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Review Article

A Comprehensive Review on Biochar - The Black Carbon: Production Technologies, Physico-chemical Properties and Utilization for Sustainable Environment

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Abstract

Biochar (BC) has now become a trending issue in both national and international level due to its numerous positive implications towards soil and environment. Conventional crop residue management (CRM) strategies like open burning of residues played havoc with the environment that has led to the evolution of sustainable route of thermochemical conversion technologies for successful CRM. BC is a carbon-rich, solid residue material obtained by thermo-chemical conversion processes from various natural organic materials, by-products and wastes (collectively known as biomasses) under oxygen-deprived environment. Among all the thermo-chemical conversion technologies established till now, pyrolysis is found to be the most outstanding in terms of yield and other desirable attributes. These carbonaceous materials possess a number of remarkable properties including aromaticity, porosity, charged surface, high internal surface area, resistance to degradation that can be effectively utilized in several domains. As soil ameliorants, they improve soil basic properties and improve essential nutrient dynamics. Since the potential benefits of BC in soil are governed by type of biomasses and production methodologies, therefore, source of biomasses and operational parameters need to be critically analyzed before its specific recommendation to distinct fields.

The current review provides a critical insight on current research on various aspects regarding the variety of different feedstocks used for BC production, an array of different thermo-chemical strategies and their controlling factors for effective biomass conversion, and the physico-chemical characteristics of BC. Additionally, a brief account is contributed on the implications of BC on soil biochemical properties and nutrient dynamics. Major constraints of biochar yield and application are also reviewed along with future outlooks.

Keywords: Biomass, black carbon, pyrolysis, soil ameliorant, nutrient dynamics

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Introduction

In recent years, biochar and the wide range of its possible applications have been extensively investigated by researchers worldwide. However, the concept of biochar, also called black carbon, is not completely new from application point of view as these high carbon residues, although not in the form we know them today, have been used since centuries. The incorporation of charcoal into the soil to enhance soil quality has been an agricultural practice for thousands of years [1]. Native pre-Columbian civilizations in the Amazon Basin combined charred residues of organic and inorganic wastes with the soils and increased their fertility. Because of their black colour and origins, these soils are known in Portuguese as Terra Preta de Indio (Indian black earth) - rich in organic matter and nutrients. Biochar is basically carbonized biomass obtained from sustainable sources and sequestered in soils to sustainably enhance their agricultural and environmental value under present and future management. In accordance with the definition specified by the International Biochar Initiative (IBI), biochar is a fine-grained product of carbonization, characterized by a high content of organic carbon and low susceptibility to degradation, which is obtained through the pyrolysis of biomass and biodegradable waste [2]. They can be utilized for energy-related purposes associated with environmental conservation and agriculture. The wide range of biochar applications is continuously expanding, mainly in such areas as industry, agriculture and operations related to the natural environment. It can be used as a soil additive, or added to fodder and silage, or applied in water treatment [3, 4]. Biochar can also be used for the immobilization of contaminants from soil, and in sewage treatment; it can be applied as a supplementary material in composting and in methane fermentation processes [5-10]. In this review we have thoroughly discussed different production technologies of biochar, their physico-chemical properties and biochemical attributes for environmental sustainability.

Importance of biochar

Several detrimental effects of crop residue burning call for an effective crop residue management for attaining agricultural sustainability. Biochemical conversion of residue to bio-ethanol has a higher scope but limited acceptance [11] whereas thermo-chemical conversion of residue biomass in absence or limited-oxygen condition resulted into liquid, gas and solid by-products [12]. These thermo-chemical technologies play significant role in crop residue management as compared to fossil fuels by producing better calorific values and cleaner fuel source by-products and are preferably promoted over other technologies recently [13, 14]. Biochar, a carbon rich by-product of thermo-chemical technology, used as a soil amendment, is considered as an effective residue management strategy for C accretion, soil fertility improvement and immobilization of pollutants [15]. It performs an important role in promoting soil physico-chemical and biological properties by improving soil C status [16, 17] and alleviating climate change by reducing harmful gases emission from the ecosystem [18, 19]. Technically, biochar is produced by heating biomass, such as wood, straw, manure or leaves by thermal degradation at temperature ranging between 300-700 ^{0}C under limited supply of oxygen [14].

Production of biochar

Biomasses for biochar production

The rapid population growth led to subsequent increases in food production, and consequently, large amounts of organic residues are produced annually [20]. Therefore, it is essential to recycle the organic residues effectively. Biochar can be produced from wide range of biomass feedstock, including agricultural and forestry by-products, animal wastes, industrial by-products and other organic wastes (**Table 1**) which governs its characteristics during conversion processes, specially calorific value, moisture and ash content, particle size, bulk density, proportion of cellulose, hemicelluloses, lignin [21]; fractions of fixed carbon and volatile components [22]; percentage and composition of inorganic substances. Producing the biochar from biomass, especially wastes offer an excellent way for the recycling of wastes into beneficial materials.

Table 1 Selected feedstocks used in biochar production

Origin of feedstocks	Types	References
Agricultural by-products	Energy crops (switch grass, willows and miscanthus), rice husk, sunflower husk, post-fermentation oats, wood chips, waste from olive oil production, straw, wheat husk, nut shells, rice hulls, tree bark	[23, 24, 25, 26]
Forestry by-products	Conifer bark, pellets from sawdust, peat, moss, beech timber	[1]
Animal wastes	Chicken litter, dairy and swine manure, cattle manure, poultry litter	[27, 28]
Industrial by-products	Sugar cane bagasse, paper sludge, and pulp	[1, 29]
Organic wastes	Waste from tea factories, Kitchen waste, sewage sludge, municipal organic waste	[29]

Production technologies of biochar

Bioenergy conversion technologies are those which are used to extract the energy out from the biomass. Various energy rich products can be obtained by the bioenergy conversion of the biomass. It is highly important to choose the appropriate method for the conversion of the biomass into energy and various value-added products so that the maximum energy can be obtained at the minimum expense keeping the environmental issues also in mind. Generally, bioenergy conversion techniques can be divided into two groups namely biochemical conversion and thermochemical conversion. Biochemical conversion involves the biological catalysts and biological organism to produce the energy from biomass while thermochemical conversion involves heat and the chemical catalyst to produce energy from biomass. Fermentation is the main process involved in biochemical process, which is widely used to obtain methanol and biodiesel from the biomass while thermochemical conversion technique can further be divided into combustion, gasification and pyrolysis. However, biochemical conversion technology is less expensive and more environment friendly as compared to thermochemical conversion technique but the rate of hydrogen production and yield is quite low in biochemical conversion method [30]. Because of this constraint, thermochemical conversion is more popular as compared to biochemical technique. Different thermochemical conversion technologies for biochar production are shown in **Figure 1**.

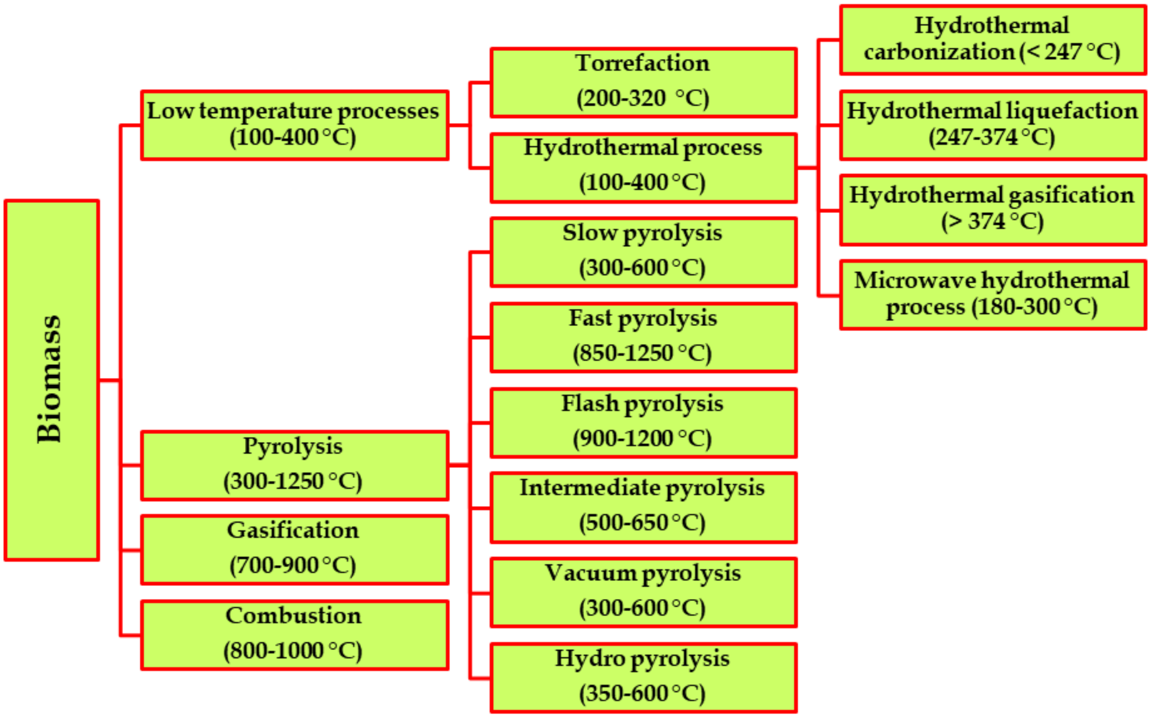

Figure 1 Different thermochemical conversion technologies for production of biochar

Low temperature processes

It includes two processes – Torrefaction and hydrothermal processes.

Torrefaction

Torrefaction technically refers to a roasting process in which biomass is heated, or pyrolyzed in an oxygen-free environment. The process increases the energy density of the biomass by removing volatiles and breaking down the complex molecules to simpler ones in which the carbon energy is more easily used. Generally, it is carried out in an inert atmosphere, e.g., nitrogen (N_2) gas. Basically, it reduces moisture, removes low weight organic compounds and, from certain temperature, also leads to depolymerisation of long polysaccharide chains [31]. The result is a biomass with higher energy density and grindability.

Hydrothermal processes

The water content in the feedstock can be a challenge for thermal processing, since drying may be economically unfeasible. Moisture contents in tropical grasses, for example, can be as high as 80-85 % [32]. In this case, the best way to treat biomass is to expose it to a hydrothermal treatment. Hydrothermal processes occur at temperatures (>100°C) and pressure conditions under which water becomes a subcritical fluid. As such, water has a completely different behaviour, switching from a polar to a relative nonpolar molecule, because the shared electron between oxygen and hydrogen atoms tends to circulate more evenly, reducing the oxygen electronegativity [33]. Simultaneously, under hydrothermal conditions, water dissociation increases dramatically (K_w ~10-11) as temperature increases, creating a highly favourable environment for hydrolysis [34, 33].

Hydrothermal processing can be grouped into three different classes [32, 35, 36]:

- hydrothermal carbonization occurs at temperatures below 247 °C, and the main product is hydrochar;
- hydrothermal liquefaction is performed at intermediate temperature (ranges between 247 and 374°C), resulting in a liquid fuel known as biocrude (a petroleum-like oil);
- hydrothermal gasification takes place at temperatures above 374°C, where gasification prevails resulting in syn-gas [37].

Therefore, not only the solid yield but also its chemical characteristics can be very different, according to the temperature of the process, different biochars will result from these hydrothermal processes.

A particular technology of hydrothermal treatment is microwave heating [38]. Mašek *et al*. mentioned as advantages of microwave heating over conventional heating the controllability and energy and cost efficiency of the process, since microwave heating at 200°C can induce similar or even stronger chemical alterations than slow pyrolysis at 350°C [39]. They compared slow (SP) and microwave pyrolysis (MW) of straw and woody biomass and found a comparable stability and similar levels of conversion between biochars but significantly lower char yields from MW pyrolysis than SP.

Pyrolysis

Pyrolysis is a thermochemical decomposition process in which ligno-cellulosic biomass is thermally degraded at an elevated temperature (ranging between 300-700^{0}C) under inert or very low stoichiometric oxygen atmosphere resulting in solid (biochar), liquid (bio-oil) and gas (syngas) products [40, 41]. Yield of products resulting from biomass pyrolysis can be maximized as follows: Biochar/charcoal (a low-temperature, low heating rate process, long residence times), liquid products (low or moderate temperature, high heating rate, short gas residence time), and fuel gas (a high-temperature, low heating rate process, long gas residence time) [42, 41]. Commercially, this process involves three steps: (1) moisture and some volatiles are lost; (2) conversion of un-reacted residues into volatiles, gases and biochar and (3) slow chemical rearrangement of the biochar [11]. It is an extremely complex process which involves so many different reactions in the reacting zone [43, 44] and it can be represented by the following reaction [45]:

$$(C_6H_6O_6)_n \rightarrow (H_2 + CO + CH_4 + \cdots + C_5H_{12}) + (H_2O + CH_3OH + CH_3COOH + \cdots) + C$$

The first part in the product side represents the gas yield with different gases being produced during the process. Second part of the product side is showing the mixture of various types of liquid products and the last term is the solid yield.

This facility in combining temperature and residence times makes pyrolysis a very versatile process, which allowed the development of many different technological possibilities. Overall, pyrolysis processes differ among each other in how fast heat is transferred to feedstock particles, the maximum temperature and residence time. They are usually classified according to these reaction conditions and product yield [35]. Differentiation of pyrolysis technology can be done on the basis of pyrolytic temperature of the pyrolytic material, residence time, size of adsorbent, pressure, heating rate and method [46-49]. Depending upon these conditions, pyrolysis process can be sub-classified into six categories. Each category is having its own merits and demerits. **Table 2** summarizes the operating parameters of all these types of pyrolysis.

Table 2 Operating conditions for different types of pyrolysis for biochar production

Type of pyrolysis	Temp (°C)	Heating rate (°C/s)	Residence time (s)	Pressure (MPa)	Particle size (mm)	Biochar yield (%)	References
Slow	300-600	0.1-1	300-550	0.1	5-50	20-40	[50, 51, 52]
Fast	850-1250	10-200	0.5-10	0.1	< 1	10-15	[50, 51, 52]
Flash	900-1200	> 1000	< 1	0.1	< 0.5	10-15	[50, 51, 52]
Intermediate	500-650	1-10	10-20	0.1	1-5	15-25	[53, 54]
Vacuum	300-600	0.1-1	0.001-1	0.01-0.02	-	25-35	[55, 56]
Hydro	350-600	10-300	> 15	5-20	-	-	[57, 58]

Note: "-" represents data not found

Slow pyrolysis

Slow pyrolysis, most traditional form having long history since charcoal production, involves heating the biomass to a relatively low temperature (300-600°C) at a lower heating rate of 0.1 to 1°C/s for long residence time (5 to 30 minutes, sometimes several hours to days). Here, approximately equal amounts of syngas, bio-oil and biochar (20-40%) are obtained by slow heating of biomass [40]. Slow heating rate and longer vapor residence period create a suitable ambience for secondary reactions to complete and allow vapors to be removed those are generated during secondary reaction. This ultimately results in the formation of solid carbonaceous biochar [50].

Fast pyrolysis

Fast pyrolysis involves quick heating of feedstock materials at 850-1250°C with rapid heating rate (10-250°C/s) for a short period of time (0.5-10 s). Therefore, the energy requirement of fast pyrolysis is significantly higher than the other techniques [49, 59]. The underlying principle is to take the biomass up to an elevated temperature at which thermal cracking can take place as well as minimize the exposure time which favors the char production. In a typical fast pyrolysis process, yield of bio-oil (60-75%) dominates to biochar (15-25%) and other non-condensable gaseous products (10-20%) [60].

Flash pyrolysis

It is the modified and improved version of fast pyrolysis used mainly to produce bio-oil. Flash pyrolysis is performed at an even shorter reaction time (< 1 s) than fast pyrolysis and so the heating rate is very high (> 1000°C/s) [41]. The process requires a special reactor configuration (parallel screw reactor, for example) and a heat conductor (as fluidized bed) must be present to receive the feedstock. The fine particles of feedstock are burnt by flash fires. High temperatures ranging from 900 to 1200°C promote rapid depolymerization and feedstock cracking, resulting in bio-oil with viscosity comparable to diesel oil [50, 51]. However, char yield is reduced (10-15%).

Intermediate pyrolysis

It is designed to maintain a balance between liquid and solid products. So, the operating conditions are kept in between slow and fast pyrolysis. Intermediate pyrolysis operates between 500-650°C, with heating rate ranging between 1 to 10°C/s with residence time 10-20 s. The typical product contains 40-60% liquid, 20-30% non-condensable gases and 15-25% biochar [54]. Unlike fast pyrolysis, it inhibits the formation of high molecular tars and produces dry char which is suitable for agricultural use or energy production along with good quality bio-oil [61].

Vacuum pyrolysis

It is the thermal degradation of biomass under extreme low pressure (0.01-0.02 MPa) in oxygen free atmosphere with very short residence time (0.001-1 s). Heating temperature and heating rate are similar to that of slow pyrolysis. Here low pressure/vacuum is used to remove the vapors instead of the purge gas which is employed in most of the pyrolysis techniques [62]. Low pressure allows the organic matrix to be decomposed at relatively low temperature and lower vapor residence time minimizes secondary reactions resulting in high yield of liquid products and moderate amount of char (25-35%) [63].

Hydro pyrolysis

This is one of the recent techniques for production of high-quality bio-oil, where hydrogen/hydrogen-based materials along with biomass are fed to the reactor at pressure higher than atmospheric pressure ranging between 5 to 20 MPa with/without use of catalyst [58]. The temperature maintained for hydropyrolysis ranges from 300 to 600°C and other operating conditions are nearly same to that of fast pyrolysis. Under this pyrolysis approach, yield of biochar hardly exceeds 10%.

Combustion

Combustion is the oldest method in which the chemical energy stored in the biomass is released in the form of heat by its direct burning in oxygenated atmosphere. Combustion can reach temperature as high as 800 to 950°C [64]. An inefficient or incomplete combustion process can result in a charcoal-rich material with high ash content.

Gasification

Gasification is a thermochemical process in which carbonaceous contents of the biomass are converted into the gaseous fuel in the presence of gaseous medium like oxygen, air, nitrogen, carbon dioxide, steam or some mixture of these gases at an elevated temperature ranging between 700°C and 900°C [64]. Unlike combustion, it is partial oxidation of biomass which extracts out the energy present in the biomass and packages it into chemical bonds in the form of gaseous products. In this process, the intrinsic chemical energy of carbon present in the biomass is converted into combustible fuel gases which can be used more efficiently and easily than raw biomass [65]. The gas produced by the gasification is generally referred as bio-syngas. This bio-syngas consists of mainly CO, CO_2, H_2 and N_2. The residues after gasification are char (solid carbonaceous material), ash, tar and some oil also [66]. The comparison of different thermochemical methods is depicted in **Table 3**.

Table 3 Comparison of thermochemical conversion techniques for production of biochar

Parameters	Low temperature processes	Pyrolysis	Combustion	Gasification
Temperature (°C)	50-300	300-1250	800-1000	700-900
Air supply	Nil	Nil	Excess	Marginal
Resources	Solid biomass	Solid biomass	Solid biomass	Solid biomass
Status	Developing	Developing	Commercial	Commercial
Pretreatment	Not required	Required	Not required	Required
Cost	Low	High	Low	High
Harmful emission	Low	Low	High	Low
Products	Char, bio-crude and syngas	Biochar, bio-oil and gaseous product	Heat	Bio-syngas, bio-oil and char
References	[52]	[50, 51]	[65, 67]	[64, 68]

Physico-chemical properties of biochar

Feedstock materials used and processing conditions are the most important factors that determine the characteristics of biochar. Amorphous and graphene carbon is the basic structural unit of biochar (**Figure 2**) [69]. The most important properties of biochar include their chemical composition, stability, specific surface and porosity. Importantly, the chemical composition of biochar mainly depends on the chemical composition of the substrates used in biochar production. Biochars contain stable organic carbon, aromatic compounds, aliphatic compounds and ash [70].

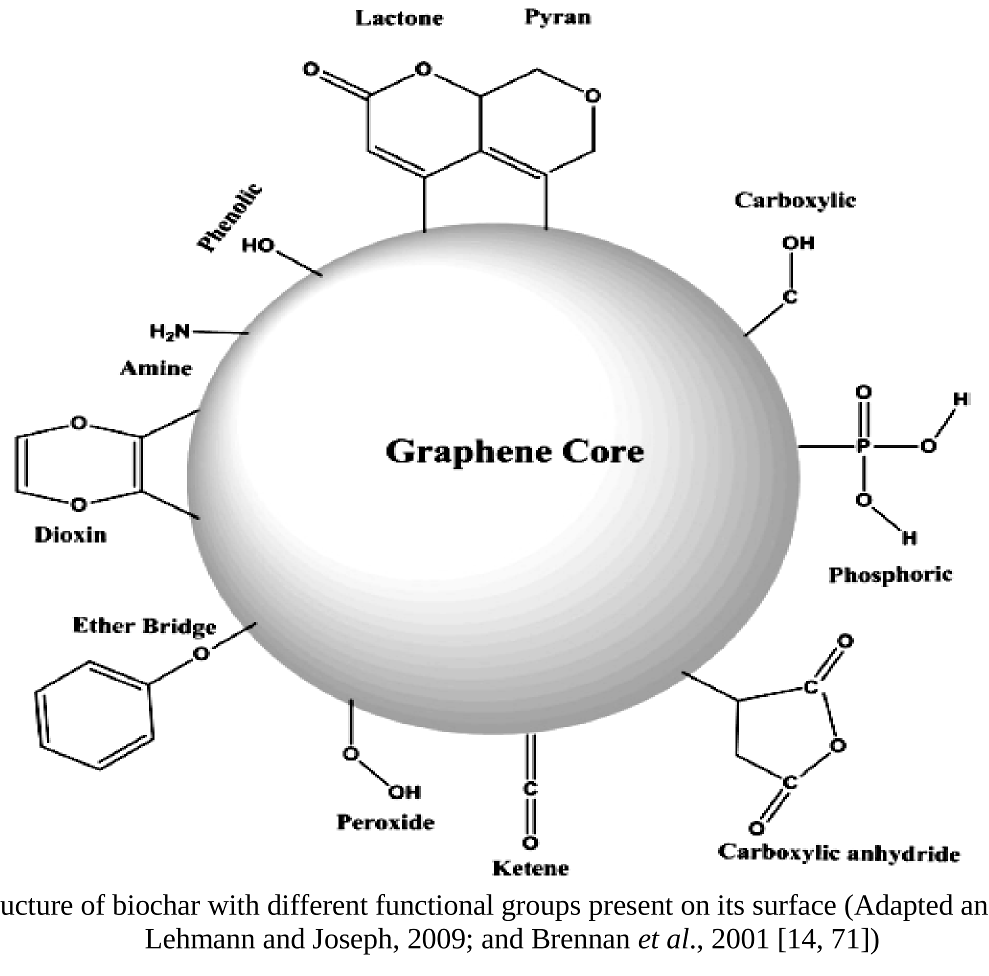

Figure 2 Structure of biochar with different functional groups present on its surface (Adapted and redrawn from Lehmann and Joseph, 2009; and Brennan *et al*., 2001 [14, 71])

Taking into account the type of biomass and parameters of thermal processing applied, the content of carbon in biochar may be in the range of 50–90%, water 1–15%, volatile substances up to 40% and mineral substances up to 5%. Carbonization products have a neutral or alkaline pH and are highly resistant to microbiological degradation and decomposition; applied in the soil they are stable in terms of their chemical composition [72]. Their porous structure on the other hand contributes to improved sorption capacity of soils (**Figure 3**).

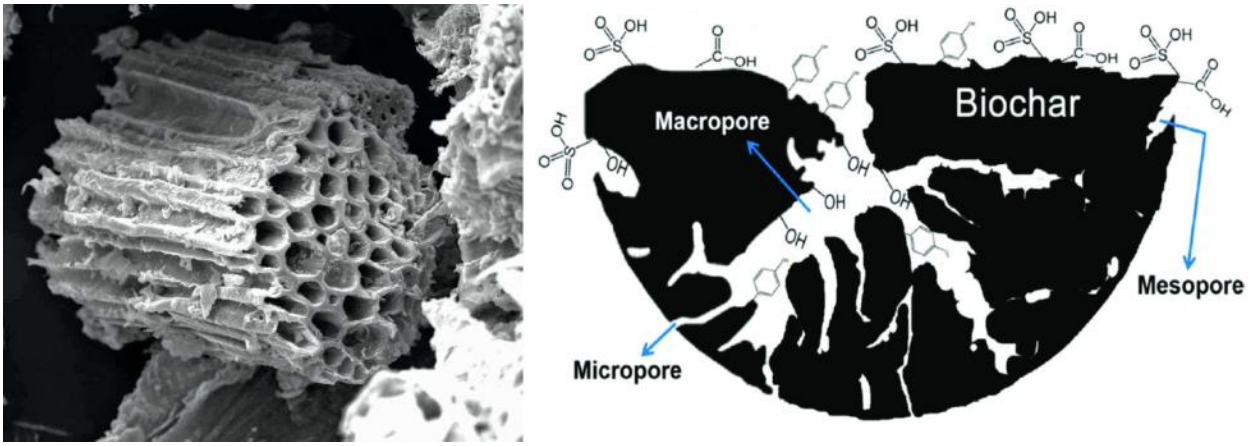

Figure 3 Electron microscopy (SEM) image of biochar (attributed to NextChar LLC) [73], and A model of porous biochar containing different functional groups [74]

Change of pyrolysis temperature causes the change of crystalline morphology of biochar [27]. Transformation of carbon structure from amorphous to aromatic takes place with the increment of pyrolysis temperature and it results in amalgamation of various graphene sheets [75]. Li *et al*. used Fourier Transform-Raman spectroscopy with peak intensities between the range of 800 and 1800 cm^{-1}, and found that the ratio of large to small aromatic ring structures was increased and oxygen-containing functional groups were decreased with increasing pyrolysis temperature [76]. Higher pyrolysis temperature not only results in increase in the order of the crystallites but also increases its surface area [77]. The vesicular structure of biochar generally contributes to its high porosity whereas high temperature condition of pyrolysis causes the formation of nano pores, which is the major contributor of biochar's high surface area [78]. Biochar has the ability to retain water and soil nutrients due to its high porosity and large surface area [79, 80]. Therefore, the overall surface area of soils, especially of coarse textured sandy soils can be increased by biochar application [77]. In this context, Hammes *et al*. reported that increase in pyrolysis temperature enhances the conversion of aliphatic-C to aromatic-C, which in turn resulted in higher surface area of the biochar [81].

Biochar properties like porous structure, charged surface and surface functional groups (like hydroxyl, carboxyl, phenolic, carbonyl etc.) play important role that influence migration, transformation and bioavailability of contaminants in soil. Besides, morphological and spectral characteristics, physical and chemical properties of biochar are also determined by feedstock material, charring temperature, heating rate, residence time [82, 83]. When production temperature is $>500^0$C, the pH of biochar ranges from neutral to alkaline [83]. According to Liang *et al*., volatile and N component of biochar were decreased while ash and fixed carbon content were enhanced with increasing pyrolysis temperature from 400 to 600^0C. Thus, biochar prepared at 600^0C had wider C:N ratio making it more stable in soil due to its reduced rate of decomposition [84]. Similarly, rice and wheat biochar produced at 400^0C were reported to have comparatively lower bulk density than maize and pearl millet biochar [85]. High temperature biochar contains reduced amounts of N and S as these compounds tend to volatilize at a temperature above 200^0C and 375^0C respectively whereas, K and P volatilize between 700^0C and 800^0C. Besides this, high temperature biochar (800^0C) have higher pH, electrical conductivity (EC) and extractable NO_3^-, while biochar produced at low temperature (350^oC) have higher amounts of extractable NH_4^+, P and phenols [86]. Krull *et al*. reported that temperatures above 350°C yield biochar with high aromatic C (specifically aryl), but they still retain some of the alkyl C characteristic to the plant [87]. However, temperatures above 500°C resulted in complete removal of the alkyl C. The degree of aromaticity of the C structures is measured by the elemental H/C and O/C ratios [87]. Hammes *et al*. observed that biochar produced at $<500^0$C have H/C ratios of >0.5, whereas < 0.5 in case of biochar prepared at temperatures >500°C, where lower H/C ratios are indicative of high degree of aromaticity [81]. Moreover, increasing pyrolysis temperature causes reduction of CEC of the biochar [83]. The high CEC of biochar is mainly due to the presence of negatively charged functional groups [88]. Brewer *et al*. found that biochar prepared from switch grass and stover contains lower lignin content and higher ash content than biochar produced from hard woody materials [89]. High hemicellulose:lignin ratio of biomass results in larger amount of volatile components, but the char yield was significantly reduced [90].

Utilization of biochar

Effect of biochar on soil nutrient dynamics

Recent studies indicate that addition of biochar to soil may enhance mineralization of soil organic carbon fractions [91, 92], releasing nutrients and improving soil fertility. According to Maestrini *et al*., in short-term incubations a positive priming effect on soil C decomposition may be induced by the presence of labile fraction in biochar whereas, long-term biochar application may cause negative priming effect through promoting physical protection of native soil organic carbon [93]. Cely *et al*. reported a negative priming effect in soil after application of wood chip biochar and a positive priming effect in soil amended with biochar which was the mixture of paper sludge, wheat husks and sewage sludge. This result was due to difference in biochar properties like carbon content, volatile matter, carbon aromaticity easily oxidizable organic C, fixed C, presence of metal and phenolic substances etc. [94]. Khan *et al*. conducted an in vitro incubation and observed that soil organic C reduced in biochar treated soils than its corresponding biomass treated soils but biochar treated soils showed higher pH, total N, phyto available N, P, K than biomass treated soil irrespective of incubation days [95].

Rondon *et al*. observed that availability of trace metals like molybdenum (Mo) and other macro and micro-nutrients like K, P, Mg, Fe and Mn were increased due to the application of biochar [96]. Uzoma *et al*. and Nigussie *et al*. reported that combination of biochar with cow manure biochar resulted in appreciable increase in N, P, K, Mg and Ca uptake, pH, total N, total C, Olsen-P, exchangeable Ca, Mg and K in the soil [97, 98]. In addition, it has been shown in literature that nutrient availability also greatly varies with the type of biochar. For e.g. biochar produced from animal source is richer in nutrient elements than those produced from plant materials [99]. Gaskin *et al*. suggested that poultry litter had higher concentration of nutrients like N, P, K, Mg, B, Ca, Fe, Mn, Zn etc. than peanut hull and pine chip biochar [100]. Another study conducted by Warnock *et al*. reported that application of mango wood and peanut shell biochar enhanced the availability of soil P but application of pine wood biochar reduced the soil P concentration [101]. The biochar produced from different feedstuffs and their physico-chemical characteristics are mentioned in **Table 4**. But when biochar was applied in combination with different organic and inorganic amendments then it affected the nutrient transformation. Brantley *et al*. reported the impact of poultry litter biochar with fertilizer (N and P fertilizers) on soil nutrient availability and growth of corn [99]. They observed that microbial biomass C and N, mycorrhizal infection were not affected by biochar alone but their combined application increased acid phosphomonoesterase activity, Mehlich-3 Mg, water soluble P, above ground plant growth etc.

Widowati *et al*. suggested that nitrogen utilization from the applied fertilizer is increased by the addition of biochar as biochar application increases CEC which enhances N use efficiency [117]. Using ^{15}N-labeled fertilizer, Steiner *et al*. observed that the plots where NPK fertilizers was applied with biochar (18.1%), N use efficiency was higher than the NPK fertilized plots without biochar (10.9%) [118]. Thus, the combined application of biochar with nitrogenous fertilizer creates a positive impact on soil quality and plant N [119, 120]. Chan *et al*. and Van Zwieten *et al*. also observed the existence of an appreciable biochar-nitrogen interaction in case of combined application of N fertilizer and biochar [121, 122]. According to Borchard *et al*., N utilization efficiency is increased by mineral retention and biological fixation when N fertilizer is applied with biochar [123]. Further, biochar application has been shown to significantly increase nitrification [124], absorb NH_4^+, reduce NH_3 volatilization [125] and denitrification [126]. Maestrini *et al*. revealed that when ryegrass-derived pyrogenic organic matter was added to a forest Cambisol it helped to increase gross N mineralization as decomposition of pyrogenic organic matter added mineral N into the soil [127]. However, Prayogo *et al*. found the reduction of N mineralization by adding willow biochar at both 0.5% and 2% [128]. Similarly, Dempster *et al*. observed that biochar had very limited effect on mineralization rate of low molecular weight dissolved organic N compounds [129]. Widowati *et al*. reported the increased rice production and reduction of need for N fertilizer due to the combined application of biochar produced from manure and litter [130]. Edward *et al*. observed the effect of combined application of biochar and inorganic fertilizer on N availability and reported that soil available nitrate concentration was enhanced by 85% at 0-15 cm soil depth but soil-ammonium N was reduced by 71% due to the combined application as compared to sole inorganic fertilizer application [131]. Gundale and DeLuca reported that biochar produced from bark and wood of two different species at two different temperatures (350°C and 800°C) influenced nitrification and N mineralization differently. Nitrification was enhanced by all biochar treatments except Douglas fir wood, which recommended that for some species wood may form less effective biochar than bark [132]. Therefore, above studies suggest that the impact of biochar on N mineralization depends on type of biochar and their interactions.

Biochar application in soil has been reported to increase phosphorus bioavailability and plant growth by reducing P sorption [133]. Zhai *et al*. showed that the availability of soil P increased with maize biochar due to high concentration of P in ash fraction (77% of total biochar) [134]. Mau and Utami observed that availability and uptake of P by plants was enhanced at 8 weeks after planting due to the combined application of biochar and mycorrhizae [135]. Biochar has the capacity to adsorb cations like Fe^{3+}, Al^{3+} which results in delayed P adsorption and precipitation in soil [136, 137]. However, biochar application did not always enhance P availability. Novak *et al*. conducted a soil column experiment and showed that the addition of biochar enhanced P retention in soil but reduced P levels in leachate solution [106]. Similarly Satriawan and Handayanto conducted an experiment to examine the effect of combined application of biochar and plant litter on soil properties and P uptake and observed that the combined application caused lower CEC, total P and exchangeable Ca. P availability was not significantly enhanced but it increased the P uptake by maize [138].

Table 4 Physico-chemical characteristics of different types of biochar

Feedstock	**Tem. (°C)**	**pH**	**%**							**CEC (c mole kg^{-1})**	**C/N ratio**	**Ash (%)**	**H/C ratio**	**O/C ratio**	**SSA (m^2 g^{-1})**	**Reference**
			C	N	P	S	Ca	Mg	K							
Peanut shell	350	8.54 ± 0.03	44.0 ± 0.5	1.01 ± 0.01	-	-	-	-	-	14.9 ± 0.3	44 ± 0.69	-	0.31	-	-	[102]
Holm oak	600	10.2	68.2	0.67	-	-	-	2.93	4.41	35.1	102	-	-	-	-	[103]
Maize straw	450	10.50	-	1.22	-	-	1.36	0.35	7.54	-	-	22.28	-	-	4.00	[104]
Corn stover	650	-	77.51	1.50	-	-	-	-	-	-	64.12	4.06	0.34	0.18	242.70	[105]
Rice husk	550	-	74.37	1.02	-	-	-	-	-	-	85.06	2.43	0.29	0.23	95.20	[105]
Peanut hull	500	8.60	82.00	2.70	0.30	0.10	-	-	-	-	30.37	9.30	0.44	0.03	200.00	[106]
Sugar cane bagasse	<500	8.63	74.02	1.00	0.24	-	0.17	0.32	2.00	69.62	74.02	12.21	0.42	0.23	92.30	[107]
Cattle waste	380	8.20	62.10	0.10	-	-	-	-	-	39.00	621.00	25.60	1.90	0.27	-	[108]
Sewage sludge	380	8.50	38.30	5.20	-	-	-	-	-	0.50	7.37	44.90	0.94	0.25	-	
Oak wood	600	6.38	87.50	0.20	-	-	-	-	-	75.70	489.00	0.01	0.33	0.07	642.00	[109]
Corn stover	350	9.39	60.40	1.20	-	-	-	-	-	419.30	51.00	11.40	0.75	0.29	293.00	[110]
	600	9.42	70.60	1.07						252.10	66.00	16.70	0.39	0.10	527.00	
Corn stalk	400	9.60	51.10	1.34	0.25	-	-	-	1.34	-	38.13	-	-	-	-	[111]
	500	10.10	48.40	0.55	0.44				2.65		88.00					
Wheat straw	425	10.40	46.70	0.59	-	-	1.00	0.60	2.60	-	79.15	20.80	-	-	-	[112]
Coco peat	500	10.30	84.40	1.02	0.03	0.27	0.06	2.30	-	-	82.75	15.90	0.41	0.10	13.70	[113]
Coconut charcoal	<500	8.86	76.50	0.20	-	-	-	-	-	-	426.60	2.90	0.12	-	-	[114]
Pinewood	<500	8.47	53.20	0.40	-	-	-	-	-	-	143.40	65.70	0.35	-	-	[100]
Eucalyptus deglupta	350	7.00	82.40	0.57	0.06	0.03	-	-	-	4.69	144.56	0.20	-	0.12	-	[96]
Hard wood saw dust	500	-	63.80	0.22	-	0.01	-	-	-	-	290.00	22.80	0.60	0.14	1.00	[115]
Chinese pine	600	8.38	66.67	2.21	-	-	-	-	-	31.58	30.17	12.50	0.58	0.31	-	[116]

Even though the effect of biochar on sulphur (S) and K transformations has received less or no attention, plant residue and biochar have a great impact on S and K mineralization. Blum *et al*. conducted an incubation experiment and reported that maximum leaching of sulphur took place after the addition of biochar and it was caused by abiotic release of mineral S and hydrolysis of ester-S. The combined application of plant residues and biochar increased the mineralization of S at earlier stage of incubation. During the earlier stage ester-S was increased but C-bonded S was reduced due to this application [139]. Liang *et al*. observed the decrement of alkaline hydrolysable N and enhancement of exchangeable K due to the addition of biochar to soil [140]. Stevenson and Cole reported that application of biochar's reduces the surface albedo of mineral soil which helps to enhance S oxidation or mineralization rates [141]. However, some researches have also shown contradictory results in case of yield, soil properties and nutrient availability with biochar application alone or in combination with other amendments [142-144]. Therefore, till date many confusions and contradictions exist about the combined effect of biochar with different amendments on the nutrient transformation in soil.

Effect of biochar on biochemical properties of soil

Enzyme activities, one of the major indicators of soil health and sustainability, are important biochemical properties of soil. The materials which help to enhance enzyme activities are considered as soil ameliorating agents. Biochar has been considered as a beneficial product in this aspect. Various studies have been reported on these properties for biochar added soil at laboratory scale but field basis studies regarding this aspect are very limited. Several studies have suggested that, application of biochar into soil helped to improve biochemical properties by increasing microbial biomass carbon (MBIOCHAR), dehydrogenase activity, catalase activity [145, 146] as well as reduced activity of hydrolytic enzymes like glucosidase, leucine amino peptidase and alkaline phosphatase due to enhanced microbial activities by modulating soil properties [147, 148]. Soil respiration and enzymatic activity were reported to be enhanced due to pH-buffering, SOM increment, nutrient retention through sorption on biochar surface [147]. Besides, increment in activities of alkaline phosphatase, aminopeptidase and N-acetyl-glucosaminidase as well as reduction in acid phosphatase activity whereas no effect on phenol oxidase, peroxidase, catalase activities were observed in biochar treated soil due to higher pH [147]. However, sorption of enzymes on biochar surface may cause reduction in extracellular enzyme activity [149] whereas higher turnover and soil respiration was observed in biochar added soil due to higher activities of belowground microorganisms [150] that was directly correlated with SOC [151]. Additionally, nitrifying enzyme activities have also been reported to be affected by biochar treatment due to its direct impact over soil nitrifiers and denitrifiers [152] and denitrifying enzyme activity is suggested to be enhanced with increasing dose of biochar addition [150]. These activities under biochar application were might be caused due to higher N-fixing gene content like *nif*H, *nos*Z, *nir*K, *nir*S. Higher biological nitrogen fixation (BNF) under biochar treatment might be due to higher nodulation [153], N-immobilization within microbial cell [154], higher micronutrient availability like B, Mo [96] and enhancement in available P content to microorganisms [155]. Therefore, addition of biochar to soil might be beneficial as it can help to enhance nutrient content of soil as well as may be a positive mechanism for prospecting its large-scale application.

Major constraints to biochar production and application technology

Though several expensive studies had been performed for establishing biochar as a suitable and potential soil ameliorant and C sequestration agent, certain confusions are still there that limit the use of biochar in soil at farmer’s level. During slow pyrolysis, poly-aromatic hydrocarbons (PAHs) are produced that remain attached with anionic surfaces of biochar, might cause pernicious impact to soil and microbial community which is one of the major limitations [156]. Besides, low molecular weight condensed ring structured toxic organic components like naphthalene, fluorine, furans etc. are produced during pyrolysis that have detrimental effect over microbial activities in soil during early days of application [157, 158]. Several other important constraints observed by workers for exploration of biochar as ameliorating agent are as follows:

- Lack of standardized application rate [156]
- Incommodious record on the behaviour of SOC or SOM under biochar application [159, 156]
- Ambiguity about long term nature of biochar under field application [150]
- Release of pollutants, toxic elements that are detrimental to environment as well as soil and human health [160]
- Reduction of the activity of pre-emergent herbicides due to addition of biochar [70]
- More heterogeneity in biochar quality because of upgraded pyrolysis technology [161]
- Higher cost of production [156]
- Variation in feedstock and pyrolysis condition affecting its properties [156]
- Negative impact on soil microorganisms because of mineralization of volatiles or labile fractions [70]
- Salinity and phytotoxicity caused by higher concentration of biochar application in soil [162]

Conclusion and Future Perspectives

Biomass is a unique resource because it is renewable and can be converted into various forms of chemical feedstock and energy products. Among various products from biomass, biochar would be the most valuable because of its interesting physical and chemical properties. The maturing field of in research on the property and use of biochar and its production techniques allow us to conclude that biochar technologies, especially as a means of improving the quality of soil and environment, will continue to flourish in the future. However, it must be accentuated that owing to the lack of specific guidelines for biochar, its commercial use is limited. In order to develop the biochar industry and to ensure environmental safety, uniform legal and quality regulations should be ensured. It should, however, be emphasized that further comprehensive research is needed to investigate the feasibility of the application of biochar and to determine the optimum methods for using this highly productive material. For large surface area and porosity of biochar, they can raise the capacity of water holding of soil and the absorption of nutrients with a view to decrease loss and an augment soil structure, so biochar might progress fertility of soil and raise crop yields in future if it is applied to soil with a suitable application rates. We hope that this summary of recent literature can lead to the foundation of new research which will exploit the great potential of biochar and biochar-based materials.

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