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Influence of Process Parameters on Synthesis of Biochar by Pyrolysis of Biomass: An Alternative Source of Energy

Krishna Yadav and Sheeja Jagadevan

Abstract

Organic matter derived from plants and animals are known as biomass. It has a great potential to be used as an alternate source of energy by employing thermochemical conversion techniques. Among the available techniques, pyrolysis is considered to be the most efficient technique used for the conversion of biomass-based waste into value-added solid, liquid and gaseous products through heating in an oxygen-limited environment. Biochar (solid fuel) is a carbonaceous material and has multiple applications in various fields such as soil health, climate stability, water resource, energy efficiency and conservation. The yield of biochar depends on organic constituents of biomass and the pyrolytic process parameters such as temperature, time, heating rate, purging gas, particle size, catalyst, flow rate, pressure and types of pyrolysis reactors. Suitable conditions for biochar production were observed to be slow pyrolysis, low carrier gas flow rate, acid-catalysed biomass or biomass mixed with some inorganic salts, low heating rate, large particle size, high pressure, longer residence time, low temperature, feedstocks with high lignin content and pyrolysis reactors with lower bed height. Thermal conversion of biomass could be a possible sustainable alternative to provide economically viable, clean and eco-friendly solid fuel.

Keywords: biomass, biochar, process parameters, pyrolysis, solid fuel

1. Introduction

Biomass refers to organic materials derived from plants and animals and is one of the natural sources of renewable energy. Organic materials present in biomass are the most abundant bio-resource that plays a key role in carbon sequestration by capturing carbon dioxide from the atmosphere through the process of photosynthesis, thereby reducing the greenhouse gases (GHGs). Biomass has a direct effect on energy, environment and economy (3E) of any country [1]. In developing countries such as India, the contribution of biomass towards societal transformations and environment is immense as people are generally directly associated with different forms of biomass. These forms of biomass may vary from forestry, small plants, trees (woody plants), organic wastes, domestic wastes and agricultural wastes. Biomass can be employed as a renewable substitute of fossil fuels because it serves

as the precursor of fossil feedstock [2]. Biomass can produce all three types of fuel, namely, solid, liquid and gaseous fuel [3]. The characteristics of biomass-derived fuel depend on several biological and thermochemical processes, and the pathway for their conversion from biomass to bioenergy is illustrated in **Figure 1**.

Biological processes such as fermentation and anaerobic digestion and thermochemical processes such as gasification, pyrolysis and liquefaction greatly influence the fuel characteristics. Out of these processes, pyrolysis is considered as the most popular and suitable method due to its lower consumption of resources and higher energy recovery [4]. Pyrolysis of biomass is a complex process in which raw biomass undergoes thermochemical conversion under oxygen-limited conditions, resulting in different products (solid, liquid and gaseous). The reaction mechanism for pyrolysis process can be summarised in three successive steps as given below [5].

Step 1: Raw biomass \rightarrow moisture + unreactive residues

Step 2: Unreactive residues \rightarrow (volatile + gas)_I + primary biochar

Step 3: Primary biochar \rightarrow (volatile + gas)_{II} + secondary biochar

In the initial step, moisture is lost and the second step leads to the synthesis of primary biochar. The rate-determining final step which involves decomposition of primary biochar at very slow rate results in the production of carbon-rich solid residue, i.e., secondary biochar along with volatiles and gases. According to the International Biochar Initiative (<http://www.biochar-international.org/biochar>), biochar can be defined as ‘a solid material obtained from the carbonisation of biomass.’ The primary constituent of biochar is carbon, followed by hydrogen, oxygen, ash content and trace amounts of nitrogen and sulphur. The elemental compositions of biochar generally changes with the nature of feedstock and pyrolytic conditions such as carrier gas flow rate, catalyst, heating rate, pressure, reactor bed height, particle size, residence time and temperature [3, 6–9].

Owing to its intrinsic properties such as large surface area, porosity and surface functionality, biochar has wide application in several fields. It can be used as a precursor of activated carbon or can be used as an adsorbent for the removal of various contaminants of water and wastewater. Biochar can also be used for soil amendments and carbon sequestration, solvent recovery, vehicle exhaust emission control and separation and purification of air [1]. In addition, high heating value and low emissions make biochar as the most suitable substitute for solid fossil fuels. With advancement in technologies, the production of renewable energy has increased from 18% in 2006 to 29% in 2018 [3]. Most countries such as Australia, Finland, Germany, the United Kingdom and Turkey are reducing the generation

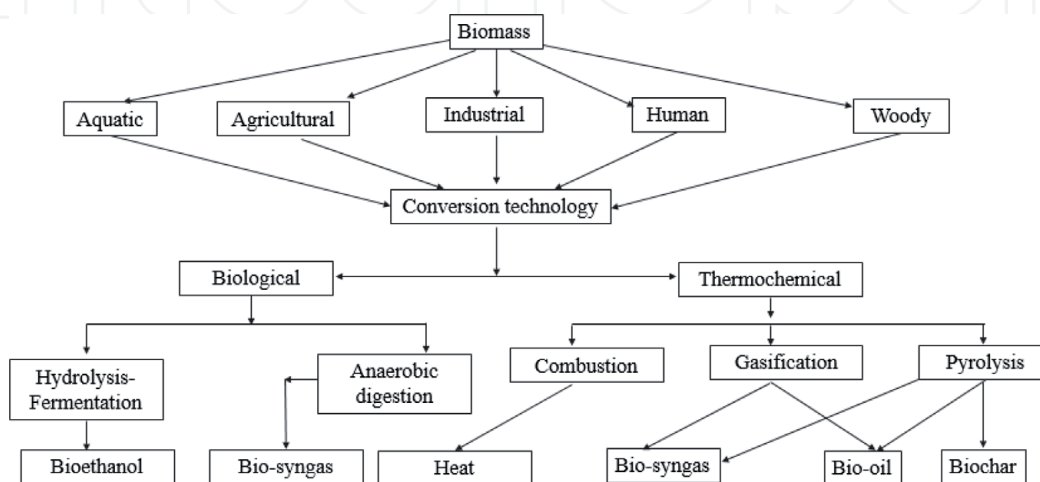


Figure 1.
Schematic pathway for conversion of biomass to bioenergy.

of electricity by thermal power plants and are encouraging generation of biomass-based electricity [10]. The primary focus of this book chapter is to delve deeper into the process parameters and know how these factors affect the characteristics of biochar produced through pyrolysis.

2. Source of biomass

Biomass can be classified based on their origin and constituents. The origin of biomass can be natural or anthropogenic (derived from processing of natural biomass), whereas the constituents of biomass may vary in terms of the polymeric structure of organic and inorganic molecules. Biomass may also be classified on the basis of their place of origin such as agricultural, animal waste, aquatic, human waste, industrial waste and woody biomass. Of these, woody biomass is abundantly found in nature, in forest area, and consists of bark, branch, chips of different trees, lumps and stem. Agricultural biomass consists of several crops, herbs and shrubs, and these biomasses ranked second in terms of abundance after woody biomass. Most countries around the world are dependent on woody and agricultural biomass for energy generation. Aquatic biomass consists of aquatic plants such as algae, blue green algae, fungi, phytoplanktons, zooplanktons and different kind of microbes. Biomass derived from humans, animal and industrial wastes includes manure from livestock; food waste generated from restaurants; waste generated from fruit industries; waste generated from paper, pulp and plastic industries and others. Energy is not only being generated and transformed into useful energy when such biomass is processed, but it also takes care of processing and handling of waste materials to a large extent.

3. Conversion techniques

It is very essential to select an appropriate technology for the extraction of energy from biomass to form a value-added product. The conversion of biomass may be achieved by two processes, namely, (i) biochemical process or (ii) thermochemical process. Biochemical and thermochemical processes make use of microorganisms and heat, respectively, to generate energy from biomass. Generation of value-added product is very less in quantity in the biochemical conversion processes. Nevertheless, this is a cost-effective and eco-friendly method and entails less production of toxic gases. Owing to the aforementioned limitations, thermochemical conversion process is a popular method and is further classified into combustion, gasification and pyrolysis.

3.1 Combustion

Combustion is considered as one of the most suitable and primitive technologies for conversion of biomass [11]. This conversion process involves a number of reactions which takes place during burning of biomass under oxygenated conditions at temperatures in the range of 800–1000°C. The biomass taken for the reaction should typically contain moisture <60% [11]. The contact between oxygen present in air and biomass determines the efficiency of the process. The efficiency can be further improved by pretreatment methods, which may enhance the total cost for the process. But the enhanced cost can be compensated by the improved process efficiency. As a result of combustion processes, various gaseous and solid products such as CO₂, H₂O, smoke, ash content and tar are produced.

3.2 Gasification

Gasification involves thermochemical conversion of carbonaceous materials into gaseous products with the help of various gaseous agents such as air, carbon dioxide, nitrogen, oxygen and mixture of gases. It is a partial oxidation occurring at elevated temperatures of 800–900°C. The primary goal of such processes is the production of gaseous products such as carbon monoxide, carbon dioxide, hydrogen and nitrogen. Solid (biochar and ash content) and liquid (bio-oil and tar) products are also produced. Biochar yield obtained during gasification is only 5–10% of raw biomass (dry basis), which is relatively lower than the yield obtained during fast pyrolysis. The composition and the heating value of the carbon and gaseous products depend upon the gaseous agents and feedstock employed. When air was employed as a gaseous medium, the syngas obtained had low heating value (4–7 MJ/Nm³), when compared to steam as a gaseous medium (heating value of syngas varied between 10 and 15 MJ/Nm³) [12]. The O/C ratio could be used as an indicator for determining the efficiency of the gasification process. Biomass having low O/C ratio will definitely have greater efficiency in the gasification process. In order to reduce the O/C ratio of raw feedstocks, a pretreatment step, namely, torrefaction is necessitated. Torrefaction is a thermochemical conversion process taking place at low temperature (250–280°C) and low heating rate. The product of torrefaction is brown/black colour, possessing little strength. Torrefaction enhances the energy density and hydrophobicity and reduces the weight and hydrophilic nature of biomass, thereby improving the calorific value and making the process commercially feasible for energy generation. Antal and Grønli [13] have reported that the wood yield and energy yield increased by 67–84 and ~77–90%, respectively. Similarly, retification of wood biomass also occurs at a lower range of temperature (~230–250°C), and the produced material is of reddish-brown or chocolate colour. Typically, these two processes (torrefaction and retification) demonstrated better resistance against biological attack and water loss to some extent [14].

3.3 Pyrolysis

Pyrolysis is thermal decomposition of biomass in the absence of oxygen or under oxygen-limited conditions. An oxygen-limited condition ensures that combustion of biomass does not take place. One of the primitive methods to obtain biochar is pyrolysis, which covers a wide range of thermal decomposition, thus making it very difficult to accurately define 'pyrolysis.' Based on literature survey, it could be understood that in the past scientists considered pyrolysis to be equivalent to carbonisation, wherein charcoal (solid) was the primary product. It is now well-known that pyrolysis is a process in which liquid (bio-oils) is the preferred product along with solid (char) and gas (syngas). These liquid products along with the solids depend on the operational conditions [15]. Generally, the process of pyrolysis occurs in two stages, i.e., primary stage and secondary stage. In the primary stage, dehydration, decarboxylation and dehydrogenation take place, whereas in secondary stages thermal cracking of high-molecular-weight compounds occurs, resulting in char and gaseous products such as CH₄, CO and CO₂ [3]. Based on the operational parameters, pyrolysis can be further subclassified into slow pyrolysis, fast pyrolysis, flash pyrolysis and intermediate pyrolysis.

3.3.1 Slow pyrolysis

Slow pyrolysis, also called as conventional pyrolysis, is an ancient technique employed for the conversion of biomass to charcoal. In this process, biomass is heated slowly (0.6–6.0°C/min) for longer residence times (5–30 min) at nearly

Process	Process temperature (°C)	Residence time	Solid product yield (mass %)	Carbon content of the solid product (mass %)	Carbon yield (mass carbon product/mass carbon feedstock)	References
Slow pyrolysis	~400	Min. to days	~30	95	~0.58	[16]
Fast pyrolysis	~500–1000	~1 s	12–26	74	0.2–0.26	[13, 17]
Gasification	~800	~10–20 s	~10	—	—	[16]
Flash carbonisation	~300–600	<30 min	37	~85	~0.65	[13]
Torrefaction	~290	10–60 min	61–84	51–55	0.67–0.85	[16]

Table 1.
Comparison of typical operational conditions and product properties associated with various processes for biochar production.

500°C. During slow pyrolysis, the production of solid (biochar) is found to be maximum when compared to liquid and gaseous products. The lower heating rate and higher vapour residence times enable the process to complete the secondary reactions. However, the vapours produced during the reactions of slow pyrolysis do not escape unlike fast pyrolysis [15].

3.3.2 Fast pyrolysis

Fast pyrolysis can be fundamentally differentiated from slow pyrolysis. Fast pyrolysis requires smaller-sized biomass (1–2 mm) having moisture content <10%, increased temperature (500–1000°C) and heating in very short span of time (1–5 s). Generally, fast pyrolysis favours liquid (bio-oil) production which contributes to 60–75% as compared to char (15–25%) and noncondensable gases (10–20%). The high temperature and minimum residence time during fast pyrolysis enable thermal cracking of biomass, resulting in char formation [15]. In addition, the high heating rate induces thermal conversion of raw biomass into liquid product before the formation of biochar [3].

Owing to its wide applicability, pyrolysis is considered as one of the most suitable techniques amongst existing technologies for conversion of biomass into value-added products. The peculiarity of this technique is its inherent flexibility, and more importantly it works based on desired products. Slow pyrolysis is recommended for higher biochar yield, whereas fast pyrolysis is the preferred choice for higher yield of bio-oil (Table 1). The characteristics associated with products of pyrolysis could be changed by varying the operational parameters. The higher cost required for pyrolysis could be compensated by setting up larger pyrolysis plants.

4. Effects of process parameters on yield of pyrolytic products

Pyrolysis is generally performed to enhance the yield of the pyrolytic products, and hence it is very essential to discuss the effect of process parameters on the production of biochar. Pyrolytic conditions can markedly affect the quantitative characteristics of the pyrolysed products.

4.1 Effect of carrier gas flow rate

In pyrolysis, the carrier gas flow rate influences the yield of products by affecting the generation of vapours during pyrolysis. If these vapours are not purged out, then they may take part in secondary reactions which definitely affects the composition and nature of pyrolysis products. There are several purging agents available such as nitrogen, argon, steam and carbon dioxide, but nitrogen is the most popular owing to its cost-effectiveness, easy availability and inert behaviour. Increase in flow rate of nitrogen from 1.2–4.5 to 50–400 mL/min led to a decrease in the biochar yield of 24.4–22.6 and 28.48–27.21%, respectively [18].

4.2 Effect of catalysts

The distribution of pyrolytic products can be affected by the presence of catalysts. Based on the catalytic effects, catalysts may be classified as primary and secondary catalysts. Primary catalysts are generally mixed prior to pyrolysis either in the dry mode or wet mode, while secondary catalysts are placed into the secondary chamber downstream to primary chamber where pyrolysis is taking place. Several catalysts such as alumina, Al-MCM-41, oxides of magnesium, oxides of nickel and ZSM-5 showed positive effects on the yield of biochar [19]. The yield of liquid (tar) and gaseous product reduces after mixing of inorganic salt to the biomass, whereas increase in the yield of solid products was observed [20]. Additionally, the yield of biochar was found to be increased after acid and base modification of biomass. Biomass catalysed with ZSM-5 demonstrated higher biochar yield than biomass modified with alumina oxide and sodium carbonate [21]. In contrary to this, some studies showed that ZSM-5 was responsible for the reduction in biochar yield, which was in accordance with the results obtained by Zhang et al. [22].

4.3 Effect of heating rate

The rate of change of heat during pyrolysis can affect the distribution of solid, liquid and gaseous products. Secondary stages of pyrolysis and thermal cracking are lacking at lower heating rates which favours the production of char. At higher heating rate, fragmentation of biomass takes place which is responsible for a higher yield of liquid and gaseous products. During pyrolysis of feedstocks such as leaves of *Ferula orientalis*, seed of safflower and leaves of *Carthamus tinctorius*, a decrement in the yield of biochar was observed as temperature was increased from 400 to 500°C along with a concurrent increase in the heating rate from 30 to 50°C/min [23, 24]. Production of bio-oil is also found to be affected by changing the heating rate. At increased heating rate from 500 to 700°C/min, 8% increment in the production of bio-oil from sawdust was observed, while there was no change observed when heating rate was increased from 700 to 1000°C/min [25]. Similar results were also observed from the biomass of cottonseed cake when it underwent pyrolysis, and heating rate was increased from 5 to 300°C/min; an increase (9%) in production of bio-oil was observed. However no change in yield of bio-oil was observed on further increase of heating rate from 300 to 700°C/min [26]. Interestingly, a reduction in the oxygen content was observed as a result of high heating rate during pyrolysis [27].

4.4 Effect of pressure

Pyrolysis carried out under increased pressure is also known to affect the yield of biochar. When the pressure inside the reactor is higher than the

atmospheric pressure, the yield of biochar gets enhanced [28]. High pressure is responsible for increasing the residence times due to which volatile matter is added to the carbonaceous material, thus resulting in high yield of biochar [29]. The volatile matter produced during pyrolysis is responsible for the generation of liquid and gaseous products as discussed in fast pyrolysis. This could be used for high biochar production either by increasing the pressure or decreasing the heating rate [29]. The concentration of carbon is also found to be enhanced by increasing pressure, which ultimately enhances the energy density of the produced biochar [13].

4.5 Effect of particle size

Biomass, being a poor conductor of heat, may create difficulties in the transfer of heat during pyrolysis. To negate this effect, particle size should be taken into consideration. As the particle size increases, the distance between the surface of biomass and the core end also increases which retards the flow of heat, resulting in high yield of solid biochar [30]. Longer-sized biomass particles were found to be responsible for reduction in the yield of liquid products due to occurrence of secondary reactions at temperatures higher than 527°C [31]. During pyrolysis, as the particle size increased from 17 to 20 mm, the water content also increased from 40 to 55% with a corresponding decrease in the carbon content of solid biochar from 78.5 to 75% [32].

The yield of biochar is also influenced by the shape of the particles. Slab-shaped and cylindrical-shaped biomass favours higher yield of biochar, whereas spherical shape favours lesser yield of biochar [33]. Some studies showed that the rate of heat and mass transfer was found to be slower with particles of spherical nature. In addition, the orientation of particles also plays an important role in explaining the pyrolytic behaviour of biomass. The permeability of flow along the particles was reported to be 10,000 times higher than that across the particles, although thermal conductivity along the particles was found to be two times higher than across the particles [34]. Heating of the perpendicular-oriented particles increased the yield of biochar and gaseous products but decreased the tar yield.

4.6 Effect of residence time

The residence time between volatile matter generated during pyrolysis and the hot biochar affects the yield of biochar. Longer residence time provides a greater chance for repolymerisation of the constituents of biomass, thereby enhancing the yield of biochar, while lower residence time decreases the yield of biochar. Popular wood and yellow brown coal biomass which underwent pyrolysis for longer residence times yielded higher biochar [35, 36]. Pyrolysis of sorghum bagasse at optimum temperatures of 525°C resulted in an increase in biochar and gaseous yield with corresponding decrease in bio-oil production (75–57%) on increasing the residence time from 0.2 to 0.9 s [37].

On contrary to the aforementioned results, some studies showed that residence time not only affects the biochar yield, but they also greatly influence the composition and quality of gaseous and liquid products. The porosity of biochar also increases due to higher residence time [38]. Fassinou et al. [39] showed an interactive effect of temperature and residence time, wherein increased temperature and residence times resulted in increase in the biochar yield, whereas lower temperature and increase in contact time reduced the yield of biochar. It is therefore difficult to make direct inferences regarding the relation between the production of biochar and the residence times.

4.7 Effect of temperature

Pyrolytic temperature is negatively correlated with the biochar yield. As the temperature increases, thermal cracking of high-molecular-weight hydrocarbons present in biomass increases which further increases the production of liquid and gaseous products, but the biochar yield decreases. Pyrolysis of biomass (hazelnut shell and sesame stalk) occurring at temperatures between 400 and 700°C resulted in decrease in yield of biochar by 10% for hazelnut shell and 17% for sesame stalk [40–42]. On increasing temperature from 365 to 606°C, a corresponding decrease in biochar yield from 31 to 17% was observed [33]. While at lower temperatures, the yield of biochar was found to be high, probably due to the partial decomposition of biomass.

The composition of biochar also gets affected by varying the temperature in which carbon content was found to be more than 85% (by dry wt.) in biochar synthesised at 500°C [32]. As temperature increases, the calorific value of produced biochar also increases [14]. The production of liquid during pyrolysis was found to be maximum as temperatures increased from 400 to 600°C. Additionally, above this range of temperature, the decomposition of vapours produced as a result of secondary reactions become more active which decreases the yield of liquid products [33]. The optimum yield of bio-oil in terms of calorific values and H/C ratio was achieved at pyrolytic temperature of 500°C [43]. However, these characteristics greatly depend on other parameters too. Pyrolysis occurring at temperatures >500°C increases the higher heating value of noncondensable gases such as carbon monoxide and methane [44].

4.8 Effect of compositions of biomass

The biomass constituents also affect the nature and composition of pyrolytic products. Several studies have reported biomass to be made up of cellulose, hemicellulose and lignin, which influence the nature of products of thermochemical processes. The production of biochar from lignin-based biomass is the result of breaking of weak bonds [45]. Some studies showed that the rate of lignin degradation depend upon the amount of lignin present in the respective biomass. The place of origin of biomass also greatly affects the production of char. Biomass obtained coniferous feedstocks are capable of producing more and stable biochar than deciduous lignin [46]. At lower temperatures, cellulose degradation leads to the formation of a more stable anhydrocellulose thereby resulting in a higher biochar yield. While at higher temperatures, cellulose is converted into more volatile compounds [47]. Furthermore, biomass rich in cellulose and hemicellulose are easily converted into a mixture of liquid products. However, lignin-rich biomass is responsible for the generation of solid product such as biochar [48]. As cellulose content in biomass increases, there is corresponding enhancement in the gaseous products, but yield of tar and char decreases. Additionally, structural differences in biomass content could lead to the compositional changes in pyrolytic products. The presence of moisture content in biomass will also affect the pyrolysis products. Studies suggested that biomass having moisture content more than 30% are not suitable for pyrolysis [1]. Biomass with low moisture content favours biochar production [49], while those loaded with high moisture content favours bio-oil production [50, 51].

4.9 Effect of reactor configuration

The thermal behaviour of various biomass has been studied with different types of pyrolysis reactors (**Figure 2**). The most exciting factor which influences the yield

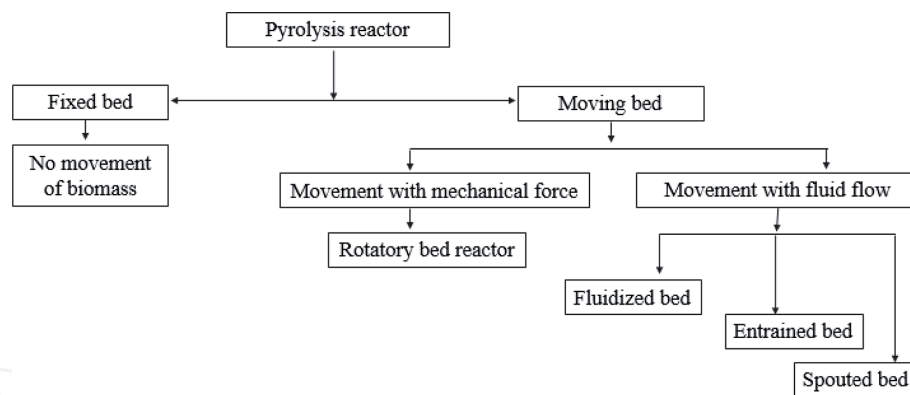


Figure 2.
Different types of pyrolysis reactor.

of pyrolytic product is the transfer of heat from the reactor to biomass particles. The transfer of heat could take place either through solid-solid mode or gas-solid mode. In the case of fixed bed reactors, solid-solid mode of heat transfer is favoured, while in the case of moving bed reactors, the dominating mode of heat transfer is a combination of conduction and convection [52].

The height of these bed reactors is also an important factor which influences the yield of pyrolytic products. The yield of biochar in both reactors remains the same, but the yield of liquid and gaseous products differs [53]. As the bed height of the reactor increases from 5 to 10 cm, reduction in the biochar yield was observed from 28.48 to 25.04% [54], while further increment in bed height results in an increase in biochar yield [22]. Higher bed height is responsible for longer vapour residence time, due to repolymerisation of biomass particles which increases the biochar yield, but an opposite effect was observed in the case of smaller bed height reactors due to less time available for repolymerisation of volatile matters.

5. Application of biochar

Biomass is a renewable substitute and precursor of fossil fuels which could be converted into different forms of valuable products. Out of these, biochar is considered as the most important product due to its intrinsic properties. Biochar has wide application in different fields such as soil, air, water and energy. In order to know the full potential of applications of biochar, it is imperative to conduct process optimization alongside minimal energy inputs and costs associated with wide applicability of the by-products at larger scales.

6. Summary and future prospects

Pyrolysis is a thermochemical conversion process in which biomass is converted into a valuable product, i.e., biochar. Synthesis of biochar depends on various process parameters such as carrier gas, catalyst, heating rate, particle size, pressure, flow rate, residence time, temperature, composition of feedstocks and types of pyrolysis reactors. Feedstocks having high cellulose content will favour tar formation, and biomass with high lignin content favours biochar formation. Suitable conditions for biochar production were observed to be slow pyrolysis, low carrier gas flow rate, acid-catalysed biomass or biomass mixed with some inorganic salts, low heating rate, large particle size, high pressure, longer residence time, low temperature, the nature of feedstocks and lower reactor bed height. Further studies need to

be done in order to incorporate the interactive effects of these process parameters by employing different statistical tools.

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Conflict of interest

There are no conflicts to declare.

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