UASB	UASB: • ↑ COD removal rate	• No effects on pH by BC • BC inert core for microbial aggregation	[50]

Biochar		Anaerobic digestion							References
Feedstock	Production	Dose of biochar	Substrate	Inoculum	Temperature [°C]	Experimental mode	Results	Possible mechanisms	
				(SS = 25.2 g L^{-}		• Continuous mode • V = 5500 mL • HRT = 12 h, 12-6 h Batch • Serum bottles • V = 550 mL	• ↑ VFAs degradation • ↑ gran. sludge conductivity and quality Batch: • ↓ lag phase by 28.6% • ↑ biogas yield • ↑ %CH_4	• Selective enrichment of microbial DIET-partners by BC	
-	Biochar	-	Grease trap waste wastewater (TSS = 1.04 g L^{-1})	-	37°C	Biochar packed bed anaerobic digester • V: 900 L +1500 L+ 1500 L • ↓ HRT (3.1 – 1.8 days)	• COD removal:68% • Total VFAs: from 4.7 (feed) to 1.46 g L^{-1} (effluent) • %CH_4 > 60% • Start-up: 59 days	• ↑ Methanogenic biofilm communities on BC • BS as packing material for growth and retention of biofilm	[53]

Biochar		Anaerobic digestion							References
Feedstock	Production	Dose of biochar	Substrate	Inoculum	Temperature [°C]	Experimental mode	Results	Possible mechanisms	
Wheat bran pellets	Pyrolysis: • 800°C • 3h	25 g L^{-1}	Food waste fermentate	Methanogenic culture (from WAS digestate)	20°C	Batch V = 120 mL	After acclimation: • ↑ rate of VFAs degradation • ↓ lag-phase	• No effects on pH via BC • No effects on NH_3 via BC • Promotion of IET by BC	[45]
Coppiced woodlands	Pyrolysis: • 500°C	-	-	-	-	-		-	
Orchard pruning	Pyrolysis: • 500°C	-	-	-	-	-		-	
Fruitwood	Pyrolysis: • 800-900°C	10 g L^{-1}	Glucose (6 g L^{-1})	AD gran.	35°C	Batch Serum bottles	• ↓ lag phase by 5.9-23.9% • ↑max CH_4 prod. rate by 23.5-47.1% • Faster VFAs degradation	• NOT NH_4 adsorption • NOT ↑ buffer capacity • DIET promotion via BC • Affinity of methanogens with BC	[44]

Biochar		Anaerobic digestion							References
Feedstock	Production	Dose of biochar	Substrate	Inoculum	Temperature [°C]	Experimental mode	Results	Possible mechanisms	
				Ammonium: 0.26, 3.5, 7 g-N L^{-1}					
Fruit wood	Pyrolysis: • 800°C	10 g L^{-1}	Nutrient solution + glucose (2 - 8 g L^{-1})	Meso. pulp sewage digestate (1 g VS L^{-1})	35°C	Batch Serum bottles V = 500 mL	• ↓ lag phase by 11.4-30.3% • ↑ Max CH_4 prod. rate by 5.2-86.6% • ↑ VFAs production and degradation	• Selective colonization of functional microbes by BC • Not ↑ buffer capacity • ? Biofilm growth on BC • ? Promotion of DIET or Hydrogen IET by BC	[48]
Pine wood	Pyrolysis: • 600°C • 2h	5 g L^{-1}	Synthetic wastewater with butyrate	WAS digestate (TSS = 13.1 g	37°C	UASB WV = 1000 mL	• ↑ CH_4 prod. rate by 25% • ↑ COD removal	• ↑ Butyrate degradation via DIET in UASB via BC • Selective enrichment of microbial DIET-partners by BC	[51,57]
			Synthetic wastewater with propionate				• ↑ CH_4 prod. rate by 16% • ↑ COD removal	• ↑ Propionate degradation via DIET in UASB via BC • Selective enrichment of microbial DIET-partners by BC	

Biochar		Anaerobic digestion							References
Feedstock	Production	Dose of biochar	Substrate	Inoculum	Temperature [°C]	Experimental mode	Results	Possible mechanisms	
-	Biochar	2.5 g L^{-1}	Synthetic wastewater with ethanol	WAS digestate (TSS = 13.1 g	37°C	UASB WV = 1000 mL ↓ HRT (24 - 8 h)	• ↑ COD removal: ≥ 93% (control: 75-83%) • ↑ CH_4 prod. rate	• (?) Promotion syntrophic metabolism via DIET with BC in UASB reactors	[29]

CIC: controlling internal circulation; COD: chemical oxygen demand; DIET: direct interspecies electron transfer; FW: food waste; HRT: hydraulic retention time; IET: interspecies electron transfer; OLR: organic loading rate; OFMSW: organic fraction of municipal solid waste; SA: surface area; S/I: substrate to inoculum ratio; SMP: specific methane potential; SS: suspended solids; TPAD: two phased anaerobic digestion; TSS: total suspended solids; UASB: up-flow anaerobic sludge blanket; VFA: volatile fatty acid; WAS: waste activated sludge; WWTP: wastewater treatment plant; WV: working volume; V: volume.

Table 7. A summary of studies reporting the selective enrichment of bacteria and archaea by BC addition during AD processes

Biochar production		Biochar properties			Anaerobic digestion					Reference
Feedstock	Pyrolysis temperature [°C]	BET-SSA $[m^2g^{-1}]$	Electrical conductivity $[S\ m^{-1}]$	Total pore volume $[cm^3\ g^{-1}]$	Temperature [°C]	Substrate	Identification technique	Enriched Bacteria	Enriched Archaea	
Wheat bran pellets	800	55 ± 1	49.9	0.0445	20	Food waste fermentate	FISH- CLSM		More Methanosarcina-like Archaea rather than Methanosaeta like Archaea	[45]
Coppiced woodlands	500	61 ± 1	1.6	0.0483						
Orchard pruning	500	13.7 ± 0.5	0.5	0.0165						
Macadamia nut shells	350	12.7	-	-	Room temperature	Food waste + water	16S rRNA sequencing	Bacteroidales Anaerolineales Syntrophobacterales	Methanoregulaceae Methanotrichaceae Methanobacteriaceae	[43]
Fruitwoods	800-900	-	-	-	35	Glucose	16S rRNA sequencing	Enterobacteriaceae	Methanobacterium Methanosaeta Methanosarcina	[44]
Fruit wood	800	-	-	-	35	Glucose	16S rRNA sequencing	Syntrophomonas Clostridium Clostridiaceae	Methanobacterium Methanosaeta Methanosarcina	[48]
Rice straw + $FeCl_3$ (3.2 g $FeCl_3$:100 g rice-straw)	500	51.14	-	0.0328	35	OFMSW + water	16S rRNA sequencing	Bacteroides Clostridiaceae Porphyromonadaceae Moraxellaceae	Methanosarcina Methanobacterium OTU in Methanomicrobiales Methanosaeta	[139]
Rice straw	500	111.5	-	-	35	Synthetic wastewater	16S rRNA sequencing	Bacteroidetes unclassified (23.65%) Bacteroidales unclassified (9.19%)	Methanosaeta (77.18%) Methanosarcina (11.65%)	[50]

								Treponema (6.43%) Smithella (5.56%) Brooklawnia (5.45%) Geobacter (5.42%)		
Sawdust	500	248.6	-	-	35	Dewatered WAS + food waste + water	16S rRNA sequencing	Anaerolineaceae Porphyromonadaceae	Methanosaeta Methanobacterium Methanolinea	[38]
Cow manure	500	112.6	-	0.0156	35	Dry beer lees	16S rRNA sequencing	Chloroflexi Bacteroides Proteobacteria	Methanospirillum Methanosarcina Methanolinea	[28]
Vineyard prunings	550	240 ± 4.8	-	-	37	Orange peels	16S rRNA sequencing	Bellilinea Trepomena Clostridium Petrimonas Proteiniphilum Bacteroides	Methanosaeta Thermogymnomonas Methanolinea Methanofollis	[47]
Vineyard prunings	550	240 ± 4.8		-	37	Sewage sludge	16S rRNA sequencing	Clostridium Longilinea Curvibacter Eubacterium Syntrophomonas	Methanosaeta Methanolinea Thermogymnomonas Methanobacterium	
Pinewood	600	209	.33 μS cm^{-1}	-	37	Synthetic wastewater with butyrate	16S rRNA sequencing	Attached sludge: Geobacter Thermanaerovibrio Syntrophomonas	Attached sludge: Methanosaeta Methanosarcina Methanospirillum	[51]
Pinewood	600	209	4.33 μS cm^{-1}	-	37	Synthetic wastewater with propionate	16S rRNA sequencing	Attached sludge: Geobacter Smithella	Attached sludge: Methanosaeta Methanobacterium	

								Syntrophus	Methanosphaerula	
Biochar	-	-	-	-	37	Grease trap waste wastewater	16S rRNA sequencing	Attached to BC: Aminobacterium Syntrophomonas Sporanaerobacter Escherichia	Attached to BC: Methanobacterium Methanosarcina Methanobrevibacter	[53]
Sawdust	500	248 ± 34	-	-	55	Food waste	16S rRNA sequencing	Coprothermobacter (36.3%) Fervidobacterium (20.0%) Syntrophothermus Treponema	Methanosaeta (43.9%) Methanosarcina (15.8%)	[46]
Corn stover	850	315.2	-	0.09	55	Primary sludge + WAS	16S rRNA sequencing	Firmicutes (Clostridia) Bacteroidetes Proteobacteria	Methanothermobacter (>90%) Methanosarcina	[34]
Pine		353.1	-	0.23						
Sawdust	500	248.6 ± 9.4	0.11 μS cm^{-1}	-	55	Food waste + Sewage sludge	16S rRNA sequencing	Defluviitoga Tepidimicrobium	Methanothermobacter Methanosarcina	[49]

NA: not available; CLSM: confocal laser scanning microscopy; FISH: Fluorescence in situ hybridization; OFMSW: organic fraction of municipal solid waste; SSA: surface area; WAS: waste activated sludge.

4.4. Effect of biochar on digestate quality

Anaerobic digestate has been considered as soil improver because it is rich in nutrients [184–186]. However, challenges related to digestate management have recently grown in association with EU regulations on ammonia, volatile organic acids, phenolic compounds, heavy metals, PAHs and PCBs [4,187]. So far, most technologies available to exploit digestate as soil improver are based on mechanical/physical (e.g. mechanical dewatering, semipermeable membranes and evaporation) or chemical processes (e.g. ammonia stripping and nutrients adjustment) (Table 8).

Table 8. Advantages and disadvantages of conventional technologies for digestate processing [188–191].

Methods	Advantages	Disadvantages
Solid-liquid separation	Rich in phosphorus and suitable for fertilizer application	Liquid fraction has been considered as a surface and ground water pollutions
Belt and drum dryers	treatment and upgrading of digestate to a solid or concentrated product	Rapid volatilization of ammonium causes severe ammonia emission
High-Tech technologies (e.g. ammonia stripping, membrane process and vacuum evaporation exist)	Production of several streams with different physical and chemical properties.	Expensive
Mixing solid digestate with desired nutrient	Increasing value per ton	-

Dehydrated digestate could be used in non-agricultural markets as a heating fuel, however, this use implies nutrient and metal losses, which in turn have negative impacts on the environment and crops. Consequently, three approaches have been conventionally applied to reduce diffuse pollution resulting from digestate application to land [19,188]:

- Nutrient recovery from digestate;
- Carbon to Nitrogen ratio adjustment;
- Increasing of nutrient retention capacity using an additive.

One of the key aspects that should be considered when supplying additives to AD process is their effects on the quality of digestate for subsequent uses, especially as soil improver. Despite literature has not explored enough the fate and properties of digestate with BC to land applications, some potential benefits of BC amendment can be identified as follows. BC remaining in digestate after AD acts as a nutrient retention improver and catalyst, mitigates leaching of heavy metals and pollutants via physical and chemical absorption of organics, phosphate, ammonium, nitrate, nitrite, metals and CO_2 [19,192]. The improvements on digestate quality can be related to BC features as SSA, surface functional groups, ash content and presence of metals (Table 9).

Table 9. Biochar properties able to improve digestate quality

Factors	Function	Literature	Reference
Textural properties (surface area, pore size)	Higher content of functional group (e.g. Si–O–Si, O–H and C=O)	HCl, $NH_3 \cdot H_2O$ and $KMnO_4$ modification were performed to obtain functional biochar from Swine manure digestate.	[193]
	Increase of the pH and cation exchange capacity	H_2O_2 and KOH modification were performed to obtain functional biochar from domestic sewage sludge digestate	[104]
Ash content	Alkali and alkaline earth metals increase the alkalinity	Pinewood and white oak biochars made digestate a great alternative to agricultural lime fertilizer.	[33]

Metals on the surface	The cation form of the metal can bind with soluble phosphorus	Ex: $3Fe(OH)_2 + 2H_3PO_4^{3-} \rightarrow Fe_3(PO_4)_2 + 6H_2O$	[151]
Functional group	Negatively charged functional groups forms complexes with heavy metals	Manganese oxide-modified biochar composite derived from corn straws improved heavy metal stabilization in the digestate	[194]

BC supplement in digesters may be beneficial to the fertilizer value of digestates. Shen et al. [34,151] have found that BC addition can cause a substantial increase of the macro- and micro-nutrients as N, P, K, Ca, Mg, and Fe in digestate. Zhang et al. (2020) [195] reported a similar rise of nutrient content in digestate amended with BC, even if concentrations of certain nutrients did not fully meet limits of EU regulation on fertilizing products (Regulation EU 2019/1009). Research has shown that the joint amendment of BC and anaerobic digestate can reduce atmospheric greenhouses emissions from fields, such as N_2O [196] and CO_2 [197–199]. A mixture of dried anaerobic digestate and BC may be an alternative to standard formulations in horticultural potting media [200]. In addition, BC may contribute to improve the composting of digestate [153,201,202], particularly in terms of process performance, compost quality and its benefits on plants [203–205].

Further research is needed to understand interactions between BC, digestate and soil for the potential use of the mixture as soil improver after AD. Future studies about the use of BC as additive in AD should also consider its effects on the agronomic value of anaerobic sludge (i.e. content in macro- and micro-nutrients, germination and phytotoxicity tests, and others [206]).

4.5. Effects on biogas upgrading

Raw biogas from AD consists mainly of CH_4 (50-70 % v/v) and CO_2 (30-50 % v/v), along with minor compounds as water vapour, H_2S, NH_3, O_2 and N_2 [207]. Upgrading and cleaning biogas are required to meet the requirements and standards for engines and pipelines, although they represent energetic and economic costs up to 55 % of the total biomethane production cost [33,208,209]. To date, conventional technologies involve water scrubbing, cryogenic separation, physico-chemical absorption, and membranes, among the others [210,211]. Recently, BC has been investigated as adsorbent of CO_2 and H_2S for in-situ and ex-situ applications, as addressed in the following paragraphs.

4.5.1. In-situ biogas upgrading

A series of studies [24,33,34,151] investigated the feasibility of in-situ biogas upgrading by the addition of BC, obtaining methane contents up to pipeline quality (Table 10). Shen et al. (2015) [151] investigated the possibility of sequestering CO_2 with BC during thermophilic AD of WAS for in-situ biogas cleaning and upgrading. They reported average methane contents of 88.5-96.7 % in BC amended reactors, compared to 67.9 % in control reactor, reaching CO_2 removals of 54.9-86.3 % and residual H_2S content below 5 ppb. They suggested that CO_2 removal could be promoted by the high porosity of BC, by the large SSA rich of basic sites and of hydrophobic sites. Shen et al. (2016) [33] assessed the AD of WAS with the addition of two woody BCs. They observed average methane content up to 92.3 % and 79.0 % in biogas from BCs amended reactors in mesophilic and thermophilic conditions compared to control reactors, corresponding to CO_2 removals by up to 66.2 % and 32.4 %, respectively. They stated that both BCs owned desirable properties for CO_2 sequestration, and in particular high values of: SSA, porosity, chemical stability, degree of carbonization and alkaline nature. Linville et al. (2017) [24] investigated the influence of particle size and dose of BC from walnut shell on AD of FW in mesophilic and thermophilic conditions. They found higher CO_2 removals compared to control reactors in the case of smaller particle size of BC (61.0 %) than coarse one (51.0 %), due to the larger SSA and ash content. However, according to other studies [33,151], they observed a reduction of methane production with higher BC doses, concluding that this could lead to inhibition caused by higher concentrations of cations released by the BC. Shen et al. (2017) [34] studied the effects of two BCs from corn stover and pine wood on AD of WAS in two-stage digesters. They reported an average methane content of 81.0-88.6 % in the reactor with BC from corn stover and 72.1-76.6 % with BC from pine wood, compared to around 70.0 % for the control. They stated that BCs would release base cations sequestrating CO_2 by chemical sorption and forming bicarbonate/carbonate salts, and that its surface structure would help CO_2 adsorption. Apart from CO_2 adsorption on BC, the major formation of CH_4 depends on the stronger syntrophic cooperation between organic acid-oxidising bacteria and CO_2 reducing methanogens [36,58], underlying the key role of efficient interspecies electron transfers. Further confirmation by other authors to the attractive findings about biogas in-situ upgrading by BC would be beneficial.

4.5.2. Ex-situ biogas cleaning and upgrading

The use of BC and other carbonaceous adsorbents for CO_2 capture from various gaseous streams recently attracted a growing attention [212–214]. Considering ex-situ applications of BC for biogas upgrading and cleaning, Table 11 shows CO_2 and H_2S adsorption capacity of different BCs. Clearly, the adsorption capacity for both CO_2 and H_2S is in a wide range, 0.4-2.3 mmol g^{-1} and 0.2-19.1 mmol g^{-1} respectively. Most of the studies regarding CO_2 capture do not specifically focus on biogas, investigating different BCs eventually subjected to activation. Sethupathi et al. (2017) [215] assessed the adsorption of CH_4, CO_2 and H_2S in a synthetic biogas stream by four BCs in fixed bed adsorbers during continuous experiments. They reported that just CO_2 and H_2S were captured by BCs, which exhibited adsorption capacities up to 0.208 mmol g^{-1} for H_2S and 0.126 mmol g^{-1} for CO_2. Creamer et al. (2014) [216] investigated the adsorption of CO_2 into BCs from bagasse and hickory wood. They found that BC could effectively capture CO_2 (adsorption capacity up to 73.55 mg g^{-1} or 1.67 mmol g^{-1}), suggesting the importance of surface area and superficial nitrogen groups in CO_2 sequestration, mainly through physical adsorption. Creamer and Gao (2016) [217] reported that the main mechanism for CO_2 sequestration by BC is physical adsorption, suggesting the importance of high SSA [100], adequate pore size (0.5-0.8 nm) [218] and pore volume, thanks to Van der Waals and electrostatic forces. However, the adsorption of CO_2 can also be influenced by BC chemical properties, such as the presence of basic surface functional groups or alkali and alkaline earth metals, hydrophobicity and non-polarity [214]. For instance, Xu et al. (2016) [219] found that the adsorption of CO_2 by three BCs during batch equilibrium tests was due to the presence of alkali and alkaline earth metals (Ca, Fe, K, Mg) by CO_2 mineralogical reactions together with physical sorption. Activation and surface treatments of BCs can provide high surface area and micropores for physical sorption and enrich surface functional groups and metal oxides for chemical sorption, leading to remarkable CO_2 adsorption capacities (5.0-7.4 mmol g^{-1}) [220].

Other studies applied BC for removing H_2S from biogas (Table 11). Sahota et al. 2018 [221] found 84.2 % removal of H_2S from biogas with BC from leaf waste. Kanjanarong et al. (2017) [222] obtained a removal of 98 % of H_2S (8.02 mmol g^{-1}) from biogas with

BC, suggesting carboxylic and hydroxide radical groups as responsible of H_2S adsorption. Finally, Pelaez-Samaniego et al. (2018) [37] found that BC from AD digestate could effectively remove H_2S from a synthetic biogas, possibly facilitated by the presence of ash, porosity, or aromatics in BC. In contrast with CO_2 for which adsorption onto BC seemed to be mainly physical, absorption of H_2S seemed to involve many chemical mechanisms with BC surface [223].

Overall, biochar seems to be a promising adsorbent for ex-situ biogas cleaning and upgrading applications. However, additional studies [215] should focus on the adsorption of CO_2 and H_2S along with NH_3 from real or synthetic biogas, considering their competitive adsorptions, along with the influence of water vapour and the eventual removal of CH_4.

Table 10. Physic-chemical properties of biochars used in biogas in-situ upgrading

Feedstock	Production temperature [°C]	BET-SA [m^2g^{-1}]	Total pore volume [cm^3g^{-1}]	Average pore diameter [nm]	H/C [molar ratio]	O/C [molar ratio]	Ash [% wt]	Reference
Corn stover	Gasification	315.30	0.09	6.50	0.075 ± 0.007	0.004 ± 0.001	45.18 ± 0.40	[34,151]
Pine pellets	Gasification	310.19	0.19	5.07	0.078 ± 0.009	0.249 ± 0.014	18.69 ± 0.44	[33,34]
White oak pellets	Gasification	296.81	0.15	4.92	0.109 ± 0.026	0.051 ± 0.010	34.90 ± 0.65	
Walnut shell	Gasification: 900 °C	86.5	0.16	7.06	0.20 ± 0.01	0.06 ± 0.01	43.2 ± 0.2	[24]

Table 11. Biochar adsorption capacity (mmol g^{-1}) of H_2S and CO_2 during ex-situ applications.

Feedstock	Pyrolysis/activation	Surface area [m^2g^{-1}]	Total pore volume [cm^3g^{-1}]	Gas	Inlet H_2S or CO_2 concentration [ppm]	H_2S Adsorption capacity [mmol g^{-1}]	CO_2 Adsorption capacity [mmol g^{-1}]	Reference

AD digestate fibres	PY/500°C/60 min	134	0.037	Synthetic biogas	2000	3.96 [a]		[37]
	PY/600°C/60min	142	0.035	Synthetic biogas	2000	15.90 [a]		
	PY/600°C/60min +Na_2CO_3	-	-	Synthetic biogas	2000	19.13 [a]		
Biomass from black liquor	C/450°C/6min	60		N_2+H_2S	1000	2.14 [a]		[224]
Pig manure	PY/500°C/4hours	47.4		Air + H_2S	1% (v/v)	1.75 [a]		[225]
Sewage sludge	PY/500°C/4hours	71.6		Air + H_2S	1% (v/v)	1.29 [a]		
Potato peel waste	C/500°C/5min	63		N_2 + H_2S	1000	1.56 [a]		[226]
Camphor	PY/400°C/5hours	20				3.21 [a]		[227]
Rice hull	PY/400°C/5hours	115				11.23 [a]		
Bamboo	PY/400°C/5hours	58				9.88 [a]		
80% wood chips 20% AD digestate	PY/600°C			Biogas	1020	8.02 [a]		[222]
Perilla leaf	PY/700°C	473.4	0.1	Synthetic biogas		0.537	2.312	[215]
Korean oak	PY/400°C	270.8	0.1	Synthetic biogas		0.178	0.597	
Japanese oak	PY/500°C	475.6	0.2	Synthetic biogas		0.167	0.379	
Soybean stover	PY/700°C	420.3	0.2	Synthetic biogas		0.308	0.707	
Sawdust	G/850°C	182.04	0.0036	N_2/CO_2			1.08 [b]	[228]
	G/850°C + monoethanolamine	3.17	0.0070	N_2/CO_2			1.02 [b]	
Sugarcane bagasse	PY/600°C	401.00					1.67 [b]	[216]
Whitewood	PY/500°C + steam activation	840	0.55	He/CO_2	30 % mol		1.34 [b]	[229]
Whitewood	PY/500°C + CO_2 activation	820	0.45	He/CO_2	30 % mol		1.43 [b]	
Whitewood	PY/500°C + KOH activation	1400	0.62	He/CO_2	30 % mol		1.77 [b]	
Walnut shell	C900°C/1.5hours	397	0.198				1.65 [b]	[230]
Pig manure	PY/500°C/4hours	31.57	0.044	N_2/CO_2			0.53 [b]	[219]
Wheat straw	PY/500°C/4hours	20.20	0.041	N_2/CO_2			0.78 [b]	
Sewage sludge	PY/500°C/4hours	10.12	0.022	N_2/CO_2			0.41 [b]	

5. Economic and environmental assessments

An economic and environmental evaluation of BC production and application in AD was performed, considering specifically four perspectives: 1. BC production according to feedstock composition and 2. to pyrolysis process conditions; 3. BC application in AD compared to current state of the art technologies addressing AD challenges; 4. integration of AD and pyrolysis processes (to our knowledge, specific studies related to the economic and environmental assessment of BC use in AD processes are not available).

5.1. Economic assessment

Considering BC production, the key parameters to evaluate the economic benefits of feedstocks (perspective 1) are: ash and lignin contents and O/C ratio, which affect pyrolysis yield, molecular weight of bio-oil and BC amount production [231]. Li et al. (2017) [232], based on regression model applied to 346 lignocellulosic feedstocks, stated that higher ash content increases BC production in a range of 12.5-15.5 %, reducing bio-oil production, and consequently the incomes coming out from bio-oil trade, which makes pyrolysis economically profitable. With lower ash content and higher O/C ratio of feedstocks, higher biofuel yields are produced, which leads to better economic performance, in fact minimum fuel selling prices for lignocellulosic feedstocks ranged from 0.53-1.1 Euro/L.

Considering the pyrolysis process (perspective 2), the investment costs for BC production from lignocellulosic feedstocks are: 43 % for pre-treatment and pyrolysis, 35 % for H_2 generation and 22 % for cooling and fractionations [232]. The average operating cost varies from 0.68 Euro/L for woody biomass to 0.86 Euro/L for straw biomass, due to the higher costs of disposal and pre-treatment of straw biomass, respectively 32 % and 34 %

of total operational costs [233]. Based on the economic analysis performed by Harsono et al. (2013) [234] and Sahoo et al. (2019) [235], the investment and operational costs related to BC production from lignocellulosic feedstock can only be balanced by a BC trade price of 470 Euro/t.

Considering perspective 3, the need to enhance AD feasibility and applicability to unconventional substrates implied higher costs, which should be exceeded by the increased methane production and therefore by the additional electric energy potentially associated. Inorganic and biological additives as iron, micronutrients and ash are conventionally employed to reduce inhibition and facilitate organic matter solubilisation, thus improving methane production. Nevertheless, the application of additives in AD accounts as 3.60-4.10 euro/L of enzyme and as 13-16 euro/L of nutrients [236]. The overall costs of BC, depending on feedstock, pyrolysis process and activating agent (Table 12), could range from 0.2 to 0.5 USD/kg, making BC cheaper than granular activated carbon (GAC), which has production costs ranging between 0.6 and 20 USD/kg.

Table 12. Comparison of granular activated carbon (GAC) and biochar (BC) production costs depending on feedstock, production process and activating agent

Additive	Feedstock	Production process/ Activating agent	Location	Cost of production (USD kg^{-1})	Reference
GAC	Poultry litter derived carbon	Steam	USA	1.44	[237]
GAC	Rice bran	NaOH	China	3.58-3.77	[237]
GAC	Red oak wood	Steam	USA	0.62-1.27	[237]
GAC - commercial	-	-	USA	1.19-16.34	[237]
GAC	Fruit processing waste	Steam	Malaysia	1.67	[237]
GAC	Rice bran	CO_2	Brazil	3.54	[237]

GAC	Acid treated rice bran	CO_2	Brazil	20.45	[237]
GAC	Wood	KOH	-	2.49	[237]
GAC	Charcoal	KOH	-	1.25	[237]
GAC	Lignite	KOH	-	2.18	[237]
GAC - commercial				1.93	[237]
BC	Empty fruit bunches	Slow PY	Malaysia	0.533	[234]
BC	Straw	Slow PY (large scale)	UK	0.203	[18]
BC	Straw	Slow PY (medium scale)	UK	0.447	[18]
BC	Straw	Slow PY (small scale)	UK	0.351	[18]
BC	Short rotation coppicing, forestry residues, short rotation forestry	Slow PY (large scale)	UK	0.266	[18]
BC	Short rotation coppicing, forestry residues, short rotation forestry	Slow PY (medium scale)	UK	0.500	[18]
BC	Short rotation coppicing	Slow PY (small scale)	UK	0.434	[18]
BC	Forestry residue	Slow PY (large scale)	UK	0.345	[18]
BC	Forestry residue	Slow PY (medium scale)	UK	0.584	[18]
BC	Arboricultural arisings	Slow PY (small scale)	UK	0.213	[18]
BC	Pine wood	Slow PY	USA	0.220-0.280	[238]
BC	-	-	European market (2014)	0.662-0.811[a]	[239]
BC	-	-	-	0.207	[239]
BC	-	-	-	0.600	[68]
BC	-	-	Global, market price (mean)	2.06	[240]
BC	-	-	USA, market price (mean)	2.48 (0.08-13.48)	[241]

GAC: granular activated carbon; PY: pyrolysis.

(a) exchange rate USD/euro (January 2014): 1.3516

Still considering perspective 3 and moving from the additive's cost to the improvement of AD performances,

The economic benefits of the integration of AD and pyrolysis technologies (perspective 4) has been explored by literature. The integrated technologies of AD of waste biomass and pyrolysis of the digestate could increase the net electricity production respect to AD alone [80] and enhance its quality as soil amendment [81] with economic and environmental benefits [242]. However, up to date, there is uncertainty regarding the balance between input costs of BC supplementation and output of energy production from AD. Qiu et al. (2019) [59] proposed the energy input-output LCA method to estimate the total energy input for biogas production, by calculating the energy associated with each component used in AD, and the actual energy return of investment. Zhang et al. (2020) [243] investigated the addition of woody BC to improve the thermophilic AD of FW. They concluded that BC supplementation could be economically feasible to enhance thermophilic AD of FW.

5.2. Environmental assessment

Considering feedstocks (perspective 1), life cycle analysis (LCA) from cradle to cradle of the pyrolysis of lignocellulosic feedstocks stated that GHG emissions for husk/shell/pit ranged from 120-250 g CO_2eq/MJ, while for other organic waste, wood and straw they ranged between 20-50 g CO_2eq/MJ [232]. This difference was due to the dominant contribution of indirect land use change from food production. Feedstocks having higher O/C ratio and 0 – 2 % ash content increased the GHG emissions [244]. Based on GREET database [245], GHG emissions reduction for lignocellulosic feedstocks was 85 - 98 % compared to the GHG emissions for petroleum fuels refining, which was equal to 93

gCO_2eq/MJ. GHG emission reductions for lignocellulosic feedstocks satisfy the 50 % share of renewable fuel standard for GHG emission reduction requirement for advanced fuels [246].

Considering BC production process (perspective 2), LCA from cradle to gate showed that BC produced from palm oil empty fruit bunches through slow pyrolysis had an energy content higher than the energy required for producing BC [234]. Furthermore, LCA cradle-to grave proved the positive energy balance of BC produced from different lignocellulosic materials [247]. Hence, the positive energy balance of BC production and application, due to the high-energy content of lignocellulosic feedstocks, represents a crucial benefit both from economic and environmental perspectives. One of the main issue of BC produced from renewable feedstocks as lignocellulose wastes (i.e. WAS, wood) and not from purpose grown feedstocks is the higher risk of having contaminants as heavy metals or organic compounds like dioxins, PAHs and PCBs [248].

Still considering BC process production (perspective 2), pyrolysis and gasification were compared from the perspective of carbon equivalent abatement (CA): pyrolysis achieved the highest CA, ranging from 0.07 to 1.25 t CO_2 eq/t feedstock, as cardboard and wood waste, while gasification reached the highest electricity generation outputs with 0.9 MWhe/t of feedstocks [249]. Activation was proven to represent a high item cost both in terms of economic and environmental perspectives [250]. BC chemical activation costs, in line with non-renewable GAC activation, range between 1.38 and 1.48 Euro/kg, respectively with acidic and basic treatments [251].

However, perspective 2 could also be explored considering the existing literature related to the conventional applications of BC as soil improver, adsorbent for water and air pollutants, catalyst for syngas upgrading and biodiesel production (Table 13). LCA studies from cradle-to-grave of conventional BC applications measured in all cases positive environmental benefits compared to conventional perspectives. BC produced from waste forestry feedstock and applied as soil improver contributed to GHGs emission reduction up to 2.74 kg CO_2 eq/ kg BC for the impact categories climate change (CC), natural gas avoided for fossil depletion (FD) and urea avoided for freshwater eutrophication (FE) and human toxicity (HT) [252]. A LCA from cradle to cradle [247] showed that BC production and application as adsorbent presented, compared to GAC deriving from virgin non-renewable feedstock, lower environmental impacts in terms of climate change (CC), fossil depletion (FD), freshwater eutrophication (FE) and terrestrial acidification (TA) impact categories, and that wood and wood chips achieved the highest environmental credits among the others feedstocks. In details, considering CC (expressed as kg CO_2/kg adsorption material), GAC produced 1.44, while wood chips and corn stover had credits ranging between -3.42 to -3.57, whereas oil palm produced 11.1 [253]. Regarding FE (evaluated as kg P eq/ kg adsorption material), BC from lignocellulosic feedstock exhibited higher values than GAC, respectively ranging between 6.2 to 10.9 % [247], due to the organic matter of renewable feedstock [254]. Considering both TA and FD (respectively estimated as kg SO_2 eq/ kg adsorption material and kg oil eq/ kg adsorption material), BC from lignocellulosic feedstock achieved higher credits than GAC, between 9.5 % and 32.0 %.

Considering BC application in AD processes (perspective 3), to our knowledge the available scientific literature only focused on sequential processes, as pyrolysis followed by AD. A LCA from cradle to grave [255] considered BC produced from corn stover applied as carburant and soil amendment with sequential AD, achieving respectively: -

2.47 kg CO_2eq/t and energy saving of -6.53 MJ/ t for the first scenario and - 4.67 kg CO_2eq/t and energy saving of -9.73 MJ/ t for the second scenario.

Table 13. Environmental assessment of biochar (BC) production and uses

	Positive effects	Negative effects
Feedstock (perspective 1)	Lignocellulosic biomass exhibited more positive effects because of higher energy potential [247] Waste biomasses presented more advantages (e.g. avoided waste management) [256]	Feedstock provision (transport) [93] Potential presence of contaminants (heavy metals, persistent organic pollutants) in waste feedstocks (sewage sludge) [256]
Production process (perspective 2)	Renewable energy from syngas and bio-oil [93] Stabilization of C in biomass feedstock [18]	Large centralized pyrolysis units higher transportation distances compared to smaller decentralized units [256]
Activation process (perspective 2)		Activation was proven to represent a high item cost both in terms of economic and environmental perspectives [250]. Use of chemicals and electricity is associated to higher impacts [257].
Applications		
Soil improver	Biochar (C) sequestration in the soil [93] Reduced fertiliser requirements [93] Reduced N_2O emissions from soil [93] Enhanced plants growth [18] Reduced fossil fuel use in irrigation and cultivation [18] Enhanced nutrient availability [258] Increased H_2O retention [258] Reduced leaching and run-off of nutrients [258]	Binding /deactivation of pesticides, herbicides and nutrients in soil [258] BC as source of potential toxicants (heavy metals, PAHs, organics) [258]
Adsorbent	BC lower impacts than activated carbon [247]	

In conclusion, focusing the environmental assessment on perspective 4, the integration of AD of waste biomass and pyrolysis of digestate, as shown in Figure 2, could increase the net electricity production respect to AD alone [80] and enhance its quality as soil amendment [81] with economic and environmental benefits [242]. In conclusion, the integrated approach has been investigated by life cycle analysis and exhibited positive environmental outcomes if compared with non-integrated processes [255,259].

6. Conclusions

This review addressed three key issues related to the comprehension of BC role in AD processes:

1. *Investigation of the influence of BC properties on AD performances and of their ability to counteract its main challenges*. It is understood that BC properties are determined by the feedstock and by pyrolysis and activation processes. The key features were SSA, porous structure and distribution, nature of surface functional groups (related to CEC and adsorption capacity, buffer capacity, ability to immobilize microbial communities), elemental composition and ash content. However, some mechanisms (e.g. BC role in ammonium adsorption and BC influence on microbial mechanisms) still need to be fully understood and explained. Other challenges for future research are related to digestate management; in detail, the influence of BC relatively high doses on the rheological properties of the digestate should be explored, as well as the eventual leaching of pollutants in the environment as a consequence of digestate recovery as soil improver.
2. *Assessment of the optimal BC production chain (i.e. feedstock-pyrolysis-activation) to achieve the desired features*. Lignocellulosic biomasses, slow pyrolysis and physical activation seemed to be a good combination in general, while other feedstocks and/or chemical activation should be evaluated for specific needs and tailor-made applications.

However, a systematic investigation of the correlations linking BC physico-chemical characteristics and AD performances, carefully exploring one by one the BC effects mentioned in this review, is highly needed for a deep understanding of BC role as additive in AD processes.

3. *Evaluation of the economic and environmental advantages connected to BC use in AD processes, compared to conventional solutions applied to address AD challenges.* The main research gap related to this issue is the absence of specific literature related to BC use in AD processes, therefore only general statements could be formulated. The use of BC as additive could be cheaper and has less environmental impacts than of conventional AD improvers (e.g. physico-chemical-biological pre-treatments) and of GAC. The integration of AD and pyrolysis achieved economic feasibility and positive environmental performances if compared with non-integrated processes. Future research could investigate the optimization of technical, economic and environmental performances of BC production chain and its integration in AD processes.

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