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Review

Production of Biochar and Its Potential Application in Cementitious Composites

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Abstract: In cement composites, usually, reinforcement is provided to restrict the crack development and their further propagation under service conditions. Typically, reinforcements utilized in cementitious composites range from nanometer scale to millimeter scale by using nano-, micro-, and millimeter-sized fibers and particles. These reinforcements provide the crack arresting mechanisms at the nano/microscale and restrict the growth of the cracks under service loads, but usually, the synthesis of nano/microfibers, and afterward their dispersion in the cementitious materials, pose difficulty, thus limiting their vast application in the construction industry. Carbonaceous inerts are green materials since they are capable of capturing and storing carbon, thus limiting the emission of CO_2 to the atmosphere. In the present study, a comprehensive review of the synthesis of low cost and environmentally friendly nano/micro carbonaceous inerts from pyrolysis of different agricultural/industrial wastes, and afterward, their application in the cementitious materials for producing high performance cementitious composites is presented, which have the potential to be used as nano/micro reinforcement in the cementitious matrix.

Keywords: cementitious composites; fracture energy; pyrolysis; biochar; high performance

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1. Introduction

Cementitious materials are one of the most used infrastructure materials worldwide due to their low cost, well-developed production methods, and well adaptability to varying environmental conditions. Cementitious composites are mainly divided into three groups, i.e., concrete, mortar and paste. Being quasi brittle, they are prone to cracking, which greatly compromises their strength and durability [1–3]. Due significance has been given to mitigate the brittle behavior of cementitious composites in the past: Various studies are available, intended at improving the tensile strain capacity of the cementitious materials. Apart from conventional steel reinforcement, inclusion of fibers has remained the focus of many studies [4–6].

Fiber-reinforced cementitious materials consist of synthetic or natural materials. The fibers are intended to provide resistance against cracking both in plastic and hardened forms of composite materials. The synthetic fibers comprise metals such as steel, aluminum or polymers such as polypropylene, polyester, nylon, acrylic, aramid, and carbon [7]. The natural fibers include coir, jute, pineapple leaf, kenaf bast, bamboo, palm, hemp, sugarcane bagasse, etc. [8,9]. In the following paragraphs, a brief introduction to the application of fibers in cementitious materials is presented.

Eren et al. studied the effect of steel fibers on the tensile strength of concrete [10]. Their study revealed that steel fibers with an aspect ratio of 80 and fiber content of 1.5% can increase the tensile strength of the concrete by 111%. Tiberti et al. evaluated the capability of steel fiber reinforced concrete in controlling cracks and reducing crack spacing [11]. They have reported that the crack spacing reduced by 30% with 0.5% fiber content and by 37% with 1% fiber content. Pająk et al. evaluated the flexural behavior of self-compacting concrete reinforced with straight and hooked-end steel fibers (0.5, 1.0, and 1.5% volume content) [12]. They have concluded that the fracture energy increased with the increase in fiber content and the fracture energy is always greater for hooked end fibers at the same dosage. Doo-Yeol et al. studied the tensile performance of ultra-high-performance concrete through straight and half-hooked steel fibers [13]. They have reported that a lesser quantity of hooked fibers, compared to the straight ones, is required for the same tensile strength. Düzgün et al. studied the effect of steel fibers on strength of lightweight pumice aggregate concrete [14]. They have reported that the reinforcement increases both strength and ductility up to 1.5% fibers. Vandewalle studied the cracking behavior of concrete beams, reinforced with combined longitudinal steel rebars and steel fibers [15]. They have reported that the combined reinforcement reduces both the crack spacing and the crack width.

Alhozaimy et al. examined the mechanical properties of concrete reinforced with polypropylene fibers (below 0.3% fiber content) [16]. They have reported an increase of 387% in flexural toughness at 0.3% fiber content. Kakooei et al. studied concrete samples reinforced with 0–2 kg/m^3 polypropylene fibers. They have reported that reinforcement of 1.5 kg/m^3 gives optimum results vis à vis compressive strength of the concrete [1]. Afroughsabet et al. evaluated the strength and durability of high strength concrete, reinforced with steel and polypropylene fibers [17]. Their resulting concrete at failure is shown in Figure 1. They have reported that 1% steel fibers enhance the splitting tensile and flexural strengths significantly. They have also claimed the best performance with 1% hybrid combination (0.85% steel and 0.15% polypropylene), with regard to mechanical strength, electrical resistivity and water absorption. Song et al. investigated the mechanical properties of concrete reinforced with nylon and polypropylene fibers at a dosage of 0.6 kg/m^3 [18]. They have reported that nylon-reinforced concrete had superior strength, and crack-resistant properties than the polypropylene reinforced one. They have attributed the enhanced properties to higher tensile strength and better distribution of nylon fibers in concrete matrix than the polypropylene fibers.

Figure 1. Concrete reinforced with steel and polypropylene fibers, reprinted with permission from Afroughsabet, Vahid., Ozbakkaloglu, and Togay. Elsevier.

As far as the incorporation of natural fibers is concerned, there are some problems, as pointed out by various researchers, which need to be addressed prior to their application for reinforcement in cementitious composites: The natural fibers have a degrading effect in alkaline cementitious environments, and their pretreatment is required prior to the utilization [19]. Bilba et al. studied the silane-treated bagasse fibers in cementitious materials, using two silane, alkyltrialkoxysilane and dialkyldialkoxysilane [20]. The SEM images of the composites reinforced with bagasse ash fibers with and without saline treatment are shown in Figure 2. Their study revealed that saline treatment improves the water resistance of the fibers and make them hydrophobic. Andiç-Çakir et al. studied the mechanical properties of coir fiber-reinforced cementitious mortars. Their study revealed that the alkali-treated coir fibers enhanced the compressive and flexural characteristics of the mortars [21]. Khan et al. studied the effect of 5 cm long coconut fibers on the strength of concrete with a fiber content of 2% by mass of cement [22]. They have reported 15% silica fume, 2% coconut fibers, and 1% super plasticizer as the optimum mix composition for enhancing the strength and cracking resistance of the mortars. Islam et al. evaluated the effect of jute fibers on concrete properties [23]. Their study revealed that smaller fiber content (0.25% by mass of cement) had positive effect on the strength of the concrete.

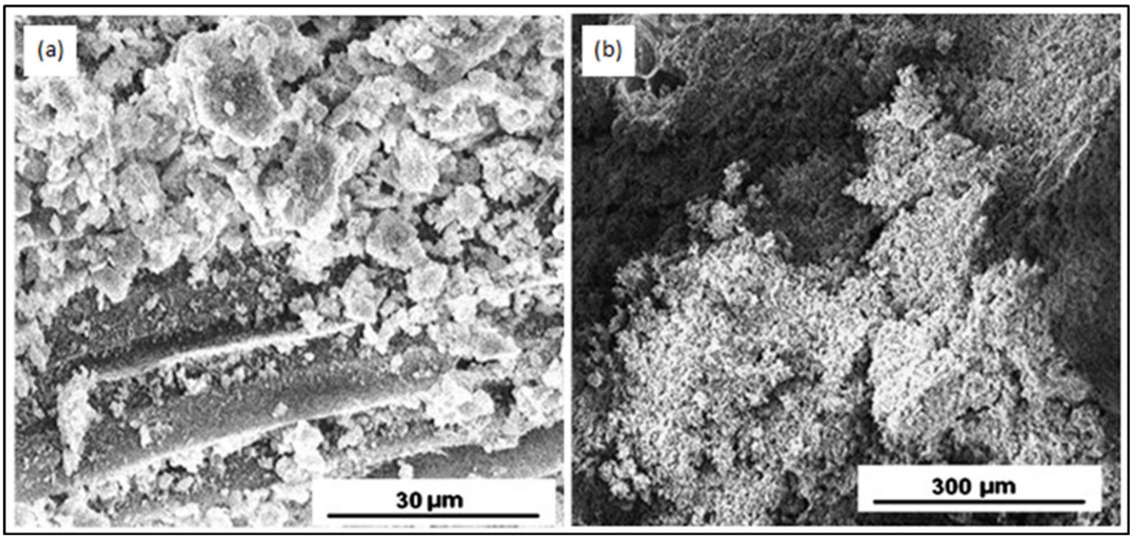

Figure 2. SEM images of composites: (**a**) composite reinforced with bagasse fiber and (**b**) composite reinforced with bagasse fiber treated with silane, reprinted with permission from K. Bilba and M. Arsene. Elsevier.

Many researchers have outlined the problems with natural fibers, including their biodegradation in an alkaline environment, their non-uniform distribution, and balling effect at higher fiber doses [19]. Special techniques, such as silane treatment, can address the issues encountered with the use of natural fibers as a crack-arresting medium in cementitious composites. Apart from fibers, another cost-effective method to enhance the fracture energy and crack resistance of the cementitious composites is the use of carbonaceous inerts (biochar) obtained from pyrolysis [24]. The biochars are reported to retain carbon from hundreds to thousands of years; thus, the synthesis and use of biochar are highly ecological, reducing the discharge of CO_2 back to the atmosphere [25]. This review paper intends to address the enhancement of crack resisting properties by using carbonaceous inerts obtained from pyrolysis of different industrial, municipal, and agricultural wastes.

2. Carbonaceous Inerts

Carbonaceous inerts are defined as materials derived from organic and/or inorganic feedstock that contain a high amount of carbon. They include coal, petroleum products, carbon black, tar, and many carbon-containing alloys. Pakistan is an agricultural country and abundant quantities of agricultural waste are produced every year. If properly refined and treated, these wastes can be employed for many useful purposes [26–28]. As in many other scientific fields, construction material technology has also benefited from agricultural wastes: These wastes have been extensively used as natural fibers, as discussed in the introduction section. Additionally, many studies have shown that if these wastes are burnt, their ashes can be used as cementing or pozzolanic materials for enhancing the properties of the cementitious composites [29–31]. The microscopic images of the burnt wheat straw ash, used by Biricik et al., are shown in Figure 3 [32]. However, it has been indicated that the direct combustion of crop residues in agricultural fields is harmful to the environment, owing to the emission of greenhouse gases [33,34]. Many researchers have suggested alternate ways for useful application of the agricultural wastes, which involve the extraction of carbonaceous inerts via several techniques such as hydrogenation, fermentation, combustion, bioconversion, etc. [35,36] According to a number of other researchers, pyrolysis is the most effective technique for extracting useful carbonaceous inerts from agricultural wastes [37–39].

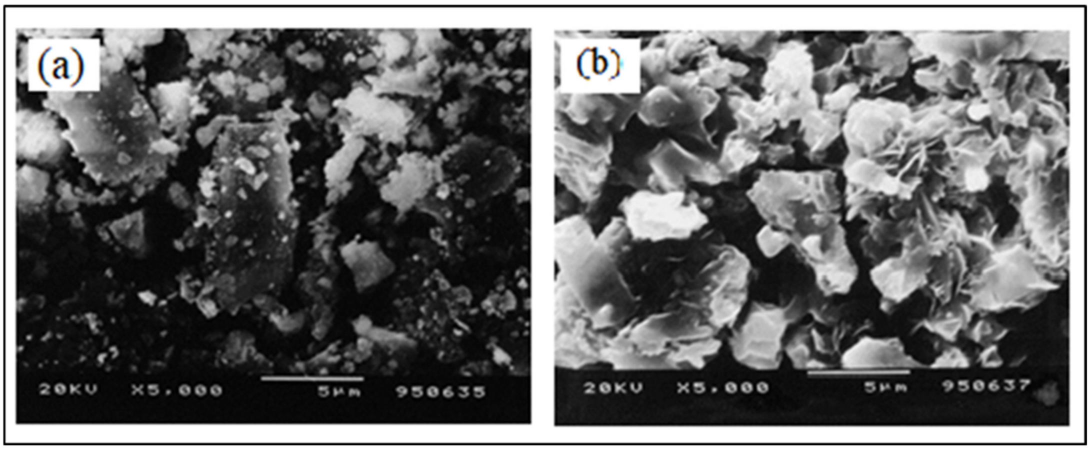

Figure 3. SEM image of wheat straw ash burned at 570 °C (**a**) and at 670 °C (**b**), reprinted with permission from Biricik, Hasan Aköz, Fevziye Berktay, I.lhan Tulgar, and Ali N. Elsevier [32].

3. Pyrolysis

Pyrolysis is an endothermic process that involves the thermochemical decomposition of raw biomass in an inert environment at a high temperature and pressure [40]. This process produces various useful products such as solid biochar, liquid bio-oil, and fuel gases, as highlighted in Equation (1) below [41]:

$$\text{Biomass} \overset{\text{Heat}}{\rightarrow} \text{Biochar}(s) + \text{Bio oil}(l) + \text{Fuel gas}(g) \quad (1)$$

Pyrolysis has the potential to transform environmentally hazardous wastes into stable valuable products, which are less harmful to life and the environment [42]. According to Ruan et al., one of the main advantages pyrolysis offers over other techniques is that the desired product (liquid, solid, or gas) can be produced by adjusting the operational parameters, i.e., temperature, pressure, heating rate, and residence time [43]. It has also been reported that biochar produced from slow pyrolysis having low heating ramp with longer residence time exhibit a more homogeneous character than those produced by fast pyrolysis [44]. A typical pyrolysis process is shown in Figure 4 in the form of a flow diagram [45], whereas the general layout of the pyrolysis process is shown in Figure 5 [46].

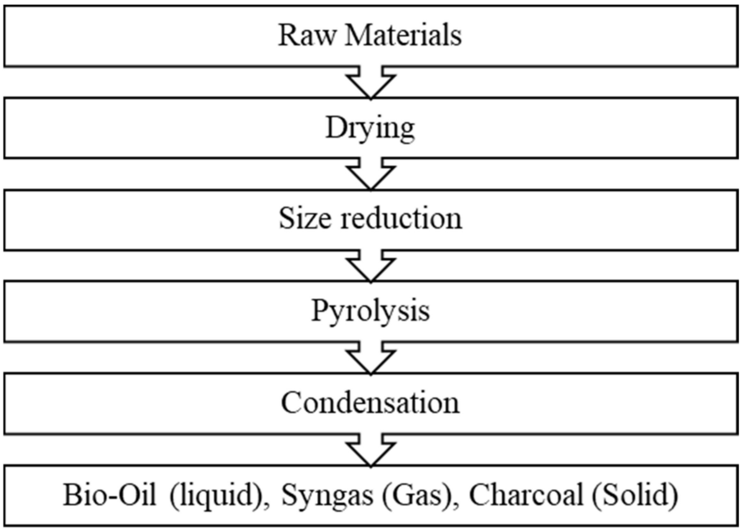

Figure 4. Flow diagram of pyrolysis.

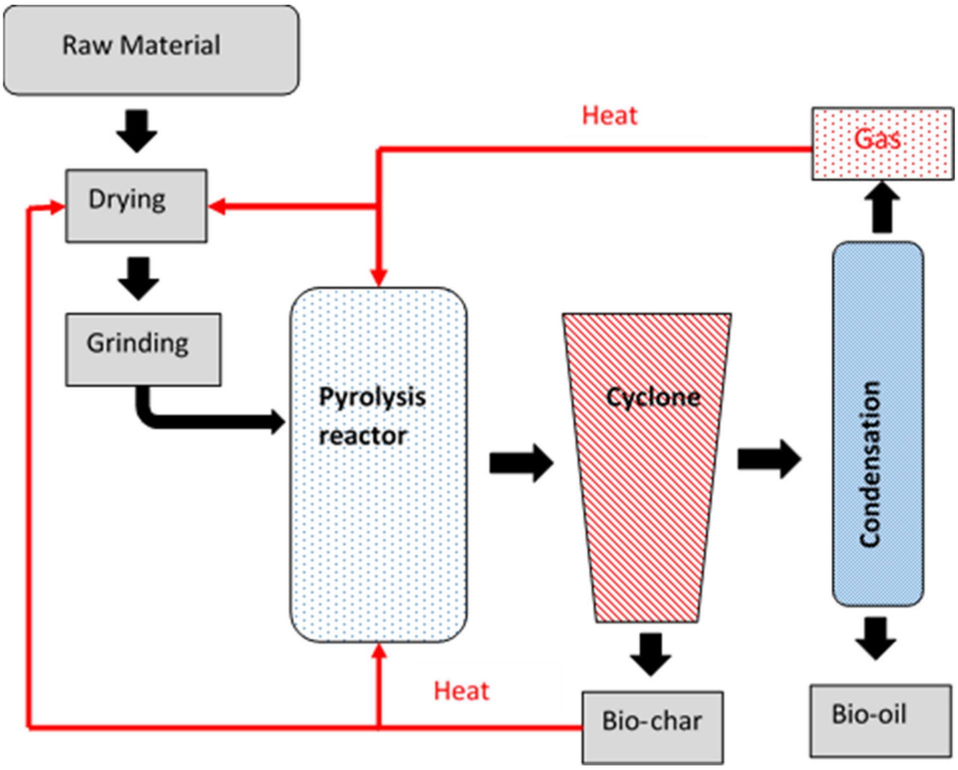

Figure 5. General layout of pyrolysis process.

Pyrolysis is termed as slow or fast, depending on the heating ramps and the operating temperature: slow pyrolysis is characterized by low heating ramp (<100 K/min) and low temperature (~300 °C), whereas fast pyrolysis refers to that carried out at high heating ramp (>100 K/min) and higher operating temperature (~500 °C or more) [47]. Pyrolysis is reported to lack synergetic effects, and it has been indicated that the yield is proportional to the percentage of biomasses in the feedstock [48].

3.1. Materials and Operating Conditions

3.1.1. Materials

Biochar is a lightweight black carbon residue, obtained after eliminating water and other volatile ingredients, mainly by pyrolysis. Various researchers have used numerous feedstock for producing biochar: They can be agricultural waste such as wheat, rice, and sugarcane or forest residues such as water hyacinth, beech trunk, hemp hurd, sawdust, etc. In the following paragraph, different raw materials used for producing biochar by pyrolysis are described.

Carnaje et al. prepared biochar briquettes from water hyacinth [49]. Their biochar is shown in Figure 6 (microscopic images). They have reported that at a temperature of 425 °C, the yield of water hyacinth biochar was 55%. Aburas et al. used oriental beech (*Fagus orientalis* L.) for the synthesis of biochar by pyrolysis at temperatures of 493,523 and 593 K [50]. They have reported a high yield of carbon-rich biochar at lower temperatures. Taralas et al. carried out steam pyrolysis of olive husk, having a particle size between 0.34 mm and 0.5 mm [51]. They have reported a yield of 29–40% at a temperature of 900 K. Gupta et al. carried out pyrolysis of untreated and phosphoric acid-treated corncob at temperatures ranging from 400 to 600 °C at a constant heating rate of 16 °C/min in a quartz reactor [52]. They have reported that the biochar yield decreases with the increase in temperature; however, pretreatment increases the yield. Akgül et al. carried out pyrolysis of tea waste at temperatures of 300–400 °C [53]. They have reported that the carbonization and aromaticity of biochar improve with the increase in pyrolysis temperature.

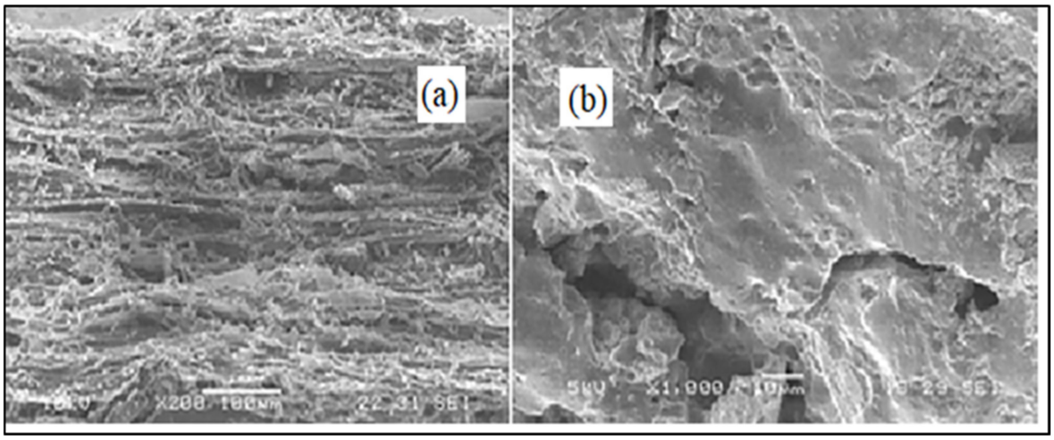

Figure 6. SEM images: (**a**) water hyacinth charcoal and (**b**) water hyacinth briquette, reprinted with permission from Carnaje, Naomi P. Talagon, Romel B. Peralta, Jose P. Shah, Kalpit Paz-Ferreiro, and Jorge. Elsevier [49].

Uçar et al. conducted pyrolysis of pomegranate seeds at temperatures, ranging from 400 °C to 800 °C [54]. They have claimed that the biochar contains high carbon content, having high bulk density and calorific value. Tay et al. prepared biochar from the pyrolysis of chemically activated soybean oil cake with K_2CO_3 and KO at 600 °C and 800 °C [55]. They have reported a high yield of biochar with K_2CO_3, having a surface area of 1353 m^2/g at 800 °C. Solar et al. carried out pyrolysis of woody waste (Pinus radiata) at a temperature range of 500–900 °C [56]. They have reported a high yield of biochar at a lower temperature. They have also emphasized that the yield decreases with the increase in temperature. Shafique Ullah et al. pyrolyzed rice husk (having a particle size of 0.5–7 mm) [57]. They obtained a 35% yield of biochar at 480 °C. Suman et al. pyrolyzed coconut husk for producing biochar at temperatures ranging from 400 °C to 1000 °C [58]. They have reported a decrease in yield and increase in aromaticity with the increase in temperature. Georgin et al. prepared biochar by conventional and microwave irradiation pyrolysis of peanut shells [59]. They have claimed that microwave irradiation followed by pyrolysis produces biochar with enhanced adsorption characteristics. Iqbal et al. carried out pyrolysis of chickpeas waste and peanut shells for biochar production, using a temperature range from 350 °C to 600 °C [60]. They have a reported biochar yield of 28% and 46%, using chickpeas waste and peanut shells, respectively, at 350 °C with a heating rate of 15 °C per minute. They have further described that the yield decreases with the increase in temperature. Jagdale et al. prepared biochar from waste coffee at 700 °C for one hour in a nitrogen atmosphere at a temperature range from 250 °C to 400 °C, using a heating rate of 5 °C/min [61]. They have reported a yield of 18%, with the biochar having high porosity and an average diameter of pores of about 7 µm. Pottmaier et al. compared two waste materials—rice husk and wheat straw—for producing biochar, using slow and fast pyrolysis [44]. Their biochar is shown in Figures 7 and 8, respectively, whereas the raw form of the materials is shown in Figure 9. They have reported 19.4% yield for rice husk and 25.4% yield for wheat straw at 900 °C. They have further emphasized that the yield decreases with the increase in pyrolysis temperature. Yang et al. pyrolyzed sawdust for producing biochar, using temperatures from 250 to 950 °C [62]. They have reported that biochar with the highest calorific value can be produced using temperatures in the range of 450 to 650 °C. Cao et al. investigated the physical and mechanical properties of biochar, prepared from sawdust, cotton stalk, and their blend at a temperature range of 400–600 °C [63]. They have reported that the density and compressive strength of the biochar briquettes first decreased and then increased with the increase in temperature. They have further elaborated that the cotton stalk biochar briquettes have superior properties than those of sawdust and the blend showed poorer characteristics than those of cotton stalk and sawdust. Liu et al. studied the pyrolysis of hemp hurd and retted hemp hurd, without and with the treatment of $ZnCl_2$ at a temperature of 800 °C, using a heating rate of 10 °C/min [64]. They have revealed that untreated hemp hurd and retted hemp hurd produced a yield of 20.7 and 20.2%, respectively. They have further elaborated that the $ZnCl_2$ activation enhanced the yield to 30.3 and 28.6%, respectively, for untreated hemp hurd and retted hemp hurd. Guo et al. produced Nano biochar using soybean and cattle manure at 500 °C in a hydrothermal reactor [65]. The SEM images of their biochar having highly porous structure are shown in Figure 10, whereas the TEM images are shown in Figure 11. The TEM images reveal carbon nanodots of sizes 2–10 nm (8.5–10% overall nano content).

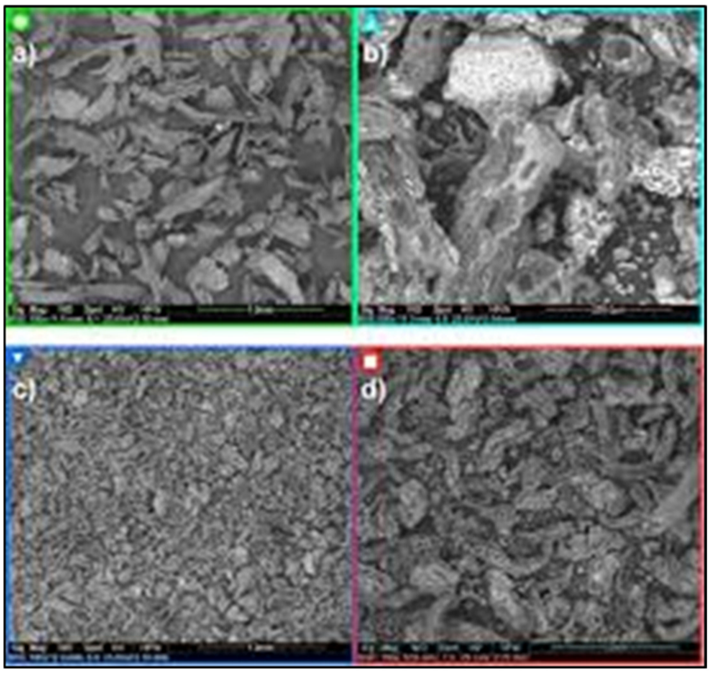

Figure 7. SEM images of rice husk: green biomass (**a**) and chars after fast pyrolysis in the DTF at 900 °C (**b**), 1100 °C (**c**), and 1300 °C (**d**), reprinted with permission from Pottmaier, Daphiny Costa, Mário Farrow, Timipere Oliveira, Amir A. M. Alarcon, Orestes Snape, and Colin. Elsevier [44].

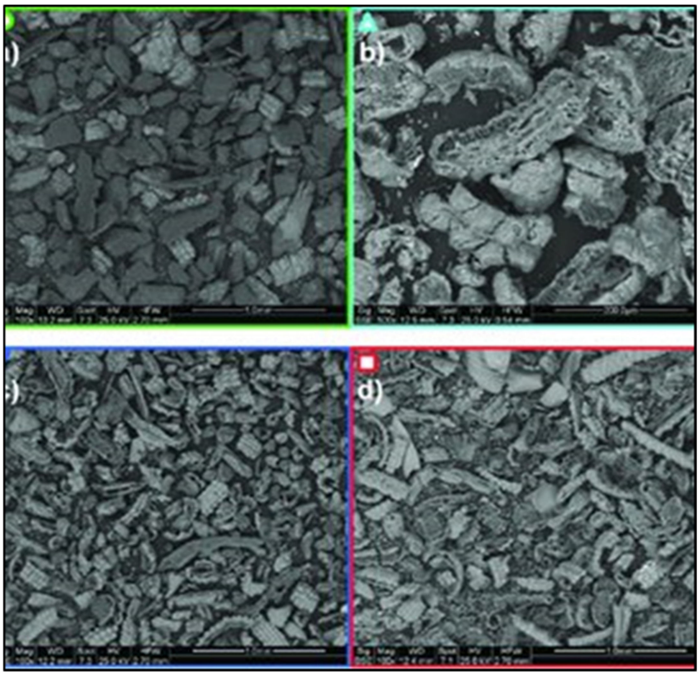

Figure 8. SEM images of wheat straw: green biomass (**a**) and chars after fast pyrolysis in the DTF at 900 °C (**b**), 1100 °C (**c**), and 1300 °C (**d**), reprinted with permission from Pottmaier, Daphiny Costa, Mário Farrow, Timipere Oliveira, Amir A. M. Alarcon, Orestes Snape, and Colin. Elsevier [44].

Figure 9. Raw forms of (**a**) wheat straw, (**b**) rice straw, (**c**) sugarcane bagasse, and (**d**) forest residues.

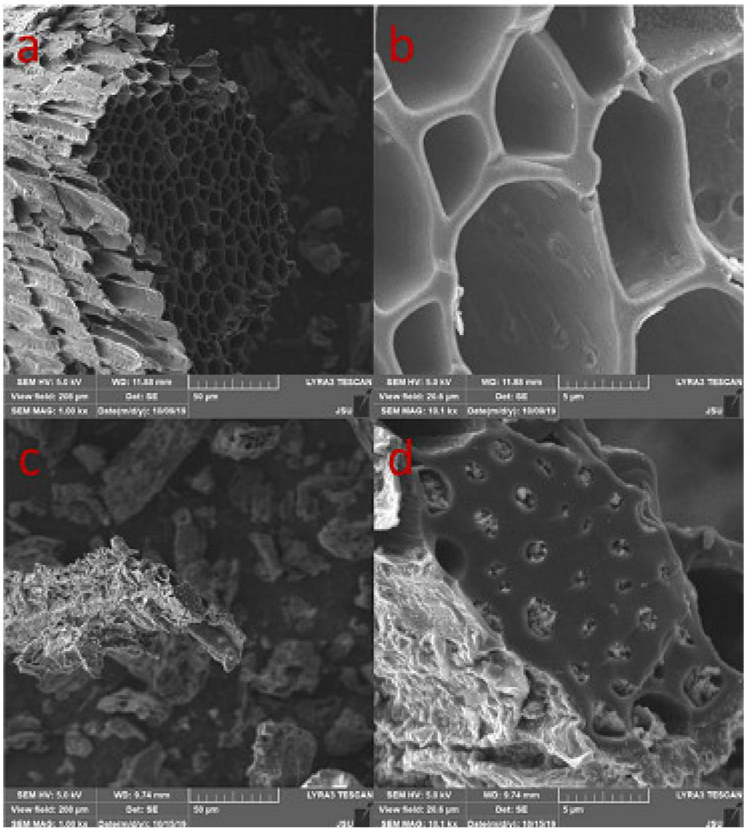

Figure 10. Microscopic images of soybean straw (**a**,**b**) and cattle manure (**c**,**d**) [65] (open access).

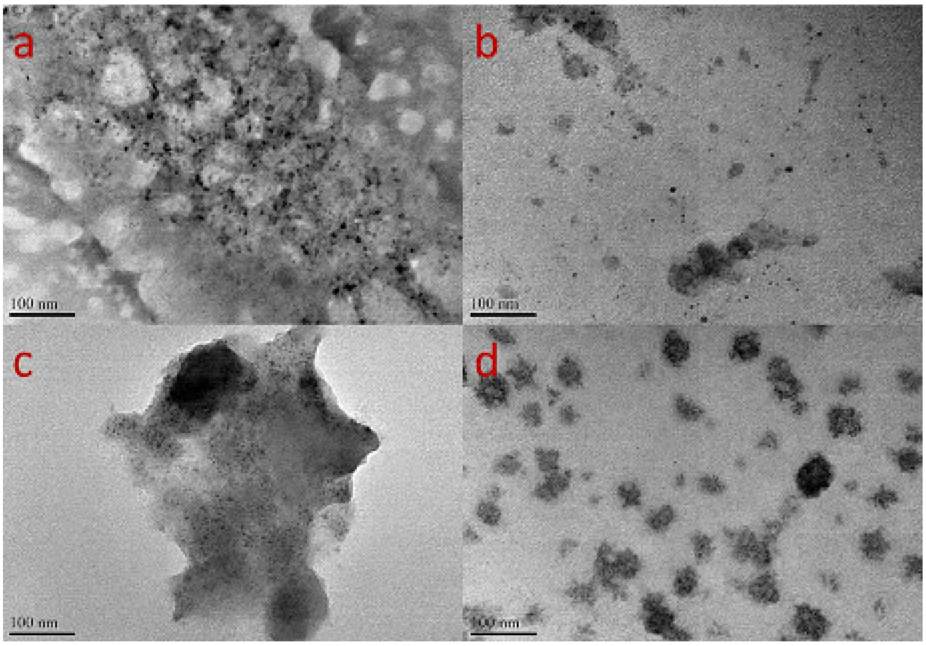

Figure 11. TEM images of soybean (**a**,**b**) and cattle manure (**c**,**d**), showing nanodots [65] (open access).

Choice of material for biochar is significant: According to Zanzi et al., the agricultural residues, having high ash and lignin (wood content of plants) contents favor biochar production and enhance its yield [66].

3.1.2. Particle Size

Manyà et al. studied the effect of particle size on the pyrolysis of vine shoots [67]. They have reported that larger feedstock particles, to a lesser extent and at higher temperatures, lead to more stable biochar products. Sundaram et al. studied the pyrolysis of coconut shells, with particle size ranging from 1.18 to 1.80 mm [68]. They have reported an increase in biochar yield with the increase in particle size. Zanzi et al. studied the fast pyrolysis of olive waste, straw, and birch (hardwood) at temperatures 800–1000 °C, using particle sizes from 0.5 to 0.8 mm and from 0.8 to 1.0 mm [66]. They have reported an increase in biochar yield with the increase in particle size. Luo et al. studied the effect of particle size (0–5 mm, 5–10 mm, and 10–20 mm) on pyrolysis of municipal solid waste, using 800 °C temperature [69]. They have reported that smaller particle size resulted in higher syngas yield with less biochar. The gas yield and weight percentages of char for plastic, wood, and kitchen garbage as a function of particle size are shown in Figure 12. They have further elaborated that smaller size also leads to the lesser carbon content in biochar.

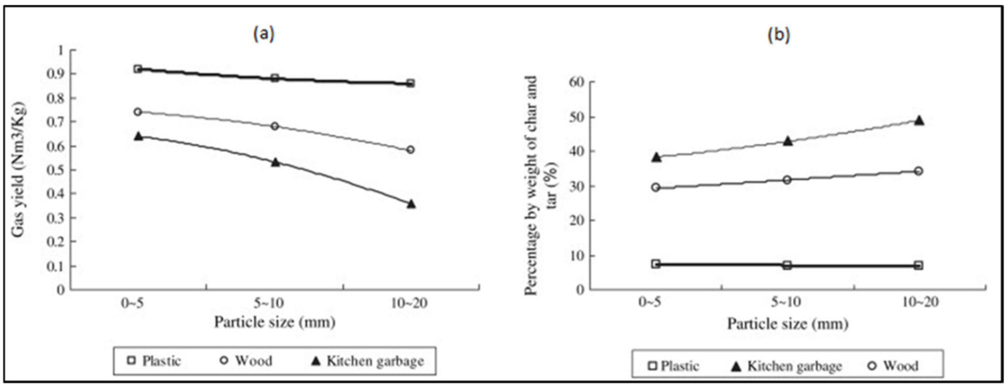

Figure 12. Gas yield of plastic, wood, and kitchen garbage as a function of particle size (**a**) and weight percentages of char and tar as a function of particle size (**b**), reprinted with permission from S. Luo, B. Xiao, Z. Hu, and S. Liu. Elsevier [69].

According to Sundaram et al. and Zanzi et al. [66,68], the larger particles induce a higher temperature gradient inside them, and therefore, the core temperature is lower than that at the surface, which leads to an increase in solid and decrease in syngas contents.

3.2. Operating Conditions

3.2.1. Temperature

The temperature has the most significant effect on the outcomes of a pyrolysis process, as pointed out by numerous researchers. Demirbas has described that the solid (biochar) content decreases, while the carbon content of biochar and the liquid (bio-oil) content increase with the increase in temperature [70]. He has mentioned that the highest liquid yield can be obtained within the range of 650 to 800 K. Zhang et al., while studying the pyrolysis of wheat straw and lignosulfonate, have mentioned that while carbon content increased, the yield of biochar decreased with the increase in temperature [71]. They have further stated that highly porous and aromatic biochar can be produced at higher temperatures. Williams et al. investigated the effect of temperature (up to 720 °C) on pyrolysis of scrap tires [72]. They have reported that the solid biochar content decreased, while the liquid and gas contents increased up to 600 °C. From the feedstock, they produced 35% solid biochar, 55% bio-oil, and 10% syngas. Hernandez-Mena et al. studied pyrolysis of bamboo at temperatures ranging from 300 to 600 °C. They have a reported a biochar yield of 80% at 300 °C, as compared to 30% at 600 °C [73]. Mimmo et al. studied the effect of temperature on miscanthus (perennial grass with bamboo-like stems) biochar at temperatures between 350 and 450 °C [74]. They have highlighted that higher temperatures result in more stable biochar materials. Kloss et al. carried out slow pyrolysis of wheat straw and woodchips in the temperature range of 400–525 °C [75]. They have reported that the surface area of biochar particles increased with the increase in temperature. Sun et al. studied the effect of temperature on the outcome of pyrolysis [76]. Their reported effect of temperature is shown in Figure 13. They have indicated that lower temperatures increased the yield, while higher temperatures increased the carbon content and produced thermally stable products.

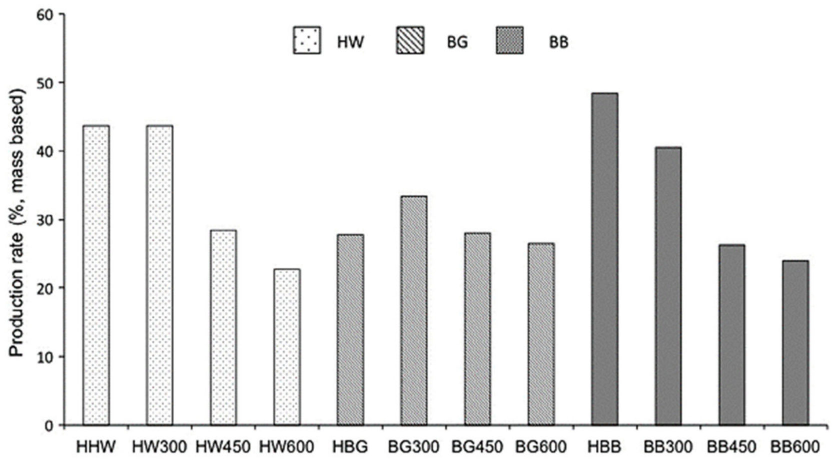

Figure 13. Production of different biochar samples, HHW, HW300, HW450, HW600, HBG, BG300, BG450, BG600, HBB, BB300, BB450, and BB600 are hydrochars and/or biochars produced from hickory wood (HW), bagasse (BG), and bamboo (BB) feedstocks under different temperatures (300 °C, 450 °C, and 600 °C), respectively, reprinted with permission from Y. Sun, B. Gao, Y. Yao, J. Fang, M. Zhang, Y. Zhou, H. Chen, L. Yang Elsevier [76].

Ahmad et al. studied the characteristics of biochar produced from soybean stover and peanut shells at 300 °C and 700 °C [33]. They have mentioned that the higher temperature enhanced the surface area and aromaticity of biochar. Li et al. studied the effect of temperature on pyrolysis of oil distillation residue by fixing three temperatures 400, 600, and

800 °C [77]. Their study revealed that higher temperatures lead to higher carbon content, surface area, and pore volume. Zhao et al. studied the effect of temperature (200–700 °C in 50 °C increment), heating ramp, and residence time on pyrolysis of rapeseed stem [34]. They have declared temperature as the most effective parameter, influencing the biochar properties. According to Zhao et al., higher temperatures increase the carbon content, surface area, and aromaticity and decrease the yield and pore size. Angın investigated the effect of temperature on pyrolysis of safflower seed press cake [78]. He is also of the view that temperature has a more pronounced effect than the heating rate. He has described that higher temperatures (~600 °C) lead to higher carbon content (80.7%) and aromaticity, and lower surface area. Devi et al. studied the effect of temperature (500–700 °C) on pyrolysis of paper mill sludge [79]. They have reported reduced yield, enhanced surface area, and higher alkalinity with the increase in temperature. Yuan et al. investigated the effect of temperature on pyrolysis of medicinal herb (Radix isatidis) residue over a range of 300–700 °C [80]. They have concluded that higher temperatures lead to higher carbon content, aromaticity, alkalinity, surface area, and porosity. Fu et al. investigated the effect of temperature (600–1000 °C) on pyrolysis of rice straw [81]. They have reported a 16% reduction in biochar yield from 600 to 1000 °C, with maximum porosity and surface area at 900 °C. Gupta et al. carried out pyrolysis of untreated and phosphoric acid-treated corncob, at temperatures ranging from 400 to 600 °C at a constant heating rate of 16 °C/min in a quartz reactor [64]. They have reported that the biochar yield decreases with increase in temperature; however, pretreatment increases the yield. Effect of (a) temperature and (b) pretreatment on % yield of biochar from corncob at different temperature and pretreatment ratio are shown in Figure 14.

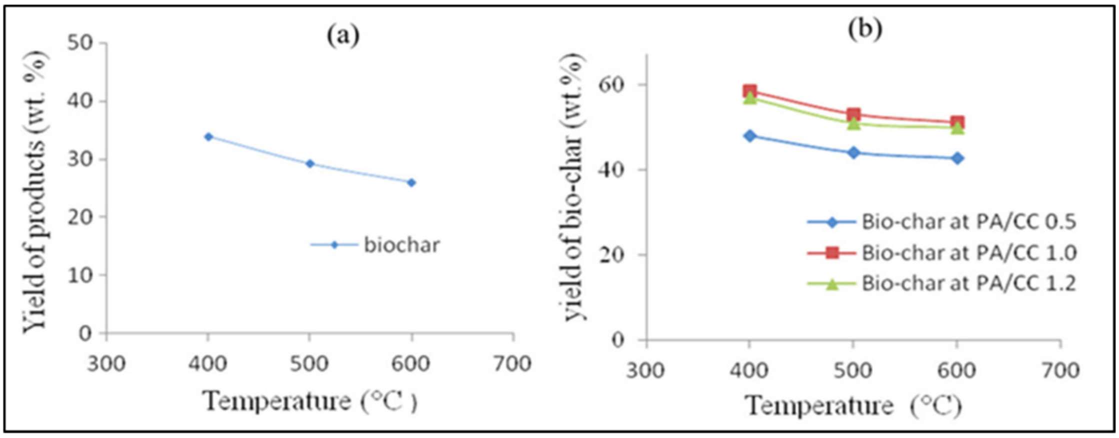

Figure 14. Effects of (**a**) temperature and (**b**) pretreatment on % yield of biochar from corncob at different temperature and pretreatment ratio, reprinted with permission from G.K Gupta, M. Ram, R. Bala, M. Kapur, and M.K. Mandol. Elsevier [52].

Based on the studies, intended to evaluate the effect of pyrolysis temperature on the production of biochar, it is concluded that regardless of material (1) temperature is the most influential parameter, controlling pyrolysis; (2) higher temperatures decrease the yield of biochar; (3) higher temperatures enhance the carbon content; and (4) higher temperatures (600 °C and above) significantly enhance porosity, pore volume, aromaticity, and alkalinity.

3.2.2. Heating Rate

Haykiri-Acma et al. studied the pyrolysis of rapeseed, using heating ramps of 5, 10, 20, 30, 40, and 50 K/min [82]. They have reported higher rates of mass loss at higher heating ramps. Cetin et al. investigated the effect of heating ramps on the pyrolysis of radiata pine (softwood) [83]. They have described that higher heating ramps resulted in the melting of the particles and imparted smoother surfaces and induced large cavities. Chen et al. studied the effects of heating rates of 5, 10, 20, and 30 °C/min on characteristics of the products using moso bamboo (Phyllostachys edulis) [84]. They have reported that higher rates lead to lower liquid and solid contents and enhance the specific area of the biochar. Williams et al. investigated the effect of heating rates (5–80 °C/min) on pyrolysis of scrap tires [72]. They have reported enhancement of surface area with the increase in heating rate. Fu et al. have reported increase in pore size and surface area of biochar with the increase in heating rate, while pyrolyzing rice straw from 600 to 1000 °C temperature [81]. Şensöz et al. studied the pyrolysis of pine chips (Pinus brutia) using temperatures (300–550 °C) and heating rate of 7 and 40 °C/min [85]. They produced the highest yield of 36% of biochar at a temperature of 300 °C with a 7 °C/min heating rate. They have described that an increase in heating rate decreases biochar yield at a particular temperature. Mani et al. investigated the effect of heating rate varying from 5 to 20 °C/min on the pyrolysis of wheat straw [86]. They have reported an increase in biochar yield with increase in heating rate.

The previous studies show that heating rate has both positive and negative effects on the production of biochar via pyrolysis. According to Mani et al., at lower heating rates, most of the materials show effective heat transfer, leading to more efficient cracking and more weight loss in the form of volatiles. This leads to an increase in biochar yield with an increase in heating rate [86].

3.2.3. Pressure

Cetin et al., while pyrolyzing radiata pine, have indicated that the pressure influences the size and the shape of the biochar particles [83]. Mok et al. studied the influence of pressure on pyrolysis [87]. They have reported that biochar yield increases with the increase in pressure. Newalkar et al. studied the effect of pressure (5–20 bar) on the pyrolysis of pine at 800 °C [88]. They have reported that pressure affects the physical and chemical properties of biochar. Yun et al. studied the pyrolysis of coal using steam under high pressure [89]. They have mentioned that the reaction rate decreases with the increase in pressure. Basile et al. studied the effect of pressure on the pyrolysis of Lignocellulose (plant dry matter) [90]. They have reported that an increase in pressure reduces the heating needs for pyrolysis. Waghmare et al. studied the effect of pressure (4, 7, and 10 bars) on the pyrolysis of rice husk and sawdust [91]. They have reported an increase in biochar yield from 4 to 7 bar pressure and an overall increase in liquid oil yield with the increase in pressure at the same temperature. Noumi et al. studied the effect of pressure on pyrolysis of Acacia wood (hardwood, native in Australia) in the range of 1–6 bar [92]. They have reported increased biochar yield and reactivity with the increase in pressure. They have further reported an optimum temperature of 617 °C and optimum pressure of 6 bar for biochar yield. Manyà et al. studied the effect of pressure on the pyrolysis of vine shoots [67]. They have reported that an increase in pressure decreases the tar content in syngas. Baiqing et al. studied the effect of pressure on pyrolysis of pine sawdust using pressures (0–50 bar) [93]. They have reported that high pressures promoted more yield of biochar by secondary cracking of oil. They have also indicated that high pressure enhances the structures and compactness of the biochar.

According to Basile et al., the enhanced pressure increases the retention time of the volatiles; the volatiles react further with the pyrolysis products, making secondary biochar. The secondary reactions are of exothermic nature and thus decrease the heating demand of pyrolysis and enrich secondary products with additional carbon content. Additionally, the overall yield of biochar increases with the increase in pressure [90].

3.2.4. Residence Time

The effect of residence time on the characteristics of biochar is often neglected; however, some researchers have highlighted that this parameter is not insignificant. Zhao et al., while studying the pyrolysis of rapeseed stem, have pointed out that an increase in residence time enhances the surface area and morphology of the biochar [34]. Cao et al. studied the combined effect of residence time (1 and 60 min) and temperature (200–700 °C) on the pyrolysis of cornstalk, rice husk, peanut husk, and tobacco stalk [94]. They have reported decreased yield, enhanced pH, and carbon content of the biochar products at higher temperatures and larger residence time. Sun et al. studied the synergetic effect of residence time (0.5, 1, 2, 4, 8, and 24 h) and temperature (300, 400, 500, and 600 °C) on the pyrolysis of different raw materials [95]. They have reported that at a lower temperature (300 °C), the biochar yield decreased, while its pH increased with the increase in residence time. They have further emphasized that at a higher temperature, residence time had negligible effects on the yield and pH of biochar. Hasan et al. studied the effect of residence time (30–75 min) on the characteristics of palm kernel shell biochar [96]. They have reported that the yield decreased and the pH of the biochar increased with the increase in residence time.

From the above paragraphs, it is concluded that lower temperatures (<400 °C), slower heating rates, shorter residence times, larger particles, and higher pressures enhance the yield, while higher temperatures, longer residence times, slow heating ramps, and high pressures lead to stable and aromatic biochars. According to Rasul et al., different reactions take place at different temperatures, and at high temperatures, the liquid and solid molecules break down enriching the gas phase [97].

3.3. Methods

According to Simmons et al., several methods of biomass pyrolysis have been developed by researchers and industrial experts [86]. They include basic or conventional pyrolysis, fast pyrolysis, catalytic pyrolysis, and thermal plasma pyrolysis. Conventional pyrolysis is carried out at low temperatures and low heating ramps and therefore favors a high yield of biochar. Fast pyrolysis is characterized by high temperature and heating rate, short vapor residence time, and rapid cooling of vapors; all favor a high yield of bio-oil [98]. According to Pattiya, fast pyrolysis liquefies solid biomass into liquid bio-oil [99]. Dhyani et al. have stated that a required amount of bio-oil can be extracted in fast pyrolysis, by controlling operating conditions, and most importantly, by quick condensation and by limiting the vapors' residence time to less than 2 s [100]. According to Jourabchi et al., rapid heating fast pyrolysis reduces bio-oil yield but enhances its calorific value and water content [101]. Catalytic pyrolysis takes place in the presence of a catalyst. The catalyst is intended to lower the reaction temperature and time. This makes the process cost effective. According to Cleetus et al., the most commonly applied catalysts for pyrolyzing plastic waste are silica, alumina, and zeolites [102]. However, some concerns have also been shown as regards performance deterioration of the catalyst with time during the pyrolysis, necessitating consideration of its lifetime and regeneration for its cost-effective use [103]. Plasma, considered to be the fourth type of matter, is produced when the atoms of a gas ionize, or more simply, it is a hot ionized gas. In thermal plasma pyrolysis, the feedstock is inserted into a plasma: This consequently heats up the raw material very rapidly. High temperature and heating rate quickly destroy the waste, producing gas and solid residue [104].

4. Use of Biochar in the Cement and Concrete

The use of biochar for enhancing soil fertility and sequestration of carbon is not a new topic [105–108]. However, its use for enhancing concrete properties is quite new. It is expected that the use of biochar in building materials might reduce as much as 25% emission of greenhouse gases into the atmosphere [109]. The use of biochar is summarized in Figure 15 and described in what follows.

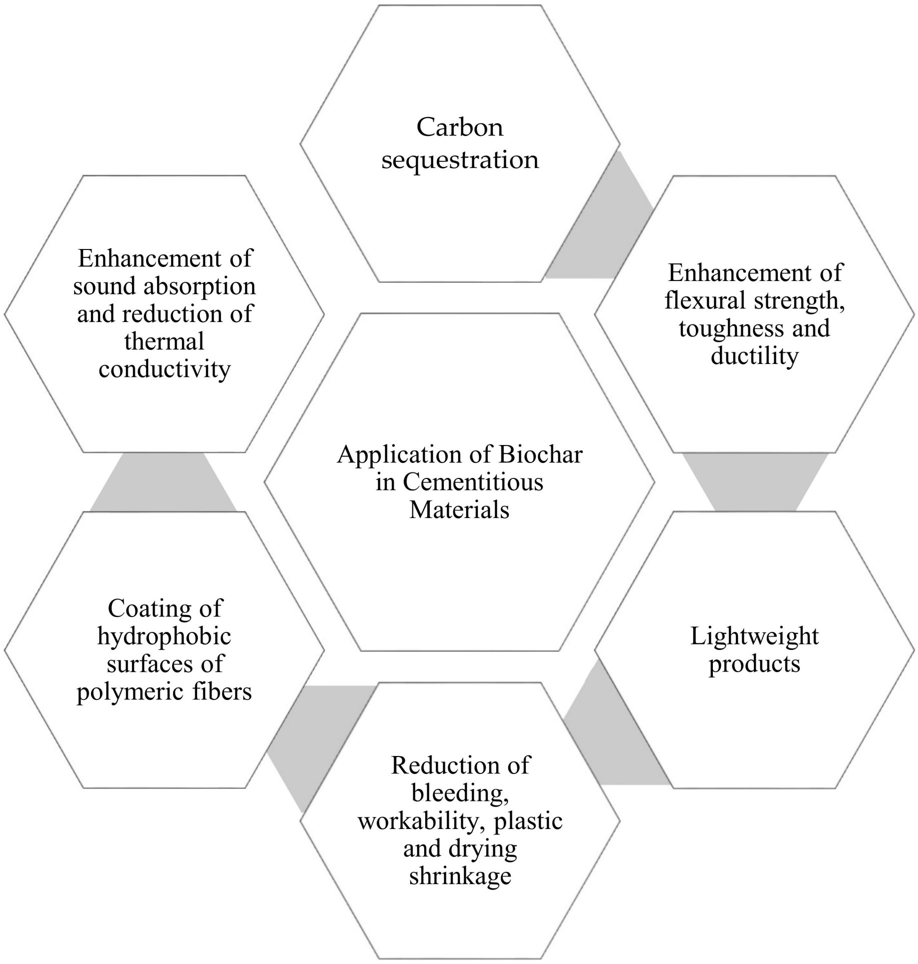

Figure 15. Benefits of biochars for cementitious composites.

Khushnood et al. studied the effect of biochar obtained by pyrolysis of peanut and hazelnut shells on the properties of cement paste [110]. They have reported that the addition of biochar by 1% mass of cement increases the flexural strength and toughness of the paste. Resheidat et al. added biochar powder at the rate of 2.5–10% by mass of cement in a concrete specimen, using accelerated curing and heat treatment [111]. They have reported a lightweight concrete with uniform porosity and a considerable saving in the overall cost of the material. Mrad et al. studied the effect of partial replacement (5–45%) of sand by biochar, obtained by pyrolysis of municipal solid waste in preparing cementitious mortars [112]. They have reported that the porous structure of biochar particles absorbs water, which is available for internal curing of the material. They have further reported that the absorption of water from micro pores leads to the densification of ITZ around biochar particles. Gupta et al. used biochar, prepared from pyrolysis of sawdust at 300 °C, as additive in cementitious mortars at the rate of 2% by mass of cement [109]. They have reported that the reinforcement enhances early compressive strength and imparts ductility, density, and imperviousness to the specimens. Restuccia et al. investigated the use of biochar, obtained by pyrolysis of hazelnut shells as an additive in mortars [24]. For pyrolysis, 3 g of feedstock was inserted, employing a heating rate of 6 °C/min, with a final temperature at 800 °C. The fine char particles ranging from a few nanometers to 10 μm were added to mortar at a rate of 0, 0.5, 0.8, and 1.0% by mass of cement. They have reported the highest flexural strength and the best post-cracking behavior with 0.8% carbonaceous materials. Choi et al. investigated the use of biochar (hardwood) obtained by slow pyrolysis process, as replacement of cement (5% by mass of cement) in mortars and concrete [25]. They have reported reduced evaporation of water and concrete compressive strength with the increase in biochar content. The reduced water evaporation was attributed to the water-retention capability of biochar, whereas reduced compressive strength was credited to lower workability and difficulty in compaction. Cuthbertson et al. investigated the use of biochar, obtained from pyrolysis of dry distillers grains from the bioethanol industry, as filler in concrete [113]. They have reported enhanced sound absorption, reduced thermal conductivity, material density, and compressive strength. The obtained results have been attributed to the porous structure of the biochar. Wang et al. investigated the effect of bamboo biochar on the characteristics of cementitious composites [114]. They have reported reduced strength, increased porosity, and pore volume. The strength decreases with the increase in biochar content and particle size. Cosentino et al. studied the effect of nano softwood biochar, obtained by pyrolysis at a peak temperature of 700 °C and added at the rate of 0.8 and 1% by mass of cement on the characteristics of cement paste [115]. They have reported enhancement in flexural strength, fracture energy, toughness, and ductility. They have further emphasized that the effect of biochar on the properties of cementitious composites is linked to the nature and particle size of the feedstock and operating conditions of the pyrolysis. Cheng studied the effect of partial replacement of sand by biochar obtained from pyrolysis of timber on the properties of cementitious mortars with fixed flow ability by adjusting water content [116]. They have reported an exponential decrease in strength with increase in biochar content. Cuthbertson studied the influence of three biochar (woodchips, Miscanthus, and distiller grains) particles (passing through 840 μm sieve) on the properties of concrete [117]. He has reported that the concrete density decreases from 2200 to 1450 kg/m^3 at 15% biochar content (by mass of concrete), the water requirements increase linearly with the increase in biochar content for a fixed workability, sound absorption and heat insulation increase, and compressive strength apparently remained unchanged with the increase in biochar content.

Biochar is a highly porous material, which leads to the reduction of workability; nevertheless, the adsorbed water is not chemically bound and is released during hydration reactions. This makes the biochar an internal curing agent that assists in developing the micropores and pore structure of the parent materials. Additionally, biochar decreases water evaporation, which is the cause of plastic and drying shrinkages in cementitious materials [25,112]. Gupta et al. studied the influence of sawdust charcoal, prepared at 300 and 500 °C, on the characteristics of cementitious mortars [118]. They have reported an enhanced early compressive strength (1–2% addition), enhanced water tightness, and no effect on flexural strength and drying shrinkage.

Carbonaceous inerts are also useful for enhancing the cracking resistance, toughness, and energy-absorbing capacity of cementitious materials. As indicated in the introduction part of this review, polypropylene (PP) fibers are added to cementing materials for many benefits; however, it has been pointed out that the smooth surface of PP fibers hinders the formation of bonds with the surrounding cement matrix [119]. Additionally, the hydrophobic surface of fibers leads to the formation of a thin water layer on PP fibers, which weakens its ITZ, known as the wall effect [120]. Gupta et al. studied the effect of sawdust biochar prepared at 300 °C, as coating material of PP fibers in cementitious mortars [121]. They have reported reduced workability, enhanced strength, post-cracking ductility, and impermeability.

According to Gupta et al., due to high water-absorbing capacity, biochars hold a significant amount of water during the mixing phase of cementitious composites, which adversely affects the flowability [121]. According to Ghani et al., biochars are hydrophilic in nature and thus have the capacity to absorb water in the early stages of hardening. This, in turn, hinders the formation of capillary pores, enhancing the density and early compressive strength [122]. The reduced plastic shrinkage can also be addressed by using biochars, owing to their hydrophilic properties. Another potential advantage with these particles might be the reduction of bleeding as pointed out by Elyamany et al. while working on the use of nonpozzolanic fillers in self-compacting concrete [123].

5. Conclusions

Biochar is a versatile material having a high potential for utilization in various fields. In the current paper, a brief summary of the literature has been reported on the subject with emphasis on the pyrolysis mechanism, the influence of operating conditions on the final products, and its potential application in the production of high-performance cement and concrete composites.

It is concluded that biochar may be produced from almost all types of feedstock; however, the characteristics of the final product strictly depend upon the constituents of the feedstock and operating conditions. On the basis of numerous research studies, it is concluded that slow pyrolysis up to 300 °C produces the optimum yield since this temperature is sufficient to decompose the cellulose, hemicellulose, and lignin effectively. The operating pressure plays an important role by increasing the biochar yield with lesser energy requirements at higher pressures.

The useful application of biochar in cementitious composites has been highlighted by various researchers and is presented in Figure 15. In cement and concrete composites, biochar produces a positive effect by increasing the strength due to the internal curing mechanism and pore refinement effect. The introduction of biochar also tends to enhance the fracture energy and tensile load carrying capacity due to the phenomenon of crack entrapment, crack bridging, and crack contouring.

However, almost all researchers have reported that the workability/flowability reduces with the incorporation of biochar in the cementitious composites, which can be overcome by using flow-enhancing admixtures. Nevertheless, the reinforcement of cementitious composites with biochar is an effective method of carbon sequestration, which is beneficial to human health and the environment.

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