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Chapter

Recent Advances in Thermochemical Conversion of Biomass

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Abstract

The chapter focuses on recent trends of biomass conversion into valuable energy, chemicals, gaseous and liquid fuels. Biomass is presently the largest source of renewable energy and the primary bioenergy resource in the world. A comprehensive discussion on different types, sources and compositions of biomass is presented. The most abundant biomass on the earth is lignocellulose and it represents a major carbon source for chemical compounds and biofuels. The chapter presents a thorough review of lignocellulosic biomass and the importance of biomass as a renewable source. It then reviews biomass classification and composition. It introduces the analysis of biomass feedstock. Biomass is converted to energy, chemicals and clean fuels using various conversion techniques such as thermochemical, chemical and biochemical. The chapter provides a thorough examination of thermochemical conversion processes that use high temperatures to break down the bonds of organic matter. It briefly introduces combustion and gasification, followed by a comprehensive review of different pyrolysis techniques.

Keywords: bioenergy, hydrothermal processing, lignocellulosic biomass, biomass composition, pyrolysis, gasification, combustion

1. Introduction

Due to industrialization, population growth, and urbanization, there has been a rapid increase in global energy demand and consumption over the past few decades. Currently, more than 80% of the world energy demand is supplied by fossil fuels. Global attention on alternative resources has increased due to the high prices and limited reserves of fossil fuels, environmental pollution and climate change. As a result, there is renewed interest in the production and use of renewable energy resources such as biomass, solar, wind, geothermal and tidal. However, biomass is the only renewable energy resource to produce transport fuels. Various biomass components, including sugars, starches and lignocellulosic materials can be used to produce transport fuels and potentially limit the use of fossil fuels. On the other hand, biomass residues and wastes (such as agricultural residue, food waste, animal manure, municipal solid waste) as resources for bioenergy production are promising alternatives to reduce environmental issues concerning waste management and disposal. If improperly managed, these residues and wastes could lead to greenhouse gas emissions, pests breeding, insects, foul odor, etc. Converting these residues and

wastes, that would otherwise have been left to decompose, into useful bioenergy is environmentally beneficial for waste management as well as to reduce the dependence on fossil fuel [1–3]. Lignocellulosic biomass (LCB) such as agricultural crop residues, wood and forestry residues are readily available, inexpensive and promising resource for biofuels. Biomass can be considered as the best option for meeting future energy demand sustainably. The efficient utilization of biomass resources is essential by having more efficient biomass production and conversion [4].

Biomass is an organic matter of plant or animal origin that is living or was living in the recent past [5]. Biomass is perhaps the oldest source of energy used by humans. People have used biomass as an energy source for cooking, heating, and lighting for thousands of years. The energy contained in biomass originally came from the sun. Plants get their energy from the sun and convert water (H_2O) and carbon dioxide (CO_2) into oxygen (O_2) and sugars (carbohydrates) in the process of photosynthesis. The energy of sunlight is stored in chemical bonds of plant organic matter. When different conversion processes break the bonds between adjacent carbon, hydrogen and oxygen molecules of carbohydrates, these substances release their stored chemical energy [6]. Biomass is a renewable energy source as it can be produced year after year and, therefore, is valuable as a fuel source. Compared to petroleum-based products, the use of biomass represents the potential to reduce CO_2 emissions, resulting in negligible or zero SO_X emissions and lower NO_X emissions [7, 8].

Biomasses include agricultural crop residues, forestry and wood residues, purposely grown bioenergy crops, aquatic biomass, sewage sludge, digestate, animal, industrial, municipal and food waste. Various types of wastes such as cow manure, poultry litter, wastepaper, sewage sludge, municipal and many industrial wastes are treated as biomass because these are a mixture of organic (and non-organic) compounds.

2. Importance of biomass

Non-renewable sources produce a significant portion of current energy supplies globally and their use is associated with the emission of CO_2 into the atmosphere. However, about 10–15% of this demand is covered by renewable resources, making biomass by far the most important renewable energy source used to date. Biomass contributes to 9% - 13% of the total energy supplies in industrialized countries. However, biomass energy is the primary energy source in many developing nations, contributing to about 20–30% of the total energy supplies. In some developing countries, biomass covers 50 to 90% of the total energy demand. In industrialized countries, biomass is used as a modern bioenergy source for industrial (heat, electricity), transportation (biofuels) and domestic (mainly heat) applications [9–11]. A significant part of the traditional use of biomass (firewood, sometimes animal waste) in developing countries is non-commercial and used for cooking and heating, generally by the poorer part of the population. The non-commercial use of biomass is poorly mapped and as a result, the contribution of biomass to the energy supply is not accurately known [12]. Solid biomass is one of the primary energy sources (mainly used for cooking) in many developing countries, especially in rural sub-Saharan Africa and South Asia. Traditional biomass use is not sustainable because it may result in soil quality degradation by depriving soil nutrients and burning it in inefficient cooking stoves can cause high levels of indoor air pollution. Most households in sub-Saharan Africa rely on the traditional use of biomass to meet their daily cooking needs. In countries such as the Democratic Republic of Congo, Ethiopia, Tanzania, Nepal and Nigeria, more than 80% of the total energy

demand is met through biomass energy sources. In developing countries, biomass is used to some extent in industries such as brick manufacturing [13, 14].

Crude oil is an excellent source of energy, it is easily transported and energy-rich, it is one of the most energy-dense fuels. The energy density of crude oil and methane are 42 MJ/kg and 55 MJ/kg, respectively. Even coal has a good energy density (27–32 MJ/kg). Compared to these fossil fuels, the energy density of biomass ranges from 8 MJ/kg for greenwood to 20 MJ/kg for dry plant matter. Biomass has low bulk density and causes a major problem during storage, handling and transportation for further processing. The bulk density of biomass varies from around 40 kg/m^3 for loose straw and bagasse, in the range of 80–100 kg/m^3 for agricultural residues and 150–200 kg/m^3 for woody biomass to the highest levels of around 250 kg/m^3 for some wood residues. This translates to needing more biomass to produce for the same amount of heat or power and higher transportation costs, processing costs, etc. [15, 16].

Most of the biomass used today is derived from agricultural and forestry biomass. Agricultural biomass includes the food-based portion and the non-food-based portion of crops. The food-based portion comprises oils and simple carbohydrates of crops such as corn, sugarcane and beet. The non-food-based portion comprises complex carbohydrates of crops such as the leaves, stalks, seed hulls, orchard trimmings, nutshells, rice husk, bagasse, coffee pulp and straw. Forestry biomass includes wood residues associated with the production of timber in the forest, as well as the processing of timber into their final products [17, 18].

The comparatively low energy density of biomass means that issues associated with land use must be taken into consideration. Expansion of land use for biomass production can lead to a high potential for environmental damage due to deforestation, erosion, nutrient runoff, emissions, etc. This reduces any potential benefit of using biomass. Large-scale cultivation of non-food perennial energy crops for bioenergy feedstock is feasible when sufficient land areas are available. The best land for agriculture must be used to grow food crops. To avoid food versus energy conflict, it is important to use infertile/marginal lands for energy crop cultivation with little use of fertilizer or pesticides and potentially needing minimal water. Energy crops should not be grown at the expense of biodiversity [15]. For productive agricultural systems, prospects of biomass production based on the factors provided by nature such as light, soil, water and nutrients with soil and water are considered as the most crucial natural resource constraints. Identifying land areas with minimal disturbance to food production is critical for technically and economically feasible biomass production. To achieve sustainable large-scale biomass production, marginal or abandoned agricultural land has been widely considered as important. Energy crops are adaptive to marginal or abandoned agricultural land. Compared with food crops, energy crops such as switchgrass and miscanthus generally require much less water to grow and are suitable to partially replace the dryland crops [19]. Beyond the vast areas of land needed to grow energy crops, the long-term impact of soil quality due to repeated removal of biomass is a concern. Water usage is another major concern. Biomass may have a moderate carbon footprint, but its water footprint is enormous. Only a small percentage of the biomass produced by photosynthesis is currently being cultivated, harvested and used, but how much can be used sustainably? As with any approach to energy generation, the massive demand for energy stresses the need to be careful in considering the use of biomass for energy generation [15].

Plants grow through photosynthesis by absorbing atmospheric CO_2 and producing carbohydrates that form the building blocks of biomass. Water and sunlight are the other two key ingredients of photosynthesis, which typically convert less than 1% of the energy available in sunlight to chemical energy. When biomass burns,

it releases CO_2 back to the atmosphere that the plants had absorbed recently. i.e., the burning of biomass does not add to the total CO_2 inventory of the earth. Therefore, biomass is considered the most important source of green carbon or carbon-neutral fuel. In order to decide the true carbon neutrality, the overall biomass chain needs to be considered, including cultivation (for energy crops), harvesting, drying, storage, transportation and processing. These represent a significant cost, energy needs and CO_2 emissions sources [7]. All these factors must be taken into consideration in life-cycle analysis for sustainability. Biomass plays an integral part in the overall sustainable energy solution, but it is not a panacea. Biomass for biochar production makes land usage more complex. The effect is not only the land usage for biomass supply but also the impacts of adding biochar to soils. The impacts may include increased productivity and, hence, reducing the land area required for food production as well as the potential for biochar to make previously unmanaged or marginal land economically productive, thereby facilitating the conversion of marginal land to agriculture [15, 20].

Besides heat and electricity generation, biomass can be used as a feedstock for biofuel production with technologies already available on the market. Biofuels are liquid or gaseous fuels produced from biomass and can be used as a replacement or blended with fossil-based fuels for different applications. This makes biomass very valuable within future energy systems based on renewable/sustainable sources of energy. The biomass potential for the energy markets needs to be evaluated without affecting the demands for food and fodder as well as for raw materials. The use of biomass has been debated critically on the background of the ongoing environmental and sustainability discussions.

2.1 Biomass classification

Biomass can be classified into different groups depending upon the origin where it is produced, including agricultural biomass, forestry and wood processing residues, dedicated energy crops (crops cultivated solely for energy), aquatic biomass, sewage sludge, digestate (remains of anaerobic digestion), industrial crops, animal, industrial, municipal and food waste. Biomass is also classified based on the chemical composition as carbohydrates, lignin, essential oils, vegetable oils, animal fats and natural resins (gums) [21–24].

Agricultural biomasses are natural products of all agriculture. These include a wide range of agricultural crop residues (the non-food based portion of crops) that are not harvested for commercial use or byproducts from harvesting or processing, such as corn stover (leaves, stalks, husks and corn cobs left in a field after harvest), sugarcane bagasse, straw residues (barley, oats, rice, rye, wheat) from grain production, waste from other food crops, horticulture and food processing. Other plant residues include husks of grains and seeds, coconut shells, fruit stones and nut shells. Straw and other agricultural residues usually have a high ash content and contain chlorides and potassium compounds, which can cause high levels of corrosion in boilers. The problems of corrosion and slagging can be mitigated by burning biomass at lower temperatures [1, 18].

Forestry and wood processing residues include trees not harvested during logging (trees that are not valuable as timber, such as imperfect commercial trees, dead wood and other non-commercial trees), biomass removed during logging (such as crowns and branches from fully-grown trees) in commercial forests, waste from forest and wood processing (such as palm kernel shells, wood pellets, woodchips, leaves, barks, lumps and sawdust) as well as materials removed during forest management operations (such as trunks of smaller trees removed during thinning, dead and dying trees removed during forest control) [1, 25].

Dedicated energy crops are another expanding and potentially larger source of biomass. Energy crops are low maintenance and high yield crop species that give the maximum energy yield. These are grown specifically for their fuel value (energy applications) on marginal land unsuitable for agriculture. Several crops can be readily used as energy sources. There are two types of energy crops, herbaceous and short-rotation woody. Herbaceous energy crops include perennials that are harvested annually after reaching maturity. It takes 2–3 years to reach complete production. These are grasses such as switchgrass, miscanthus, bluestem, elephant grass, bamboo and wheatgrass. They do not require replanting for 15 years or more. The drawback with most non-woody energy crops is that their chemical properties generally make them less suitable for combustion due to the high ash and salt content [18, 26, 27]. The woody crops are grown on short rotations, generally with more intensive management than timber plantations. These fast-growing hardwood trees are harvested within 5–8 years of planting. These crops include poplar, willow, maple, cottonwood, black walnut and sweetgum [25, 27].

Different kinds of algae, plants and microbes found in water form another class of biomass called aquatic biomass. Aquatic biomasses include macroalgae, microalgae, seaweed, kelp, water hyacinth and aquatic plants [24]. Animal, industrial, municipal and food waste and sewage sludge are other important sources of biomass. Animal and human waste biomass includes waste resulting from farm and processing operations, manure of different animals, cooked or uncooked food, fruits, paper and pulps. When these waste materials are treated and converted to useful energy products, not only energy is being produced, but the problem of disposing of these materials is also reduced to a certain extent. Industrial waste involves waste from various manufacturing and industrial processes like paper sludge from paper industry, sugar cane residues from sugar mills, waste from food processing industry, waste oils, textile industry waste and others. Animal and human waste biomass and industrial biomass are categorized differently because industrial biomass may contain different types of toxic chemicals and harmful additives. In contrast, animal and human waste are primarily free of these types of harmful materials [28]. Municipal solid waste (MSW) includes waste from residential, commercial and industrial sectors that contains a significant amount of biomass (such as paper, cardboard, wood, food, leather, textiles and yard trimmings) with energy content. Food waste contains residues from food and drinks manufacture, preparation and processing, post-consumer waste, animal fat, used cooking oil etc. Other biomasses include Industrial crops (crops developed to produce specific chemicals or feedstocks such as kenaf), construction and demolition waste, building material waste, abandoned furniture etc. [18, 25].

2.2 Composition of biomass

The chemical composition of biomass is different from fossil fuels. The most abundant biomass on the earth is LCB, including agricultural biomass, forestry and wood processing residues, dedicated energy crops, industrial crops and food waste, hence, the following sections primarily focus on LCB. Plant biomass is a complex mixture of polymers consisting of three key elements: 42–47% of carbon (C), 40–44% of oxygen (O) and 6% of hydrogen (H), all percentages in dry matter, whose total content generally reaches above 95% [24, 29]. Plant biomass also contains macronutrients such as nitrogen (N), phosphorus (P), potassium (K), magnesium (Mg), sulfur (S), calcium (Ca). These inorganics are required in relatively high amounts (> 0.1% of dry mass) and essential for plant life cycle and biomass production. In addition, plants need a small amount of micronutrients (essential elements required in relatively small amounts, 100 mg/kg of dry mass)

such as chlorine (Cl), iron (Fe), boron (B), manganese (Mn), zinc (Zn), copper (Cu), molybdenum (Mo), nickel (Ni). Trace elements like sodium (Na), silicon (Si), selenium (Se), titanium (Ti), vanadium (V), cobalt (Co), aluminum (Al) and other heavy metals may also be present in plant biomass at different levels depending upon the plant species and the environment [24, 30–32].

Plant biomass has a carbon-to-oxygen (C/O) ratio of almost one. Because of this high oxygen level, the energy density of biomass is relatively low relative to fossil fuels. The major component of plant biomass is cellular lignocellulosic material, which is the non-starch fibrous part of the plant materials. Cellulose, hemicellulose and lignin are the three major constituents of LCB constituting the cell wall of plants [5, 15, 21]. The main component of the plant cell wall is cellulose (a linear homogeneous structural polysaccharide composed of D-glucose units with molecular weight (MW) > 100,000), which provides structural support. The second most abundant polymer in LCB is hemicellulose, a ramified heterogeneous structural polysaccharide composed of D-xylose, L-arabinose, D-mannose, D-galactose and D-glucose units. The third most abundant polymer in LCB is lignin, a phenylpropanoid polymer composed of guaiacyl, p-hydroxyphenyl and syringyl units [33, 34]. The compositions (cellulose, hemicellulose and lignin) of common LCB are listed in **Table 1**. Cellulose macromolecules form tough microfibers that function as the skeleton material of the cell wall. The inner space is packed with branched amorphous hemicellulose and lignin linking material. Cellulose connects with hemicellulose or lignin mainly through hydrogen bonds, while hemicellulose connects with lignin via both hydrogen and covalent bonds. Lignins and carbohydrates link tightly together in lignin-carbohydrate complexes, which results in residual carbohydrate or lignin fragments in extracted lignin or hemicellulose samples. Wooden biomasses are usually rich in cellulose, leaves and grasses are rich in hemicellulose and the shells are mostly rich in lignin. Cellulose is thermally more stable than hemicellulose. Knowledge of cellulose, hemicellulose and lignin composition in LCB can be helpful in controlling the product chemistry [32, 37].

In addition to the three major components, some other compounds present in LCB include inorganic compounds and organic extractives. These exist as non-structural components that do not constitute the cell walls or cell layers. Organic extractives can be extracted by nonpolar solvents (such as toluene and hexane) or polar solvents (such as water and alcohol). These include fats, waxes, proteins, terpenes,

Lignocellulosic material	Cellulose %	Hemicellulose %	Lignin %
Hardwood stems	40–55	24–40	18–25
Softwood stems	45–50	25–35	25–35
Almond shells	29.0–31.1	28.0–38.0	27.7–35
Corncobs	45	35	15
Grasses	25–40	35–50	10–30
Wheat straw	30	50	15
Flax straw	36.70	34.40	28.90
Leaves	15–32	80–85	0
Sugar cane bagasse	32–44	27–32	19–24
Coastal Bermuda grass	25	35.7	6.4
Switch grass	45	31.4	12

Table 1.
Composition of common LCB [35, 36].

simple sugars, gums, resins, starches, alkaloids, phenolics, pectins, glycosides, mucilages, saponins and essential oils. Often these compounds are responsible for the smell, color, flavor and natural resistance to rotting of some species. A common classification divides them into aliphatic compounds (mainly fats and waxes), terpenes and terpenoids, and phenolic compounds. The inorganic compounds constitute less than 10% by weight of LCB, forms ash in the pyrolysis process [21, 32].

LCB contains varying amounts of inorganic materials (including alkali and heavy metals, chlorine, phosphorus and sulfur) collectively called ash. The ash contents in LCB depend on feedstock type, the environment in which it was grown, fertilizer use, and contamination with soil particles. Typically, softwood and hardwood have ash contents below 1 wt%, short-rotation woody crops have around 2 wt%. Herbaceous crops have high levels of potassium and silicon and ash contents up to 7 wt%. Ash content is also not uniformly distributed within biomass; bark has higher concentrations of inorganics [38]. Water in wet biomass contains in three phases: bound water (hygroscopic or adsorbed, in cell walls, believed to be hydrogen-bonded to the OH groups of primarily cellulose and hemicelluloses of the biomass); free or unbound water (liquid water in cell cavities or voids of the biomass if the moisture content is higher than the fiber saturation point); and water vapor which fills the cell cavities or voids of the biomass [23]. Depending on the type of LCB, the cellulose, hemicellulose and lignin content fall in the range 40–60%, 15–30% and 10–25%, respectively. Both cellulose and hemicellulose are carbohydrates (polymers of sugars) and can be hydrolyzed into fermentable sugars, which in turn can be converted into fuels and chemicals. Wood biomass contains much higher amounts of the three main components (~90%), while agricultural and herbaceous biomass contains more extractives and ash [21, 32].

2.2.1 Cellulose

Cellulose is the most abundant organic polymer on the planet. It is one of the main structural constituents of the lignocellulose cell wall of green plants and is found in an organized fibrous structure. Cellulose is a polysaccharide consisting of d-glucose (pyranose) units linked by β-1,4 glycosidic bonds. The β-linkages in cellulose form linear chains. The degree of polymerization (DP) is about 300–15,000, depending on the plant variety. Cellobiose is the repeating glucose disaccharide of cellulose. Because of its long and linear molecules, cellulose does not dissolve readily in water. The chemical formula of cellulose can be written as $(C_6H_{10}O_5)_n$, where n is the DP. It is the long flexible natural polymer in fibers that predominately gives trees and wood of their strength. Cellulose chains are grouped to form cellulose fibers, which are interlinked by hydrogen bonds and van der Waals forces, resulting in long microfibrils. These microfibrils are arranged as a mesh in the cell wall, giving it strength and shape. Hemicelluloses and lignin cover the cellulose microfibrils. Cellulose is highly stable and resistant to chemical attack because of the high degree of hydrogen bonding between cellulose chains [15, 32, 37, 39, 40].

The hydroxyl (OH) groups present on the inner and outer surfaces of cellulose forms intra- and intermolecular hydrogen bonds, which stiffens the chains and promotes aggregation into a crystalline structure. The crystallinity and stabilization of cellulose mainly originate from the presence of OH groups. As three OH groups are available in each glucose molecule, the inner and outer surfaces of cellulose are covered by OH groups. These OH groups make hydrogen bonds with other OH groups and other groups (such as O, N and S) available in lignocelluloses. The crystalline structure of cellulose leads to chemical stability and provides strength

and toughness to the roots and stems of a plant. Cellulose molecules have different orientations throughout the structure resulting in different levels of crystallinity. The energy of hydrogen bonds in water and cellulose is 15 and 28 kJ/mol, respectively and the energy of van der Waals in water is only 0.15 kJ/mol. The strength of cellulose mainly originates from the existence of hydrogen bonds rather than van der Waals forces. The interchain hydrogen bonds introduce order (crystalline) or disorder (amorphous) into cellulose structure, creating two forms of cellulose: crystalline and amorphous. Cellulose requires severe hydrolysis conditions for breaking it into simple glucose units due to its crystalline structure. As suggested by some authors, cellulose consists of three regions: true crystal, subcrystalline (disordered structure in true crystal regions) and or noncrystalline (subscrystalline) regions. The crystallinity index (CrI) usually characterizes the crystallinity of cellulose, increasing CrI leads to decreasing chemical and biological hydrolysis of cellulose [41, 42].

2.2.2 Hemicellulose

Hemicellulose is the second most abundant natural organic polymer after cellulose on the planet. In contrast to the linear or one-dimensional structure of cellulose, hemicellulose is a two-dimensional polymer composed of short chain branched heteropolysaccharides side connections. It is one of the major constituents of plant cell walls and is strongly linked to the surface of cellulose microfibrils. Hemicellulose is a random heterogeneous polysaccharide of pentoses (xylose and arabinose), hexoses (galactose, glucose and galactose) and their acidified derivatives such as glucuronic and galacturonic acids. Because of the branched nature, hemicellulose is amorphous, which is relatively easy to hydrolyze (by dilute acids, bases and hemicellulose enzymes) to its constituent sugars compared to cellulose. The content and structure of hemicellulose differ among LCB. The general nature of the hemicellulose structure depends on the type of plant, with the result that certain types of lignocellulosic materials are easier to hydrolyze than others. The various sugar units are arranged with different substituents and in different proportions. Hemicellulose has a degree of polymerization of 80–200. It is much smaller than cellulose, with a relatively low MW (< 30,000). The general chemical formula of hemicellulose can be written as $(C_6H_8O_4)_m$, where m is the DP. Lateral chains of hemicellulose form the tightly bound network through hydrogen bonds with cellulose microfibrils. It makes a highly rigid matrix of the cellulose-hemicellulose-lignin with interaction of lignin via covalent bonds [15, 32, 37, 39, 43, 44].

The different groups of polysaccharide molecules such as xylans, mannans, galactans and arabinogalactans make up hemicellulose. Xylan is the most common polysaccharide in hemicellulose consists of backbone chains that contain a varying number of D-xylopyranose linked by β –1,4 linkage (70–130 in softwood xylan and 150–200 in hardwood xylan). Mannans are made up of β–1, 4-linked D-mannose backbone mixed with D-glucose and D-galactose residues. These compounds include mannan (made up of mannose monomer), galactomannan (made up of mannose and galactose monomers), glucomannan (made up of mannose and glucose monomers), glucuronic acid (made up of mannose and glucuronic monomers). Galactan is composed of repeating galactose units as a polymer. Arabinogalactans consist of arabinose and galactose monosaccharides. The dominant hemicellulose component in hardwood, agricultural residues and herbaceous crops is xylan, with a small degree of acetylation and arabinose side groups. The main form of hemicellulose in softwood is glucomannan, highly acetylated and containing glucose and mannose [15, 32, 37, 44].

2.2.3 Lignin

After cellulose and hemicellulose, lignin is the third largest heteropolymer that occurs predominantly in the cell walls of woody plants. It is the main non-polysaccharide constituent of plant biomass and the amount of lignin vary widely with plant species. Lignin primarily consists of macromolecules that contain highly branched phenolic compounds. Lignin is composed of three different phenyl propane (three-carbon chain attached to rings of six carbon atoms) monomers, including coniferyl alcohol (guaiacyl propanol), p-coumaryl alcohol (p-hydroxy-phenyl propanol) and syringyl alcohol (sinapyl alcohol). The phenyl propane monomeric units in lignin are linked in different ways (alkyl-aryl, alkyl-alkyl and aryl-aryl ether bonds): through oxygen bridges between two propyl and phenyl groups, between a phenyl and a propyl group or through carbon–carbon bonds between the same groups. Lignin is generally considered as the natural phenolic glue that tightly binds cellulose and hemicellulose of LCB together; thus, leading to a strong cell wall structure and making it insoluble in water. The functions of lignin, an amorphous and highly complex aromatic hydrophobic biopolymer, are (a) to provide mechanical strength to the plants. It plays a cementing role for linkages (van der Waals, hydrogen bond and covalent bond) between cellulose and hemicellulose to form a 3-dimensional structure of lignin-polysaccharide complex in cell wall leading to a strong cell wall structure; (b) to provide sealing for water-conducting system linking roots with leaves. Polysaccharide components of the plant cell wall are hydrophilic and permeable, while lignin is hydrophobic and impermeable. The cross-linking between polysaccharides and lignin is a barrier for water absorption to the cell wall that create vascular tissues for efficient conduction of water in plants. Lignin exists in all vascular plants; and (c) to protect plants against biodegradation. It forms a natural protective shield protecting cellulose and hemicellulose in plants and makes plants resistant to pathogens, oxidative stresses and biodegradation by enzymes and microorganisms [42, 45–47].

The distinctive feature that differentiates lignin from cellulose and hemicelluloses is the presence of aromatic monomers. Lignin is less polar than cellulose or hemicellulose. Physically, cellulose microfibrils encrust hemicellulose whose empty spaces are filled up with lignin. Lignin is embedded within hemicellulose to provide additional rigidity to the plant. These lignin-hemicellulose fibers characterize woody plants, whereas the fibers in herbaceous plants are more loosely bound, indicating a lower amount of lignin [15, 35, 47]. The lignin content of plants varies with species and age. It is originated from not only content but also monomeric units and linkage types. The lignin content of softwood is in the range of 25–40%, which is higher than that of hardwood (18–25%), herbaceous crops (10–20%) and annual plants (10–12%). LCB with lignin percentage up to 40% has been reported. Softwood lignin is primarily made from coniferyl alcohol (>95%), with the rest consisting of coumaryl alcohol derived units and trace amounts of syringyl alcohol derived units. Hardwood lignin is composed of coniferyl alcohol and syringyl alcohol derived units in varying ratios. Lignin in grassy biomass has all three types of monomers. Annual plants lignin is composed of coumaryl alcohol. The elemental composition of lignin is approximately 61–65% carbon, 5–6% hydrogen and the remaining is oxygen. The carbon to oxygen (C/O) atom ratio for lignin is higher than 2:1, which is at least double that of hemicellulose and cellulose, where the C/O ratio is nearly 1:1. Therefore, lignin is a more energy-dense substance than polysaccharides. Lignin structure has many polar and hydroxyl groups allowing the establishment of strong intramolecular and intermolecular hydrogen bonds. These make lignin insoluble in any solvents except alkaline solutions [23, 37, 42, 44, 48].

3. Analysis of biomass

Analysis of biomass feedstock is an integral part of understanding the behavior of biomass in energy use. The proximate analysis, ultimate analysis and higher heating value (HHV) of biomass can provide a clear understanding of its thermochemical conversion characteristics.

3.1 Proximate analysis

The proximate analysis provides information on the biomass in terms of volatile matter (VM), ash content, fixed carbon (FC) and moisture (M). VM of biomass is the condensable and non-condensable gases released from the biomass during heating. The amount of VM depends on the heating rate and the final temperature to which biomass is heated. Ash is the solid residue left after the biomass is completely burned. FC shows the percentage of biomass burned in the solid states, while VM indicates the percentage of biomass burned in the gaseous state. The ash content indicates the quantity of non-combustible ash remaining on the fire grates or ash pit or entrained with flue gases. These are of fundamental importance for biomass energy use and such information for specific LCB are depicted in **Table 2**. Such data provides the furnace designer with essential information for the furnace design, including sizing and location of primary and secondary air supplies, refractory, ash removal and exhaust handling equipment etc. [49, 50].

The composition of ash depends on the type of biomass which includes mostly inorganic residues such as silica, aluminum, iron, calcium and small amounts of magnesium, titanium, sodium and potassium may also be present. Even though ash content of biomass is usually very small, it may play a significant role in biomass combustion or gasification if biomass contains alkali metals (such as potassium) or halides (such as chlorine). Straw, other agricultural residues and grasses generally contain potassium compounds and chlorides are particularly susceptible to this problem and can cause severe agglomeration, fouling and corrosion in boilers or gasifiers. The ash obtained during biomass conversion does not necessarily come from biomass itself but also from other sources such as contamination as well. Biomass can pick up a considerable amount of dirt, soil, rock and other impurities during collection and handling. These also partly contribute to ash content. FC is

Lignocellulosic Material	VM	FC	Ash	Moisture
Hardwood	72.3	25	2.7	7.8
Softwood	70	28.1	1.7	8.8
Almond shells	79.7	4.9	2.3	8.7
Corncobs	80.6	18.2	1.2	9.7
Reed canary grass	82.5	12.1	5.5	4.7
Wheat straw	63	23.5	5.5–13.5	8.5
Flax straw	80.3	8.8	3.0	7.9
Hazelnut seedcoat	71.20	27.0	1.8	6.8
Sugar cane bagasse	84.00	1.64	4.5–9	8.5
Elephant grass	65	14.66	6.0	10

Table 2.
Proximate analysis (wt%) of common LCB [35].

the solid carbon (non-volatile) in the biomass that remains in the char in the pyrolysis process after devolatilization. The amount of FC is related to VM, moisture (M) and ash by the equation: $FC = 1 - \mathrm{M} - VM - ASH$ [18, 49].

The relationship between FC and charcoal yield in biomass is positive, while VM and ash relate negatively to charcoal yield. It is expected that the greater biomass VM lead to greater gas production instead of the solid phase. Moisture content will have a significant impact on the biomass conversion process. High moisture content is a major concern in biomass. Biochemical conversion processes can use biomass with high moisture content, while thermochemical conversion processes generally require biomass with low moisture content. However, gasification processes require some moisture to produce hydrogen and the amount of hydrogen produced will increase with moisture content. The moisture content of some biomass, such as water hyacinth, can be very high (> 90%). As the energy used in evaporation is not recovered, moisture drains much of the deliverable energy during conversion [49–51].

3.2 Ultimate analysis

The ultimate analysis provides the composition of biomass, including major elements (C, H, O, S, N and Cl), moisture and ash on a gravimetric basis. The ultimate analysis of common LCB are listed in **Table 3**. The ultimate analysis is generally reported on a dry and ash-free basis. These are useful in understanding biomass processes and performing mass balances on biomass conversion processes. Elemental chemical composition, moisture, ash and volatiles are essential for thermal/ thermochemical conversions of biomass. Additional information on the polymeric composition of biomass is important for conversions like torrefaction, pyrolysis and gasification. A typical ultimate analysis of the biomass in terms of its basic elements, moisture (M) and inorganic constituents (ASH) can be written as: $C + H + O + \mathrm{N} + \mathrm{S} + ASH + \mathrm{M} = 100\%$. The hydrogen or oxygen content in the ultimate analysis includes only the hydrogen and oxygen present in the organic components of the biomass it does not include the hydrogen and oxygen in the moisture. The moisture in the biomass is expressed separately as M. The ultimate analysis is useful in calculating the quantity of combustion air required to sustain the combustion reactions. Generally, sulfur and nitrogen content of biomass is very low. As a result, biomass produces minimal SO_X and NO_X pollutants. Particulate emissions of unburned carbon in the flue gases can present pollution problems [49, 51].

Lignocellulosic Material	C	H	N	S	O
Hardwood stems	48.6	6.2	0.4	—	41.1
Softwood stems	52.1	6.1	0.2	—	41.0
Almond shells	54.7	7.5	0.3	0.3	37.4
Corncobs	43.6	5.8	0.7	1.3	48.6
Grasses	48.3	5.7	0.8	—	39.4
Wheat straw	53.9	7.0	3.0	—	36.1
Flax straw	43.10	6.20	0.68	0.09	49.90
Hazelnut seedcoat	52.90	5.6	1.4		42.7
Sugar cane bagasse	45.13	6.05	0.3	—	42.77
Switch grass	48.6	5.5	0.5		39.5

Table 3.
Ultimate analysis (wt%) of common LCB [35].

4. Biomass conversion

Biomass conversion is the key step to produce heat, biofuels or chemicals from LCB. Biomass can be converted to these products through chemical, biochemical and thermochemical conversion processes. Selection of the conversion process depends on number of factors, including the desired form of end products (heat, biofuels or chemicals), biomass feedstock (type, quantity and characteristics) available, environmental standards, policy, economic conditions and specific factors related to the project. In most situations, the selection is based on two main factors, i.e., desired form of end products and the available feedstocks [5, 21, 52]. The moisture content of biomass primarily determines the conversion process for the selected biomass. Thermochemical conversions like pyrolysis, gasification or combustion are ideal for dry biomasses such as wood or straw. These processes are often unsuitable for wet biomass because of low energy density due to high moisture content. The high moisture content significantly increases the transportation cost and energy cost for drying. Wet conversion processes such as hydrothermal processing and biochemical processing (fermentation and anaerobic digestion) have gained growing attention and are more suitable to process high moisture content biomass like aquatic biomasses, sewage sludge, food waste and manures. Despite consuming less energy, biochemical conversion processes require more time compared to thermochemical conversion processes. Subsequently, much attention has been placed on hydrothermal processing, which is more cost-effective than conventional thermal drying followed by thermochemical conversion. The additional parameters (like cost and feasibility of drying etc.) need to be considered when selecting the correct conversion process, primarily if the moisture content lies between wet and dry regions [6, 21, 53, 54]. Biomass has substantial quantities of free and bound water. Wet biomass requires drying before pyrolysis, gasification or combustion; hence, additional energy and facilities are needed. Drying biomass outside the pyrolysis reactor is beneficial (produce pyrolysis vapor with high calorific value and bio-oil with low water content) [23].

The important biochemical conversion processes include anaerobic/aerobic digestion, fermentation and enzymatic or acid hydrolysis. In biochemical conversion, biomass molecules are broken down into smaller molecules by bacteria or enzymes. This process is much slower than the thermochemical conversion process but does not require much external energy. In anaerobic digestion, bacteria take oxygen from the biomass itself instead of atmospheric oxygen. The products of anaerobic digestion are biogas (a mixture of methane, carbon dioxide) and solid digestate. Only 5–10% of the feed into the digester is digested by the anaerobic bacteria. The digestate consists of remaining indigestible material. Aerobic digestion, commonly known as composting, takes place in the presence of oxygen. It uses different types of microorganisms that access oxygen from the air, producing carbon dioxide, heat and solid residue (compost). In fermentation, starch is converted into sugars using acids or enzymes. Then sugar is converted into ethanol or other chemicals with the help of yeast. The fermentation of lignocellulosic feedstock requires additional pretreatment (hydrolysis) to breakdown the cellulose and hemicellulose into simple sugars. Hydrolysis can be achieved by the use of acids, enzymes or hydrothermally [5, 21, 52].

The lignin is not converted and is left for thermochemical conversion. Major thermochemical conversion processes include combustion, gasification, pyrolysis, torrefaction and hydrothermal processing. These are further discussed in the following sections. Thermochemical conversions generally offer many advantages over biochemical conversions, such as handling a wide variety of feedstocks, better

conversion efficiency, high energy efficiency and shorter reaction times. As a result, in recent years, thermochemical conversions have received greater attention for biofuels production [3, 21].

5. Thermochemical conversion

There are many types of thermochemical conversion processes through which biomass is converted to solid, liquid and gaseous products. Thermochemical conversion processes use high temperatures to breakdown the bonds of organic matter. Thermochemical conversion routes can be classified according to the oxygen content used in the process, including combustion (complete oxidation), gasification (partial oxidation) and pyrolysis (thermal degradation in the absence of oxygen). Torrefaction is also performed in the absence of oxygen. Hydrothermal processing is an alternative route to process wet biomass using heat and pressure in the presence of water, which can also be considered a thermal degradation in the absence of oxygen. The typical products of thermochemical conversion of biomass are carbon-rich solid residue (biochar), condensable vapors (bio-oil or tar) and non-condensable gases. The distribution of products (biochar, bio-oil/tar and gases) depends primarily on the conversion process [21]. A brief description of biochar, bio-oil and gases are given below.

Biochar - Biochar is a porous carbonaceous material with a high degree of aromatization and strong antidecomposition ability. The physical, chemical and mechanical properties of biochar will depend on the feedstock material characteristics and pyrolysis conditions used for the production of biochar. It has a wide range of potential applications in various agronomic and industrial sectors. Biochar is used in agriculture to upgrade the soil quality, in waste treatment to remove organic contaminants, heavy metals and different types of dyes and pigments from textile industries and in power generation as a fuel. The most successful approach for high-yield biochar production is via slow pyrolysis [21].

Bio-oil - Bio-oil is a dark brown, free-flowing organic liquid mixture. It generally comprises of 15–35 wt% water (resulting from both the original moisture and as a pyrolysis product) and a mixture of organic compounds, such as acids, alcohols, ketones, aldehydes, phenols, ethers, esters, sugars, furans, alkenes, nitrogen compounds, miscellaneous oxygenates and solid particles. The final water content of bio-oils depends on the initial moisture content of biomass feedstock and water formation during pyrolysis. Water cannot be removed from bio-oil by conventional methods like distillation. Bio-oil has a low (15–20 MJ/kg) HHV in comparison to conventional petroleum fuel HHV of 42–45 MJ/kg due to the increased oxygen content (35–40 wt% on a dry basis). Bio-oil density is approximately 1200 kg/m^3; the viscosity ranges from 25 to 1000 cP (depending on the composition). It is acidic in nature (pH value of 2–4) due to the presence of organic acids such as formic and acetic acid and, hence, corrosive. Bio-oil has a large amount of oxygenated compounds and organic material; it is highly polar. As a result, bio-oil is hydrophilic. A distinct aqueous phase is only observed with bio-oil having water content in the range 30–45 wt% [23, 55]. Bio-oil will not mix with hydrocarbon liquids. Bio-oil has a complex mixture of oxygenated compounds that provide the potential and challenge for its utilization. It has a range of uses in energy applications, can be used in boilers for heat and power generation, cofired with natural gas/coal in power plants or blended with other fuels such as ethanol or gasoline. Bio-oil can be converted into fuels (ethanol and diesel) and chemicals through hydrocracking/hydroprocessing [56].

Non-condensable gases – Gases produced in biomass pyrolysis may consist of carbon dioxide (CO_2), carbon monoxide (CO), hydrogen (H_2), methane (CH_4), ethane (C_2H_6) and ethylene (C_2H_4), and small amounts of other gases, such as propane (C_3H_8), ammonia (NH_3), nitrogen oxides (NO_X), sulfur oxides (SO_X) and alcohols of low carbon numbers. The composition of the non-condensable gases will be determined by the pyrolysis temperature and the vapors condensing temperature. Lower pyrolysis temperatures (such as torrefaction) result in higher amounts of CO and CO_2, while higher pyrolysis temperatures result in increased content of CH_4 and H_2.

5.1 Combustion

Combustion is simply the burning of biomass in air. Chemically it is high-temperature exothermic oxidation of biomass in the presence of oxygen. Complete combustion of biomass involves the production of heat due to the oxidation of carbon and hydrogen of biomass to CO_2 and H_2O, respectively. The process consists of consecutive heterogeneous and homogeneous reactions. Biomass combustion basically depends on the properties of the feedstock and particle size, temperature and combustion atmosphere. Char (contains some organic carbon) and ash (typically includes inorganic oxides and carbonates) are the solid byproducts of combustion. Combustion temperatures are usually in the range of 700–1400°C [52, 57].

Energy stored in biomass can be converted into heat and power via combustion. The chemical composition and the combustion properties of biomass vary considerably depending on the biomass type. A wide range of biomass sources can be considered for combustion. Seasonal, regional variances and parts of the plant (bark, branches and leaves etc.) of the woody biomass (wood chips, wood pellets and waste woods etc.) can result in differences in the chemical composition of the feedstock. Straw is also considered as having potential as an alternative feedstock. Straw is essentially a waste product from agricultural crop production. This feedstock does not compete with agricultural products for the limited land resources. Besides wood and straw, a wide variety of waste products such as rice husks, wheat bran, peanut shells, coffee grounds, bagasse, etc., can be used as feedstock. These can be used as an inexpensive fuel to produce heat or electricity needed for industrial processes. The best quality fuels contain high amounts of carbon and hydrogen and low amounts of other elements (oxygen, nitrogen, sulfur and trace elements). Biomass usually contains higher levels of oxygen than fossil fuels. Impurities such as sulfur and nitrogen are associated with the emission of SO_X and NO_X. Trace elements such as potassium and sodium can cause fouling; chlorine leads to corrosion and silica causes excessive wear to milling equipment [52, 57].

Fresh woodchips can contain 50% moisture and leaves can be over 90% moisture. Most furnaces and boilers recommended biomass with less than 20% moisture. It is extremely difficult to maintain combustion with a moisture content of more than 55%. Higher levels of moisture affect combustion efficiency and increase the amount of smoke emitted. The water content also increases the combustion time of a biomass particle and, thus, extends the required residence time in a boiler/furnace. Torrefaction upgrades biomass by removing lighter volatiles and moisture. It improves the heating value of biomass, increases the hydrophobicity and stability and, thus, can be stored under the open sky [52, 57].

Combustion can be split into four stages: drying, pyrolysis (devolatilization), volatiles combustion and char combustion. When biomass particles enter a hot environment, moisture in the particles starts to evaporate. On further heating, volatile gases and tars are released from biomass particles, followed by the combustion of volatiles. The remaining char will essentially retain its original shape. In the

char combustion stage, char reacts with oxygen to form mainly CO_2 (and CO due to incomplete combustion) and ash remains after combustion is completed. Detailed chemical reactions kinetics that takes place during biomass combustion are complex [52, 57, 58].

The initial combustion stage requires heat to evaporate moisture; hence, it is necessary to have biomass with minimal moisture content. Biomass has a significantly higher volatile matter content compared to coal and the fixed carbon to volatile matter (FC/VM) ratio is significantly low. Lower values of the FC/VM ratio leads to high ignition behavior. Biomass releases VM at a lower temperature and more rapidly than coal, thus, reducing ignition temperature compared to coal. Proper design of the air supply is important due to the faster release of VM in order not to delay combustion. Combustion of VM is fast compared to combustion of solid charcoal and a low ratio of FC/VM decreases the residence time in the boiler/furnace [52, 57, 58].

Incomplete combustion results in the formation of intermediates, including pollutants such as CO, CH_4 and particulate matter (PM). Ash handling, high emissions of NO_X, SO_X, CO_2 and particulate matter make combustion environmentally challenging. Biomass is more corrosive, tends to foul heating surfaces, ash from biomass tends to agglomerate. The boilers have to be redesigned to burn biomass properly. Depending on the condition and combustion properties of the biomass to be burned, different furnace designs and combustion parameters can be selected to ensure optimum efficiency. Direct combustion is currently the principal method of generating electricity around the world [52, 57, 58].

5.2 Gasification

Biomass gasification is a thermochemical process of converting solid biomass into a gaseous fuel known as synthesis gas or producer gas under a reduced oxygen atmosphere to avoid complete combustion [59, 60]. Gasification aims to maximize the conversion of biomass feed into useable gases. In the gasifier, feed is exposed to a high temperature atmosphere, which heats the biomass leading to thermal decomposition. In contrast to pyrolysis, the feed is brought into contact with a gasifying agent (air). At the gasifier temperature, reactions between oxygen and carbon take place. A mixture of many gases, primarily carbon monoxide and hydrogen, is released as the output product of the gasification process. The gas contains various percentages of CO, H_2, CH_4, CO_2, H_2O and N_2 depending on the quality of the biomass used and the way gasification is conducted. It also produces liquids (oils, tars, and other condensates) and solids (char, ash) from solid biomass feedstocks [5, 61, 62]. A simple way of representing the gasification reaction is shown below

$$\begin{aligned} Biomass + O_2(\mathrm{g}) \rightarrow\ & CO(g) + H_2(g) + CO_2(g) + CH_4(g) \\ & + Tar(l) + H_2O(l) + Char(s) + TraceSpecies \end{aligned} \tag{1}$$

Gasification processes are designed to generate fuel or synthesis gases as the primary product that can be used in internal and external combustion engines as well as fuel cells, offering a viable solution to overcome energy demands. Currently, such syngas is used as fuel to generate heat and electricity or as a feedstock for many products in the petrochemical and refinery industries, like methanol, ammonia, synthetic gasoline, etc. The overall gasification process is endothermic, requiring energy input for the reactions to proceed, most of which operate between 600°C and 1500°C [59, 63]. The energy needed for this endothermic reaction is obtained by oxidation of part of the biomass through a direct heating (autothermal) or an

indirect heating (allothermal) phase. The main operating parameters of gasification include type and design of gasifier, gasification temperature, flow rates of biomass and oxidizing agents (air or steam), type and amount of catalysts, and biomass type and properties [64]. In addition to the operating conditions of the gasifiers, the properties of biomass such as size, shape, density, chemical composition, energy content and moisture content affect biomass gasification. Gasifier reactors are simple in construction and their designs are generally categorized into the following types: downdraft, updraft, entrained flow, and fluidized bed.

If air is used as the gasifying agent, the producer gas is usually diluted by atmospheric nitrogen. As a result, producer gas has a relatively low calorific value of 4–6 MJ/m^3 (normal cubic meter) compared to the calorific value of natural gas of 39 MJ/m^3. Because of its low calorific value, larger volumes of producer gas are required to achieve a given energy output compared to natural gas. In some more applications, oxygen-enriched air, oxygen or even steam may be used as the gasifying agent, resulting in the production of syngas with higher calorific value in the range of 10–15 MJ/m^3 due to the absence of diluting nitrogen [16].

5.3 Pyrolysis

Pyrolysis is a thermal decomposition process that takes place in the absence of oxygen to convert biomass into three distinct product fractions: solid residue (biochar), condensable vapors resulting liquid product fraction (bio-oil) and non-condensable gaseous products. Once oxygen is removed, combustion cannot occur; instead, pyrolysis happens. Pyrolysis temperatures are usually between 300 and 700°C, depending on the pyrolysis process employed. Pyrolysis is the most promising technique to convert biomass into biochar and bio-oil. Lower pyrolysis temperatures and longer residence times tend to produce more biochar. High temperatures and longer residence times increase the production of gas. Moderate temperatures and short residence times tend to produce more liquids. Higher pyrolysis temperatures tend to produce a higher proportion of aromatic carbon [65, 66].

Depending on the operating conditions (heating rate, solid residence time and temperature), pyrolysis processes are classified as torrefaction, slow (conventional) pyrolysis, intermediate pyrolysis, fast pyrolysis, flash pyrolysis, and microwave pyrolysis. Various operating conditions are used in these processes; residence time can vary from less than 1 second to hours, heating rate can vary from less than 1°C/s to more than 1000°C/s and temperature ranges from 300 to 700°C or higher. As each type of pyrolysis produces different proportions of the three types of products (biochar, bio-oil and gas), careful selection of the pyrolysis process is essential to obtain the final desired product [21].

The primary conversion of biomass during the pyrolysis process can be described by three pathways; char formation, depolymerization and fragmentation. Char formation is generally favored by intra- and intermolecular rearrangement reactions resulting in higher thermal stability of the residue. This pathway is characterized by the formation of benzene rings and the combination of these rings into an aromatic polycyclic structure. These rearrangement reactions are generally accompanied by the release of water or non-condensable gas (devolatilization). Depolymerization is a dominant reaction during the initial stages of pyrolysis, characterized by the breaking of polymer bonds. This occurs when the temperature is sufficiently greater than the activation energies for the bond dissociation. Depolymerization increases the concentration of free radicals. It is followed by stabilization reactions to produce monomer, dimer and trimer units. These volatile molecules are condensable at ambient conditions and found in the liquid fraction. Fragmentation consists of breaking polymer bonds and even monomer bonds result

in the formation of non-condensable gases and a range of organic vapors that are condensable at ambient conditions [55, 58, 67].

The decomposition of cellulose, hemicelluloses and lignin releases a mixture of condensable vapors and non-condensable gases. The condensable vapor contains (apart from water vapor) methanol, acetic acid, acetone (all three mainly from hemicellulose), hydroxyacetaldehyde, anhydrous monosaccharides (both mainly from cellulose), phenols and heavier tars (from lignin decomposition). The heavier, water-insoluble tars contain larger molecular fragments obtained after splitting the ether and C-C bonds in lignin. The resulting complex mixture, once condensed, is referred to as bio-oil. The main parameter that determines the degree of devolatilization of the biomass is the pyrolysis temperature. Yang et al. [68] observed great differences among the pyrolysis behaviors of the three components, cellulose, hemicellulose and lignin. These three forms of polymers are responsible for most of the physical and chemical property modification during the pyrolysis process. The mechanisms of pyrolysis of these polymers are chemically different from biomass species to species. Cellulose and hemicellulose decompose over a narrower temperature range, whereas lignin degrades over a wider temperature range than cellulose and hemicellulose. Pyrolysis of lignin is known to produce more biochar than pyrolysis of cellulose and hemicellulose. Biomass pyrolysis consists of three main stages: (a) initial evaporation of moisture, (b) primary decomposition and (c) secondary reactions (oil cracking and repolymerization). At the initial heating stage, when the biomass temperature is increased to about 100°C, the mass of biomass decreases due to the evaporation of free water. Bound water is then removed in heating the biomass to temperatures up to 160°C. At this stage, the heating value of pyrolysis gases is negligible. Thermal decomposition of biomass begins with devolatilization/ decomposition of extractives at temperatures <220°C. Hemicellulose is the least stable polymer and breaks down first at temperatures of 220 to 315°C with maximum mass loss at 268°C [23, 38, 55, 67, 68].

The reactions are endothermic between 180 and 270°C, sometimes becoming exothermic at temperatures above 280°C. The nature of pyrolytic decomposition reactions explains this phenomenon. Devolatilization and decomposition in pyrolysis is not a single step reaction and a difference can be made between primary and secondary reactions. The gas and vapor products of primary conversion are unstable under pyrolysis temperatures and, with sufficient residence time, can undergo secondary reactions such as cracking and/or repolymerization of primary volatile compounds. Cracking reactions consist of the breaking of volatile compounds into lower MW molecules. Repolymerization involves combining volatile compounds into higher MW molecules, which may not be volatile under pyrolysis temperatures. Repolymerization reactions become effective at later stages of pyrolysis, leading to the formation of char. It also results in the formation of secondary char. Primary char can act as a catalyst to the secondary reactions. Primary reactions are highly endothermic, while secondary reactions are exothermic and result in the production of secondary char and non-condensable gases at the expense of volatiles in the vapor phase. Decomposition of vapors to coke and secondary vapors has been suggested as the reason for exothermicity. The extent of secondary decomposition reactions determines the overall exothermicity of the pyrolysis reaction and the overall char (primary and secondary) yield. The occurrence of primary and secondary reactions in the thermal decomposition of biomass highlights the fundamental difference between fast pyrolysis and slow pyrolysis [38, 55, 67].

Cellulose has a high degree of polymerization and exhibits higher thermal stability. It decomposes in the temperature range 315 to 400°C. The secondary reactions continue to occur within the solid matrix with further increasing of the temperature. At temperatures above 400°C, the less volatile components are

gradually driven off from solid char residue resulting in higher fixed carbon content and lower volatile carbon content of the solid char residue. As the temperature increases above 600°C, the condensable vapor components undergo cracking and polymerization reactions, resulting in a lower bio-oil yield. Lignin is the most difficult component to pyrolyse, which decompose in a wide temperature range from 160 to 900°C, the rate of lignin degradation reactions is slower than cellulose and hemicellulose [23, 38, 55, 68].

The combination of low heating rate and longer residence time allowed for repolymerization reactions to maximize biochar yield. A low temperature, high heating rate and short gas residence time would be required to maximize bio-oil yield. A high temperature, low heating rate and long gas residence time would be preferred to maximize the gas yield. As a result of high heating rates and short residence times, fast pyrolysis tends to yield higher proportions of bio-oils. In contrast, slow pyrolysis produces higher proportions of biochars because of slow heating rates and longer residence times. Pyrolysis requires relatively dry feedstock (usually moisture content <30 wt%, but moisture contents of ~10 wt% are preferred) and ground to different particle sizes based on the type of pyrolysis. Feedstock with high moisture content consumes more energy to account for increasing heat of vaporization during the heating of biomass towards the pyrolysis temperature. Additionally, the gases and vapors produced in pyrolysis using a high moisture feedstock are diluted with steam and have a lower calorific value [21, 61].

The molar H/C and O/C ratios of LCB are approximately 1.5 and 0.7, respectively. During pyrolysis, the biomass undergoes devolatilization and the solid portion gets enriched in carbon. The H and O are preferably removed over C and the H/C and O/C ratios tend to decrease as biomass undergo its transformation into biochar. The H/C and O/C ratios are used to assess the degree of aromaticity and maturation. Low-temperature chars have high H/C and O/C ratios, the values close to the original biomass. After pyrolysis, a significant decrease in the H/C and O/C atomic ratios is reported and it decreased straightly with increasing pyrolysis temperature. When the pyrolysis temperature is below 500°C, the reduction in H/C and O/C is mainly attributed to major decomposition reactions of biomass, including dehydration (water removal), decarboxylation (CO_2 removal) and decarbonylation (CO removal). Above 500°C, the H/C ratio decreases drastically compared to the O/C ratio, which indicated direct dehydrogenation and demethanation of the chars occurred [38, 69].

5.3.1 Torrefaction

Torrefaction is a pretreatment for upgrading biomass primarily for energy production. Torrefaction, a mild or incomplete form of pyrolysis, involves heating the feedstock to temperatures of 200 to 300°C at slow heating rates (less than 1°C/s) in the absence of air under atmospheric pressure conditions. The residence time depends on the particle size and ranges between several seconds and an hour. Torrefaction removes water as well as superfluous volatiles and partly decomposes the biopolymers (cellulose, hemicelluloses, and lignin) by giving off organic volatiles. It tends to yield higher proportions of solid (torrefied biomass) in addition to liquid and non-condensable gaseous products [21]. Decomposition can be further subdivided into (a) drying, (b) depolymerization and recondensation, (c) limited devolatilization and carbonization, (d) extensive devolatilization and carbonization. Hemicellulose is the least stable of three major polymers, soften between 150 and 200°C and break down via various dehydration, deacetylization and depolymerization reactions at processing temperature range 200–300°C. Predominant hardwood hemicellulose is xylan, while predominant softwood hemicellulose is

glucomannan. Xylan tends to break down more quickly than glucomannan at lower temperatures. Therefore, hardwood has a higher mass loss (higher breakdown of hemicellulose) than softwood when treated at the same temperature. This indicates that different biomass species have different torrefaction kinetics. The cellulose and/or lignin degradation during torrefaction is small. A greater degradation has been reported at temperatures above 270°C. Different biomasses have different physical properties such as porosity, specific heat capacity, thermal conductivity, particle size distribution etc., which results in non-homogenous torrefied biomass. A narrower particle size distribution is required for efficient torrefaction and optimized product quality [23, 70].

As specified by the EBC [71], the molar oxygen to carbon (O/C) ratio of biochar should be less than 0.4. But torrefied biomass tends to have higher oxygen to carbon (O/C) ratio than the ECB specification of biochar. Therefore, torrefied biomass cannot be referred to as biochar. Torrefied biomass has physicochemical properties in between that of raw biomass and biochar. Torrefaction is a pretreatment method that is used primarily for moisture removal and densification of biomass, which will reduce the cost of transportation and increase the heating value of biomass. Torrefaction has higher conversion efficiencies compared to slow pyrolysis. Torrefied biomass yield has a maximum of 35 wt% (on a weight basis of dry, ash-free biomass feedstock). A typical mass yield from torrefaction is 70–80% and energy yield is 80–90%. The lower heating value (LHV) of torrefied biomass is about 20.4 MJ/kg compared to the LHV of charcoal between 28 and 33 MJ/kg. Torrefaction increases the hydrophobicity, stability, grindability and reduces biodegradability compared to the untreated biomass feedstock. Torrefied biomass can be stored long-term without degradation [21].

The heating value of torrefied biomass on a weight basis increases compared to its original biomass. Its heating value on a volume basis is not necessarily increased as torrefied biomass has relatively low bulk density. Torrefied biomass can be pelletized or briquetted to account for low bulk energy density. Consequently, bulk energy densities between 14.9 and 18.4 GJ/m^3 can be achieved.

5.3.2 Slow pyrolysis

Slow pyrolysis is characterized by moderate temperatures (300–550°C), slow heating rates (0.1–0.8°C/s) and longer residence time (5–30 min or even 25–35 h) [56]. Slow pyrolysis aims at maximizing the yield of biochar by promoting secondary reactions, which is achieved by longer vapor residence times. The biochar produced in slow pyrolysis consists of both primary and secondary char. The slow heating rate with moderate pyrolysis temperatures also promotes the production of biochar. Biochar yield and physicochemical properties depend on the feedstock properties and pyrolysis conditions such as processing temperature, heating rate and pyrolysis environment. In addition, moisture content and particle size also significantly affect biochar yield [28, 56, 72].

The biomass composition plays a significant role in the resulting biochar yield and the physicochemical nature of the biochar. Biomass cell wall constituents (cellulose, hemicellulose and lignin) behave differently in terms of decomposition and devolatilization in pyrolysis. As lignin decomposes at lower reaction rates and contains aromatics, it is known to contribute to high biochar yields in slow pyrolysis. Consequently, if high biochar yield is required, then lignin-rich biomass feedstocks are preferable. The extractives in biomass will evaporate and end up in the vapor phase or may be cracked, thereby contributing to char and non-condensable gas formation [38]. High ash contents in the biomass affect the slow pyrolysis process and the physicochemical properties of biochar in multiple ways. Alkaline and earth

alkaline metals exhibit catalytic activity in pyrolysis. They catalyze secondary reactions of primary vapor components favoring higher yields of non-condensable gases and biochar or they may catalyze different primary decomposition reactions altogether. Biomass containing more minerals yields less biochar [67, 72–74]. Most of the constituents in ash (mainly the alkaline and heavy metals) are non-volatile within the range of temperatures typically employed in slow pyrolysis processes. Thus, ash remains in the solid biochar product, potentially affecting the use of biochar in downstream processes. If biochar (with high ash content) is used in combustion or gasification processes, slagging and equipment fouling occurs. Chlorine and sulfur lead to higher corrosion. Some downstream applications, such as soil amendment, can benefit from higher ash contents in biochar (nutrient recycling). High ash content biochar can be treated with leaching, which involves soaking of biochar in hot water or hot dilute acid. Washing with pure water at 80°C is sufficient to remove about 90% of the potassium found in biochar, produced at 550°C. The leaching process has been successfully applied to treat potassium and chlorine of biochar. Extra dewatering and drying processes are required after leaching in addition to handling and treatment of leachate, which may contain heavy metals extracted from biochar [38].

The process variables that affect the biochar yield and properties include pyrolysis temperature, heat transfer (to and in the biomass), biomass residence time and operating pressure. The primary biomass constituents (hemicelluloses, cellulose and lignin) undergo decomposition and devolatilization over different temperature ranges. Decomposition of hemicellulose occurs at temperatures below 300°C. The resulting gas and vapor products include non-condensable gases (such as CO, CO_2, H_2 and CH_4), water vapor and low MW oxygenated organic compounds (mainly acetic acid, formic acid, methanol, acetone and furfural). Extensive devolatilization of lignin and cellulose occurs at temperatures higher than 300°C (slow pyrolysis temperatures). Peak devolatilization occurs at temperatures around 500°C, yielding typical vapor products including levoglucosan, hydroxyacetaldehyde, acetic acid and hydroxymethyl furfural (HMF) all originate from cellulose [38, 74, 75].

Phenolic compounds (both in monomeric and oligomeric form) are typically liberated from lignin [76]. Further increase in temperatures causes secondary vapor phase cracking reactions to dominate, yielding additional non-condensable gases and secondary biochar. The higher the pyrolysis temperature, the lower the biochar yield. The additional secondary char formation occurring at higher temperatures is offset by further devolatilization of the primary biochar. The net effect is a decreasing biochar yield with increasing slow pyrolysis temperature. Slow pyrolysis uses low heating rates resulting in biomass conversion being rate limited by heat transfer. Additionally, the slow devolatilization resulting from a slow heating rate ensures maximum secondary char formation. The heat transfer is of less critical importance in slow pyrolysis (compared to fast pyrolysis) as very long biomass residence times are used [38]. Biochar yield increases with increasing residence time, decreasing pyrolysis temperature and lower heating rate. With increasing residence times, vapors are restrained and reacted with solid-phase extensively for more biochar yield [28, 56, 72].

Slow pyrolysis favors biochar production at the expense of bio-oil production. The biochar, bio-oil and gas yields are typically 35 wt%, 30 wt% and 35 wt%, respectively. The overall slow pyrolysis process can generally be exothermic due to the extensive occurrence of secondary reactions. Slow pyrolysis can accept a wide range of particle sizes (5–50 mm). Large biomass particles are frequently used when rapid heating rates are not required or when the desired product is biochar [21, 55].

5.3.3 Intermediate pyrolysis

In intermediate pyrolysis, the reaction is faster than slow pyrolysis but slower than fast pyrolysis. Intermediate pyrolysis differs from fast pyrolysis in terms of heat transfer to biomass feed. It occurs in the temperature range of 450–550°C and even lower temperatures are used (350°C). The heating rates are much lower than fast pyrolysis (100 to 500°C/min) with residence time ranging from 10 to 30 s and produce less biochar than slow pyrolysis [65, 77]. Intermediate pyrolysis occurs at controlled heating rates, thus, inhibiting the formation of high MW tars and yielding products (biochar, bio-oil and gases) with different product qualities. In intermediate pyrolysis, the biomass particles sizes and shapes are less critical than in fast pyrolysis. It can process a wider variety of biomass, larger particles up to pellets, chips and dust and also material with a water content of up to 40%. High cooling rates are needed for the vapors to reduce thermal post-decomposition reactions. A higher amount of bio-oil than slow pyrolysis can be produced through intermediate pyrolysis. More controlled chemical reactions occur and, thus, the reaction conditions offer a broad range of variation for process optimization. The typical product distribution of intermediate pyrolysis is 40–60% of bio-oil, 20–30% non-condensable gases and 15–25% biochar [77].

The biochars produced by intermediate pyrolysis have a high carbon and low volatile contents. The bio-oil produced by intermediate pyrolysis has a high calorific value; the oil fraction easily separates into organic and aqueous phases. Compared to bio-oil generated from fast pyrolysis, the liquid fraction from intermediate pyrolysis has some beneficial characteristics, including low tar yield, improved viscosity and heating value. These characteristics may result from a relatively long residence time and contact with biochar [78]. Intermediate pyrolysis at 400°C yielding 35% solid (biochar), 46% liquid and 19% gaseous products has been reported. The liquid fraction separates into an aqueous phase (38% with 50% water; HHV of 7 MJ/kg) and organic phase (8% pyrolytic lignin, phenols, etc., HHV of 24 MJ /kg) [79].

5.3.4 Fast pyrolysis

The fast pyrolysis typically involves high heating rates (10–1000°C/s), short residence times (0.5–2 s) [56] and temperatures between 450 and 550°C. It decomposes biomass quickly to generate liquid (bio-oil), solid (biochar) and gaseous products. The bio-oil, biochar and gas yields are typically 60–70 wt%, 12–15 wt% and 13–25 wt% on a dry basis, respectively [55].

Fast pyrolysis suppresses secondary reactions from taking place by having short vapor residence times (rapid removal and quenching of the condensable primary volatile vapors) and maintaining high biomass heating rates, thereby maximizing the yield of condensable vapors (bio-oil). In this way, secondary reactions of cracking and repolymerization are prevented. The intermediate products of flash degradation of hemicellulose, cellulose and lignin are rapidly quenched and condensed to bio-oil before further reactions break down higher MW components into gaseous products. This freezing of intermediates results in bio-oil containing many reactive species, contributing to its unusual characteristics. Condensable vapors are formed by rapidly and simultaneously depolymerizing and fragmenting cellulose, hemicellulose and lignin fractions with a rapid increase in temperature. Rapid quenching traps many of these products that would further react (depolymerize, decompose, degrade, crack or condense with other molecules) to form more non-condensable gases if the residence time at high temperature was extended [61, 80].

The distribution of products (bio-oil, biochar and gases) depends on the biomass composition and rate and duration of heating. If bio-oil is the product of interest, the optimum pyrolysis temperature range is 425–600°C, with the peak temperature below 650°C to strike a balance between thorough devolatilization and minimal secondary cracking of vapors. The optimum yield in vapor products translates to the quantity of bio-oil formed. However, the peak temperature can be up to 1000°C if gas production is of primary interest [5]. Woody biomass (poplar, sawdust, forest and wood residue) produces the highest bio-oil yield (around 75%). The second highest bio-oil yield is from energy crops (reed), followed by agricultural residues (wheat straw, flax straw etc.). This is due to the higher cellulose and hemicellulose in wood than energy crops and agricultural residues. Product (bio-oil, biochar and syngas) yields in fast pyrolysis are affected by the feed particle size. The heat transfer rate decreases with increasing particle size, thus, increasing biochar yield and decreasing bio-oil and syngas yield. Smaller particle size is better for internal heat transfer, which increases bio-oil yield. Both pyrolysis temperature and feedstock particle size need to be optimized for maximum bio-oil yield [56, 80].

A finely ground biomass feed (usually <1 mm) is required to achieve very high heat transfer rates and thereby very high heating rates, which reduce the mass and heat transfer limitations. The biochar yield in fast pyrolysis is generally low as only primary char is being produced (secondary reactions are suppressed) and high reaction rates also minimize biochar formation. The overall fast pyrolysis process is highly endothermic due to the absence of secondary reactions. Fast pyrolysis prefers biomass with low moisture content (< 10 wt%) in order to minimize the water in the product bio-oil. Low moisture content also facilitates grinding the feed to give sufficiently small particles to ensure rapid heating and fast pyrolysis [65].

5.3.5 Flash pyrolysis

Flash pyrolysis aims to maximize the liquid yield (bio-oil). It is characterized by high temperatures, higher heating rates (> 1000°C/s) and shorter residence times (< 0.5 s). Very fine particles of biomass feed (< 0.2 mm) are usually required. Flash pyrolysis is extremely fast, thus, leading to a reduced time for processing of the feedstock. It occurs in the temperature range of 800–1000°C [77]. The product containing condensable and non-condensable gas is cooled, thus increasing the liquid yield while reducing biochar production. The main product distributions of flash pyrolysis are similar to that of fast pyrolysis. The small particle sizes of biomass feed result in small particles of biochar. The liquid (bio-oil) yield is typically 75–80 wt% and biochar yield is 12–13 wt%. Biochar particles need to be removed because it can catalyze the polymerization of some of the products and increase bio-oil viscosity. Special reactors, such as appropriately designed fluidized bed or entrained flow reactors, are typically required [21].

5.3.6 Microwave-assisted pyrolysis

In conventional heating, heat is transferred to the material surface (by convection, conduction and radiation) and subsequently from the surface to the interior of the material by conduction as a result of temperature gradients. On the other hand, microwave energy is delivered directly into materials within an electromagnetic field. The electromagnetic field enters the material and generates thermal energy throughout the penetration depth by dielectric heating through interaction with polarizable dipoles present in the material and heat the material from

inside. Microwave heating requires a material with a high dielectric constant. The dielectric constant is a measure of the ability of a material to absorb microwave energy. Biomass has a relatively low dielectric constant. As a result, microwave pyrolysis requires catalysts as well as microwave absorbers to improve the heating. The presence of water in biomass may increase the heating rate of microwave pyrolysis due to the high dielectric constant of water in comparison with biomass. Microwave-assisted pyrolysis usually operates in the temperature range of 400–800°C [72, 81].

Some of the advantages of microwave-assisted pyrolysis over conventional pyrolysis include uniform heating throughout, rapid heating rate, cleaner products due to no agitation, volumetric and selective heating. Microwave heating provides ease of operation by instant on/off control and improves the yield and quality of the products. It reduces the formation of hazardous products and minimizes pollutants emission, making the technique environmentally friendly [72, 81]. The other advantages include high heating efficiency as heating is in situ, the ability to handle wet biomass without drying and the ability to pyrolyse large biomass particles. The disadvantage of microwave-assisted pyrolysis is that it requires electricity which is expensive high-quality energy compared to the heat generated by the combustion of pyrolysis gases and vapors in conventional pyrolysis. Microwave pyrolysis generally needed pre-treatment and catalysts before heating [21].

5.4 Hydrothermal processing

Most biomass materials are wet and have moisture contents range up to 95 wt%. Biomass with more than 30 wt% moisture content requires energy costly drying operation prior to pyrolysis, which is one of the leading technical barriers in using wet biomass. For high moisture content biomass, the heat of moisture evaporation is greater than the heat available from the biomass, thus becoming a net energy consumption. Wet biomass, typically with 70 wt% or more water, can be converted using hydrothermal processing, which involves applying heat and pressure to convert biomass in the presence of water into carbonaceous biofuel. In hydrothermal processing, water plays an active role as a solvent and reactant. It uses subcritical or supercritical water to convert biomass into end products in the absence of atmospheric oxygen. Hydrothermal processing is a promising technique to convert wet biomass into carbonaceous solids at relatively high yields by omitting the energy-intensive drying before or during the process. Hydrothermal processing can be classified into three processes: hydrothermal carbonization (HTC), hydrothermal liquefaction (HTL) and hydrothermal gasification (HTG) based on reaction parameters such as temperature, pressure and residence time [21].

5.4.1 Hydrothermal carbonization

When biomass feedstock in water is heated at low temperatures (< 200°C) in a sealed vessel at autogenous pressure, mostly solids (called hydrochar) are formed in a process known as HTC. The decomposition temperature of hemicellulose is usually around 160°C in subcritical water, while cellulose and lignin decompose in the temperature range 180 to 200°C and above 220°C in subcritical water, respectively. The three products of HTC are hydrochar (solid fraction), aqueous solution (bio-oil mixed with water) and a small volume of gas (mainly CO_2). HTC aims to maximize the yield of hydrochar. The product distribution and characteristics will mostly depend on three factors: type of biomass, the pH and the maximum temperature used. The reaction time and the solids concentration in biomass water mixture

also has a relatively smaller influence. A minimum HTC temperature of 160°C is needed for the hydrochar formation from glucose. The overall HTC reaction extent is negligible below these processing conditions. The maximum hydrochar yield is obtained at 200°C and then it decreases gradually. A decreasing trend of hydrochar formation with the increase in temperature is due to the higher temperatures favoring gasification reactions. Consequently, part of hydrochar is lost in the formation of volatile compounds. The process energy requirements and final product composition depend on the input biomass feed and the process conditions. The main product of HTC is hydrochar which can be easily separated from the liquid fraction due to its high hydrophobicity and homogeneous properties. The solid fraction can be used to produce dried hydrochar pellets for energy production and mono sugars can be recovered from the liquid fraction. HTC generates less harmful gases such as CO and CO_2 and produces hydrochar mass yields varying from 35% up to 80%, with hydrochar carbon content similar to lignite. Residence time varies from minutes up to several hours [21, 70, 82, 83].

5.4.2 Hydrothermal liquefaction (HTL)

At elevated temperatures (between 200 and 350°C) and pressures (5–20 MPa), HTL takes place and the biomass feedstock is mainly converted into a liquid product (aqueous soluble). Free radical and ionic reactions are considered to be the main reactions in HTL [21, 84]. The dielectric constant of water decreases rapidly with increasing temperature. At ambient conditions, the dielectric constant (a measure of hydrogen bonding) of water is about 80 F/m. It drops to about 27 F/m at 250°C and 5 MPa and to about 14 F/m at 350°C and 25 MPa. Water starts to display less polar behavior due to decreasing number of hydrogen bonds. The dissociation of water also increases with the increase of temperature. The ionic product of water (pK_w) decreases from 14 at 25°C to 11 at 250°C. The viscosity of water decreases with increasing temperature. Thus, mass transfer is enhanced and any mass-transfer-limited chemical reactions are accelerated [84, 85].

5.4.3 Hydrothermal gasification (HTG)

HTG operates near and/or above the critical point of water at temperatures of 400–600°C and pressures of 23–45 MPa. The biomass is mainly converted into a mixture of non-condensable gases (H_2, CO, CH_4 and CO_2). HTG is capable of producing syngas enriched with H_2. The conversion efficiency is highly improved when water reaches the critical point (374°C and 22.1 MPa) [21]. HTG involves the splitting of biomass polysaccharides with supercritical water (SCW). Due to higher reaction temperature, HTG progresses at a faster rate and complete decomposition of biomass is achieved. This is a distinctive feature of HTG in comparison with other hydrothermal treatments (HTC and HTL). The difficulty of byproducts treatment is one of the problems with HTC and HTL. Undesirable byproducts produced by HTC and HTL are occasionally dissolved in the water phase. HTG typically decomposes biomass into gas with a conversion higher than 0.8. The amount of organic compounds in the liquid fraction is low; hence, post-treatment is unnecessary or easily carried out. HTG usually requires wet biomass; other biomasses can also be used. Conventional thermal gasification technologies are available when biomass is not wet. Conventional thermal gasification cannot be effectively employed when the feedstock is wet or has a high moisture content (> 80%). Conventional thermal gasification is achieved by partial oxidation using air. Syngas is partially diluted with nitrogen in addition to tar production. Syngas from HTG does not contain tars; even if produced, they remain in the liquid phase and are not diluted with nitrogen [21, 86].

6. Conclusions

Biomass is a sustainable source of energy. Natural biomass is bulky and usually has a high moisture content which complicates the direct use of biomass as a fuel. Biomass is a complex mixture of polymers consisting of three key elements carbon, oxygen and hydrogen. In addition, there are macronutrients, micronutrients, trace elements and other heavy metals. The three major components of LCB are cellulose, hemicellulose and lignin. Other compounds present in LCB include inorganic compounds and organic extractives. The components of biomass behave differently during thermochemical conversion.

The proximate and ultimate analysis is vital for describing biomass and thus product distribution. Thermochemical conversion is an increasingly feasible route to use biomass sources to fulfill energy needs. Designing effective thermochemical conversion systems that result in proper combinations of biomass feedstocks and conversion technologies is vital. It involves the design of efficient supply chains and conversion technologies suitable to manage variations in biomass properties. It needs to be cost-effective while minimizing harmful emissions and maintaining product quality.

Different thermochemical conversions of biomass are employed to yield varying amounts of gaseous, liquid and solid products of interest. Torrefaction aims to maximize the yield of solid product, torrefied biomass. It is performed at longer residence time, slow heating rates and low temperatures (<300°C). The improved properties of torrefied biomass include increased energy density, hydrophobicity, grindability and reduced biodegradability compared to the initial biomass feed, thus, allowing cheaper transport, handling and processing of the torrefied biomass. Torrefied biomass has a higher O/C ratio than biochar. Biochar is the desired product in slow pyrolysis, and yield is maximized by conversion at longer residence time, slow heating rates, and moderate temperatures. Biochar applications include use as a soil amendment, as an adsorbent or as fuel in power generation. In fast pyrolysis, bio-oil is the desired product and yield is maximized by conversion at short vapor residence times, high heating rates and around 500°C. The gap between biomass feedstock and a usable product can be bridged by incorporating additional processes such as drying and grinding of biomass feed, palletization or briquetting of biomass feed and/or product and mineral leaching of products to treat high ash content. These additional processes have cost implications.

High moisture content is a major barrier in biomass handling and processing. Moisture content has a significant impact on the biomass conversion process. The main problem with the pyrolysis of high moisture biomass is that it requires a large amount of energy to evaporate moisture. Hydrothermal processing is a useful processing technique for biomass feedstocks with high moisture as it does not require the drying and/or dewatering processes, thereby reducing the operating costs.

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References

[1] Bhat AH, Dasan YK, Khan I. Extraction of Lignin from Biomass for Biodiesel Production. In: Hakeem KR, Jawaid M, Alothman OY (eds) *Agricultural Biomass Based Potential Materials*. New York: Springer, 2015, pp. 155-180.

[2] Kataki R, Chutia RS, Mishra M, et al. Feedstock Suitability for Thermochemical Processes. In: Pandey A, Bhaskar T, Stöcker M, et al. (eds) *Recent advances in thermochemical conversion of biomass*. Oxford: Elsevier, 2015, pp. 31-74.

[3] Okolie JA, Nanda S, Dalai AK, et al. A review on subcritical and supercritical water gasification of biogenic, polymeric and petroleum wastes to hydrogen-rich synthesis gas. *Renew Sustain Energy Rev* 2020; 119: 109546.

[4] Chandra R, Takeuchi H, Hasegawa T. Methane production from lignocellulosic agricultural crop wastes: A review in context to second generation of biofuel production. *Renew Sustain Energy Rev* 2012; 16: 1462-1476.

[5] Basu P. *Biomass Gasification, Pyrolysis and Torrefaction: Practical Design and Theory*. Second. Oxford: Elsevier, 2013.

[6] McKendry P. Energy production from biomass (part 1): Overview of biomass. *Bioresour Technol* 2002; 83: 37-46.

[7] Pilon G, Lavoie JM. Pyrolysis of switchgrass (*Panicum virgatum* L.) at low temperatures within N_2 and CO_2 environments: Product yield study. *ACS Sustain Chem Eng* 2013; 1: 198-204.

[8] Ruan R, Zhang Y, Chen P, et al. Biofuels: Introduction. In: Pandey A, Larroche C, Dussap C-G, et al. (eds) *Biofuels: Alternative Feedstocks and Conversion Processes for the Production of Liquid and Gaseous biofuels*. Oxford: Academic Press, 2019, pp. 3-43.

[9] Ernst M, Walter A, Schurr U. Biomass Production. In: Kaltschmitt M, Themelis NJ, Bronicki LY, et al. (eds) *Renewable Energy Systems*. 2013, pp. 510-521.

[10] Faaij APC. Biomass Resources, Worldwide. In: Kaltschmitt M (ed) *Energy from Organic Materials (Biomass)*. New York: Springer, 2019, pp. 299-350.

[11] Panwar NL. Biomass for Domestic and Agro-Industrial Applications. In: Botannini LF (ed) *Wood: Types, Properties and Uses*. New York: Nova Science Publishers, 2011, pp. 81-109.

[12] Faaij APC. Technical and Economic Potentials of Biomass until 2050: Regional Relevance for Energy Security. In: Brauch HG, Spring ÚO, Grin J, et al. (eds) *Facing Global Environmental Change: Environmental, Human, Energy, Food, Health and Water Security Concepts*. Berlin: Springer-Verlag, 2009, pp. 379-394.

[13] IEA. *World energy outlook 2020*. Paris, 2020.

[14] Timilsina G, Shah KU. Energy Technologies for Sustainable Development Goal 7. In: Adenle AA, Chertow MR, Moors EHM, et al. (eds) *Science, Technology and Innovation for Sustainable Development Goals: Insights from Agriculture, Health, Environment and Energy*. New York: Oxford University Press, 2020, pp. 36-63.

[15] Carpenter NE. *Chemistry of Sustainable Energy*. Boca Raton, FL: CRC Press, 2014. DOI: 10.1201/b16687.

[16] Champagne P. Biomass. In: Letcher T (ed) *Future Energy: Improved, Sustainable and Clean Options for our Planet*. Oxford: Elsevier, 2008, pp. 151-170.

[17] Corro G, Pal U, Bañuelos F, et al. Generation of biogas from coffee-pulp and cow-dung co-digestion: Infrared

studies of postcombustion emissions. *Energy Convers Manag* 2013; 74: 471-481.

[18] Wolf JP. Biomass combustion for power generation: an introduction. In: Rosendahl L (ed) *Biomass Combustion Science, Technology and Engineering*. Cambridge: Woodhead, 2013, pp. 3-8.

[19] Li R, Chen J. Planning the next-generation biofuel crops based on soil-water constraints. *Biomass and Bioenergy* 2018; 115: 19-26.

[20] Cowie A, Woolf D, Gaunt J, et al. iochar, carbon accounting and climate change. In: *Biochar for Environmental Management: Science, Technology and Implementation*. Oxon: Routledge, 2015, pp. 763-794.

[21] Daful AG, Chandraratne MR. Biochar Production From Biomass Waste-Derived Material. In: Hashmi S, Choudhury IA (eds) *Encyclopedia of Renewable and Sustainable Materials*. Oxford: Elsevier, 2020, pp. 370-378.

[22] Gundekari S, Mitra J, Varkolu M. Classification, characterization, and properties of edible and non-edible biomass feedstocks. In: Hussain CM, Sudarsanam P (eds) *Advanced Functional Solid Catalysts for Biomass Valorization*. Oxford: Elsevier Inc., pp. 89-120.

[23] Nachenius RW, Ronsse F, Venderbosch RH, et al. Biomass Pyrolysis. In: Marin GB, West DH, Li J, et al. (eds) *Advances in Chemical Engineering, Volume 42. Chemical Engineering for Renewables Conversion*. Oxford: Elsevier, 2013, pp. 75-139.

[24] Sanchez J, Curt MD, Robert N, et al. Biomass resources. In: Lago C, Caldés N, Lechón Y (eds) *The Role of Bioenergy in the Emerging Bioeconomy: Resources, Technologies, Sustainability and Policy*. Oxford: Elsevier Inc., pp. 25-111.

[25] Hodge BK. *Alternative Energy Systems and Applications*. Hoboken, NJ: John Wiley & Sons, 2017.

[26] Mansoori GA, Enayati N, Agyarko LB. *Energy (Sources, Utilization, Legislation, Sustainability, Illinois as Model State)*. Danvers, MA: World Scientific, 2016.

[27] Quader MA, Ahmed S. Bioenergy With Carbon Capture and Storage (BECCS): Future Prospects of Carbon-Negative Technologies. In: Rasul M, Azad A, Sharma S (eds) *Clean Energy for Sustainable Development Comparisons and Contrasts of New Approaches*. Oxford: Elsevier, 2017, pp. 467-481.

[28] Tripathi M, Sahu JN, Ganesan P. Effect of process parameters on production of biochar from biomass waste through pyrolysis: A review. *Renew Sustain Energy Rev* 2016; 55: 467-481.

[29] Wang S, Luo Z. *Pyrolysis of Biomass*. Berlin: Walter De Gruyter GmbH, 2017.

[30] Vassilev S V., Baxter D, Andersen LK, et al. An overview of the chemical composition of biomass. *Fuel* 2010; 89: 913-933.

[31] Vassilev S V., Baxter D, Andersen LK, et al. An overview of the organic and inorganic phase composition of biomass. *Fuel* 2012; 94: 1-33.

[32] Wang S, Dai G, Yang H, et al. Lignocellulosic biomass pyrolysis mechanism: A state-of-the-art review. *Prog Energy Combust Sci* 2017; 62: 33-86.

[33] Godin B, Agneessens R, Schmit T, et al. Chemical Composition and Biofuel Potentials of a Wide Diversity of Plant Biomasses. *Energy and Fuels* 2013; 27: 2588-2598.

[34] Akhtar J, Amin NAS. A review on process conditions for optimum bio-oil yield in hydrothermal liquefaction of biomass. *Renew Sustain Energy Rev* 2011; 15: 1615-1624.

[35] Dhyani V, Bhaskar T. A comprehensive review on the pyrolysis of lignocellulosic biomass. *Renew Energy* 2018; 129: 695-716.

[36] Potumarthi R, Baadhe R, Bhattacharya S. Fermentable Sugars from Lignocellulosic Biomass: Technical Challenges. In: Gupta V, Tuohy M (eds) *Biofuel Technologies: Recent Developments.* Berlin: Springer-Verlag, 2013, pp. 1-27.

[37] Dhyani V, Bhaskar T. Pyrolysis of Biomass. In: Pandey A, Larroche C, Dussap C-G, et al. (eds) *Biofuels: Alternative Feedstocks and Conversion Processes for the Production of Liquid and Gaseous Biofuels*. Oxford: Elsevier, 2019, pp. 217-244.

[38] Ronsse F, Nachenius RW, Prins W. Carbonization of Biomass. In: Pandey A, Bhaskar T, Stöcker M, et al. (eds) *Recent advances in thermochemical conversion of biomass*. Oxford: Elsevier, 2015, pp. 293-324.

[39] Pant KK, Mohanty P. Biomass, Conversion Routes and Products – An Overview. In: Hornung A (ed) *Transformation of Biomass Theory to Practice*. Chichester: John Wiley & Sons, 2014, pp. 1-30.

[40] Sannigrahi P, Ragauskas AJ, Tuskan GA. Poplar as a feedstock for biofuels: A review of compositional characteristics. *Biofuels, Bioprod Biorefining* 2010; 4: 209-226.

[41] Karimi K, Shafiei M, Kumar R. Progress in Physical and Chemical Pretreatment of Lignocellulosic Biomass. In: Gupta V, Tuohy M (eds) *Biofuel Technologies: Recent Developments.* Berlin: Springer-Verlag, 2013, pp. 53-96.

[42] Zheng Y, Shi J, Tu M, et al. Principles and Development of Lignocellulosic Biomass Pretreatment for Biofuels. In: Li Y, Ge X (eds) *Advances in Bioenergy -Vol 2*. Oxford: Elsevier Ltd, pp. 1-68.

[43] Nanda S, Mohammad J, Reddy SN, et al. Pathways of lignocellulosic biomass conversion to renewable fuels. *Biomass Convers Biorefinery* 2014; 4: 157-191.

[44] Tursi A. A review on biomass: Importance, chemistry, classification, and conversion. *Biofuel Res J* 2019; 6: 962-979.

[45] Agbor VB, Cicek N, Sparling R, et al. Biomass pretreatment: Fundamentals toward application. *Biotechnol Adv* 2011; 29: 675-685.

[46] Demirbas A. *Biorefineries: For Biomass Upgrading Facilities*. London: Springer, 2010. DOI: 10.1007/978-1-84882-721-9.

[47] Dheeran P, Reddy L. Biorefining of Lignocelluloses: An Opportunity for Sustainable Biofuel Production. In: Kumar S, Sani R (eds) *Biorefining of Biomass to Biofuels: Opportunities and Perception, Biofuel and Biorefinery Technologies 4*. Cham, Switzerland: Springer, 2018, pp. 1-23.

[48] Amidon TE, Wood CD, Shupe AM, et al. Biorefinery: Conversion of woody biomass to chemicals, energy and materials. *J Biobased Mater Bioenergy* 2008; 2: 100-120.

[49] Basu P. *Biomass Gasification, Pyrolysis and Torrefaction: Practical Design and Theory*. 2nd ed. London: Elsevier, 2018. DOI: 10.1016/B978-0-12-812992-0.00003-0.

[50] Nunes LJR, Matias JCDO, Catalão JPDS. *Torrefaction of Biomass for Energy Applications- From Fundamentals to Industrial Scale*. Oxford: Elsevier, 2018. DOI: 10.1016/b978-0-12-809462-4.00001-8.

[51] Jameel H, Keshwani DR. Thermochemical Conversion of Biomass to Power and Fuels. In: Cheng JJ (ed) *Biomass to Renewable Energy Processes*.

Boca Raton, FL: Taylor & Francis, 2018, pp. 375-421.

[52] Adams P, Bridgwater T, Lea-Langton A, et al. Biomass conversion technologies. In: Thornley P, Adams P (eds) *Greenhouse gas balance of bioenergy systems*. London: Elsevier, 2018, pp. 107-139.

[53] Jafri N, Wong WY, Doshi V, et al. A review on production and characterization of biochars for application in direct carbon fuel cells. *Process Saf Environ Prot* 2018; 118: 152-166.

[54] Maniscalco MP, Volpe M, Messineo A. Hydrothermal carbonization as a valuable tool for energy and environmental applications: A review. *Energies* 2020; 13: 04098. DOI: 10.3390/en13164098.

[55] Kan T, Strezov V, Evans TJ. Lignocellulosic biomass pyrolysis: A review of product properties and effects of pyrolysis parameters. *Renew Sustain Energy Rev* 2016; 57: 1126-1140.

[56] Roy P, Dias G. Prospects for pyrolysis technologies in the bioenergy sector: A review. *Renew Sustain Energy Rev* 2017; 77: 59-69.

[57] Mando M. Direct combustion of biomass. In: Rosendahl L (ed) *Biomass Combustion Science, Technology and Engineering*. Cambridge: Woodhead, 2013, pp. 61-83.

[58] Ranzi E, Faravelli T, Manenti F. Pyrolysis, Gasification, and Combustion of Solid Fuels. In: Marin G, West D, Li J, et al. (eds) *Advances in Chemical Engineering, Volume 49, Thermochemical Process Engineering*. Oxford: Elsevier, 2016, pp. 1-94.

[59] Cerinski D, Baleta J, Mikulčić H, et al. Dynamic modelling of the biomass gasification process in a fixed bed reactor by using the artificial neural network. *Clean Eng Technol* 2020; 1: 100029.

[60] Luo X, Wu T, Shi K, et al. Biomass Gasification: An Overview of Technological Barriers and Socio-Environmental Impact. In: Yun Y (ed) *Gasification for Low-grade Feedstock*. London: IntechOpen, 2018, pp. 3-18.

[61] Demirbas A. Biorefineries: Current activities and future developments. *Energy Convers Manag* 2009; 50: 2782-2801.

[62] Neubauer Y. Biomass gasification. In: Rosendahl L (ed) *Biomass Combustion Science, Technology and Engineering*. Cambridge: Woodhead, 2013, pp. 106-129.

[63] Safarian S, Saryazdi SME, Unnthorsson R, et al. Gasification of woody biomasses and forestry residues: Simulation, performance analysis, and environmental impact. *Fermentation* 2021; 7: 1-14.

[64] Kumar A, Jones DD, Hanna MA. Thermochemical biomass gasification: A review of the current status of the technology. *Energies* 2009; 2: 556-581.

[65] Bridgwater A V. Review of fast pyrolysis of biomass and product upgrading. *Biomass and Bioenergy* 2012; 38: 68-94.

[66] Harris Z, Milner S, Taylor G. Biogenic Carbon-Capture and Sequestration. In: Thornley P, Adams P (eds) *Greenhouse gas balance of bioenergy systems*. London: Elsevier, 2018, pp. 107-139.

[67] Collard FX, Blin J. A review on pyrolysis of biomass constituents: Mechanisms and composition of the products obtained from the conversion of cellulose, hemicelluloses and lignin. *Renew Sustain Energy Rev* 2014; 38: 594-608.

[68] Yang H, Yan R, Chen H, et al. Characteristics of hemicellulose, cellulose and lignin pyrolysis. *Fuel* 2007; 86: 1781-1788.

[69] Krull ES, Baldock JA, Skjemstad JO, et al. Characteristics of Biochar: Organo-chemical Properties. In: Lehmann J, Joseph S (eds) *Biochar for Environmental Management*. London: Earthscan, 2009, pp. 53-65.

[70] Lam PS, Tooyserkani Z, Naimi LJ, et al. Pretreatment and Pelletization of Woody Biomass. In: Fang Z (ed) *retreatment Techniques for Biofuels and Biorefineries*. Berlin: Springer-Verlag, 2013, pp. 93-116.

[71] EBC. *European Biochar Certificate - Guidelines for a Sustainable Production of Biochar. Version 6.3E*. European Biochar Foundation, Arbaz, Switzerland. 2012. DOI: 10.13140/RG.2.1.4658.7043.

[72] Yu KL, Lau BF, Show PL, et al. Recent developments on algal biochar production and characterization. *Bioresour Technol* 2017; 246: 2-11.

[73] Patwardhan PR, Satrio JA, Brown RC, et al. Influence of inorganic salts on the primary pyrolysis products of cellulose. *Bioresour Technol* 2010; 101: 4646-4655.

[74] Ronsse F, Bai X, Prins W, et al. Secondary reactions of levoglucosan and char in the fast pyrolysis of cellulose. *Environ Prog Sustain Energy* 2012; 31: 256-260.

[75] Ronsse F, Dalluge D, Prins W, et al. Optimization of platinum filament micropyrolyzer for studying primary decomposition in cellulose pyrolysis. *J Anal Appl Pyrolysis* 2012; 95: 247-256.

[76] Mohan D, Pittman CU, Steele PH. Pyrolysis of Wood/Biomass for Bio-oil: A Critical Review. *Energy & Fuels* 2006; 20: 848-889.

[77] Bhaskar T, Pandey A. Advances in Thermochemical Conversion of Biomass – Introduction. In: Pandey A, Bhaskar T, Stöcker M, et al. (eds) *Recent advances in thermochemical conversion of biomass*. Oxford: Elsevier, 2015, pp. 3-30.

[78] Corton J, Blanco-Sanchez PP, Khan Z, et al. The Impact of Biomass Feedstock Composition and Pre-treatments on Tar Formation during Biomass Gasification. In: Singh LK, Chaudhary G (eds) *Advances in Biofeedstocks and Biofuels*. Hoboken, NJ: John Wiley & Sons, 2016, pp. 33-54.

[79] Dahmen N, Henrich E, Kruse A, et al. Biomass Liquefaction and Gasification. In: Vertes A, Qureshi N, Blaschek H, et al. (eds) *Biomass to Biofuels: Strategies for Global Industries*. Cham, Switzerland: John Wiley & Sons, 2010, pp. 91-122.

[80] Bridgwater A. Fast pyrolysis of biomass for the production of liquids. In: Rosendahl L (ed) *Biomass Combustion Science, Technology and Engineering*. Cambridge: Woodhead, 2013, pp. 130-171.

[81] Li J, Dai J, Liu G, et al. Biochar from microwave pyrolysis of biomass: A review. *Biomass and Bioenergy* 2016; 94: 228-244.

[82] Heidari M, Dutta A, Acharya B, et al. A review of the current knowledge and challenges of hydrothermal carbonization for biomass conversion. *J Energy Inst* 2019; 92: 1779-1799.

[83] Titirici MM, Funke A, Kruse A. Hydrothermal Carbonization of Biomass. In: Pandey A, Bhaskar T, Stöcker M, et al. (eds) *Recent advances in thermochemical conversion of biomass*. Oxford: Elsevier, 2015, pp. 325-352.

[84] Singh R, Prakash A, Balagurumurthy B, et al. Hydrothermal Liquefaction of Biomass. In: Pandey A, Bhaskar T, Stöcker M, et al. (eds) *Recent*

advances in thermochemical conversion of biomass. Oxford: Elsevier, 2015, pp. 269-291.

[85] Toor SS, Rosendahl L, Rudolf A. Hydrothermal liquefaction of biomass: A review of subcritical water technologies. *Energy* 2011; 36: 2328-2342.

[86] Matsumura Y. Hydrothermal Gasification of Biomass. In: Pandey A, Bhaskar T, Stöcker M, et al. (eds) *Recent advances in thermochemical conversion of biomass*. Oxford: Elsevier, 2015, pp. 251-267.

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