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Multifaceted application of crop residue biochar as a tool for sustainable agriculture: An ecological perspective

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ABSTRACT

Lignocellulosic crop residue biomass, in surplus, is of vital importance due to its multifaceted utilization potential on- and off-site to agricultural systems; therefore, its management is essential for sustainable agriculture. The malpractice of open crop residue burning leading to the brown cloud phenomenon and contributing significantly to atmospheric heterogeneity through enhanced gaseous and particulate emissions is of greater off-late concern. Available traditional crop residue management (CRM) technologies have not achieved wider adaptation; therefore, recently thermochemical conversion has been foreseen as an interesting tool for potential CRM under changing climate scenario. Biochar, a by-product of thermochemical processes, has been evaluated as a potential soil ameliorant and C sequestration agent. As soil ameliorant, it improves soil basic properties directly along with subdued release of greenhouse gases from agroecosystems, provides adsorption surface to agrochemicals and improves essential nutrient dynamics. Since the potential benefits of biochar in soil are governed by initial pyrolysis conditions and soil types; therefore, its wider utilization potential as suitable tool in sustainable agriculture and climate change mitigation needs to be critically analyzed before its specific recommendation to an agroecosystem. The present review provides a critical insight on current research on various aspects, particularly ecological, of crop residue biochar starting from the feedstock sources, pyrolysis conditions and changes after application. Additionally, a brief account is given on the agronomic relevance and major constraints of biochar amendment as an ecological engineering tool for sustainable agriculture. After reviewing various aspects of crop residue as feedstock, we recommend its use as a blend, rather than sole use, along with several other lignocellulosic materials under pyrolysis process as well as ameliorating agent.

1. Introduction

The agricultural management introduced by green revolution to meet the food requirements have fallen about in context of sustainable development due to major grassroot-level drawbacks viz., decreased soil organic matter (SOM), poor soil health, reduced microbial and mesofaunal activities associated with biodiversity loss, increased open crop residue burning, enhanced use of persistent agrochemicals (e.g., pesticides and fertilizers) and their health impacts, etc. As a consequence of increased grain productivity, green revolution also resulted into a proportionally surplus crop residue generation in developing and urbanized countries. As estimated by Lal (2008a), about 4000 MT/yr crop residue is produced worldwide from 27 food crops, with a 75% share of lignocellulosic residue produced by cereal crops. Rice and wheat are the main crops grown in Asian countries and contributing around 30% of the global lignocellulosic biomass generation from cereal crops (FAO online database, 2006; Buranov and Mazza, 2008; Haefele et al., 2011). Such a massive crop residue generated following intensive agricultural activities may be utilized as a valuable resource in agroecosystems further because of its impact on plant nutrients availability and soil organic matter (SOM) level, thus, improvement in soil properties (Westeman and Bicudo, 2005; Tang et al., 2013).

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Globally, open crop residue burning is a very common practice in general, which leads to the release of various air pollutants including non-methane hydrocarbon compounds (NMHCs) (Jain et al., 2006) and particulate matter ($PM_{2.5}$ and PM_{10}) consisting primarily of ash, polycyclic aromatic hydrocarbons (PAH), and soot (organic carbon & black carbon) in the atmosphere (Radke, 1989; Crutzen and Andreae, 1990). Such pollutants interrupt with radiative–convective coupling of the Sun–Earth system and also considered as the potent source of Asian Brown Clouds (ABCs) (Ramanathan and Carmichael, 2008). These detrimental effects of crop residue burning call for an effective crop residue management (CRM) system for attaining agricultural sustainability. However, CRM has received less space in R&D community, but its probable contribution to improved soil health and fertility leading towards sustainable agriculture with substantial carbon sequestration is of great significance (Erenstein, 2011). Several alternatives (like physical, chemical and thermochemical conversion processes) have been suggested for CRM to avert from open residue burning. Physical or mechanical processes involve removal of crop residue manually or mechanically from field for livestock feed, conservation agriculture practices and burning at a common place (Thakur and Kumar, 2005; Singh, 2011). Biochemical conversion of crop residue to bio-ethanol as an additive to fossil fuel has a greater scope but limited acceptance so far (Demirbas, 2006; Rass-Hansen et al., 2007; Lal, 2008a). Thermo-chemical conversion of crop residue biomass in absence or limited-oxygen environment resulted into liquid, gas and solid valuable by-products (Fig. 1). Massive crop residue biomass, which was earlier considered as a waste, is now considered as a suitable feedstock for biofuel conversion technologies (Lehmann, 2007a,b; Lal, 2008a; Buranov and Mazza, 2008). Moreover, better calorific values and cleaner fuel source by-products from thermochemical technologies as compared to fossil fuels have significant role in CRM and are preferably promoted over other technologies recently (Lehmann, 2007a,b; Lehmann and Joseph, 2009).

Biochar is a by-product of biofuel technology which is extensively studied as soil ameliorant worldwide. Therefore, of various thermochemical technologies, biochar transformation technology (BTT), having multiple ecosystem services such as soil quality improvement, waste management, climate change mitigation and green energy production (Fig. 1), is viewed among the most reliable alternative to open residue burning (Lehmann and Joseph, 2009). BTT provides great opportunities as conservation technologies for sustainable agro-ecosystem practices, leading to evergreen revolution against the existing one (Tillman, 1998; Conway, 1999) because biomass C to biochar C conversion facilitates more C retention to soil i.e., retains about 50% (for long time) of parent C compared to traditional conservation agriculture systems i.e., burning (only 3%, rest releases instantly to atmosphere) and microbial degradation (10–20% for 5–10 years) (Lehmann et al., 2006).

To achieve long term food security by maintaining agricultural sustainability, management of SOM reserves in harmony to nutrient cycling and water use efficiency (WUE) has been proposed as a central idea in the era of climate change (Jones et al., 2012). Further, soil C sequestration (Renforth et al., 2009; DeJong et al.,

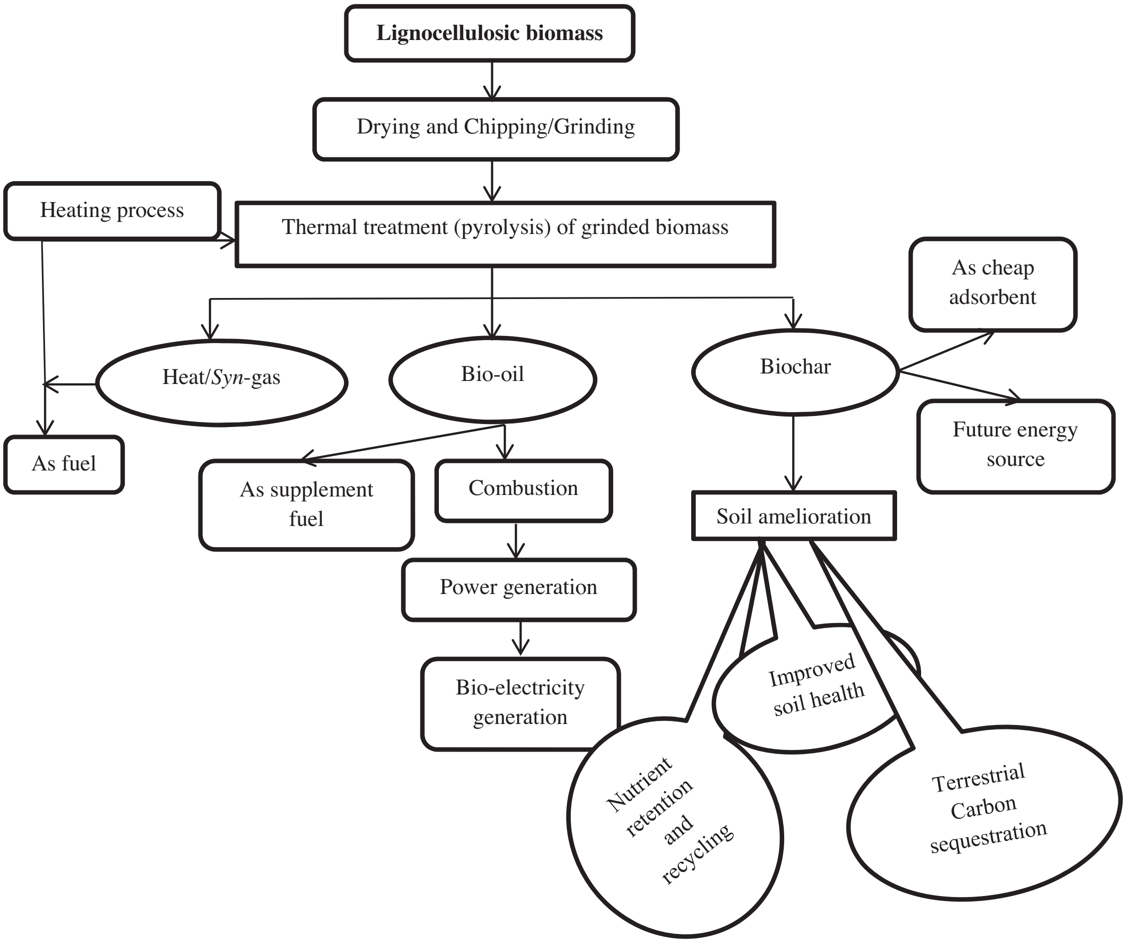


Fig. 1. Sustainable thermochemical conversion process of lignocellulosic biomass to bioenergy and valuable products such as future energy source, cheap adsorbent and soil ameliorating agents.

2011), biochar addition (Lehmann, 2007b), and phytosequestration (Jansson et al., 2010) have been proposed for mitigating climate change through agroecosystems. Adoption of best management practices is unable to manage overall emissions, thus, an active net withdrawal of carbon dioxide (CO_2) from the atmosphere for long term is required (Lackner, 2003). BTT from crop residue suits best in this regard. Crop residue has been an established material for biochar sequestration technology, there is a need of holistic study on crop residue biochar (CRB) in varying pyrolysis conditions and its multifaceted use as an ecological engineering tool for sustainable agriculture in the present era of climate change (Fig. 2).

Therefore, the present review initially deals with crop residue inherent properties and its suitability as feedstock for pyrolysis. In general, extensive literatures are available on biochar formation, characterization and its potential applications (Lehmann and Joseph, 2009) as soil ameliorant, adsorbents (Mohan et al., 2014), impact on soil biota (Lehmann et al., 2011), impact on bioremediation of contaminated soil (Tang et al., 2013), GHGs emission reduction (Cayuela et al., 2014), however, these literature have focused on biochar derived mainly from wood with little emphasis on CRB. Thus, the present review would strictly focus on CRB, its properties, applicability as soil amendment for sustainable agriculture, changes it undergoes after application to soil and the possible constraints to wider applicability.

2. Crop residue biochar (CRB): preparation and characterization

Lignocellulosic biomass is the most abundant renewable energy resource gaining worldwide attention for its carbon-neutrality, heterogeneity and macromolecular characteristics, thus, versatile use as fuel, power, heat and valuable chemicals (Ragauskas et al., 2006; Stocker, 2008; Gallezot, 2012). Such biomasses are mainly composed of variable proportions of cellulose (38–50%), hemicellulose (23–32%), lignin (15–25%) and a small amount of extractives (Fig. 3) (McKendry, 2002; Mussatto et al., 2008). In general, wood cannot be considered as a sustainable feedstock for Asian countries where substantial crop residues are available (Mandal et al., 2013). Thermochemical conversion of biomass leads to formation of various black carbon species such as solid combustion residues as well as condensation products like char, charcoal, biochar, soot, graphite black C and graphite specified on the basis of their O:C ratios (Fig. 4) (Schmidt and Noack 2000; Spokas et al., 2010). Of them, biochar is a form of solid residual black carbon derived from the thermo-chemical decomposition of renewable biomass feedstock such as wood, crop residues, manure or leaves, heated in a closed container at relatively lower temperature (<700 °C) under oxygen-limited condition and specifically prepared for soil amelioration and C sequestration (Goldberg 1985; Kuhlbusch and Crutzen 1995; Lehmann, 2007a,b; Lehmann and Joseph, 2009). The exact chemical nature of CRB depends upon the type of biomass (feedstock type and size) and pyrolysis conditions (e.g., pyrolysis temperature, temperature hold time and heating rate) used (Fig. 5; Table 1) which are summarized in later sections (Lehmann and Joseph, 2009).

3. Pyrolysis conditions

Thermo-chemical processes comprises of direct combustion, pyrolysis, hydrothermal conversion, hydrolysis, torrefaction and gasification for the conversion of lignocellulosic material to energy or other value-added chemicals e.g., small molecular syngas, chemicals, liquid fuels and/or high grade biochars (Cao et al., 2014). Of these processes, pyrolysis (i.e., the thermal decomposition of materials in limited oxygen) (Mohan et al., 2014) is more favored and acceptable process due to rationale yields of small compounds formed by decomposition i.e.,volatiles (bio-oil and syn-gas) and biochar produced from the condensation/polymerization of lignocellulosic biomass (Nowakowski and Jones, 2008; Couhert et al., 2009; Shen and Gu, 2009; Qu et al., 2011; Carrier et al., 2013; Nanda et al., 2013; Cao et al., 2014). Pyrolysis process is further distinguished into various types depending on operating conditions used such as the feedstock's heating rate, residence time and pyrolysis temperature (Fig. 5) (Czernik and Bridgwater, 2004; Mohan et al., 2006). For example, conventional or slow pyrolysis, fast pyrolysis, flash pyrolysis, ablative pyrolysis, etc. involving different pyrolysis temperature, heating rate and vapor residence time, thus, having varying yield and properties of the resulting materials (Fig. 5) (Mohan et al., 2006). Basic stages involved in pyrolysis process (Fig. 6) are delineated under Box 1, whereas various important factors governing biochar yield and its further characteristics are described in Box 2.

4. CRB important characteristics

As described earlier in Box 1 and 2, characteristics of CRB are very much variable depending upon various pyrolysis conditions (Lehmann and Joseph, 2009). Biochar varies from other organic matter due to its higher aromaticity of fused carbon structures

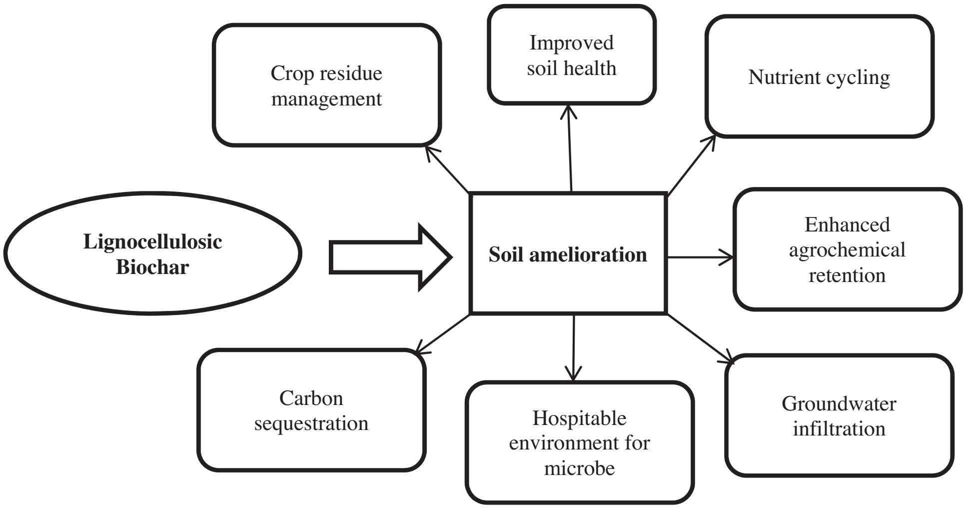


Fig. 2. Multifaceted benefits of biochar as soil ameliorant for sustainable agriculture.

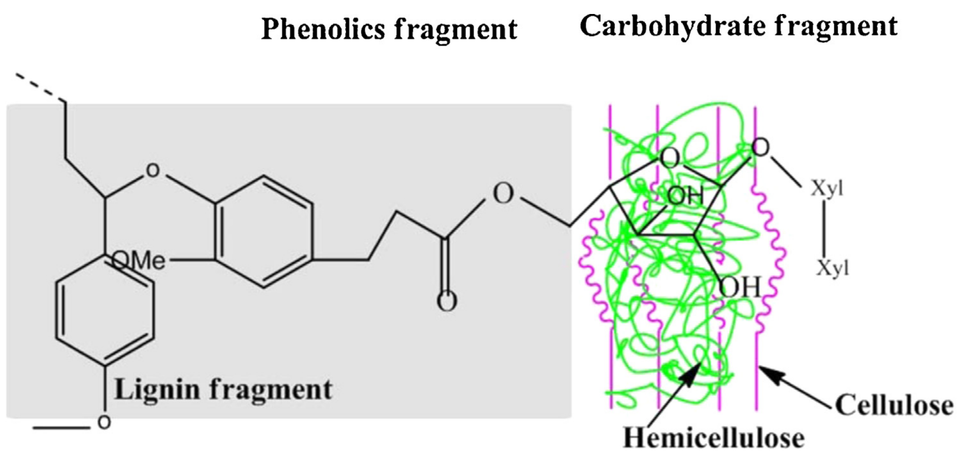


Fig. 3. Lignocellulosic component of wheat crop residue biomass (Adapted and redrawn from Sun et al., 1997; Buranov and Mazza, 2008).

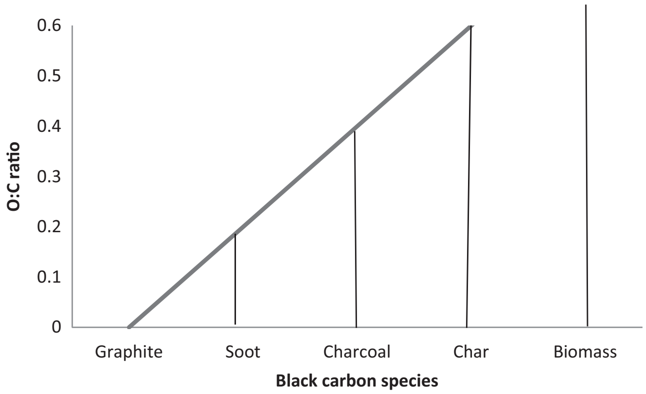
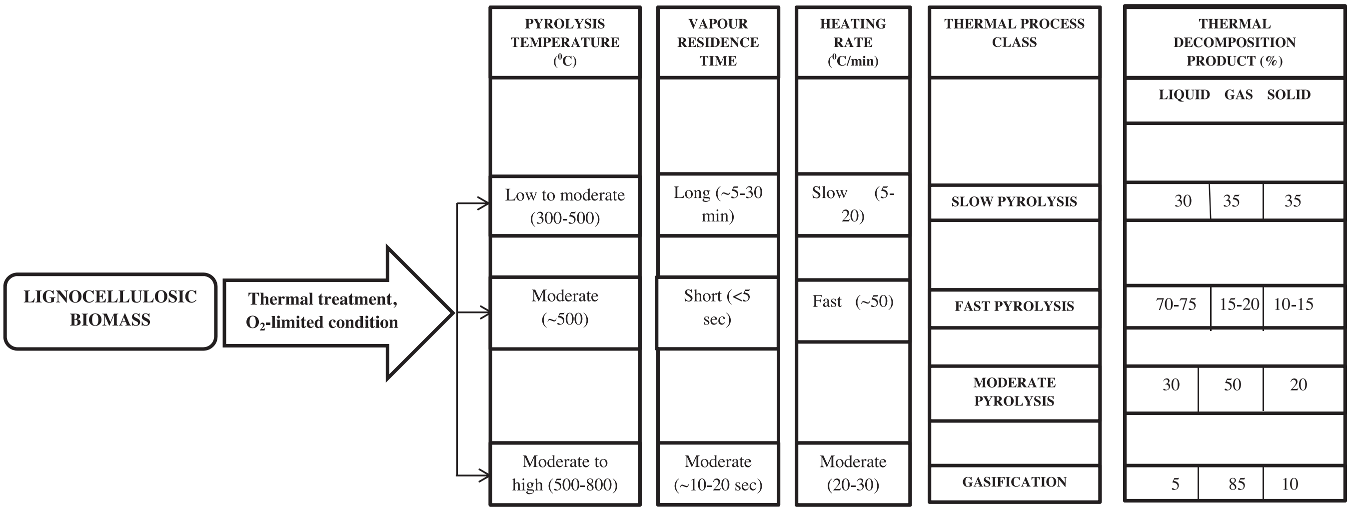


Fig. 4. An illustrative representation of various black carbon species along with lignocellulosic biomass categorized on the basis of O:C ratios.

(Schmidt and Noack, 2000). Biochar prepared at lower temperature is dominated by amorphous C whereas turbostratic C at higher temperature (Keiluweit et al., 2010; Nguyen et al., 2010). The International Biochar Initiative (IBI) has categorized biochar in three classes on the basis of carbon content as Class 1 biochar having >60% C, Class 2 biochar having 30–60% C and Class 3 biochar having 10–30% biochar (http://www.biocharinternational.org/sites/default/files/Guidelines_for_Biochar_That_Is_Used_in_Soil_-Final.pdf). Further elaboration is given as:

4.1. Proximate and Ultimate analyses of CRB

Proximate and ultimate analyses of different feedstock materials vary significantly. In general, wood-derived biochars have lower ash content, soluble elemental components and pH in comparison to crop residue-derived and grass-derived biochars (Brewer et al., 2011; Spokas et al., 2011a,b; Kloss et al., 2012), whereas reverse is true for thermal stability and surface area (Kloss et al., 2012). Carbon content of wood-biochar is generally higher as compared to herbaceous feedstock and it further increases with increasing pyrolysis temperature (PT) (Enders et al., 2012) due to volatilization and formation of stable C structures. Proximate analysis of CRB indicates a negative trend in volatile matter (VM) content and a positive trend in ash content and fixed carbon (FC) content with increasing PT due to volatilization as well as higher salt content (e.g., silica SiO_2) (Kloss et al., 2012; Mukherjee, 2011; Mukherjee et al., 2011; Wu et al., 2012). Lignocellulosic biomass generally has a VM/FC ratio of 4.6 (Lee et al., 2013). It is also supported by FTIR spectral analyses that pyrolysis of lignocellulosic biomass yields VM mainly composed of CO_2, CO, carbonyl compounds (C=O), alkanes (C—C), and ethers (C—O—C), however, lignin component derived volatiles dominated by CO, CO_2, CH_4, and some organics with carbonyl, aromatic ring, alkane, and ether groups (Cao et al.,



PYROLYSIS TEMPERATURE (°C)	VAPOUR RESIDENCE TIME	HEATING RATE (°C/min)	THERMAL PROCESS CLASS	THERMAL DECOMPOSITION PRODUCT (%)		
				LIQUID	GAS	SOLID
Low to moderate (300-500)	Long (~5-30 min)	Slow (5-20)	SLOW PYROLYSIS	30	35	35
Moderate (~500)	Short (<5 sec)	Fast (~50)	FAST PYROLYSIS	70-75	15-20	10-15
			MODERATE PYROLYSIS	30	50	20
Moderate to high (500-800)	Moderate (~10-20 sec)	Moderate (20-30)	GASIFICATION	5	85	10

Fig. 5. Typical thermal treatment of lignocellulosic biomass in O_2-limited conditions and normal decomposition product yield.

Table 1
A comparative assessment of wood- and crop residue biochar properties.

S. N.	Parameter	Wood biochar	Crop residue biochar	Reasons for a particular variation	References
1	Yield	Higher	Lower	Wood have higher lignin content which is less decomposable	(Mandal et al., 2013; Cao et al., 2014)
2	H and O content	Lower	Higher	Higher lignin content is dominated by interlinked-aromatic C-rings	(Mohan et al., 2014)
3	Surface area/ adsorption capacity	Higher	Lower	Have very high porosity due to various interchange mechanisms under C rings structures of wood biochar involved during pyrolysis process leading to very high porosity	(Kloss et al., 2012)
4	C content	Higher	Lower	Crop residue is dominated by cellulose and hemicellulosic components (highly decomposable) as compared to lignin content of wood which is less decomposable	(Enders et al., 2012)
5	pH increase	Higher	Lower	With increasing pyrolysis temperature wood biochar pH increases	(Enders et al., 2012)
6	pH neutralization capacity	Higher	Lower	Wood biochar have higher liming properties due to presence of carbonaceous species	
7	Electrical conductivity (EC)	Lower	Higher	Crop residues have higher salt content than wood	(Kloss et al., 2012)
8	Cation exchange capacity (CEC)	Lower	Higher	Crop residues have higher salt content than wood	(Kloss et al., 2012)
9	Water-extractable micronutrient	Lower	Higher	Higher salt content and availability in crop residue biochar	(Kloss et al., 2012)
10	Soil amelioration potential	Lower	Higher	Due to easy and frequent availability than wood resource	(Cornelissen et al., 2013)

2014). Higher PT leads to more condensed and aromatic (Box 1 and 2) i.e.,biologically resistant biochar formation (Almendros et al., 2003; Bruun et al., 2014). Further, VM content of biochar varies with vapor residence time (VRT) (Spokas et al., 2011b). It is generally higher for longer VRT like slow pyrolysis process as compared to shorter ones like fast and flash pyrolysis processes (Spokas et al., 2011b) due to re-condensation and surface adsorption processes.

Ultimate analyses of various biochar samples revealed that biochar elemental composition significantly varies with pyrolysis conditions (Enders et al., 2012; Mohan et al., 2014; Xu et al., 2014). In general, biochar have a carbon (C), nitrogen (N) and ash content in the range of 40–60%, 0.1–1.0% and 1–88%, respectively which is comparatively higher than the feedstock material (Kloss et al., 2012; Sanna et al., 2011; Enders et al., 2012; Mohan et al., 2014; Xu et al., 2014). Pyrolysis of biomass leads to changes in elemental composition of biochar as compared to feedstock material, thus, encompasses variations in C/N, O/C and H/C ratios; structural properties (e.g., porosity, surface area and crystallinity), and functional groups (such as increased aromatic C=C and decreased O—H and aliphatic groups) (Baldock and Smernik, 2002; Graetz and Skjemstad, 2003; Zabaniotou et al., 2008; Chan and Xu, 2009; Krull et al., 2009). A linear decrease in H/C and O/C and (O + N)/C ratios is observed with increasing PT due to formation of aromatic condensed carbon structures formed by the continuous dehydration and decarboxylation reactions (Enders et al., 2012; Cao et al., 2014; Mohan et al., 2014) which revealed the higher degree of aromaticity and stability of biochar approaching towards pure carbon (Krull et al., 2009; Van Zwieten et al., 2010; Kumar et al., 2013; Lee et al., 2013). It is further supported by van Krevelen plot that with the increase in pyrolysis temperature H/C and O/C ratios decreased causing a substantial aromatization of the product (Kloss et al., 2012; Wu et al., 2012; Cao et al., 2014; Mohan et al., 2014).

4.2. Physicochemical characteristics of CRB

Various physicochemical properties such as surface area (SA), porosity, bulk density (BD) and water holding capacity (WHC) (due to decreased hydrophobicity), pH, electrical conductivity (EC), cation exchange capacity (CEC), etc. of CRB significantly varies with pyrolysis conditions (Kinney et al., 2012; Mukherjee and Lal, 2013). Biochar has large SA, high pore space (micropores, mesopores and macropores) and permeability, lower bulk density and high WHC than its feedstock material (Lehmann and Rondon, 2006). PT has a very important role in determining the characteristics and application of biochar as biochar prepared at low temperature can be used for controlling release of nutrients from fertilizers (Day et al., 2005) and high temperature leads to the formation of activated carbon like material (Ogawa et al., 2006). For example, SA of biochar increases with increase in PT due to loss of VM, thus, in turn leading to increase in porosity and decrease in bulk density; however it is substantially 100 times less than the SA of activated charcoal. In general, higher SA could be obtained at pyrolysis over >500 °C (Kloss et al., 2012). Further, SA of biochar is mainly responsible for increased WHC, fixing of nutrients and fertilizers from washing away (Karhu et al., 2011; Lee et al., 2013). Condensation of organic volatiles which possibly blocks the pores at lower PT is supposed as a reason for lower SA. Increased pore spaces and voids created in the biochar matrix by volatilization process may lead to increase in SA with increased PT (Downie et al., 2009). Some key parameters having relevance as soil ameliorant are discussed in the later sections.

4.2.1. pH and alkalinity

pH of biochar increases from acidic to alkaline range with increase in PT due to separation as well as accumulation of alkali salts due to significant mass loss especially carbonates derived from the feedstock material at higher temperatures (Chan and Xu, 2009; Van Zwieten et al., 2010; Mohan et al., 2014). However, CRB showed less increase in pH as compared to wood and waste derived biochar with increasing PT (Enders et al., 2012). In a study Cornelissen et al. (2013) found that wood biochar have greater pH neutralization and higher CEC as compared to corn cob biochar. Generally, ash content and alkali matter contents (Na, K, Mg and Ca) of biochar are directly correlated with biochar pH (Singh et al., 2010; Lehmann et al., 2011; Enders et al., 2012). Occurrence of wollastonite ($CaSiO_3$) has been reported at 350 °C by Bruun et al. (2014), which further reacts with CO_2 to form carbonates after cooling. These carbonates as well as base cations are the major cause of the alkalinity for the biochar product which provides liming property to it (Singh et al., 2010; Van Zwieten et al., 2010; Lehmann et al., 2011,b; Yuan et al., 2011a,b), whereas, oxidation of C to acidic carboxyl compounds leads to pH decrease (Cheng et al., 2006).

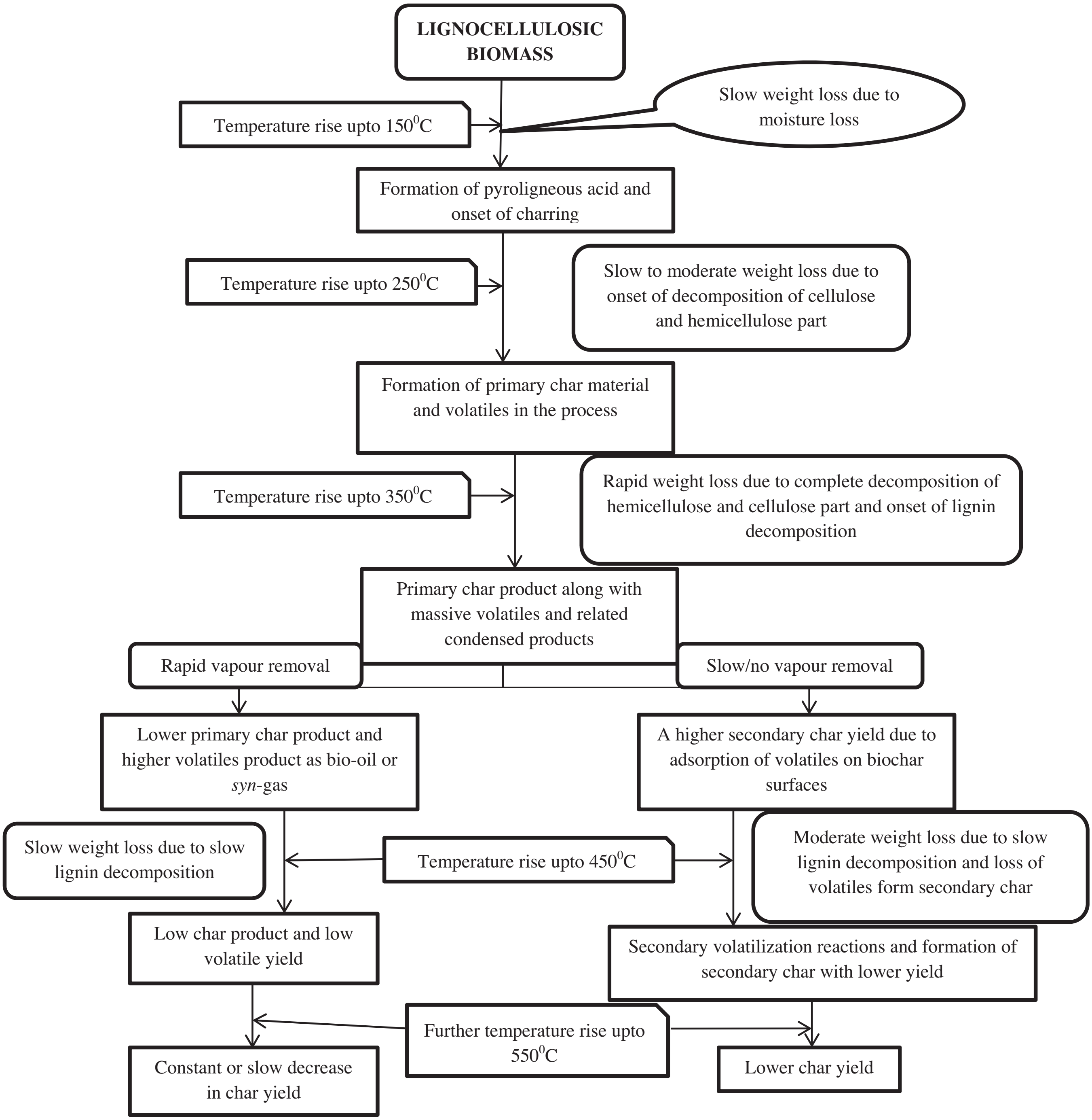


Fig. 6. A detailed mechanistic exploration of pyrolysis process and product yield from lignocellulosic biomass source.

4.2.2. Electrical conductivity (EC)

Biochar has significantly higher electrical conductivity (EC) with a wider range of from 0.42 to 4.92 mS cm^{-1}, in general, as compared to feedstock material, thus, have high salinity as well (Kloss et al., 2012). EC further increases with increase in PT (Singh et al., 2010; Kloss et al., 2012) due to separation as well as accumulation of alkali salts at higher temperatures (Chan and Xu, 2009; Van Zwieten et al., 2010). CRB generally have higher EC as compared to wood biochar (Kloss et al., 2012).

4.2.3. Cation exchange capacity (CEC)

CRB have higher CEC as compared to wood biochar (Kloss et al., 2012), possibly due to higher salt content (Lehmann et al., 2011); however, it is lower than SOM or natural clay soil or humic components (Lehmann, 2007b; Chan and Xu, 2009). Fresh biochar has net positive or net negative charge on its surface, thus, have higher CEC as compared to feedstock. CEC and charge density of biochar are higher due to enrichment of oxidized functional groups like pyranone, phenolic, carboxylic, lactone and amine (Fig. 7) on its surface through pyrolysis process (Brennan et al., 2001; Liang et al., 2006) even for low PT biochar (Wu et al., 2012). However, it decreases with increase in PT (generally after 400 °C) due to loss of cations and decrease in surface charge densities through loss of volatile components at higher PT up to 600 °C (Kloss et al., 2012; Lehmann et al., 2011; Wu et al., 2012).

Box 1. Basic stages of pyrolysis.

Biomass undergoes various structural transformations resulting into increased aromaticity during pyrolysis process mainly governed by feedstock material and the operating conditions such as temperature, heating rate, pressure, purge gas and particle size (Antal and Gronli, 2003; Enders et al., 2012). It covers a range of thermal decomposition reactions such as condensation polymerization, dehydration, dehydrogenation, deoxygenation and decarboxylation reactions (Fig. 6), thus, a very complex process to define precisely (Demirbas, 2000). Crop residue is mainly composed of lignocellulosic components (Fig. 3) (Sun et al., 1997; Buranov and Mazza, 2008). The cellulosic and hemicellulosic components of biomass (60–75%) started decomposing at 200–400 °C, whereas, lignin component (15–25%) to 300–700 °C (Fig. 6) (Cao et al., 2014). Lanzetta and Blasi (1998) proposed two possible steps involved in any pyrolysis process comprising of devolatilization of the materials where different zones can appear corresponding to (a) the thermal decomposition of the main constituents leading to dehydration, dehydrogenation, decarboxylation and decarbonylation reaction; and (b) secondary pyrolysis, which covers the secondary decomposition reactions in solid matrix, as well as secondary reactions between the volatiles release or between the volatiles and the carbonaceous residue. This leads to the process known as cracking, where heavy compounds further break into gases, or char is also converted into gaseous as well as partially oxidized products (Fig. 6) (Lanzetta and Blasi, 1998).

Thermo-gravimetric analysis (TGA) of crop residue also support the two stage decomposition of biomass during pyrolysis (Xiao et al., 2001; Kim et al., 2012; Cao et al., 2013; Lee et al., 2013). Loss in weight of biomass is observed initially at 1000C which is due to release of moisture from crop residue. Second significant mass loss stage was observed near 200–300 °C and 300–400 °C which is due to degradation and decomposition of hemicellulosic and cellulosic components of biomass, respectively (Fig. 6) (Kim et al., 2012). However, the char obtained at this stage is significantly rich in lignocellulosic components which get further decomposed upon raising the temperature to 400 °C and above, resulting in the release of volatiles with lower char yield (Fig. 6) (Cao et al., 2013).

4.2.4. Macro-nutrients

Chemically, biochar is a highly aromatic compound that contains random stacks of graphitic layers (Schmidt and Noack, 2000) i.e., high C followed by O, H and N contents, thus, variable C/N, H/C and O/C ratios and lesser VM content than the parent feedstock material (Spokas, 2010). The effect of PT lead to a considerable variation such as decrease in N, H and O contents, increase in C, P, and pH of biochar (Woods et al., 2009; Spokas et al., 2011b; Yuan et al., 2011a). Biochar having higher soil nourishing properties can be obtained at lower PT and THT (Barrow, 2012). For example, biochar generated at 400 °C and 500 °C from rice straw and Geodae-Uksae-1 (*Miscanthus*), respectively, can be considered better for supplementing soil properties (Wu et al., 2012; Lee et al., 2013). In general, total N content varies invariably with changing PT such as it increases initially and decreases with further increase in PT due to N enrichment at lower PT, whereas loss through volatilization at higher PT (Wu et al., 2012). However, C/N ratio of biochar (ranging from 63 to 80) is less affected by PT as compared to feedstock material in terms of N immobilization (Kloss et al., 2012).

Alkali matter contents viz., Ca, Mg, K, Na in addition to macro- and micronutrient contents such as P, Fe, Zn, Co, Mo, B, etc. have been reported to present in significant amount in biochar (Xu et al., 2014) in the form of SiO_2, $CaCO_3$, KCl, and $CaSO_4$ as well as nitrates, oxides, and hydroxides (Parr and Sullivan, 2005; Amonette and Joseph, 2009; Wu et al., 2012). However, these salt and ion concentrations mainly vary with feedstock elemental composition (Enders et al., 2012). For example, CRB have more salts and ions as compared to wood-derived biochar (Kloss et al., 2012). Xu et al. (2014) reported that wheat straw biochar have 1% Ca, 0.3% P, 0.6% Mg, 0.4% Fe and 2.6% K. Total P content of biochar increases with increasing PT due to concentration of P in ash, however, its availability decreases due to decreased availability of cations (Wu et al., 2012). However, because of its higher adsorption capacity in comparison to soil, biochar can be regarded as a better soil P retaining material (Warnock et al., 2007). Thus, the nutrient profile

Box 2. Factors affecting CRB yield.

Feedstock composition and pyrolysis conditions are determining factors for the CRB yield and its physical and chemical properties (Baldock and Smernick, 2002; Enders et al., 2012; Wu et al., 2012).

2.1 Effect of feedstock material

Feedstock composition having varying proportions of cellulose, hemicellulose and lignin resulted into significant variation in yield and other properties (Fig. 8). Cellulose has greater potential of decomposition whereas lignin the least due to its thermal stability (Yang et al., 2007; Cao et al., 2014). The resulting volatiles from lignin decomposition are mainly composed of aromatic compounds as compared to aliphatic compounds from cellulose and hemicellulose (Cao et al., 2014).

2.2 Pyrolysis temperature (PT)

Lignocellulosic biomass pyrolysis generally occurred at a range of 200–700 °C (Figs. 5, 7 and 8) (Cao et al., 2014). A significant decrease in biochar yield (i.e., from ~50% at 200 °C to ~10% after 500 °C) is reported by several workers with increase in pyrolysis temperature for different feedstock materials (Wu et al., 2012; Kumar et al., 2013; Lee et al., 2013). Further, a drastic mass loss was observed in between 300–400 °C which can be due to complete decomposition of cellulosic and hemicellulosic components whereas initial decomposition of lignin, however, mass loss decreases after 500 °C due to thermal stability of heterogeneous lignin components (Figs. 6 and 8) (Sanna et al., 2011; Kumar et al., 2013; Lee et al., 2013; Cao et al., 2014).

2.3 Temperature hold time (THT)

Pyrolysis processes are generally classified on the basis of vapour residence time or peak temperature hold time (THT). CRB yield has been reported to decrease with increased THT (Kuo et al., 2011; Peng et al., 2011; Kumar et al., 2013).

2.4 Heating rate

Various studies have been performed at different heating rate ranging from 10 °C/min (Wu et al., 2012; Lee et al., 2013) to 45 °C/min (Cao et al., 2014). Higher heating rate leads to rapid carbonization of biomass, thus, resulted into extensive cracking and micropores generation producing high surface area (Mukherjee and Lal, 2013).

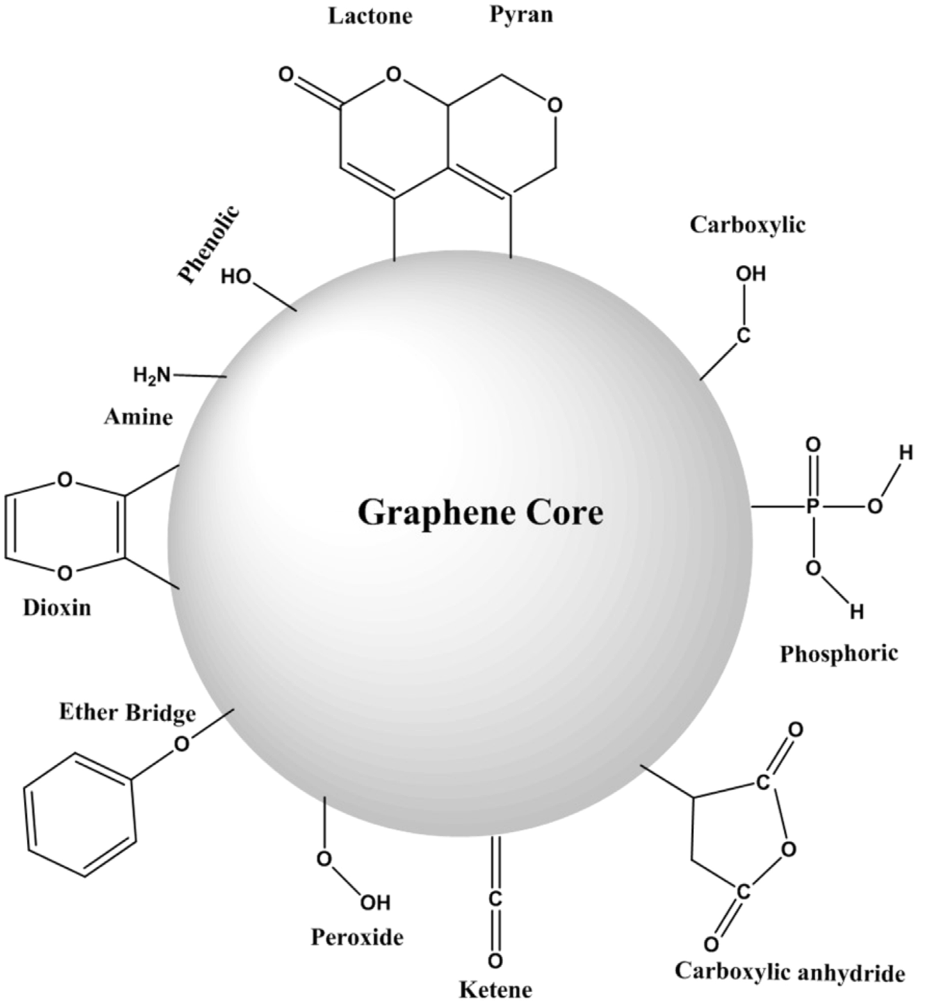


Fig. 7. Structure of biochar with different functional groups present on its surface (Adapted and redrawn from Brennan et al., 2001; Lehmann and Joseph, 2009).

of biochar and nutrient retention capacity supports its ability as potential fertilizer and soil nourishing agent (Wu et al., 2012).

4.2.5. Micro-nutrients

Biochar is considered as an important source of micronutrients like Fe (present in the form of small ferromagnetic clusters) (Freitas et al., 2002), B, Cr, Cu, Ni, Mo, etc. due to concentration of these elements from feedstock with increasing PT (Kloss et al., 2012). However, they vary with feedstock type as CRB have higher water-extractable Ni, Cr and Mo whereas lower B content as compared to wood biochar (Kloss et al., 2012). Although, excess amount of micronutrient is not recommended for soil amelioration, but various studies suggests that the micronutrient content of biochar is lesser than the other ameliorants such as composts, poultry litter, and coal fly ash – amended manure compost (Ciba et al., 2003; Toor et al., 2007). Thus, this could be advantageous for soil amelioration of biochar as higher concentration of micronutrient may lead to microbial toxicity within rhizosphere.

5. Potential uses of CRB for sustainable agriculture

Crop residues have been regarded as potential feedstock for biochar production (Lehmann, 2007a,b,b); however its properties after soil amelioration vary from the previously suggested wood biochar. Biochar production from crop residues is cost-effective, thus, it could be explored as a potential soil ameliorant (Beesley et al., 2011). Biochar has been found as a potential soil ameliorant for improving the deteriorating soil quality and has been reported

Box 3. Possible mechanism of organic contaminant adsorption on biochar surface under soil environment.

In biochar, native organic matter interact with native mineral matter and get sorbed on its surface which further leads to suitable interaction in environment (Palumbo et al., 2004). Biochar having graphene like arranged carbon matrix alongwith highly porous structures (Fig. 6) provides a suitable surface for contaminants binding on its surface, thus, reduce the availability to the other components of the environment (Masto et al., 2013). Various sorption isotherms and sorption kinetics studies on biochar sorption revealed that the basic mechanism involved for the adsorption process are surface adsorption (adhesion of pollutants on surface) at high temperature having carbonized structure and partition of pollutant molecules in micropores of biochar at lower temperature having less-carbonized structure (Tang et al., 2013). However, adsorption is highly dependent on pH with a reported optimum adsorption by biochar at pH 2.0 (Mohan et al., 2014). High pH of biochar leads to increase in soil pH which further leads to immobilization of heavy metal cation in soils (Beesley et al., 2011).

to apply in various agroecosystems. Biochar application to soil has been found to have multifaceted advantages viz.,improve soil physical and nutrient profile such as soil C, N and P as like fertilizer (Park et al., 2011); cause detoxification of soil by adsorbing various contaminants (Josko et al., 2013); and provide hospitable environment to soil micro- and meso-faunal communities, etc. (Fig. 2). In the following sections a critical insight is given on multifaceted application of biochar as soil ameliorant with respect to sustainability in agriculture.

6. As adsorbent material for contaminants from soil system

Adsorbents are the materials which have ability to neutralize the contaminant's effectiveness through lowering either their toxicity or bioavailability by reducing mobility (Josko et al., 2013). Biochar, having higher surface area and structural composition having different functional groups on its surface (Fig. 7) (Mohan et al., 2014), can be considered as a potential adsorbent for removing a range of organic and inorganic contaminants such as polyaromatic and polyaliphatic hydrocarbons, toxic chemicals, metals and elements from soil, sediments and water environments (Hale et al., 2012; Mohan et al., 2014). Possible mechanism of organic contaminants on biochar surfaces under different soil systems is described in Box 3. Though, biochar derived from lignocellulosic biomass usually have higher H and O contents as compared to activated carbon (highly carbonized), thus, have slightly lesser adsorption capacity than activated carbon (Mohan et al., 2014). Evaluation of CRB as soil adsorbent is very much necessary for its establishment as soil ameliorant for sustainable agriculture.

Substantial literature are available worldwide on biochar sorption of contaminants such as heavy metals (Cao et al., 2009; Uchimiya et al., 2010; Chen et al., 2011) as well as organic and inorganic contaminants (Mohan et al., 2014). Further, highly porous biochar structure qualified it as a supplement with nanocomposite sorbents for improved removal of environmental contaminants (Zhang et al., 2013a; Zhou et al., 2014). In an adsorption study, Zhou et al. (2014) found that biochar-nacomposites (in various proportions of iron oxide and bicohar) have greater ability to remove arsenic (As (V)) as compared to the individual adsorbents. Mohan et al. (2014) reviewed biochar adsorption potential for various organic and inorganic contaminants and found that biochar prepared at higher PT have high adsorption capacity. Also, high temperature aromatic biochar sorb generally non-polar or weakly polar organic solutes (Lehmann et al., 2011).

6.1. Reduction of metal toxicity from contaminated soil

Biochar application alongwith other soil ameliorant cause a synergistic effect over metal toxicity reduction. Biochar amended heavy metal contaminated soil have been reported to have significantly lower amount of metals in grain (Cui et al., 2011a, 2012; Bian et al., 2013). Bian et al. (2013) found 20–90% reduction in Cd content in rice grain with a 40 t/ha biochar amended Cd-contaminated rice field, possibly due to biochar-mediated pH change led reduction in Cd pool-availability. Furthermore, biochar increases soil CEC and base saturation, thus, provide liming effect to acidic soils contaminated with elevated Al and Fe oxides (Cao et al., 2009; DeLuca et al., 2009; Major et al., 2010; Chien et al., 2011; Yuan et al., 2011a,b). Also, increased CEC leads to immobilization of heavy metals and persistent organic pollutants (POPs) on biochar surface (Beesley et al., 2010; Gomez-Eyles et al., 2011; Uchimiya et al., 2010). A reduction in extractable heavy metals such as Cd, Cu, Ni and Pb is reported from several contaminated sites receiving combined application of biochar with lignite fly-ash, possibly due to increased soil pH after composite application (Masto et al., 2012, 2013). Further, biochar-mediated pH change indirectly improves contaminated soil fertility through adsorbing metals on its surface and releasing metal-binded available P (Major et al., 2010; Beesley and Dickinson, 2011). However, biochar itself contains various polyaromatic hydrocarbons adsorbed on its surface which could be considered as a contaminant to the soil, thus, it must be kept in consideration before applying biochar (Hale et al., 2012; Mccormack et al., 2013). However, a recent study by Kołtowski and Oleszczuk (2015) revealed that drying of biochar before application leads to reduction in PAHs content.

6.2. Sorption and activity of agrochemicals in a biochar amended agroecosystems

In addition to sorption of metal contaminants, biochar also adsorbs various agrochemicals (viz., pesticides, herbicides and fertilizers) on its surface and reduce their bioavailability to soil fauna, thus, reduced efficacy of those agrochemicals (Yang et al., 2006; Smernik, 2009; Yu et al., 2010; Zheng et al., 2010; Lehmann et al., 2011). In addition, immobilization of residual agrochemicals on biochar surface improve seedling emergence and growth (Yang and Sheng, 2003; Jones et al., 2011a) and indirectly leads to reduction in agrochemical application rate and frequency. Therefore, this could be a reason for improved environmental health and food safety due to reduced uptake by crops and leaching

Box 4. Mechanistic explanation of adsorption of agrochemicals and heavy metals on biochar surface in cropland.

Biochar having high CEC and low zeta potential thought to decrease heavy metal and organic contaminant toxicity by increasing negative charge on soil surface by several mechanisms such as electrostatic interaction and precipitation for heavy metals and surface adsorption, partition and sequestration for organic contaminants (Dong et al., 2011; Peng et al., 2011; Jiang et al., 2012; Tang et al., 2013). It is supposed that ion exchange is mainly governed by the basic properties such as ionic radius and electronegativity of metal ions, for example, metal ions having smaller ionic radii and higher electronegativity showed higher degree of adsorption (Gorgievski et al., 2013). Surface adsorption through partitioning process has been observed for biochar prepared at lower PT having less carbonized and residual organic matter. However, biochar prepared at higher PT are more carbonized having lower H/C and O/C ratios and act as potential surface for adsorption. In addition, such biochar are highly hydrophobic in nature dominated by sp^2 hybridisedaromatic carbons with smaller sp^3 hybridised alkyl carbons, thus, shows weak p-H-bonding and broader p–p interactions (Sun et al., 2011). Oh et al. (2013) reported that microscopic graphene like structure dominated by surface functional groups, such as (hydro)-quinones, or redox-active metals, such as Fe, Cu and Mn in a high temperature biochar help in adsorption and electron transfer from the adsorbates. Biochar may also act as electron shuttle transferring electron from one state to another (Cayuela et al., 2013). Therefore, CRB could be a potential ameliorant for the contaminated and less-productive sites.

of these chemicals in soil layers under biochar applied systems (Yu et al., 2010; Lehmann et al., 2011). Further elaboration on mechanism involved for agrochemical adsorption on biochar surface is outlined in Box 4.

7. As soil ameliorating agent

Historical background of biochar use as soil amendment has been revealed by Japanese horticulture practices and Terra Preta sites near to the Central Amazon Basin as early as appearing in the literature in 1697 (Lehmann, 2007b; Brewer et al., 2009; Lehmann and Joseph, 2009; Lehmann et al., 2011). However, work on Terra Preta was pioneered by the late Wim Sombroek and further recent exploration is performed by Sohi, Woods, Glaser, and Lehmann (Sombroek et al., 2003; Lehmann et al., 2003a; Woods et al., 2009; Sohi et al., 2010), but biochar found its initial worldwide attention through the study on sustained fertility of Terra Preta soil by Lehmann et al. (2003a). Further, biochar addition to soil had been argued by James Lovelock in the UK media as the only hope for mitigation of catastrophic climate change (Barrow, 2012). Biochar gets its global potential recognition through 18th World Congress of Soil Science in Philadelphia (2006), International Agrichar Initiative Conference (2007), Conference of the IBI: “Biochar, Sustainability and Security in a Changing Climate” (2008), and 1st Asia Pacific Biochar Conference in Australia (2009) (Barrow, 2012). Also, biochar is viewed as potent ameliorant in present agronomic scenario because of its dual role for mitigating climate change through long-term C sequestration and improving soil health by reducing land degradation via supplementing soil C and N pool (Lehmann, 2007b; Roberts et al., 2010; Whitman and Lehmann, 2011; Lehmann et al., 2011; Barrow, 2012; Seleiman et al., 2013). Therefore, its addition to soil has been further promoted by several professional bodies such as “The United Nations Convention to Combat Desertification (UNCCD)” and “United Nations Framework Convention on Climate Change (UNFCC)” for ‘Enhanced Action on Mitigation’ programme (Barrow, 2012).

CRB is more suitable for soil amelioration due to easy availability, whereas wood biochar will pose extra pressure on forest resources (Cornelissen et al., 2013). Broad level ecosystem services of biochar include enhanced soil microorganism dynamics (Liang et al., 2010; Smith et al., 2010; Jones et al., 2011a,b; Lehmann et al., 2011), suppressed plant diseases (Elad et al., 2010), reduced GHGs emission (Taghizadeh-Toosi, 2011), reduced nutrient leaching loss (Lehmann et al., 2003b), decreased fertilizer run-off (Lehmann, 2007b), ameliorate soil acidity (Yuan et al., 2011a), soil quality and plant growth (Fig. 2 and Box 5) (Lehmann et al., 2011). These observations on CRB impact after soil amelioration are consistent as reviewed by Sohi et al. (2009) and Woolf et al. (2010). Liu et al. (2012) studied on rice straw biochar in rice agroecosystem and found it as a potential ecological engineering tool enhancing soil fertility, rice productivity and reducing N_2O emission from the rice fields. In addition, biochar application along with various organic and inorganic materials has been reported for soil amelioration studies (Thind et al., 2012; Masto et al., 2013). Biochar has been viewed as a new ecological engineering tool for the sustainable use of fly-ash (Masto et al., 2013). Masto et al. (2013) studied on applications of fly-ash and biochar under laboratory conditions and found that the combined material have positive synergistic effect such as improved nutrient accessibility, microbial activities, buffering pH and reducing toxic metal availability, thus, significantly affected growing crop and soil properties. In addition, combined material have significant effect over soil C pool, increase P bioavailability due to liming effect of both materials (DeLuca et al., 2009; Palumbo et al., 2009; Van Zwieten et al., 2010; Xu et al., 2013). Although, biochar amendment varies with soil conditions as detailed in Box 6. Further, biochar as blending material with inorganic materials like fly-ash lead to adsorption of metals on its surfaces or formation of organic-metal complexes; thus reduces the bioavailability of heavy metals from fly-ash (Dar et al., 2012).

7.1. Agronomic evaluation of CRB

Evaluation of agronomic benefits of biochar conducive to soil and crop is quite difficult as compared to its characterization in soil (Enders et al., 2012). However, in terms of agronomy, biochar showed both positive and negative effects after its amendment to soil (Lehmann et al., 2003a,b, 2011; Novak et al., 2009; Atkinson et al., 2010; Major et al., 2010; Spokas et al., 2011a). Therefore, Novak and Busscher (2011) and Spokas et al. (2012) suggested scientific communities not to recommend biochar as ‘one size fit-all paradigm’ instead of detailed studies on its behavior in varying soil environment. For example, biochar impact on SOM dynamics still needed to be explored as various studies reported increase in SOM whereas others reported decrease in native SOM initially for biochar applied fields (Wardle et al., 2008; Liang et al., 2010; Seleiman et al., 2013). Also, biochar produced at lower PT have higher VM content which inhibits plant growth and reduces N uptake in soil (Deenik et al., 2010). Thus, it is suggested by Enders et al. (2012) that for effective biochar application to soil and related crop growth issues, a proper understanding of soil–crop–climate conditions should be required. Also, many agronomic benefits observed at laboratory scale are not reflected in field-level studies which further emphasized the need of detailed field-level studies on agronomic performance of biochar (Jones et al., 2012).

7.2. Effect on soil basic characteristics after biochar application

Biochar and such amendments have been reported to have significant effects over various soil chemical and nutrient properties. Biochar is a rich source of mineral matters (macro- and micro-nutrients favoring biological activities), thus its application is supposed to increase soil basic properties (Lehmann et al., 2011). These chemical species get concentrated and incorporated into aromatic structure during pyrolysis process forming organo-mineral compounds (Lehmann et al., 2011). Various laboratory- and field-scale studies reported variable effects of biochar on soil properties after its application (Masto et al., 2013; Mukherjee and Lal, 2013; Prendergast-Miller et al., 2014). A brief description of biochar on soil priming is described in

Box 5. Mechanistic explanation of biochar as potential soil ameliorant.

Biochar have large surface area and micropores (Mukherjee et al., 2011), thus, its addition to soil changes soil key properties such as surface area, pore size distribution, bulk density and water holding capacity (Mukherjee and Lal, 2013). It increases nutrient bioavailability for plants by altering pH, liming effect, CEC (Liang et al., 2006; Van Zwieten et al., 2010); direct nutrient supply such as Na, K, P and Ca; and reducing nutrients loss from fertilizers via leaching and run-off (Lehmann et al., 2003b; Yuan et al., 2011a; Enders et al., 2012; Cheng et al., 2012; Xu et al., 2012; Lee et al., 2013).

Box 6. Amendment rate of biochar to soil.

Biochar has been applied in soil at varying rate depending on the site conditions. Mostly laboratory-scale studies are available for observing biochar effect on soil properties. Thus, it is difficult to analyze amendment rate effect in general, as it varied from % w/w of soil to t/ha. For example, 1, 5, and 10% w/w amendment rate was studied by Xu et al. (2013, 2014) reflecting 10, 50, and 100 g/kg of soil weight; 1–2% by Mukherjee and Lal (2013); 5% by Cornelissen et al. (2013); 20 g/kg by Kumar et al. (2013); 9 t/ha by Stewart et al. (2013); 25 and 50 t/ha by Jones et al. (2012); and 20–40 t/ha by Bian et al. (2013) and Liu et al. (2012) which showed significant improvement in soil properties such as surface area, porosity, water holding capacity, bulk density, plant available water content, reduced GHG emissions, metal adsorption from contaminated soil and N fertilizer availability, in general. Thus, the amount of biochar incorporation in soil requires the understanding of soil characteristics and climatic conditions. Although, after performing various experiments on biochar application to soil, especially for crop production, Lehmann (2007b) concludes that: “crops respond positively to biochar addition upto 50 Mg C/ha and may show growth reduction only at very high applications”.

Box 7. Mechanistic exploration of biochar over soil priming.

The mechanisms suggested for C mineralization and stabilization of biochar amended soil system are: (1) mineralization interaction with soil clay components (Liang et al., 2008; Joseph et al., 2010), (2) increased mineralization or co-mineralization of biochar C in the presence labile soil C source (Hamer et al., 2004; Kuzyakov et al., 2009), and (3) protection or stabilization of soil-biochar C along with soil aggregate or heavy organo-mineral fractions of soil (Brodowski et al., 2006; Liang et al., 2008). However, a decrease in carbon mineralization was observed in terra preta soil (Anthrosols) after labile C source application (Liang et al., 2010) probably due to sorption of labile C fraction on biochar surface (Hilscher et al., 2009). Thus, it may be possible that with aging biochar may suppress SOM mineralization (Kuzyakov et al., 2009; Zimmerman et al., 2011). This might be due to enhancement in surface functional group leading to higher CEC and sorption of labile carbon C on its surface. Therefore, C mineralization at spatio-temporal scale needs furthermore exploration at laboratory-as well as field-scale level including certain basic conditions such as: (1) proper source characterization and defined pyrolysis condition, (2) proper characterization of biochar product either produced at lower PT or higher PT, (3) holistic approach on soil characterization including its physical, chemical and biological properties, (4) detailed description of climatic condition such as rainy and dry conditions, (5) standardized application rate for a particular climatic condition, and (6) holistic monitoring of C flux in biochar amended and control soil for long time. Though, several studies have been performed caring some of the above said points, but carbon dynamics needs to be explored further.

Box 7. Further elaboration of biochar effect on various basic soil properties are critically assessed and described in the later sections.

7.2.1. Effect on soil physiochemical properties

Addition of biochar, a highly porous structure, is reported to have marginal effect on soil bulk density, soil moisture content (SMC) and WHC (Masto et al., 2013; Mukherjee and Lal, 2013); however, soil aggregation percentage (Mukherjee and Lal, 2013), soil porosity and permeability which affect nutrient dynamics (Prendergast-Miller et al., 2014) are significantly increased. Interconnected pores/microsites provide nutrient retention and mobilization capacity to the soil–root system (Prendergast-Miller et al., 2014). Biochar initially have lesser impact over soil compaction, but with aging of biochar alteration is projected in long term (Cheng et al., 2008; Cheng and Lehmann, 2009; Mukherjee, 2011). Soil pH, electrical conductivity (EC), cation exchange capacity (CEC), alkalinity, and acidity (Luo et al., 2011; Liu et al., 2012; Cornelissen et al., 2013; Kumar et al., 2013; Masto et al., 2013) have been reported to change after biochar amendment. These are critically analyzed in the later sections.

7.2.1.1. Soil pH and acidity. In general, pH of biochar varies from slightly acidic to alkaline range (mostly in alkaline range from pH 8.0–10.0). Therefore, various laboratory- and field-scale studies reported that biochar addition increases soil pH (generally approaches towards neutral in acidic soil and highly alkaline soil) (Luo et al., 2011; Liu et al., 2012; Wu et al., 2012; Kumar et al., 2013; Xu et al., 2013). Soil pH modification is subjected to either due to addition of high concentration of alkali and alkaline metal oxides by biochar or reduction in concentration or availability of acidic ions (e.g., Al^{3+} due to sorption on its surface) from soil matrix (Kumar et al., 2013; Masto et al., 2013). Changes in soil pH in addition to surface area under biochar amendment affect nutrient sorption and their bioavailability indirectly in addition to a direct nutrient source (Xu et al., 2013). However, soil pH neutralization capacity is generally higher for wood biochar having higher CEC amended soil than CRB (Cornelissen et al., 2013).

Inherent pH of biochar decreases after its application to soil (Jones et al., 2012), therefore, pH change projection should be taken under consideration before long term biochar amendment. It has liming effect on acidic soil, however, the alkalinity associated with it get lessened and fully neutralized with aging (Jones et al., 2012; Cayuela et al., 2014). Possible reasons for increasing acidity of biochar amended soil over time may be due to (1) later oxidation of its surface groups viz., carboxylic acid to phenols and cyclic acid anhydride derivatives; (2) solubilization and uptake through microbial activities into carbonyl and carboxyl groups; and (3) complete loss of associated alkaline metals (Cheng et al., 2006, 2008; Jones et al., 2012; Cayuela et al., 2014). However, biochar derived from animal manure reported to retain its liming property for long time (Slavich et al., 2013).

7.2.1.2. Soil electrical conductivity (EC). Several studies reported an increase in soil EC under biochar amended soil due to presence of high concentration of soluble salts (Masto et al., 2013). However, a significant decrease in inherent EC of biochar was observed after its application to soil (Jones et al., 2012). Significant increase in EC could be problematic initially due to sudden availability of soluble salts. Also, higher salt concentration of CRB may restrict its potential as soil ameliorant. Therefore, it needs further exploration at spatiotemporal scale before recommending it for soil amelioration.

7.2.1.3. Soil cation exchange capacity (CEC). Change in soil CEC after biochar amendment is a function of feedstock material, pyrolysis conditions and oxidation of the biochar within soil. Cornelissen et al. (2013) in a three-year field-scale study observed that wood biochar (having higher CEC) increases soil CEC at a greater extent as compared to CRB. Soil CEC increase under biochar amendment may be due to oxidation of biochar surfaces having various anionic functional groups like pyranone, phenolic, carboxylic, lactone and amine (Fig. 7) (Brennan et al., 2001), behaving as cation exchange resin either leading to retention of essential cations for exchange or conversion to more acidic and ionic species (Cheng et al., 2006, 2008; Liang et al., 2006). The increased soil CEC is possibly responsible for the growth of plant, leading to increased crop productivity (Chan et al., 2007; Asai et al., 2009). However, long term behavior of soil CEC change under CRB amendment is needed to further foolproof its wider adoptability.

7.2.1.4. Effect on soil nutrient conditions. Biochar has an excellent nutrient retention property which leads to longer retention of nutrients in topsoil after fertilizer application. Concentration and incorporation of various minerals of feedstock during pyrolysis process under aromatic structure as organo-mineral compounds make biochar a rich source of essential mineral matters (Lehmann et al., 2011). Thus, biochar addition leads to increase in SOM (Masto et al., 2013), in particular, and cationic species such as Na, K, Mg and Ca in soil (Xu et al., 2013). Josko et al. (2013) found significant increase in K under biochar amended soil possibly due to inherent higher amount of biochar K content. However, in a three-year study, Jones et al. (2012) observed that biochar amendment have less or no effect on dissolved organic carbon (DOC) and nitrogen (DON), nitrate (NO_3^--N), ammonium (NH_4^+-N), C turnover and N mineralization, ammonia (NH_3) volatilization, denitrification, NH_4^+-N sorption. In addition, a significant reduction in alkali and alkaline metals was observed with biochar aging; however, P and NH_4^+-N availability are less affected with biochar aging (Jones et al., 2012). Various aspects of soil after biochar addition in terms of sustainable agriculture have been dealt in this section.

7.2.1.4.1. Biochar and C mineralization. Biochar is a good source of SOM (an indicator of soil quality and health) (Masto et al., 2013); however, variable reports are available for biochar C and N dynamics in soil after application (Liu et al., 2012; Xu et al., 2013). For example, it is important to analyze the mineralization rate of biochar C in varying environmental conditions. Contrasting reports are available on biochar C mineralization (Box 7). One school of thought support that biochar application slow down C mineralization from soil, thus can be used for soil C sequestration (Kuzyakov et al., 2009; Zimmerman et al., 2011; Junna et al., 2014). Such changes are subjected to the pyrolysis conditions (Box 8). PT affect biochar mineralization in soil (Bruun et al., 2014) as high temperature biochar is more recalcitrant, thus, remain in soil for long term whereas low temperature biochar consists of more labile components (Fig. 8 and Box 8). Jones et al. (2012) observed less effect of biochar on SOM mineralization considering whole soil profile in a three year field-scale study. Similar observations were also reported for short term studies by Smith et al. (2010) and Bell and Worrall (2011).

On contrary, second school of thought suggest that either biochar C mineralization increases with aging or it enhances the inherent soil organic carbon (SOC) mineralization, thus increased CO_2 evolution, after its application to soil (Luo et al., 2011; Rogovska et al., 2011; Bruun et al., 2014). However, this is found more frequent when sufficient labile C source is available adjacent to biochar due to priming effect (Box 7 and 8). In an extensive laboratory-scale study on soil C mineralization using wheat straw biochar prepared at varying PT with and without wheat straw under alternate drying–wetting conditions Junna et al. (2014) found that mineralization rate was higher for wheat straw followed by wheat straw and biochar combination, low PT biochar applied soil, and high PT biochar applied soil. Lower C mineralization from combined wheat straw and biochar applied soil system elucidate that biochar organic carbon get adsorbed on biochar surface, thus, mineralization decreases (Junna et al., 2014). Initial C mineralization was also reported by Kuzyakov et al. (2009) in a three year study; however, mineralization rate decreases over time.

In another study on biochar application to different soils Bruun et al. (2014) reported higher evolution of CO_2 after biochar application; however, it was possibly due to dissociation of carbonates and other labile form of C instead of biochar C mineralization. This was further correlated with carbonate dissociation by biotic and abiotic factors in early phase of biochar applied soil (Bruun et al., 2014). However, this is mostly due to abiotic activity induced CO_2 evolution; thus, ignoring this consideration would lead to an overestimation of SOM-derived C release (Jones et al., 2011b). The increased mineralization under biochar amended soil was due to biochar C breakdown. Therefore, such studies further signifies that presence of labile carbon such as plant residues, glucose, etc. could lead to positive short term priming effect on soil C mineralization (Kuzyakov et al., 2000; Wardle et al., 2008; Luo et al., 2011). Initial priming effect under biochar applied soil is possibly due to presence of water-soluble

Box 8. Effect of pyrolysis temperature on biochar C mineralization and nutrient properties.

Pyrolysis temperature, leading to variaition in basic properties of biochar, has significant effect over organic C behavior. As biochar prepared at lower temperature (<300 °C) have higher labile C whereas biochar prepared at higher temperature (>400 °C) have more turbostratic or recalcitrant C (Wu et al., 2012), thus, a lower mineralization rate of C species (Luo et al., 2011; Junna et al., 2014). Effect of PT and feedstock source on biochar initial properties and changes after its application has been explored recently along with various soil properties like pH, texture and labile SOM (Luo et al., 2011; Wu et al., 2012; Bruun et al., 2014). Luo et al. (2011) found a higher rate of C mineralization of high temperature (700 °C) biochar in high pH soil. In a similar study on biochar produced at low and high PT in presence and absence of ryegrass as a labile carbon source in two different pH conditions, Luo et al. (2011) observed a significant short term increase in C mineralization for high PT bicohar in presence of ryegrass as compared to low PT biochar for low and high pH soil. CO_2 evolution was observed significantly for low PT biochar under highly clayey soil wheareas lower for high PT biochar under low clayey soil (Bruun et al., 2014). Further, Bruun et al. (2014) found that in contrast to initial priming effect, CO_2 evolution was high from low PT biochar applied soil at low and high pH soil as compared to high PT biochar with aging (>180 days) of biochar in soil system. Biochar prepared at lower temperature from a crop residue feedstock have high levels of extractable cations, available P, thus, high alkalinity and CEC having a good candidature as soil ameliorant (Wu et al., 2012). Further, high temperature biochar is inert and recalcitrant, thus, less decomposable and less bioavailable to microorganisms (Glaser et al., 2002a). Charring at high temperature resulted into significant decrease in labile components of carbon (Junna et al., 2014).

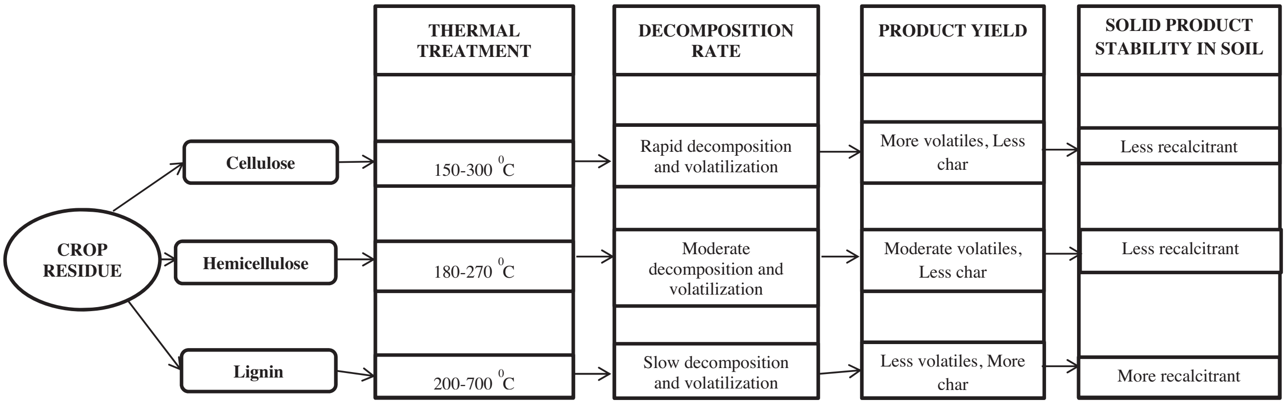


Fig. 8. Effect of biomass composition and its behavior in thermochemical process alongwith nature of biochar product stability (Modified from Lanzetta and Blasi, 1998).

component of biochar (Luo et al., 2011). Thus, biochar have varying effect over C mineralization with aging. Such priming effects generally observed in early phase of biochar amendment leading to significant carbon dynamics (Kuzyakov et al., 2000); however, such processes need further investigation with mechanistic explanation. This is also an important consideration before recommending biochar as soil C sequestration (Luo et al., 2011).

7.2.1.4.2. Nitrogen (N) dynamics under biochar applied soil system. Nitrogen is a critical element required for various processes within plant system. It ranges between 1 and 6% in plant system absorbed in the form of soluble nitrate and ammonium from soil components (Havlin et al., 2005; Barker and Pilbeam, 2006). Thus, any material leading to increment in soil-N will improve soil fertility and productivity. Biochar having concentrated N derived from crop residue has been reported to increase soil NH_4^+-N concentration while decrease NO_3^--N recovery (Nelson et al., 2011). N dynamics can be explained by considering its multiple available forms under different biochar applied soil systems. Biochar derived from lignocellulosic biomass usually prepared at moderate pyrolysis temperatures (300–400 °C) is reported to have higher N content (Yuan et al., 2011a; Bird et al., 2011; Sanna et al., 2011; Wu et al., 2012). In a study on ^{15}N-labelled biochar application to soil, Taghizadeh-Toosi et al. (2011) found that biochar nitrogen was plant-available which support biochar as a nutrient carrier. Further, N-enrichment in biochar applied soil was observed possibly due to ammonia sorption (Spokas et al., 2012) which react with surface oxygen groups to form amines and amides (Seredych and Bandosz, 2007), as well as hetroaromatic compounds like pyrroles, pyridines, NH_4^+-N, etc. at high PT (Jansen and van Bekkum, 1994). Ammonia sorption on biochar surface is considered as bioavailable N source due to its property to dissolve and dissociate in water at ambient atmospheric conditions, however, this sorption process is generally reversible for biochar prepared at low PT (Spokas et al., 2012). A brief light is given on various factors responsible for N dynamics under CRB amended soil system in Box 9.

Biochar addition to soil has been contrastingly reported to reduce the net N mineralization in an incubation study by Jones et al. (2012) due to: (1) adsorption of plant available N on biochar surface (Ding et al., 2010; Nelson et al., 2011), or (2) through binding of NH_4^+-N ions on cation exchange sites of biochar (Jones et al., 2012), or (3) neutralization of alkalinity of biochar (Jones et al., 2012). In addition, several studies reported good N mineralization in soil prior to biochar amendment due to inhibition of nitrifier activity with biochar addition (DeLuca et al., 2006; Kolb et al., 2009; DeLuca et al., 2009). This reduction in N mineralization potentially lead to reduction in crop yield due to poor crop establishment, reduction in foliar N, leaf chlorophyll content and seed quality (Ding et al., 2010; Nelson et al., 2011; Campbell et al., 2011).

7.2.1.4.3. Soil phosphorus availability in biochar applied soil. Phosphorus (P) is an essential component of plant tissue ranging from 0.1 to 1.0%. Plant commonly uptake P as dihydrogen phosphate or monohydrogen phosphate from soil system (Havlin et al., 2005; Barker and Pilbeam, 2006); which is mainly affected by soil properties such as pH, acidity, and variation in Al- and Fe-bound P availability (Murphy and Stevens, 2010; Xu et al., 2013, 2014). Biochar has been reported to have significant amount of P and have tendency to modulate soil properties, thus increases P-availability resulting into improved plant growth (Lehmann et al., 2003b; DeLuca et al., 2006, 2009; Xu et al., 2013). It increases P sorption in acidic soil by increasing Ca-bound and Al-bound P fraction availability; however, reverse is true for alkaline soil possibly due to Ca-ion induced chemical reactions (DeLuca et al., 2009; Xu et al., 2014). In addition, biochar can be proved as a suitable candidate for P concentration and availability under external P addition in a highly P deficient and acidic soil systems by altering soil pH and releasing Fe-, Al-metal bound P either from soil

Box 9. Factors affecting N dynamics under biochar applied soil systems.

Soil pH, CEC and acidic surface groups are the major factors regulating the N cycling (N adsorption and retention) in biochar applied soil system (Seredych and Bandosz 2007; Huang et al., 2008; Molina-Sabio et al., 2011). However, it is also well proved that increase in soil pH resulted into neutralization of NH^{4+}-N with freely available OH^-, thus leads to volatilization of NH3 easily (Xu et al., 2013). Simmilarly, biochar (having high C/N ratio) addition lead to N immobilization, thus, resulted into decreased bioavailability for plant processes (Lehmann et al., 2003b; Deenik et al., 2010). Inherent biochar N is reported in some studies as unavailable (recalcitrant or black-N) form due to its presence in heteroromatic structures as well as more evaporative loss of labile N form from aged biochar surfaces (Gaskin et al., 2010; Lin et al., 2012). It was further observed that biochar prepared at lower temperature have higher labile fraction of N and is more prone to immobilization through microbial activities (Deenik et al., 2010).

or other amendments (Cui et al., 2011b; Masto et al., 2013). In general, higher rate of biochar amended soil leads to increase in Ca-bound P sorption whereas decrease in Al- and Fe-bound P sorption in acidic soils (Murphy and Stevens, 2010; Xu et al., 2013, 2014). However, precipitation of Ca-bound P with pH change is the major limitation and leads to decrease in P availability in biochar amended soils (Xu et al., 2013).

As reviewed by DeLuca et al. (2009) and the present literature survey on role of biochar on soil P, possible reasons for enhanced P availability in biochar amendment, irrespective of the production process include: (1) direct release of P from biochar and other amendment in combination (Chan et al., 2007; Atkinson et al., 2010; Xu et al., 2013), (2) release of bounded form of P (Fe-, Ca- or Al-bounded) to the soil system through pH variation (Murphy and Stevens, 2010; Wang et al., 2012; Yuan et al., 2011a,b; Xu et al., 2013), (3) adsorption of available P on its surface, thus increasing bioavailability to the rhizospheric region via increased CEC (Xu et al., 2014), (4) by changing P sorption and desorption mechanism through pH change after its application to soil system (Xu et al., 2014). Further, biochar in combination with other soil ameliorant such as fly-ash increases P as well as other essential metals availability e.g., K increases significantly by the sorption on its surface (Masto et al., 2013). Mechanistic explanation of P availability under CRB applied soil system is given in Box 10. Thus, biochar application can be beneficial in acidic soil reclamation and the soil that has been degraded by long term continuous cultivation (Kimetu et al., 2008).

7.2.1.4.4. Mechanism of nutrient retention. Possible mechanisms proposed for nutrient retention under varying biochar applied soil systems are dominated by higher sorption potential for high PT biochar whereas partition on the organic matter part for low PT biochars (Chun et al., 2004). Further, increased nutrient retention in biochar applied soil may be attributed by increased CEC, surface adsorption, inducing abiotic and biotic reactions, pH variation, etc. (Lehmann et al., 2003b; Cheng et al., 2006, 2008; Sohi et al., 2009; Murphy and Stevens, 2010; Sohi et al., 2010; Xu et al., 2013). Highly negative biochar surfaces may lead to higher absorption and cation retention by ionic interaction, bond formation and thus, reduced leaching (Liang et al., 2006; Dunisch et al., 2007; Steiner et al., 2008a; Ding et al., 2010; Zimmerman et al., 2011; Luo et al., 2011). Surface adsorption processes lead to retention of labile nutrient sources like organic fertilizers, manures composts and mulch for further decomposition by microbes (Mccormack et al., 2013).

7.2.2. Effect of biochar on biochemical properties of soil

Soil biochemical properties such as enzyme activities are one of the important indicator of soil health and therefore, sustainability of soil system. Any material having tendency to improve these activities can be considered and recommended for soil amelioration. Extensive studies have been performed on these properties for biochar applied soil at laboratory-scale, though field-scale detailed studies considering various abiotic factors are limited. Various studies on biochar added soil have been reported as beneficial, in general, to soil biochemical properties such as active microbial biomass carbon (AMBC), dehydrogenase (DHA: an indicator of microbial activity) (Nannipieri et al., 1990; Paz-Ferreiro et al., 2012) and catalase activities increase, whereas decrease in hydrolytic enzyme such as glucosidase, leucine amino peptidase and alkaline phosphatase activities due to improved microbial activities by modulating soil properties (Galvez et al., 2012; Nannipieri et al., 2012; Kumar et al., 2013; Masto et al., 2013). pH-buffering, SOM enrichment, nutrient retention through sorption on biochar surfaces could lead to increased enzymatic activity, soil respiration, active microbial biomass carbon (AMBC), etc. (Masto et al., 2013). However, some studies reported increase in activities of alkaline phosphatase, aminopeptidase and *N*-acetyl-glucosaminidase (Jin, 2010; Bailey et al., 2011); decrease in acid phosphatase activity; whereas no effect on peroxidase, phenol oxidase and catalase activities in biochar amended soil samples possibly due to increase in soil pH (Masto et al., 2013). In addition, extracellular enzyme activity also decreases due to sorption of such enzymes on biochar surfaces (Jin, 2010; Liang et al., 2010). Increase in turnover and soil respiration has been observed in biochar applied soil due to increased belowground microorganism's activities (Jones et al., 2012) which is directly correlated with SOC (Liu et al., 2006).

Further, combined application of biochar with compost affects nitrifying enzymes activities due to its direct effect over soil nitrifier and denitrifier communities (Wang et al., 2013a,b,b). In addition, denitrification enzyme activity is reported to increase with higher dose of biochar amendments (Jones et al., 2012; Ducey et al., 2013). Possible reasons for these activities under biochar application proposed by Ducey et al. (2013) include increase in N-fixing gene content viz., *nif*H (N fixation), *nos*Z (nitrous oxide reductase), *nir*K (nitrite reductase), and *nir*S (nitrite reductase) of microbial communities. In general, based on present literature survey, the possible mechanisms involved for improved biological nitrogen fixation (BNF) in biochar amended nutrient poor soils include: (1) increase in nodulation (Ogawa and Okimori, 2010; Rillig et al., 2010), (2) immobilization of available N within microbial cell (Bruun et al., 2011; Nelissen et al., 2012), (3) increase in micronutrients availability (e.g., Mo and boron B, critically required for BNF enzyme activity) (Rondon et al., 2007), and (4) increase in available P content to microorganisms (Nelson et al., 2011; Brewer et al., 2012). Therefore, improved biochemical properties under biochar applied soil system can be a positive mechanism for prospecting its large-scale application.

7.2.3. Effect on soil biota

Growth of various microorganisms beneficial to agriculture has been reported in biochar amended soil. Biochar favors microbial soil communities like N_2-fixing bacteria (Brussaard et al., 1990), arbuscular mycorrhizal (AM) and ectomycorrhizal fungi colonization and sporulation (Robson et al., 1994; Saito and Marumoto, 2002; Brussaard et al., 2007; Warnock et al., 2007) and several

Box 10. Mechanism of P availability in biochar amended soil system.

Soil pH change under biochar added soil is attributed to change in surface charge density through increase in ionic strength and alkaline metal exchange (Murphy and Stevens, 2010). Increase in pH cuases early precipitation of Fe- and Al-oxides (Murphy and Stevens, 2010; Yuan et al., 2011b), whereas Ca and Mg precipitation occurs at highly alkaline condition (Agbenin, 1995; Cui et al., 2011b; Xu et al., 2014). Therefore, under biochar amended soil an increase in Fe and Al oxide content and Ca and Mg content in soil system is reported. Biochar surfaces are more preferable for cation exchange than anion exchange (Cheng et al., 2008; Silber et al., 2010; Mukherjee et al., 2011). It leads to exchange of metal cations especially Ca^{++} in soil system which increases P sorption released from Fe- and Al-oxides through pH changes resulting into further availability of Ca-bound P through precipitation (Murphy and Stevens, 2010; Xu et al., 2013). However, further increase in pH leads to anionic repulsion and decrease in P sorption due to inhibition of HPO_4^{2-} formation (Haynes, 1982; Murphy and Stevens, 2010).

other meso-faunal organisms like earthworms (Li et al., 2011), by providing them protection from predators and desiccation, space and nutrients (Ogawa, 1994; Pietikäinen et al., 2000; Ezawa et al., 2002; Saito and Marumoto, 2002; Warnock et al., 2007; Thies and Rillig, 2009). Biochar aggregate consists of organic carbon with porous structure having potential to hold nutrients and soil moisture, thus, providing a suitable habitat for microbial communities (Tisdall and Oades, 1982). A recent review on biochar effect on soil biota by Lehmann et al. (2011) suggests that its addition affects microbial community composition and enzyme activities significantly by modulating various biochar-induced soil properties such as surface area, pore structure, pH and mineral matter as well as sorption of growth-inhibiting substances, thus, flourishing biotic communities (see: Lehmann et al., 2011). They further identified the possible major processes involved for microbial abundance in biochar surfaces as surface adsorption, flocculation, covalent bonding to carriers, bacterial cell bridging, entrapment of bacterial cell to the biochar matrix or encapsulation in a biochar mediated polymer gel on its surface. However, microbial abundance in biochar amended soil system is a function of soil–biochar interaction (Lehmann et al., 2011).

Biochar is more prone to degradation because a small fraction of carbon is present in the labile form, thus less resistance in its initial phase of application (Krull et al., 2006). Further, the high porosity and larger surface area of soil after biochar amendment would lead to the growth of microorganism, thus, leading to better symbiosis of the crop with bacteria and fungi, which results in the dissolution of nutrients and bioavailability of nutrients for the crop (Warnock et al., 2007). In addition, alkaline pH leads to better functioning of soil microbial communities and resurrecting buffering capacity to soil after its application (Yuan et al., 2011a,b,b).

Bacterial communities generally favors alkaline pH range whereas at neutral to slightly acidic pH range fungal communities dominate in soil system (Rousk et al., 2009). Thus, addition of alkaline biochar in soil changes fungal/bacterial growth ratio and stimulate the microbial communities shift towards bacterial growth community in one way (Jones et al., 2012) and on the other way highly porous structure provide protection to the fungal hyphae. In addition, sorption of bacterial communities on biochar surface via electrostatic or hydrophobic attraction reduces leaching to soil whereas fungal communities remain stable with hyphal network (Pietikäinen et al., 2000). However, presence of moderate microbial predators induce SOC release from microbial systems (Box 11) through hyphal growth and enzyme activities whereas high grazer abundance lead to accumulation of SOC due to decreased microbial population, thus, protection of microbes from predators through fine porous biochar structure lead to reduction in soil nutrient flux due to immobilization in microbial biomass (Bardgett, 2005). Thus, higher microbial activities signifies rapid SOM turnover, modulate nutrient cycling and plant growth (Wardle et al., 2008; Kuzyakov et al., 2009; Liang et al., 2010), and ultimately less microbial C sequestration (Jones et al., 2012; Mccormack et al., 2013). In addition, alkaline biochar application can be a suitable candidate for acidic soil having damaging effects on microbial communities due to increased availability of toxic metals like Al (Bardgett, 2005). Liming of acidic soil increases soil pH towards neutral, thus, favor bacterial community which may further enhance nutrient mineralization and reduce microbial carbon sequestration (Bardgett, 2005; Fornara et al., 2011).

On the other hand, decrease in certain microbial activities have been reported in some studies possibly due to addition of recalcitrant carbon, or with induced mineralization of native SOM with biochar addition (Seiler and Crutzen, 1980; Glaser et al., 2002a; Liang et al., 2010; Jin, 2010). Also, decrease in mycorrhizal abundance has been observed in various studies possibly due to modified environments with biochar addition as it increased soil moisture, soil pH, nutrient source, P availability; or sometimes high heavy metal and salt contents having detrimental effects over such associations; or sorption of available C source to its surface (Covacevich et al., 2006; Gryndler et al., 2006; Chan and Xu, 2009). However, these ambiguous explanations on biochar and microbial activities has been thought to be sorted out by applying certain basic information in each study, as proposed by Joseph et al. (2009) and Lehmann et al. (2011), such as physico-chemical properties (surface area, pore size and volume, microbially available C, pH, ash content, elemental content) as well as feedstock material and production conditions alongwith comparative analysis of different biochar types on microbial activities. Furthermore, biochar has been suggested as a suitable inoculant carrier either alone or as a blend with other traditional carriers for various microorganisms such as *Azotobacter, Bacillus, Clostridium, Frankia, Pseudomonas*, or *Rhizobium* due to its cheap and easy availability as compared to expensive, non-renewable and GHG emitting carriers such as peat, press mud, compost and farmyard manure (Beck, 1991; Deaker et al., 2004).

7.2.3.1. Biochar effect on soil meso- and macro-fauna. Interactions of soil meso- and macro-faunal communities with any material to be incorporated in soil are of vital importance for further degradation and mineralization with the help of microbial communities. Biochar interactions with soil mesofauna such as nematodes, microarthopods, etc. have been less studied except detailed studies on biochar and earthworm interactions in soil system (Lubbers et al., 2013). An increase in microarthropods such as clams, polychaetes and amphipod activities in biochar amended soil has been reported due to decreased availability of toxicants and increased fungal nutrient pool (Moore et al., 1988; Millward et al., 2005; McLeod et al., 2007). Biochar application decreases mites abundance, thus, consequently could increase decomposition rate of nutrients through enhanced microbial

Box 11. Biochar-induced microbial C mineralization.

Drying has significant effect over microbial activities (Xiang et al., 2008). Rewetting of soil have been reported to increase r-strategist community having higher soil respiration and labile C mineralization tendencies (Fierer and Schimel, 2003; Mavi and Marschner, 2012). Biochar having larger surface area maintains soil moisture, thus protects microbes from dehydration (Glaser et al., 2002a; Liang et al., 2006; Downie et al., 2009); and further stimulate r-strategist microbial communities (Junna et al., 2014). Therefore, increase in "r-strategist" microbial communities leads rapid mineralization of labile C in moist condition after biochar addition (Kuzyakov et al., 2000; Wardle et al., 2008; Mukherjee and Lal, 2013). Microbial activities vary with the presence of stable SOM source as bicohar and soil mineral matter interaction lead to formation of stable soil aggregates (Six and Jastrow, 2002; Kyung-Hwa et al., 2010; Mukherjee and Lal, 2013). Addition of external labile C source further enhances mineralization of SOM and biochar C due to co-metabolic decomposition by rapid growth of "K-strategist" microorganisms having potential to decompose recalcitrant carbon (Hamer et al., 2004; Kuzyakov et al., 2009; Luo et al., 2011).

activities (Kajak, 1995). Therefore, elaborative studies on interactions of biochar with soil meso- and macro-faunal communities would be of further relevance from microbial point of view.

Earthworm, natural soil engineer, improves soil properties, increase bio-availability of nutrients (Don et al., 2008; Roithmeier and Pieper, 2009) and increase fluxes of soil contaminants (Sizmur and Hodson, 2009). Their activity in presence of biochar has been extensively studied. Earthworm shows assimilatory behavior for fresh organic matter as compared to old and recalcitrant one (Edwards and Bohlen, 1996). However, it clearly ingests biochar and modifies the biochar properties by changing microbial activities and act as a transporting agent to deep in soil (Lehmann et al., 2011). Heavy metal accumulation in earthworm tissues in observed in a biochar amended soil system (Beesley and Dickinson, 2011). The bioturbation activity performed by earthworm (anecic), causes vertical mixing of biochar in soil profile (Carcaillet, 2001). Van Zwieten et al. (2010) studies on earthworm affinity to biochar by using behavioral experiment and found that it vary with soil type, e.g., it was higher in Australian Ferrosol whereas less preferable for Calcarosol. In another experiment on soil amended with hardwood biochar, Gomez-Eyles et al. (2011) observed reduction in weight of earthworm, possibly due to higher PAHs content in biochar. Earthworm activities are affected by soil pH, as its presence is reported in neutral environment having moderate pH and aridity (Liesch et al., 2010). Further, soil moisture and soil temperatures altered by biochar addition are the major regulatory factors for earthworm activity and related faunal communities such as soil respiration (Lou and Zhou, 2006; Oguntunde et al., 2008; Beesley and Dickinson, 2011; Genesio et al., 2012).

7.3. Biochar and crop yield

For qualifying the criteria of sustainable agriculture, any amendment material should have capability to improve the crop yield along with conservation of natural resources. From the above discussion, it is obvious that biochar can fulfill the key criterias of being sustainable material for agricultural systems; however, its potential for improving yield is needed to further exploration. In the present section, a brief account of biochar effect on various crop yields has been given. Biochar application has been reported to have varying effect over different crop performance and yield due to variation in cropping system and inherent soil properties (Yamato et al., 2006; Asai et al., 2009; Van Zwieten et al., 2010). Enders et al. (2012) suggested that for proper evaluation of agronomic performance of a crop in a particular type of soil, there should be a library containing key limiting factors for soil–crop–climate before applying a biochar material. A brief account of biochar–crop interactions has been delineated in Box 12. In a meta-analysis on effect of biochar on crop yield, Jeffery et al. (2011) found crop yield ranging from −28% to +39% (grand mean +10%) with varying soil and crop type under different climatic conditions (see: Jeffery et al., 2011). Long-term field studies on such variation are limited; however, a long-term field study has been started from June 2009 at Rothamstead Experimental Station (UK) for evaluating the effects of biochar application on soil properties and crop yield (Barrow, 2012).

A few short-term studies on biochar application rate and crop yield under different agroecosystems have been reviewed here. Improvement in yield for various important staple cereal crops under biochar application have been reported for rice crop (Singh et al., 2010; Liu et al., 2012; Tang et al., 2013), for corn (Van Zwieten et al., 2010; Rajkovich et al., 2012) and maize (Jones et al., 2012; Cornelissen et al., 2013). Yield gain under biochar amendment may possibly be attributed to improved soil physico-chemical properties such as WHC, bulk density, SOC, decrease in Na content, enhanced availability of P, N, Mg, N-metabolism (Van Zwieten et al., 2010; Rajkovich et al., 2012) and K (Josko et al., 2013) contents, and, thus increasing leaf protein metabolism (Tang et al., 2013), as well as nutrient use efficiency under biochar applied soils than control soils (Liu et al., 2012). Potassium (K), a key element required for enzyme formations and acts as co-factor in various plant-reactions, thus would lead to increase in crop productivity and fertility of soil (Maathuis, 2009). However, soil inherent nutrient conditions are considered as the major determinant because yield increase trend observed is generally high for low SOM, marginal for moderate SOM and no yield gain for high SOM containing soils (Liu et al., 2012).

Similarly, a three-year field study by Jones et al. (2012) on impact of biochar on agronomic performance for a fertile soil suggests that biochar application to fertile soil is not so effective in terms of agronomy such as crop growth, crop nutrition and soil quality, even on the fertilizer input rate because it did not reflected into maize crop growth performance i.e., germination efficiency, seedling emergence rates and leaf chlorophyll content (Jones et al., 2012). As long-term benefits, biochar leads to increase in nutrient retention through reduced leaching and increased adsorption, thus, resulted into improved soil fertility (Dunisch et al., 2007; Steiner et al., 2008a; Ding et al., 2010; Zimmerman et al., 2011; Luo et al., 2011). Possible benefits to soil and crop due to biochar amendment has been suggested by Sohi et al. (2009) as changes in soil chemistry by supplementing native composition of soil particles, providing catalytic sites for useful soil reactions, and by benefitting root growth and nutrient flux by ameliorating soil properties.

Biochar amendment has been found to have less effect on crop nutritional qualities such as C, N, P, K, Na or Ca content in its earlier phase of application, whereas a significant reduction in alkali and alkaline metals but not for P and NH_4^+-N availability was observed with biochar aging (Jones et al., 2012). The increase in phosphatase activity would lead to increased soil P content, thus, increased soil fertility (Jin, 2010; Masto et al., 2013). Biochar in combination with NPK fertilizer have been found to increase grain yield in a Brazilian oxisol (Christoph et al., 2007). Further, biochar amendment in combination with conservation agriculture practices such as no tillage may have positive yield effect even for fertile soils possibly due to higher interaction of biochar to root system reflecting fertilizer retention in rhizosphere, increased base saturation and

Box 12. Biochar–crop interactions.

Rhizosphere is a primary point of interaction between any materials and growing plants. However, limited detailed studies are available on the biochar-root interactions (rhizosphere) (Prendergast-Miller et al., 2014). In a rhizoboxmesocosms study for biochar application to spring barley (*Hordeumvulgare* L.), Prendergast-Miller et al. (2014) found that biochar provide direct nutrient such as soluble P and available N (as nitrate) supply to plant roots. Possible mechanisms involved for forbiochar-root interactions include: (1) by changing soil physico-chemical properties (Jones et al., 2012), (2) by changing microbial biodiversity (Rondon et al., 2007; Prendergast-Miller et al., 2014), (3) by decreasing residual effects of herbicides and allelochemicals by sorption on its surface (Jones et al., 2011a), and (4) changing flux of secondary metabolite affecting root growth (Spokas et al., 2010).

CEC (Cornelissen et al., 2013). Thus, spatio-temporal exploratory studies on biochar application with conservation agricultural practices or as inherent conservation agricultural principles are required.

8. Crop residue biochar and GHGs emissions

Agricultural systems are regarded as one of the most potential greenhouse gases (GHGs) emission sources worldwide (Cheng et al., 2011) contributing about 10–12% per year of the global anthropogenic emissions (IPCC, 2007; Smith et al., 2008; Davidson, 2009), and 24% including forestry and land use (AFOLU) sectors (Houghton et al., 2012; Tubiello et al., 2013; IPCC, 2014). However, it is supposed that by managing rather increasing SOC pool or decreasing non-CO_2 GHGs emissions with proper crop improvement, net GHGs emissions can be slowed down (Mosier et al., 2006; Smith et al., 2008). In addition, the nutrient retention capacity of biochar leads to the reduction of fertilizer use, so it indirectly results in reduction in production, energy and environmental cost. Also, biochar application to soil leads to subdued release of N_2O and CH_4 like potent GHGs (Dalal et al., 2008; Yanai et al., 2007). Further, combined application of biochar with compost affects nitrifying enzymes activities due to its direct effect over soil nitrifier and denitrifier communities (Wang et al., 2013a,b,b). Thus, biochar in addition to other amendments is directly correlated with N_2O emissions from soil through several enzymes (like nosZ, nirK, and nirS) activities (Wang et al., 2013a).

In general, it is very difficult to give any conclusive remark on biochar application and GHGs emission reductions after reviewing available literature and recently published reviews (see: Cayuela et al., 2014) because of the versatility of biochar characteristics, application, inherent soil properties and climatic conditions (Rondon et al., 2005; Van Zwieten et al., 2009; Verhoeven and Six, 2014). Further, the results on GHGs fluxes performed under laboratory conditions have not replicated in the field scale studies (Scheer et al., 2011). However, a preliminary calculations on biochar (produced from crop residue wastes worldwide) application to surface soil suggest that about 2.5% of the above produced biochar might be caused a decrease in atmospheric CO_2 levels as low as to pre-AD 1752 by 2050 (Jacquot, 2008). In general, mechanistic explanation of biochar addition and GHG fluxes are still lacking or unable to explain why GHGs emission is reduced in some cases and increased in the others (see: Mukherjee and Lal, 2013). In elaborative terms, various GHGs emitting processes such as methane oxidation and denitrification (Yanai et al., 2007; Van Zwieten et al., 2009), nutrient flux (DeLuca et al., 2009), and C mineralization (Kuzyakov et al., 2009; Liang et al., 2010) have been found to have variable effects in biochar applied systems (Lehmann et al., 2011).

Management of SOM is more important because reduction in SOM pool is one of the key contributors of global climate change (Cramer et al., 2001). As an inherent practice of conservation agriculture, crop residue retention has been found to improve soil fertility by increasing SOC, though in addition its degradation causes significant release of CH_4 (Chidthaisong and Watanabe, 1997). Thus, it would be a wise option to incorporate crop residue-derived biochar to soil instead of crop residue which improves soil health and nutrient status and reduce GHGs emissions to a great extent especially in a paddy field (Watanabe et al., 1998; Lou et al., 2007; Zhang et al., 2013a). GHGs emissions from a biochar added soil is crop-dependent. Zhang et al. (2013b) reported that wheat straw biochar applied soil emitted significantly low GHGs with lower intensity for wheat crop, whereas the trend was not similar for rice crop. Even in a biochar amended soil having fresh organic matter input, N_2O emissions was not found to be reduced (Karhu et al., 2011). Recently, several elaborative reviews and meta-analyses are available on the biochar additions and GHGs fluxes (see: Cayuela et al., 2014) dealing with various aspects of biochar amendment, GHGs emissions and climatic conditions. In general, varying results are available for GHGs emission reductions from a biochar amended agroecosystems and this is further needed to be explored with respect to interrelationships among crop-specific, climate-specific, biochar-source and properties-specific as well as including other abiotic factors analyses to overcome this potential constraint for sustainable agriculture.

9. Life cycle analysis and C sequestration potential of crop residue biochar

Soil has tremendous potential of C storage having as much as 95% of the total C stock on land (Ostle et al., 2009). Long term terrestrial C sequestration is a potential strategy to mitigate present enhanced CO_2 induced global climate change, as terrestrial resources holds more than 2.5 times higher carbon than atmosphere (Fowles, 2006). To enhance terrestrial carbon pool focusing mainly on plant and soil C sequestration, various geo- and eco-engineering approaches such as plant sequestration, no-tillage or geological carbon sequestration, biochar sequestration, etc. (Lehmann, 2007b; Galaz, 2012) have been proposed. Among these approaches, biochar sequestration to soil has been found as an effective and low-risk strategy to mitigate climate change because of its higher recalcitrance (fused ring aromatic structure having amorphous and turbostratic carbon) (Lehmann, 2007a,b,b; Keiluweit et al., 2010; Nguyen et al., 2010) against microbial activities and subsequent improvement of soil environment (Lehmann, 2007b). According to an estimation of Woolf (2008), all the crop residues of the world if converted into biochar, would sequester about 1 gigatonne of carbon to soil and is assumed to be a better carbon capture and storage (CCS) alternative for mitigating Climate Change. About 50% plant biomass carbon is converted to inactive carbon pool whereas remaining 50% can be used as energy and fuels by the pyrolysis process, thus, have a carbon-negative effect (Lehmann, 2007a; Lehmann, 2007a; Lal, 2008a,b). Biochar technology can be estimated to store 2.2 GT carbon annually worldwide by 2050 (IBI, 2012).

Biochar stability and lability has been evaluated by using certain indices such as recalcitrance index developed by Harvey et al. (2012) which represents thermal stability of biochar. Similarly, stable organic matter yield index (SOMYI) proposed by Kumar et al. (2013) is a measure of biochar stability calculated by char yield multiplied by stable organic matter. SOMYI decreases with increasing temperature; with maximum value at temperature range of 300–350 °C. Here, stable organic matter represents the extra proportion of carbon excluding organic matter (i.e., loss-on-ignition (LOI) – organic matter) (Kumar et al., 2013). Further, carbon lability (ratio of organic carbon/LOI) decreases with increasing pyrolysis temperature and residence time. Thus, Kumar et al. (2013) suggested that 300–350 °C temperature range can be used for preparing a biochar having greater potential of C sequestration. Biochar stability to soil has been estimated as centennial to millennial by several workers, however, any definite result is unavailable. However, various lab-scale studies have predicted that biochar has a mean residence time of 1300–4000 years in soil (Cheng et al., 2008). Its degradation and mineralization is very slow, therefore, it is considered as a good method for mitigating Climate change by locking a huge amount of atmospheric CO_2 (Lal, 2008b).

Terra Preta soils are considered as a proxy of biochar longevity to soil. However, biochar stability is approximated by the volatile content as biochar with 40% volatile matter have decomposition of about 10% for about 100 years (Hunt et al., 2010; Zimmerman, 2010). As estimated by Glaser et al. (2002b) and Lehmann et al. (2006) slash-and-char practice will be resulted into 50% biomass carbon retention as recalcitrant material to soil as compared to slash-and-burn (about 3% retention). In addition, Nguyen et al. (2009) estimated that biochar amelioration to soil is long-lived (more than 100 years) as compared to addition of ash and charcoal (less than 100 years). However, biochar stability is greatly affected by clay content of soil (Bruun et al., 2014). Two possible reasons have been supposed for higher stability of biochar in soil viz., the graphene-like structures of biochar i.e., chemical recalcitrance and reduction of accelerated decomposition of labile carbon of soil through co-metabolism (Baldock and Smernick, 2002; Czimczik et al., 2002; von Lützow et al., 2006; Lehmann and Joseph, 2009; Novak et al., 2009). However, microbial activities have been thought to be stimulated initially by labile fractions of biochar for short period (Cheng et al., 2006; Steiner et al., 2008b).

Biochar recalcitrance increases with increasing PT (Wu et al., 2012; Kumar et al., 2013); however, biochar produced from herbaceous feedstock at low PT may decompose earlier as compared to higher PT biochar (Wu et al., 2012). Further, biochar stability is a function of O:C ratios in addition to H:C and volatile matter content (Spokas, 2010; Spokas et al., 2011b). Further, Spokas (2010) reviewed on biochar stability and volatile matter content and found that biochar having very high VM (>80% w/w) showed less C sequestration potential whereas biochar having moderate VM (<80% w/w) in addition to high O:C (>0.2) and H:C (>0.4) ratios showed moderate sequestration ability; however, biochar having less VM (<80%) as well as less O:C (<0.2) and H:C (<0.4) ratios showed very high C sequestration potential. Further, evaluation under various abiotic and biotic conditions is needed to explore its potential.

Early C mineralization from biochar in soil has been further supported by various short-term (almost 3 years) laboratory studies (Baldock and Smernik, 2002; Hamer et al., 2004; Bruun et al., 2008; Kuzyakov et al., 2009; Nguyen et al., 2010; Zimmerman, 2010). Also, various studies suggested that a fraction of C (present as mineral carbonates and organic molecules) from biochar, called labile C content, is mineralized abiotically and biotically to CO_2 within a short period of time (Lehmann and Joseph, 2009). In terms of carbon sequestration, as evaluated by Lee et al. (2013) using ultimate analysis of biomass for biochar sample prepared at 500 °C that a biochar having 27% yield with 79% C content at the same PT would sequester 79 wt% CO_2 of the feedstock biomass. In addition, biochar addition would indirectly reduce the GHGs emissions from N fertilizer industries by increasing the nitrogen use efficiency (NUE) (Gaunt and Lehmann, 2008). Incubation experiments (Bruun et al., 2008; Kuzyakov et al., 2009; Bruun and El Zahery, 2011; Zavalloni et al., 2011) and chronosequencing (Nguyen et al., 2009) of biochar further support its stability to soil as compared to other natural organic additives. Biochar decomposition is also affected by various soil parameters such as soil aggregates, SMC, inherent SOM and aerobic environment (Liang et al., 2006; Cheng et al., 2008; Lehmann et al., 2011).

10. Major constraints to crop residue biochar production and application technology

Instead of extensive studies carried out for pyrolysis processes to establish biochar as potential soil ameliorant and C sequestration agent, certain questions still remain to be answered which limit the application of crop residue biochar to soil at farmer's level. Poly-aromatic hydrocarbons (PAHs) production during slow pyrolysis which remains attached with the anionic surfaces of biochar and might cause negative impact to soil and microbial diversity can be considered as most important limitation (Sparkes and Stoutjesdijk, 2011). It include various low molecular weight two- or three-condensed rings-structured toxic organic compounds such as naphthalene, fluorene, etc. (Barbosa et al., 2006), polychlorinated dibenzo dioxins and furans (PCDDs/Fs) developed during pyrolysis (or incomplete combustion) which have detrimental effect over soil microbial processes during early days of application (Kloss et al., 2012; Hilber et al., 2012). PAHs is produced significantly during fast pyrolysis and gasification processes whereas in a temperature range of 350–550 °C for slow pyrolysis (Hale et al., 2012). Thus, slow pyrolysis produces biochar with minimal PAHs and dioxin content (Barrow, 2012). In a study on PAHs formation and its toxicity effect with varying pyrolysis temperature by Kloss et al. (2012), PAHs composition showed variation with pyrolysis conditions irrespective of any particular trend and naphthalene was the dominating one. This finding further recommended a detailed study to find out the gap between the PAHs formation and pyrolysis condition. Other major limitations observed and reviewed by various workers for exploration of crop residue biochar as soil ameliorant include:

1. Lack of standardized application rate (Sparkes and Stoutjesdijk, 2011).
2. Uncertainty about its long term behaviors under agricultural soil (because once applied to soil, it would be difficult to retrieve) (Jones et al., 2012).
3. Inconvenient evidence on SOM or SOC behavior under biochar applied soil system (Wardle et al., 2008; Sparkes and Stoutjesdijk, 2011).
4. Possibility of soil contamination by introduction of xenobiotics such as PAHs.
5. Reduced activity of pre-emergent herbicides in presence of biochar (Jones et al., 2011a,b; Lehmann et al., 2011).
6. Release of pollutants, detrimental to human health, during pyrolysis process (Kato et al., 2004; Mara dos Santos Barbosa et al., 2006).
7. Unqualification of bio-oil as primary fuel produced via pyrolysis due to high water content, low energy content, high oxygen content, acidic nature, high viscosity and delayed ignition during combustion and poor stability (Czernik and Bridgwater, 2004; Mohan et al., 2006; Wang et al., 2013b).
8. Greater heterogeneity in biochar quality due to upgraded pyrolysis technology basically focused on liquid and gaseous product quality (Verhoeven and Six, 2014).
9. Reduction in efficacy of agrochemicals through surface binding (Sparkes and Stoutjesdijk, 2011; Tang et al., 2013).
10. Negative effects on soil biota due to mineralization of volatiles/labile fraction (Lehmann et al., 2011; Dempster et al., 2012).
11. Salinity and phytotoxicity caused by increased concentrations of CRB application affecting soil and crops (Belyaeva and Haynes, 2012; Enders et al., 2012).
12. Change in reflection of solar radiation by reducing soil albedo leading to increase in soil temperature, decrease in soil moisture affecting soil fauna (Oguntunde et al., 2008; Genesio et al., 2012).
13. Accumulation of ash containing trace metals after pyrolysis.
14. Heterogeneity of biochar feedstock and pyrolysis conditions affecting its properties (Sparkes and Stoutjesdijk, 2011).
15. Generally higher cost of production (Sparkes and Stoutjesdijk, 2011).

11. Future perspective and recommendations

Enhanced SOM mineralization and soil nutrients depletion are currently considered as two important limitations for the sustainable agriculture (Renner, 2007). Soil fertility and agricultural productivity are supplemented by SOM pool, thus, its improvement by addition of stable organic matter (e.g., biochar) rather than less stable biomass (fast mineralization) source (Keith et al., 2011), is necessitated for long term sequestration of atmospheric C (Lehmann, 2007b; Khare and Goyal, 2013). Biochar, having high adsorption and nutrient retention capacity and more stable nutrient source, suits more as an effective soil ameliorant than compost and organic manure in the present scenario (Chan et al., 2007). Further, biochar can also be applied alongwith other soil amendment such as manures, fertilizers, fly-ash in conservation agriculture systems (Lehmann, 2007b; Masto et al., 2013). Co-application of biochar with inorganic material such as fly-ash has been supposed to enhance soil physico-chemical properties and improve crop yield (Masto et al., 2013). On the basis above discussion, a few recommendations for the crop residue biochar (CRB) can be outlined:

- Crop residue as sole feedstock should not be advertised; therefore, it should be used as blend with other organic or inorganic feedstock either in traditional pyrolysis or under catalytic pyrolysis processes. Further, the blended product obtained after catalytic pyrolysis are needed to be evaluated critically for agronomic and ecological benefits.
- Crop residue-biochar integrated approach as a partial retention and partial removal with closed loop model of reversion can be considered as a better option under conservation agriculture scenario as biochar get concentrated under rhizospheric zones.
- Optimization of pyrolysis processes for CRB preparation so that a biochar with suitable salt, PAH and trace metal content could be obtained, as these are the major limitations for its widespread and sustainable application.
- Long term pH change studies under varying CRB applied soil systems in relation to crop-climate understanding are needed.
- However, it is found to have good result with soil N and P availability and movement, it is further needed to be explored under different soil conditions.

12. Conclusion

Crop residue burning practices contribute significantly to global climate change. Carbon sequestration and storage with substantial emphasis on crop residue management is need of the hour. Biochar formation from crop residue and its reutilization in the crop field for soil improvement would be a good practice for sustainable agriculture. Technological initiatives for biomass to biochar formation have not been able to impress policymaker or the society so far as a whole. Rice straw, in particular, is essential crop requiring CRM practice due to the features like surplus amount, lower livestock utility and less cropping gap. Thus, potential need for exhaustive studies on crop residue biochar, its characterization and changes after application to soil is required. A closed loop cycle for a crop residue management with carbon sequestration and storage with soil-specific carbon management is required. In addition crop residue incorporation as a blend with various other lignocellulosic biomasses such as weeds can also be used for the sustainable management through thermochemical decomposition process. Its further incorporation as a blend in soil amelioration with other inorganic materials like sewage sludge and fly-ash needed to be explored in terms of sustainable agriculture. Further, massive work is still needed to describe the stability of biochar in different soil environment and its Life-cycle assessment, so that biochar addition to soil can be unambiguously recommended in sustainable agriculture.

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