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Review

Pyrolysis of Biosolids to Produce Biochars: A Review

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Abstract: The continuing increase in population means an increasing demand for products and services, resulting in huge amounts of waste being discharged into the environment. Therefore, waste management requires the application of new and innovative solutions. One new approach involves converting waste into value-added chemicals and products for use directly or after further processing into higher value-added products. These processes include biological, thermochemical, and physiochemical methods. Furthermore, biosolids, including treated sewage sludge (SS), represent one of the major by-products of human activities, constituting a major environmental hazard and requiring the treatment of contaminated wastewater with associated health hazards. Sustainable solutions to manage and dispose of this type of waste are required. In this review, pyrolysis, a thermochemical conversion technology, is explored to convert biosolids to biochars. The review addresses previous studies, by providing a critical discussion on the present status of biosolids processing, the potential for energy recovery from the pyrolysis bio-oil and biogas, and finally some benefits of the production of biochars from biosolids.

Keywords: pyrolysis; biosolids; biochar; waste management; waste-to-energy

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1. Introduction

1.1. Background

With a projected increase in population amounting to approximately 9.8 billion by the year 2050 [1], it is anticipated that as a result there will be multiple dilemmas world-wide. The dilemmas include depletion of natural resources, increased waste generation and subsequent increased emissions, the need to increase food production, competition between the allocation of available resources and climatic change among others. Industrial expansion, human activities and the continuing national development of the emerging nations are the main drivers of such changes and their problems, and with them comes the creation and generation of all kinds of wastes. There is a need to manage urban and industrial wastes sustainably if we aim to avoid serious, irreversible effects that will shift the Earth towards further damaging changes. The issues impacting on the world at present are illustrated in Figure 1.

The current negative environmental problems and phenomena are results of the linear economic model, which leads to increasing substantial quantities of wastes and prolonged pollution. The adoption of the concept of a circular economy and the development of biorefining [2] should facilitate the transition of societies and companies to a world that is characterized by being more sustainable and having more sustainable supply chains [3–6], which should aid in alleviating the burdens placed on the planet due to the generated wastes and the increased levels of production to cope with the increase in population. The lack of information on sludge processing technologies and the development of integrated biosludge management systems has been reported [7,8]. Nevertheless, a circular economy is considered to be a rising major research area that requires additional consideration and study [9]. Among the many options that can be considered is the application of thermochemical technologies, such as, gasification [10,11] and pyrolysis [12,13], which can efficiently convert different waste streams into several value-added products. Hence, implementing the concept of a circular economy, in addition to creating additional markets for waste and opening new doors for their industrial uses. The types of wastes that can be used are varied and can range from sewage sludges, pharmaceutical wastewaters, plastics, woods, animal and plants wastes, algae, and other biomass wastes [14–17]. Recent advances in the use of sustainable waste materials and the subsequent conversion of these wastes into different useful products are key drivers for the application of pyrolysis for other wastes like biosolids. For instance, [18] utilized calcinated chicken eggshells in the fabrication of a supercapacitor, while [19] utilized mango seed husk in the production of sustainable porous carbon materials suited for super-capacitors applications. Moreover, exceptional biochars (solid fractions) were manufactured from bagasse for applications in antibiotics removal from water in the work of [20], whereas leather waste was converted into biochars and other value-added products in the work of [21].

Figure 1. Global issues and consequences faced by today's world.

One of the by-products of urban and industrial activities is sewage sludge (SS), which constitutes a major issue due to its large volume and deleterious effects on the environment. It is a result of the treatment of primarily domestic wastewater and is associated with a number of contaminants and health hazards [22]. Therefore, there is a pressing need for its processing and subsequent use, in addition to the appropriate disposal if needed. The use of sewage sludges in other useful forms is motivated by the amounts of sewage sludges that are rising due to the many wastewater treatment plants that produce them in vast quantities. On the other hand, the conversion of biosolids to biochars resonates well with the sustainability goals of conserving resources and finding new methods for the production of goods, while offering a sustainable pathway for future generations.

1.2. What Constitutes a Biosolid/Biosludge and Why Should It Be Treated?

A term that is commonly used in the scientific literature is biosolids or biosludges, which in this review will refer to any form of sludge that has undergone some form of treatment (e.g., chemical, biological, heat treatment, etc.) in order to transform it into a less hazardous and organic form [23,24]. Additional forms of SS resulting from industrial activities involving the above are also considered (e.g., due to the use of a bioreactor or from the pharmaceuticals industry). Biosludge management practices are generally based on disposal or utilisation in three categories [25,26]:

(i) Land application technologies: composting, direct agricultural use, forestry enhancement and land reclamation [27],
(ii) Energy source production/recovery: incineration, gasification, pyrolysis, anaerobic digestion, bioethanol production, direct/hydrothermal liquefaction, and hydrogen production [28]; and thirdly,
(iii) Materials applications: water treatment absorbents, adsorbents, filtration media, composites, cement, construction, and asphalt manufacturing [29].

In many cases with biosludges, especially treated sewage sludge using biofilm reactors [30] the elemental composition varies with the climatic season and the geographic region and these factors are important in the designations of biosludge treatment applications.

Solids resulting from wastewater are either applied to land as soil amendment and nutrient source, incinerated, or landfilled [31]. These solids are full of micropollutants that include organic chemicals originating from consumer-based products, which end up in the sewer drains during disposal (e.g., pharmaceuticals, antimicrobial compounds, personal care products, medicines and hormones, etc.) [32,33]. Therefore, the sewage sludges and wastewater treatment sludges and their by-products from these locations require new and innovative handling methods that alleviate environmental burdens, while producing value-added products, e.g., capacitors [34]. The thermal process of pyrolysis to biochars has been reported to combat some of these issues, for instance, the destruction of organic molecules, the destruction of microorganisms and the fixation of heavy metals, preventing them from leaching out into the soil. The agricultural benefits that can be derived from the thermal processing of biosolids are shown in Figure 2.

Figure 2. Expected agricultural improvements resulting from the application of biosolids-derived biochars.

1.3. Application of Pyrolysis as a Thermochemical Treatment Process and Biochar Production Technology

The pyrolysis process holds great potential as a thermal treatment method [35,36], that is capable of transforming biomass into value-added products. Typically, a biomass feedstock will undergo thermal treatment to an elevated temperature that goes beyond 400 °C in the pyrolysis process in an inert environment, that involves partial or total removal of oxygen. In addition to containing the gas produced resulting from the thermal degradation of the organic components [37,38], the pyrolysis process results in the production of three major products, namely, biochar, bio-oil, and biogas as shown in Figure 3.

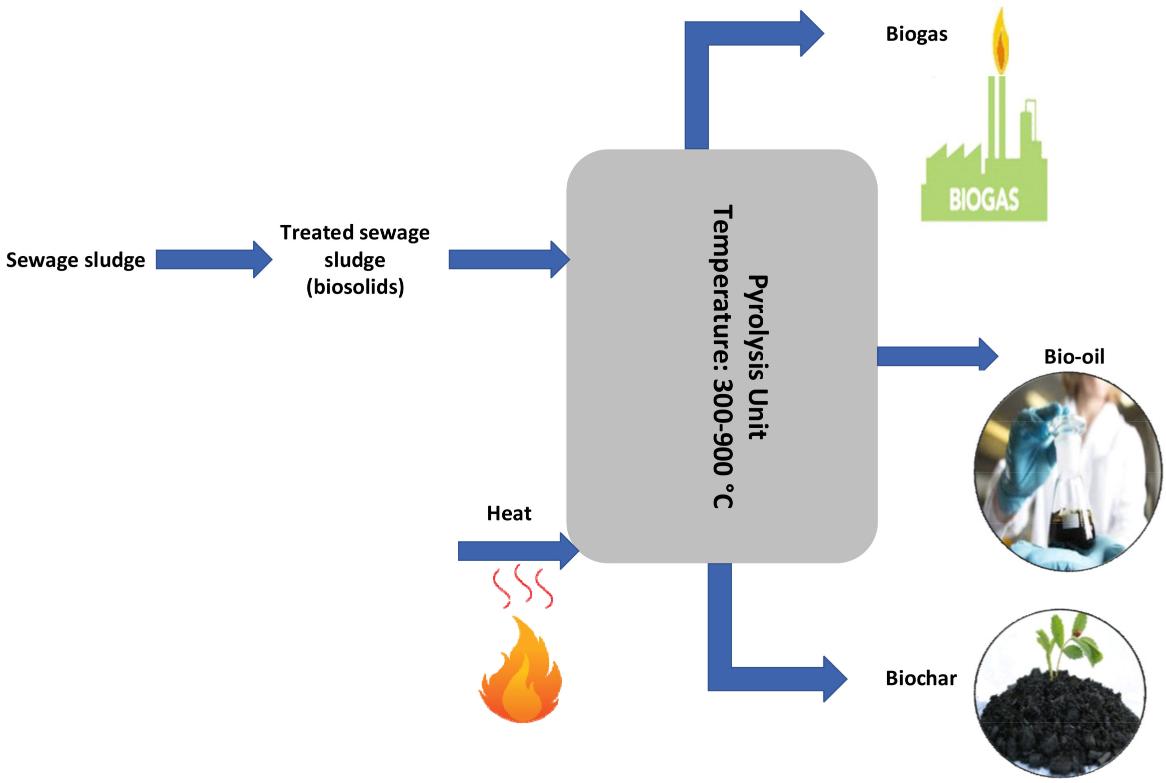

Figure 3. Schematic of a typical conversion of biosolids into biochar through the pyrolysis process.

Pyrolysis processing is classed into a variety of categories primarily based on the product requirement, the operating conditions, and the feedstock type. The general classification of pyrolysis groupings and the most frequently used techniques include: slow, fast, and flash pyrolysis [39]. It should be noted that both pyrolysis and gasification are two processes for producing biochars, but greater char yields are usually obtained from the pyrolysis reaction.

1.3.1. Pyrolysis Technologies

This section sheds light on the common types of the pyrolysis process. The various types of pyrolysis have been presented in detail in the work of [39,40] and are summarized here:

Slow Pyrolysis

Slow pyrolysis, as the name suggests, is based on applying slow or low heating rates and extended hold-up times [39]. The biosolids feedstock undergoes pyrolysis most commonly in the range of 350–550 °C, with low heating rates in the order of 0.10–1.0 °C/s for reaction durations of 5 to 30 min. Slow pyrolysis has been found to benefit and optimize char formation, while producing lower amounts of the two byproducts bio-oil and biogas [41]. The most popular reactors that are typically employed in the slow pyrolysis mode are: rotary kilns, drums and screw augers [42,43]. The choice of the most suitable reactor design has been reviewed by [44].

Fast Pyrolysis

Fast pyrolysis is applied to processes by heating the biosolids between 800–1300 °C, but using heating rates in the range 10–200 °C/s for a very short period of time ranging from 1.0 to 10.0 s [39]. The process of fast reaction pyrolysis enhances the production of bio-oil over the other two byproducts. Reported yields of the different products are varied. For example, yields of biofuel liquid products were in the range 60–75%, while non-condensable gaseous products were in the range 10–20% and a yield of 15–20% was obtained for solid biochars [45]. Unlike slow pyrolysis, which involves a long exposure time that favors the production of higher char yields, fast pyrolysis is designed such that thermal cracking is achieved, while minimizing the exposure time [46]. To achieve rapid heating rates and high heat transfer rates, the types of reactors suited to these conditions are rotating cones, entrained flow, fluidized/bubbling bed reactors, ablative and vacuum reactor types [47].

Flash Pyrolysis

Flash pyrolysis is an extension of fast pyrolysis [48], which concentrates on the production of high bio-oil yields. The process is performed at only moderate thermal processing conditions circa 500–550 °C), having very low vapour phase residence times in the order of 0.5–1.0 s and the application of high heat transfer rates. This set of conditions leads to the maximization of the bio-oil yields due to the secondary stage cracking chemical reactions causing the decrease in the yield of liquid products [46,49–51]. Flash pyrolysis of biosolids results in the production of approximately 60–80 wt% bio-oil yields, 10–20 wt% biogas and char yields in the range15 to 25 wt% [46,50].

1.3.2. Benefits of Pyrolysis

Pyrolysis is a relatively uncomplicated technology requiring no complex process plant compared with incineration and gasification and it is quite environmentally friendly [52]. Additional benefits include its ability to handle many waste types [53], while directly producing several product materials (for example, biochars, bio-oils and syngas) [54,55]. In terms of the limitations of the sustainability of the pyrolysis process for a treatment alternative, the issue for wet biosolids feedstock is a problem but it has been stated recently that the introduction of low-cost pre-drying solutions can improve the outcomes, prior to pyrolysis [40]. For example, solar drying methods are promising techniques as a low-cost drying pretreatment in arid environmental conditions, having plentiful sunlight and a low humidity environment. Alternatively, flue gases, available from the combustion of the bio-oils/biogas, in the temperature range 140–180 °C could achieve the same objective and even indirect heat exchange with the hot outlet pyrolysis gases.

This focused review paper aims to shed light on biochars produced from different pyrolysis methods and using different biosolids or treated sewage sludge. It should be noted that both types of sludges will be later referred to as bio-sludge as there seems to be no consistency in the literature regarding the use of these terminologies and types of sewage sludges—based on their level of treatment. Furthermore, the paper briefly discusses the available options for the recovery of energy from the pyrolysis products as reported in the literature. Both biogas and bio-oil for energy are useful byproducts of the biosludge pyrolysis process for the production of biochars. Finally, an overview of the role of biochars as a soil amendment additive is presented.

1.3.3. Limitations of the Pyrolysis Process

The pyrolysis process, whether fast or slow, is associated with a number of challenges which have been recently discussed in the work of [56] who has explored the use of wet biomass for bioenergy production. Briefly, the use of fast pyrolysis is typically associated with the requirements for dewatering or drying [40] stages, in addition to the resulting low yield and poor quality bio-oil. It also places significant pressure on vapor condensation and the gas cleaning system. Slow pyrolysis is also associated with a number of challenges that need remediation steps that are also outlined in the work of [56]. Such limitations include high energy requirements of the process in addition to the requirements for vapors separation and gas cleaning systems.

2. Treatment of Sludge Prior to Pyrolysis

Most of the studies focus on the pyrolysis process itself and the characterization of the end-products, while assigning minimal reference to the major pretreatment requirement of the sludge that was obtained prior to the pyrolysis. Mostly, these studies indicate that the biosludge was received in a dry form with certain characteristics [57,58]. Furthermore, some studies report further drying of the obtained sludge, such as the work of [59], who obtained their sludge from a printing and dyeing plant. In Poland, [60] obtained sewage sludge (SS) from two municipal wastewater treatment plants (WWTPs) based on MBT; mechanical and biological treatment. After the sewage sludge anaerobic digestion process in the WWTPs, samples of the sewage sludge were harvested in summer, at the final processing stage. Another treatment of sewage sludge was reported by [61] who implemented a triple oxidation ditch processing stage for the wastewater treatment step.

Another problematic sludge is oil sludge from oil refineries [62]. Initial efforts to make use of this sludge sought to convert it into useful resources such as lower molecule organic compounds and carbonaceous chars by the application of pyrolysis, but with very limited success [63]. In a later study, the oil sludge was the feedstock for the pyrolysis reaction which resulted in a unique product distribution and characteristics. Table 1 provides a summary of the recent work on the pyrolysis of treated sewage sludge and other biosludges.

Table 1. Previous studies on the pyrolysis of treated sewage sludge.

Pyrolysis Method	Feedstock Type	Process Conditions			Products			References
		Temperature	Time	Pressure	Char	Oil	Gas	
Slow pyrolysis	Air-dried biosolids	300 °C and 500 °C	Residence time of 30 min	-	86 ± 8 and 65 ± 4%	-	-	[64]
Slow pyrolysis	Three different biowastes including biosolids	550 °C	Held for 1.5 h	-	18.6%	-	-	[65]
Microwave assisted pyrolysis in a customised single-mode microwave chamber connected to a 1.2 kW microwave source	Biosolids	600 °C	Holding time of 10 min	-		-	-	[66]
Fast microwave-assisted	Continuous biomass (SS)	450–600 °C	-	-	63–34%	17–26%	20–40%	[67]
Microwave pyrolysis technology	Biosolids	The quartz crucible outer temperature was reported in the range 300 °C to 350 °C immediately after each experimental run; but the sample temperatures were in the range 600 °C to 650 °C	-	-	59.93%	2.37%	37.7%	[68]
Microwave assisted pyrolysis in a customised single-mode microwave chamber connected to a 1.2 kW microwave source	Biosolids	300–800 °C	Mean residence time of 6.38 s for the nitrogen in the pyrolysis chamber	The control valve was manually adjusted to maintain the pressure within −15 kPa gauge pressure	0.91–0.77 g	-	-	[69]
Slow pyrolysis	Biosolids	300–750 °C	-	-	67.5 ± 1.2 to 48.1 ± 0.4% and 70.1 ± 1.2 to 44.4 ± 0.2	-	-	[70]

Table 1. *Cont.*

Pyrolysis Method	Feedstock Type	Process Conditions			Products			References
		Temperature	Time	Pressure	Char	Oil	Gas	
Co-pyrolysis	Anaerobically digested and thermally dried SS	525 °C	-	1.01×10^5 Pa	28%	58%	14%	[71]
Co-pyrolysis	A triple oxidation ditch process was used for wastewater treatment and the SS feed samples were taken from the dewatering stage	400–600 °C	Pyrolysis for 1 h	-	44.5–44.1%	-	-	[61]
Flash pyrolysis	Anaerobically digested and thermally dried sewage sludge	450–600 °C	1 s vapor residence time	-	24–10%	70–73%	5–17%	[72]
Slow pyrolysis	Four different anaerobically digested sewage sludges	500–700 °C	Pyrolysis time of 5 h	-	Ranged from 54.5 to 40.2%	-	-	[73]
Fast pyrolysis	Biophysical dried sludge	500–900 °C	-	-	63.10 ± 0.50 to 53.31 ± 0.48%	-	-	[74]
Slow pyrolysis	Digested wastewater sludge/biosolids	300–700 °C	-	-	72.3 ± 2.5 to 52.4 ± 2.6%	-	-	[75]

3. Pyrolysis Methods for Sewage Sludge

In previous research work, sewage sludge processing was carried out using different methods such as slow [76], fast [77], and microwave-assisted pyrolysis technology [78]. Each method, together with the selection of raw materials and operating conditions result in a unique product distribution and characteristics.

3.1. Summary of Pyrolysis Methods and Conditions

In an attempt to valorize urban wastewater derived sewage sludge, [72] investigated the flash pyrolysis of this material using the conical spouted bed reactor where the focus was on the yield and composition of the liquid product. The product yield was studied in a temperature range 450–600 °C, and a maximum yield of liquid of 77 wt% was obtained at 500 °C. With respect to the char product, which is also of significant importance, it was observed that the majority of the heavy metals in the original sludge sample were retained and immobilised in the char [79], indicating a possible application in agriculture or as an adsorbent. The results were assessed based on a 100 g sample of sewage sludge and were reported based on a dry, ash free analysis basis (DAF). Table 1 provides a summary of the results obtained on a DAF basis.

Another approach to sewage sludge pyrolysis is the use of microwave-assisted technology which was explored by several researchers such as [67,80]; their work aimed to test sewage sludge as a feedstock using a continuous microwave-assisted pyrolysis scheme. Furthermore, the influence of the pyrolysis processing temperature on the bio-oil compositions and products yield were investigated. In addition, sewage sludge was shown to be a promising biomass resource because of the high HHV of bio-oil and gas, and the fact that biochar produced from the pyrolysis process has a porous structure, which enables its use as a carbon adsorbent for contaminant removal.

The microwave-assisted technology was also employed by [68] who explored the potential of biochar from biosolids as a growing media amendment. The produced chars were shown to have high mesoporosity, moderate surface area, high nutrient levels, and quite low concentrations of heavy metals, when compared to several other biosolids-derived biochars reported in the literature. The authors also reported the results of a greenhouse experiment that involved the microwave pyrolyzed biochar (MB) and other growing media mixes, where the goal was to stimulate the uptake of nutrients and monitor plant growth, while minimizing the loss of leachate. It was concluded that the addition of peat containing 60% MB by volume resulted in the reduction of leachate losses of phosphate and nitrate from this medium, while the loss of ammonium in the leachate increased. From an energy recovery perspective, it was shown that from the HHV that around 90% biosolids elements were recovered in the pyrolytic product stream as follows: biochar-11%, bio-oil-6%, syngas-73%. Moreover, the interaction synergy between MB and fertilizer that led to the enhanced plant growth performance and improved nutrient uptake were then further investigated by adding MB alongside fertilizer to increase plant growth capability and plant phosphorus and nitrogen uptake ability.

Roberts et al. [70] produced biochar from biosolids including and excluding alum over several temperatures, in addition to trying to monitor the longer-term leaching of phosphorus (P) and metals by simulating the oxidative aging of the chars. According to the findings of the study, above 90% of the P in the biosolids existed as plant-available P in the biochars after pyrolysis even though extremely low quantities of plant-available P were detected in the biosolids containing alum. On the other hand, the conversion of biosolids with no alum into biochar resulted in only a minute increase in the available P, while increasing the available P pool available post oxidation. Although both biosolids led to the leaching of substantial quantities of metals post oxidation, the biochars were again associated with extremely low quantities of metals content, which did not lead to an increase in oxidation and hence demonstrated a stable metal content. The results of the study imply that pyrolysing biosolids is an efficient waste management strategy for biosolids [81], especially those containing alum, and which can efficiently promote the reduction of the leaching of metals as well as the beneficial re-use of P by increasing the efficiency of recycling of P.

Ruiz-Gómez et al. [71] evaluated the viability of co-pyrolysing sewage sludge (SS) and digested manure (DM) as a promising management technology for such residues. A stirred batch reactor, inerted using $N_{2,}$ was used to conduct the pyrolysis studies of blends of sewage sludge/manure (50:50%), which were carried out at 525 °C. Pyrolysis runs were conducted both using individual components and blends of the two components. The results demonstrated that the char yield of DM (on a dry ash free basis) was greater than the product produced using SS alone. This can be attributed to the lower extractive contents and higher lignin composition. On an individual basis, the pyrolysis of SS generated a gas containing a higher LHV, whereas the biochar resulting from DM demonstrated better characteristics for energy related applications. In addition, more water and organic compounds (dry ash free basis) were produced by the pyrolysis of SS, indicating higher proteins and extractive components. With respect to the co-pyrolysis of DM and SS, there were small synergistic effects, which are attributed to similarities in the ash content from SS and DM. It was concluded that, given the above findings, the co-pyrolysis of SS and DM in regions where both of these wastes are generated in close proximity constitutes a great management alternative opportunity. This is due to the fact that the advantages and the disadvantages of co-pyrolysis resemble and are quite similar to those of the pyrolysis of the pure residues.

Another implementation of co-pyrolysis is the work of [61], who co-pyrolyzed bamboo sawdust with raw sewage sludge to produce a novel biochar as summarized in Table 1. The results indicated that co-pyrolysis led to lower biochar yields and with the biochars having higher C contents in the final products, when comparing with using sludge alone as the raw feedstock material. Among the benefits provided by the co-pyrolysis process, the study demonstrated the transformation of the toxic heavy metals contained in the sludge into more stable components, which led to a significant drop in the toxicity and bioavailability in the co-pyrolyzed product biochar. This is in line with the objective of the study, which was to demonstrate that the co-pyrolysis technology provided an alternative and feasible solution that allows the disposal of metal-containing sewage sludge safely.

Hence, minimizing the environmental risk resulting from mobilizing the toxic metals by using the biosludges directly following agricultural/soil applications.

An investigation undertaken by [73] produced biochars from the slow pyrolysis of sewage sludge using a pre-heated quartz tube placed in a heated furnace at 500, 600, and 700 °C. The results indicated that the properties of sewage sludges had a significant impact on the produced chars, in addition to the difficulty to predicting the final product properties based on the initial material properties. Another important parameter influencing sewage sludge pyrolysis is the temperature, as it affects the biochar yield and controls the properties of biochars. The results have also shown that higher temperatures of 600 °C and above favored the production of biochars with an alkaline pH. Additionally, increases in the temperature range 500 °C to 700 °C increase the ash content of the biochars, which makes the ash content in the biochars relatively greater in relation to the values in the original sewage sludge of course. Moreover, higher temperatures also promoted the formation of biochars having higher concentrations of nutrient components.

In order to systematically examine the effect of pyrolysis temperature on the adsorption of heavy metals and on the properties of municipal sludge derived biochar, biophysically dried sewage sludge was used for pyrolysis at temperatures ranging from 500 °C to 900 °C in the work of [74]. It was observed that increasing the temperature of the pyrolysis reaction achieved a decrease in the biochar yield, whereas the ash content remained relatively constant, and hence driving the biochar properties into the alkaline region. Moreover, an increase in the temperature resulted in a porous structure development, while a low concentration of surface functional groups was observed to be developing under these conditions. The leachate toxicity tests of the biochars yielded metal concentration results that were less than 20% of the Chinese environmental leachate toxicity test standard concentration limits, even though the biochars had relatively high heavy metals content. In comparison with the performance of commercial activated carbon, the adsorption removal potential of the biochars showed an improvement at the higher biochar production temperature in the batch adsorption tests for cadmium (II) removal, particularly at 800 °C and 900 °C. This is an order of magnitude greater than that of the commercial activated carbon. Additionally, the optimal pyrolysis temperature was found to be 900 °C for both heavy metal removal and energy recovery purposes. The higher pyrolysis temperatures support the development of high surface area, greater porosity, and increased concentrations of thermally activated surface functional groups. The findings indicate that biochars from biosolids may be considered important candidates in applications involving the removal and adsorption of heavy metals and other contaminants from water.

Biochars were also produced from biosolids in the work of [75], who studied the production of wastewater sludge biochar and the influence of the pyrolysis temperature on the product characteristics. Additionally, the properties required for agronomic applications were evaluated. In this study, the pyrolysis was carried out in a laboratory scale reactor using wastewater sludge obtained from a treatment plant for processing urban wastewater, and it was revealed by the results that increasing the pyrolysis temperature, in the range 300 °C to 700 °C, resulted in a decrease in the biochar yield, which is in agreement with most other studies involving the production of biochars through pyrolysis. According to the study, wastewater sludge biochar generated at high temperature (700 °C) is acidic, whereas biochar produced in a low temperature range (300–400 °C) is alkaline. A twofold application can be achieved by using biochar in agriculture. In the case of a soil with an acidic nature, the biochars obtained at 700 °C or higher can be applied to neutralize alkaline soils and improve soil fertility in addition to sequestering carbon. On the other hand, biochars generated at a lower temperature, being alkaline in nature, will be beneficial for acidic soils to combat acidity issues. Furthermore, a wide range of elements of key importance in crop cultivation existed in the biochar, such as K, P, N, and other micronutrients. Increasing the temperature was linked with a decrease in the concentration of nitrogen while micronutrients were found to increase. Variations in the concentration of trace metals were observed with varying temperatures, which were primarily enriched in the biochar.

Other recent applications involving the pyrolysis of biosolids for the production of biochar include the work of [64] and the work of [65], who employed slow pyrolysis in the conversion of biosolids to value-added products. [64] focused on biochars derived from biosolids (BBC) and the effects of such biochars on soil phosphorus (P) pools. According to their results, these biochars have the ability to increase the total P and the organic, inorganic, and available P fractions regardless of the pyrolysis temperature, which leads to maintaining these high values for long periods of time (e.g., two years) even when their application is stopped. In general, the treatment of soils, in the studied cropping seasons, with BBC surpassed other treatments with P content that is twice the content of other treatments. The content of P in their study involves some uncertainty since soils themselves could have some P in them in addition to the P released from BBC. Hence, it is important to employ analytical techniques to study how P is released from biochar to soils. Furthermore, [65] used three different biowastes for the production of biochar, including biosolids. The results of the study and characterization of biochars resulted in the production of alkaline materials that are similar but with differences in their characteristics, dependent on type of feedstock used. Additionally, the properties showed good stability of these derived biochars in soil, making them suitable as soil amendment agents, sorbent materials for wastewater and soil decontamination, and carbon sequestration agents [82]. In addition, there is a potential for their use for liming purposes as soil additives.

In recent years, biochars produced by the pyrolysis of sludges and other biomass resources have been used in a number of trial applications due to their distinctive characteristics. [83] reviewed a wide range of applications of biochars as catalysts, which have been tested in several research areas, including; esterification, reforming and cracking, gasification/pyrolysis, hydrolysis, electrochemistry, photocatalysis and certain oxidation reactions.

3.2. Critical Discussion of Previous Work

3.2.1. Effect of Process Conditions and the Type of Pyrolysis Method

It was noticed that most of the studies only emphasize on the effect of temperature alone when it comes to the production of biochars from treated sludges using pyrolysis. Hence, there is missing information like the influence of process pressure, residence time, blends of feedstocks and particle size among others. As with the pressure effect studies, this could be due to the economics of the process and the fact that it was set at standard conditions. With respect to temperature, biochar production was seen to increase at lower temperatures and decrease at higher temperatures regardless of the method of pyrolysis used. In terms of the pyrolysis method used, it was noticed that different studies utilized different pyrolysis processes for the production of biochar from biosolids. Variations involved the use of different process conditions together with the process type. In general, slow pyrolysis was associated with the highest biochar yield as opposed to the use of fast pyrolysis, which is typically used to produce higher yields of bio-oil. The selection of the pyrolysis is governed by the desired product and the process requirements needed to achieve it.

To date, several recent studies on the use of biomass wastes have looked at the effect of heating rates and the resulting products. For instance, [84] looked at the effect of two heating rates, typical of slow pyrolysis, in the production of biochars from food wastes and found that increasing the heating rate from 5 to 10 °C/min had minimal effect on the yield results. This implies the importance of further research looking at higher heating rate and conducting a comparative study. Furthermore, [13] looked at the effect of heating rate in the pyrolysis of camel manure. The results indicated that the increase in heating rates increased the starting and ending temperatures (decomposition) of manure components. Char yields were shown to increase, while there was an insignificant effect on the kinetic parameters of the camel manure components. Hence, it is important to extend the analysis to biosolids pyrolysis studies to understand how temperature and heating rates affect yield, product composition and performance of the process.

The effect of increasing temperature on biochar formation is to reduce the biochar yield but produce a biochar product of higher carbon content and of higher surface area and porosity. The loss in the biochar yield as the temperature is increased is accounted for by the production of bio-oil products and as the temperature is increased still further, >600 °C, the production of biogas becomes the dominant biosolids decomposition product.

The effect of feedstock particle size was also addressed in recent work on biomass waste and showed that the grinding has a major role on the final composition and structure of the produced chars and byproducts [85,86]. Grinding is associated with differences in the final product composition and results. For instance, fine grinding is associated with higher percentages of CO, CH_4 and higher heating values and energy conversion rate of gases. It is suggested to investigate the effect of fine and coarse grinding on the effect of product composition, feed mixing, and product yield when utilizing biosolids as feedstocks and other types of biomasses.

Typically overlooked in the literature, residence time is a crucial factor and the process parameters in the pyrolysis process. Slow pyrolysis conditions provide higher char yields because slow heating rates and longer residence times in the reactor result in slower decomposition [87]. Research has shown that physical properties and chemical composition are influenced by residence time [88–90].

Further discussion on the importance of process parameters and the pyrolysis of biomass waste is detailed in the work of [39].

3.2.2. Effect of the Type of Feedstock on Biochar Yield

In general, the biochar yields observed in the previous studies were higher than those obtained from the plant-based biomass pyrolysis investigations [91–93], food waste [94–96], and other pyrolyzed treated SS [97,98]. This could be because of the higher inorganic composition in the sewage sludge in comparison to other biomasses.

It should be noted that some authors omit the type of feedstock and the treatment it has undergone in their studies, which makes it difficult to judge the impact of the feedstock type used on the results of the biochar, as well as the final application of the biochars (e.g., plant growth). It is also another challenge to differentiate the impact treated SS has on biochars versus untreated SS [31].

3.2.3. Comparison between the Properties of Biosolids-Based Biochar and Other Feedstocks

Stylianou et al. [65] recently investigated the use of three different biowastes and their effects on the produced biochars. In terms of the yield, biochar produced from biosolids resulted in the lowest yield, but had the second highest calorific values and pore volume. The other feedstocks were cattle manure and spent coffee grains. These are the only results found so far where the yield of biochar derived from biosolids is lower than other feedstocks, which indicates the need for further studies investigating the impact of a number of feedstocks and comparing them with biosolids.

The elemental properties and composition of biosolids-derived biochars are known to be rich in phosphorus and other elements that are essential for plant growth, but low in carbon when compared to other feedstocks. [31] presented a recent comparison of the elemental composition of biosolids-based biochar and other biochars at different temperature ranges. In their study they provide detailed list of the composition of each biochar and the implications. The important role of biosludge derived biochars in providing plant nutrients is receiving more attention [99]. For instance, it was concluded that wastewater sludge derived biochars are associated with higher concentrations of key nutrients essential for healthy plant growth like potassium (K), phosphorus (P), and nitrogen (N), also this trend was found in the case of treated sewage effluent [33,100]. Since these nutrients are available in abundance in many wastewater biochars, they are considered highly suitable for use as a soil-amendment agents for agriculture. Other biochars, on the other hand, that are associated with high carbon contents might be best suited for use as adsorbents and filtration media. Others with high ash (silica contents) are suitable for cement production and construction applications [101,102].

Moreover, wastewater sludge biochars resulted in surface areas and pore volumes that are within the range reported for various biomass derived biochars. These two parameters are significant if the objective is to utilize biochars as the adsorbents for a range of compounds [103].

Table 2 presents a summary of research studies that have addressed the different properties of the produced biochars from biosolids and conventional biomass wastes. It should be noted that data are reported without taking into account statistical variance in order to have a general sense of the results.

Table 2. Summary of biochar properties resulting from biosolids versus conventional biomasses.

Biomass Type	Process Conditions	Biochar Properties										Reference
		Yield	Surface Area	Porosity	C (%)	H (%)	N (%)	S (%)	O (%)	Ash (%)	pH	
Biosolids	Temperature of 600 °C	-	80 m^2/g	Micropore area of around 67 m^2/g	45.5	0.9	3.4	-	-	59.1	8.1–10.2	[104]
Biosolids	Temperature of 600 °C	0.599 g/g	75 m^2/g	pores with average width of 4.46 nm	11.8	0	0.7	0.53	-	82.6	7.31	[68]
Banana peel	Temperature of 600 °C	35.7%	1.07 m^2/g	Pore size of 1.93×10^{-6} m	67.5%	-	0.36	0.09	16.7	22.58	-	[90]
Crop residues	Temperature of 600 °C	35%	Specific area of 12 m^2/g	Pore diameter of 8 nm	50	1.5	-	-	6	35	10	[85]

Two water treatment plant biosludges were considered for biochar production and the biochar properties are presented in the first two rows. The third and fourth rows list the properties of two waste food-banana peel/crop biomass derived biochars respectively. All four biochars were produced at 600 °C. In terms of the yields the biosludge biochars tend to be higher, in the range 50 to 60% by weight, but comprising a high ash content. The biomass biochar yields are both in the range 35 to 36% by weight, the results are quite typical and the carbon contents of the biomass biochars being higher but the ash contents significantly lower. The BET nitrogen surface areas and porosities are higher for the biosludge biochars, 75 and 80 m^2/g, most probably due to the pore development catalytic effect from the metal content in the ash—due in turn from the added water treatment chemicals to dewatering the sludge; alum and iron most commonly used. Elemental oxygen is higher in the biomass biochars originating from the high presence of cellulose and hemicellulose in the raw biomass. The pH values for all the biochars are in the alkali range typically found for the higher biochar production pyrolysis temperatures.

4. The Potential for Energy Recovery from the Pyrolysis Bio-Oil and Biogas

Although the focus of this review is on biochar production, it is important to take into account the two major by-products, biogas and bio-oil, because their effective utilization will have a tremendous benefit on the economic attractiveness of the pyrolysis process package [11]. Besides biochars, the pyrolysis products from biosolids include bio-oil and biogas, which are associated with the energy content that can be potentially recovered and utilized. Table 3 presents a summary of high calorific values or higher heating values (HHV) reported by several studies.

Table 3. HHV of bio-oil and biogas from the literature.

Reference	Bio-Oil HHV	Biogas HHV
[105]	27.8–31.4 kJ/kg in nitrogen and hydrogen atmosphere	-
[106]	12.19–22.32 MJ/kg	-
[107]	Energy yield of 1042–7762 kJ/kg-fuel	Energy yield of 22–3745 kJ/kg-fuel
[108]	25.1 MJ/kg	-
[109]	23.9–27.9 MJ/kg	13–17.5 MJ/kg
[110]	36–39 MJ/kg-oil	-

The study conducted by [110] report the HHV of bio-oil and char only, where HHV of 36–39 MJ/kg-oil was observed for the process. The HHVs were not influenced by the operating temperatures nor the sludge type as per the study. Another promising results were demonstrated by the work of [107] in which the energy content of biogas and bio-oil was always greater than the energy required for the pyrolysis study.

Woody and non-woody biomass materials were used in the production of bio-oil and biochar, with the investigation of HHV of both products [106]. The HHV of bio-oil was comparable to other studies mentioned in Table 2, with values in the range 12.19–22.32 MJ/kg. It is evident that the slight variations in the reported values for HHV are due to the type of biomass used, its composition and the type of pyrolysis used. Moreover, bio-oil HHV was influenced by the inert environment used with heating value increasing from 27.75 MJ/kg to 31.40 MJ/kg when using nitrogen and then hydrogen in the work of [105]. The results imply the importance of the type of gases in the subsequent values of HHV of bio-oil products.

The energy recovery from both streams comes with some challenges. For instance, the liquid oil is heterogenous with fractions that contain dissimilar HHV [111], in addition to being a corrosive material. It is, however, a very attractive source of energy when compared to both the gas and char products' energy content. The inclusion of the by-products into the economic analysis can improve the economic effectiveness by 2 or 3 fold [11].

5. Benefits of Biosolids-Derived Biochars

It is crucial to distinguish between biochars produced from biosolids and those obtained from other types of biomass materials. There are commonalities in the uses of all types of biochar and as such the same benefits are expected from biosolids-derived biochars. From the results of previous work on biochars produced from other types of biomasses, the different biochar products found successful use in amending soils in commercial potting soil mixes, green roofs, and commercial agriculture [31]. However, the same benefits from biochars derived from biosolids require further research to determine its applicability, opening room for more research opportunities in the applied side of this type of research.

The use of biosolids-derived biochars in reducing the uptake of soil heavy metals by plants, as an application in soil amendment and plant growth, have been reported by [112]. Additionally, high levels of electrical conductivity can negatively affect plant growth, which leads to a reduction in water uptake by plant roots and nutrient imbalances. Therefore, deriving biochars from sewage sludge pyrolysis and applying them in reducing salinity is considered a smart management option and remediation technique for enhancing plant growth.

Furthermore, the addition of different biochars to soils promotes plant growth. This addition is associated with interesting biological and chemical changes such that a shift in rhizosphere microbial and fungal communities to more favorable compositions for plant growth is attained. The same changes can be achieved through the contribution of some chemicals to the soil-system that lead to similar increases in nutrient concentrations [31,113,114].

There are several added advantages of the use of biochars, in addition to the before mentioned applications. For instance, and according to biochar studies, biochar addition reduces nutrient leaching rates from soils, which leads to improved stormwater runoff quality [115,116]. Another key advantage of the application of biochar in general and biosolids-derived biochar in particular is the reduction in soil greenhouse gases [117], making it an environmentally friendly solution to the release and production of such harmful gases. Lastly, biochar has been reported to suppress health risks associated with potentially toxic elements in rice. This is indicative of the fact that the application of biochar produced from wastewater byproducts is associated with a reduction in cancer risk resulting from the edible consumption of crops planted in soils treated with such biosolids biochars [118].

6. Conclusions and Recommendations for Future Work

In this review, the use of the pyrolysis process in converting biosolids into the value-added biochar products was explored. Municipal wastewater facilities generate large volumes of biosolids including treated sewage sludge. This is a result of the continuous increase in population and urbanization, which in turn require upgrades to existing facilities or the commissioning of new treatment plants. Moreover, several pyrolysis technologies were reported in the literature and biochar yields were observed in the previously mentioned studies to be higher than those obtained from the plant-based biomass and other types of wastes. Only one study found in the literature reported a lower yield of biochar that is derived from biosolids when compared to other feedstocks. However, other properties and characteristics in the same study were reasonable. There is a need to further investigate and compare the use of biosolids against other feedstocks. Also, it is recommended to study the use of co-pyrolysis [119] and catalytic co-pyrolysis [120] and the use of biosolids in blends with other feedstocks and examine the impact on the final product (e.g., yield, sorption capacity, etc.). More R&D is required on the pilot scale testing which is very limited for biosolids and co-pyrolysis [119]. Biosolids are composed of nutrients and energy content that can be utilized in different highly beneficial applications. The products from the pyrolysis of biosolids can be implemented in agriculture, water treatment, and energy processes, among other uses.

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