Biochar from Biomass: A Strategy for Carbon Dioxide Sequestration, Soil Amendment, Power Generation, and CO_2 Utilization

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Contents

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Abstract

Biochar is a stable form of carbon produced via the pyrolysis of biomass for use in sustainable environmental and agricultural practices. The concept of biochar was originally triggered from the ancient practice in which humans deliberately mixed carbonized biomass into soils to enrich the soil quality and fertility. According to the International Biochar Initiative (IBI), biochar can be defined as “A solid material obtained from the thermo-chemical conversion of biomass in an oxygen-limited environment.” Biomass-derived biochar production has been demonstrated as a potentially viable strategy for developing negative carbon emission technologies for climate change mitigation and also as a material for effective amendment of relatively poor agricultural soils. Most interestingly, ongoing biochar research work has expanded broadly, stretching from its traditional core in the environmental and agricultural science to include studies in the use of biochar for energy generation and as adsorbents for pollution treatment applications. However, the use of biochar for carbon sequestration and soil amendment has attracted more interests by research scientists globally. The use of biochar as a material for soil amendment is closely linked with its potential for climate change mitigation by carbon sequestration. Specifically, the properties of biochar include resistance to microbial degradation and chemical transformations, high surface areas, high water retention capacity, cation-exchange capacity, and its effectiveness as support and substrate for soil microbes. These characteristics endow biochar with a greater potential to become a highly useful source of materials for improving agricultural productivity through soil quality enhancement while simultaneously sequestering CO_2 from the atmosphere to mitigate climate change. On a separate front, a recent study of acoustic and photochemical interactions of CO_2 with carbonaceous materials seems to warrant feasibility research in the future for exploring novel routes of CO_2 utilization and CO_2 capture. Moreover, biochar’s ability to absorb electromagnetic radiation and emit far-infrared wavelength radiation has promoted research, development, and commercialization of biochar’s applications in medical and health therapies.

Introduction

For decades, significant interest has been paid to research activities on biomass-derived biochar for environmental and agricultural purposes. The key properties such as resistance to microbial degradations, chemical transformations, and preservation for geological time periods have provided recognition for biochar application as a potential strategic material for carbon sequestration and soil improvement. The concept of biochar originated from the ancient practice in which humans were deliberately mixing burned biomass into soils to enrich the soil quality (O'Neill et al. 2009). These enriched soil deposits, known as terra preta and found in the Amazonian Basin, appear to have substantially altered soil properties and led to long-term carbon storage and crop improvement (Lehmann 2003; Lehmann et al. 2009).

Biochar, being a thermochemically derived recalcitrant carbon, has multiple definitions based on its production conditions and intended applications. The International Biochar Initiative (IBI 2012) provided a standardized definition for biochar as "A solid material obtained from the thermo-chemical conversion of biomass in an oxygen-limited environment." Lehmann and Joseph (2009) described biochar as "A carbon-rich product obtained when biomass such as wood, manure or leaves is heated in a closed container with little or unavailable air" (Lehmann and Joseph 2009), whereas two more definitions given by Shackley et al. (2012) and Verheijen et al. (2010) were "The porous carbonaceous solid produced by the thermo-chemical conversion of organic materials in an oxygen depleted atmosphere that has physicochemical properties suitable for safe and long-term storage of carbon in the environment" (Shackley et al. 2012), and "Biomass that has been pyrolyzed in a zero or low oxygen environment applied to soil at a specific site that is expected to sustainably sequester carbon and concurrently improve soil functions under current and future management, while avoiding short- and long-term detrimental effects to the wider environment as well as human and animal health"(Verheijen et al. 2010).

Biomass-derived biochar has been increasingly discussed by experts as a potential strategy for developing negative carbon emission technologies, climate change mitigation, soil quality, and food security (Lal 2004; Lehmann et al. 2009; Lehmann and Joseph 2009; Manya 2012; Paustian et al. 2000; Xu et al. 2012; Zhao et al. 2013a). To mitigate global climate change and ensure food security for a growing global population, biochar-based techniques have been extensively used for many years to improve the environment by carbon sequestration, reduce greenhouse gas emissions, and enhance soil quality and crop productivity (Laird 2008; Lehmann 2007; Lehmann et al. 2006; Sohi et al. 2010). The multiple benefits associated with biochar are shown diagrammatically in Fig. 1.

Figure 1 shows how human activities impact global climate change and this is represented in two categories and designated carbon negative and carbon positive. Carbon negative is a phrase used to describe any activity that removes more carbon or CO_2 from the atmosphere. For example, the process of photosynthesis is a classic carbon neutral phenomenon. Ultimately, the world will need to become carbon negative if the increasing buildup of atmospheric CO_2 is to be reversed. Thus, a sustainable global environmental future requires strategies to facilitate the use of energy resources that enable the reduction of concentrations of CO_2 and other greenhouse gases in the atmosphere. Low-cost and sustainable ways to achieve net negative carbon emissions from human activities involve the use of technologies such as the hydrogen fuel cell, solar and wind power, and other renewable energy sources. They are critical to achieving the net negative emission goal. On the contrary, carbon positive processes are those which add carbon to the environment. Whereas the thermochemical transformation of biomass into biochar is carbon positive with respect to the atmosphere, the addition of biochar to soil is carbon

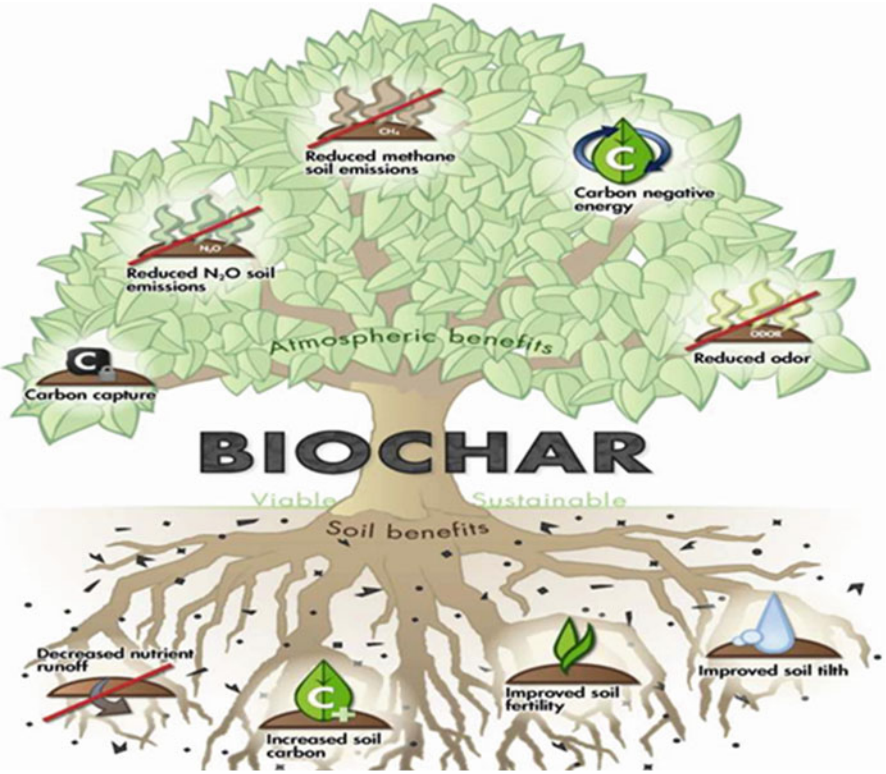


Fig. 1 Environmental and agricultural benefits associated with biochar (Source: International Biochar Initiative (IBI); http://www.biocharinternational.org/)

negative and desirable. Converting biomass carbon to biochar carbon is known to help in sequestering 50 % of the initial carbon compared to the low amounts retained after burning or normal biological decomposition. The stabilization of biomass carbon to carbonized biochar under sustainable procedures is an imperative component in a multi-phased strategy to reduce and offset GHG emissions globally. An added benefit to this solution is the potential for simultaneous enhancement in agricultural production through increased soil carbon content, improved soil fertility and soil tilth, water retention capacity, and reduced nutrient depletion. The physical properties of biochar contribute to its intrinsic multifunctional ability as a tool for environmental management. When biochar is present in the soil, its contribution to the physical nature of the system may involve significantly influencing texture, structure, porosity, and consistency through changing the bulk surface area, pore-size distribution, particle-size distribution, density, and packing. The effect of biochar on soil physical properties may then have a direct impact on plant growth because the penetration depth and availability of air and water within the root zone is determined largely by the physical makeup of soil horizon (Downie et al. 2009). In this chapter, the authors have summarized information related to biochar production techniques, characterization methods, and its potential benefits for carbon sequestration and soil amendment purposes.

Biochar Production Pyrolysis

Pyrolysis is a thermochemical process involving conversion of organic material into a carbon rich solid (char/biochar/charcoal) and volatile materials such as gases (syngas) and liquids (bio-oil) by heating in the absence of oxygen (Demirbas and Arin 2002). The solid product obtained in pyrolysis process is known as char/biochar or charcoal and contains around half of the carbon of the original organic matter. A simple schematic representation of main products of pyrolysis is shown in Fig. 2. Pyrolysis process has been used for decades. Production of charcoal as an unintentional residue from cooking fires by Cro-Magnon man has been reported 38,000 years ago (Antal and Grønli 2003). Pyrolysis and gasification methods have been used for the production of synthetic crude oil from coal since Victorian times.

Based on the heating rate applied to the biomass in order to reach the intended pyrolysis temperature, pyrolysis is classified into slow pyrolysis and fast pyrolysis. Techniques such as intermediate pyrolysis, flash pyrolysis, and hydrothermal carbonization and gasification methods have also been employed but less frequently compared to slow and fast pyrolysis.

Slow Pyrolysis

Slow pyrolysis involves slower heating rates and longer solid and vapor residence times. The temperatures used in slow pyrolysis are typically 400 °C and the heating rate is about 5–7 °C/min. In slow pyrolysis, the yield of biochar is higher compared

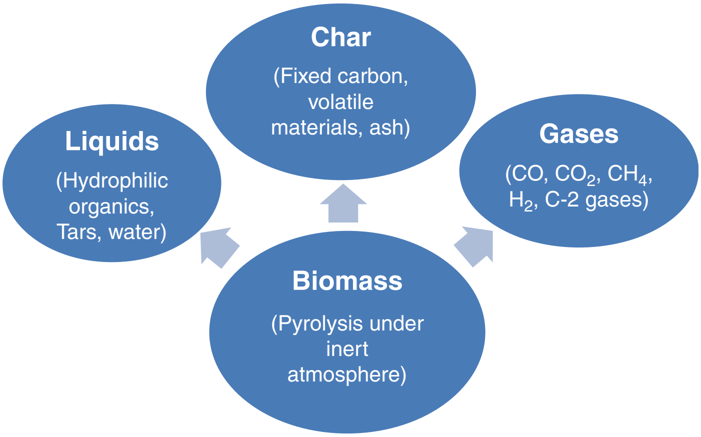


Fig. 2 Major products formed in biomass pyrolysis

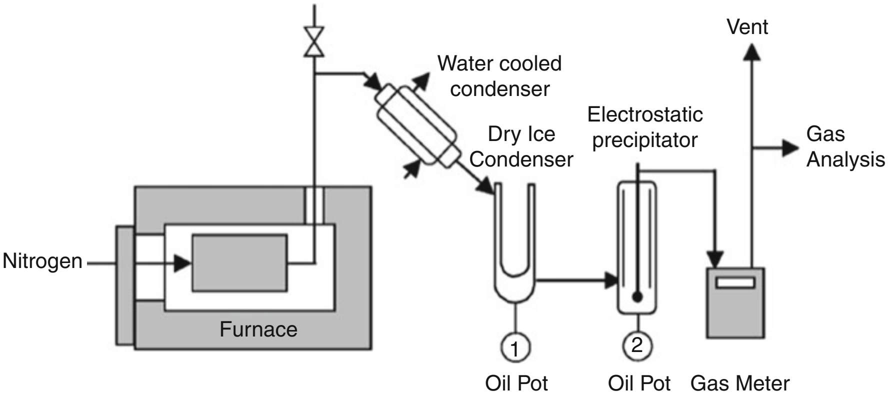


Fig. 3 Schematic representation of slow pyrolysis setup (Bridgwater et al. 2007) (Copyright © 2014 Interscience Enterprises Ltd)

to liquid and gas products formed. In the past, slow pyrolysis of biomass using pits and mounds or kilns was common practice. Bridgwater et al. (2007) demonstrated product yields and characteristics in slow pyrolysis of eucalyptus mallee, and the experimental setup reported in this study is shown in Fig. 3 (Bridgwater et al. 2007).

Fast Pyrolysis

Fast pyrolysis involves high heating rates and short vapor residence times. The pyrolysis reaction temperature applied in this process is usually around 500 °C. Fast pyrolysis requires feedstocks with smaller particle size (<2 mm) and a setup that is capable of removing vapors quickly from the presence of the hot solids. Fluid beds, stirred or moving beds, and vacuum pyrolysis system designs have been used for this application. Commercial processes using fast pyrolysis method have been reviewed and reported (Bridgwater et al. 1999; Bridgwater and Peacocke 2000). In fast pyrolysis the biomass heating rate is very rapid (>300 °C/min) and used specifically to obtain high yields of single-phase bio-oil. A fast pyrolysis experimental setup reported by Bridgwater et al. (2007) is shown in Fig. 4. Since the fast pyrolysis process yields higher concentrations of volatiles, its value for soil applications is limited. Fast pyrolysis produces 50–85 % of bio-oil, 5–25 % of solid char, and 10–20 % of gases, depending on the nature of feedstock and operating conditions.

Other Techniques

Methods such as intermediate pyrolysis, flash pyrolysis, hydrothermal carbonization, and gasification have also been reported. Intermediate pyrolysis was used in electronic waste disposal feedstock (Hornung 2013). The performance of this

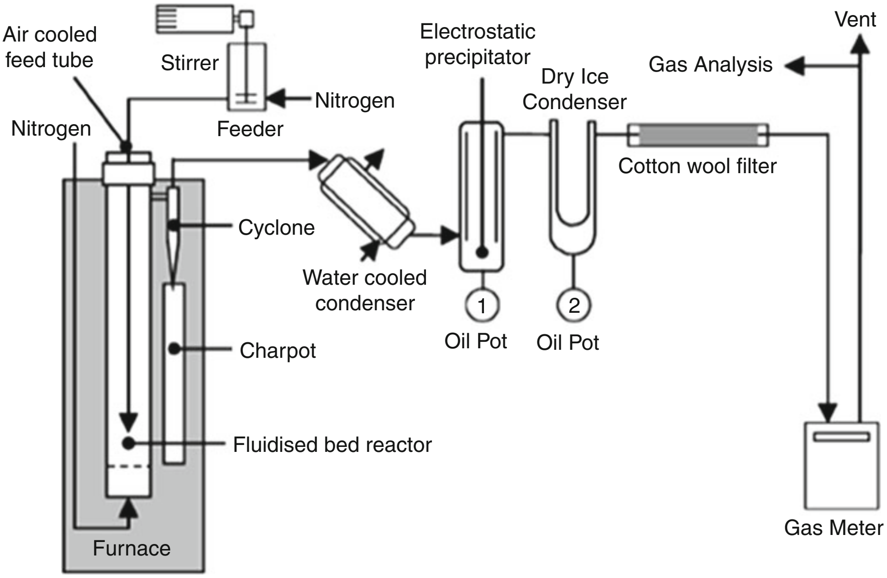


Fig. 4 Schematic representation of fast pyrolysis setup (Bridgwater et al. 2007) (Copyright © 2014 Interscience Enterprises Ltd)

method is very similar to slow pyrolysis and there is not much literature available. Flash pyrolysis methods are similar to fast pyrolysis but required higher temperatures and shorter residence times (Demirbas and Arin 2002). However, hydrothermal carbonization is used in the conversion of biomass into carbon-rich solids in water at high temperatures and pressure (Kruse et al. 2013). Since water is used in hydrothermal carbonization process, there is no need to dry feedstock prior to carbonization and it is a useful method for liquid biomass conversion. The gasification method involves partial combustion of biomass in a gas flow containing a controlled level of oxygen at high temperatures ranging from 500 °C to 800 °C. The main product in this process is syngas.

During pyrolysis, the heat transfer rate is one of the important parameters for determining the product yield and properties. According to IEA (2007), biochar product yields in slow and fast pyrolysis are 35 % and 12 %, respectively (IEA 2007). Depending on the pyrolytic conditions such as temperature, heating rate, vapor residence time, and biomass feedstock composition, the physiochemical properties and quality of biochar vary widely (Enders et al. 2012; Ronsse et al. 2013). Masiello (2004) explained that at low temperature, biochar chemical composition is closer to the original feedstock, while high temperature biochar is closer to graphite (Masiello 2004). Biochar produced at low temperature has high volatile matter and lower fixed carbon and ash contents than its high temperature counterpart (Bourke et al. 2007). Earlier studies have demonstrated that biochar with high volatile organic content contributed to nitrogen immobilization and microbial activity reduction which negatively affected plant growth (Deenik et al. 2010; Spokas et al. 2012). Thus, it is clear that improving the yield of biochar for carbon sequestration and agricultural purposes has been associated with slow pyrolysis in which production gas and liquid co-products will be reduced (Angın 2013; Crombie et al. 2013; Demiral and Ayan 2011; Demirbas 2004; Hossain et al. 2011; Manya 2012; Mašek et al. 2013; Ronsse et al. 2013). Prior to use, a key step involves the evaluation of biochar characteristics that are responsible for its quality and efficacy for the intended application. The details of various biochar characterization methods have been summarized.

Biochar Characterization

The physicochemical properties and composition of the feed biomass are a function of the content of cellulose, hemicellulose, lignin, and extractives. Once the biochar is produced, determining key characteristics using relevant analytical techniques enable the understanding of the potential of the biochar product for proposed applications. Especially the temperature used in the pyrolysis process has shown an impact on both biochar production distribution and the nature of biochar (Kim et al. 2010; Méndez et al. 2013). When the pyrolysis temperature is higher, less biochar is generated and the microstructure develops more effectively. If the temperature is too high, the loss of carbon and other functional group elements on the surface is excessive. The chemical composition, pH, surface charge, and thermal stability of biochar, as well as the heavy metal fate in the biochar body, are also functions of pyrolysis temperature. The information obtained by physicochemical characterization of biochar may help understand the environmental and agronomic functions and facilitates production of desired biochar which offers specified benefits. Properties such as bulk density, elemental composition (ultimate analysis), pH, proximate analysis, and surface properties will help in assessing the biochar quality (Okimori et al. 2003). The details of analytical methods used to characterize biochar properties have been summarized.

Bulk Density

Since the solid density of biochar is directly related to its mechanical strength, it can be used to estimate the biochar's relative ability to withstand wear and tear during soil applications. Generally, the biochar has a higher density than the biomass feedstock from which it was derived. Bulk density is defined as weight per unit volume of material and expressed in kilograms per cubic meter (kg/m^3). Bulk density of biochar is measured by adding a known amount of mass into a container of known volume. Generally, biochar bulk density is around 0.2–0.5 g/cm^3 (Brewer et al. 2014; Özçimen and Karaosmanoğlu 2004).

Elemental Composition

Elemental analysis is generally performed by combusting biochar under excess oxygen using an Elemental Analyzer (EA). This analysis includes quantitative estimation of carbon, hydrogen, nitrogen, sulfur, and oxygen. Also, elemental ratios of C:O, O:H, and C:H are reported as reliable methods to measure the extent of pyrolysis of biochar (Cheng et al. 2008; Kuzyakov et al. 2009). Chan and Xu (2009) reported that during pyrolysis, biomass carbonizes to yield biochar which is highly recalcitrant in nature and has a potential impact on soil health and productivity (Chan and Xu 2009). Thus, quantification of elemental components and their ratios of biochar samples are very important to assess their quality as they may influence soil properties.

pH

Measuring pH is crucial to choose the right char for soil applications depending on the soil nature. The simplest way to measure pH is to make a char and water slurry and use a standard laboratory pH meter. Biochar pH is known to be neutral to basic.

Functional Group Analysis

Qualitatively, Fourier transform infrared spectroscopy (FTIR) is frequently used to detect functional groups in biochar samples. The information is helpful in comparing biochar samples produced under different conditions. Some of the selective stretching group frequencies of biochar samples in IR spectra include O-H (3,400 cm^{-1}), aliphatic C-H (3,000–2,860 cm^{-1}), aromatic C-H (3,060 cm^{-1}), and the carbonyl ($C = O$) (1,700 cm^{-1}) functionalities.

Proximate Analysis

Proximate analysis of biochar includes parameters like volatile organic compounds (VOCs), moisture content, ash content, and fixed carbon. Biochar VOCs are formed during pyrolysis by breakdown or rearrangement of chemical structures present in biomass feedstock. Biochar VOCs have greater impact on plant and microbial responses to biochar amendments because they are known to inhibit/stimulate microbial and plant processes (Baldwin et al. 2006; Klinke et al. 2004). Analyzing VOC content in biochar prior to soil amendment may avoid adverse agronomic effects. Analytical methods such as pyrolysis-gas chromatography/mass spectrometry (pyr-GC/MS) methods have been developed for VOC analysis in biochar samples (Clough et al. 2010; Galipo et al. 1998; Spokas et al. 2011). Thermogravimetric analysis (TGA) has been used routinely to determine the moisture content, volatiles, percentage of fixed carbon, and ash content in biochar samples (Garcia et al. 2013; Kim et al. 2010; Kim and Agblevor 2007; Ottaway 1982; Slaghuis and Raijmakers 2004).

Surface Property Characterization

The surface area characteristic is expressed in the extent of porosity of the biochar which in turn depends on the cell structure of the starting materials. The best-known and most commonly used method for evaluating specific surface areas of biochar materials is the Brunauer-Emmett-Teller (BET) nitrogen physisorption method. For example, if feedstock has larger pore sizes, it can yield biochar with larger surface area resulting in greater nutrient retention properties. These larger pores can also enhance microbial activity (Warnock et al. 2007). In addition, scanning electron microscopy (SEM) has been used for studying the morphology of biochar materials. SEM analysis helps in obtaining details about pore structure and their distribution among the biochar produced under different pyrolysis conditions and from different biomass sources (Fang et al. 2013; Özçimen and Karaosmanoğlu 2004; Shaaban et al. 2013). Figure 5 shows SEM images of biochar produced from wood sources (Fig. 5a), sugarcane bagasse (Fig. 5b), and goat droppings (Fig. 5c) and pyrolyzed at 550 °C. Different physical microstructural property is represented in these images. The macroporous structures in wood derived biochar are arranged in an array of parallel domains, whereas that for the sugarcane bagasse is expressed in a radial distribution. Biochar from goat dropping may only be microporous.

Other analytical instruments used to determine biochar properties include X–ray photoelectron spectroscopy (XPS), energy dispersive X-ray spectroscopy (EDX), near-edge X-ray absorption fine structure (NEXAFS) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, gas chromatography/mass spectrometry (GC/MS), and total organic carbon (TOC) analyzer (Chintala et al. 2012; Fernandes and Brooks 2003; Keiluweit et al. 2010; Lee et al. 2010; Moon et al. 2013; Srinivasan and Sarmah 2014). Studies on characterization of biochar properties have been respired in the literature (Abdel-Fattah et al. 2014 ; Ahmad et al. 2014; Brewer et al. 2014; Chia et al. 2014; Hmid et al. 2014; Jindo et al. 2012; Liu et al. 2014; Mimmo et al. 2014; Novak et al. 2009; Pujol et al. 2013; Rajkovich et al. 2012; Shaaban et al. 2013; Stanger et al. 2013; Zhao et al. 2013b). Overall, detailed characterization of biochar samples provides valuable information useful in understanding the environmental and agronomic efficacy of biochar samples in depth.

Biochar Benefits: Carbon Sequestration

For the past few decades, CO_2 emissions in the atmosphere have been increasing significantly each year. It has been estimated that each year approximately 2 Gt of carbon is set free as CO_2 in response to deforestation and degradation of soils.

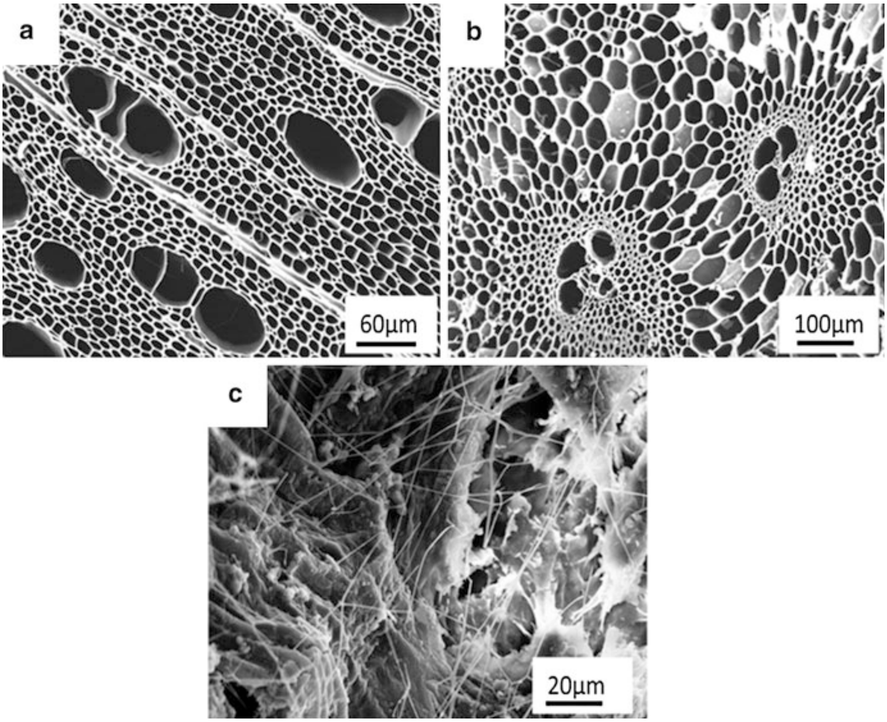


Fig. 5 Scanning electron microscope (SEM) images showing macroporosity of a wood-derived (**a**), sugarcane bagasse (**b**), and goat dropping (**c**) biochar produced by slow pyrolysis: The biochar samples were gold coated and imaged with beam energy of 20 kV on a Zeiss EVO 50VP SEM

The US Department of Energy (USDOE) has estimated that by 2020 the global, annual net production of CO_2 will be 33.8 billion metric tons (USDOE 2010). Energy sources, fires, deforestation, and soil degradation activities have been contributing to increasing the levels of CO_2 emissions into the atmosphere. Since CO_2 is the foremost greenhouse gas (GHG), its enrichment in the atmosphere triggers an increase in atmospheric temperature and ultimately results in global climate change. Researchers have been looking for potential strategies to mitigate climate change by either reducing greenhouse gas emissions or by carbon sequestration, e.g., in aboveground soils. In the past, the Intergovernmental Panel on Climate Change (IPCC) has listed several climate change mitigation options: (1) carbon capture and storage, (2) energy efficiency, (3) switch to low-carbon fuels, (4) nuclear power, (5) renewable energy, (6) enhancement of biological sinks, and (7) reduction of non-CO_2 greenhouse gas emissions (IPCC 2005). Among these options enhancing biological sinks and carbon capture and storage can balance CO_2 in the atmosphere. But again carbon capture and storage concept is associated with high energy consumption generating additional emissions associated with carbon capture. However, the other mitigation approaches are only

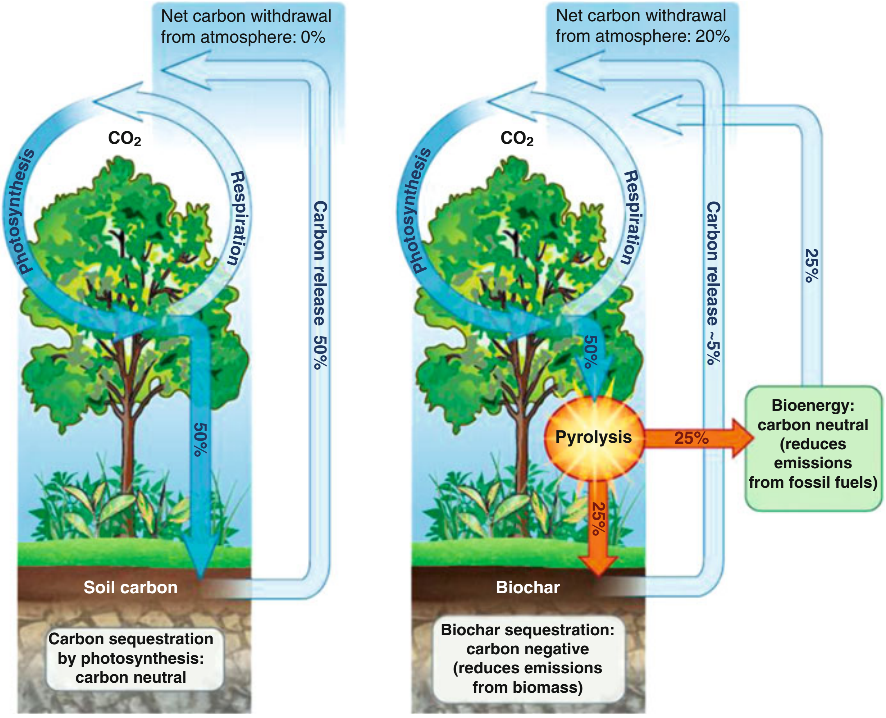


Fig. 6 Illustration of normal and biochar-based carbon cycles (Lehmann 2007) (Copyright © 2007 Nature Publishing Group)

preventive or controlling measures. The carbon cycle function in natural and biochar-based scenarios is shown in Fig. 6. In the case of normal cycle, plants absorb atmospheric carbon dioxide as part of the biological carbon cycle but they are inadequate to handle huge amounts of carbon dioxide released in the atmosphere. So the net carbon withdrawal by the natural carbon cycle from the atmosphere is zero. In addition, plants decay and this biomass releases captured carbon dioxide into the atmosphere. If this biomass is converted into biochar and used to amend soil, the net carbon withdrawal from the atmosphere is 20 % as shown in Fig. 6. Additionally, biochar-based carbon cycle can reduce emissions by 12–84 % and offers the opportunity to convert bio-energy into a carbon-negative strategy (Lehmann 2007).

During the biomass pyrolysis, bio-oil, biochar, and syngas are the three main products. These products can influence the global carbon cycle in the following ways. All the main products obtained during pyrolysis can be used as energy sources which can reduce fossil energy use. In general, biomass decomposition can release a significant amount of carbon dioxide into the atmosphere. By pyrolyzing the biomass, the biochar with enriched stable carbon is produced and will remove carbon dioxide from the atmosphere that would otherwise be released into the atmosphere through bacterial decomposition in the soil. This biochar added into soil becomes a carbon sink and long-term carbon storage.

Biochar carbon sequestration is fundamentally different from other forms of carbon sequestration. It refers to the capture and subsequent storage of carbon to prevent it from being released into the atmosphere (Duku et al. 2011). The primary effect of biochar production on greenhouse gas fluxes is the avoidance of emissions that would have occurred had the biomass been left to decompose. For example, biochar from herbaceous and woody feedstock sources is found to have a carbon content of 60.5–66.7 % and 74.5–80 %, respectively. One can assume from these figures that for every ton of biochar applied to the soil, 0.61–0.80 t of carbon (equivalent to 2.2–2.93 t of CO_2) can be sequestered (Galinato et al. 2011). Using the highest carbon content of the wood-based biochar (i.e., 80 %) and the CO_2 offset price range of \$1 to \$31/MT CO_2 (West and McBride 2005), the approximate value of biochar carbon sequestration is \$2.93–\$90.83/MT biochar. Biochar carbon sequestration might avoid difficulties such as accurate monitoring of soil carbon due to spatial and temporal variation which are the main barriers to inclusion of agricultural soil management in emissions trading. Using the turnover rate and the quantity of carbon has been suggested as a method to be used in assessment of the carbon sequestration potential and that could be done independently from biochar use as soil amendment or other non-fuel purposes.

Biochar Benefits: Soil Amendment

Since biochar is produced from waste biomass such as crop residues, manures, timber and forestry residues, and green waste, its use as a soil amendment has been suggested as a sustainable approach in achieving soil fertility and enhanced crop productivity along with other environmental benefits (Chan et al. 2007). In the past, highly fertile carbon-rich terra preta soils in Central Amazonia are widely cited as evidence that charcoal addition to soils brings benefits to the soils (Lehmann 2003). Due to the increasing recognition for the potential of the terra preta as a model for modern agriculture, the use of biomass-derived biochar has raised a lot of research and development interests (Lehmann 2003; Lehmann et al. 2009). Biochar soil amendment becomes a practice to improve soil fertility and crop productivity while maintaining high levels of soil carbon (Ibrahim et al. 2013; Lehmann et al. 2011). Biomass-derived biochar has been proposed as a potential strategy to enhance soil fertility and crop productivity that can boost food security. Studies have shown that the application of biochar to soil enhances soil fertility by increasing the soil cation-exchange and water retention capacities as well as microbial activity, thereby improving agricultural productivity (Lehmann 2007; Lehmann and Rondon 2006).

Enhanced Soil Fertility and Crop Productivity

Effect of Biochar pH and Surface Properties on Nutrient Availability and Cation-Exchange Capacity (CEC)

Once biochar was amended into soil, it exists as soil aggregates rather than free organic matter, thus making up the overall structure of the soil (Liang et al. 2008). According to Sohi, the soil texture and chemistry can be modified based on biochar's pH and surface properties (Sohi 2012). Also, the chemically active biochar surface properties change soil nutrient dynamics and can act as a catalyst for soil functions. A statistical meta-analysis undertaken by Jeffery et al. (2011) to evaluate the relationship between the application of biochar and crop productivity showed an overall small, but statistically significant benefit of biochar application to soils on crop productivity. Even though the grand mean increase is 10 %, the mean results for each analysis performed within the meta-analysis covered a wide range (from −28 % to 39 %) with the greatest (positive) effects with regard to soil analyses being observed in acidic (14 %) and neutral pH soils (13 %) and in soils with a coarse (10 %) or medium texture (13 %). This observation suggests that two of the main mechanisms for yield increase may be a liming effect and an improved water holding capacity of the soil, along with improved crop nutrient availability (Jeffery et al. 2011). Generally, biochar pH values are neutral to basic ranging from pH 6.2 to 9.6 (Chan and Xu 2009). Effects of biochar on soil chemistry appear to arise from modification of soil pH. In the case of acidic soil, there is a reduction in cation-exchange capacity (CEC) and nutrient availability observed with lower pH values. In addition to the nature of the feedstock, a significant importance to biochar properties is the temperature of production. The production temperature influences properties such as the biochar surface chemical characteristics (pH), bulk surface area, and carbon content. Although it has been argued that other factors such as soil type, soil chemistry, organic matter content, and climate may be of greater importance to the agricultural impact of biochar incorporation, the importance of production temperature cannot be overlooked (Mukome et al. 2013). Typically, there is little or no cation-exchange capacity of soil organic matter at very low pH, but this increases with higher pH, and biochar is no exception. However, the point at which the CEC (cation-exchange capacity) of biochar is zero (point of zero charge, pzc) is dependent on the production temperature. It is seen from Fig. 7 that both pH and surface area of biochar appear to increase with production temperature, as carbon yield decreases and so the optimum temperature is probably within the range of 450–550 °C.

CEC is a measure of the surface charge in a soil or a biochar and refers to the ability of a soil/biochar to hold onto nutrients. The benefits for soil work both ways as it will absorb nutrients and prevent leaching yet release the nutrients when required by plants. The level of CEC of biochar gives an indication of the abundance of negatively charged sites on the biochar which can retain exchangeable cations that are essential plant macronutrients, e.g., NH_4^+ and Ca^{2+} (Carrier et al. 2012). For example, Lehmann (2003) demonstrated that biochar reduced leaching of NH_4^+, maintaining it in the surface soil where it is available for plant uptake. The production of a partially oxygenated biochar that possesses enhanced cation-exchanging

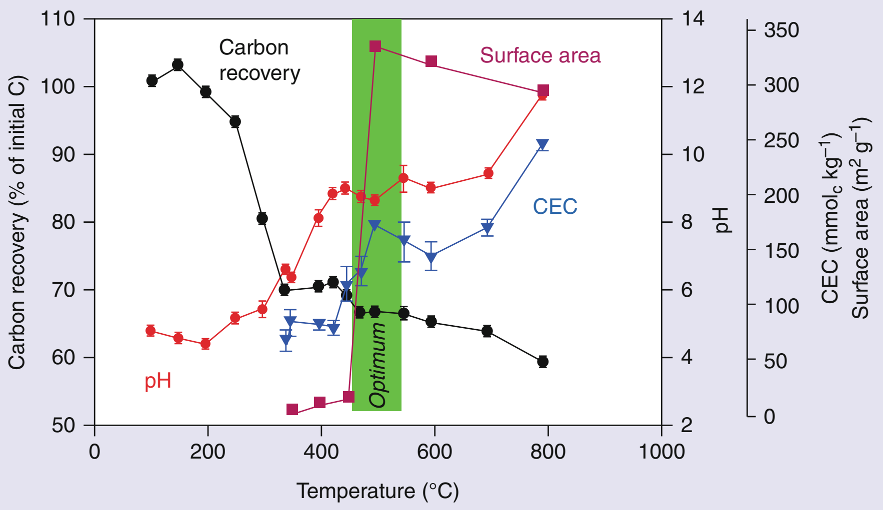


Fig. 7 The impact of temperature on biochar properties. Temperature effects on carbon recovery, cation-exchange capacity (measured at pH 7), pH, and surface area are shown here (Lehmann 2007) (Copyright © 2007 Ecological Society of America)

property by reaction of the biochar source with oxygenating compounds such that the biochar homogeneously acquires oxygen-containing cation-exchanging groups has been reported with oxygenated biochar possessing CEC of at least 140 mmol/kg (Lee et al. 2011, 2013). This concept is based on the experimental finding that the O: C atomic ratio in biochar material correlates with its cation-exchange capacity. Along with aging, the CEC capability increases as evidenced in the terra preta soils of the Amazon (Glaser et al. 2002). Charges on the high surface area can increase cation-exchange capacity (CEC), thereby increasing a soil's ability to retain and supply nutrients. It is well known that both organic and mineral fractions of soil contribute to cation-exchange capacity. The cation-exchange capacity controls the flush of ammonium ions after fertilizer application and mineralization of soil organic matter. This mineralization of organic matter helps in mitigating loss of nitrate leaching. Ash content, phosphorus, potassium and other trace elements present in biochar may impact on crop growth (Steiner et al. 2007).

It is important to note that even though the CEC of biochar is hampered at the pzc, the biochar surface is still available for sorption interactions with other chemical species through hydrogen bonding. For example, the hydrophobic surface of wood-derived biochar has been demonstrated to enhance perchlorate adsorption via H-bonding to oxygen containing groups on the biochar surface (Fang et al. 2013). The principle is illustrated in the schematic in Fig. 8. The totally hydrophilic aliphatic biomass surface (which is unreceptive to ClO_4^- anion) when subjected to pyrolysis and transformed into biochar acquires an aromatic hydrophobic nature. The newly created hydrophobic surface interacts through H-bonding with the ClO_4^- anion. Fang et al. (2013) suggested that it is possible to tune the sorption properties

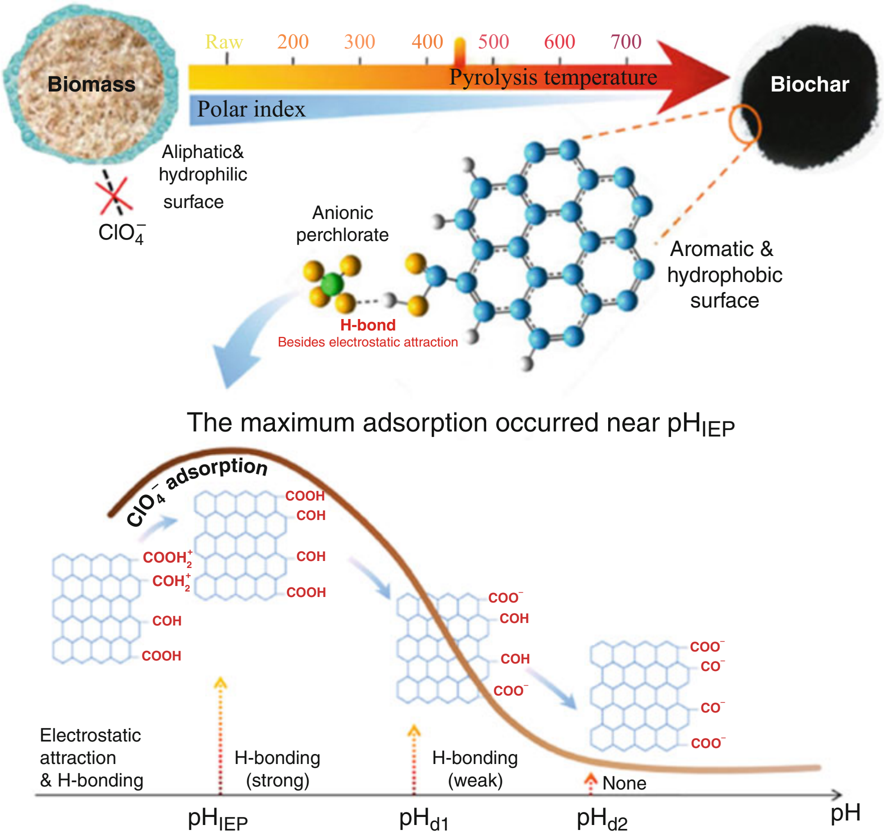


Fig. 8 The schematic of pH-dependent perchlorate (ClO_4^-) adsorption mechanisms onto high temperature biochar with different structural properties and surface functional groups. The maximum adsorption occurred at the point of zero surface charge (Fang et al. 2013) (Copyright © 2013 American Chemical Society. IEP = isoelectric point; d1 =; d2 =)

of biochar by changing the solution pH and concluded that the maximum adsorption interaction occurs at the point of zero charge. The surface area of biochar has a significant impact on the magnitude of interactions between biochar and the soil environment. The surface properties of biochar derived from biomass is crucial in understanding water retention, nutrient retention, sorption capability, and microbial activity of biochar (Day et al. 2005; Fernandes and Brooks 2003; Yu et al. 2006).

Habitat for Microbial Activity

Biochar addition to soil has been shown to increase microbial activity as well as microbial efficiency. In fact, enhanced microbial activity influences the nutrient availability, moisture retention, and cation-exchange capacity (CEC) and is associated with plant growth. Due to porous nature, biochar has been shown to improve soil microorganism abundance and cause effects on nutrient cycle and soil structure

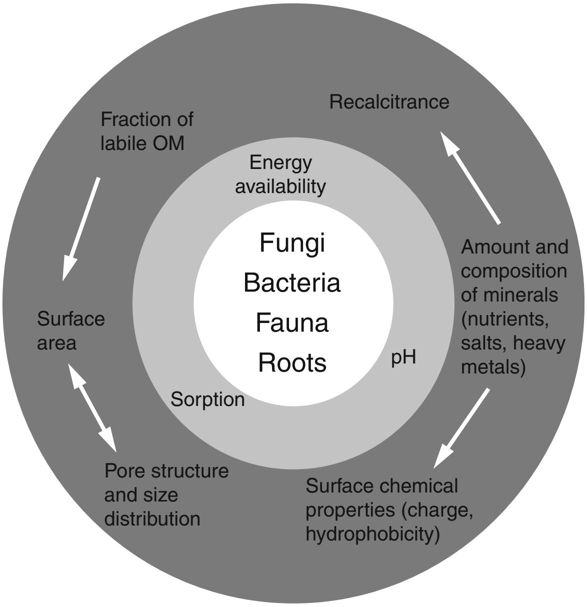


Fig. 9 A schematic overview of correlation between biochar properties and soil microbial community: outer circle represents biochar properties; intermediate circle denotes soil process which influences the microbial community, whereas inner circle shows a qualitative estimation of the strength of the connection. White arrows indicate influence between biochar properties (Lehmann et al. 2011) (Copyright © 2011 Elsevier Ltd. OM =)

that leads to soil growth (Grossman et al. 2010; O'Neill et al. 2009; Pietikäinen et al. 2000; Rutigliano et al. 2014). This scenario has been evidenced further in terra preta soils of the Amazonian Basin (Atkinson et al. 2010). Various biochar properties that influence the soil microbial community and relation between biochar properties and soil microbial community have been documented (Lehmann et al. 2011). The proposed correlation between biochar properties and soil microbial community reported by Lehmann et al. 2011 is illustrated in Fig. 9. Substantial research evidence documenting stimulation of indigenous arbuscular mycorrhizal fungi by biochar has positive impact on plant growth due to increase in nutrient availability, moisture retention, and cation-exchange capacity (Rondon et al. 2007; Warnock et al. 2007). Biochar has demonstrated its function as soil conditioner by making nutrients available to plants and improving soil structure. The surface area and pore structure properties of biochar can increase soil water holding capacity, and the micro-pore spaces with positively charged surfaces can improve soil water retention and in turn reduce nutrient loss through leaching (Lehmann and Joseph 2009; Verheijen et al. 2010). In addition to the chemical stabilization of nutrients, modification of the physical structure of the bulk soil may result in biochar not simply increasing the capacity of soil to retain water, but also nutrients in soil solution. CEC of biochar may be due to leaching of hydrophobic compounds from biochar or by increasing carboxylation of carbon through abiotic oxidation (Cheng et al. 2006).

Mobility and Bioavailability of Heavy Metals

Growing human activities and industrial revolution have resulted in the concentration of metal such as cadmium (Cd), copper (Cu), and lead (Pb) in contaminated soils. These heavy metals may have negative consequences on agricultural productivity and human health. Thus, in contaminated soils, heavy metals such as Cd, Cu, and Pb and their mobility and bioavailability are of agricultural and environmental concern. Biochar soil amendment has been considered to be an alternative remediation method to not only promote plant growth but also reduce the mobility of metals in contaminated soil (Beesley et al. 2010, 2014; Houben et al. 2013; Uchimiya et al. 2011b). Several studies have demonstrated that biochar soil amendment was successful in retaining these heavy metals in contaminated soils (Clemente et al. 2010; Tang et al. 2013; Uchimiya et al. 2010, 2011a). The presence of various functional groups and the highly porous nature of biochar have demonstrated it to be very effective in the adsorption of heavy metals. The pH of biochar also plays an important role in controlling the mobility of heavy metals. Studies have explained that an increase in pH and CEC affects the metal immobilization process (Beesley et al. 2011; Uchimiya et al. 2011a). Therefore, biochar has been considered a potential amendment for promoting the establishment of a plant cover and phytostabilization strategies on contaminated soils (Beesley et al. 2011).

Pesticide Sorption

Biochar is considered as a universal sorbent. Compared to natural soil, biochar-amended soil has greater sorption ability due to its large surface area and charge density (Liang et al. 2006). Application of biochar as sorbent is a cost-effective approach and has shown strong affinity for organic contaminants (Yang and Sheng 2003; Yu et al. 2010). The usage of pesticides in agricultural practice poses a potential risk of groundwater pollution. These environmental contaminants have been monitored in groundwater. Based on solubility and dissipation behavior in soil, these contaminants may represent elevated risk of leaching. This leaching process is affected by sorption and desorption behaviors in soil. Biochar works as a super sorbent and decreases the leaching potential of these contaminants in soils which further helps to mitigate groundwater contamination (Ahmad et al. 2014; Guo et al. 2006; Loganathan et al. 2009). The mechanism for the sorption characteristic of biochar has been proposed by Ahmad et al. (2014) and the details have been illustrated in Fig. 10.

The large surface area (1,000 m^2/g), micro-, meso-, and macro-porosity, diverse surface and bulk properties of biochar has imparted to it different sorption properties of biochar (Downie et al. 2009). It is unsurprising that the presence of biochar in soil plays an influential role in the sorption properties of soil. The application of biochar to the sorption or removal of organic and inorganic pollutants has been tested using four theoretical isotherm models, namely, Langmuir, Freundlich, Dubinin-Radushkevich, and Temkin models (Zhang et al. 2011). The Langmuir model is described by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 K_L} + \left(\frac{1}{Q_0}\right) C_e \tag{1}$$

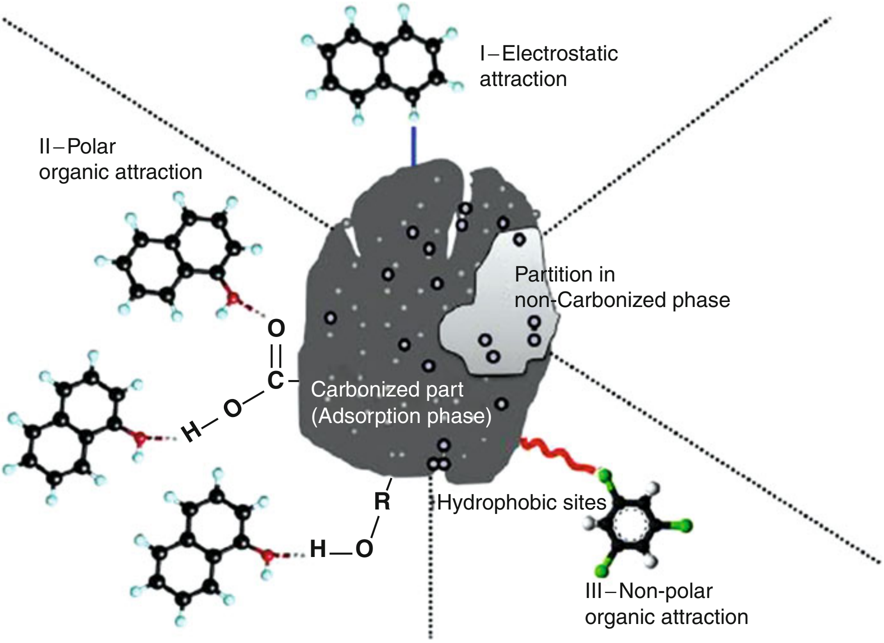


Fig. 10 Biochar interaction with organic contaminants: Electrostatic attraction between biochar and organic contaminant (I), polar organic contaminant (II), and non-polar organic contaminant (III). (Ahmad et al. 2014) (Copyright © 2014 Elsevier Ltd)

where q_e and C_e are, respectively, the amount adsorbed per gram of adsorbent (mg/g) and the solute concentration in solution (mg/l) at equilibrium and Q_0 and K_L are constants related to the maximum adsorption capacity (mg/g) and the intensity of adsorption(l/mg), respectively. An essential characteristic of the Langmuir isotherm is explained in terms of the dimensionless separation factor (R_L) defined by the equation

$$R_L = \frac{1}{1 + K_L C_i} \tag{2}$$

where C_i is the initial concentration.

The Freundlich's model is described by the equation

$$In\, q_e = In\, K_F + \left(\frac{1}{n}\right) In\, C_e \tag{3}$$

where K_F (mg/g) is the adsorption capacity of the adsorbent and n gives an indication of how favorable the adsorption process is.

The Dublin-Radushkevich equation has a linear representation of the form

$$In\, q_e = In\, Q_0 - K_{DR}\, \varepsilon^2 \tag{4}$$

where K_{DR} (mol^2/K^2) is a constant related to the mean adsorption energy and ε is the Polanyi potential which can be calculated from the equation

$$\varepsilon = RT\, In\left(1 + \frac{1}{C_e}\right) \tag{5}$$

A plot of In q_e versus ε^2 gives K_{DR} as the slope and Q_0 and the intercept.

The Temkin equation is also given in a linear form as

$$q_e = B_T\, InK_T + B_T\, InC_e \tag{6}$$

where $B_T = RT/b_T$, the constant b_T is related to the heat of adsorption, and K_T is the equilibrium binding constant corresponding to the maximum binding energy.

The Langmuir and Freundlich models have been most commonly used to describe adsorption isotherms. These adsorption isotherms describe the relation between the adsorbate loading on the adsorbent (Q_e) and the liquid-phase concentration of the adsorbate (C_e) at equilibrium conditions. The Langmuir model corresponds to the homogeneous monolayer adsorption, whereas the Freundlich model defines the adsorption onto adsorbents with heterogeneous surface (Yang et al. 2014). Additionally, the dynamics of an adsorption process in terms of the order and the rate constants has been evaluated using the pseudo-second-order kinetic equation given as

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_{\max}^2} + \frac{1}{Q_{\max}} t \tag{7}$$

$$Q_t = K_w\, t^{1/2} + I \text{ (Weber} - \text{Morris model)} \tag{8}$$

where $Q_{\max}$ and Q_t are the adsorption capacities (mg/g) at the equilibrium and at time t, respectively; K_2 and K_w are the constants of pseudo-second-order and the Weber-Morris model, respectively; and I is the intercept (Yang et al. 2013, 2014). The units of K_2 and K_w are g/(mg. min) and (mg/g).min$^{-1(½)}$, respectively.

Altering Nitrous Oxide (N_2O) Emissions

Global nitrous oxide (N_2O) emissions mainly originate from soil due to the extensive use of nitrogen (N) fertilizers in agriculture. N_2O is one of the potent greenhouse gases (GHG) released into the atmosphere from both natural (about 60 %) and anthropogenic sources (approximately 40 %), and its atmospheric concentration in 2013 was about 325.9 parts per billion. Its estimated impact on climate is 298 times greater than equal emissions of carbon dioxide, over a period of 100 years. Biochar addition to soils reduces nitrous oxide (N_2O) emissions by slowing down the nitrogen cycle, possibly as results of an increase in the carbon/nitrogen ratio (Ussiri et al. 2009). Further, crop productivity enhancement is possible with biochar amendment with no or minimal fertilizers, which helps in mitigating other greenhouse gas emissions from soil and on indirect emissions. Irrigation costs can be reduced by biochar amendment.

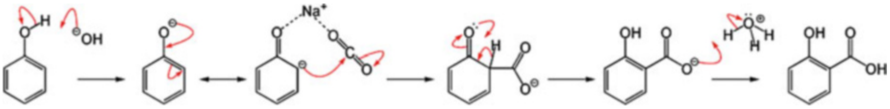
Emerging Applications in Power Generation

Scientific Background

With the goals of developing novel CO_2 capture and utilization technologies, a recent study by Chen et al. (2014) used biochar as a substrate in their study of CO_2 reactions with carbonaceous materials at temperatures below 100 °C. Their study synthesized scientific observations and principles from disparate fields: chemically and photochemically induced CO_2 fixation on carbon, acoustic physics and chemistry, structural characteristics of biochar, and solvent-induced swelling of carbonaceous materials. Each of these strands will be described below. The relevant hypotheses, tests of these hypotheses, and technological implications are discussed in later sections.

Chemically and Photochemically Induced CO_2 Fixation on Carbon

At the outset of their efforts, Chen et al. (2014) sought new CO_2 fixation processes, such as the Kolbe-Schmitt reaction R1 below (Kolbe 1860; Schmitt 1885; Lindsey and Jeskey 1957) that could represent the initial steps for viable CO_2 utilization and capture.



(*R*1)

The reverse reaction of R1, i.e., the desorption of CO_2, has a desorption energy of 24–29 kJ per mole of CO_2 (Dewar et al. 1988; Bonneau-Gubelmann et al. 1996) which is within the range for the CO_2 desorption by amines that has been considered the most viable means of CO_2 capture and desorption. The hydroxyl groups can also be functionalized by amine through a linker such as sulfonic acid. Since the synthesis procedure is designed mainly for CO_2 capture (Brunelli et al. 2012) but not directly for CO_2 utilization or reuse, no detailed discussion is given here.

While reaction R1 might be considered for CO_2 capture, the resultant product is expected to have a lower heating value than the reactant phenol, so the reaction cannot be considered as a major CO_2 recycle route for fuel production. On the other hand, photochemical or photocatalytic CO_2 fixation, recently reviewed by Kumar et al. (2012) and by Izumi (2013), could add heating value through reductive photocarboxylation, in which the aromatic structures are also reduced by the addition of hydrogen. This was first accomplished by Tazuke et al. (1975, 1986) by Hg-lamp irradiation of a solution of an aromatic hydrocarbon and CO_2 in the presence of an electron donor (*N*,*N*-dimethylaniline, DMA) and a hydrogen atom donor (dimethylformamide, DMF). Instead of using a liquid solvent, Chateauneuf et al. (2002) used supercritical CO_2 in their reductive photocarboxylations. The reaction equilibrium favors carboxylated product under high CO_2 pressure. Nearly complete conversion of anthracene was observed at 35 °C and 2,000 psi, with DMA as the electron donor and 2-propanol as the hydrogen atom donor. About 57 % of the product was dihydrocarboxylic acid. This carboxylation reaction can be stated as

$$\begin{aligned} \mathrm{PAH} + h\nu \rightarrow \mathrm{PAH}^{*} + \mathrm{DMA} \rightarrow \mathrm{PAH}^{\bullet -} + \mathrm{CO_2} \\ \rightarrow \mathrm{PAH}^{\bullet} - \mathrm{CO_2}^{-} + \mathrm{iPrOH} \rightarrow \mathrm{H} - \mathrm{PAH} - \mathrm{CO_2}^{-} \end{aligned} \qquad \text{(R2)}$$

The key to the remarkably high conversion of anthracene rests on the role of the electron donor in forming the reaction intermediate $PAH^{\bullet -}$, a charged free radical, by electron transfer to the photochemically excited PAH*.

The thermal carboxylation of phenolic PAHs R1 and reductive photochemical carboxylation R2 of PAHs promoted the authors' interests in fixing CO_2 on naturally available carbonaceous materials. These CO_2 fixation reactions could serve as a major step for CO_2 capture and CO_2 utilization. Due to the reductive nature of the photochemical R2, the resultant product should have higher heating value than the reactant PAH, and thus the CO_2 is recycled to an energy source in a cradle-to-cradle carbon cycle. The process would be most attractive if the carbonaceous material were a renewable biomass, as will be described below.

Sonochemical and Sonophysical Effects

Acoustic cavitation consists of at least three distinct, successive stages: nucleation, bubble growth, and implosive collapse (Ince et al. 2001). During the collapse stage, the energy released is so extreme that trapped gases undergo molecular fragmentation, which is the underlying phenomenon in homogeneous sonochemistry. This collapse is accompanied by the emission of light, or sonoluminescence (SL) (Suslick and Flannigan 2008). Spectroscopic analyses of SL reveal that the temperature and pressure can reach 20,000 K and several thousand bar, respectively (Suslick and Flannigan 2008). Water splits during the bubble-collapse stage, and the formation of oxygen, hydroxyl, and peroxyl radicals is attractive for oxidizing organic waste in water and for the oxidative desulfurization of fuels (Mason 1990). Strongly reducing protons also form during water splitting.

Sonication has been widely adopted to enhance mixing and reduce mass transfer limitations in liquid/solid interactions. Ultrasound is also capable of leaching fine minerals such as K, Na, S, Cl, P, Mg, Ca, Fe, and Al, from porous carbonaceous materials (Ahmed et al. 2004). As a result of mineral leaching, the internal surface

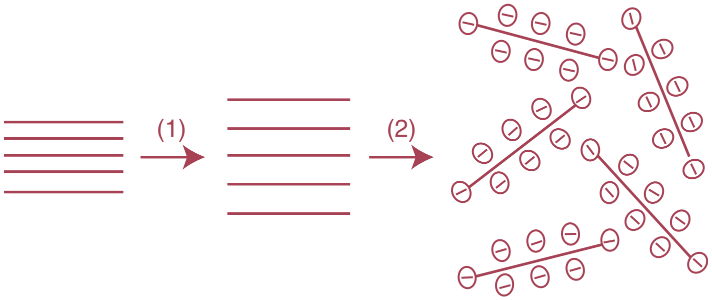


Fig. 11 Graphite can be oxidized to graphite oxide (Step 1), which can be exfoliated into single-layer platelets of graphene oxide (GO) by ultrasound (Step 2)

area of carbon increases, which, in turn, creates higher heating value and higher rates of fluid-surface reactions such as gasification, thus improving the efficiency of the carbon fuel.

Graphite can be oxidized to graphite oxide, producing intercalated hydroxyl and epoxide groups and a disrupted sp^2-bonded carbon network. Stankovich et al. (2006) demonstrated that graphite oxide in phenyl isocyanate is completely exfoliated by ultrasound (150 W) for 1 h, producing single-layer graphene oxide (GO); see Fig. 11. GO platelets are expected to be more reactive than graphitic oxide clusters due to the higher contact area in GO, a feature that will be discussed below. The interests in conducting ultrasound treatment on biochar (see below) were to induce positive benefits on the heating value of the biochar by inducing exfoliation of its graphite oxide, along with mineral removal and water splitting.

Structural Characteristics of Biochar

Chen et al. (2014) chose biochar (Fig. 12) for their ultrasonic and photocatalytic treatments for several structural reasons.

First, biomass-derived (Hammes and Schmidt 2009) and coal-derived (Franklin 1951) chars and petroleum coke (Yen et al. 1961) contain stacks of graphite oxide clusters with reactive carbon edges which could serve as binding sites for CO_2. Ultrasound-exfoliated GO will be even more reactive than the raw char. Second, biochar is more porous than coal-derived char and petroleum coke and is expected to have a higher rate of fluid/solid reactions. Third, the acidic ions of dissolved CO_2 in water can enhance the dissolution of metal ions in the biochar. Fourth, TiO_2 in char is a known semiconductor; it could serve as an electron donor in photocatalytic reductive fixation of aromatics and CO_2, while H_2O can serve as the desired hydrogen donor. Biochar is thus an attractive, renewable carbonaceous material to investigate the treatments proposed.

Solvent-Induced Swelling of Carbonaceous Materials

It has been demonstrated that coal, biomass, and coal-derived chars can be swelled by solvents, including CO_2 and H_2O, after breakage of the cross-links in their macromolecular structure (Gathitu et al. 2009; Mirzaeian and Hall 2006, 2007).

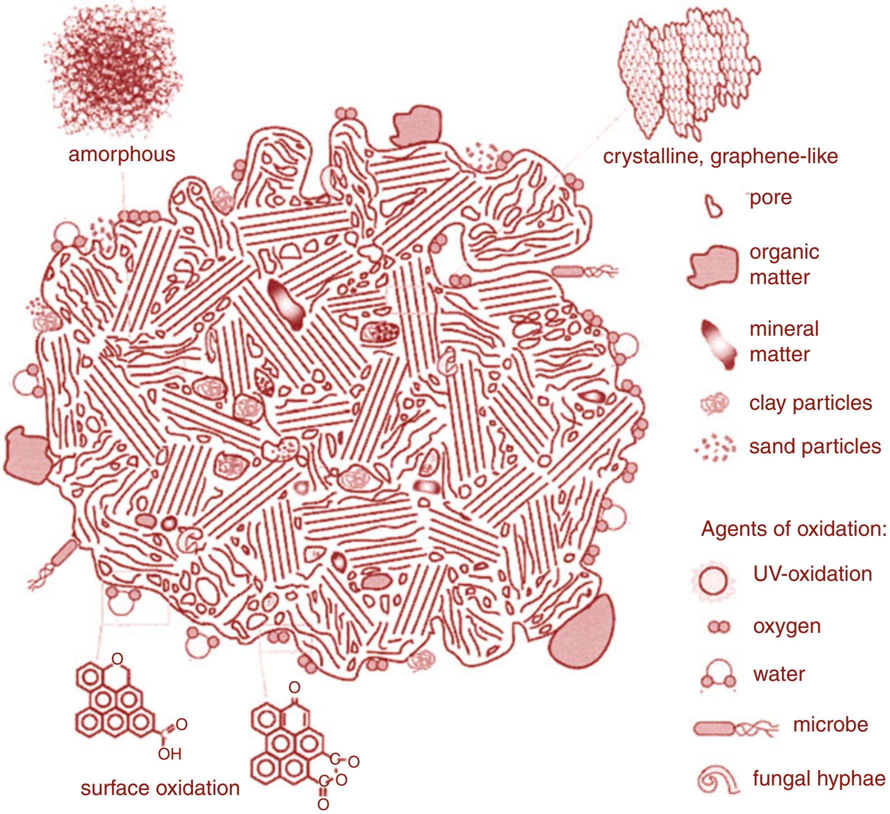


Fig. 12 Graphite oxide clusters form the backbone of the biochar structure (Hammes and Schmidt 2009)

Hydrogen bonds, especially those contributed by hydroxyl and carboxyl groups, have been considered by many as the major cross-links between aromatic clusters (Larsen and Gurevich 1996). The swelled carbonaceous materials have higher porosity and, therefore, higher gas/solid reactivity in processes such as gasification (Wall et al. 2002), which suggests the potential benefits of treating carbon with CO_2 and H_2O (see Fig. 13).

Tested Hypotheses and Technological Implications

Hypotheses

Consideration of the acoustic and photochemical interactions of CO_2 with PAHs as discussed above led Chen et al. (2014) to a set of hypotheses. To start with, they hypothesized that in a single reactor of biochar with CO_2 and H_2O, ultrasound would simultaneously induce the following synergistic chemical and physical processes:

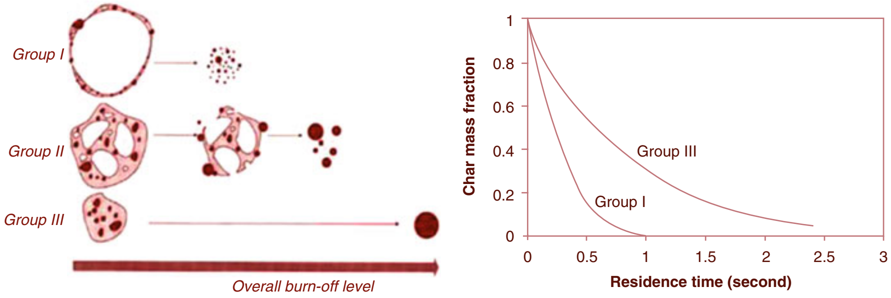


Fig. 13 Porous carbons (Group I particles) possess a higher gasification rate than non-porous carbons (Group III particles) (Wall et al. 2002) (Copyright © 2002 Elsevier Science Ltd)

graphite oxide exfoliation, water splitting, leaching of minerals, carboxylation, hydrogenation, and swelling. As a result, the treated biochar would have a higher heating value, higher reaction rates, and fewer operational and maintenance problems in the subsequent power-generation processes. Moreover, any CO_2 fixed reductively on biochar could be recycled in power/heat generation, thus creating a cradle-to-cradle carbon cycle.

Secondly, Chen et al. (2014) hypothesized that in a single contactor of biochar with CO_2 and H_2O and suitable donors, solar irradiation would induce the following synergistic chemical and physical processes simultaneously: carboxylation, hydrogenation, water splitting, and swelling. As a result, the treated biochar would have a higher heating value and higher reaction rates.

Results of Hypothesis Testing

Ultrasonic and photocatalytic treatments of a sorghum-derived biochar with CO_2 and H_2O at 60 °C resulted in the following observations (Chen et al. 2014):

- Remarkable increases in heating value (HV) for both treatments: 50 % increase for ultrasonic treatment and 20 % increase for photochemical treatment
- Large increases in internal surface area (up to 16-fold) for both types of treatment
- Significant leaching of minerals (60–98 % of Si, K, and Na) that are detrimental to power generation but beneficial to soil after they are captured in the leachate (water)
- Significant hydrogenation, calculated as 9 % additional hydrogen after ultrasonic treatment and 24 % additional hydrogen after photochemical treatment
- Carbon fixation, calculated as 13 % additional carbon after ultrasonic treatment and 16 % additional carbon after a simultaneous photochemical and ultrasonic treatment
- No significant change in oxygen content of the biochar

Further, Fourier transform infrared (FTIR) spectroscopy suggests that carboxylation occurs during photochemical treatments (Chen et al. 2014). The increase in internal surface area (by N_2-BET) during ultrasound treatment is lower than that from photochemical treatment, suggesting the possibilities of surrendering mesopore volume by exfoliated GO platelets during ultrasound treatment. The increases in heating value result from the combined processes of carbon fixation, mineral removal, and, in the photochemical treatment, hydrogenation. The observed increases in carbon and hydrogen content are attributable, in part, to carboxylation, water splitting, and hydrogenation; H_2O and CO_2 are the only H and C sources in the treatments. These observations are consistent with their hypotheses, although much work remains to optimize the conditions and elucidate the responsible mechanisms.

Implications for Sustainable Technologies

The results discussed above suggest new paradigms for the following technologies:

- Ultrasonic pretreatment of biochar (or other selected carbon feedstock) prior to gasification for simultaneously increasing thermal efficiency, decreasing CO_2 emissions, and reducing operational issues
- Photochemical pretreatment of biochar (or other selected carbon feedstock) prior to gasification, for increasing hydrogen content
- CO_2 capture by functionalized nanographene oxide (GO), phenolic compounds, and char-derived polycyclic compounds that have not been the focus of a systematic CO_2 capture study

Figure 14 illustrates the major streams and variables in a pretreatment process, ultrasonic or photochemical, before the char is fed into a gasifier and combustor.

Power generation with a pretreatment unit offers several sustainable benefits since it is expected to:

- Have higher thermal efficiency due to the 20–50 % higher heating value of the char
- Have a higher power-generation rate due to the more porous nature (16×) of the char

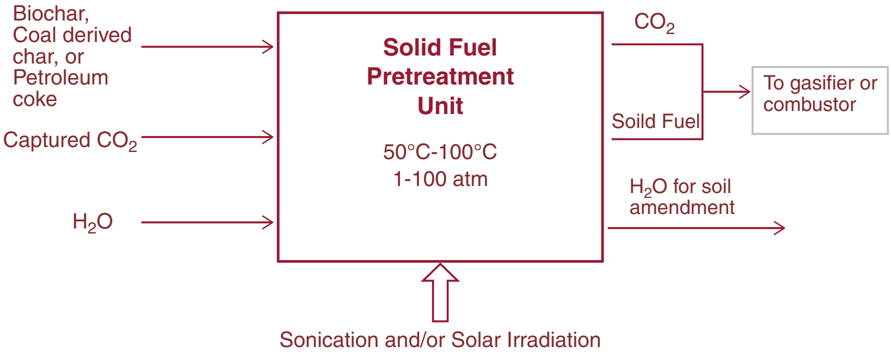


Fig. 14 Streams and variables of a pretreatment process

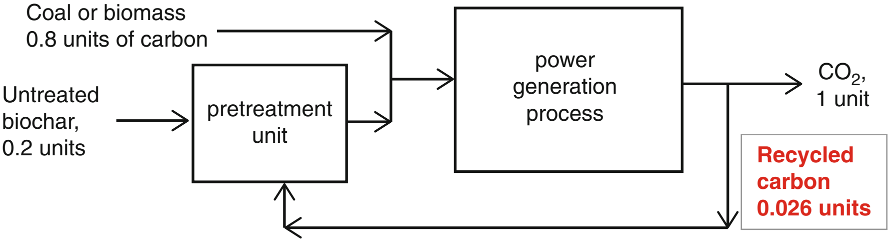


Fig. 15 The ultrasound-treatment unit recycles 2.6 % carbon in the feed, thus creating a cradle-to-cradle carbon cycle

- Exhibit fewer operational and maintenance issues such as fouling and slagging due to the removal of detrimental minerals K, Na, and Si (60–98 %)
- Offer a new CO_2 capture and utilization route since carbon in biochar picks up CO_2 in treatment
- Offer a waste (biochar) utilization route
- Return the soil nutrients, K and Na, in the leachate back into the soil

The benefits of such treatment on thermal efficiency and CO_2 recycling are not merely incremental. Assuming char's heating value increases by 50 % and 20 % of such increase is used by the pretreatment process, the energy output from char combustion will be 1.40 times that of the untreated char. For a co-generation power plant that uses char as only 20 % of its fuel source, with the rest from coal or biomass (see Fig. 15), the overall energy output will increase to 28 % (20 % × 1.40), resulting in a net gain of 8 % in the total output. This would be considered a significant improvement for power plants.

A carbon balance has been conducted for a co-gasification process where 20 % of carbon in the feed comes from biochar based on the 13 % increase in biochar's carbon content during treatment. Figure 15 illustrates the impact of introducing an ultrasonic biochar pretreatment unit on CO_2 emissions prior to biochar's injection into a gasifier. It suggests that the pretreatment unit renders it possible to recycle about 2.6 % of burned carbon fixed in the char. In a co-generation process shown in Fig. 15, the treatment results in 13 % carbon fixation on char and, therefore, 2.6 % carbon recycle – creating a cradle-to-cradle carbon cycle. The scale of this CO_2 uptake is noteworthy. The anthropogenic production of CO_2 is so high that the current total CO_2 utilization does not account for even 1 % of overall CO_2 emissions, and a single technology capable of using 1 % of its CO_2 emissions can be considered a major contribution (Styring et al. 2012).

The efficiency of ultrasound energy output was estimated by using a short treatment time of 3 min, which results in a 19 % increase in heating value (see Fig. 16). The energy consumed by the sonicator during the 3-min treatment was 0.65 kcal/g, which is less than the increase in heating value of the biochar, 0.91 kcal/g, during the 3-min treatment (from 4.83 to 5.74 kcal/g). Although the energy gain (the difference between these two quantities) seems to be limited, it is expected that a

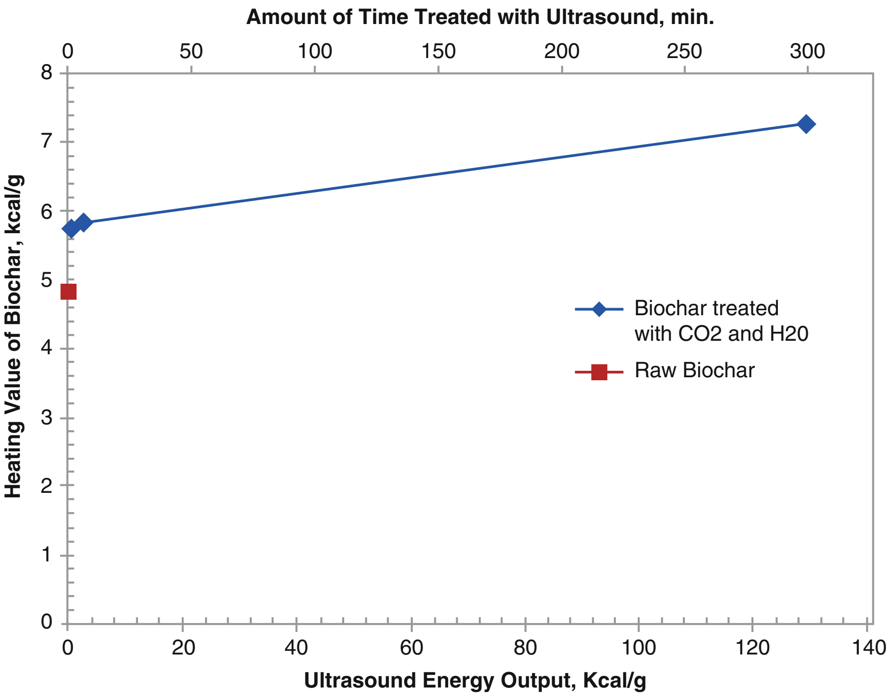


Fig. 16 Ultrasound power increases biochar's heating value. Biochar was treated with (CO_2 + H_2O) and 90-W ultrasound transducer (Chen et al. 2014) (© 2014 American Institute of Chemical Engineers)

majority of the ultrasound energy was dissipated in its surroundings through several modes in the initial apparatus, in which cavitation consumes only a small fraction of the energy. Ultrasound treatment induces energy gain mainly through the loss of mineral content and increases in hydrogen and carbon contents as a result of the treatment. These synergistic physical and chemical processes are believed to be the results of carboxylation, water splitting, hydrogenation, graphite oxide exfoliation, leaching, swelling, etc.

In practice, ultrasonic energy can be used much more efficiently by directly inserting a high-power ultrasonic horn into the solution in the treatment reactor. Thus, the test data indeed support the potential benefits in energy efficiency and the economics of installing a biochar pretreatment reactor prior to gasification or combustion. The pretreatment concept is technically viable. For instance, Mahamuni and Adewuyi (2010) reviewed the costs of various commercial advanced oxidation processes (AOPs) involving similar ultrasound devices for waste-water treatment, containing ideas for further reducing the costs for advanced ultrasound-treatment processes. Pretreatment is also viable because CO_2, H_2O, and residual heat are usually readily available in power plants.

Medical Applications

Biochar has many technological applications even though it is usually considered a by-product in biofuel production. As discussed above, biochar has been adopted in soil amendment and remediation of organic and inorganic contaminants in soil and water. Interests in biochar have intensified in the last decade mainly due to biochar's stability in sequestrating carbon in soil and its use for soil amendments. More recently, Nguyen and Pignatello (2013) evaluated biochar's ability in recovery and containment of marine oil spills. The study of ultrasonic and photochemical interactions of biochar with CO_2 and water (Chen et al. 2014) has provided foundations to explore novel technologies for CO_2 utilization and CO_2 capture.

On a separate front, biochar's medical applications have been scrutinized. We include only a short discussion for completeness since it is not directly related to mitigating climate change. Interestingly, most of these applications were developed with bamboo biochars in China, Japan, and Taiwan where bamboo is widespread. As stated by Zhong et al. (2010), bamboo can be harvested more than 20 times than trees on the same area. It can be harvested annually and regenerated without replanting. It sequestrates up to 12 t of CO_2 per hectare and generates 30 % more oxygen than trees during its growth.

Most of the medical applications of bamboo biochars are based on their abilities to generate far-infrared (FIR) radiations and negative ions (Lou et al. 2007). Bamboo biochar has 15.3–24.1 cmol/kg cation-exchange capacity. Bamboo biochar adsorbs nitrate-nitrogen more effectively than activated carbon (Mizuta et al. 2004). The negative ions generated by bamboo biochar remove the odors and refresh air.

Bamboo char has high electrical conductivity; chemically modified bamboo biochar has been used for developing lithium-sulfur batteries (Gu et al. 2015). Bamboo charcoal can generate a good amount of negatively charged ions that have the property of giving electrons to nearby matters, while charcoal adsorbs positive ions. Bamboo char dissipates electromagnetic (EM) waves emitted by devices such as television, personal computers, cell phones and microwave over, etc., by bouncing them, and the released EM waves can be absorbed by bamboo char due to its high electrical conductivity. The absorbed energy is then dissipated as far-infrared (FIR) emissions. Teraoka et al. (2004) reported that FIR emitted by bamboo biochar at wave lengths between 4 and 16 μm inhibits the growth of Henrietta Lacks (HeLa) cervical cancer cells in vitro at 37 °C. At ambient temperatures, ~25 °C, FIR inhibits tumor growth in mice (Nagasawa et al. 1999; Udagawa et al. 2000; Hamada et al. 2003). Ishibashi et al. (2008) found that the FIR-induced inhibitions of proliferations of cancer cells are controlled by basal expression level of heat shock protein 70A. Moreover, whole-body FIR irradiation at wave length between 7 and 12 μm is believed to improve human health and sleep by keeping the body warm, enhancing the blood circulation, and reducing blood pressure (Honda and Inoue 1988; Inoue and Kabaya 1989; Wang et al. 2006). A number of bamboo char-based food, beauty care, textile, sleepwear and health support products are commercially available.

Conclusions

Pyrolysis process converts biomass organic matter to biochar and increases the recalcitrance of carbon which becomes more resistant to chemical and/or biological decay. Due to its recalcitrant nature, biochar has long-term stability and its soil amendment utilization has been proposed as a way to store carbon in the soil for longer periods than if biomass was left to decay. The physical and chemical properties of biochar support soil health by altering the pH in acidic soils, increasing water retention capacity, and enhancing nutrient availability and microbial activity. Since biochar has high sorption capacity, its agricultural soil amendment will be helpful in reducing leaching of pesticides and pollutants in soil. Much more research is required to establish characterization methods and best management practices for biochar applications in various fields that can help to understand the mechanisms underlying biochar applications for soil amendment and environmental applications. In conclusion, based on the extensive research evidence, it is clear that biochar is indeed a viable soil amendment option for agricultural and environmental purposes worldwide.

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