Synthesis of Engineered Biochar from Green Waste and Its Application

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Abstract

Biochar has raised a great deal of interest in the research field. The feedstock of biochar commonly from biomass or biowaste such as dry leaves and twigs, rice husk, and wheat straw; which are widely available and low-cost. Furthermore, it can be utilized to reduce contaminants, carbon sequestration, and soil amendment. The feedstock and synthesis method of biochar affects its physicochemical properties and various applications. The production of biochar was generated by thermochemical conversion in anaerobic (oxygen-deficient) conditions. Some research have been conducted to produce biochar using pyrolysis, gasification, torrefaction, and hydrothermal carbonization process. Biochar can be modified by physical, chemical, and biological methods. Based on its variety of feedstock, biochar production methods are categorized into two major types; dry-based method and wet-based method. In this study, we itemize efficient production methods of biochar from agricultural waste for consideration. Subsequently, we explicate the intended application of biochar in an industrial scale.

Keywords: biochar, hydrothermal carbonization, wet method, dry method

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1. Introduction

Green waste is an inscapable by-product, resulted from the green public areas preservation, urban parks, and agriculture. In this context, we can frequently find it in urban areas, office, schools, and universities. Green waste from agricultural sector is composed of herbaceous biomass consists of tree or plant parts as a residue of garden trimmings [1]. According to the waste management data by Direktorat Jenderal Pengelolaan Sampah, Limbah dan B3 and the Direktorat Penanganan Sampah of Indonesia, the green waste such as leaves, twigs, and wood waste produced during 2021 reached 13.1% of the total waste in Indonesia [2]. Similar to other types of waste, this created a major issue that must be faced to buttress our society. In this case, utilizing green waste for implementation of cost-effective bioenergy production can be a potential solution.

Biochar has been highlighted by the researchers in recent years as the bioenergy products from biomass waste, for instance, sugarcane straw [3], acacia tree [4], [5], [6], conocarpus [7], Bermuda grass [8], and bunch of forest litter, fallen-shredded leaves, twigs and branch cuttings generated by urban landscape maintenance or lopping of trees [9], [10], [11], [12], [13]. Biochar derived from green waste has many advantages for environmental sustainability, such as removing contaminants [8], [14], [15], improving soil conditions [4], [16], and reducing greenhouse gases[17], [18], [19]. The biochar derived from biomass is a highly rich source of carbon [20]. The production of biochar has now sought the real-world interest nowadays for the effective adsorption purposes [21]. Biochar also shows the potential to complement solid fuels, while addressing important issues related to the environment [22]. Actually, there are still a few researchers have conducted studies on biochar from green waste, whereas green waste is closely related to daily human life. This study is focused on summarizing various effective methods for producing engineered biochar from green waste. Engineered biochar derived from green waste can be used in a variety of sustainable applications which are also useful for industrial purposes.

2. Biochar Production Method

Biochar is characterized as a carbon enriched solid product generated by thermoconversion process of organic molecules in an oxygen-limited environment, with excellent physical and chemical characteristics [8], [23]. It used widely in agricultural, environmental, and biorefinery operations owing to its decreased density, enhanced stability, and

adsorption capacity [24]. Biochar plays a vital role in decreasing atmospheric greenhouse gas emissions [24], enhancing soil fertility [25], and contributing for soil carbon storage [26]. The unique properties of biochar such as wide surface area, stability, high porosity and functional group are corresponding for various application in worldwide [27]. Even more, biochar has rapid and simple production method, low-cost [28], recyclability, and environmental safe [29]. Biochar overcomes the disadvantage of traditional activated carbon's expensive price [30].

The thermoconversion process used for biochar production can be either biochemical or thermochemical. Biochemical usually use the role of microorganisms during the process [31], [32]. Whereas the most widely applied process is the thermochemical conversion process. Thermochemical conversion of biochar in terms of operating conditions and yields can be classified into four: pyrolysis, hydrothermal carbonization, gasification, and torrefaction [24], [33]. The differences can be shown on the Table 1. According to the type of media used during the process, biochar production methods can be run with dry process or wet process. The dry process here includes pyrolysis, gasification, and dry torrefaction. While the wet process requires a liquid to the process which are hydrothermal carbonization or wet torrefaction.

2.1. Dry Process

Pyrolysis is a thermochemical process to convert organic matter into biochar, bio-oil, and syngas in an anaerobic condition that may be used to treat a wide range of biomass-based products at temperatures ranging around 350 to 900 °C [34], [35]. Overall, the primary mechanism of pyrolysis consists of a process of breaking chemical bonds from raw materials and releasing volatile compounds in the reactor under thermal conditions, which will undergo further reactions in the secondary mechanism [36]. Some experiments on biochar production using pyrolysis process have been carried out by Kaudal [37] using municipal softwood garden waste, Bin Ji [38] using fallen Magnolia Grandiflora L. leaves, Ben Salem [39] using Date Palm leaf (DPL) waste, and Wang [40] using *Platanus acerifolia* leaves as raw material.

Since biochar is not the primary product of pyrolysis process, the yield of biochar produced depends on the temperature, residence time, heating rate, and feedstock used[24]. Increase in pyrolysis temperature and residence time causes decreasing biochar yield [8]. Biochar produced from pyrolysis has comparatively less surface area, low pore volume, and less functional groups. Pyrolysis is well known for converting biochar into rich carbon products [41], [42]. It can be classified according to its operating condition (e.g., heating rate and residence time): slow, intermediate, fast, flash, vacuum, and microwave pyrolysis [6].

2.1.1. Fast Pyrolysis

Fast pyrolysis is commonly carried out at high temperatures (550-1000°C) and heating rates (≥200 °C/min) [34]. If the addition of biomass or feedstock occurs when the reactor temperature reaches a desired level with several seconds of residence duration, then it named fast pyrolysis [24]. Abdallah et al. [43] has conducted a fast pyrolysis on

walnut, pumpkin, and corncob samples then exhibit complete conversion (dm/dt=0) at lower temperatures than slow pyrolysis samples. For example, the biochar obtained after fast pyrolysis by steam-based biomass activation of corncob residue and coconut shell produce biochar with high surface area of 1210 m^2g^{-1} after ash removal [44]. This is convenient previous reports that high heating rates promote the development of favorable biochar characteristics that support gasification.

A number of fast pyrolysis technologies have been widely used, such as fluidized bed systems, systems using ablative reactors, and systems using Pyrolysis Centrifuge Reactors (PCR) [45]. The high heating rate pyrolysis deteriorates natural morphology to increases surface area and generates higher micropore volume [43]. Biochars produced from fast pyrolysis are characterized by relatively high volatile matter contents[46]. Yet, fast pyrolysis produce less biochar than other type of pyrolysis. The products by fast pyrolysis are 65–75% of bio-oil, 10–20% biochar, and 10–15% syngas[47]. Since the yield of biochar only up to 20%, this process is suggested to produce liquids rather than solid biochar[48].

2.1.2. Intermediate Pyrolysis

Intermediate pyrolysis is generally utilized to make a balance products between liquid and solid phase. This type of pyrolysis operates in between slow and fast pyrolysis condition [49]. Intermediate pyrolysis occurs in the temperature between 450 and 550 °C while takes 10–30 s to produce less biochars than slow pyrolysis [20]. This method equipped with a cylindrical tube reactor, cyclone, quenching system and electrostatic precipitator[50]. But a fixed bed reactor also can be used for this process, as if Ahmed [6] used acacia tree to produce biochar with high percentage of carbon and hydrogen content which is suitable for energy applications [51] with a decent calorific value analyzed by SEM-EDX. The biochar produced by intermediate pyrolysis commonly applied for energy production or as feedstocks to produce different value-added products and chemicals[6]. Due to low quantity of reactive tar over the fast pyrolysis, it can be used directly in boilers and engines [52]. Moreover, the biochar has a brittle texture and less toxic compounds [53]. It is suitable for further applications, such as a solid fuel or as a soil amendment and/or as a fertilizer.

2.1.3. Slow Pyrolysis

Slow pyrolysis exhibited a relative low heating rates (<10 °C/min) whereas a long residence time (10 min-hours) over a wide range of temperature (300-700 °C), accompanied with relatively higher yield of biochar compared to other type of pyrolysis [54]. The yield of biochar produced in this process ranged from 30 to 60% [24], [34]. Biochar from lab-scale slow pyrolysis [55] has good quality in O/C and H/C molar ratio and specific surface even still low. Pyrochar also presents a low amount of Polycyclic Aromatic Hydrocarbons (PAHs) [55]. In slow pyrolysis, the vapor phase reaction in which the pyrolysis steam persists for a long time in the reactor at low temperature will continue to increase the char yield [48]. Modern SP often takes place in continuous reactors, e.g., drum pyrolysers, rotary kilns, or screw pyrolysers [45].

Now with technological advancements, the flash, vacuum, and microwave pyrolysis becomes the recent techniques used for biochar production. The pyrolysis process known due to its extremely fast nature process called flash pyrolysis. It is modified form of fast pyrolysis. Flash pyrolysis depends upon by which heat and mass are transferred across the feedstock along with chemical kinetics of the reactions and phase transition behavior of the biomass [36]. Moreover, flash pyrolysis has limited application on industrial scale because of the reactor configuration in which the input feedstock reside for a very short time under the high temperature range [24], [49].

In case of vacuum pyrolysis, the process taken place in very low pressure between 0.01 and 0.20 MPa and temperature range between 450 and 600°C [56]. The vacuum (low pressure) conditions are used to remove steam instead of cleaning gas [49]. This process does not require any carrier gas which is used in most other pyrolysis techniques [57]. The rapid removal of organic vapors formed during primary pyrolysis also reduces vapor residence time significantly which reduces the secondary reactions [49]. This process allows the formation of large quantities of pyrolysis oil and solid char. In terms of viscosity and calorific value, the organic phase formed by vacuum pyrolysis reveals promising qualities [58].

While the most recent advancing method in pyrolysis known as microwave pyrolysis. In microwave pyrolysis, the energy is delivered directly into materials within an electromagnetic field[59]. Microwave-assisted pyrolysis provides several benefits over traditional pyrolysis, including uniform overall heating, fast heating rate, volumetric and selective heating [20]. This method produce high quality biochar because of dielectric heating in less temperature as well as heat energy is transferred and increase the calorific value of biochar [24]. The downside of microwave pyrolysis is that it requires catalyst as well as microwave absorbers to improve the heating [59] and its electricity consumption [20].

2.1.4. Gasification

Gasification needs a high temperature (often greater than 700 °C). Temperature has key role as it determines the production of hydrogen, carbon monoxide, and carbon [24]. This process is basically decomposed biomass as carbon source into syngas with limited oxidizing agents, including a mixture of oxygen (O_2), air, steam, and gas [60], [61]. Biochar is actually known as the carbonaceous residue of the gasification process. Biochar quantity produced from gasification process is very much less than other method.

The mechanism of gasification can be summarized into four main stages, which are drying, devolatilization or pyrolysis, oxidation, and gasification [56]. Each step cannot be separated from the others clearly in terms of temperature and pressure [48].

2.1.5. Dry Torrefaction

Forestry and agricultural wastes are more suited for torrefaction process in which hemicellulose decomposition takes place at 240 °C and cellulose decomposition takes place above 280 °C [24]. Dry torrefaction is a thermochemical pre-treatment of biomass consists of slow heating rate (less than 50 °C/min) at 200 to 300 °C [62]. It is kind of incomplete pyrolysis that occurs in lower temperature [24]. Dry torrefaction is a typical method to improve the fuel properties of lignocellulosic biomass. It can improve biomass as cofiring materials for energy generation [63]. The four stages of dry torrefaction (Fig. 3) are the heating, drying (includes pre-drying and post-drying), torrefaction, and chilling phases process [56].

Similar to other methods, in dry torrefaction produced three type of products: biochar as solid product; permanent gases including hydrogen (H_2), carbon dioxide (CO_2), carbon monoxide (CO) and methane (CH_4); and condensed liquid consist of water, organic compounds and lipids[64]. Among the three, biochar is the primary product for about 70% mass and 90% energy of the raw biomass[64], [65]. The biochars by this process present more concentrated combustion range and are closer to coal properties [63]. Lee et al.[66] shows that biochar from spent coffee grounds through torrefaction process has higher resistance against biodegradation and thereby can be stored longer.

2.2. Wet Process

Hydrochar is a name that refers to the final product in the wet process of biochar production. This method occurs in the aqueous phase with the addition of water as a medium in the production process. Wet processes that have been widely developed are wet torrefaction and hydrothermal carbonization. Several studies have stated that the two methods are very similar due to the operating condition and working principle, but there are slight differences between the two.

2.2.1. Hydrothermal Carbonization

Hydrothermal carbonization (HTC) is a new technology to convert biomass by contacting the feedstock with hot pressurized water into solid rich-carbon material at temperatures of 180 – 260 °C[67] which has many chemical reactions[68] and then placed inside a sealer reactor [69]. The technology of HTC is based on the use of water at high temperatures and under-high pressures (subcritical water: 180 – 373 °C and 1.5 – 22 MPa)[70].

In hydrothermal carbonization occurs some chemical reactions includes hydrolysis, dehydration, decarboxylation (resulting in the realese of CO_2), demethanation, and aromatization[68]. HTC does not need drying pretreatment to minimize the intensive-energy used in the drying stage[70], it is essential for producing carbon-rich hydrochar by reducing the hydrogen to carbon (H/C) and oxygen to carbon (O/C) ratios [24]. The energy density of biochar increased with increasing temperature, with higher heating values [71]. Some researches found an optimum temperature of 250 °C for hydrothermal carbonization of waste biomass for the production of biochars for heat generation [55], [60], [71], [72].

HTC is a low cost and eco-friendly technology in the enclosed system without any chemical reagents, but only water as a carbonization medium [68]. Hydrothermal treatment also offers various advantages for biomass conversion including the lack of an energy-extensive drying process, high conversion efficiency, and relatively low

operation temperature among thermal method [71]. The biochar from hydrothermal treatment was composed of more alkyl moieties [73]. Hydrothermal biochar can be used to remove methylene blue, iodine and copper ions because of its high affinity. Jian et al.[74] has been calculated the maximum copper removal capacity of rice husk hydrochar at 220 °C using Langmuir and Freundlich models which resulting 169.3 mg kg-1 maximum copper adsorbed in wastewater. Furthermore, combination of hydrothermal carbonization and a subsequent low alkali modification has proved as an effective method to prepare a high-performance adsorbent [73]. These results indicate that the main adsorption processes of hydrochars are ion exchange and complexation [74].

2.2.2. Wet Torrefaction

Wet torrefaction is developed from the concept of hydrothermal carbonization, invented by the German Nobel laureate Friedrich Bergius [64]. It also treats biomass in the aqueous phase and pressurised condition (15 – 160 bar) at temperature range 175 – 225 °C for 10 – 60 minute to produce 70 – 90wt% of biochar yield[63]. Wet torrefaction process shown in Fig. 5 uses subcritical water conditions below its critical point of 374 °C temperature and 22.1 MPa pressure[65]. The complex reaction in the liquid medium and the different extraction efficiency of organics and inorganics can be achieved under the optimal wet torrefaction condition [75].

Yek et al.[63] exhibited that biochar from wet torrefaction process has potential catalytic approach to treat waste palm shell and generating a higher yield with improved properties. In other study, wet torrefaction also affected reactivity and structure of PIW-derived biochar more than that of POW-derived biochar [75]. Moreover, Jiang et al.[76] has been compared dry and wet torrefaction for production of pine biochar. It explained that both methods can significantly decrease the equilibrium moisture content of torrefied products. While the hydrophobicity of the biochar produced by wet torrefaction is better than that by dry torrefaction at the same temperature.

Wet torrefaction produces solids with energy density greater than that obtained from dry torrefaction [62]. The biochar produced has higher surface area and can realize the higher thermal efficiency with lower pollutant emission compared to dry torrefaction [75]. Its products exhibit more prosperous surface functional groups and higher crystallinity [63]. The development of microwave wet torrefaction can produce high porosity solid biochar which can be utilized as a higher value bio-adsorbent for environmental remediation [63]. Microwave wet torrefaction system coupled with steam can perform torrefaction and partial gasification simultaneously to convert biomass into porosity biochar [63]. In spite of the researches about microwave wet torrefaction process for biochar production from green waste was scarce, this process has been able to convert sludge [29], plant seeds and shells [77], or microalgae [78] into high-quality biochars. The microwave torrefaction significantly increased the energy density of pellets compared to conventional torrefaction [63]. Microwave wet torrefaction exhibited as a promising method to produce biochat and recorded a catalytic

torrefactiob with hight heating rate and lower mass yield conversion, also present high porous structure [63].

3. Physicochemical Properties

The operating conditions of biochar production exhibited obvious influence to its physicochemical properties, such as aromaticity, hydrophobicity, polarity, porous structure, and crystalline mineral components, etc [79]. This variability affects the performance of biochar in soil amendment, water and soil treatment, carbon sequestration and emission reduction [36]. Overall, biomass pretreatment, reaction temperature, heating rate, reactor type, flow rate, residence time, pressure, and post-modification method of biochar are the main operating parameters that affect the physical structure of biochar. For example, biochar formed at high temperatures has a large specific surface area and high porosity structure; and is rich in surface polar functional groups (H/C)[80]. Chiappero et al.[81] concluded that among its physicochemical properties, the surface area, porosity, hydrophobicity, and alkaline metal contents in the ash were the most significant properties of biochar.

3.1. Physical Properties

Biochar has been extensively researched for various environmental applications due to its physical properties: surface area, pore volume, bulk density, and pore diameter that indicate the distribution of porous structure and influence the activated adsorption sites [23]. The carboxylic (COOH), hydroxyl (OH), amine, amide, and lactonic groups are vital functional groups on the biochar surface that contribute to its adsorption capacity [42]. As well known, biochar with high surface area and porosity will have a higher adsorption capacity. These physical properties were influenced by temperature of the production process. Fig. 7 represent that surface area, pore volume and pore size of green waste derived biochar increase significantly with increasing pyrolysis temperature. In addition, hydrothermal conditions of the reaction also related to the escalation of specific surface area: the degradation/ depolymerization of hemicellulose and cellulose generated the formation of slightly porous structures of hydrochars [82].

Biochar develops a porous surface during the production process due to increased water loss during dehydration process [27]. Moreover, the ash content of biochar affected by high pressure steam which promotes biomass decomposition and resulting in ash accumulation. The calorific value and ash content of biochar increases with temperature, which is composed of a fixed carbon content accompanied by a simultaneous decrease in the oxygen and hydrogen content [83], [84]. Ronsse et al.[10] have investigated the physicochemical properties of biochar from agricultural waste. The biochar produced from green waste shows an increase in ash content and fixed carbon content as the slow pyrolysis temperature increases. Conversely, when the biochar yield reaches 98.4%, it only produces very low fixed carbon content of 25.7% and an ash content of 3.6% at a temperature of 300 °C.

3.2. Chemical Properties

Some factors that may influence the chemical properties of biochars include the types of feedstocks,

pyrolysis temperature, SSA, and DOC content of biochar [85]. Biochar principally contains five elements: hydrogen, oxygen, nitrogen, sulphur, and carbon [24]. A study reported by Chen et al. [86] compared the chemical properties of woody biochar (WB) and pig carcass biochar (PB) using method based on Yang et al. . This case shows that WB had higher C% and specific surface area than the PB [86]. In the other hand, polymerization in hydrothermal carbonization are intensified with temperature rise. The produced hydrochar becomes more chemical stable. These are detrimental to the reactivity of carbon substrate material [82]. In general, biochars have neutral to alkaline pH (6.11–10.01) [80]. Biochar is generally alkaline and has a high pH value at higher operating temperatures [10]. Srinivasan and Sarmah [14] have attested this by examining biochar from green waste at various temperatures of 350, 450, and 550°C. In the experiment, the pH of pyrolyzed biochar at 350°C only 5.3. Meanwhile, green waste derived biochar (GWB) at pyrolysis temperatures of 450 and 550 °C showed pH value of 5.8 and 8.4 respectively. This correlation also proved by Méndez[87] in the previous studies on sewage sludge biochar production and M. Nisar[8] that produced green waste derived biochar with the highest pH value of 11.88 from a pyrolysis temperature of 800 °C. This could be obtained by the transformation of minerals and metal oxides into alkaline media during pyrolysis. In addition, Bin Ji [38] has observed a correlation of increasing the pH value of biochar from fallen leaves of *Magnolia Grandiflor L.* ranging from 5 to 12 enhanced the adsorption capacity of the biochar, as shown in Fig. 7.

4. Biochar Engineering

Biochar properties can be affected by pre-treatment and post-modification during the production process[27]. In addition to the influence of the type of raw material and the operating conditions, the engineering process of biochar also affects its efficiency [88]. Engineered biochar can be defined as a carbon-rich solid fabricated from biomass or waste materials using thermochemical conversion method combined with modification technique such chemical, physical, or biological [34].

Engineered biochar can becomes a viable, cost-effective and long-term platform for environmental applications, especially for adsorption due to changes in its surface area, H/C molar ratio, carbon content, aromatic structure, and ash content [88]. Changes in the functional portion of the surface facilitate electrostatic interactions, ion exchange, and/or complexation mechanisms[88]. Engineering biochar has been reported to produce biochar with higher specific surface area, adsorption capacity, and cation exchange contaminants from wastewater[34]. Sugarcane leaf biochar has been engineered by Suwanree et al.[89] to reduce biomass burning in the field. A pre-treatment applied with DAP or PA in the presence of MgO produces biochar with slow P release which is controlled by the dissolution of $Mg_2P_2O_7$ crystals formed during pyrolysis. There are physical and chemical activation method can be used to enhance the biochar physicochemical properties.

4.1. Physical Modification

In physical method, enhancing the porosity if biochar at high temperature and its specific surface area can also be observed. Based on many literatures, parameters such as activation temperature and time is directly proportional to the porosity growth and pore size distribution[24]. For example, the activation using H_3PO_4 steam conducted by Zhang[90] which causes the rate of color removal and total organic carbon in $Al_2(SO_4)_3$ solution by coconut shell derived biochar are 96.2% and 93.8%, respectively. Other physical activation was also reported by Shakiya et al.[91] to increase oxygen-containing functional groups on the surface of biochar thereby increasing the efficiency of pollutant adsorption.

Physical modification biochar recognized to enhance specific surface area, pore structure with more plentiful micropores, mesopores, and oxygen-containing functional groups, resulting in a higher adsorption capacity for heavy metals, nutrients, and organic pollutants than unmodified biochar [92]. Also compared to pristine biochar, ball-milled nano-biochar has been reported improved physicochemical properties including larger external and internal surface area and more acidic surface functional groups. Thus, the removal of contaminates was much higher than that of bulk biochar [22].

4.2. Chemical Modification

The chemical method is heating biochar in the presence of various types of chemicals and non-reactive gases [34] at 450-900 °C [93]. Biochar is impregnated with acidic or basic chemicals to oxidize and improve the availability of functional groups, cation exchange capacity, and surface area [34]. Chemical activation can be carried out through one-step or two-step thermal treatment[15]. Char is doped with chemicals so that the micropore surface is formed by dehydration and subsequent oxidation [48].

Although chemical activation has several disadvantages, such as corrosion of equipment by chemicals, difficult chemical recovery, and high chemical costs [48], it is more preferred because of high efficiency, low temperature, higher carbon content, increased surface area, and increased microporosity [24]. Yadav and Jagadevan [94] has been conducted a research analyzing adsorption mechanism of engineered biochar on groundwater. Their iron-modified biochar BCF-700 exhibits maximum removal efficiency due to thermal stability, specific morphological structure, surface functionality coupled with very high surface area and the presence of varying oxidation states of iron. However, the chemical modification approach is costly and lengthy as it often requires extra washing steps to remove the excess chemicals that remain [34].

5. Application
5.1. Biochar as Fuel Energy

Biochar produced by the pyrolysis method has a high calorific value and high carbon content, making it suitable for power production and other heat uses [24]. In terms of environmental and metallurgical considerations biochar which injected in blast furnace tuyeres is a viable substitute to coal. The effect of using biochar instead of coal in a blast furnace reveal that CO_2 emission might be reduced by 18-40%[24]. Yan Yu et al.[95] found the comprehensive flammability index S was increased to 22.1 and 19.8 for their

HT180 and HT220 pellets. The combination of hydrothermal carbonization and pelletization is efficient for using discarded Ginkgo leaf residue as a solid biofuel due to its high durability, minimal water absorption and improved pyrolysis performance. The cellulose and hemicellulose contents in lignocellulosic biomass enable biochar to replace coal by extending its life cycle[29]. Using the FTIR spectrum, Kim et al.[70] also confirmed that their biochar produced by HTC at 220 °C witnesses the change in chemical structure shown by its CO bond peaks and potentially applied as solid fuels.

5.2. Biochar as Adsorbent

Biosorption defined as the property of certain types of biomass (or their derivatives) to bind the selected molecules or ions in aqueous solutions [28]. Biochar adsorption processes have an advantage over other methods, especially because of the simplicity of the procedure and cost-effective and eco-friendly adsorbent [96]. Since it has wide surface area, porosity, and an abundance of functional group, biochar is possible to adsorb heavy metal and aromatic molecules which will get adhered to surface, eliminating pollutants from wastewater and soil [24]. But, the adsorption characteristics of biochar depend on the feedstocks used [48] and the operating temperature applied during the production process. Liao et al.[97] has conducted experiments to produce biochar from bamboo, rice husk, and corn cobs at different temperature to test the adsorption ability of the biochars. It found that the specific surface area and total pore volume change with increasing pyrolysis temperature. The highest economic value reached by rice husk biochar.

Similar research has been investigated by James et al.[98] using biochars form rush *Juncus effuses* for minewater remediation. Aromaticity and the specific surface area are the two factors that entirely relies on the adsorption capability of the pollutants present in water [24]. The presence of carboxylic acid and hydroxyl groups on the surface of biochar is the main principle behind the heavy metal adsorption [24]. Utilizing biochar as adsorbent can contributes to minimize the total cost of adsorption and increase in oxygen groups in biochar also increase contaminant adsorption [27].

Recently, many researchers have studied the adsorption mechanism of heavy metal by biochar derived from green waste. It has reported that biochar has excellent adsorption capacity for heavy metals. Jain et al.[74] illustrated in Fig. 9 that the oxygen-containing group on the biochar surface are associated with the hydrolysis and decomposition of the main biopolymer components in rice husks. Therefore, the ion metals in aqueous solution can be removed by functional groups through iron exchange and complexation reactions. Yin et al. (2022) converted *Platanus orientalis* Linn leaves into an oxidant-modified biochar and showed high performance for Cd^{2+} chemical adsorption. Similar work by F. Liu et al. [100] reported that lotus leaves biochar can contributed to the degradation of SMX in polluted water bodies.

5.3. Biochar for Construction Industry

The world now is looking for a substitute for cement for the construction of building to reduce the GHG emissions to the atmosphere due to construction. The reduction in cement consumption and net negative CO_2-equivalent associated with production of biochar [101]. When the biomass undergoes slow pyrolysis, it reduces the surface area of the biochar and the carbon free radicals in it which helps in creating a low flammability property of the biochar produced[24]. Javed et al.[102] reported that biochar-based cement paste requires slightly more water to produce an adequate mixture due to its large surface area. It absorbs more water and resulting in a more cohesive mixture. The best result of compressive strength test were achieved at a replacement rate of 2% by weight of biochar relative to cement for biochar-based mortar.

Biochar may be an appropriate candidate for the production of green concrete. The incorporation of agricultural or green wastes biochar into concrete had great effects on the compressive and tensile strengths [103]. The good mechanical properties was achieved due to their high specific surface area and amorphous silica levels. The use of biochar in concrete allows agriculture and forestry wastes to adsorb carbon instead of releasing the CO_2 and methane. In this case, it prevents the climate change effects of concrete production. According to Tommaso and Bordonzotti [104], it is estimated that if only 1% of biochar (by mass of concrete) is incorporated in concrete. It can be calculated that roughly 0.5 Gt of CO_2 would be sequestered each year by the concrete sink convenient to about 20% of the total yearly emissions of CO_2 generated by the cement industry.

Biochar has low thermal conductivity and chemical stability that plays a vital role as suitable material for construction [24]. The temperature and feedstock used in biochar production process can impact the pore size present on the biochar, which is the most important factor of low thermal conductivity [24]. Several studies of biochar applications using various types of green waste have been summarized by Liu et al.[105]. Regarding the long-term behavior, the effect of biochar on strength development is more visible in compression. An experiments conducted by Sirico et al.[106] showed the best improvement was obtained during 365 days of dry treatment by the addition of 5% biochar, the average increase in compressive strength was 12%.

5.4. Biochar for Soil Amendment

Biochar is an excellent supplement for agricultural soils due to its unique properties. The use of biochar as a soil amendment is usually proposed sequentially to increase groundwater retention, especially in dry climates that experience water scarcity [18]. It has been developed to modify soil permeability, moisture content, pH, and size of unstable C and N pools in soil and which significantly affect soil CO_2 emissions [20]. Many studies have also shown that biochar can help reduce greenhouse cutting-edge and nitrogen losses if applied in agricultural soils [24]. Application of biochar to soil can not only storage carbon, but also improve the soil quality by neutralizing acidic soil, enhancing the CEC of soil, and increasing the activity of soil microorganisms [48].
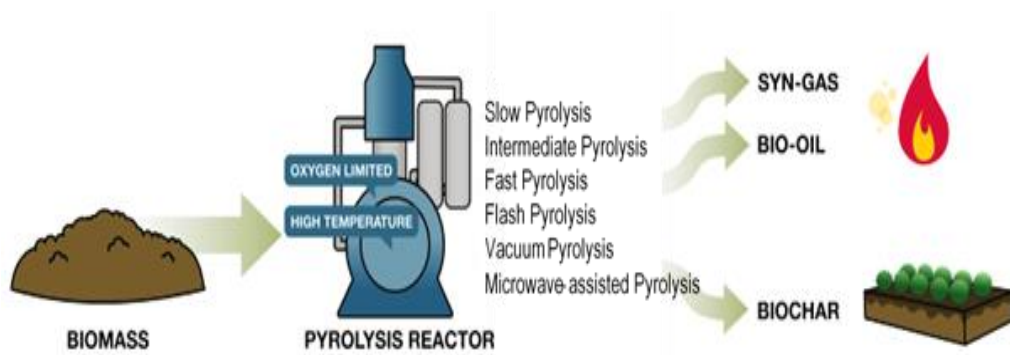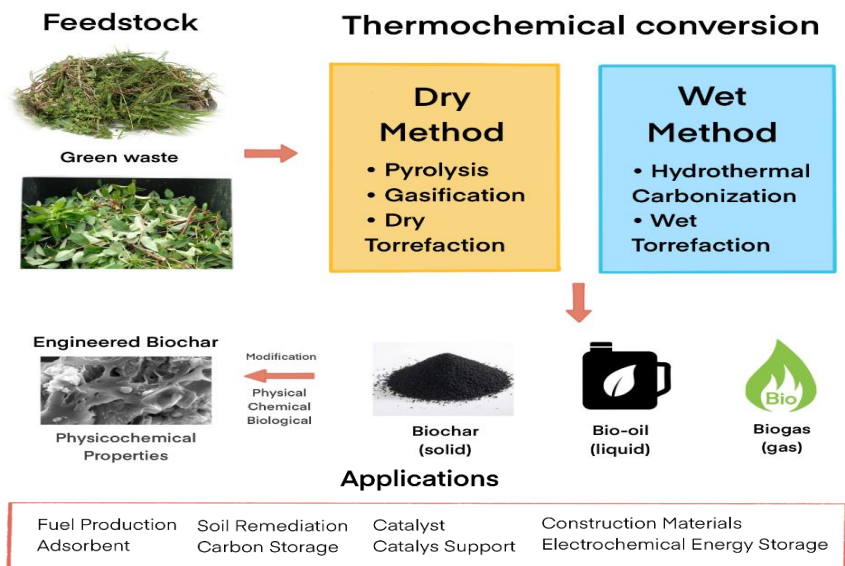
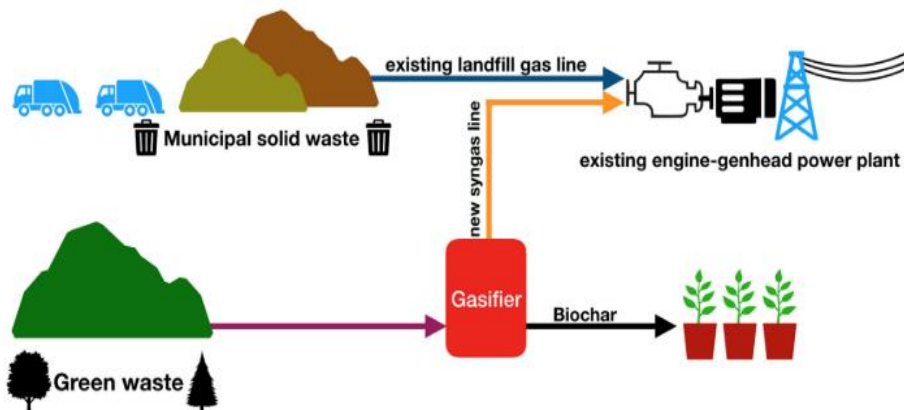**Figure 1.** General Concept of Pyrolysis. Adapted from Sanford et al.[111]

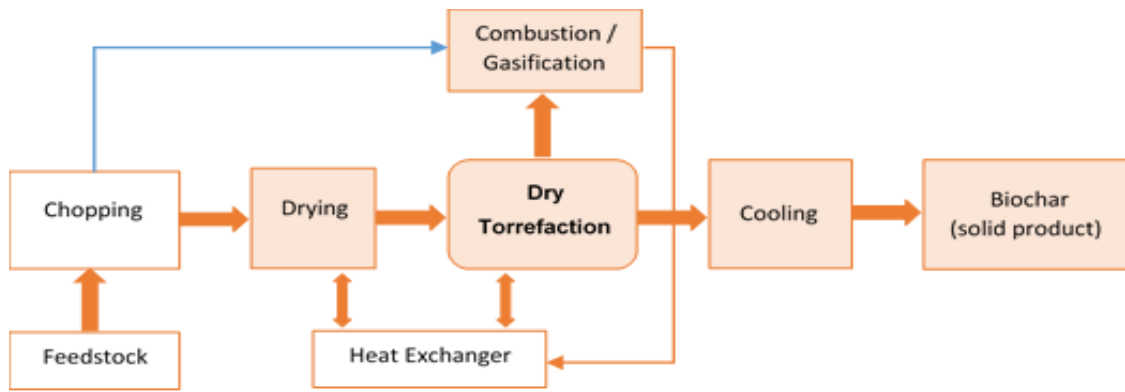**Figure 1.** GreenWaste Gasification System[1]

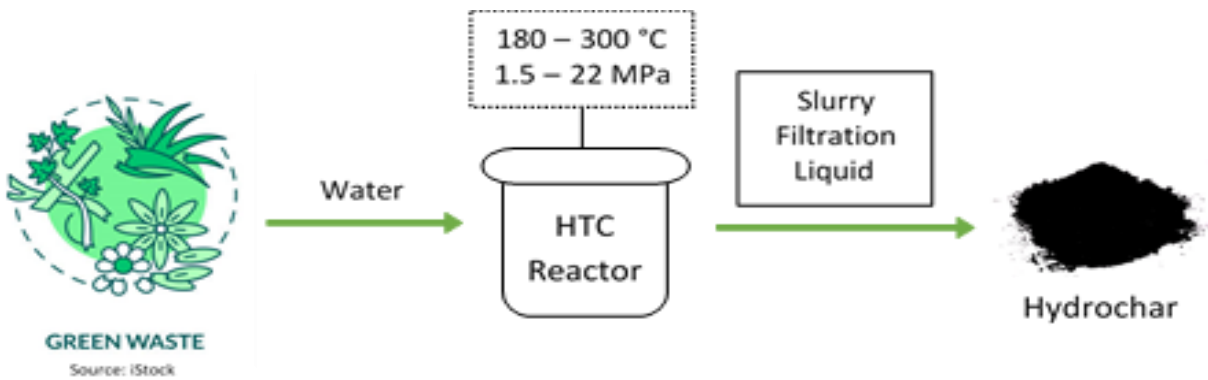**Figure 3.** Process Diagram of Dry Torrefaction with Heat Integration

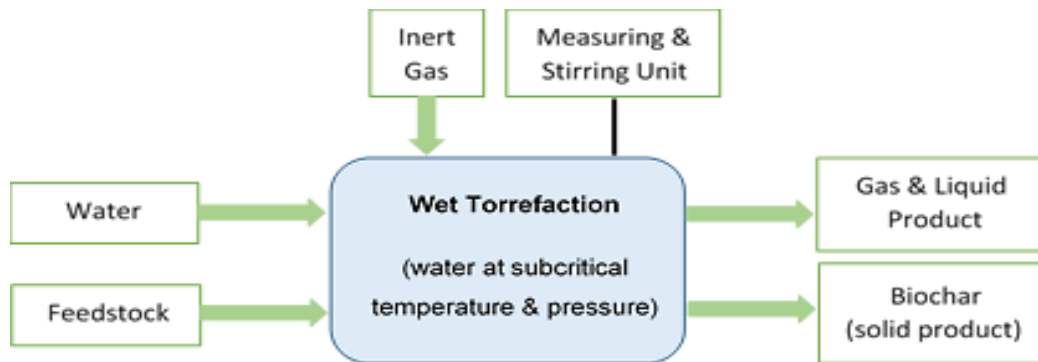**Figure 4.** Hydrothermal carbonization of Green Waste. Adapted from [27]

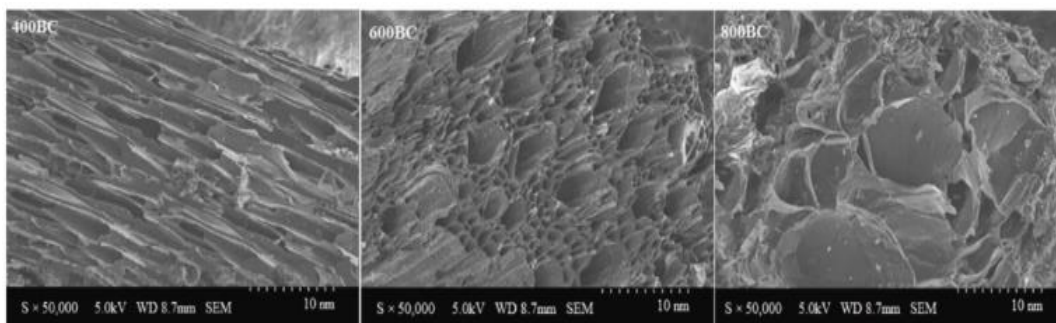**Figure 2.** Wet Torrefaction Basic Process[65]

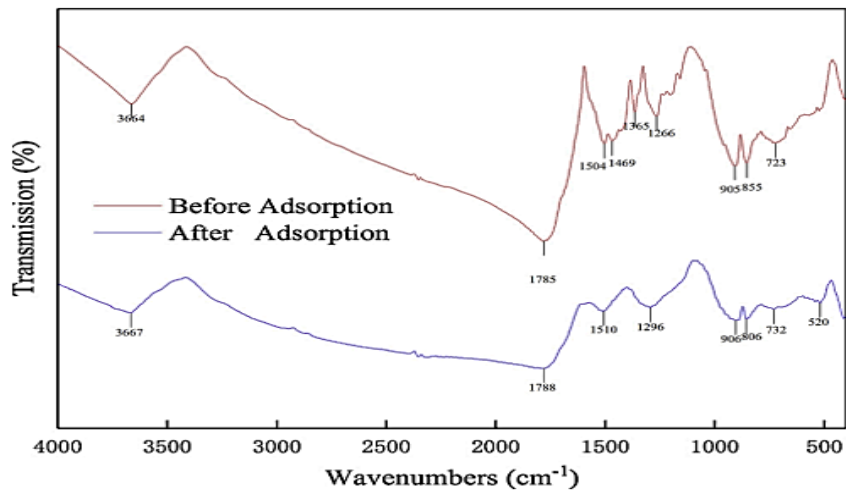**Figure 3.** SEM images of 400BC, 600BC and 800BC [8]

Figure 4. FTIR Analysis of *Magnolia grandiflor* Biochar [38]
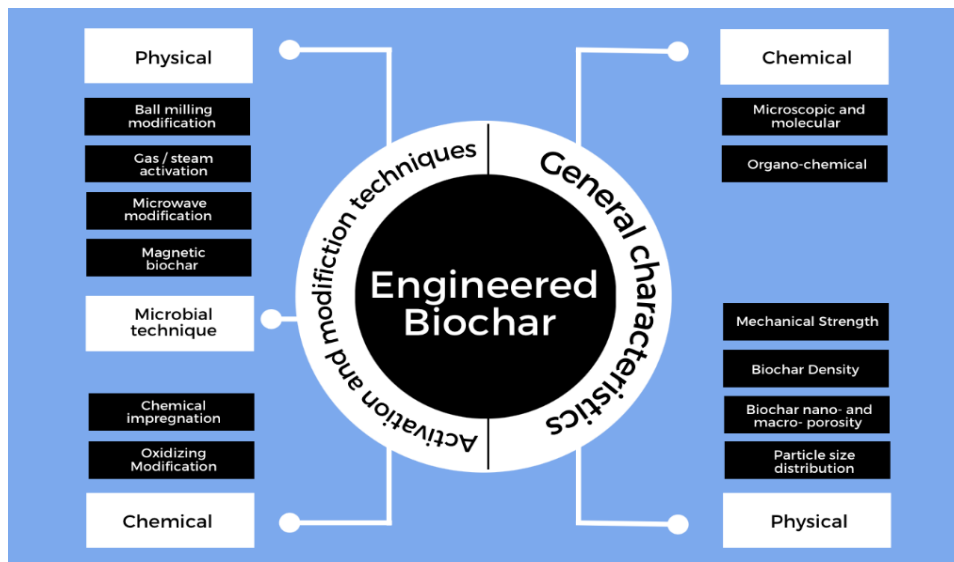

Figure 5. Characteristics and production (i.e. activation and modification techniques) of engineered biochar[92]
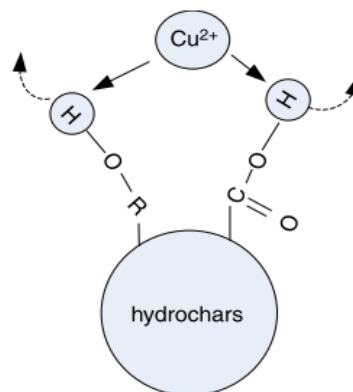

Figure 6. The Mechanism of Ion Exchange and Complexation for Adsorption of Cu^{2+} on Hydrochars

Table 1. Biochar Production Methods

Production Process		Operating Condition				Yield of Biochar	Reference
		Temperature (°C)	Heating Rate (°C/s)	Residence Time (s)	Pressure (MPa)		
Dry Process	Slow Pyrolysis	$300 - 500$	$0.1 - 1$	$300 - 10000$	0.1	30–50%	21,22
	Intermediate Pyrolysis	$350 - 650$	$0.25 - 10$	$30 - 1500$	0.1	20–35%	23,24
	Fast Pyrolysis	$500 - 1200$	$10 - 1000$	$0.5 - 10$	0.1	10–20%	8,21
	Flash Pyrolysis	$700 - 1200$	>1000	<1	0.1	–	6,24
	Vacuum Pyrolysis	$300 - 600$	$0.1 - 1$	$0.001 - 2$	$0.01 - 0.2$	28–32%	11,24
	Microwave-assisted Pyrolysis	$400 - 800$	>1000	–	–	~30 %	19,25,26
	Gasification	$750 - 2000$	$0.8 - 1$	$10 - 20$	$2 - 10$	5 – 10%	24,27
	Dry Torrefaction	$200 - 300$	–	$600 - 7200$	0.1		28
Wet Process	Hydrothermal Carbonization	$180 - 300$	<1	$3600 - 57000$	$1.5 - 22$	50–80%	21,29
	Wet Torrefaction	$180 - 265$	–	$300 - 14400$	$1 - 20$	60–88%	30,31

Ash in biochar contains hydroxide and carbonate functional groups which in dissolution result in an increase in the pH value of the soil [85]. Biochar has shown enhanced crop production due to the improvement in the chemical, physical, and biological qualities of soil [24]. The biochar obtained from the copyrolysis of rice husk by Bian et al.[41] contained high nutrients. The cultivation of cabbage in their country (Brassica chinensis L.) at 0.5% yield improved significantly. As a result of its surface features and basic structure, biochar has gained considerable interest in soil remediation in agricultural sectors [27]. In a long-term experiment on oaks, Tanazawa et al.[107] reported that P_n increase in trees grown in biochar amended soil due to improvements in physiological activities (i.e., higher maximum carboxylation rate and maximum electron transport than not amended ones). However, they assumed that the effects observed may only help the tree for a limited period (tree establishment phase).
The application of biochar can moderate fluctuations in soil temperature by narrowing the temperature range[108].

Biochar also can effectively improve soil structure and increase groundwater availability [85] by immobilizing both inorganic and organic pollutants by immobilizing both inorganic and organic pollutants [109], [110] due to its high specific surface area and cation exchange capacity, porous structure, active surface functional groups, and aromatic surfaces. Moreover, biochars can react with heavy metals in the soil to reduce their mobility and bioavailability through physisorption, chemisorption, and precipitation reactions. In addition, biochar effectively reduces metal uptake by plants [85].

5.4. Biochar for Electrochemical Energy Storage

Carbon-rich materials are commonly used in electrochemical energy storage devices, which have high electrical conductivity, strong mechanical properties, and easy accessibility [60]. The rich functional groups and good cation exchange performance of biochar indicated its potential as electrochemical materials, such as fuel cell [112], supercapacitor [113], electrochemical biosensor, etc [114]. Between the conventional thermochemical and capacitor batteries, biochar as superconductor has high power density, long life and fast charge/discharge capability, which can be used as uninterrupted power source in electric vehicles, digital communication systems, etc [60]. Engineering the appropriate electrode is the key to fully realizing the potential of microcarbons in electrochemical energy storage.

A biochar produced from biowaste such as wood straw, chips, grass, and garden waste at 800 °C [115] showed a specific capacitance of 228 Fg^{-1} at 1 Ag^{-1} in 1 M H_2SO_4 and a rate capability of ~84.1% when current density increased up to 191.9 Fg^{-1}. Intrinsically, the biochar-800 also showed an excellent energy density of 7.91 $Whkg^{-1}$ in current electrolyte solution and improved cycling stability 88% capacitance retention after 5000 cycles at a high current density of 10 A g^{-1}. However, based on the study of Wan [116], the electrochemical test results showed that the conductivity of biochar decreased along with the lower adsorption capacity of biochar to ions. In short, after the biochar participates in the catalytic process, the pore structure is not damaged, but the surface adsorption capacity decreases.

5.5. Biochar as Catalyst Support

Due to high stability and decent textural properties such as high surface area and mesoporous structure, biochar could be used as catalyst support. Biochar has been used as catalyst support in various reaction systems [117]. A biochar obtained by steam gasification process applied to support nickel catalysts for tar cracking [117] then resulting 6 wt% Ni loading catalyst and shows good catalytic cracking performance. Compared with other support materials such as Cu, Co, K, and Mo, Ni has low cost and low toxicity. Nitrates and chloride solutions of Ni, such as $Ni(NO_3)_2$ is often used as impregnation precursor [118].

Most studies have reported that the enhancement of catalytic activity by biochar can be achieved by providing a stable mesoporous structure. Additionally, biochar could contribute to catalytic effects due to the presence of AAEM, which could catalyze certain reactions [119]. For catalyst support preparation, a wide range of biomass has been used covering different types of woody and non-woody biomass and interestingly, an attempt using seaweed biomass was also reported. In addition, there are some studies used used rice husk, corn stalk, and wheat straw for tar cracking [120]. The benefit of using biochar as catalyst support is to help improve the dispersion of active metal and provide higher metallic sites with smaller crystallites to improve the catalytic activity and selectivity [119]. One point worth mentioning is to further investigate the synergetic effect between metal and biochar support.

5.6. Biochar as Catalyst

Biochar can play a role as catalysts, which have been widely applied in environment [121], energy [122], agriculture [93] and other aspects. Its relatively larger specific surface area benefits its catalytic activity by providing more active site for the reaction. As carbon material, biochars can play a role as green and efficient catalysts in advanced oxidation processes to remove various organic contaminants, as they are chemically stable and can be reused in reaction solutions without introducing metal ions [119]. Biochar can be easily separated from the catalyst by oxidation to recover the precious metal [59]. A study about carbocatalyst applied for water decontamination process has been conducted by Shi et al.[123] using Preserved Wood Biochar (PWB). They exhibits outstanding BPA degradation capabilities. The metal compounds, especially Cu metal and biochar in PWB dominate the radical and non-radical PMS activation mechanisms, respectively [123].

However, it should be noted that even without introducing any metals from external sources, produced biochar might contain some AAEM due to their presence in the original raw materials. The most-reported catalytic effect is to reduce the tar and increase yield and selectivity towards different compounds in the liquid or gas phase of the final products [119]. Catalytic pyrolysis of bamboo waste with N-doped biochar catalyst for phenol products reached 82%, while inhibiting the formation of O-species and acetic acid, with the release of more CO_2 and H_2O [124]. Even when introduced into the reaction system to function as the catalyst, biochar may also show different functions as an adsorbent and reactant [119]. The modified surface area and adequate mechanical properties allow biochar to adapt to different chemical reactor configurations. As one of the common by-products in biorefinery processes, biochar as a catalyst will increase production efficiency, reduce waste generation, help maintain economically viable production [118]. Economically and environmentally sustainable processes were determined for agricultural and food waste containing 30.1% (w/w) oil for biodiesel production (96.3%) using a biochar catalyst [125]. Therefore, the application of biochar as a catalyst will not only increase its utilization but also encourage the development of various catalysts [59].

6. Conclusions

The diversion of green waste in urban areas to biochar seems to be an even better alternative for the environmental application. Biochar engineering can be a solution to enhance the quality of biochar through improving the physicochemical properties of biochar. The dry method (i.e. pyrolysis, gasification, and dry torrefaction) and the wet method (i.e. hydrothermal carbonization and wet torrefaction) have developed in recent years into more effective and efficient for various application. In addition, there are many factors that can affect the physicochemical properties of biochar, such as the type of raw material, production techniques, operating conditions, or the method of activation or modification. The effect of biochar in various applications has been well proven, but further research on biochar derived from green waste is recommended to increase the commercial value of the use of biochar in the real world.

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