REVIEW

Biomass pyrolysis technologies for value-added products: a state-of-the-art review

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Abstract

Biomass pyrolysis has been the focus of study by several researchers as a viable means of producing biofuels and other useful products. This paper gives a comprehensive, elaborate and updated review of pyrolysis technology as an efficient thermochemical route for biomass conversion. Pyrolysis products include pyrolytic gas, bio-oil, and solid biochar. Depending on the operating conditions, pyrolysis is usually classified as slow, intermediate, fast, and flash pyrolysis. The utilization of special catalysts can help facilitate pyrolytic gas production, while specific pretreatment processes can help facilitate bio-oil production. The efficiency of the pyrolysis process is affected by a number of factors such as temperature, heating rate, residence time, particle size, biomass type, and biomass pretreatment method. In this review, thermogravimetric analysis and kinetic modelling of biomass pyrolysis were also emphasized while the various constraints encountered during biomass pyrolysis have been highlighted and suggestions made to address them. More recently, more advanced experimental methods have been developed for biomass pyrolysis research, and these include Py-GC–MS/FID, TG-MS/TG-FTIR, in situ spectroscopy for reaction progress analysis, isotopic labelling, and intermediate product analysis techniques that enable the monitoring of the biomass devolatilization process as well as identification of the functional groups of the volatiles and monitoring of the changes in the functional groups on the surface of biomass in the course of pyrolysis. No doubt, biomass pyrolysis will continue to provide several benefits and serve as a sustainable means of producing biofuels, biochemicals, and other valuable products with far-reaching areas of applications.

Keywords Pyrolysis · Renewable energy · Bio-oil · Biochar · Kinetic modelling

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1 Introduction

The steady supply and availability of energy in a sustainable way will continue to be a major concern in the coming years considering the growing global population and the accompanying demand for energy. Renewable energy is rapidly gaining popularity as a viable substitute for conventional fuels because the use of conventional fossil-based fuels is unsustainable as a result of the increasing environmental consequences.

In particular, the production of liquid transportation fuels from biomass materials is attracting a lot of attention. This is because of the advantages accruing from utilizing biomass materials as feedstocks for fuel production (Bridgwater 2003). This option has the potential to reduce the over dependence on fossil-based sources of energy. Biomass-based energy has been projected to satisfy as much as 40% of global energy demand in the coming decades (Czernik and Bridgwater 2004).

Through suitable biomass conversion methods, surplus amounts of energy, chemicals, and transportation fuels can be obtained from biomass alongside the production of biochemicals and biomaterials (Bridgwater 2003; Czernik and Bridgwater 2004). Biochemical and thermochemical methods exist for the conversion of biomass materials into useful products. However, there is need for further investigation to engineer these conversion methods for higher efficiency (Demirbas 2001).

Numerous studies are available in the area of biomass conversion for the production of biofuels: bio-oil, biochar, and biogas (Demirbas 2001; McKendry 2002; Brownsort 2009; Laird et al. 2009; French and Czernik 2010; Bridgwater 2012a; Veses et al. 2015; Kan et al. 2016; Mohamed et al. 2016; Dhyani and Bhaskar 2017; Garrido et al. 2017; Wang et al. 2017; Bensidhom et al. 2018; He et al. 2018; Huang et al. 2018a; Kabir et al. 2018; Zhao et al. 2018). Biomass pyrolysis is an efficient conversion method offering several possibilities for the conversion of low-value, readily available biomass such as grasses, shells, stalks, bagasses, husks, waste woods, stalks, and sawdust into valuable products. However, further research needs to be carried out to overcome inherent technical and economic challenges in order for it to compete favourably with conventional fossil fuel-based techniques (Bridgwater 2004). For instance, the type and composition of biomass have been reported to have an influence on the pyrolysis process and products formed in a number of ways. In the first instance, the relative ratios of the organic and inorganic components of the biomass material vary from one biomass to the other in addition to depending on the growth and harvesting time (Dhyani and Bhaskar 2017). The general composition of the components (cellulose, hemicellulose, and lignin) of lignocellulosic biomass materials varies from one biomass to another, and this makes the possible interactions between the components to differ from one biomass to another, and this consequently affects the performance of the pyrolysis process and to some extent determine the characteristics of the products formed during pyrolysis (Wang et al. 2017). For example, cellulose and hemicellulose are mainly responsible for the formation of bio-oil while lignin is mainly responsible for the formation of biochar. Higher compositions of lignin in biomass result in more viscous bio-oils with lower moisture content (Kan et al. 2016). Thus, an understanding of lignocellulosic biomass materials becomes necessary if they are to be considered as ideal feedstocks for producing value-added products via pyrolysis.

2 Lignocellulosic biomass

A large portion of biomass consists of lignocellulose which is the non-edible part of the plant that is fibrous in nature. Unlike food crops, its use for energy purposes does not interfere with nor threaten the world's food supply (Basu 2010). Cellulose, hemicellulose, and lignin are the most important constituents of lignocellulose with little amounts of inorganic materials and plant extractives (McKendry 2002).

Cellulose accounts for the largest percentage in terms of the composition of lignocellulosic biomass and represents the most commonly found organic polymer in plant cell walls (Dhyani and Bhaskar 2017). Cellulose is made up of crystalline and amorphous fractions. Structurally, cellulose chains are bound together by hydrogen bonds to form cellulose fibrils which are surrounded by a three-dimensional lignin matrix which serves to inhibit hydrolysis of the cellulose by acids and enzymes (Fig. 1). In terms of composition, cellulose is composed of repeating units of D-glucose linked by β-1,4 glycosidic bonds (Fig. 2) (Hendriks and Zeeman 2009). The interaction between the hydroxyl groups in the six-carbon ring via hydrogen bonding bequeaths cellulose with its crystalline structure, high mechanical, and chemical stability (Lauria et al. 2015; Harmsen et al. 1184; Xu et al. 2016).
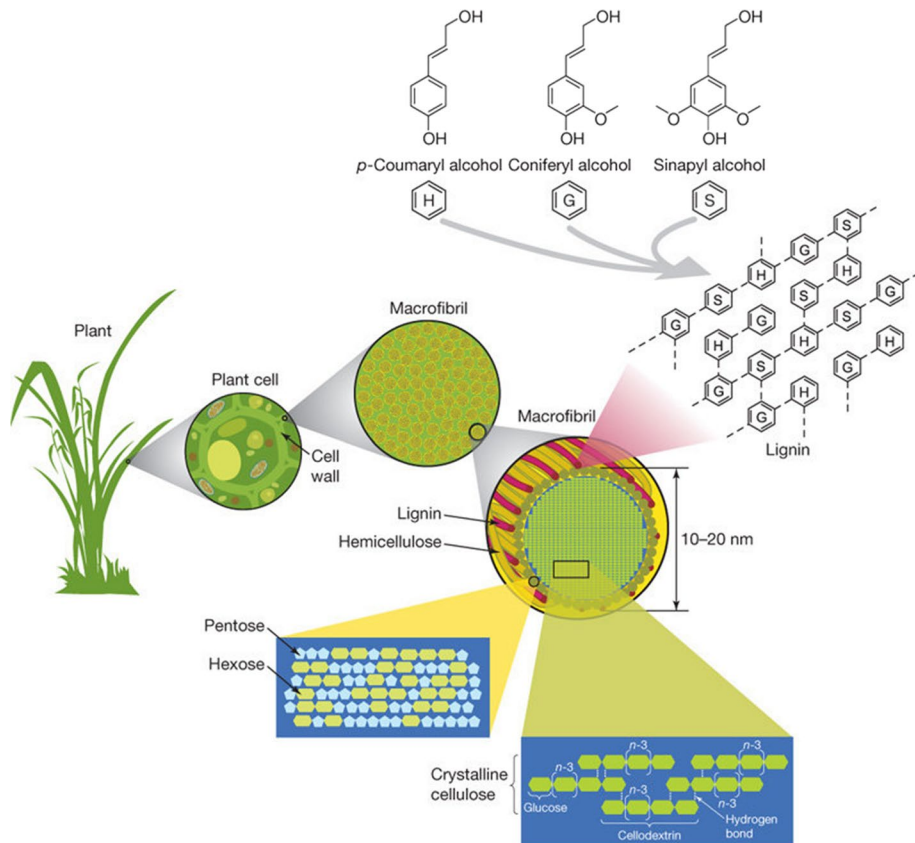
Fig. 1 Structure of lignocellulose (Lauria et al. 2015)

Fig. 2 Structural units of cellulose (**a**), hemicellulose (**b**), and lignin (**c**) (Xu et al. 2016)
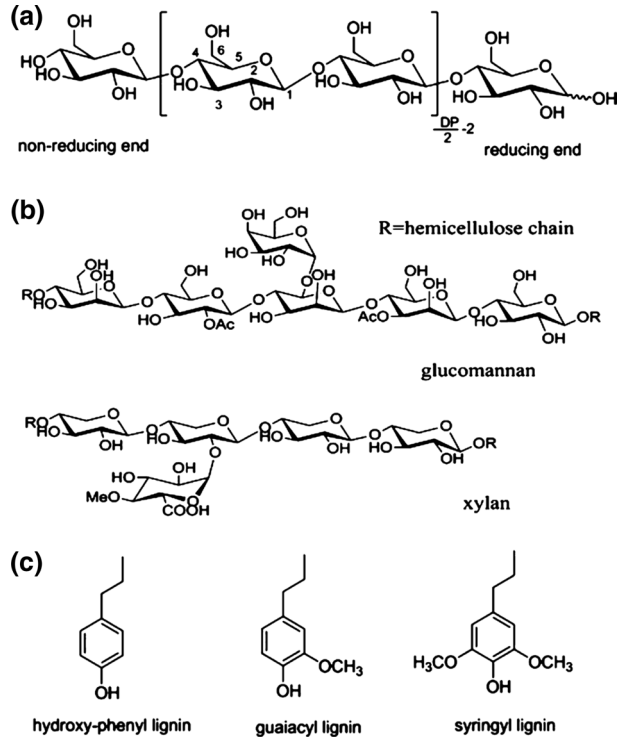
Hemicellulose is a complex polymeric material made up of units of five carbon sugars like xylose and arabinose; six carbon sugars like glucose, mannose, and galactose; and sugar acids (Fig. 2). The hemicellulose component of lignocellulose serves as the link between cellulose and lignin. Compared to cellulose, hemicellulose has lower molecular mass and contain chains of sugar units that are readily amenable to hydrolysis (Saha (2003)). Structurally, hemicellulose is amorphous and its mechanical and chemical stability is not comparable to that of cellulose (Laureano-Perez et al. (2005)). Xylan and glucomannan are examples of hemicelluloses in hard and soft woods. Acetylglucuronoxylan makes up about 30% of hemicelluloses in hardwoods, with xylose and galactose as its primary constituents. Glucomannan and galactoglucomannan on the other hand make up about 15% and less than 8%, respectively, of hemicelluloses in softwoods with glucose, mannose, and galactose as the primary constituents (Carrier et al. 2011).

The third most abundant component of lignocellulose after cellulose and hemicellulose is lignin. It is amorphous in nature and made up of three different types of substituted phenylpropane units. The units which include syringyl, guaiacyl, and p-hydroxylphenyl are bundled together in different forms (Carrier et al. 2011; Mohan et al. 2006). The presence of lignin in lignocellulose confers structural support, microbial and oxidative resistance, and impermeability. All of these and its water insolubility and optical inactivity makes lignin resistant to degradation (Dhyani and Bhaskar (2017); Hendriks and Zeeman 2009).

Aside the three major components, lignocellulosic biomass materials also contain extractives. These extractives comprise of saponins, phenolics, gums, essential oils,

starch, alkaloids, terpenes, mucilages, glycosides, waxes, resins, pectins, simple sugars, proteins, and fats (Dhyani and Bhaskar 2017). These extractives play vital roles in the plant by acting as a defence system which protects the plant from attacks by microbes and insects and the metabolism of the plant by acting as intermediates, while serving as a reserve for energy in the plant (Mohan et al. 2006; Kundu et al. 2018). Table 1 shows the approximate composition of some lignocellulosic biomass materials.

Several types of lignocellulosic materials have been used for pyrolysis. These materials can be grouped into woody biomass, agricultural wastes, and energy crops as shown in Table 1. Woody biomass include pine, redwood, spruce, birch, oak, beech, etc. Agricultural wastes materials that have been utilized for pyrolysis include corn stalk, rice straw, cotton stalks, cotton stalks, corn stover, almond shell, sorghum bagasse, etc. The use of agricultural waste materials as feedstock for pyrolysis is highly welcome as it does place less burden on the cultivation of land (Kundu et al. (2018)). Energy crops are crops that possess high energy values and examples include bamboo, sorghum, and grasses such as elephant grass, Bermuda grass, switch grass, etc. (Basu 2010). The use of these types of feedstock is also desirable because they can be cultivated on land that is otherwise unsuitable for agricultural purposes (Dhyani and Bhaskar 2017).

Table 1 Examples of lignocellulosic biomass for pyrolysis

Material type	Feedstock	Composition (%)			Reference
		Cellulose	Hemicellulose	Lignin	
Woody biomass	Pine	45.6	24.0	26.8	Ingemarsson et al.(1998)
	Douglas fir	45.0	19.2	30.0	Bok et al.(2014)
	Spruce	50.8	21.2	28	Velden et al.(2010)
	Beech	45.8	31.8	21.9	Blasi et al. (2000)
	Birch	25.7	40	15.7	Minkova et al.(2000)
	Oak	43.2	21.9	35.5	Yu et al.(2017)
Agricultural waste	Almond	29.0–31.1	28.0–38.0	27.7–35	Savova et al. (2001)
	Hazelnut	22.9	15.7	51.5	Koçkar et al.(2000)
	Millet husk	33.3	26.9	14	Raveendran et al. (1995)
	Corn stover	51.2	30.7	14.4	Agblevor et al. (1996)
	Corn stalk	22.8	43.0	156	Lanzetta and Blasi (1998)
	Cotton stalk	77	16	0	Pütün (2002)
	Coir pith	2806	15.3	31.2	Mohan et al. (2006)
	Sorghum bagasse	41	24	10	Cardoso et al.(2011)
	Banana waste	13.2	14.8	14	Sellin et al. (2016)
	Wheat straw	27.3–30	27.3–50	15–16.4	Lanzetta and Blasi (1998)
	Tea waste	30.2	19.9	40	Demirbaş (2001)
Energy crops	Bamboo	26–43	15–26	21–31	Posom et al. (2017)
	Canary reed grass	29.7	42.6	7.6	Bridgeman et al. (2008)
	Bermuda grass	25	35.7	6.4	Agblevor et al. (1996)
	Elephant grass	22	24	23.9	Agblevor and Besler (1996)
	Switch grass	45	31.4	12	Agblevor and Besler (1996)

3 Lignocellulosic biomass pretreatment

The composition of the particular lignocellulosic biomass used for pyrolysis has an effect on the pyrolysis products (Agblevor and Besler 1996). For instance, in bio-oil, levoglucosans and oligomeric anhydrosugars are very important precursors to essential products in the chemical and pharmaceutical industries. To ensure higher yields of these compounds, attention has to be focused on the pyrolysis reactions so that the depolymerization of cellulose is favoured over its fragmentation (Kan et al. 2016). Consequently, pretreatment of lignocellulosic biomass is carried out in order to selectively favour certain pyrolysis reactions that will result in the formation of desired products.

The goal of pretreatment is to make the cellulose and hemicellulose components of the biomass material readily assessable (Fig. 3). This is achieved by changing the structure of the lignocellulosic material so that the efficiency of the pyrolysis process can be increased.

Pretreatment strategies for lignocellulosic biomass can be categorized into physical, chemical, thermal, and biological pretreatment, and these are discussed in the following sections.

4 Physical pretreatment

Physical pretreatment methods include washing, crushing, densification, and extrusion. Washing of the biomass feedstock can remove most of the alkali present in the biomass since they are readily soluble in water. This is required if high oil yield is desired (Scott et al. 2000). Crushing is a common size reduction pretreatment operation which reduces the biomass material into smaller sizes. The crushed biomass is then sieved to obtain particle sizes suitable for the selected pyrolysis process. Better heat and mass transfer are achieved when smaller particle sizes are used due to increased biomass surface area per unit mass. Densification (pelletization) is used to compact biomass materials such as sawdust, wood chipping, straws into uniformly packed solids. This process alters the physical properties of the biomass as well as its energy content while simplifying the process of biomass handling, storage, and transportation (Wang et al. 2017). Extrusion on the other hand serves to increase the energy density of the biomass, reduce its moisture content, and produce pellets under high pressure with small cylindrical shapes (Kan et al. 2016).

Fig. 3 Effect of pretreatment on lignocellulosic biomass material (Scott et al. 2000)
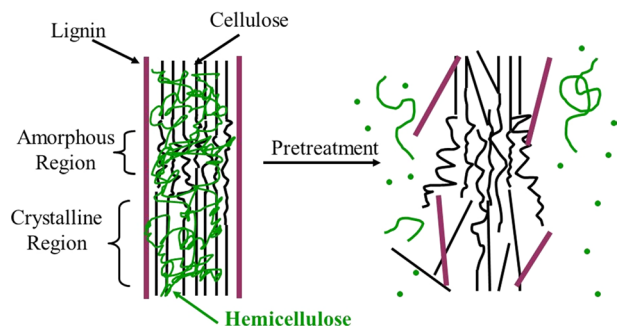
5 Chemical pretreatment

The amounts of inorganic minerals present in biomass affect the pyrolysis process and consequently its yield. Higher amounts of glucose can be obtained using chemical pretreatment through the removal of hemicellulose and lignin (Putro et al. 2016). Chemical pretreatment methods are discussed in the following sections.

5.1 Acid pretreatment

Acid pretreatment generally involves the use of inorganic acids (mineral acids) such as phosphoric acid (H_3PO_4), sulphuric acid (H_2SO_4), hydrochloric acid (HCl), nitric acid (HNO_3), etc. It can be further grouped into dilute acid pretreatment method, concentrated acid pretreatment, and organic acid pretreatment methods using acetic acid (CH_3COOH), propionic acid (CH_3CH_2COOH), formic acid (HCOOH), etc. With dilute acid, the reaction process is usually fast and the acid does not need to be recycled, whereas with concentrated acid, the hydrolysis reaction is slow requiring acid recovery due to its toxic and corrosive nature. However, very high sugar conversion rate is achieved using strong acid with a conversion rate higher than 90% for both cellulose and hemicelluloses (Xu et al. 2016). Pretreatments carried out using dilute acids have high hemicellulose sugar recovery which makes them suitable for use with biomass that have low amounts of lignin since little or no lignin is removed. Other advantages of concentrated acid hydrolysis include mild temperature requirement, no need for enzymes subsequent to the acid hydrolysis, and flexibility for different feedstocks (Amenaghawon et al. 2014). Acid pretreatment can be used to remove the mineral matter available in the biomass feedstock. Messina et al. (2017) carried out acid pretreatment on peanut shells before pyrolysis to determine its impact on the characteristics and yields of the products obtained. The acid pretreatment was performed using a solution of 10 wt% hydrochloric acid for 1 h at a temperature of 80 °C, after which distilled water was used in rinsing the de-mineralized shells until a pH value of 5.5 was reached before they were dried for 24 h at 60 °C temperature. Higher products yield for biochar, bio-oil, and biogas were obtained in comparison to that of the untreated pyrolyzed peanut shells. The pyrolyzed acid pretreated peanut shells yielded more bio-oil than those of untreated peanut shells in the same temperature range. The amount of ash contained in the biochar obtained via the pyrolysis of acid pretreated de-mineralized shells was very low compared to that of the biochar obtained from the pyrolysis of untreated peanut shells. Due to the lower ash content, biochars produced using acid pretreatment would minimize fouling, slagging, and corrosion when used in combustion engines. Garrido et al. (2017) carried out pretreatment of Phragmites australis (referred to as common reeds) prior to pyrolysis to examine the effects on the yield, selectivity, and properties of the products obtained. Acid hydrolysis (phosphoric acid was used) combined with torrefaction was used for the pretreatment which controlled the product yield and selectivity of the pyrolysis process by producing a feedstock rich in cellulose and low in inorganic content. The presence of cellulose in high amounts in biomass is of importance because it can cause selective pyrolysis to occur leading to the formation of bio-oil rich in chemical components derived from cellulose, while serving to enhance the quality of the bio-oil produced. With 4% phosphoric acid hydrolysis and torrefaction pretreatment, maximum yield and bio-oil quality was obtained by decreasing the inorganic content, production of high amounts of levoglucosenone, and hindering the formation of aldehyde, acid, and ketones. More so,

the biochar yield increased from 24.3% which was obtained from untreated phragmites to about 60%–70% after pretreatment with phosphoric acid. They also reported higher amount of fixed carbon as well as reduced inorganic matters in the biochar produced using acid pretreated biomass.

5.2 Alkaline pretreatment

Alkaline pretreatment mainly involves eliminating the lignin available in the biomass in order to improve the reactivity of the residual polysaccharides. The acetyl and other uronic acid substitutes present in the hemicellulose which restricts enzymes from accessing the surface of the cellulose and hemicellulose are also removed during alkaline pretreatment (Holtzapple et al. 1992). Alkaline pretreatment is mainly performed with dilute alkaline solutions (sodium hydroxide (NaOH), calcium hydroxide, $Ca(OH)_2$, ammonium hydroxide (NH_4OH), etc.) under operating conditions of 60 C–90 °C, 10–60 min. retention time, 1 MPa–3 MPa pressure, and liquid–solid ratio of 1%–2% w/w (Mohammed et al. 2017). Xu et al. (2016) reported that alkali-based pretreatment can enhance conversion of lignocellulosic biomass materials, and this was linked to the expansion of lignocelluloses resulting in increased internal area, lower crystalline structure and degree of polymerization, and the breakdown of chemical bonds within the carbohydrates and lignin and is capable of destroying the structure of the lignin. Pretreatment using dilute alkali makes the ensuing enzyme hydrolysis easier, while enhancing the reactions of the polysaccharides remaining.

5.3 Ammonia pretreatment

Ammonia pretreatment occurs at elevated temperatures, lowers the lignin content, decrystallizes the cellulose, and removes some hemicelluloses. Examples of ammonia pretreatment methods are ammonia fibre explosion (AFEX), ammonia recycle percolation (ARP), and soaking in aqueous ammonia (SAA). In AFEX, liquid ammonia is used in treating the biomass (Fig. 4). This technique is usually performed with a ratio of 1 kg–2 kg ammonia/kg dry biomass held for 30 min. at a temperature of 90 °C. Ammonia fibre explosion pretreatment method lowers the amount of lignin, eliminates portions of the hemicellulose, and breaks down the crystalline structure of the cellulose (Teymouri et al. 2005). According to (Sendich et al. 2008), more than 90% of the cellulose and hemicellulose can be converted at optimum conditions into valuable product using AFEX for different lignocellulose feedstocks.

More so, the highly volatile nature of ammonia makes it possible for the ammonia to be recovered and reused, followed by enzyme hydrolysis of the dried biomass remaining. AFEX pretreatment is suitable for herbaceous and agricultural residues. The liquid ammonia rapidly expands leading to the incomplete decrystallization of the cellulose and the physical disruption and swelling of the biomass fibres. AFEX makes it easier for the lignocelluloses biomass to be broken down through the process of deacetylation.

An important benefit of ammonia pretreatment methods is that inhibitors are not produced into the downstream biological processes making the use of wash water unnecessary. Aqueous ammonia is used for ammonia recycle percolation (ARP) pretreatment method. The biomass and aqueous ammonia are made to pass through a compact reactor bed having operating conditions of 140 °C–210 °C temperature, 5 mL/min percolation rate, for a period of 90 min. (Sun and Cheng 2002). Soaking in aqueous ammonia (SAA) pretreatment method was used by (Kim et al. 2008) for bioethanol production from barley hull.

Fig. 4 Schematic of an AFEX equipment set up (Balan et al. 2009)
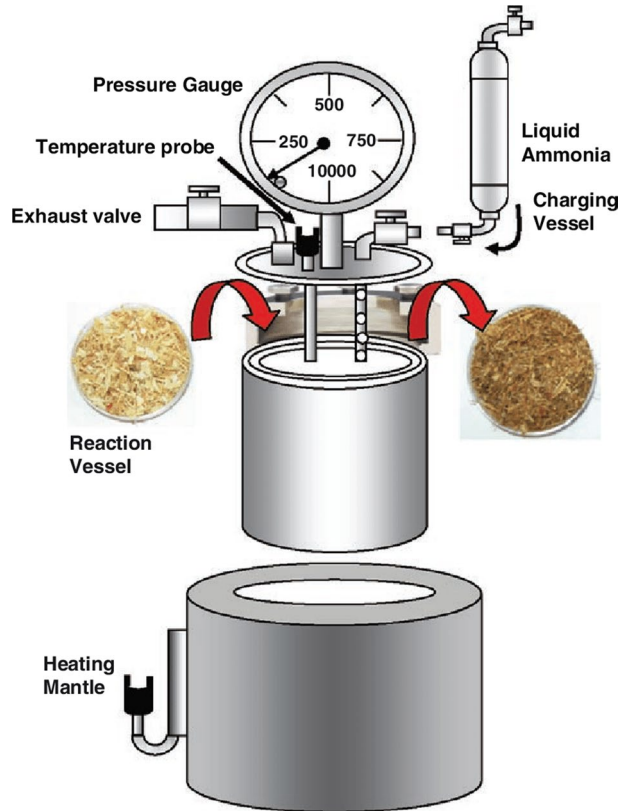
Lower temperatures of 40 °C–90 °C, with increased residence time, were employed for the preservation of the xylan and glucan present in the samples before they were fermented by the process of SSCF (simultaneous saccharification and co-fermentation).

5.4 Ionic liquid (IL) pretreatment

The use of ionic liquids (ILs) is a promising option for lignocellulosic biomass pretreatment. It is an evolving green chemical that can readily hydrolyze the cell walls of plants with the application of moderate heat (Putro et al. 2016). ILs are materials made of negative and positive ions only, which gives them their unique properties. ILs are referred to as green chemicals with unique properties which include high thermal stability, non-flammability, low volatility, efficient recyclability, and less toxicity. Their low vapour pressure makes them highly recoverable and reduces the risk of exposure thereby preventing loss of solvent due to evaporation (Negi and Pandey 2015). Examples of commonly used ionic liquids are 1,3-dialkylimidazolium, 1-ethyl-3-methylimidazolium acetate, 1-ethyl-3-methylimidazolium chloride, 1-ethyl-3-methylimidazolium diethylphosphate, etc. Studies recently carried out using ionic liquid pretreatment methods have been reported in the literature (Perez-Pimienta et al. 2015; Elgharbawy et al. 2016; Financie et al. 2016; Papa et al. 2017; Raj et al. 2018; Husson et al. 2018).

5.5 Organosolv pretreatment

Organosolv pretreatment, an abridged term for organic solvent pretreatment method, is commonly used for extracting lignin with high purity containing small amounts of phenolic and aliphatic hydroxyl from lignocelluloses materials with the aid of acidic or alkaline catalysts. Organosolv pretreatment method makes it possible for the main constituents of the biomass to be used as precursor materials for conversion into biofuels and the production of chemicals, while the isolated lignin can be used for other purposes (Putro et al. 2016).

6 Thermal pretreatment

Thermal pretreatment methods for biomass materials include drying, torrefaction, and steam explosion. Since most biomass materials contain varying degrees of water in them, drying can be used as a pretreatment process to reduce the moisture content in the biomass and also improve the efficiency of pyrolysis process in terms of energy consumption. Drying of the biomass before it is used for pyrolysis helps in preventing the feeding system from being clogged due to excess moisture in the feedstock and increases the energy content of the bio-oil formed (Cummer and Brown 2002). This drying process is referred to as torrefaction which requires the application of heat to the biomass in the absence of oxygen at a temperature range of 200 °C–300 oC. Energy densification occurs with the product obtained containing about 85% of its initial energy value and 70% of its original weight (Pach et al. 2002). The modified biomass (torrefied biomass) has several advantages over the untreated biomass feedstock such as easier feeding to the pyrolysis reactor, higher resistance to biological degradation, higher energy content, and reduction in size.

Steam explosion is frequently used in biomass pretreatment considering its low energy consumption and minimal use of chemicals. High-pressure saturated steam is brought in contact with the biomass in a reactor for a short interval ranging from seconds to a couple of minutes, after which the pressure is abruptly decreased creating an explosive decompression in the feedstock materials with the degradation of hemicelluloses and matrix interference of the lignin. According to Sun and Cheng (2002), steam explosion is dependent on factors such as temperature, residence time, moisture content, size of particle, and has the advantages of accommodating the use of larger particle size, avoidance of needless use of acid catalyst (unless when softwood is used), and its potential of being applied for industrial purposes. However, a drawback of steam explosion is that some degraded products formed during the process can hinder subsequent operations (García-Aparicio et al. 2006).

7 Biological pretreatment

In this process, microorganisms are used in degrading the biomass constituents. Microorganisms commonly used are white-rot fungi, soft-rot fungi, and brown-rot fungi. The white-rot fungi are generally the most important naturally occurring microorganism for the degradation of lignin from lignocellulosic materials due to their extracellular oxidase which helps to degrade lignin to into water (H_2O) and carbon dioxide (CO_2). Cellulose is mainly degraded by brown-rot fungi with cellulose and lignin degraded by soft- and white-rot fungi. The ability of white-rot fungi to degrade lignin is due to the presence of

laccase and peroxidases which act as enzymes during the degradation of lignin (Kumar et al. 2009). Biological pretreatment method although very slow, have low energy requirement, are safe and more environmentally friendly.

8 Biomass pyrolysis

Pyrolysis is a thermal decomposition process that involves the conversion of organic materials into solids rich in carbon (biochar), condensable liquids (bio-oil), and non-condensable volatiles (gases) via the application of heat in an oxygen-free environment (Demirbas and Gonenc 2002). Pyrolysis is an integral part of biomass thermochemical conversion processes. It can be an individual technique to form energy products as well as an initial process of gasification and combustion (Sadhukhan et al. 2008). Pyrolysis consists of multiple spontaneous reactions which are affected by several process variables such as reactor temperature, time of reaction, pyrolysis heating rate, particle size, pressure, biomass composition, and moisture content (Slopiecka et al. 2011; Vhathvarothai 2013). Through the process of pyrolysis, products rich in energy content can be obtained while serving as an efficient means of converting biomass to biofuels (Rasul and Jahirul 2012). Biomass pyrolysis process is an intricately linked process comprising of several spontaneous and continuous reactions when heat is applied in the absence of air. At temperature conditions of 350 °C–550 °C, the biomass constituents begin to degrade and this process continues to a temperature of about 800 °C. This results in the breakdown of carbon, hydrogen, and oxygen linkages in the biomass, thereby leading to the production of solid, liquid, and gaseous pyrolysis products. These reactions can be grouped into primary and secondary reactions. The pathway for the primary reaction consists of dehydration and charring reactions. Primary products alongside intermediates are formed during this process. The intermediates obtained during the primary reactions are subjected to secondary reactions which breakdown the intermediates. The secondary reaction pathway involves degradation and volatilization reactions (Akhtar and Amin 2012). During the process of pyrolysis, the primary constituents of the biomass do not degrade uniformly. The rate and extent of their degradation will depend on the pyrolysis process conditions. Hemicellulose is usually the first to undergo degradation, followed by cellulose, then lignin which decomposes under a wider range of temperature (Colantoni et al. 2010; Zhang et al. 2010).

The glycosidic bonds that bind the glucose units of cellulose are easily broken under conditions of high temperature (Anastasakis et al. 2011). Thus, cellulose is liable to degrade rapidly during the initial stages of pyrolysis resulting in a reduction in its degree of polymerization (DP). The formation of furans and levoglucosans is largely attributed to the breaking of the glycosidic bonds (Fig. 5). Mettler et al. (2012) determined the distribution of products formed during pyrolysis of cellulose and six glycosyl oligomers. Their findings revealed that almost the same product categories were obtained from starting materials. In another study, Zhou et al. (2014) examined the pyrolysis of cellulose, maltohexaose, cellobiose, and glucose at 500 °C in a micro pyrolyzer. Their findings showed that the yield of levoglucosans increased from 8.1 to 54.5% with increase in the degree of polymerization. Thus, the formation of levoglucosans was linked with the cleavage of the glycosidic bonds.

The thermal weight loss of cellulose has also been linked to the degree of polymerization. The thermogravimetric analysis results presented by Wang et al. (2016), revealed that the maximum weight loss occurred at a temperature which was above that of the microcrystalline cellulose. This observation was attributed by them to the higher molecular
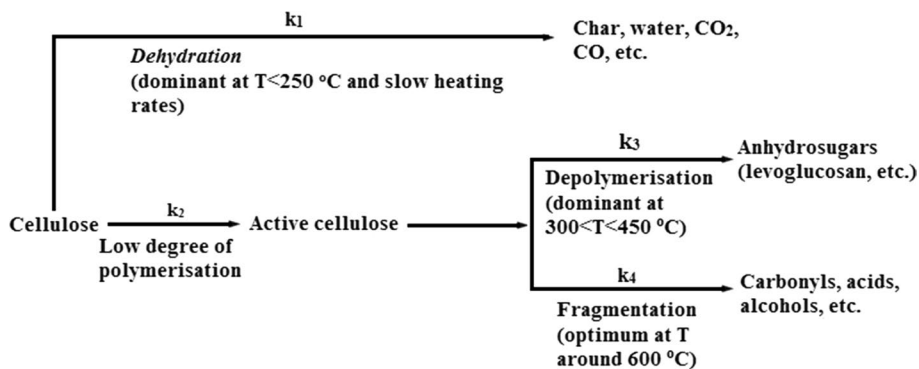
Fig. 5 Schematic of cellulose decomposition (Kan et al. 2016)

weight of the extracted cellulose. Kim et al. (2010) investigated the thermal degradation of some cellulose samples of varying levels of crystallinity. Their results revealed that the maximum temperature and initial thermal decomposition temperature obtained from differential thermal analysis and derivative thermogravimetric curves increased as the level of crystallinity increased.

The complex nature of the structure of hemicellulose could be the reason for the difference in pyrolysis behaviour when compared to simple monosaccharides. Werner et al. (2014) studied the thermal degradation behaviour of some hemicellulose samples such as xylan, xyloglucan, glucomannan, galactomannan, arabinogalactan, arabinoxylan, and β-glucan. They found that different hemicellulose species displayed different weight loss rate behaviour. They, however, noted that the glucan-based hemicellulose species were more thermally stable while the xylan-based ones were the least thermally stable.

Compared to cellulose and hemicellulose, lignin possesses an aromatic matrix bound together by various linkages with ether linkages being the most prevalent Wang et al. (2016). The ether linkages are generally easy to break to form phenolic compounds. This is in contrast with the carbon–carbon linkages which are difficult to break. Thus, the thermal decomposition of lignin presents a wider peak in its derivative thermogravimetric curves in comparison with cellulose and hemicellulose.

9 Types of pyrolysis

9.1 Slow pyrolysis

Slow pyrolysis usually occurs over a longer period of time using heating rates that are very slow, typically less than 10 °C/min to give char, gas, and liquids/bio-oil whose yields are dependent on the feedstock and process utilized. Pyrolysis reactors that accept bigger particle sizes (above 2 mm) can be referred to as a type of slow pyrolysis reactor (Garcia-Perez et al. 2010a). Traditional slow pyrolysis is mainly employed when char (charcoal) is the preferred product. This process is referred to as carbonization and is the oldest method used for the pyrolysis of biomass. A temperature of about 400 °C is used, and the residence times can be for as long as many days. During carbonization, the vapours are usually not condensed but can be channelled to supply heat during the carbonization process.

Torrefaction is another type of slow pyrolysis which uses moderate temperatures of about 225 °C–300 °C to enhance the heating properties and energy density of the biomass (Prins et al. 2006). Gaitán-Álvarez et al. (2018) in their study of torrefied woody biomass reported the best torrefaction temperatures to be 200 °C and 225 °C, respectively, for both light and medium torrefaction. However, at 250 °C, severe torrefaction was noticed which resulted in the degradation of the material.

The product obtained after torrefaction is a dark and dried solid material called torrefied biomass. In the course of the torrefaction process, the moisture content and volatiles in the biomass material are totally removed resulting in the formation of a material that is richer in energy value in comparison to the original material. An advantage of torrefaction is easier transportation of the biomass since the volume and weight of the biomass is reduced, making long haulages of the biomass to where they are needed easier while also reducing transportation cost. It is also possible to store the torrefied biomass for an extended period without it absorbing water due to their hydrophobic nature.

Conventional pyrolysis on the other hand gives all the three products of pyrolysis (biochar, bio-oil, and syngas) in reasonable amounts. It is typically performed at about 600 °C using a moderate heating rate. Balagurumurthy et al. (2015) investigated slow pyrolysis of rice straw within a temperature range of 300 °C–450 °C under nitrogen environment. The optimum temperature was reported as 400 °C for slow pyrolysis of the rice husk. Further investigation showed that the yield of bio-oil increased as the temperature increased from 300 to 400 °C. However, as the temperature was further increased, the yield of the bio-oil decreased. Al Arni (2018) also carried out slow pyrolysis on sugarcane bagasse. Heating rates of 45 °C/min–50 °C/min, with temperature range of 663 K–1253 K, and residence time of 60 min were used. Their results showed that more syngas was produced when the temperature was increased. Furthermore, the production of methane rather than hydrogen was favoured at the low temperature while hydrogen production was favoured at high temperature.

9.2 Intermediate pyrolysis

Intermediate pyrolysis is mainly used to obtain a combination of slow and fast pyrolysis products. Slow pyrolysis gives high solid yields with low liquid yields while fast pyrolysis gives high liquid yields with low solid yields. Pyrolysis conditions of 300 °C–600 °C temperature and 0.1 °C/min–10 °C/min heating rates are usually used. Within this low temperature range, desirable process reactions occur resulting in a wider variable range for the optimization of the process. Typical yields obtained from intermediate pyrolysis are 15%–25% (biochar), 40%–60% (bio-oil), and 20%–30% (gas) (Tripathi et al. 2016). The bio-oil produced from intermediate pyrolysis contains low amounts of tars and low viscosity unlike that obtained from fast pyrolysis. Varying particle sizes can be used in intermediate pyrolysis unlike fast pyrolysis where finely ground particles are required.

9.3 Fast pyrolysis

Fast pyrolysis involves the use of very high heating rates, very short residence time, and prompt vapour cooling to obtain bio-oil with high yields. Bio-oil is the primary product obtained from fast pyrolysis with 70%–80% product yields obtained (Demirbas and Gonenc 2002; Sukumar et al. 2015). In fast pyrolysis, biomass with small particle sizes is used in order to quickly attain maximum temperatures which prevent the occurrence of secondary

reactions. Nonetheless, biomass with bigger particle sizes can also be used through a process called ablative pyrolysis (Luo et al. 2017a).

During the fast pyrolysis process, rapid degradation of the biomass occurs with the formation of essentially vapours and aerosols, and little amounts of chars and gas. These vapours and aerosols condense after cooling to form a single-phase liquid with a darkish brown appearance having a calorific value which is roughly half of the value present in oils obtained from fossil sources. Biomass materials with little ash contents produce bio-oil with higher yields. It is important to note that for fast pyrolysis with focus on high liquid yield, small particle size of the biomass feedstock (usually less than 3 mm) is required to ensure very high heat transfer during the pyrolysis reaction since biomass generally have low thermal conductivity (Bridgwater 2012a). Secondary cracking reactions can be minimized using very short reaction time (less than 2 s) followed by speedy cooling of the hot vapours. Pyrolysis conditions of about 500 °C temperature are suitable for most biomass materials to obtain bio-oil with high yields. The need to develop advanced fast pyrolysis processes has gained wider recognition due to renewed interest in the area of bio-oil production from biomass. Fast pyrolysis offers a reliable and convenient means of converting low value biomass materials into bio-oil and numerous useful products. Fast pyrolysis processes are usually performed using bubbling fluidized bed or circulating fluidized bed reactors. Al Arni (2018) compared fast and slow pyrolysis of sugarcane bagasse. Heating rates of 120 K/min–127 K/min, residence time of 20 min., and temperature of 653 K–1053 K were used for the fast pyrolysis. They observed that as the temperature increased, the losses and solid yield also increased. However, the highest loss recorded was less than 15%, but this was nevertheless higher than what was recorded for the case of conventional pyrolysis. The loss was attributed to the longer residence time adopted.

9.4 Flash pyrolysis

Fast pyrolysis adopts high heating rates for the conversion of biomass to value-added products, mainly bio-oil. In contrasts with the other types of pyrolysis, flash pyrolysis utilizes even higher heating rates and the main products are gases and bio-oil. Flash pyrolysis is gaining popularity as a suitable medium for the production of liquid fuels from biomass using very high temperature and shorter reaction time with the sole aim of avoiding the re-polymerization of decomposed products (Akhtar and Amin 2012). With flash pyrolysis, it is possible to achieve above 75% bio-oil yields (Demirbas and Gonenc 2002). The flash pyrolysis process usually involves fast devolatilization of the biomass in an oxygen-deficient environment, occurring under high temperature (about 1000 °C) and high heating rates within a very short time. Madhu et al. (2016) reported bio-oil yield of about 48.2% at a temperature of 500 °C, 1 mm particle size, and 2 m^3/h sweep gas flow rate using flash pyrolysis. Technological limitations of flash pyrolysis process are poor thermal stability, high acidity and viscosity of the bio-oil, production of pyrolytic water, presence of char in the bio-oil, and the dissolution of alkali in the char (Cornelissen et al. 2008). Table 2 summarizes the major differences between slow, fast, and flash pyrolysis.

9.5 Hydro pyrolysis

Hydropyrolysis is an emerging technique used for the production of bio-oil with high quality from biomass. It is a pyrolysis process that takes place in an inert environment with hydrogen as the inert gas. The biomass material alongside hydrogen is introduced into the

Table 2 Different types of pyrolysis processes Boyt (2003)

Method	Temperature (°C)	Residence time	Heating rate (°C/s)	Major products
Conventional/slow pyrolysis	Medium–high 400–500	Long 5–30 min	Low 10	Gases, char, bio-oil (tar)
Fast pyrolysis	Medium–high 400–650	Short 0.5–2 s	High 100	Bio-oil (thinner), gases, char
Ultra-fast/flash pyrolysis	High 700–1000	Very short <0.5 s	Very high>500	Gases, bio-oil

reactor at above atmospheric pressures (about 5 MPa–20 MPa). The presence of hydrogen helps in hindering the formation of free radicals resulting in a reduction in the number of unsaturated hydrocarbons and an increase in the bio-oil quality produced (Dhyani and Bhaskar 2017). Hydropyrolysis can be referred to as a type of fast pyrolysis occurring in a hydrogen-based environment under high pressure due to its similar process conditions: temperature, heating rate, reaction time interval, with that of fast pyrolysis (Tripathi et al. 2016). Balagurumurthy et al. (2015) used hydropyrolysis for their study. Rice straw was pyrolysed in a hydrogen environment. The optimum temperature was reported to be 400 °C at a high pressure of 30 bars. The bio-oil obtained was more selective to phenolic compounds. However, the yield of the bio-oil obtained was lower compared to the bio-oil yield obtained at the same conditions using nitrogen environment.

10 Pyrolysis products

10.1 Biochar

Biochar is obtained after pyrolysis alongside amounts of ash and unconverted biomass. Biochar is the carbonaceous and porous solid product of the pyrolysis process. The process conditions under which the pyrolysis occurs determines its composition. The use of high temperature increases the carbon content in the biochar while the type of biomass used determines the amount of ash present in the char (Anca-Couce 2016). The decomposition of hemicelluloses and lignin under the application of heat causes the volatiles in the material to be lost, after which a solid-amorphous carbon structure known as biochar is produced. About 10%–35% yields of biochar can be obtained based on the type of biomass used and the process conditions under which the pyrolysis was performed, which consists mainly of carbon, hydrogen, and several inorganic matter. As pyrolysis occurs, the aromaticity of the material increases while the functional groups which have oxygen attached to them reduce, thus making the material hydrophobic and also increasing its energy content (Kloss et al. 2012). No sudden modification in the internal structure of the biochar occurs at low heating rates. At low heating rates, the structure is similar to that of the starting material which permits volatiles to be released due to its porous nature. However, as the temperature increases to 400 °C and above, distinct changes begin to occur in the morphology of the material and the surface area of the biochar increases. At temperatures between 600 and 800 °C, biochar with very high surface areas is obtained from woody biomass (Vhathvarothai 2013). The application of high heating rates causes the walls of the material to melt and the cellular structure of the material to be lost (Guerrero et al. 2005). Above 800 °C, the structural order of the material increases as the micropores within the material collapses, thereby decreasing the surface area of the biochar (Antal and Grønli 2003).

Properties of biochar can be determined by characterizing the biochar produced. Biochar is made up of carbon, hydrogen, nitrogen, oxygen, inorganics, with little or no sulphur. The particular composition of these elements as well as the physical, chemical, and mechanical properties of biochar vary from one feedstock to another (Kan et al. 2016). Some important properties of biochar are its porosity and pore size distribution, density, surface area, high reactivity, ease of storage, and surface functional groups (Laird et al. 2009). To produce biochars with high elemental carbon, biomass materials with low oxygen-to-carbon (O/C) and hydrogen-to-carbon (H/C) ratios are required (Nsamba et al. 2015). Biochars from soft and hard woods usually have low ash and intermediate ash contents, respectively,

while biochars obtained using corn/wheat stover produce high amounts of ash (Laird et al. 2009). Table 3 summarizes the characteristics of biochar obtained from different feedstock materials.

Biochar as it were can be used as solid fuel for heating and combustion purposes. The unique microscopic nature of the surface of the biochar produced during pyrolysis bequeaths it with special properties which can be taken advantage of for filtration as well as adsorption of organic and inorganic contaminants, particularly after activation of the chars with mineral acids, bases, and salts (Kan et al. 2016). Biochar can serve as raw material for the production of chemicals, carbon nanotubes, hydrogen rich gas, and soil additives (Laird et al. 2009; Wang and Lee 2018; Nathaniel et al. 2013). Biochar can be utilized as carbon sink for carbon sequestration thus mitigating the emissions of greenhouse gases. It can also be used as soil amendment to improve soil properties, increase soil nutrients, and soil fertility (Nsamba et al. 2015; Rondon et al. 2007). The increase in soil fertility as a result of biochar addition further increases the productivity of crops and also reduces the use of chemical fertilizers (Brownsort 2009). It also finds application in energy generation through direct combustion as substitute for coal to produce heat or co-fired in existing coal-fired plants (Roy and Dias 2017). Biochar can be used for combustion purposes. It has a heating value of about 18 MJ/kg with low sulphur content which makes it suitable for both domestic and industrial combustion processes. Biochar can suitably be used as adsorbent for the removal of odorants from air streams and as feedstock in the steel industry during the smelting of iron ores (Laird et al. 2009). The similar electrical properties of biochar to graphite make it suitable for potential use as a semi-metal. More so, emerging researches on the production and application of charcoal/biochar is a sign of wider and further interest

Table 3 Characteristics of representative biochar obtained from different feedstock materials (Dhyani and Bhaskar 2017; Wang and Lee 2018)

Feedstock material	Composition (%)					
	Carbon	Hydrogen	Nitrogen	Sulphur	Oxygen	Ash
Almond shells	87.90	2.5	1.10	0.50	7.80	2.80
Bamboo	76.67	1.69	0.57	0.28	5.81	8.70
Corn stover	56.70	1.89	0.75	0.22	–	5.00
Beech	73.60	3.40	0.20	–	6.30	–
Corn cobs	67.70	3.20	0.50	–	9.20	–
Iroko	68.40	3.40	0.20	–	15.30	–
Eucalyptus	79.50	2.77	0.17	0.27	–	5.00
Olive husk	78.68	2.83	0.98	0.032	12.88	–
Rice husk	51.52	2.14	0.46	0.021	9.77	–
Banana leaves	48.00	3.20	1.20	0.33	–	23.50
Spruce	72.90	3.30	0.20	–	12.80	–
Switch grass	87.23	2.71	1.33	0.00	8.73	–
Rice straw	67.89	1.50	1.12	0.28	8.96	–
Sugarcane	41.30	2.90	0.40	0.10	–	33.80
Grape seeds	84.70	1.30	1.60	0.30	12.10	13.10
Wheat straw	64.27	2.39	0.48	0.30	14.31	–
Miscanthus	44.30	5.73	0.46	–	49.51	8.79

in the applications and usage of biochar as solid fuels, adsorbents, soil conditioners, among others (Antal and Grønli 2003; Yaman 2004).

10.2 Pyrolysis gas

Pyrolysis gases consist of hydrogen (H_2), carbon monoxide (CO) (commonly referred to as syngas), carbon dioxide (CO_2), nitrogen (N_2), methane (CH_4), ethene (C_2H_4), ethane (C_2H_6), etc. The distribution of these gas constituents is dependent on the type of biomass used and the operating conditions under which the pyrolysis is performed. Varma and Mondal (2017) obtained gaseous products after pyrolyzing sugarcane bagasse at a temperature of 500 °C with the following composition: H_2 (5.7 mol %), CO_2 (36.8 mol%), CH_4 (11.9 mol%), and CO (45.6 mol%). At higher temperatures, the cracking of hydrocarbons produces hydrogen (H_2), while further breakdown of partly oxygenated compounds results in CO and CO_2 formation which signify that oxygen is present. The formation of C_2H_4, CH_4, C_2H_6 can be attributed to reforming and cracking reactions of tars and heavy hydrocarbons present in the vapour phase (He et al. 2010). Pyrolysis gas yield of about 35% can be obtained when slow pyrolysis is used. Higher gas yields can be achieved with flash pyrolysis at high temperatures (Kantarelis and Zabaniotou 2009). Al Arni (2018) obtained maximum gas yield of 41% using slow pyrolysis at a temperature of 1143 K. Imam and Capareda (2012) reported syngas yield of 26% at 600 °C from the pyrolysis of switch grass. In another study, Wang and Lee (2018) investigated the fast pyrolysis of Miscanthus in a fluidized bed reactor. They reported an increasing trend of pyrolysis gas yield with respect to pyrolysis temperature during the process and recorded a maximum gas yield of about 60% at a temperature of 550 °C.

The production of pyrolysis gas is mainly dependent on the pyrolysis temperature which also affects the pyrolysis process and quantity of product yields obtained. Increase in the pyrolysis temperature first causes the moisture content present in the biomass to be given off, followed by the devolatilization and decomposition of the biomass. This leads to the release of volatile matters and the formation of tars which pass through several reforming and cracking reactions (deoxygenation, decarbonylation, decarboxylation, dehydrogenetaion) to produce the gaseous products (Kantarelis and Zabaniotou 2009; Jahirul et al. 2012). Thus, more tar-to-pyrolysis gas conversion occurs as the temperature increases thereby increasing the product gas yield while the biochar and bio-oil yields decreases (Fegbemi et al. 2001; International Energy Agency (IEA). Pyrolysis Reactors. IEA Bioenergy Task (2020) Available online a https://task34.ieabioenergy.com/pyrolysis-react ors/ 2020). The presence of moisture in the biomass affects the transfer of heat during the pyrolysis process and also reduces the quantity of gas produced. The same observation was recorded by Hodgson et al. (2010) who investigated the impact of fertilizer application of the biomass characteristics of Miscanthus.

Pyrolysis gases can be used as supplementary energy source to the reactor during pyrolysis. The amount of hydrogen available in the pyrolysis gas can be increased with the introduction of catalysts. This hydrogen fuel can be further applied in heating and transportation operations (Chen et al. 2003a). Pyrolysis gases can also be used in combustion engines and gas turbines for the generation of power and as an alternative to cooking gas. This is because of its higher heating value which exceeds that of conventional gasification gas (Chen et al. 2003b). It is possible to retrofit available engines which are powered with diesel and petrol fuels from crude oil to run on gaseous fuels obtained from pyrolysis for transportation purposes, power generation, and heating operations.

10.3 Bio-oil

Bio-oil is the liquid product formed during pyrolysis. It is the main product of fast/flash pyrolysis of biomass with yields as high as 70%–80% (Meier and Faix 1999). It is basically a combination of about 80% polar organics and 20% water. Bio-oil consists of several compounds and different functional groups which include phenolic compounds, carboxylic acids, alcohols, hydroxyketones, esters, hydroxyaldehydes, sugars/anhydrosugars, lignin-derived oligomeric compounds, and furan/pyran ring derivatives (Patwardhan 2010). Bio-oil produced over an extended temperature interval and residence time of about 5 s are more suitable for use as liquid fuels even though a reduction in the yield may occur due to the secondary reactions of volatiles which occurs beyond 500 °C and the condensation reactions of the vapours taking place below 400 °C. When very short residence times are used, the depolymerization of the lignin content in the biomass is not completed as a result of inter-reactions and random bond formations of the lignin macromolecule. However, using longer residence time can give rise to secondary cracking of the primary products which significantly affects the properties of the bio-oil and the yield obtained (Bridgwater et al. 1999; Xiao and Yang 2013). Some oligomeric fractions of lignin can also be found in bio-oil in appreciable amounts, and they are usually characterized by high molecular weight (Zhang et al. 2006). The major components of bio-oil produced from some selected feedstock materials are summarized in Table 4.

On the other hand, the physicochemical properties that characterize bio-oil include oxygen content, moisture content, viscosity, acidity, and ash content as summarized in Table 5 (Kan et al. 2016). Bio-oil is characterized by high water content (15%–30%), and this is usually dependent on the type of biomass used and the operating conditions under which the pyrolysis was carried out (Patwardhan 2010). However, moisture content as high as 40–60% was reported by (Heo et al. 2010) for bio-oil produced via pyrolysis of furniture sawdust. Increase in moisture content of the bio-oil produced particularly from woody feedstock materials has been attributed to the occurrence of etherification and esterification reactions within the bio-oil components (Czernik et al. 1994). Bio-oil is also characterized by high oxygen content (35–40%), and this distinguishes it from other hydrocarbon fuels. Other properties include low pH value (<3), low stability, high acidity (which makes it corrosive), wide range of volatility distribution, and viscosity (35–1000 cP at 40 °C) (Patwardhan 2010). The high energy density of bio-oil potentially makes it suitable for use in many applications such as heat, power, transportation fuels, and chemicals (Fig. 6) (Brownsort 2009; Sadhukhan et al. 2008; Vhathvarothai 2013; Akhtar and Amin 2012; Colantoni et al. 2010).

Bio-oil can be used in boilers and combustion engines for heat and power generation. It can be co-fired with fossil fuel which leads to higher efficiency and lower investment cost when compared to setting up wholly biomass plants (Lehto et al. 2014). Bio-oil can be further refined to produce other liquid fuels like diesel and ethanol or blended with them (Roy and Dias 2017). Bio-oil can serve as feedstock for the production of useful chemicals compounds like olefins and aromatics via hydroprocessing or hydrocracking and as petroleum fuel substitutes (Zhang et al. 2014a). Other applications are recovery of commodity chemical from pyrolysis liquids like calcium salts for use in the de-icing of roads and recovery of phenolics which is utilized in phenol–formaldehyde resins (Diebold and Bridgwater 1997). The composition of bio-oil composition makes it a potential precursor for the production of chemicals. However, separating these products in an economical way for the chemical market and for use as liquid fuels is still a challenge (Meier and Faix 1999).

Table 4 Organic compounds found in bio-oil

Feedstock material	Component	Reference
Spruce	Sugars, non-aromatic aldehydes, non-aromatic ketones, guaiacols, acids, furans, pyrans	Azeez et al. (2010)
Palm kernel shell	Acids, ketones, alcohols, phenol, furans	Islam et al. (1999)
Corn cob	Acids, non-aromatic aldehydes, non-aromatic ketones, sugars,	Azeez et al. (2010)
Cotton residue	Aromatic ethers, phenols, ketones	Krishna et al. (2016)
Rice straw	Esters, phenols, alcohols, acids, ketones, furans	Xiao and Yang (2013)
Palm frond	Aldehydes, acids, ketones, alcohols	Rinaldi and Simanungkalit (1803)
Rice husk	Acids, aromatic and heterocyclic compounds	Ji-Lu (2007)
Beech	Non-aromatic aldehydes, non-aromatic ketones, acids, furans, sugars, pyrans	Azeez et al. (2010)
Pine	Acid, phenols	Zhang et al. (2017)
Miscanthus	Ketones, alcohols, phenols, alkanes, aldehydes, organic acids	Wang and Lee I2018)

Table 5 Physicochemical properties of bio-oil (Oasmaa et al. 2009)

Property	Value
Nitrogen (%)	<0.4
Sulphur (%)	<0.005
Ash (%)	0.01–0.1
Moisture content (%)	20–30
Suspended solids (%)	<0.5
pH	2–3
Viscosity at 40 °C (cSt)	15–35
Density (kg/dm^3)	1.10–1.30
Flash point (°C)	40–110
Pour point (°C)	−9 to −36
Lower heating value (MJ/kg)	13–18
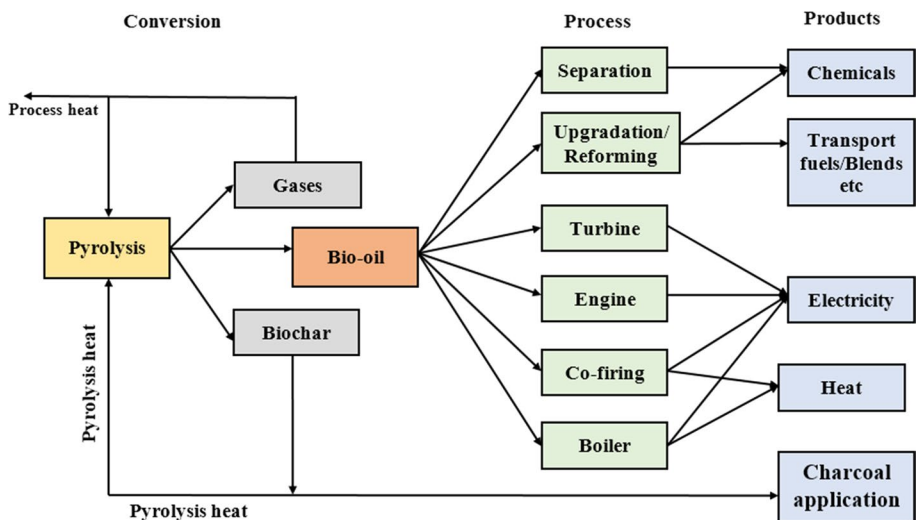
Fig. 6 Application routes for different pyrolysis products (Dhyani and Bhaskar 2017)

Bio-oil is usually regarded as a crude product which needs to be upgraded through further processing into high quality liquid fuels and chemicals (Nathaniel et al. 2013). Bio-oil produced during biomass pyrolysis usually have high amount of oxygen and high moisture content (15%–60%) (Bridgwater 2012b) which affects its performance in combustion engines when used directly, thereby reducing its suitability as a substitute for conventional petroleum fuels (Collard and Blin 2014). Bio-oil from biomass pyrolysis has low stability with a tendency to form a gel when left for a period of time under cold conditions due to its acidic nature. It is also corrosive requiring the use of stainless steel and other corrosion-resistant materials when burnt directly in boilers and other combustion engines. Thus, there is need to improve the oil stability and reduce its acidity (Laird et al. 2009). These challenges can be overcome by upgrading the bio-oil to improve its quality. Bio-oil can be upgraded to meet the quality of fossil-derived transportation fuels. However, more research is still required to fully develop the process. Fisher-Tropsch fuels and methanol which are

useful transport fuels can be obtained from bio-oil using synthesis gas techniques (Jahirul et al. 2012).

Bio-oil upgrading can be carried out using physical upgrading methods. The viscosity of the oil can be improved by adding little amounts of suitable solvents. For instance, when alcohols are used as solvent, the calorific content and storage properties of the bio-oil are increased. However, modifications would be needed on the equipment where this bio-oil will be used in other to accommodate its chemical properties (Ringer et al. 2006). During physical upgrading, the separation of char present in the bio-oil can be accomplished using cold or hot filtration methods and the volatile products can be removed using steam-stripping.

Chemical upgrading can be used to obtain bio-oil with properties similar to that of petroleum fuels, thereby eliminating the need for modifying end-use devices. Chemical upgrading basically involves the deoxygenation and subsequent reforming of the remaining hydrocarbons. This can be achieved via catalytic cracking and catalytic hydrotreating (full hydrotreating and mild hydrotreating) (Ringer et al. 2006). Hydrotreating is a simple non-destructive process that involves the use of hydrogenation to upgrade the quality of bio-oil. This is borne out of the fact that the fuel properties of a fuel typically increase with an increase in the level of hydrogen. This process can be accomplished under atmospheric conditions and temperatures of about 500 °C. Several researchers have adopted this procedure in the upgrading, and the operating conditions and kinetics were evaluated (Su-Ping 2003; Sheu et al. 1988; Wang et al. 2011; Leng et al. 2013). Considering the intended application, chemical or physical upgrading can be carried out to make the bio-oil more stable, increase the heating value, minimize char, and ash content, reduce viscosity and acidity, and make it more suitable for blending with fossil fuels. Table 6 summarizes the typically used upgrading techniques for improving the quality of bio-oil. The merits and demerits of each techniques are also provided.

Bio-oil can also be upgraded via catalytic cracking using bifunctional or metallic catalysts. This process is characterized by the production of large amounts of lighter products, but is, however, possible only at conditions of high temperature and pressure which severely affects the economics of the process (Xiu and Shahbazi 2012). Zhang et al. (2014b) examined the upgrading of bio-oil produced from pyrolysis of Aspen lignin, and they reported a significant increase in the heating value of the resulting product. In another study, Adjaye and Bakhshi (1995) reported hydrocarbon content as high as 89% in the organic distillate fraction obtained after upgrading pyrolysis oil from maple wood in the presence of alumino-silicate catalysts.

Steam reforming has also been investigated as an option for upgrading bio-oil. This process entails the conversion of hydrocarbons in the bio-oil to syngas (a mixture of hydrogen and carbon monoxide) by reacting it with steam at high temperatures. This route to bio-oil upgrading has been extensively studied by the National Renewable Energy Laboratory (NREL) (Wang et al. 1997, 1998; Czernik et al. 2007).

A number of chemical substances such as phenol, triacetonamine, volatile organic acids, n-alkanes, etc., can be extracted from bio-oil and these find applications as resins, asphalt binder, wood flavour, etc. (Fini et al. 2010; Gallivan et al. 1980; Cao et al. 2010).

Bio-oil upgrading via emulsification is an important procedure to adopt if the oil is intended for use as a transportation fuel. In its natural form, bio-oil is not miscible with hydrocarbon fuels, but this can be remedied through the application of suitable surfactants. This process has been investigated by several researchers, and positive results were reported (Chiaramonti et al. 2003; Ikura et al. 2003; Jiang and Ellis 2009; Garcia-Perez et al. 2010b).

Table 6 Summary of techniques used for bio-oil upgrading Xiu and Shahbazi (2012)

Method	Operating conditions	Description	Merits	Demerits
Hydrotreating	Low pressure and temperatures around 500 °C. Typically done in the presence of catalysts	The bio-oil sample is hydrogenated without cracking	Economically attractive and commercially viable	Characterized by the generation of high amounts of coke. Fuel quality obtained is not too desirable
Catalytic cracking	High pressure and temperature around 350 °C. Catalysts are also required	Hydrogenation of the bio-oil sample accompanied by cracking	More lighter products are formed	Capital intensive. There is also the problem of catalyst deactivation
Steam reforming	Very high temperatures are required in the range of 800–900 °C. Also carried out in the presence of a catalyst	Upgrading of bio-oil takes place through catalytic steam reformation accompanying the water–gas shift reaction	Hydrogen, a clean source of energy is a major product	The process is complex
Emulsification	Done under mild condition in the presence of a surfactant	The surfactants facilitate the mixing of bio-oil with diesel	The process is not complicated	Characterized by high energy requirement
Chemical extraction	Done under mild condition in the presence of a suitable solvent	Involves solvent extraction or distillation	Valuable chemicals can be extracted	Still characterized by huge capital and operating costs

11 Characterization of pyrolysis products

Characterization refers to the process of elucidating the properties of a substance. Methods typically adopted include spectroscopy, microscopy, calorimetry, light or radiation scattering, chromatography, gravimetric procedures. A host of analytical methods have been adopted to elucidate the physical and chemical characteristics of bio-oil, biochar, and gases produced during pyrolysis, and this is summarized in Table 7.

Chen et al. (2016) analysed the water content of bio-oil using Karl-Fischer titration method, while an elemental analyzer was used to carry out the ultimate analysis. Gas chromatography–mass spectrometer (GC–MS) was used to analyse the organic components present in the bio-oil. From the results they reported, over a hundred compounds were identified which were grouped into seven categories: anhydrosugars, phenols, ketones, aldehydes, acids, furans, and hydrocarbons. In another study, Açıkalın and Karaca (2017) used FTIR and GC–MS analyses to characterize the bio-oil produced from the pyrolyzed walnut shells. The results obtained showed that the bio-oil comprised of several oxygenated compounds and aromatics which included ketones, aldehydes, carboxylic acids, phenols with other 32 compounds identified. The carbon distribution and molecular weight of the compounds were reported to be between C_2–C_{10} and 60–182 g/mol, respectively. Imam and Capareda (2012) obtained highly oxygenated bio-oil (37%) which had a high heating rate of 36.3 MJkg^{-1}. The viscosity of the bio-oil was observed to be very high (10 cST) when compared to that of diesel (2.1) and gasoline (0.12). The liquid product (bio-oil) had two distinct phases: an oil phase and an aqueous phase. After analysing both phases, it was observed that the oil phase comprised of phenols, acids, hydrocarbons, ketones, alcohols, and aromatics making it a complex mixture while the aqueous phase had acetic acid and branched ketones as the main composition.

Wang and Lee (2018) utilized FTIR and GC–MS to analyse the products of Miscanthus pyrolysis carried out in a fluidized bed reactor. A bio-oil yield of 34.3% was obtained and the oil had a higher heating value of 11.05 MJkg^{-1}. The viscosity of the oil was reported as 1.57 cSt. FTIR and GC–MS analyses revealed the presence of ketones, alcohols, phenols, alkanes, aldehydes, organic acids. In a similar study, Bok et al. (2013) evaluated the yields and product characteristics of bio-oil produced via fast pyrolysis of Miscanthus in a fluidized bed reactor. The highest yield of bio-oil was recorded as 48.9 wt% at 500 °C and 50.01 wt% at 450 °C in rectangular and cylindrical reactors, respectively. Furthermore, GC–MS analysis revealed that the bio-oil contained compounds such as phenols, furans, non-aromatic ketones, sugars, guaiacols, etc.

Scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), or a combination of SEM–EDX can be used to carry out surface and elemental analysis of the biochar produced. BJH method (Barrett Joyner Halenda) is suitable for determining the pore distribution of the biochar. The thermal degradation of the material can be performed by thermogravimetric analysis (TGA) and/or differential scanning calorimetry (DSC). BET (Brunauer, Emmet, and Teller) analysis is also a surface analysis technique that is used to determine the surface area and pore structure of the biochar. X-ray diffraction (XRD) analysis can be used to determine the crystalline nature of the biochar. Fourier transform infrared spectroscopy (FTIR) which is an analytical method can be used to characterize the solid product (biochar produced) by determining the functional groups and other compounds which are present. X-ray fluorescence (XRF), a non-destructive procedure, can also be used to analyse the elemental composition of the biochar. Imam and Capareda (2012) using Brunauer, Emmett,

Table 7 Typical methods used for characterizing pyrolysis products

| Product	Property analysed	Analytical method	Ref
Bio-oil	Elemental composition	ASTM D5373	Li and Suzuki (2009)
	Sulphur content	ASTM D4294 by energy-dispersive X-ray fluorescence (EDXRF) spectrometry	Kanaujia et al. (2014)
	Moisture content	ASTM E203	Kanaujia et al. (2014)
	Identification and quantification of components	Gas chromatography–mass spectrometry (GC–MS), high performance liquid chromatography (HPLC)	Kanaujia et al. (2014)
	Molecular weight distribution	Gel permeation spectroscopy (GPC), Matrix-assisted laser desorption/ionization (MALDI) mass spectroscopy	Cao et al. (2011)
	Higher heating value	Theoretical estimation	Li and Suzuki (2009)
	Carbon residue	ASTM E203 by destructive distillation method	Kanaujia et al. (2014)
	Acid number	ASTM D664 by potentiometric titration method	Kanaujia et al. (2014)
	Flash point, pour point and boiling range (°C)	ASTM D93, D97, and D2887, respectively	Kanaujia et al. (2014)
	Density at 15 °C (kg/m³)	ASTM D4052 by digital density meter	Kanaujia et al. (2014)
	Kinematic viscosity (mm²/s)	ASTMD445–03	Kanaujia et al. (2014)
	Functional groups	Fourier transform infrared (FTIR) spectroscopy and near-IR (NIR)	Kanaujia et al. (2013)

Table 7 (continued)

Product	Property analysed	Analytical method	Ref
Biochar	Proximate analysis	ASTM D1762-84, 2007	Kim et al. (2014)
	Ultimate analysis	ASTM standard D3176-89, 2002	Kim et al. (2014)
	Functional groups	Fourier transform infrared (FTIR) spectroscopy	Rogovska et al. (2014)
	Aromaticity	^{13}C Nuclear magnetic resonance (NMR) spectroscopy	Brewer et al. (2009)
	Crystalline phases	X-ray diffraction (XRD)	Azargohar et al. (2014)
	BET Surface area	Nitrogen gas adsorption	Shaaban et al. (2014)
	Surface morphology	Scanning electron microscopy	Azargohar et al. (2014)
	Particle size distribution	Laser sizing equipment	Shivaram et al. (2013)
	Electrical conductivity	Conductivity meter	Uras et al. (2012)
	Mass and heat effects during heating in gaseous atmospheres	Thermogravimetric analysis with differential scanning calorimetry (TGA/DSC)	Shaaban et al. (2014)
	Cation exchange capacity	Ion chromatography (IC)	Carrier et al. (2013)
	Surface acidity and alkalinity	Boehm titration	Boehm (1994)
	Elemental surface distribution	Scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM/EDX)	Shaaban et al. (2014)
	Organic carbon	DPI in-house method 236	Guizani et al. (2014)
Pyrolytic gas	Identification of gas components and quantification	Gas chromatography (GC); mass spectrometry (MS); non-dispersive infrared (NDIR) analysis	Kan et al. (2010)
	Functional groups	Fourier transform infrared (FTIR) spectroscopy	Kan et al. (2013)
	Hydrogen sulphide content	Lead sulphur precipitate through reaction between H_2S and lead nitrate	Karayildirim et al. (2006)
	Lower heating value	Theoretical estimation	Li and Suzuki (2009)

and Teller (BET) analyses calculated the pore volume and surface area of the biochar produced. After degassing the biochar samples at a temperature of 300 °C for 12 h, adsorption measurements were carried out. The biochar surface area was reported to have increased from 0.1 to 1.0 m^2/g as the temperature increased from 400 to 600 °C. The total pore volume per gram was 0.7 cm^3/g at 500 °C–600 °C, with higher heating values (HHV) of 29.4 MJ/kg obtained from the biochar at 600 °C. (Chen et al. 2016) characterized the biochar obtained in their study as follows. A bomb calorimeter was used to calculate the higher heating value of the biochar, while surface analysis to determine the specific surface area and pore distribution of the biochar were performed using BET method. A sample mass of 0.35 mg was measured out, then degassed at a temperature of 300 °C for 15 h after which the nitrogen adsorption isotherm of the sample was recorded at −196 °C. Specific surface area of 411.06 m^2/g and total pore volume of 0.1819 cm^3/g which were the maximum values recorded were obtained at a heating rate of 30 °C/min. Varma and Mondal (2017) used the following method to characterize the biochar obtained in their study from the pyrolysis of sugar bagasse. FTIR spectrometer using pellet technique was used for measuring the biochar infrared spectra. A bomb calorimeter was also used to calculate the higher heating rate of the biochar, and a thermogravimetric analyzer was used for the thermal analysis of the biomass feedstock and biochar product. X-ray diffraction (XRD), field emission scanning electron microscope, and energy-dispersive X-ray (EDX) were also used in characterizing the biomass and biochar. The results obtained for fixed carbon, ash content, pH value, and HHV were 59.75%, 16.25%, 8.1, and 24.31 MJ/kg, respectively. From the FTIR spectra of biochar, the numbers of peaks representing the biochar structure were observed to have high peaks at 1589 cm^{-1} attributed to the stretching vibrations of double carbon bonds which is an indication that alkenes and aromatics are present in the biochar. In another study, Scholze and Meier (2001) utilized FTIR technique to understand the ageing processes of pyrolysis oil. FTIR analysis was also used by Yin et al. (2013) to characterize bio-oil and biochar obtained via the fast pyrolysis of sweet sorghum. With this method, they were able to investigate the changes in the chemical composition of the feedstock in the course of fast pyrolysis. For the XRD analysis, part of the cellulose crystalline structure was lost indicating that degradation of the cellulose occurred during the pyrolysis process, while EDX analysis showed that the biochar comprised of several inorganic elements including N, Na, K, Si, Al, Ca, Fe, and Mg which are essential nutrients required for fertile soils making them suitable as soil amendments. Pore volume of 0.011 cm^3/g, BET surface area of 10.85 m^2/g, and pore size of 4.37 nm were obtained after characterizing the biochar.

For characterization of the gaseous products, gas chromatography (GC), and mass spectrometry (MS) are usually used. FTIR can also be used. Jie et al. (2008) investigated the pyrolysis of waste printed circuit board under conditions of varying temperature. The gases produced which mainly comprised of CO, CO_2, H_2, CH_4 and in small part of O_2 were quantified using GC–MS. It was also observed that increasing the temperature increased the composition of CH_4 and H_2 in the pyrolytic gas stream (Fig. 7). Varma and Mondal (2017) also used gas chromatography alongside thermal conductivity detector (TCD) to characterize the pyrolysis gas produced. Tedlar bags were used to collect the gaseous products during the pyrolysis process. The carrier gas used was argon with a gas flow rate of 30 mL/min, a sample volume injected of 60 μl, an injector temperature of 80 °C, an oven temperature of 50 °C, and a detector temperature of 90 °C.

Fig. 7 Effect of pyrolysis temperature on the composition of gas liberated during pyrolysis of waste printed circuit board (Jie et al. 2008)
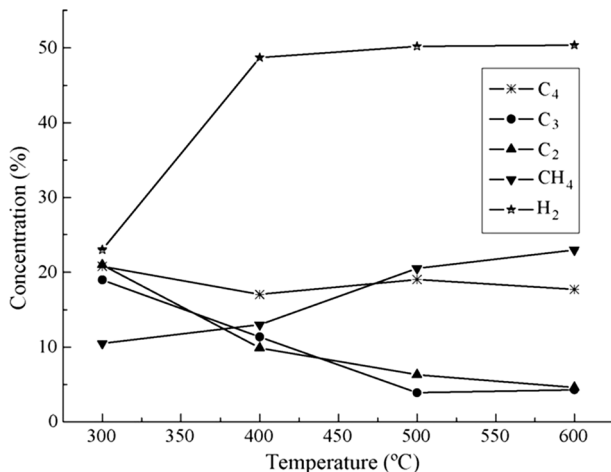
12 Reactors configurations for pyrolysis

Biomass pyrolysis reactors have been referred to as the heart of the pyrolysis process which is a very apt and befitting description for it. This is because the selected pyrolysis reactor determines to a large extent the pyrolysis product to be obtained in terms of its quality, quantity, properties, and characteristics (He et al. 2010).

12.1 Fixed-bed reactors

The fixed-bed reactor is a commonly used pyrolysis reactor for the conversion of biomass into useful biofuels and valuable products. It is an efficient pyrolysis system with a simple design which can be used with biomass having varying uniform sizes and minimal amounts of fines. It is made up of firebricks or steel reactors which consist of feeding unit, cooling system, ash cleaning unit, and an exit for the gas. General operating features of fixed bed reactors are long residence times for the biomass, high carbon conservation, reduced ash entrainment, and low sweeping gas velocity. They are usually used for small-scale systems for energy generation. Fixed-bed reactors have a challenge of tar removal which affects the product gas. Fixed-bed reactors have been used in several studies for biomass pyrolysis. In the study by Chen et al. (2016), a fixed-bed laboratory scale reactor was used for the pyrolysis polygeneration of poplar wood. They evaluated the effect of temperature and heating rate on the pyrolysis process. They identified the optimum BET surface area, HHV of the non-condensable gases, and bio-oil as 411.06 m^2/g, 14.56 MJ/m^3, and 14.39 MJ/m^3, respectively, and these were obtained at a temperature and heating rate of 600 °C and 30 K/min, 600 °C and 50 K/min, 550 °C and 50 K/min, respectively. Messina et al. (2017) pyrolysed peanut shells pretreated with acid using a fixed bed reactor to improve the product yield of the bio-oil at 400 °C, 500 °C, and 600 °C temperature values. A temperature of 500 °C was identified as the optimum for the pyrolysis. Furthermore, more bio-oil (42%) was obtained for the treated biomass compared to the untreated one (33%). The BET surface area of the char obtained from the treated biomass was as high as 300 m^2/g pointing to their possible use as an adsorbent. Açıkalın and Karaca (2017) studied the effect of various process parameters on product yields using a fixed-bed reactor and also characterized the

solid and liquid products obtained. The pyrolysis conditions used were heating rate (40 K/min), pyrolysis temperature (350 °C–650 °C), nitrogen gas flow rate (50 mL/min–450 mL/min), and residence time (10–50 min). Maximum liquid yield of (48.2%) was obtained at operating conditions of 500 °C, 30 min, and 150 mL min^{-1}. Ma et al. (2018a) also used a fixed-bed reactor in their study within temperature intervals of 400 °C–600 °C to produce bio-oil from rice husks through pyrolysis and fractional condensation. They found that increasing the pyrolysis temperature favoured the production of phenol products while an increase in condensation temperature also favoured the production of phenol compounds and dehydrated carbohydrates.
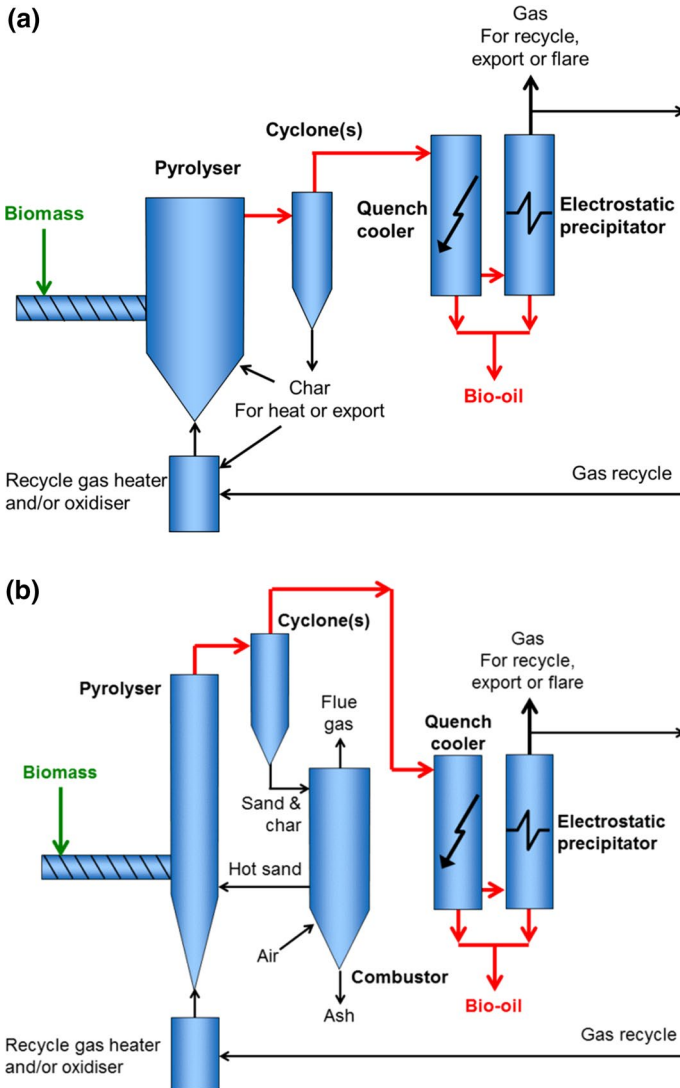
12.2 Fluidized bed reactors

Fluidized bed reactors are most suitable and frequently used for fast pyrolysis processes due to their very fast heat transfer rates, increased velocity, surface area contact, and ability to control the residence time of the vapour during the pyrolysis reaction. In fluidized bed reactor, the biomass is brought in contact through mixing with sand particles which is heated to an elevated temperature. Mixing the biomass material with sand increases the heat and mass transfer within the reactor. The reactor bed is heated externally and the heat can be transferred directly or indirectly (Dhyani and Bhaskar 2017). There are basically three configurations of fluidized bed reactors which are the bubbling fluidized bed reactor, entrained fluidized bed reactor, and circulating fluidized bed reactor (Fig. 8).

Carvalho et al. (2017) carried out fast pyrolysis of sweet sorghum bagasse using fluidized bed reactor. The products obtained were characterized and compared with vapours generated during analytical pyrolysis. Particle sizes between 500 μm and 1000 μm were used. They attributed the difference in the results obtained to certain factors such as solvent used, secondary reactions, condensation efficiency, and post-condensation polymerization. Lisa et al. (2016) examined the pyrolysis of pine using catalysts (in situ and ex situ) in a bench-scale fluidized bed reactor. They found that the *in situ* system performed slightly better than the *ex situ* system. Madhu et al. (2016) performed flash pyrolysis of palmyra palm fruit bunch in a fluidized bed reactor to investigate the effects of temperature, particle size, and sweep gas flow rate. The maximum bio-oil yield obtained was 48.22% at 500 °C temperature, 1 mm particle size, 2 m^3/h sweep gas flow rate.

12.3 Microwave reactor

These types of reactors are a recent approach to biomass pyrolysis which have a couple of advantages when compared to slow pyrolysis reactors liked fixed-bed reactors which makes it suitable for the recovery of useful chemical from biomass. The drying process occurs in the oven chamber of the microwave reactor that is connected to a power source. An inert gas is used to provide an oxygen-free environment for the process. Energy is transferred due to the interaction taking place among the molecules and atoms. Microwave reactors have very good heat transfer. The heating process can be better controlled, and the chemical reactions taking place are enhanced which hinders the formation of unwanted products (Fernández and Menéndez 2011). Studies in which microwave reactors have been used are available in the literature (Mohamed et al. 2016; Bu et al. 2016). Yu et al. (2018) studied the effect of temperature, catalyst–feed ratio, and feeding rate on the product distribution of chemical composition of bio-oil-produced from Chinese tallow kernel oil in the presence of silicon carbide catalyst. They reported a maximum yield of 89.71% aromatic

Fig. 8 Bubbling fluidized bed reactor (**a**) and circulating fluidized bed reactor (**b**) (International Energy Agency (IEA). Pyrolysis Reactors.IEA Bioenergy Task (2020) Available online at https://task34.ieabioenergy.com/pyrolysis-reactors/ 2020)

components in the oil when the reaction conditions were set as 300 °C temperature, 1:2 catalyst/feed ratio, and 1 ml/min feed rate. Zhao et al. (2012) used a microwave reactor to analyse the impact of microwave on the pyrolysis of biomass. Their findings showed that temperature positively influenced the process, and this was reflected in the increase in the proportion of combustible gases as well as an improvement in the characteristics of the biosolids produced. Tarves et al. (2016) also used a microwave reactor to investigate the effect of gas atmospheres on the properties of bio-oil produced from fast pyrolysis of lignocellulosic biomass. Their results showed that the use of a CO atmosphere had little to

no influence on the process. However, the use of H_2, CH_4 and model pyrolysis gas atmospheres resulted in the formation of more deoxygenated products and lower oxygen content.

12.4 Ablative reactor

The ablative reactor is a more complex reactor due to its intensity and mechanically driven process. It involves the transfer of heat from the walls of the reactor to a section of the particles with the application of pressure which quickly removes the volatiles formed. At temperatures of about 600 °C, high velocity is attained within the particles in the reactor. Advantages of the ablative reactor include high heating with good heat transfer, high efficiency in terms of energy and cost, compact designs with small contact time, and less emphasis on size reduction (Bahng et al. 2009). The applications of ablative reactors are becoming popular for industrial purposes due to their high heating and high mass transfer rates and their suitability for use in fast pyrolysis without much emphasis on biomass size reduction. Commonly used ablative reactors are vortex and rotating disc reactors.

In vortex reactors, the transfer of heat takes place as the particles come in contact with the walls of the reactor. A surge of steam with a velocity of 1200 m/s is used to force small particles of the biomass to spin within the walls of the reactor heated to about 625 °C temperature. The separate solid and liquid products which rise to the top in the course of the process are then removed via friction. The solid materials that were not fully converted are fed back into the reactor, and a cyclone is used to separate the hot char (Meier and Faix 1999). The vapours formed on the walls of the reactor are rapidly removed using carrier gas in less than 100 ms. High yield of bio-oil, about 65%, have been achieved using vortex reactor which makes it suitable for biomass fast pyrolysis. A schematic of a vortex reactor design at the NREL is shown in Fig. 9. Some experimental and numerical simulation works on biomass pyrolysis using the vortex reactor have been carried out and different levels of successes have been recorded (Gonzalez-Quiroga et al. 2017; Kulkarni et al. 2018; Miller and Bellan 1998; Marin 2017).

Rotating cone reactors do not require the use of an inert gas. The biomass is mechanically mixed with hot sand and fed into the reactor through the base of the cone, from where they are moved to the tip of the cone via spinning by centrifugal force. The vapours

Fig. 9 Schematic of a vortex reactor designed at the NREL (International Energy Agency (IEA). Pyrolysis Reactors.IEA Bioenergy Task .(2020) Available online at https://task34.ieabi oenergy.com/pyrolysis-reactors/ 2020)
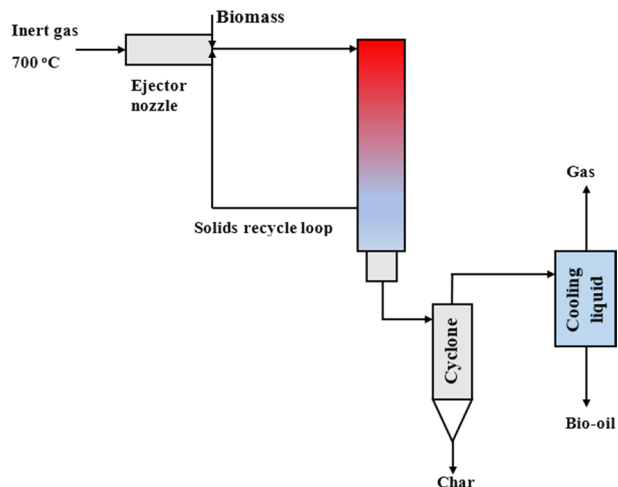
produced are condensed as the reach the top. The char formed is returned as feed alongside new feedstock into the reactor (Fig. 10). Despite the complex nature of rotating cone design configuration, they are attractive due to their high yield of bio-oil (Pattiya et al. 2008). Several works on biomass pyrolysis using the rotating cone reactor have been carried out and different levels of successes have been recorded (Wagenaar et al. 1994; Westerhout et al. 1998; Guoxin et al. 2008).

12.5 Auger reactor (screw reactor)

The auger reactor is a viable pyrolysis technology ideal for mobile applications and areas where access and infrastructure are not easily available due to its operating ease and maintenance. The feedstock together with hot sand is introduced into the reactor at one end, with the screw conveying the feed and ensuring the mixing of the sand and the biomass materials with good control of reaction time (Fig. 11). Advantages of the auger reactor are low temperature and the ability to utilize small reactor sizes. The disadvantages are long vapour residence time resulting in low pyrolysis oil yield due to further vapour cracking and mechanical unreliability due to exposure of movable parts in the hot zone (Papari et al. 2017).

Brassard et al. (2016) investigated the influence of pyrolysis parameters: temperature (450 °C–650 °C), solid residence time (60–120 s), and N_2 flow rate (1 Lmin^{-1}–5 Lmin^{-1}) on the products yields and biochar characteristics using a vertical auger reactor. Papari et al. (2017) used a pilot auger reactor to carry out a parametric study of forest residues pyrolysis for the production and characterization of bio-oil. Pyrolysis oil yield (53%) was obtained for softwood shavings at temperatures of 450 °C − 475 °C and feed rate of 4 kg/h.

Other types of pyrolysis reactors are vacuum reactor, pyros reactor, plasma reactor, and solar reactor (Zeng et al. 2015; Li et al. 2016a,b; Ma et al. 2017, 2018, Pradhan et al. 2017; Bardalai and Mahanta 2018;Fan et al. 2018; Sánchez et al. 2018). Vacuum pyrolysis is carried out under vacuum conditions. The process utilizes lower heating rates with the objective of increasing bio-oil yield. By operating under a vacuum, the residence time of the vapours is

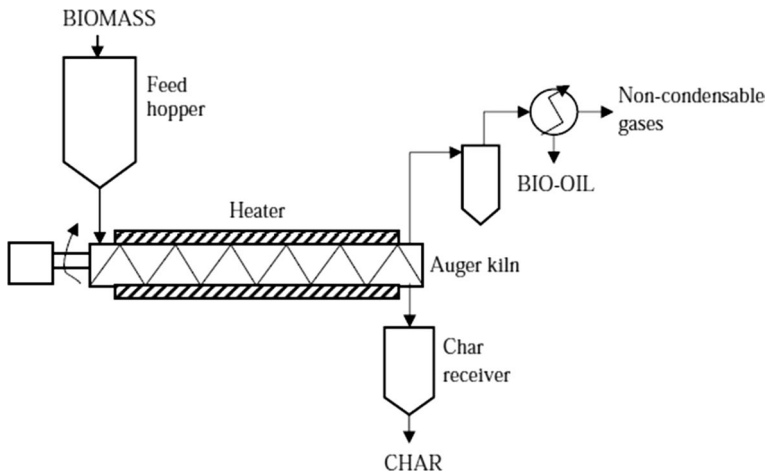**Fig. 10** Schematic of a rotating cone reactor (Dhyani and Bhaskar 2017)
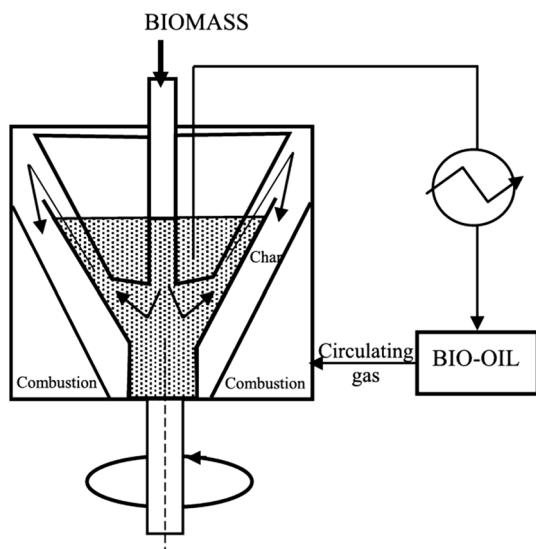
Fig. 11 Schematic of an auger/screw pyrolysis reactor (Dhyani and Bhaskar 2017)

reduced, and this prevents the proliferation of secondary reactions. For this process, a carrier gas is not required and larger particle size can be used because of the low heating requirements. Fan et al. (2018) examined the upgrading of bio-oil in a vacuum reactor. Their findings showed that despite the decrease in the bio-oil yield, the properties of the oil were found to improve in the course of the process. Li et al. (2018) also investigated the catalytic upgrading of pyrolysis vapours from rape straw under vacuum conditions. Their results revealed that the yield of hydrocarbons was increased when 5 wt% of the catalyst was used.

Plasma pyrolysis is an innovative technology for the conversion of high calorific waste materials to synthesis gas (syngas) by means of thermal plasma. The process makes use of extremely high temperature in an oxygen-deficient environment to completely convert waste materials into syngas. Ma et al. (2017) investigated the pyrolysis of coal to produce acetylene in a rotating hydrogen-plasma reactor. They reported that the use of plasm improved stirring of the materials facilitated movement of the particles and enhanced the mixing of coal with high heat transfer efficiency. In another study, Li et al. (2016a) examined quenching conditions and its effect on the yield of acetylene produced from pyrolysis of coal tar in a thermal plasma reactor. Their findings indicate that the quenching operation and quenching media flow rate significantly affected the yield of acetylene.

Solar pyrolysis involves the facilitation of the pyrolysis process with solar energy in the form of high-temperature process heat. This technique can potentially produce products with higher calorific value and is usually characterized by lower carbon emissions compared to the conventional pyrolysis processes. Zeng et al. (2015) studied the effect of temperature and sweep gas flowrate on the distribution of products formed during pyrolysis of wood in a laboratory-scale solar reactor. Their results showed that gas production was favoured by increasing the temperature, but the reverse was the case for liquid yield.

13 Application of catalysts in biomass pyrolysis

Catalytic pyrolysis of biomass is increasingly gaining attention among researchers. The application of catalysts in the pyrolysis of biomass has potential for a significant positive impact on the quality and distribution of pyrolysis products if suitable catalytic materials can be found (Chen et al. 2003a). Through catalytic pyrolysis, it is possible to directly produce bio-oil and hydrocarbons from biomass with higher quality than those produced through the conventional non-catalytic pyrolysis process (Venderbosch 2015). Catalysts can be used in the primary decomposition of biomass, to facilitate certain useful reactions while inhibiting unwanted reactions of the pyrolysis products. Bio-oil can be upgraded through catalytic cracking in the presence of catalysts by deoxygenation (i.e. elimination of oxygen) which is achieved via dehydration, decarbonxylation, and decarbonylation reactions (French and Czernik 2010). In catalytic fast pyrolysis, the pyrolysis vapours are upgraded by bringing the vapours into contact with the catalyst prior to condensation at atmospheric pressure (Fernández and Menéndez 2011). Catalytic pyrolysis can be carried in two ways namely: *in situ* and *ex situ*. For *in situ* catalytic pyrolysis, a single reactor is used and the catalyst is placed inside the pyrolysis reactor. It has a simple design configuration, leading to low capital cost which makes it advantageous. In *ex situ* catalysis pyrolysis, the pyrolysis vapours passes through a different reactor before condensation. *Ex situ* catalytic pyrolysis has the potential to isolate the contaminants from the catalyst in the biomass and also separately maximize both the catalytic upgrading and pyrolysis process (Lisa et al. 2016).

Commonly used catalysts are metal oxide catalysts (e.g. Al_2O_3, SiO_2-Al_2O_3) and zeolite catalysts. Zeolites are the commonly used catalysts in the pyrolysis of biomass. Unlike silica-alumina catalysts, zeolites have better aromatization reactions. This is because of their varied acidity and shape selectivity (Kabakcı and Hacıbektaşoğlu 2017). Zeolites are crystalline in nature and are made up of SiO_4 and $[AlO_4]^-$. They are comprised of micropores which have several structural dimensions which serve as access points into the internal active sites of the zeolite material from where the diffusion of small molecular reactant takes place (Wang et al. 2017). ZSM-5 is a type of zeolite catalyst frequently used in biomass pyrolysis and oil industry because of its unique pore size, solid acidity, thermal stability, steric hindrance, and shape selectivity (Shirazi et al. 2008; Mihalcik et al. 2011). Naqvi et al. (2014) examined the pyrolysis of paddy husk using catalyst for the production of bio-oil in temperature ranges of 300 °C–600 °C. The bio-oil obtained had higher energy value, low oxygen, and high carbon contents when compared with that obtained without using catalyst. The bio-oil yield was highest at 450 °C with a catalyst loading ratio of 0.5. Veses et al. (2015) used mineral clay materials as low-cost catalysts to produce upgraded bio-oil from the pyrolysis of wood in an auger reactor. With catalyst loading ratio of 1:6 and temperature of 450 °C, highest yield of bio-oil was obtained. The bio-oil was found to have high viscosity and high heating rates, while the acidity level was reduced alongside its oxygen content. Khanday et al. (2016) studied the role of catalysis in the pyrolysis of oil palm mesocarp fibre. They observed higher bio-oil yield (37.98%) for the catalysed process compared to the uncatalysed one (31.95%). They further noted that the catalyst adopted enhanced the selectivity of phenol compounds and lighter aromatics. Long et al. (2017) investigated acid catalysed pyrolysis of cellulose in the temperature range 50 °C–325 °C. Their findings indicated that dehydration reactions were dominant during the process. More so, the formation of glucose oligomers as reaction intermediates was observed. Muhammad et al. (2015) utilized zeolite catalysts for the pyrolysis of plastic

wastes obtained from electrical and electronic equipment. They found that the introduction of the catalysts did not enhance the production of bio-oil; however, it did facilitate the production of gases.

14 Factors affecting biomass pyrolysis

The pyrolysis products and their yields are influenced by the biomass constituents such as hemicelluloses, lignin, cellulose, ash contents, and by the operating conditions which include heating rate, residence time, particle size, pyrolysis temperature, and configuration/design of reactor.

14.1 Pyrolysis temperature

Temperature is considered as a major and important process parameter during biomass pyrolysis. Controlling the temperature profile is vital because of its over-reaching influence on other pyrolysis parameters. Results obtained from studies have shown that at higher temperatures, the char yield reduces, and this is considered to be as a result of secondary reactions occurring that enhances the formation of liquid fractions and further decomposition of the chars leading to the production of more pyrolysis gases at temperatures above 600 °C (He et al. 2018; Chen et al. 2016; Lisa et al. 2016; Bridgewater and Peacocke 2000). At temperatures below 150 °C, the formation of tars usually does not occur; as the temperature steadily increases, biochars are formed which in turn results in the formation of pyrolysis gases and a reduction of char yields. This is caused by further degradation of the biomass which leads to the decrease in the liquid products resulting in increase in gas production, apparently due to the degradation of the cellulose and hemicellulose components of the biomass materials (Aquino 2007). In the study by Aquino (2007) using cotton-gin trash feedstock, about 10% reduction was reported in the char produced by increasing the temperature from 600 to 800 °C, while more than 12% increase was obtained for the liquid yields and above 13% increase was obtained for the pyrolysis gas produced. Tan et al. (2017) examined the composition of the pyrolysis gas obtained from durian shell. They found that increasing the pyrolysis temperature resulted in a reduction in the amount (%) of CO_2 in the gas, unlike that of CO, C_2H_4, CH_4, C_2H_6 whose quantities increased with increasing temperatures. CO_2 was the major gas product at 250 °C. At 350 °C, amounts of CO were detected in the gas product (25.43%) which increased to 29.44% at 450 °C temperature. With further increase in temperature, the presence of light hydrocarbon gases were detected. At a temperature of 550 °C, 5.07% of CH_4 was obtained while 2.14% and 1.58% of C_2H_4 and C_2H_6, respectively, were obtained at a temperature of 650 °C. Putun et al. (1999) investigated the pyrolysis of hazelnut shells under conditions of varying temperature. They attributed the increase in liquid and gas yields as temperature increased to further conversion of the biomass to volatile materials at elevated pyrolysis temperature. They also observed that the liquid yields obtained began to decrease at higher temperatures, while the gas yields continued to increase which they also attributed to the fast devolatilization of the cellulose and hemicellulose components of the biomass at elevated temperature. Imam and Capareda (2012) obtained product yields at three separate temperatures of 400 °C, 500 °C, and 600 °C. As the temperature was varied from 400 to 600 °C, the bio-oil and pyrolysis gas yields increased from 22 and 8% at 400 °C to 37% and 26% at 600 °C, respectively, while the biochar yield decreased from 48% at 400 °C to 25% at

600 °C. A mass loss of 12%–22% was reported for this study which was attributed to losses during the gas and liquid collection. Mullen et al. (2010) reported mass losses of 19%–26% which was due to unconverted biomass deposited inside the pyrolyzer. Ma et al. (2018a) obtained increased gas yields with increase in pyrolysis temperature especially at a temperature range of 550 and 600 °C. However, the solid product yields decreased with increasing temperature with maximum yield at 400 °C. They attributed this partly to be as a result of incomplete pyrolysis reaction at lower temperature. Thus, as the temperature profile increased, more thermal cracking reactions occurred leading to higher product yields of liquid and gases and a decrease in the yield of the solid product. However, increasing the temperature further (between 450 and 550 °C) caused the liquid product yields to decrease. Similar trends were reported by He et al. (2018). The liquid yields increased from 300 °C to 500 °C before decreasing from 500 °C to 600 °C. The highest liquid yields were observed between 450 °C and 500 °C. The biochar yields of the crop residues decreased sharply with temperature from 300 °C to 400 °C, followed by a gradual decrease till 500 °C, while the gas yields gradually increased as the temperature was increased between the defined temperature ranges.

14.2 Heating rate

The heating rate is also a very important factor during pyrolysis that can affect the yield and composition of the pyrolysis products Garcia-Perez et al. (2010a). Based on heating rates, pyrolysis is usually divided into two categories: slow pyrolysis with heating rates of about 10 K/min and fast pyrolysis with heating rates approaching 1000 K/min. When fast/high heating rates are used with moderate temperatures of about 400 °C–600 °C, higher yields of volatiles and liquid are obtained, whereas the use of slow heating rates at moderate temperature produces higher char yields. Applying slow heating rates minimizes the thermal cracking reactions taking place within the biomass, thereby producing higher yields of char. The use of high/fast heating rates, on the other hand, promotes the thermal fragmentation and cracking reactions taking place which hinders the formation of chars, thereby increasing the liquid and gas yields (Al Arni 2018). With slow heating rates, the volatiles are gradually removed from the reactor which allows the occurrence of secondary reactions between the volatiles and chars leading to the formation of secondary chars (Basu 2010). From research works published, it has been reported that high rate of heating promotes the formation of volatile compounds, while the use of slow heating rates favours the production of biochars. About 75% bio-oil yield with biochar yield of 15% is usually obtained using high heating rates for the pyrolysis of lignocellulosic feedstock (Garcia-Perez et al. 2010a). To achieve high rates of heat transfer, the use of biomass with very small particle size (less than 2 mm) is usually required. Efika et al. (2015) investigated the pyrolysis behaviour of refuse derived fuel (RDF) using slow and fast heating rates (5, 20, 90, and 350 K/min) in a horizontal tubular reactor at high temperatures of 700 and 900 °C. At 800 °C temperature and residence time of 20 min, the following results were obtained. Increasing the heating rate resulted in an increase in gas yield from 14.4 wt% at 5 K/min to 46.9 wt% at 350 K/min. The bio-oil and solid residue yields decreased from 55 to 23 wt% and 25 to 22.8 wt%, respectively, when the heating rate was increased to 350 K/min from 5 K/min. However, no clear distinction existed for the product yields obtained at heating rates of 5 K/min and 20 K/min, an indication that wider disparity between heating rates could be needed to cause significant changes in the product yields. The surface area and biochar heating value (HHV) also decreased with increasing heating rates from 169.7 m^2/g

and 18.5 MJ/kg at 5 K/min to 84.4 m^2/g and 16.4 MJ/kg at 350 K/min. (Efika et al. 2015) also reported in their study that pyrolysis carried out using slow heating rates produced bio-oil with high amounts of oxygenates, alkenes (C_8–C_{20}), and alkanes (C_8–C_{39}) when compared with bio-oil produced using rapid/fast heating rates which had higher amounts of aromatics. They suggested that this was likely caused by an increase in Diels–Alder type of reactions.

14.3 Residence time

As important as temperature and heating rate are during biomass pyrolysis, the residence time also plays a vital role. Residence time refers to the duration the pyrolysis material spends in the reactor during the pyrolysis process. Zanzi and Sjotrom (2002) observed that the residence time influenced the pyrolysis products produced and that longer residence time may lead to secondary reactions taking place which will result in the formation of secondary products. Aquino (2007) varied the pyrolysis time during batch pyrolysis of cotton gin wastes. It was observed that the yield of the biochar decreased considerably, while the yield of the pyrolysis gas increased when the pyrolysis residence time was increased. The highest char yield obtained was 40 wt% at 600 °C and reaction time of 30 min. Further increase in the residence time caused the solid yield to decrease. However, this led to the production of more pyrolysis gases for the various temperature values used. The maximum gas yield (57.80 wt%) was obtained after 60 min at a temperature of 800 °C, while the highest liquid yields was obtained at 800 °C after 30 min. Hence, the production of pyrolysis gas is favoured by the use of longer residence time since the biomass is further converted to volatile gases. Açıkalın and Karaca (2017) studied the effect of residence time at five different intervals (10, 20, 30, 40, and 50 min) on product yields using an operating temperature of 500 °C and nitrogen gas flow rate of 250 mL/min. The different residence time had minimal effect on the bio-oil and biogas yields. The yield of liquid produced was 47.14% after 10 min and 47.39% after 20 min which later decreased to 44.67% as the residence time was further increased to 50 min. The yield of the pyrolysis gas produced was 25.11% after 10 min and 28.34% when the residence time was 50 min. About 27% biochar yield was obtained with the varying reaction time used having no effect on the yield of the solid product.

14.4 Particle size

The size of biomass particles to be used for pyrolysis should be given important consideration. This is because particle size can affect the rate of heat transfer from the surface to the interior of the particle (Zabaniotou and Karabelas 1999). With large particle sizes, the distance between the particle surface and its core increases, and this slows the flow of heat from the hot to the cold regions of the particle. Several studies have reported that the composition and yields of the pyrolysis products were affected by the particle size of the biomass used (Zanzi and Sjotrom 2002; Luo et al. 2010; Oladeji et al. 2015). Zanzi and Sjotrom (2002) using a free fall reactor to pyrolyse wood and agricultural residues observed that the use of smaller particle sizes for pyrolysis caused the char yield to decrease but increased the yield of the pyrolysis gas produced. They also observed that using pelletized wheat straw produced higher char yields than that obtained after pyrolysis of untreated straw. Weerechanchai et al. (2011) characterized the products obtained after pyrolyzing cassava pulp and palm kernel cake residues. Their findings showed that higher

yields of char were obtained when particle sizes less than 2.03 mm were used while the liquid yield decreased. Their explanation for this was that the reduced particle sizes of the biomass resulted in greater heat transfer within the material which led to the production of more gases and volatiles. Furthermore, the denser packing of the particles due to their very small sizes could hinder the flow of the sweeping gas which would invariably prolong the time spent by the pyrolysis products in the reaction zone, resulting in secondary reactions taking place such as thermal cracking, re-polymerization, and re-condensation, thereby furthering the decomposition of heavy volatiles into pyrolysis gases, thus reducing the liquid yield produced and increasing the solid char formed (Das and Sarmah 2015). Particle size affects the pyrolysis process by determining the rate of heat transfer during the reaction. With bigger particle sizes, the amount of heat transferred from the surface of the particle to its core is limited resulting to increased char yields (Tripathi et al. 2016). Balagurumurthy et al. (2015) examined the effect of particle sizes on the yields of pyrolyzed durian shells at operating parameters of 550 °C temperature and 200 mL/min nitrogen gas flow rate. The range of particle sizes used were <0.5, 0.5–1, 1–2, and 2–5 mm. Maximum char yield of 28.30 wt% and liquid yield of 46.29 wt% were obtained using durian shells with particle size of 1 mm–2 mm, while particle sizes less than 0.5 mm produced gaseous product with the highest yield (29.21 wt%). They attributed the increased gas yields at particle sizes <0.5 mm to increased heat and mass transfer operations which favours the fragmentation of the material into smaller volatiles compared with those of larger sizes. Madhu et al. (2016) used four different particle sizes; 0.6 mm, 0.71 mm, 1 mm, and 1.25 mm to investigate the effects of biomass size on pyrolysis product yields. From their study, the size of the biomass used had significant effect on the product yields obtained. For a particle size of 0.6 mm, 34.54% yield of bio-oil was produced at a temperature of 500 °C. This bio-oil yield increased to 44.13% as the particle size used was increased to 1 mm. However, increasing the particle size further from 1 mm to 1.25 mm resulted in a decline in the yield of the bio-oil from 44.13% to 41.15%. Their explanation for this was that as the particle size increased from 1 mm–1.25 mm, the surface-to-core distance of the material also increased, thereby reducing the transfer of heat between the reactor and the material leading to incomplete reactions which caused the decline in the bio-oil yields. The gas yield increased with decreasing particle sizes with maximum yield of pyrolysis gas (35.94%) produced using 0.6 mm particle size. The solid product on the other hand decreased with decreasing particle sizes.

15 Kinetic modelling of biomass pyrolysis

To understand the decomposition/devolatilization reactions occurring throughout the pyrolysis process and the dependence of reaction rate on pyrolysis process variables, kinetic study of the process is very necessary. A comprehensive understanding of the pyrolysis kinetic triplets (activation energy, pre-exponential factor, and reaction model) is essential in the design of highly efficient reactors and their optimization. Kinetic studies are usually done using a thermogravimetric analyzer (TGA). To carry out this analysis, low heating rates, small particle size, and sample mass are usually used to maintain a kinetically controlled regime by minimizing heat and mass transfer effects (Kok and Ozgur 2017; Cai et al. 2018; Hatakeyama and Hatakeyama 2004; Burnham et al. 2015).

Kinetic models of the pyrolysis process can be grouped into three broad areas: single step (one stage) multiple reactions; one stage global decomposition models where an irreversible

first-order reaction is used to denote the thermal degradation of the material; and two step (two-stage semi-global) model which describes the primary and secondary reactions of the pyrolysis process (Patwardhan 2010). Generally, kinetic models can be obtained using model-fitting methods and model-free/isoconversional approach.

16 Model-fitting methods

Model-fitting methods fit various reaction models (differential or integral) into the general kinetic equation and estimates the activation energy (Ea) and pre-exponential factor (A) by regression analyses. See the following references for more details (Vyazovkin and Wight 1999; Grønli et al. 2002; Burnham and Dinh 2007; Khawam 2007; Blasi 2008; Vyazovkin et al. 2011). Different groups of the kinetic parameters are fitted into the equation, and the curve generated by the equation which closely fits the experimental curves is then considered for selection as a possible solution.

In model-based procedures, the first step is to assume a reaction model. Commonly selected reaction models are the first- and nth-order reaction models. Model based techniques can be grouped into Isothermal model-fitting methods (conventional method) and non-isothermal model-fitting methods. In Isothermal model-fitting methods, the rate constant (k) for the reaction model which best fits the data is first determined, followed by the activation energy (Ea) and frequency factor (A) which are calculated from Arrhenius equation. For non-isothermal model-fitting methods, several methods can be used to determine the kinetic parameters (activation energy, reaction model, and frequency factor). These methods include Freeman-Carroll (difference-differential) method (Freeman and Carroll 1958), direct differential method, and Coats-Redfern method (Coats and Redfern 1965).

16.1 Model-free/isoconversional methods

Model-free methods unlike model-fitting do not require any prior assumption of a model. The reaction activation energy (Ea) is usually evaluated without assuming any model from the slope of the linear equation which has parameters for reaction model and frequency factor in its intercept. However, from the intercept of the equation, it is possible to also determine the frequency factor (A), but a model will have to be assumed in order to carry out such estimation. Hence, model-free/isoconversional methods typically give values of activation energies only. Model-free methods are derived from the isoconversional principle where the rate of reaction at fixed conversion is mainly determined by temperature (Vyazovkin and Wight 1999; Grønli et al. 2002; Burnham and Dinh 2007; Khawam 2007; Blasi 2008; Vyazovkin et al. 2011). They can be grouped into isothermal and non-isothermal isoconversional method. Isothermal model-free methods include the standard isoconversional method and Friedman's isoconversional methods (Friedman 1964). Non-isothermal methods require the use of temperature integrals. Examples of these methods are Ozawa, Flynn and Wall (OFW) method (Ozawa 1965; Flynn and Wall 1966), Vyazovkin (VYZ) method, and modified Coats-Redfern method.

17 Challenges in the design and operation of biomass pyrolysis processes

17.1 Feedstock problems

Although several feedstocks can be used for biomass pyrolysis, the nature and properties of the material affects the pyrolysis process and its products. This variability in biomass makes it difficult to obtain consistent quality and yields of products. Some of these factors are chemical and physical characteristics of the material, its morphology, size, moisture content, mode of harvesting, and means with which the materials are collected. Handling of the biomass material in terms of transportation and storage is another source of concern. The amount of ash present in the material is also a challenge.

17.2 Processing problems

For bio-oil quality and reproducibility to be maintained, a generally accepted processing standard and specification will be required. The inability of current end-use-systems to directly use the pyrolysis products is a process challenge requiring the upgrading of the pyrolysis products and/or modification of the end-use-systems. Also, due to the presence of undesirable substances and impurities (e.g. tars, dust, heavy metals) in the products, efficient cleaning systems will be required. Another challenge is the high amounts of oxygen present in the bio-oil which reduces its energy content, increases its acidity (making it corrosive), thereby limiting its application (Seshan 2014).

33.3.Product problems.

Collection of the product liquid product after pyrolysis is a major challenge due to the volatile tendency of liquid thus requiring the use of various quenchers. Poor stability of the bio-oil during storage and thermal stability is also a problem as the molecular weight and viscosity of the oil increases with the passage of time. The pyrolysis process in addition to storage conditions of the bio-oil also affects its stability (Meier and Faix 1999). For instance, contents of char and ash present in the bio-oil affect its colour, quality, and stability. Hot gas filtration can be used to remove these solids during pyrolysis, thereby enhancing the quality of the bio-oil. According to Meier et al. (Meier and Faix 1999) the reactions responsible for the ageing of the oil are condensation reactions occurring within the aromatic units and formaldehyde, formation of acetals among alcohol and carbonyl groups, and polymerization of aryl-vinyl, aryl-crotonyl, aryl-allyl fragments of the lignin. Nevertheless, substituting wood and fossil fuel with bio-oil results in lower tar, dust, and carbon monoxide (CO) emissions. Besides, in comparison with bulk biomass materials, transportation and storage of bio-oil is much easier and cost effective.

17.3 Current state-of-the-art

Biomass pyrolysis is no doubt a promising method for the thermochemical conversion of lignocellulosic biomass materials to renewable fuels. The challenges that the technology faces have prompted a lot of interest in optimizing reaction design and conditions, developing more efficient catalysts, optimizing choice of feedstock and product upgrading to

improve the economics of the process (Perkins et al. 2018). In the subsequent sections, the current state-of-the-art of biomass pyrolysis in terms of recent developments to overcome the challenges encountered are discussed.

17.4 Recent experimental methods

Most of the research efforts recorded in the twentieth century were centred mainly on optimizing product yield and improving the quality of the products. This was typically done by carrying out pyrolysis in common reactors (fixed bed, fluidized bed, rotating cone, ablative, etc.) and characterizing the products formed. Recently though, research efforts have now shifted in the direction of studies aimed at understanding the chemistry of the pyrolysis reactions. Thermogravimetric analysis is the most popular and extensively used tool in analytical pyrolysis studies. However, to have a deep understanding of the mechanisms that drive the process, more detailed information is needed. In recent times, cutting-edge experimental techniques have been developed for biomass pyrolysis research, and these include Py-GC–MS/FID, TG-MS/TG-FTIR, in situ spectroscopy for reaction progress analysis, isotopic labelling and intermediate product analysis techniques (Seshan 2014). For the Py-GC–MS/FID, a micropyrolyzer is combined with gas chromatography (GC), mass spectrometry (MS), and flame ionization detection (FID). This is very useful and convenient tool for quantitative investigation of the distribution of products obtained from biomass pyrolysis, and it has been utilized in many researches (Patwardhan et al. 2009, 2011; Lourenço et al. 2015; Kim et al. 2018; Romagnoli et al. 2018). Despite the obvious advantages of the Py-GC–MS/FID, it can, however, not be used to obtain information on the production profile with respect to time or temperature. This problem is overcome with the use of the TG-FTIR which couples TG with FTIR and the TG-MS which couples TG with MS. With this technique, the process of devolatilization of biomass can be monitored. Beyond that, the functional groups of the volatiles can be readily identified. This method has been utilized in many researches (Huang et al. 2018b; Shen et al. 2018; Wei et al. 2018; Ma et al. 2018b).

Tools like *in situ* FTIR is used for monitoring the changes in the functional groups on the surface of biomass in the course of pyrolysis (Cheng et al. 2017; Tian et al. 2017). Isotopic labelling is useful for studying the mechanism of biomass pyrolysis. It can help to elucidate the origin of specific atoms of interest within the pyrolysis products (Wang et al. 2017).

Also, recently, more novel and advanced reactors have been designed to improve the efficiency and performance of the pyrolysis process (Hossain et al. 2018; Luo et al. 2017b; Fu et al. 2018; Rony et al. 2018; Valdés and Chejne 2018; Liaw et al. 2018).

17.5 Commercial scale pyrolysis plants

Modern pyrolysis reactor configurations have been discussed in previous sections (Chen et al. 2016; Açıkalın and Karaca 2017; Ma et al. 2018a, 2017; Carvalho et al. 2017; Lisa et al. 2016; Fernández and Menéndez 2011; Bu et al. 2016; Yu et al. 2018; Zhao et al. 2012; Tarves et al. 2016; Bahng et al. 2009; Gonzalez-Quiroga et al. 2017; Kulkarni et al. 2018; Miller and Bellan 1998; Marin 2017; Pattiya et al. 2008; Wagenaar et al. 1994; Westerhout et al. 1998;

Guoxin et al. 2008; Papari et al. 2017; Brassard et al. 2016; Fan et al. 2018; Li et al. 2018, 2016a, 2016b; Pradhan et al. 2017; Bardalai and Mahanta 2018; Zeng et al. 2015; Sánchez et al. 2018). Industrial-scale pyrolysis reactors have also been reviewed previously by Bridgewater (Bridgwater 2012) as well as Strezov and Evans (Press 2014). Some of these are summarized in Table 8. Amongst the reactors discussed, the bubbling and circulating fluidized bed as well as the rotating cone reactors have been commercialized while others are still at the level of pilot scale and laboratory demonstration (Table 9). Some pyrolysis plants that are operating at commercial scale are summarized in Table 10.

17.6 Future prospects

Although continuous work is being carried out in the area of pyrolysis as a thermochemical route for the conversion of lignocellulosic materials into biofuels and other valuable products, there are several areas of the pyrolysis process in which further studies should be done. These research areas include improvement of the pyrolysis process, reactor performance, and design which will help in maximizing the quantity and quality of specific pyrolysis products of interest; production and isolation of chemicals and valuable products from the pyrolysis products; development of advanced catalytic pyrolysis systems with high selectivity for specific products with reduced coke formation; improvement in properties and characteristics of the pyrolysis oil through suitable upgrading; understanding the underlying reaction schemes taking place on the catalysts active sites coupled with the effect of mineral built-up on the catalysts; and adapting current end-user systems for use with pyrolysis products.

18 Conclusion

Biomass pyrolysis as a thermochemical conversion route provides several benefits and potentials for the production and application of biofuels, biochemicals, and other valuable products. The different pyrolysis process routes: slow, intermediate, fast, or flash pyrolysis, and reactors types have been considered alongside the interactions of pyrolysis process parameters. The heating rate, pyrolysis temperature, particle size, time of reaction, and the nature of the biomass feedstock have influence on the pyrolysis process and the product yields obtained. Pretreatment of the biomass helps to improve the quality of the biomass, thereby improving the yield of the pyrolysis product and efficiency of the pyrolysis process. The high oxygen content as well as that of moisture usually present in the bio-oil which makes it unstable and acidic can be improved through suitable upgrading to the quality level of conventional fuels and for the production of valuable chemicals. Catalysts can also be used to directly produce bio-oil and hydrocarbons with higher quality from biomass compared to those produced using the conventional pyrolysis process and also influence the quality and distribution of product yields during pyrolysis. It is expected that in the nearest future, with the current research drive in the area of biomass pyrolysis, most of the present technical and economic challenges limiting the pyrolysis of biomass and its application would have been overcome, leading to the realization of an advanced concept of bio-refinery and bio-refining.

Table 8 Characteristics of some biomass pyrolysis reactors (Mohan et al. 2006; Press 2014)

Reactor configuration	Feed particle size	Bio-oil yield	Complexity	Ease of scale-up	Scale and status
Bubbling fluidized bed	<2 mm	75%	Medium	Easy	2–20 t/h, commercial
Rotating cone reactor	<6 mm	70%	High	Medium	200–2000 kg/h, commercial
Circulating fluidized bed	<6 mm	75%	High	Easy	2–20 t/h, commercial
Heated kiln	5–50 mm	–	Low	–	<4000 kg/h, commercial
Ablative	<20 mm	75%	High	Difficult	1–20 kg/h, laboratory
Auger	5–50 mm	60%	Medium	Medium	20–200 kg/h, pilot
Vacuum	5–50 mm	60%	High	–	200–2000 kg/h

Table 9 Examples of research scale pyrolysis plants (Kan et al. 2016; Jahirul et al. 2012; Perkins et al. 2018)

Organization and location	Reactor type	Feed rate (kg/h)	Product
RTI, USA	Fluidized bed	0.001	Bio-oil
BTG, Netherlands	Rotating cone reactor	0.001–3	Bio-oil
CRI Criterion/Shell India, India	Bubbling fluidized bed	0.001	–
University of Twente, Netherlands	Rotating cone reactor	7	Bio-oil
Laval University, Canada	Vacuum reactor	30	Bio-oil
University of Waterloo, Canada	Bubbling fluidized bed	3	Bio-oil
University of Massachusetts, USA	Bubbling fluidized bed	< 1	–
GTI International, USA	Bubbling fluidized bed	0.4	Gas
Ensyn, Canada	Circulating fluidized bed	10–40	Bio-oil
KIT, Germany	Twin screw reactor	50	Bio-oil
Zhejiang University, China	Rotating cone reactor	3	Bio-oil
Canmet, Canada	Bubbling fluidized bed	10	Gas

Table 10 Examples of commercial scale pyrolysis plants (Kan et al. 2016; Jahirul et al. 2012; Perkins et al. 2018)

Organization and location	Reactor type	Feed rate (t/day)	Product
Dynamotive, Canada	Bubbling fluidized bed	100–130	Bio-oil
Mitsubishi Heavy Industries, Japan	Indirect heating rotary kiln	100	Gas
Ensyn, Canada	Circulating fluidized bed	100	Bio-oil
BTG, Malaysia	Rotating cone reactor	50	Bio-oil
Choren, Germany	Heated kiln followed by gasification	180	Syngas
AbriTech, Canada	Auger reactor	50	Bio-oil
Fortum, Finland	Circulating fluidized bed	274	Bio-oil

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