

Chapter 6

Thermochemical Conversion of Cellulose and Hemicellulose



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Abstract Thermochemical conversion process is an important and potential route to transform biomass feedstocks into powers, fuels, and a variety of chemical platforms. The chapter describes general characteristics of thermochemical processes of biomass including combustion, pyrolysis, liquefaction, and gasification, with the focus on the thermal decomposition of individual biomass components such as cellulose and hemicellulose. Thermochemical processes occur at a wide range of temperatures and pressures with or without catalysts, in which cellulose and hemicellulose undergo serial primary and secondary reactions to form a variety of product types and yields. Primary reactions of cellulose and hemicellulose are associated with the dehydration and depolymerization process to smaller fragments, monosaccharides units, and volatiles which further decompose to low molecular weight compounds at severe conditions of temperature, times, pressures, and catalysts. Thermochemical decomposition of cellulose and hemicellulose typically produces various fuel sources including bio-char, bio-oil, bio-crude, and syngas, along with diverse substances such as anhydrosugars (levoglucosan, mannosan, galactosan), furans (furfural, 5-hydroxymethylfurfural), organic acids (acetic acid, formic acid, levulinic acid), ketones, and aldehydes. Cellulose and hemicellulose are the most abundant constituents in lignocellulosic biomass. Understanding the mechanism of thermochemical conversion of cellulose and hemicellulose leads to the choice of suitable biomass feedstocks and the transformation process for targeted production.

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6.1 Introduction

Thermochemical conversion processing is the use of heat to decompose and transform biomass feedstocks into power, fuels, and chemical products. Thermochemical processing occurs at high temperatures from several hundred to 1000 °C or even higher. Therefore, thermochemical processes take place in a short time, in seconds or minutes, compared to hours or days for biochemical processing. Thermochemical processes can be classified into combustion, pyrolysis, gasification, and liquefaction. Biomass combustion has long been used to supply heat and power in the industry. Combustion is the complete oxidation of all organic matters in biomass using sufficient oxygen, while gasification of biomass is performed by partial oxidation of solid biomass feedstocks to produce a mixture of gases at high temperatures using a controlled amount of oxygen. Pyrolysis is the thermal decomposition of biomass into bio-char, bio-oil, and syngas in the absence of oxygen. Liquefaction produces liquid fuels and various chemical platforms from biomass that occurs at mild temperatures in the presence of pressurized water or solvent (Buendia-Kandia et al. 2020; Robert and Kaige 2017). Each process has its own characteristics and uses different reaction conditions, such as temperature, heating rate, residence time, pressure, purge gas flow rate, and catalyst. The yield and composition of the product depend not only on the operating parameters but also on the physicochemical properties of biomass feedstock. Lignocellulosic biomass is mainly composed of cellulose, hemicelluloses, and lignin. Cellulose is rigid and dense because of its highly ordered structure. Hemicelluloses are heterogeneous polymers of hexose and pentose sugars and are less stable than cellulose. Lignin is much more difficult to completely decompose as compared to cellulose and hemicellulose due to its complex aromatic structure. These components that vary from one biomass to another are able to make interactions with each other during thermochemical processes, thus resulting in diverse products with different yields and qualities (Patel et al. 2020). For a better understanding of the mechanism of thermochemical biomass conversion, the processing of the individual components such as cellulose and hemicellulose have been widely performed and investigated. Understanding the decomposition mechanism of each biomass component can provide important information for the effective transformation of biomass into target products, such as energy, power, or chemical products. In this chapter, we discuss the characteristics and behaviors of thermochemical conversion processes of cellulose and hemicellulose including combustion, pyrolysis, liquefaction, and gasification, and their main products (Fig. 6.1).

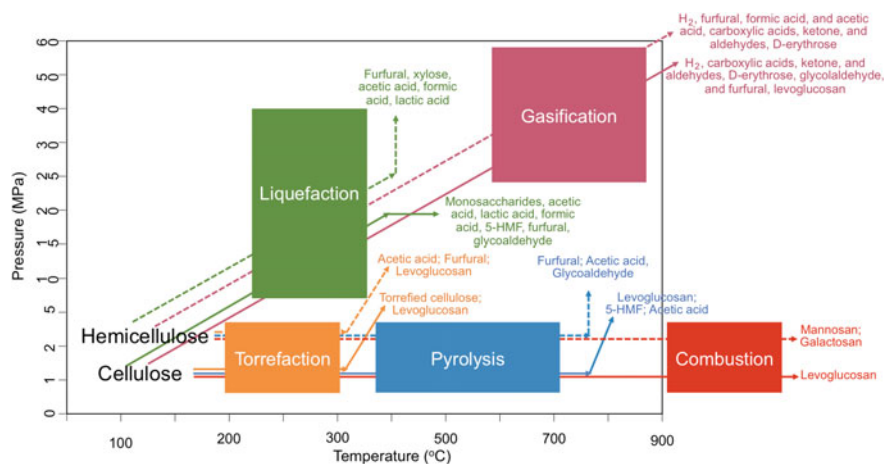


Fig. 6.1 General behaviors of thermochemical conversion technologies and their main products. Dotted line: conversion of hemicellulose; solid line: conversion of cellulose

6.2 Cellulose

Cellulose is the most abundant organic polymer on earth, which is an important structural component of the plant cell wall (Börjesson and Westman 2015). Cellulose is a linear homo-polysaccharide composed of D-glucose monomers linked together by β -1,4 glycosidic bonds. The degree of polymerization of cellulose depends on its source and ranges from several hundred to over ten thousand. Structurally, cellulose is made up of highly ordered crystalline regions and amorphous parts (Amenaghawon et al. 2021; Collard and Blin 2014; Hendriks and Zeeman 2009). These crystalline regions give mechanical stability, hydrophobicity, and chemical recalcitrance to cellulose microfibrils. These microfibrils are arranged and bound to biomass matrices such as hemicellulose and lignin to form bundles or macrofibrils. In addition, multiple hydroxyl groups in the cellulose can form intermolecular hydrogen bonds among different cellulose chains or intramolecular hydrogen bonds within the polymer itself. The high crystallinity and high degree of hydrogen bonds in the cellulose microfibrils give cellulose fibers strength and stiffness (Börjesson and Westman 2015; Pinkert et al. 2009).

6.3 Hemicellulose

Hemicellulose is a heterogeneous and complex polymer of different sub-constituents such as pentoses (xylose and arabinose), hexoses (glucose, mannose, galactose), hexuronic acids (4-O-methyl-D-glucuronic acid, D-glucuronic acid, and D-galacturonic acid), acetyl groups, and small amounts of L-rhamnose and L-fucose

(Patel et al. 2020; Zhou et al. 2018). Hemicellulose accounts for 15–30% of lignocellulosic biomass compositions (Wang et al. 2021). Compared to cellulose, hemicellulose has a lower molecular mass and degree of polymerization. Unlike cellulose, hemicellulose is made up of amorphous regions and branched, making it less stable and more prone to decomposition than cellulose (Amenaghawon et al. 2021; Laureano-Perez et al. 2005). Hemicellulose is cross-linked with cellulose and lignin to strengthen the plant cell wall structure. The types and compositions of hemicellulose vary according to their source. Xylan is the predominant hemicellulose in hardwood and herbaceous biomass, while mannan is found mainly in softwood (Carrier et al. 2011; Zhou et al. 2016). Xylan usually consists of a backbone of β -(1–4)-linked xylose monomers which might attach side chains containing 4-O-methyl-glucuronic acid, glucuronic acid, arabinose, galactose, and glucose (Ebringerová et al. 2005). Mannan is composed of a backbone of β -(1–4)-linked mannose units or β -(1–4)-linked mannose and glucose (glucomannan) with/without galactose-containing side chains (Amenaghawon et al. 2021; Zhou et al. 2016) (Table 6.1).

6.4 Combustion

Combustion is the most feasible and conventional way to utilize biomass as a renewable energy source by cleaving the chemical bonds of fuel and generating a series of reactions in the presence of air or oxygen under the heat. To evaluate combustion performance, it is important to recognize the chemical composition and physical characteristics of biomass. Thermogravimetric analysis (TGA) is typically used to investigate thermal decomposition characteristics of solid materials based on weight change at the determined heating rate as a function of time or temperature. The structure and chemical composition of lignocellulosic fibers (cellulose, hemicellulose, and lignin) greatly influence their thermal degradation, and the differential thermal analysis is an effective method to investigate the thermal behavior of the biomass (Chen et al. 2017; Jiang et al. 2017; Sefain et al. 1985).

6.4.1 Combustion of Cellulose

TGA analysis showed that the combustion of pure cellulose showed only one peak, which could be explained by the occurrence of only the combustion of the volatile fraction of cellulose (Boukaous et al. 2018). Combustion kinetics can be gained by using a multi-Gaussian-distributed activation energy model and density-functional theory (Wang et al. 2021; Yu et al. 2021). For combustion of cellulose, reactive force field molecular dynamics (ReaxFF-MD) simulations were applied to study the thermal decomposition of amorphous and partially crystalline cellulose (i.e., microfibrils). By following the complete transformation of cellulose into low molecular weight products, scientists found the decomposition begins with glycosidic bond

Table 6.1 Major mechanisms and recent applications of thermochemical conversion technologies

Technologies	Major mechanisms	Applications	Hemicellulose
Combustion	<ol style="list-style-type: none"> 1. Heat (high, > 900 °C) 2. Low pressure 3. With oxygen 	<p>Cellulose</p> <ul style="list-style-type: none"> – Electrode materials, metal oxides, and ceramics (Kumar 2019) – DOPO–Cinnamoyl cellulose–DCC (Liu et al. 2021) – High-performance lithium-ion battery (Zhu et al. 2016) 	<ul style="list-style-type: none"> – Mannosan and galactosan (Kuo et al. 2008; Li et al. 2019; Ruan et al. 2020; Segato et al. 2021)
Pyrolysis	<ol style="list-style-type: none"> 1. Heat (>300 °C) 2. Pressure (<5 MPa) 3. No oxygen 	<ul style="list-style-type: none"> – Anhydrosugars (levoglucosan etc.) (Junior et al. 2020) – Low molecular weight (LMW) compounds (glycoaldehyde, pyruvaldehyde, hydroxyacetone, and glycerlaldehyde) (Patwardhan et al. 2011; Wang et al. 2012, 2020b) – Furans (5-hydroxymethylfurfural, furfural, 2-furan methanol, 3-furan methanol, and 5-methyl furfural) (Patwardhan et al. 2011; Yang et al. 2020b) 	<ul style="list-style-type: none"> – Char and bio-oils (Chen et al. 2019b; Zhou et al. 2016, 2018) – Light oxygenated compounds: glycoaldehyde, acetaldehyde, 1-hydroxy-2-propanone, 4-hydroxy-5,6-di-hydro-(2 H)-pyran-2-one, and 1-hydroxy-2-butanone (Usino et al. 2020; Werner et al. 2014) – Furfurals (Chen et al. 2019b; Wang et al. 2015)
Liquefaction	<ol style="list-style-type: none"> 1. Temperature (280–370 °C) 2. Pressure (10–25 MPa) 3. No oxygen 4. Aqueous liquefaction (using water) 5. Nonaqueous liquefaction (methanol, ethanol, isopropanol, phenol, etc.) 6. Required catalyst (Brønsted or Lewis acids, MnO, CaO, CeZrOx, Raney Ni-NaOH, Na₂CO₃, Fe-zeolite, Na₂CO₃-Fe) 	<ul style="list-style-type: none"> – Monosaccharides and further to acids, aldehydes, ketones (Gagic et al. 2018; Wang et al. 2020a; Jasinukaitė-Grojzdek et al. 2021; Liu et al. 2020; Sun et al. 2020a) – Lactic and formic acid (Xu and Li 2021) – Photothermal plastic (Sun et al. 2021; Zimmermann et al. 2021) – Biopolyols and polyurethane (Ge et al. 2018; Kosmela et al. 2018) 	<ul style="list-style-type: none"> – Oligosaccharides, monosaccharides, furfural, glycerlaldehyde, acetic acid, lactic acid, etc. (Ghimire et al. 2021; Song et al. 2020; Yang et al. 2020a) – Xylose and 4-O-methyl glucuronic (Ghimire et al. 2021)

(continued)

Table 6.1 (continued)

Technologies	Major mechanisms	Applications	
Gasification	1. Temperature (> 700 °C) 2. Pressure (> 2.5 MPa) 3. Oxygen 4. Steam 5. Required catalyst (MnO, CaO, Raney Ni-NaOH, SiO ₂ , Fe-zeolite, Na ₂ CO ₃ -Fe)	Cellulose – Carboxylic acids, ketone, and aldehydes (Ong et al. 2019; Soomro et al. 2018; Yang et al. 2020a; Yu et al. 2018) – Syngas (Craven et al. 2020; Zou et al. 2018; Minami et al. 2018)	Hemicellulose – Xylose, 4-O-methylglucuronic furfural, formic acid, and acetic acid (Berthet et al. 2016; Hassan et al. 2020) – Hydrogen (Garcia-Jarana et al. 2020; Okolie et al. 2020)

cleavage. Particularly, the crystallinity has no appreciable effects on the mechanism or kinetics of chain scission (which is generated by glycosidic bond cleavage occurs during cellulose decomposition), the evolution of the molecular weight distribution, or the low molecular weight products (Paajanen et al. 2021).

Stochastic reactive molecular dynamics (RMD) simulations were used to identify and analyze the primary thermal decomposition reactions of an isolated cellulose molecule at a range of temperatures from 1400 to 2200 K (1127–1927 °C), and the results suggest that the decomposition occurs primarily through random cleavage of the (1–4)-glycosidic bonds by an activation energy of (171 ± 2) kJ.mol⁻¹ (Paajanen and Vaari 2017). When cellulose is combusted at temperatures above 300 °C, levoglucosan (1,6-anhydro-β-D-glucopyranose) is the most abundant monosaccharide anhydride that was released. Levoglucosan is considered as a molecular marker for the combustion of cellulose (Kuo et al. 2008; Li et al. 2019; Ruan et al. 2020; Segato et al. 2021).

Cellulose combustion typically releases carbon monoxide and carbon dioxide. The mechanism of carbon monoxide release in cellulose combustion was investigated by using molecular dynamics (MD) simulations together with ReaxFF to analyze reactions of cellobiose oxidation at different temperatures. Basically, this approach uses molecular dynamics simulations equipped with a reactive force field to study the formation of cellobiose from the cellulose oxidation process. The production of carbon monoxide is highly dependent on the abundance of formyl and carboxyl groups, which are formed through cellobiose decomposition. Elevated temperatures cause more carbon monoxide to be released. Subsequently, the formed carbon monoxide is oxidized into carbon dioxide, where reaction steps for the formation and decomposition of the carboxyl group are involved. The simulation results help to identify critical reaction steps and lead to the development of a method to reduce the concentration of free radicals, which then allows the formation of carbon monoxide to be reduced (Barzegar et al. 2020; Hao et al. 2020; Luo et al. 2018).

6.4.2 Recent Applications of Cellulose Combustion

A new synthetic method known as combustion synthesis (CS) has emerged and gained considerable research attention due to it being fast and economic and involving simple synthesis steps. Using a thin cellulose paper, the technique called “Cellulose Assisted Combustion Synthesis” (CACS) or “Impregnated Layer Combustion Synthesis” (ILCS) has been applied for the synthesis of electrode materials, metal oxides, ceramics, catalysts, plus other products (Kumar 2019). Cellulose-based materials with their excellent film-forming properties, mechanical properties, and flame-retardancy, have found application in the battery industry. In this process, cellulose was prepared in a membrane, with excellent infiltration of the electrolyte and flame-retardant performance, namely DOPO–Cinnamoyl Cellulose (DCC), then assembled into a lithium-ion battery. The corresponding battery characterization was then tested for its cycle and rate stability. The test results showed excellent characteristics and

enhanced battery performance making the cellulose-based composite materials a very promising separator for high power applications, which broadens their uses in the field of energy storage devices (Liu et al. 2021).

Cellulose combustion can also be applied in making Ni–MgO catalysts with cellulose paper being impregnated with $\text{Mg}(\text{NO}_3)_2$, $\text{Ni}(\text{NO}_3)_2$, glycine solutions, and their different combinations. It was established that the combustion mechanism changes as a function of the impregnated media composition, and after combusting, the resulting materials had a highly porous, sponge-like microstructure (Danghyan et al. 2020). Using a single-step nitrate-cellulose combustion synthesis, a novel method was proposed to produce MnO/carbon composites, in which the MnO nanoparticles were embedded into a porous carbon matrix, that resulted in a MnO/carbon composite with enhanced cycling performance and capacity retention, as it had potential to be an anode alternative for high-performance lithium-ion battery (Zhu et al. 2016).

To have a deep understanding of the mechanism, scientists developed a novel model for the combustion of reactive solutions impregnated into a cellulose carrier, which were shown to be effective in the synthesis of metallic oxides with a nanoscale microstructure, that made the cellulose-assisted combustion materials suitable for catalyst applications. Basically, the model involved three reactions: (1) combustion of the carrier matrix, (2) an endothermic reaction related to the decomposition or gasification of the synthesis reaction precursors, and (3) the exothermic oxide synthesis reaction. The results indicated that manipulation of the cellulose burning reaction was the most favorable to increase the reaction yield of the composite materials (Lennon et al. 2011).

6.4.3 Combustion of Hemicellulose

Hemicellulose combustion occurs via a two-step process: (1) Reduced degree of polymerization in the first step; and (2) Decomposed into volatiles and char in the second step. The ignition temperature is the temperature at which the combustion reaction begins, while the final temperature indicates the end of the combustion reaction, which is essential to ensure the perfect design of the combustor and avoid unburned solid fuel at the outlet of the reactor. In the first step, hemicellulose requires the lowest ignition temperature and also gains the lowest final temperature. However, in the second step, the ignition and final temperature of hemicellulose are higher than those required for the other components and just only lower than that of lignin. TGA characteristic curves showed the presence of three peaks, two of them were completely overlapped and could be explained by the heterogeneity of hemicellulose, which is mainly constituted of xylose along with small parts of glucuronic acid and other sugars (Boukaous et al. 2018). Through the process, mannosan and galactosan are considered as molecular markers for the combustion of hemicellulose (Kuo et al. 2008; Li et al. 2019; Ruan et al. 2020; Segato et al. 2021).

6.5 Pyrolysis

Pyrolysis is the thermochemical conversion process of biomass feedstock in the absence of oxygen to break down the large complex polymers present in the biomass into smaller fragments and molecules. The pyrolysis process is initiated by the evaporation of water, followed by primary decomposition and secondary reactions. Primary decomposition consists of three pathways including char formation, depolymerization, and fragmentation (Collard and Blin 2014; Lu et al. 2011; Van de Velden et al. 2010; Wooten et al. 2003). The charring process involves the formation of aromatic polycyclic structures of chars in which benzene rings are formed, combined, and rearranged (Cho et al. 2010; McGrath et al. 2003). Depolymerization breaks down the linkages in the biomass polymers, resulting in a decrease in the degree of polymerization of the chains and releasing volatile compounds (Azeez et al. 2011; Madhua et al. 2020). Fragmentation occurs in the linkage of the polymers even within the monomer units, leading to the formation of small condensable organic compounds and incondensable gases (Collard and Blin 2014; Kostetsky and Broadbelt 2020). Secondary reactions include cracking or recombination (Chen et al. 2019a). Cracking reactions involve the breaking of chemical bonds within the unstable and volatile compounds, which results in the formation of lower molecular weight molecules (Collard and Blin 2014; Neves et al. 2011). In contrast, released volatile compounds can be recombined together to yield higher molecular weight molecules (Orcid et al. 2017; Wei et al. 2006). The products of pyrolysis are divided into three groups including carbon-rich solids (char), liquid products of condensable vapors (tars and oils), and non-condensable species (Abhijeet et al. 2020; Patel et al. 2020; Robert and Kaige 2017). The yield of each fraction depends on the heating rate and residence time. The slow heating rates and long residence times favor the production of solid char, while high heating rates and short residence times facilitate the production of vapor products. It is considered as slow pyrolysis when the heating rate is below 10 °C/s, fast pyrolysis when it is higher than 100 °C/s, and flash pyrolysis when the process is performed at higher than 500 °C/s. Biomass pyrolysis has been used for centuries and continually improved since it provides many benefits and serves as a sustainable means of producing biofuels, biochemicals, and other commodities (Amenahawon et al. 2021; Robert and Kaige 2017).

6.5.1 *Slow Pyrolysis*

Slow pyrolysis is the oldest form of biomass pyrolysis that usually occurs over a long period of time using slow heating rates to produce charcoal or bio-char as the main product. Lower heating rates and long residence times facilitate the re-polymerization reactions of the biomass constituents, which may generate a polycyclic carbon structure and maximize the yield of solid bio-char. Most of the slow pyrolysis literature focused primarily on the production of carbon-rich solids, thus

the process is called carbonization (Gabhane et al. 2020). Carbonization is carried out over a wide temperature range from 300 to 900 °C.

Temperature plays the most important role in the production of bio-char by slow pyrolysis. The processing temperature determines the structural and physicochemical properties of bio-char such as surface area, pore structure, surface functional groups and elemental composition (Tag et al. 2016). It was found that high pyrolysis temperature resulted in increased specific surface area, pore-volume, and carbon content of bio-char but reduced bio-char yield, nitrogen, oxygen, and hydrogen content (Chatterjee et al. 2020; Dhar et al. 2020; Ferraro et al. 2021; Moradi-Choghamarani et al. 2019; Salam et al. 2020). Bio-char with a high specific surface area, large pore size, and elevated carbon content have potential applications in pollution remediation, soil fertility improvement, and carbon sequestration (Agnieszka et al. 2020; Tag et al. 2016).

Torrefaction is another type of slow pyrolysis which is performed at mild temperatures between 200 and 300 °C in the absence of oxygen to produce torrefied biomass (Boateng, 2020). During the torrefaction process, water and volatile compounds in the biomass feedstock are released resulting in the formation of a dark solid material (torrefied biomass) that exhibits higher energy density and greater homogeneity compared to the original feedstock (Amenaghawon et al. 2021). Currently, torrefaction has been investigated intensively and is gaining a high capability to be implemented at an industrial production scale.

6.5.1.1 Torrefaction of Cellulose

Previous studies mainly investigated the effects of torrefaction pretreatment on the chemical structure and pyrolysis behaviors of whole biomass, while a few studies focused on the structural transformation of cellulose. The reaction temperature significantly affects the distribution of the products from cellulose pyrolysis. The torrefaction of cellulose slowly occurred at 200 °C to produce solid char as the main product, along with a small amount of bio-oil, but no gaseous products were generated at below 250 °C. As the temperature was increased, the yield of bio-char decreased while bio-oil production was elevated (Zhang et al. 2021). The formation of an intermediate product called “active cellulose” or anhydrocellulose was reported during the processing below 300 °C (Paajanen and Vaari 2017). Active cellulose is obtained from partial depolymerization of the cellulose, whereas anhydrocellulose is formed after the dehydration reactions. For application, cellulose can be directly used for the production of hydrocarbon-rich bio-oil using integrated microwave torrefaction and ZSM-5 catalyst, but the results are not equal in comparison to those from biomass (Bu et al. 2021; Shen and Gu 2009; Zhou et al. 2020). Significant influences of metal salts, such as chlorides (CaCl_2 , ZnCl_2 , MgCl_2 , and Al_2O_3), hydroxides ($\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$), and acetates ($\text{Ca}(\text{CH}_3\text{COO})_2$) on the torrefaction of cellulose, indicated that the conversion mechanism of torrefaction process needed to be intently considered before scaling up to the industrial application (Atienza-Martínez et al. 2017; Tancredi et al. 2017; Zhao et al. 2020; Zhou et al. 2020).

6.5.1.2 Torrefaction of Hemicellulose

According to the TGA profile, the thermal decomposition of hemicellulose occurs at a temperature range of 200–350 °C (Collard and Blin 2014; Zhou et al. 2016). The lower thermal stability of hemicellulose compared to cellulose is attributed to its amorphous structure and its lower degree of polymerization. Therefore, hemicellulose requires lower temperature and activation energy for thermal decomposition (Chen et al. 2019b; Negi et al. 2020; Zhou et al. 2016). The structural changes in hemicellulose after torrefaction, even disappeared at higher torrefaction temperatures (250–300 °C), probably is caused by the removal of hydroxyls in hemicellulose resulting in the generation of carboxyl and conjugated ketone, based on two-dimensional perturbation correlation analysis using Fourier transform infrared spectroscopy (Chen et al. 2015; Wang et al. 2016a). After torrefaction, oxygen content decreases significantly, leading to the increase of a high heating value. The results obtained from analyzing two-dimensional perturbation correlation based on diffuse reflectance infrared Fourier transform spectroscopy showed that the dehydration of hydroxyls and the dissociation of branches were the main reactions at low torrefaction temperature, but when the temperature was increased, the depolymerization of hemicellulose and the fragmentation of monosaccharide residues occurred. Via the activation energy model, the results showed that hemicellulose torrefaction process enhanced the activation energy but decreased the yields of torrefied products (Cahyanti et al. 2021; Wang et al. 2016b). The torrefaction process strongly affects the degradation of hemicellulose, that leads to the increase of carbon content, decreased H/C and O/C ratios, increased mass energy density, higher heating value, better grindability, higher hydrophobicity, and resistance to biodegradation (Niu et al. 2019; Zheng et al. 2021).

6.5.2 Fast Pyrolysis

In contrast to slow pyrolysis, fast pyrolysis involves the use of a high heating rate, short residence time (<2 s), and rapid vapor cooling to obtain bio-oil, mixed gases, and solid char (Pawar et al. 2020). During the fast pyrolysis process, rapid decomposition of the biomass occurs with the formation of vapors and aerosols, which are condensed after quenching to recover a darkish brown liquid known as bio-oil. Slow pyrolysis gives high solid yields with low liquid yields, while fast pyrolysis gives high liquid yields with low solid yields (Amenaghawon et al. 2021). Fast pyrolysis is the most popular technique for the production of liquid fuels and various commodity chemicals.

Recently, bio-oil produced through the fast pyrolysis process has attracted considerable attention since it provides potential uses as renewable biofuels source, biofuel additives, and as a precursor for the production of specialty chemicals (Patel et al. 2020). The quality and yield of bio-oil produced by fast pyrolysis are affected by not only processing conditions but also the chemical composition of the biomass

feedstock. Many studies have shown that the optimum temperatures for obtaining high liquid yields were between 450 and 550 °C, and bio-oil yields varied according to the type of biomass used. It was reported that biomass feedstocks with moisture content less than 10% and particle size of 2–3 mm were the primary requirements for achieving a high heating rate and heat transfer during fast pyrolysis (Pandey et al. 2015).

Moreover, the pyrolysis reactor must be designed and controlled to heat up the biomass rapidly and cool the vapor phase to make it condense to form the bio-oil products in seconds (Robert and Kaige 2017). Several configurations of reactors are used for pyrolysis including bubbling fluidized bed, circulating fluidized bed, conical spouted bed, ablative reactor, rotating cone, vacuum pyrolysis reactor, entrained flow reactor, wire mesh reactor, and auger (twin screw) reactor. The fluidized bed is the most widely used pyrolysis reactor because it is simple to design, construct, and operate. Moreover, it is proven to exhibit a high heat transfer rate, good temperature control, temperature uniformity, and large heat storage capacity (Boateng 2020; Pandey et al. 2015). A circulating fluidized bed reactor is similar to a bubbling fluidized bed except for the velocity of the gas used to fluidize the bed. In the circulating fluidized beds, the gas velocity is set high enough to transport char and heat carrier particles (e.g., sands) to the second combustor. The sand stream is reheated through the char combustion process and then recirculated to the fluidized bed to heat up the biomass feedstock. Circulating fluidized bed reactors have been used for obtaining a high yield of bio-oil from sugarcane bagasse (78%) (Treedet and Sunti-varakorn 2018), sawdust, giant Miscanthus, and empty fruit bunch (60%) at pilot scale (Park et al. 2019). Another technology is the rotating cone reactor in which biomass feedstock and hot sand are fed near the bottom of a cone at the same time. The centrifugal forces generated by the rotation of the cone enable the particles to move upwards without the need for large volumes of carrier gas. Hot sand is then recycled back to the rotating cone reactor. The Biomass Technology Group (BTG) has commercialized this reactor that converts biomass feedstock into bio-oil as the main product in just 2 s. It has been reported that a conical spouted bed reactor is suitable for the fast pyrolysis to obtain high bio-oil yields from rice husk (70%) (Alvarez et al. 2014) and eucalyptus waste (75.4%) (Maider Amutio et al. 2015). The outstanding features of the spouted bed reactor include high heating and mass transfer rates, short residence time, and continuous char removal, which accelerate de-volatilization reactions and minimize the cracking of these components (Alvarez et al. 2014; Amutio et al. 2012).

6.5.3 Flash Pyrolysis

Efforts have been carried out to increase the heating rate and minimize the residence time of the vapor phase to improve the production yield of bio-oil from biomass pyrolysis. High bio-oil yields of 75–80% can be achieved by flash pyrolysis occurring at high temperatures (>800 °C) using very high heating rates (>1000 °C/s) and

very short residence times (<0.5 s) (Pawar et al. 2020). Feedstock particle size less than 0.2 mm is a primary requirement to achieve such a high heating rate and heat transfer rate (Amenaghawon et al. 2021; Balat et al. 2009; Dada et al. 2021). Rotating cone and conical spouted bed reactors are considered good configurations for the flash pyrolysis process due to their high heat transfer rates and short residence time (Amutio et al. 2012; Papari and Hawboldt 2015).

6.5.4 Pyrolysis of Cellulose

TGA is the most common analytical method used to study the mechanism of polymer degradation. TGA of cellulose showed that the cellulose is thermally degraded at a temperature range of 300–400 °C with the highest decomposition rate between 330 and 370 °C (Collard and Blin 2014; Zhou et al. 2016). The reaction temperature significantly affects the distribution of the products from cellulose pyrolysis. Bio-oil yield increased with increasing temperatures and was maximized at 450–500 °C. Further increase in the temperature resulted in a gradual decrease in the yield of tar and bio-oil. In contrast, the conversion of cellulose into gaseous products was dominant at above 600 °C and the yield of syngas including CO, CO₂, CH₄, and H₂ significantly increased with increasing temperatures (Zhang et al. 2021).

Pyrolysis of cellulose produces several products classified into three groups: anhydrosugars, low molecular weight (LMW) compounds, and furans. Anhydrosugars are formed by transglycosylation reactions (Junior et al. 2020). Levoglucosan (LG) is the most abundant anhydrosugar (up to 80% in relative peak area) from cellulose pyrolysis (Collard and Blin 2014; Junior et al. 2020; Yang et al. 2020a). The yield of levoglucosan is affected by processing temperatures, residence times, and the degree of polymerization of the cellulose chains (Wang et al. 2020a; Yang et al. 2020a). The subsequent decomposition of LG produces LMW compounds, such as 1-pentene-3,4-dione, acetaldehyde, 2,3-dihydroxypropanal, and propanedi-aldehyde from C–O bond breaking reactions (Zhang et al. 2012). The levoglucosan vaporized above 500 °C contributes mainly to gaseous and liquid streams rather than solid char formation (Banyasz et al. 2001; Basu 2013). Other anhydrosugars were found in much smaller proportions than LG, such as levoglucosone, 1,4:3,6-dianhydro- α -D-glucopyranose, 2,3-anhydro-D-mannosan, and 1,6-anhydro- β -D-glucofuranose. LMW compounds from cellulose pyrolysis include glycoaldehyde, pyruvaldehyde, hydroxyacetone, and glyceraldehyde (Patwardhan et al. 2011; Yang et al. 2020a). Organic acids such as formic acid, acetic acid, and propionic acid also were detected among the LMW pyrolytic products (Patwardhan et al. 2011; Wang et al. 2012, 2020b). Furans are formed by open-ring reactions and dehydration from the glucopyranose structure (Junior et al. 2020). The yields of furans (5-hydroxymethyl furfural, furfural, 2-furan methanol, 3-furan methanol, and 5-methyl furfural) varied with operating conditions. It is noted that the furan ring is very stable, but its side groups (methyl or oxygenated groups) are less stable and are readily cleaved or rearranged with increasing temperatures. Decomposition of

furans led to an increase in the formation of low molecular weight compounds and gaseous species. 5-Hydroxymethyl furfural (5-HMF) and furfural, the attractive platform chemicals, were found to be the most abundant furans (Patwardhan et al. 2011; Yang et al. 2020a). In a previous study, the furans content reached the highest value, about 35% (in relative peak area), and changed little with increasing temperature. It is proven that the thermal degradation of pentose sugars (xylose and arabinose) tends to yield furfural, whereas the processing of hexose sugars (glucose, mannose, and galactose) tends to produce 5-HMF (Zhou et al. 2016). Further decomposition of 5-HMF via fast pyrolysis at 600 °C was performed and resulted in the release of 72.8% furfural. This evidence demonstrated the presence of furfural as a predominant secondary product of cellulose pyrolysis reported in the literature (Collard and Blin 2014; Wang et al. 2012).

6.5.5 Pyrolysis of Hemicellulose

According to the TGA profiles, the entire thermal degradation of hemicellulose could take place in three steps. The first step includes the dehydration and cleavage of the side chains of hemicellulose with slight mass loss. The dissociation of side chains in xylan occurs readily due to its relatively low energy of activation (Dai et al. 2021). Acetic acid was reported as the major product in xylan pyrolysis which was formed by the cleavage of acetyl groups attached to the backbone of xylan (Zhou et al. 2016). The main pyrolysis, which occurs in the second step, is responsible for the most mass loss through a sequence of reactions such as dehydration, decarboxylation, and decarbonylation. Finally, in the third step, further decomposition of hemicellulose occurs to release volatiles from the residue resulting in a slight mass loss (Collard and Blin 2014; Peng and Wu 2010).

Xylan is the most abundant hemicellulose in nature. Xylan is typically used as a model compound for understanding the mechanism of hemicellulose pyrolysis. Pyrolysis of xylan typically yields 20–30% char, 10–20% non-condensable gas species, and 40–60% bio-oil (Zhou et al. 2018). The non-condensable gaseous products include H₂, CO, CO₂, and light hydrocarbons such as CH₄, C₂H₆, and C₃H₈. Bio-oil mainly includes acids (acetic acid and formic acid), furans (furfural), anhydrosugars (anhydroxylose and dianhydroxylose), aldehydes, ketones, and minor aromatic compounds (Zhou et al. 2016, 2018).

Hemicellulose is composed of heterogeneous and diverse monomers. Pyrolysis of hemicellulose generates more complicated and various product distributions compared to cellulose pyrolysis. Hemicellulose pyrolytic products are mainly categorized into two groups including light oxygenated compounds and furans. Light oxygenated compounds mainly include glycoaldehyde, acetaldehyde, 1-hydroxy-2-propanone, 4-hydroxy-5,6-di-hydro-(2 H)-pyran-2-one, and 1-hydroxy-2-butanone, among which glycoaldehyde is detected as the most abundant compound (Werner et al. 2014). Furfural is widely reported as a major furan in hemicellulose pyrolysis (Zhou et al. 2018). Furfural is derived from thermal degradation of pentose units or by

secondary decomposition of 5-hydroxymethyl furfural (5-HMF) (Usino et al. 2020). Hemicellulose rich in acetyl groups attached to its backbone yields more acetic acid as a major product (Wang et al. 2015). Furans and acetic acid contents decrease with increasing temperatures (Wang et al. 2015).

6.6 Liquefaction

Liquefaction (hydrothermal liquefaction) is a process responsible for the conversion of lignocellulosic biomass into bio-liquid and/or crude oil-like products at temperatures of 280–370 °C and pressures of 10–25 MPa in the absence of oxygen (Khatiwada et al. 2021; Yang et al. 2020a). This technology has much attraction to produce renewable fuels due to its low operating temperatures and fast reaction rates, and the use of wet feedstocks without the need for an energy-intensive drying process (Amarasekara and Reyes 2020; Khatiwada et al. 2021; Song et al. 2020). There are two types of liquefaction, which include aqueous liquefaction (using water) and non-aqueous liquefaction (using organic solvents such as methanol, ethanol, isopropanol, phenol, and others). The aqueous liquefaction is typically carried out in subcritical water and requires catalysts such as Brønsted or Lewis acids and metal oxides such as MnO, CaO, CeZrOx, Raney Ni-NaOH, Na₂CO₃, Fe-zeolite, Na₂CO₃-Fe. Aqueous liquefaction generally gives higher quality and quantity of bio-oil compared to non-aqueous liquefaction (Amarasekara and Reyes 2020; Feng et al. 2018; Song et al. 2020; Yang et al. 2020a).

6.6.1 Liquefaction of Cellulose

Under thermochemical liquefaction, cellulose is mainly hydrolyzed into monosaccharides and further to acids, aldehydes, ketones, and other products. Cellulose is decomposed into soluble sugars (cellobiose, lactose, and glucose) as primary products in subcritical water at 200–300 °C. Soluble sugars subsequently undergo secondary reactions of isomerization, dehydration, and retro-aldol condensation to form D-erythrose, glycolaldehyde, and furfural, which are further degraded to smaller species. A significant decrease in soluble products was observed with increasing reaction times because the sugars were readily degraded to carboxylic acids, ketone, and aldehydes (Gagic et al. 2018; Wang et al. 2020a). These products then can be upgraded to liquid fuels, platform biochemicals, and commodity chemicals such as ethanol, liquid alkanes, 5-hydroxymethylfurfural (5-HMF), furfural, and acetic acid. The results obtained in several studies showed that cellulose could be liquefied with high efficiency (Li et al. 2020; Peng et al. 2018; Wang et al. 2020b; Xu et al. 2019).

Catalyst is one of the key factors that affect the quantity and quality of liquefaction products. In addition to acidic, alkali, and metal catalysts, glycol organosolv and supercritical ethanol (with 2,2,6,6-Tetramethylpiperidinoxy-TEMPO) processes

have recently received much attention, due to their environmental benefits, low viscosity, and high solubility (Jasiukaitytė-Grojzdek et al. 2021; Liu et al. 2020; Sun et al. 2020a). Hydrothermal liquefaction with metallic-Fe catalyst is still the most effective process for producing water-soluble fraction, thereby enhancing the hydrocarbon yield (Hirano et al. 2020).

Cellulose liquefaction shows great promise for using cellulose as a supporting substrate or template material in photothermal plastic due to its renewability, degradability, abundant availability, and low cost. In fact, cellulose composite materials have been successfully developed and applied in various fields such as antibacterial compounds, UV shielding, catalysis, flame retardant, fluorescence, metal ion adsorption, and supercapacitor (Sun et al. 2021b; Zimmermann et al. 2021). In liquefaction technology, solvent is one of the key factors. Water, low-carbon alcohols, supercritical fluids, and hydrocarbon-based solvents such as n-alkanes are often employed in cellulose liquefaction (Li et al. 2021).

The increasing trends of using biomass as an alternative to fossil fuels lead to the formation of the biorefinery concept, which now utilizes a range of biomass and known conversion technologies to produce green chemicals and polymers without impacting food and feed security. Among them, biopolyols and polyurethane obtained by direct conversion of separated cellulose or lignocellulosic biomass through liquefaction technology were listed among the “Top 10” platform chemicals in a report prepared by the Pacific Northwest National Laboratory (PNNL) and the National Renewable Energy Laboratory (NREL) (Ge et al. 2018). Interestingly, polyurethane foams were produced via cellulose liquefaction in the presence of crude glycerol, which indicated that cellulose could be a good alternative material to produce polyurethane (Ge et al. 2018; Kosmela et al. 2018).

6.6.2 Liquefaction of Hemicellulose

Due to its heterogeneous and complex structure, the product profile of hydrothermal liquefaction of hemicellulose is complicated and includes a variety of chemicals such as oligosaccharides, monosaccharides, furfural, glyceraldehyde, acetic acid, lactic acid, plus others (Ghimire et al. 2021; Song et al. 2020; Yang et al. 2020a). Hemicellulose decomposition in subcritical water at below 220 °C yielded monosaccharide sugars, mainly xylose and 4-O-methylglucuronic acid, which were further degraded into small molecule products such as furfural, formic acid, and acetic acid at temperatures higher than 220 °C. Xylan usually is used as a model compound in many studies. Xylan liquefaction resulted in different product distributions through hydrolysis and oxidation reactions depending on operating conditions. Hydrolysis occurs via the depolymerization of xylan to soluble sugars, while oxidation promotes the formation of organic acids. The released organic acids subsequently catalyze the degradation of the hydrolyzed products into small molecules. Catalysts are typically used in liquefaction. The presence of a high concentration of oxidizing agent (H_2O_2) and/or pressurization facilitates strong oxidative reaction and/or acidic hydrolysis,

yielding xylo-oligosaccharides, xylose, arabinose, glucose, acetic acid, and their decomposition compounds, which include furans and organic acids (Phaiboonsilpa et al. 2020; Zhou et al. 2016). In the presence of ethylene glycol, xylan was decomposed and transferred to the liquid phase, with the average molecular weight of xylan significantly decreasing after liquefaction. The products from the liquefaction of xylan in ethylene glycol are ethylene glycol derivatives, alcohols, aldehydes, ketones, some acids, and their esters (Wang et al. 2016a).

6.7 Gasification

Gasification is a thermochemical conversion process that involves complex reactions, pressure changes, and heat and mass transfer. In general, gasification is used to convert solid fuels (coal or biomass) into value-added products or to release heat for heating and power generation at high temperatures without combustion. Gasification requires oxygen, air, and steam to convert carbonaceous materials into gaseous fuels. Fixed bed and fluidized bed gasifiers are common technologies. Basically, gasification consists of four steps: (1) Drying or dehydration, in which evaporation of moisture occurs under 150 °C; (2) Pyrolysis, in which devolatilization occurs at a temperature range of 150–700 °C; (3) Combustion, in which fuel constituents oxidize and exothermic reactions occur in the temperature range of 700–1500 °C; and (4) Reduction, in which endothermic reactions occur in the temperature range of 800–1100 °C (Ong et al. 2019; Soomro et al. 2018; Yang et al. 2020a; Yu et al. 2018).

6.7.1 Gasification of Cellulose

Cellulose consists of several hundred to many thousands of β -glycosidic bonds linking D-glucose units, which are not stable and tend to cleave at high temperatures. It was observed that cellulose began to decompose at 180 °C and the reaction rate was much faster with increasing temperature and residence time, leading to sugar degradation to carboxylic acids, ketone, and aldehydes. Glucose was completely decomposed in 60 s at 300 °C, but only in 0.5 s at 460 °C (Yang et al. 2020a). Degradation of levoglucosan, the major volatile intermediate being produced from cellulose gasification, was completed at a temperature range of 550–700 °C within only 0.11–0.45 s (Fukutome et al. 2017).

Normally, gasification requires a catalyst to increase efficiency while reducing temperature and time. Among these, alkali and alkaline earth metals and Ni-based catalysts are commonly used in the gasification process (Ong et al. 2019). Cellulose gasification produces the largest amount of H₂ in the absence of steam and catalyst, but adding the Ni-based catalyst significantly increases the gas yield, particularly for H₂ production (Hassan et al. 2020). Moreover, nickel-based catalysts were used and

gained the highest H₂ yield from gasification, especially in the presence of SiO₂ (Sun et al. 2020b; Taylor et al. 2020). To enhance H₂ production, scientists have proposed using pure cellulose instead of lignocellulosic biomass and also suggested that a combination of gasification of cellulose and dark fermentation may give a higher hydrogen yield (Hassan et al. 2020). Ca-Fe oxygen carrier is a potential material for efficient lignocellulose conversion and hydrogen-enriched syngas production, acting as catalysts to promote cellulose decomposition (Tang et al. 2021). CaO sorption enhanced the gasification efficiency of biomass for hydrogen-rich syngas production, demonstrating its potential as an inexpensive catalyst for the gasification process (Mbeugang et al. 2021). In addition, the highest carbon monoxide (CO) concentration was found in cellulose gasification compared to those originated from hemicellulose and lignin, which may be due to the abundance of C–O compounds in cellulose (Hassan et al. 2020).

Reliance on catalysts is one of the bottlenecks of gasification, so scientists have proposed other options, in which physical catalysts (Ce/Fe, Ni, etc.) were not used but replaced by a plasma-catalyst system to produce a cleaner syngas. The results provided an alternative and cleaner way for gasification, although it still needs to be evaluated further (Craven et al. 2020; Zou et al. 2018). Recently, scientists proposed a very low temperature gasification system for cellulose (around 50 °C) by using glow-discharge plasma. Due to the low temperature, pyrolysis did not occur, but a very long retention time (90 h) was required. Interestingly, no tar formation was observed, indicating that all of the cellulose was decomposed into gaseous products. This achievement demonstrated that clean and complete gasification of cellulose and/or hemicellulose could be achieved with plasma technology (Minami et al. 2018).

6.7.2 Gasification of Hemicellulose

Xylose and 4-O-methylglucuronic acid were mainly detected in the degradation of hemicellulose at a temperature below 220 °C, but low molecule weight products such as furfural, formic acid, and acetic acid were observed at higher temperatures (Berthet et al. 2016; Hassan et al. 2020). Xylose was completely decomposed in less than 5 s at a temperature of 300–450 °C and 25 MPa. The decomposition behavior was similar to that of glucose as they have a homoeologous molecule structure, except that xylose has one less CH-OH group than glucose. The formation of furfural via dehydration of xylose was considered to be analogous to that of dehydration of glucose (Fukutome et al. 2015; Hassan et al. 2020; Tang et al. 2021).

Hydrothermal gasification in either subcritical or supercritical water is an attractive approach to produce hydrogen from cellulose and hemicellulose, in which hydrogen yields from hemicellulose normally were higher than those from cellulose (García-Jarana et al. 2020; Okolie et al. 2020). Moreover, the use of hemicellulose isolated from biomass not only helps to understand and analyze the catalytic gasification characteristics of natural biomass material with high hemicellulose content, but also gives a considerable method to produce H₂ from only hemicellulose, with

the highest amount of H₂ produced but a lower amount of gasification solid residues than the whole biomass used (Gökkaya et al. 2020).

6.8 Conclusion

For efficient use of biomass, technologies that employ thermochemical conversions, including combustion, pyrolysis, liquefaction, and gasification, have demonstrated high efficiencies and improved environmental performance, leading to their recognition worldwide. Process mechanisms and characteristics of each technology applying to cellulose and hemicellulose, which are two main components of biomass, have been investigated and the reported results have been helpful in identifying potential applications and useful products. Before they can be implemented in industrial applications, the related technologies need more research and development efforts followed by a demonstration at semi-commercial scales. Among the thermochemical conversion processes, combustion offers potential direct applications, especially in the innovation of new materials, whereas liquefaction may become a new route for the production of liquid fuels. Pyrolysis, particularly torrefaction, has been applied widely for heat and electricity generation, but the technology required sophisticated designs for specific equipment in industrial scales, while gasification often consumes extensive energy to reach the required temperatures and pressures. Advances in biomass processing such as pretreatments and fractionation as well as in system and engineering process design may enhance the effectiveness of biomass thermochemical conversion into fuels and value-added products with better performance and cost competitiveness.

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