

Waste to Wealth: Types of Raw Materials for Preparation of Biochar and Their Characteristics



Sarita Joshi, Sudipta Ramola, Bhupender Singh, Prathmesh Anerao, and Lal Singh

Abstract Biochar is carbonaceous material prepared from thermo-chemical conversion of biomass-based raw materials. These include agro-waste, forestry waste, animal manure, sewage sludge, and municipal waste. Different pyrolysis conditions and raw materials alter the properties of biochar such as pH, surface area, porosity, cation exchange capacity, nutrient availability, and water holding capacity. These physico-chemical properties further influence the functional properties of biochar for its different applications. In the present chapter, role of different raw materials used for the preparation of biochar, their effects on the properties, and characterization of biochar are discussed.

Keywords Biochar · Pyrolysis · Cation exchange capacity · Pore structure · Hydrothermal carbonization

1 Introduction

Industrialization and urbanization are the need of today's world which are very important for the sustenance of human beings on earth (Rajaeifar et al. 2019). The problems associated with rapid industrial development are air pollution especially the release of polyaromatic hydrocarbons (PAHs) (Kumar et al. 2021a), water pollution including surface water and groundwater (Bolan et al. 2022), generation of sludge and

S. Joshi

Department of Environmental Science, School of Vocational Studies and Applied Science, Gautam Buddha University, Greater Noida 201308, Uttar Pradesh, India

S. Ramola

College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310014, China

B. Singh

Central Research Facility, Indian Institute of Technology Delhi, Delhi 110016, India

P. Anerao · L. Singh (✉)

CSIR-National Environmental Engineering Research Institute (CSIR-NEERI), Nehru Marg, Nagpur 440020, Maharashtra, India

e-mail: lalsingh@neeri.res.in

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lignocellulosic waste (Kumar and Thakur 2018; Kumar et al. 2021c), soil pollution due to release of organic and inorganic pollutants (Zhou et al. 2022; Sarkar et al. 2021), carbon dioxide emissions leading to climate change (Kumar et al. 2018; Thakur et al. 2018). To remediate these pollutants, various techniques have been adopted recently to reduce the pollutants load and simultaneously generate value-added products (Bhujbal et al. 2022; Gupta et al. 2022; Maddalwar et al. 2021).

Lignocellulosic biomass is considered as one of the potential raw materials for generation of heat via direct burning, but simultaneously it produces gaseous pollutants such as greenhouse gases, trace gases, aerosols, particulate matter (PM_{2.5} and PM₁₀), polycyclic aromatic hydrocarbons (PAH), and non-methane hydrocarbon compounds (NMHCs) (Mishra et al. 2020; Prabha et al. 2021, Ramola et al. 2020a). Thermochemical conversion of biomass to biochar is one of the possible strategies to manage environmental waste such as lignocellulosic (Kumar et al. 2021b; Fuke et al. 2021; Ramola et al. 2020a), municipal waste (Mishra et al. 2021), and algal waste (Kumar et al. 2020a).

Biochar has large surface area, small bulk density, strong adsorption capacity, high stability, and diverse structural properties (Bolan et al. 2021; Lyu et al. 2016). Production of biochar is also environmentally and economically feasible (Kumar et al. 2020b; Ahmad et al. 2014; Ramola et al. 2021a). It is of multifaceted utility as has been used for adsorption and treatment of varied pollutants from water such as polyaromatic hydrocarbons (PAHs), volatile organic compounds (VOCs), dyes, pharmaceuticals, nutrients, pesticides, and trace metals (Kumar et al. 2020c; Yao et al. 2012; Wathukarage et al. 2019; Ramola et al. 2020b, 2021a, b).

The major raw materials for the production of biochar are biomass-based wastes. The choice of raw material for the preparation of biochar is also a key component in characterizing and classifying the biochar. Biomass is referred as an organic, complex biological material derived from living organisms. It is categorized as woody biomass and non-woody biomass (Tomczyk et al. 2020). The woody biomass comprises natural biomass residues obtained from forestry and trees that have high calorific value, low moisture content, high bulk density, and low ash. Non-woody biomass comprises mainly agricultural wastes, especially crop residue, animal wastes, industrial solid, and urban wastes that have high moisture content, low calorific value, high ash content, and low bulk density (Jafri et al. 2018). The moisture content in these raw materials is prominently responsible for the biochar formation. If the moisture content is more in raw material, then it not only reduces the calorific value but also requires more energy for pyrolysis and hence inhibits the biochar formation. Therefore, for production of efficient and economically viable biochar, the moisture content should be low (Tripathi et al. 2016).

Different types of wastes produced as agricultural by-products and crops residues including wood wastes are characterized as efficient raw material for the production of biochar (Lyu et al. 2020). The conversion of raw material to biochar is carried out by thermo-chemical processes which usually includes pyrolysis, gasification, and hydrothermal carbonization (Wang et al. 2018; Ramola et al. 2020a). The biomass contains different constituents like lignin, cellulose, and hemicellulose which is responsible for the different amount of biochar produced during pyrolysis

(Xie et al. 2015). The selection of raw material biomass affects the overall yield, content, and structure of biochar. Generally, for high biochar yield, a high lignin containing raw material is preferred. On comparing the yield of biochar from different raw materials, the animal-based biomass shows the best results because of its high inorganic components that prevent the loss of volatile substances which is responsible for the mesoporous structure within the biochar (Pan et al. 2020). The activation and adsorption properties of biochar depend on the elemental content present in it that forms the relation between nitrogen and double bond oxygen holding functional group of biochar on its surface (Rajapaksha et al. 2016). This elemental content changes at high pyrolysis temperature that results in increase of aromatic properties which mainly increase the carbon (C) content and decrease the polarity due to the decrease in the content of hydrogen (H) and oxygen (O). In general, biochar prepared using wood waste, sewage sludge and livestock manure have high C and O content in comparison to other raw materials (Pan et al. 2020).

2 Biochar Characterization

Characterization of biochar is done to understand the properties of biochar for its use in various purposes. In this context, on November 2015, International Biochar Initiative (IBI) has issued guidelines for defining biochar properties to be used in soil. Similarly, the European Biochar Foundation (EBC) has issued guidelines for production of biochar as agricultural amendment. These guidelines mostly focus on the production of biochar and its properties according to the need without compromising its utilities (Igalavithana et al. 2017). To evaluate various properties of biochar, generally five preferable characterization methods have been reported such as physico-chemical, surface, molecular, proximate, and ultimate analysis (Fig. 1).

3 Classification of Biochar

Unlike characterization, the classification of biochar is also related with the selection of biomass and its constituents. Classification can be carried out on a different basis, but majorly the carbon content is accepted prominently. On the basis of carbon content, the biochar is classified into three groups, i.e., biochar with high carbon content (BHC), biochar with medium carbon content (BMC), and biochar with low carbon content (BLC) (Hu et al. 2021).

BHC is produced from unprocessed raw materials like bamboo, wood, grass, and agricultural residues. BHC has carbon content $>75\%$ and higher ash content, which illustrate its impact on soil improvement and yield of plant biomass. Whereas the biochar having low ash content shows high porosity and increased carbon stability in the soil. It is suitable for the remediation of contaminated land and also as a supplement to animal feed (Hu et al. 2021). BMC is composed of mixture of unprocessed

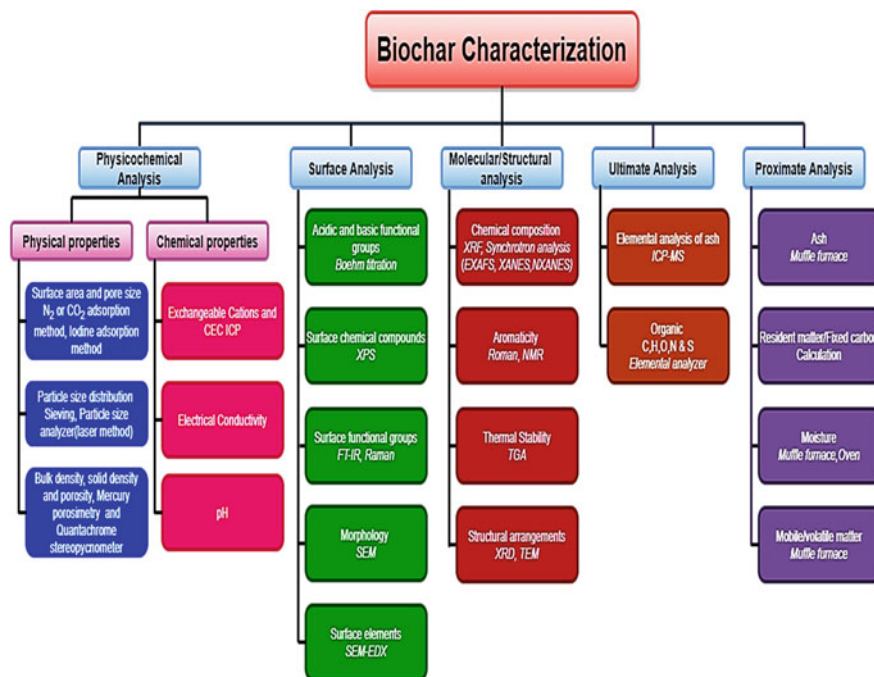


Fig. 1 Schematic representation of biochar characterization methods

raw materials (wood, bamboo, and mineral mixtures) and agricultural crops residues. This has moderate carbon content (approximately 55%) and used mainly as additive in livestock manure processing and bioenergy production (Hu et al. 2021). BLC is prepared by sludge, food waste, crop residue, manure, and wood mineral mixtures. This has < 30% of carbon content which can be used (post balancing the elemental concentration and adjustment of pH) as a major source of micro and macronutrients for agricultural crops and plants (Ghosh et al. 2016).

On the basis of requirement and availability of biomass, the biochar can be produced via various methods such as pyrolysis, hydrothermal carbonization, gasification, etc. (Kumar et al. 2020b, c; Ramola et al. 2020a). Due to an increase in pyrolysis temperature carbon graphitization takes place in the layers of biochar which is associated with deoxygenation and dehydration of biochar and it progressively results in the atomic H/C ratio and O/ C ratio of the biochar (Bogusz et al. 2015; Li et al. 2017). Different instruments are used for comprehensive structural and functional characterization of biochar which includes high-resolution transmission electron microscopy (HR-TEM) (Santhosh et al. 2020), X-ray diffraction (XRD) (Shaaban et al. 2013), Raman spectroscopy (Xu et al. 2020), energy-dispersive X-ray (EDX) spectroscopy (Ma et al. 2016), Fourier transform infrared spectroscopy (FTIR) (Singh et al. 2016), field-emission scanning electron microscopy (FE-SEM)

(Ma et al. 2016), inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Pourret and Houben 2018). BET is extremely helpful for the textural analysis of biochar (Zhu et al. 2018). Carbon nanostructure can be characterized by high-resolution transmission electron microscopy (HR-TEM) and XRD (Martin et al. 2019). The degree of weight gain and loss of the biomass raw material is determined by an analytical method popularly known as Differential thermal gravimetric analysis (DTGA) (El-Sayed and Mostafa 2014; Ramola et al. 2020b).

4 Raw Materials for the Preparation of Biochar

The type of raw material plays a vital role in the determination of the biochar properties (Amonette and Joseph 2009). Cellulose and hemicellulose contribute in producing bio-oil whereas, lignin contributes in producing high yield of biochar (Kan et al. 2016). Gymnosperms plants contain 47–50% carbon content whereas, angiosperm plants contain comparatively high cellulose to lignin ratio and they both are suitable as raw material for biochar (Pandey 1999). Residues from mill and forests are also proved to be potential raw materials for the production of biochar. Residues from agricultural lignocellulosic biomass are also used for biochar production for example sorghum (Kotaiah Naik et al. 2017), corn stover (Zhu et al. 2015), sugarcane bagasse, bamboo, rice husk (Ramola et al. 2014, 2021a, b), wheat straw (Junna et al. 2014), forest residues thinning (Puettmann et al. 2020), cardboard waste (Ghorbel et al. 2015), paper waste and paper mill sludge (Yoon et al. 2017), switchgrass (Koide et al. 2018), paper mill waste (Van Zwieten et al. 2010), logging residues (Campbell et al. 2018), municipal solid waste (Jayawardhana et al. 2016), wastewater organic sludge (Bolognesi et al. 2021), energy crops (Blanco-Canqui 2016), banana peduncle (Karim et al. 2014), and aquatic biomass (Mokrzycki et al. 2021).

4.1 *Effect of Type of Raw Material on Biochar Properties*

Plant biomass used as raw material for biochar preparation is composed of hemicellulose, cellulose, and lignin. The relative amount of these compounds in the raw biomass determines the extent of chemical, physical, and structural changes in the biochar during pyrolysis. Weight loss at low temperature is due to the evaporation of water. These components are gradually pyrolyzed with the increase of temperature. The major decomposition process occurs between 200 and 500 °C. Hemicelluloses degradation happens in the low temperature range from 200 to 260 °C, whereas cellulose degradation occurs between 240 and 350 °C. Lignin is much more recalcitrant (degradation between 250 to 500 °C) than hemicellulose and cellulose during pyrolysis (Lehmann and Joseph 2015; Fan et al. 2017; Wani et al. 2021). It has been reported in most of the studies that the biochar derived from herbaceous biomass for example grass, corn stover, sugar bagasse, hydrophytic weeds, and wheat straws

showed appreciably high content of inorganic elements than the biochar obtained from woody biomass (Bakshi et al. 2020). The biochar derived from microalgae was found to have highest fixed carbon, i.e., 24.8% followed by *Camellia oleifera* shells (21.95%) and pruned plum (21.07%) (Voca et al. 2016; Fan et al. 2017; Hossain et al. 2017).

4.1.1 Effect of Raw Material on Surface Area and Porosity

Similar to pyrolysis temperature, the properties of biochar are also equally affected by the composition of raw material. Ippolito et al. (2015) have described the selection of raw material as the most important influence on final biochar properties. Biochar prepared from lignin rich biomass is porous with large surface area, high aromatic organic components, and low ash content. Thermal cracking which contributes to surface area expansion occurs frequently in wood biochar as a result of unequal shrinkage of interior parts and exterior surfaces of the inflexible wood masses. During the pyrolysis, micro-molecule organic compounds are increasingly lost which create voids within the biochar matrix and consequently increases overall surface area and pore volume (Quicker and Weber 2016). Whereas, biochar from manures/biosolids has low surface area due to deformation, structural cracking, or micropore blockage (Ahmad et al. 2014), along with less distinct porous structures in the raw material itself as compared to wood-based biochar (Ippolito et al. 2015). The herbaceous raw material contains high percentage of silica components that often produce porous biochar with high ash composition. Animal manures as starting raw material are not very porous but it is shown that their porosity improves through pyrolysis (Yavari et al. 2015).

In general, for biochar production, a biomass with high lignin content yields macroporous structure, whereas biomass with high cellulose content yield microporous structures (Li et al. 2017). Another, important factor that can further deteriorate the surface area and pore volume is prolonged pyrolysis time which can cause melting, shrinkage, and elemental realignment. This destruction may be more pronounced for softwood biomass, resulting in a reduced adsorption capacity (Yavari et al. 2015; Ramola et al. 2021a). Biochar also tends to show different surface functionalities in relevance with hydrophobicity and hydrophilicity in correspondence with basic and acidic environmental conditions. The biochar contains stable and unstable C composition which is also responsible for surface chemistry and the varied heterogenous nature of biochar (Batista et al. 2018).

Surface chemistry plays a very integral role in influencing the surface behaviour of biochar in different environments for example it shows hydrophilic functionalities in an acidic environment and hydrophobic functionalities in basic environment (Ebrahimzadeh Omran et al. 2020). The studies were done on pine wood biochar and rice husk biochar showed that adsorption of Pb by pinewood biochar showed effective adsorption than rice husk biochar (Liu and Zhang 2009). During pyrolysis the dehydration of the biochar takes place which simultaneously increases the pore space in the biochar. The pore size in biochar is highly variable and is classified as

nanopore, micropore, and macropore, i.e., <0.9, <2 nm, >50 nm, respectively (Li et al. 2017). The preparation of biochar is the most important factor, as the activation process (chemical and physical activation process) used during biochar formation enhances the surface area and porosity of the biochar (Kim et al. 2012; Ramola et al. 2021a).

4.1.2 Effect of Raw Material on Cation Exchange Capacity and pH

In comparison to woody biomass, the biochar prepared from non-woody biomass such as crop waste, grasses, and manures has more CEC and pH. During pyrolysis, formation of oxygenated surface and inorganic functional groups take place, which increases the CEC (Briggs et al. 2012). The treatment of soil with woodchip biochar results in higher saturated hydraulic conductivities than manure-based biochar (Zhu et al. 2015).

The biochemical composition and structure of seaweeds are significantly different from lingo-cellulosic biomass. The seaweed-derived biochar is generally characterized by high yield, nutrient content, and CEC but relatively low organic carbon content and surface area (Roberts et al. 2015). It has been now well-established fact that the O/C ratio is directly proportional to the CEC value of the biochar (Huff et al. 2018). The highest cation exchange capacity is reported in the biochar produced at low pyrolysis temperature. The average obtained CEC at the pH range from 1.5 to 7.5 at 250 °C for grass, oak, and pine is reported to be 51.9 ± 15.3 mol C/kg. Pyrolysis done at 600 °C gives the CEC value in the range of 21.0 ± 17.2 mol C/kg (Mukherjee et al. 2011; Zhou et al. 2018).

The biochar produced from hydrothermal carbonization process leads to the production of organic acids and hence, results in the decrease of pH of the hydro chars (acidic hydro chars) (Quicker and Weber 2016). After pyrolysis, the ash content is increased significantly this results in increase in pH which get enhanced with the increase in degree of carbonization process (Ippolito et al. 2015). The studies done on spelt, nut shells, sewage sludge, grass, miscanthus, manure, and bamboo biochar had pH in the range of 10–12. The pH can also be increased by increasing the residence time for the first 5–10 min of hydrothermal carbonization (Conti et al. 2014).

4.1.3 Effect of Raw Material on Nutrients of Biochar

In general, wood-based biochar contain more C and lower plant available nutrients, manure-based biochar contains less C and more plant available nutrients whereas grass-based biochar typically falls somewhere in between woody and manure biochar (Ippolito et al. 2015). Less than 0.002% of the total N, 2.2% of the total P and 17% of the total K present would be supplied by hardwood biochar, whereas the biochar from

soft wood can supply 27% and 6% of the total P and K present (Dieguez-Alonso et al. 2018; Ippolito et al. 2015). The biochar derived from the animal materials has high amount of trace elements such as magnesium, potassium, calcium, and phosphorus than the biochar derived from plant materials. The comparative studies between wheat straw and pig manure biochar showed that biochar derived from pig manure contains calcium and magnesium in considerable amounts whereas, the biochar derived from wheat straw did not contain these elements in a mentionable amount when elemental studies were done by Xu et al. (2014).

5 Conclusion

As there is a tremendous increase in urbanization and industrialization, huge quantity of solid waste is generated that causes threat to human health as well as environment. In India, about 75–80% of the municipal waste gets collected and out of this only 22–28% is processed and treated whereas the remaining waste is disposed off indiscriminately at dump yards. It is projected that by the year 2031, the MSW generation shall increase to 165 million tonnes and to 436 million tonnes by 2050. One most prominent solution to this increasing problem is to convert the solid waste in biochar. Different raw materials and pyrolysis conditions affect the chemical and physical properties of biochar along with their bulk properties. The increase in the pyrolysis temperature results in the increase in surface area, elemental content, pore size, carbon mass fraction, micropore volume, carbon stability, and fixed carbon. Maximum efficiency can be obtained by optimizing activation of biochar and its properties. Standard characterization techniques can also be used for more insights into the properties of biochar. Some specific points also need to be addressed for example the combined modification methods for different biochar, the determination of the stability of different biochar produced from different raw materials, and final fate of biochar in the environment.

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