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Chapter

Hydrothermal Conversion of Lignocellulosic Biomass to Hydrochar: Production, Characterization, and Applications

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Abstract

The high moisture content poses a major technical barrier to using wet biomasses in thermochemical conversions. Hydrothermal conversions open efficient ways to convert wet biomass into carbonaceous products as an alternative to thermochemical methods such as pyrolysis, gasification, and combustion. Three types of hydrothermal conversions, hydrothermal carbonization (HTC), hydrothermal liquefaction (HTL), and hydrothermal gasification (HTG), use different operating conditions to convert wet biomass into distinct products: solid (hydrochar), liquid (aqueous soluble bio-oil), and gaseous fractions. Water plays a dominant role in hydrothermal conversions. HTC uses relatively mild conditions. HTL and HTG use subcritical and supercritical conditions, respectively. Conversion mechanisms and the effect of process parameters are also discussed in detail. The solid product hydrochar (HC) has properties comparable to biochar and activated carbon, hence a range of potential applications. Current and emerging applications of HC, including energy production and storage, soil amendment, wastewater treatment, carbon capture, adsorbent, and catalyst support, are discussed.

Keywords: bioenergy, hydrothermal carbonization, bio-oil, biofuel, thermochemical conversion, biomass composition, pyrolysis

1. Introduction

Over the past few decades, the world has seen a rapid increase in energy demand and consumption. Currently, fossil fuels (oil, natural gas, and coal) are the primary source of global energy supply. The combustion of fossil fuels releases greenhouse gases into the atmosphere, resulting in global warming, environmental pollution, and climate change. Due to higher prices and a finite supply of fossil fuels and to reduce greenhouse gas emissions and mitigate climate change, more attention has been given to finding a sustainable long-term alternative to fossil fuels. As a result, renewable energy resources (such as biomass, solar, wind, geothermal, and tidal) are gaining popularity. Biomass, available abundantly at a relatively low cost, is

considered a promising alternative renewable energy source to substitute for fossil fuels. It is a clean, environmentally friendly, and carbon-neutral source of energy. Burning biomass or fossil fuel releases carbon dioxide (CO₂), a greenhouse gas. However, when biomass burns, it releases CO₂ back into the atmosphere that the plants have absorbed recently by photosynthesis during the growth process producing biomass. Thus, burning biomass does not add to the total CO₂ inventory of the earth and is considered carbon neutral. Nevertheless, the overall biomass chain, including planting, harvesting, processing, and transporting, needs to be considered for true carbon neutrality of biomass. In addition, burning biomass releases a variety of pollutants, including carbon monoxide (CO), nitrogen oxides (NO_x), and particulate matter [1–4].

2. Lignocellulosic biomass

Biomass is defined as a plant or animal-based organic matter of recent origin. Biomass includes agricultural crop residues (residues of agricultural crops that are not harvested for commercial use, including stalks, leaves, husks, etc.), forestry and wood residues (residues associated with the production of timber in the forest, as well as the processing of timber into their final products), dedicated energy crops (herbaceous and short rotation woody energy crops), aquatic biomass (algae, plants, and microbes found in water), sewage sludge, digestate (remains of anaerobic digestion), industrial crops, animal, industrial, municipal and food waste [1, 5]. A detailed discussion on biomass sources, classification, composition, and analysis is available in [1, 5]. If improperly managed, these biomass residues and waste could lead to environmental issues, including water contamination, greenhouse gas emissions, pests and insects breeding, and foul odor. Converting biomass residues and wastes into bioenergy (a) reduces the burden on waste management, (b) energy generated reduces the dependence on fossil fuels, and (c) reduces the amount of decomposing waste and associated environmental issues [5–7].

Biomass is a complex heterogeneous mixture mainly of organic matter (and a small amount of inorganic matter). Biomass is also classified based on its chemical composition as carbohydrates, lignin, essential oils, vegetable oils, animal fats, natural resins (gums), etc. The most abundant biomass on earth is lignocellulosic biomass (LCB), which includes agricultural crop residues, forestry and wood residues, dedicated energy crops, industrial crops, and food waste. LCB is a complex mixture of biopolymers consisting of carbon (C), oxygen (O), and hydrogen (H), with total content reaches typically above 95%. The elemental composition of C, O, and H in plant biomass on a dry basis is 42–47%, 40–44%, and 6%, respectively. Plant biomass has a substantial amount of oxygen with a carbon-to-oxygen (C/O) ratio of almost one. Because of the higher level of oxygen content, the energy density of biomass is relatively low compared to fossil fuels. Plant biomass also contains macronutrients, micronutrients, trace elements, and other heavy metals, which are present in varying amounts, depending on the plant species and environment, summing all together up to about 4% [1, 4, 8–10].

The three major constituents of LCB are cellulose, hemicellulose, and lignin. These constitute the cell wall of plants. The most abundant polymer of the lignocellulosic plant cell wall is cellulose, which provides structural support that gives trees and wood their strength. It is a linear polymer chain composed of D-glucose (pyranose) units linked by β -1,4 glycosidic bonds. Cellulose has a high (300–15,000)

degree of polymerization (DP) depending on the plant species. Cellobiose, glucose disaccharide, is the repeating unit of cellulose. Cellulose chains are grouped to form elementary fibrils, which are interlinked by hydrogen bonds and Van der Waals forces to form long microfibrils. Microfibrils represent the main component of the cell wall. Because of the high degree of hydrogen bonding, cellulose is highly stable and resistant to chemical attack. Interaction of hydroxyl (OH) groups present on the inner and outer surfaces of cellulose forms hydrogen bonds (intra- and intermolecular), which stiffens the chains and provides crystalline structure to cellulose. The interchain hydrogen bonds create crystalline (uniform and ordered) and amorphous (loose and disordered) regions of cellulose. The amorphous regions are more reactive than crystalline regions. The crystalline structure of cellulose leads to its mechanical strength and chemical stability and provides strength and toughness to leaves, roots, and stems. Cellulose is insoluble in almost any solvent [4, 5, 8, 11–13].

Hemicellulose is the second most abundant polymer in LCB. It is a branched heterogeneous structural polysaccharide composed of C5 and C6 sugars, including D-xylose, L-arabinose, D-mannose, D-galactose, and D-glucose units. Hemicellulose has a lower DP (80–200) than cellulose. Because of the branched structure, hemicellulose is amorphous and easy to hydrolyze by dilute acids, bases, and enzymes. Hemicellulose lateral chains form a tightly bound network with cellulose microfibrils through hydrogen bonds, which makes a highly rigid cellulose-hemicellulose-lignin matrix with the interaction of lignin *via* covalent bonds [4, 9, 11, 12].

Lignin is the third most abundant polymer in LCB. Lignin is an aromatic polymer composed of three phenylpropanoid monomers: guaiacyl, p-hydroxyphenyl, and syringyl. The phenylpropanoid monomers in lignin are linked in alkyl-aryl, alkyl-alkyl, and aryl-aryl ether bonds. Lignin, an amorphous and highly complex aromatic hydrophobic biopolymer, is the natural phenolic glue that tightly binds cellulose and hemicellulose. Lignin plays a cementing role for linkages between cellulose and hemicellulose to form a 3-D structure of lignin-polysaccharide complex in the cell wall, leading to a strong cell wall structure that makes it insoluble in water and provides mechanical strength to plants. Lignin provides sealing for a water-conducting system linking roots with leaves. The cross-linking between polysaccharides (hydrophilic and permeable) and lignin (hydrophobic and impermeable) creates vascular tissues for the efficient conduction of water in plants. Lignin 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 [5, 14, 15].

The key component in woody biomass is cellulose. Leaves and grasses are rich in hemicellulose, and lignin is the major component in shells. Hemicellulose is thermally least stable, and lignin is the most stable of all three. The cellulose, hemicellulose, and lignin content vary with the biomass falling in the range of 40–60%, 15–30%, and 10–25%, respectively. In addition to three major components, inorganic compounds and organic extractives, including fats, waxes, proteins, simple sugars, gums, resins, starches, phenolics, pectins, essential oils, and mineral compounds, are also present in biomass as nonstructural components, which are responsible for the smell, color, flavor, and natural resistance to decaying of some species. Inorganics present in LCB include nitrogen (N), phosphorus (P), potassium (K), magnesium (Mg), sulfur (S), calcium (Ca), chlorine (Cl), iron (Fe), boron (B), manganese (Mn), zinc (Zn), copper (Cu), molybdenum (Mo), nickel (Ni), selenium (Se), silicon (Si), sodium (Na), aluminum (Al), titanium (Ti), cadmium (Cd), and chromium (Cr). Woody biomass contains a high (~90%) amount of cellulose, hemicellulose, and lignin, whereas agricultural and herbaceous biomass contain more extractives and ash [5, 8, 11, 12].

Biomass analysis, including proximate and ultimate analysis, as well as higher heating value (HHV), is essential in understanding the behavior of biomass in energy applications. The proximate analysis determines the volatile matter (VM), fixed carbon (FC), ash (noncombustible solid residue), and moisture (M) content. VM is the vapors/gases released during heating. FC is the nonvolatile solid carbon that remains after devolatilization. Inorganic matter, including silica, calcium, iron, aluminum, potassium, sodium, magnesium, and titanium, are the main constituents of ash. High-ash content biomasses include agricultural residues, grasses, and straws. Contamination of biomass with dirt, soil, rock, and other impurities during collection and handling partly contributes to ash content. Moisture content has a significant impact, and high moisture content is a major concern in biomass conversion. The moisture content of some biomasses, such as water hyacinth, can be very high (> 90%). Moisture can affect the storage and handling of biomass. High moisture content significantly increases transportation and energy costs. It lowers the calorific value as the energy released is used in the evaporation of moisture, which is not recovered. Moisture drains much of the deliverable energy during conversion. The ultimate analysis expresses biomass composition in terms of major elements (C, H, O, S, and N) on a mass percent, dry, and ash-free basis. These are useful for performing mass balances on biomass conversion processes. Typically, the sulfur and nitrogen content of biomass is very low. The characteristics of raw biomass include high moisture content, low bulk density, low energy density (calorific value), poor grindability, compositional non-homogeneity, hygroscopic nature, higher biological degradation, and lower storability [9, 16–18].

3. Biomass conversion

The primary goal of biomass conversion is to break down the rigid and complex structure of biomass polymers into smaller and lower molecular weight (MW) compounds. Typically, the reaction time, temperature, and reaction medium influence the rate of destruction of the biomass polymeric structure. Chemical, biochemical, and thermochemical conversion processes convert biomass into end products such as chemicals, biofuels, or heat. Chemical conversion processes use chemicals to convert biomass into biofuels. Biochemical conversion processes utilize microorganisms or enzymes to convert biomass into products. Thermochemical conversion processes employ high temperatures in oxygen free, reduced, or normal oxygen environments. The thermochemical conversion approaches are applicable for a wide range of biomass types using different temperatures to break down the bonds of organic matter in a relatively short period. The advantages of thermochemical conversions over biochemical conversions include better conversion efficiency, handling a wide variety of feedstocks, shorter reaction times, and high energy efficiency. In most situations, the selection of the conversion process is based on the biomass feedstock available and the desired form of end products. Environmental standards, policy, economic conditions, and specific factors related to the project may influence the selection process. The moisture content of biomass is a primary aspect determining the conversion process. Thermochemical conversions, such as pyrolysis, gasification, or combustion, generally require relatively dry biomass with a moisture content of less than 30 wt.%, but moisture contents of 10 wt.% are preferred. The low energy density of wet biomass due to higher moisture content makes it unsuitable for these processes. The biochemical conversion process, a wet conversion process, is suitable for processing high moisture

content biomass. Hydrothermal (HT) processing is a thermochemical conversion that involves applying heat (and pressure) in subcritical or supercritical water. It can process high moisture content (> 70 wt.%) biomass feedstock without dewatering or drying. Biochemical conversion consumes less energy compared to HT processing but requires more time. Subsequently, cost-effective HT processing has gained growing attention as a method suitable for processing wet biomass [1, 5–8, 19, 20].

4. Hydrothermal (HT) processing

Biomass with a moisture content of more than 30 wt.% needs to be dried before being suitable for some thermochemical processes such as pyrolysis, combustion, and gasification. Drying is a highly energy-intensive process and requires a large amount of energy. As a result, for biomass with high moisture content, the heat of moisture evaporation is higher than the heat available from biomass, becoming a net energy consumption. Wet biomass, typically with 70 wt.% or more water, can be converted using HT processing without energy-intensive drying [1, 5, 8].

HT processing applies heat and pressure in subcritical or supercritical water in a closed reactor. The biomass is surrounded by water during the reaction, and the presence of water speeds up biomass conversion. HT reactions are supported by water, which plays an active role as a solvent, reactant, and even a catalyst or catalyst precursor in the hydrolysis reactions. Due to the high ionic product in subcritical conditions, water shows both acidic and basic properties and behaves as a catalyst. As a result, the addition of acid or base catalyst can be avoided. Water behaves as a catalyst precursor due to relatively high concentrations of hydronium (H_3O^+) and hydroxide (OH^-) ions resulting from the dissociation of water. In HT processing, water is used as a reacting medium. It is cheap, environmentally friendly, nontoxic, inherently present in wet biomass, and a better alternative to corrosive chemicals and toxic solvents. In HT processing, the reaction pressure is usually not controlled, but the temperature maintains the autogenic pressure corresponding to the saturation vapor pressure of water. It is an attractive process to convert wet biomass into three distinct product fractions, solid (HC), liquid (bio-oil/water), and a mixture of non-condensable gases. All three product fractions (solid, liquid, and gaseous) are formed at all temperatures in HT processing. However, reaction temperature (and pressure) determines the product distribution. The reaction shifts from solid products at low temperatures through liquid products at medium temperatures to gaseous products at high temperatures. The advantages of HT processing include the elimination of energy-intensive drying, high conversion efficiency, and relatively low operating temperature. Depending on the operating conditions, HT processes can be classified into three processes as hydrothermal carbonization (HTC), hydrothermal liquefaction (HTL), and hydrothermal gasification (HTG) [1, 5, 8, 21–23].

The physicochemical properties of water are strongly affected by pressure and temperature. Water exhibits gas-like behavior at or around the critical point with low density, low viscosity, high compressibility, and high diffusivity. Some physical and chemical properties of water at various conditions are shown in **Table 1**. Above the critical point, a single homogeneous fluid phase exists, and the density, viscosity, compressibility, and diffusivity of water are very sensitive to pressure and temperature changes. This unique property of water is a result of hydrogen bonding. When water is heated, hydrogen bonding in the water molecules becomes weak, allowing the dissociation of water into H_3O^+ and OH^- ions. The characteristics of water change

	Ambient	Subcritical water	Supercritical water
Temperature (°C)	0–100	100–374	> 374
Pressure (MPa)	0.003 (24°C)	0.1 (100°C)–22.1 (374°C)	> 22.1
Density (kg/m ³)	997	958 (101°C, 0.11 MPa) 692 (330°C, 30 MPa)	between gas-like and liquid-like densities 252 (410°C, 30 MPa)
Viscosity (mPa s)	0.89 (25°C, 0.1 MPa)	0.11 (250°C, 5 MPa) 0.064 (350°C, 25 MPa)	0.03 (400°C, 25 MPa) 0.07 (400°C, 50 MPa)
Dielectric constant	78.5 (25°C, 0.1 MPa)	27.1 (250°C, 5 MPa) 18.2 (330°C, 30 MPa) 14 (350°C, 20 MPa)	5.9 (400°C, 25 MPa) 10.5 (400°C, 50 MPa)
Ion product K_w (mol ² /L ²)	10 ⁻¹⁴ (25°C) 10 ⁻¹² (100°C)	10 ⁻¹² (100°C) 10 ⁻¹¹ (300°C)	10 ⁻²⁰ (400°C) 10 ⁻²³ (550°C)
Heat capacity C_p (kJ/kg K)	4.22 (25°C, 0.1 MPa)	4.86 (250°C, 5 MPa) 10.1 (350°C, 25 MPa)	13 (400°C, 25 MPa) 6.8 (400°C, 50 MPa)
Thermal conductivity (W/m K)	0.608 (25°C, 0.1 MPa)	0.62 (250°C, 5 MPa)	0.16 (400°C, 25 MPa) 0.438 (400°C, 50 MPa)

Table 1.

Physical and chemical properties of water at various conditions [24–27].

from a polar solvent at ambient conditions to a nonpolar solvent at supercritical conditions. At ambient conditions, organic compounds, and gases are poorly miscible in water. But the high dielectric constant (about 80) makes water a good solvent for salts. The dielectric constant decreases rapidly with increasing temperature to about 27 (at 250°C and 5 MPa) and about 14 (at 350°C and 20 MPa). Under HT conditions, water displays less polar behavior due to decreasing dielectric constant and the miscibility of organic compounds is improved, which opens new reaction pathways. Temperature and pressure can be controlled to adjust reaction rates. Above the critical point, organic compounds are completely miscible. Below the critical point, organic compounds are miscible. When HT processing products are cooled down to ambient conditions, water, and organic compounds are separated again [23, 26, 28–30].

4.1 Hydrothermal carbonization (HTC)

HTC is carried out in compressed water at temperatures between 180 and 260°C under autogenous pressures (up to 4 MPa), and biomass feedstock in water is converted mostly to solids (HC). The residence time of HTC varies from minutes up to several hours. HTC aims to maximize the yield of HC. In addition, HTC produces bio-oil mixed with water in the liquid fraction (aqueous solution) and a small volume of gases (consisting of H₂, CH₄, and CO₂). The product distribution and characteristics primarily depend on the process conditions and the type of biomass feed. The reaction temperature remains the main process parameter even though both reaction time and temperature influence the physicochemical characteristics of products. Solids concentration has a relatively smaller influence. The characteristics of HC are significantly affected by the chemical composition of the feedstock. The liquid fraction contains valuable chemical compounds, including organic acids (acetic acid, formic acid, lactic acid, levulinic acid, and propionic acid), furan compounds

(furfural, furfuryl alcohol, and 5-hydroxymethylfurfural (5-HMF)), esters, phenolic compounds, lignin fragments, amino acids, sugars, and some nutrients (nitrogen and phosphorus) that are formed *via* the biomass polymers degradation. Hemicellulose degradation temperature in subcritical water is usually around 180°C and cellulose decomposition in subcritical water usually starts above 200°C, while lignin decomposes above 220°C [5, 8, 21, 31–34].

During HT decomposition, the physical structure of biomass is altered through a series of reaction mechanisms such as hydrolysis, dehydration, decarboxylation, aromatization, polymerization, and condensation. These reactions do not run sequentially; instead, they show simultaneous and interconnected reaction paths and the mechanisms depend on the feedstock type. Hydrolysis has a lower activation energy than most decomposition reactions, which initiates biomass HT degradation [35–37]. Under HTC conditions, marked changes in water properties (such as dielectric constant, ionic product, and polarity) catalyze the hydrolysis of biomass. These property changes unlock different reaction pathways that are not possible in other conversion conditions such as pyrolysis, liquid water, or steam at atmospheric pressures. The dissociation of water into H_3O^+ ions facilitates hydrolysis reactions. As a result of property changes, under HTC conditions, water acts as a reagent for various reactions and as a solvent for a wide range of organic biomass compounds. In hydrolysis, biomass polymers (such as hemicellulose, cellulose, extractives, and lignin) react with water and break ester and ether (mainly β -1-4 glycosidic) bonds creating oligosaccharides and fragments of lignin that enter the liquid phase. Consequently, complete disintegration of the physical structure of biomass may occur. Rapid degradation and depolymerization of hemicellulose and cellulose chains following hydrolysis produces a wide range of fragments, including water-soluble oligomers (cellobiose, celotriose, cellotetraose, cellopentaose, cellohexaose, arabinose, etc.) and monomers (glucose and fructose). Hydrolysis of lignin fragments gives rise to phenolic compounds. Most extractables possess good water solubility and are eluted simultaneously [35–37].

Subsequently, two important reactions (dehydration and decarboxylation) occur simultaneously, reducing both the oxygen and hydrogen content of the biomass. The extractables increase dehydration and decarboxylation, leading to a condensation reaction. The reaction mechanism of the HTC process mainly involves dehydration, decarboxylation, and polymerization. Dehydration is favored at low temperatures (< 300°C) [38, 39]. The soluble hydrolysis products undergo further dehydration, which removes water from the biomass by eliminating hydroxyl (-OH) groups. It also releases more water into the reaction medium and carbonizes biomass by lowering the H/C and O/C ratios. Decarboxylation removes CO_2 from the biomass, eliminating carboxyl (-COOH) groups. Condensation and polymerization convert these compounds to larger molecules, which undergo further aromatization. The net result for LCB is highly aromatized fragments combining phenolic structures derived from the lignin dehydration with aromatization resulting from the carbonization of carbohydrates. The fragments undergo condensation and polymerization to form humic acid and bitumen-like material and partly precipitate to form HC [23, 40].

The main reason for a significant decrease in oxygen content could be the elimination of carboxyl groups, mainly from hemicellulose, cellulose, and extractives. Aromatization occurs because of dehydration and decarboxylation. In the process, hydroxyl and carboxyl groups in biomass are replaced by C=O and C=C bonds. Aromatic carbon structures formed are considered the building block of HC. The furfural compounds generated undergo hydrolysis, which further breaks them down

into acids, aldehydes, and phenols. Due to the formation of organic acids such as acetic acid, lactic acid, formic acid, propionic acid, and levulinic acid pH of biomass and process water decrease as HTC proceeds, which further promotes hydrolysis and dehydration of small-chain polymers and monomers into much smaller fragments. The dehydration process of eliminating OH groups is sometimes called chemical dehydration. During the HTC of biomass, physical dehydration also occurs in addition to chemical dehydration. In physical dehydration, the reduction in the hydrophilic nature of biomass expels water out of the biomass matrix [35, 36].

The dehydration and decarboxylation of hydrolyzed products (fragments and extractable) lead to the formation of intermediate compounds. The 5-HMF generated from C6 sugars (D-fructose and D-glucose) and furfural generated from C5 sugars (D-xylose) are well-known dehydration intermediate compounds of sugars. The HTC process under acidic conditions allows the effective conversion of D-glucose to 5-HMF. D-glucose first isomerizes to D-fructose, and then undergoes dehydration to form 5-HMF. The 5-HMF ($C_6H_6O_3$) is C6 heterocyclic aldehyde containing aldehyde and alcohol functional groups. It has formyl (-CHO) and hydroxy methyl (-CH₂-OH) functional groups attached to 2 and 5 positions, respectively. The 5-HMF, one of the “top 10 biomass derived value-added chemicals” defined by the US Department of Energy, is a versatile platform chemical for a wide range of fuel and chemical products, including 2,5-furan dicarboxylic acid (FDCA), 2,5 dimethylfuran (DMF), 2 methyl furan, levulinic acid, formic acid, furfuryl alcohol, adipic acid, caprolactam, and maleic acid. The furfural ($C_5H_4O_2$) is C5 heterocyclic aldehyde containing aldehyde (-CHO) and two olefins (-CH=CH-) functional groups. Furfural can undergo various chemical reactions due to its aldehyde and olefin functional groups are considered a promising platform chemical that can be used to produce a range of chemical products, including DMF, tetrahydrofuran (THF), furan, furfuryl alcohol, 2-methyl furan, and levulinic acid [1, 35, 38, 39, 41, 42].

There are two pathways to HC formation: solid-to-solid conversion (primary char) and polymerization of aqueous phase intermediate compounds (secondary char). The carbon-rich intermediate compounds (such as furfural and 5-HMF) resulting from hydrolysis and dehydration undergo condensation, polymerization, and aromatization to produce bio-oil. After successive polymerization and aromatization, bio-oil converts into a solid product with or without auto nucleation to form secondary char [37]. A high concentration of HMF favors secondary char formation. The typical HTC temperatures are too low to convert lignin completely, and lignin forms primary char *via* solid-to-solid conversion. Sequential hydrolysis, dehydration, and isomerization producing furfurals and cleavage reactions yielding intermediate organic acids are thought to have resulted in secondary char. These dissolved intermediates can lead to the precipitation of the furfurals as a secondary organic phase, which polymerizes as microspheres. Both primary and secondary chars are called HC when they are formed by HTC, despite their different chemical structures [34, 43].

The solid fraction of the HTC is in the form of slurry mixed with an aqueous fraction, and it has to pass through a series of steps such as mechanical dewatering (compressing), filtering, and drying before it can be used as a fuel. HC has high hydrophobic and homogeneous properties and can be easily separated from the liquid fraction. HTC process removes part of oxygen from biomass during decarboxylation and dehydration. Consequently, by mechanical dewatering, the moisture content of solid fraction can be reduced to 50% (only 70–75% moisture content can be achieved in mechanical dewatering of wet biomass). This reduces

the energy and time required for drying. Dried HC (moisture content <5%) pellets can be produced from the separated solid fraction, which can be used for energy production [21, 44].

Initially, the liquid fraction was considered a waste, hence higher costs for wastewater treatment and disposal. Recently, it has been considered a potential added resource of the HTC process as it contains various valuable organic and inorganic compounds, including organic acids, furan compounds, esters, phenolic compounds, lignin fragments, amino acids, sugars, and some nutrients. Mono sugars and chemicals can be recovered from liquid fraction. The gas fraction contains less CO and CO₂ and is less harmful [5, 8, 21, 31–34].

The inorganic elements (Ca, Mg, P, K, Na, S, and Fe) present in LCB remain in ash as oxide forms (CaO, MgO, P₂O₅, K₂O, Na₂O, SO₃, and Fe₂O₃) after combustion. Even though the ash content of LCB is usually minimal, these oxides can cause severe agglomeration, fouling, clinker formation, and corrosion during combustion, pyrolysis, and gasification. Inorganic compounds are very stable and may remain unchanged under HTC conditions, but the degradation of biomass polymers might release inorganics from the solid structure; hence some of the ash-forming elements can leach out from the biomass to the aqueous solution reducing the overall ash content of the HC. In addition, the HTC process can convert organic chlorine to inorganic chlorine reducing chlorine content in HC, which reduces the potential for corrosion and dioxin formation in combustion [21, 22].

Some of the advantages of the HTC process include (a) fewer emissions, low carbonization temperatures, and lower energy consumption than pyrolysis; (b) a greater variety of wet and dry feedstocks can be processed in an aqueous medium (no drying is required); (c) higher solid yields; (d) final product with lower ash content; and (e) inexpensive process. Feedstock material and processing conditions significantly influence the performance and properties of the HC. HC obtained from HTC has the following properties: (a) versatile properties make it suitable for a wide range of applications in the energy and environmental sectors, (b) oxygenated functional groups at the surface (OH, C=O, and COOH groups), (c) controlled porosity can be easily introduced using activation procedures, thermal treatments, etc., (d) uniform spherical micro-sized particles, (e) easily controlled surface chemistry and electronic properties *via* additional thermal treatment, and (f) specific physicochemical properties tailored for particular applications can be obtained by adding other components (such as inorganic nanoparticles) to biomass [1, 37–39].

HC is more energy dense, hydrophobic, and easily friable and has a lower H/C ratio and O/C ratio than the feedstock used. H/C and O/C ratios of selected biomasses and HC are given in **Table 2**. This is a result of reducing the oxygen and hydrogen content of the biomass through dehydration and decarboxylation, disrupting colloidal structures, and reducing the hydrophilic functional groups. A complex series of reactions, reducing hydrophilic functional groups, take place in HT medium, including the removal of hydroxyl groups through dehydration, removal of carboxyl and carbonyl groups through decarboxylation, and cleavage of many ester and ether bonds through hydrolysis [23, 40]. Specific characteristics, including H/C ratio, O/C ratio, elemental composition, porosity, conductivity, morphology, energy content, etc., are needed for applications in many fields such as solid fuel in soil amendment, adsorbent in water purification, power generation, and carbon capture. The characteristics of HC can be modified by combining HTC with other processes. The initial use for the HTC process was organic materials degradation, liquid and gaseous fuels,

Feedstock	Temperature, time, B/W	H/C**	O/C**	Fuel Ratio (FC/VM)	HHV (MJ/kg)	Ref.
Sewage sludge	220°C, 12 h, 1/75	2.07*, 1.77	0.52*, 0.36	0.12*, 0.22	9.26*, 5.97	[45]
Peanut shells	220°C, 12 h, 1/75	1.58*, 0.99	0.75*, 0.27	0.36*, 0.76	12.6*, 28.14	[45]
Orange peel	220°C, 12 h, 1/75	1.76*, 1.02	0.86*, 0.27	0.23*, 0.83	12.06*, 28.21	[45]
Fallen leaves	220°C, 12 h, 1/75	1.63*, 1.21	0.63*, 0.26	0.25*, 0.5	18.4*, 27.21	[45]
Rice straws	240°C, 1.5 h, 1/12	1.74*, 1.11	0.86*, 0.28	0.22*, 0.73	16.93*, 20.6	[46]
Waste textile	240°C, 1.5 h, 1/12	1.39*, 0.81	0.58*, 0.36	0.2*, 0.29	19.23*, 22.11	[46]
Waste wood	240°C, 1.5 h, 1/12	2.13*, 1.29	0.74*, 0.28	0.4*, 1.53	18.04*, 26.46	[46]
Wastepaper	240°C, 1.5 h, 1/12	2.07*, 1.2	0.9*, 0.29	0.16*, 0.53	14.28*, 24.05	[46]
Waste food	240°C, 1.5 h, 1/12	2.25*, 1.44	0.54*, 0.15	0.18*, 0.94	21.33*, 25.65	[46]
Hornbeam wood	225°C, 1 h, 1/20 250°C, 1 h, 1/20 275°C, 1 h, 1/20	1.51*, 1.17 1.08 1.02	0.69*, 0.57 0.49 0.47	0.17*, 0.32 0.95 1.36	17.29*, 18.45 19.91 20.46	[47]

*B/W — biomass to water ratio, * Values of biomass, ** atomic ratios.*

Table 2.
Properties of biomass and hydrochar.

and basic chemical production. In recent years, the technology gained research interest to produce solid HC and as a technique to synthesize nano- and micro-size carbon particles [1, 31, 32, 48].

The HC produced by HTC directly from LCB lacks porosity. Only a small porosity is developed after further carbonization at a higher temperature. This is due to HC being pre-carbonized material produced under autogenic pressures and temperatures between 160 and 200°C. The high surface area and porosity of HC are essential for most industrial applications, such as adsorption or catalysis. This would ensure efficient transport and diffusion throughout the material. Different techniques have been developed to improve porosity [1, 32].

4.2 Hydrothermal liquefaction (HTL)

HTL is carried out at temperatures between 260 and 350°C under autogenous pressures of 5–20 MPa (subcritical); biomass in compressed water is primarily converted to an aqueous fraction (bio-oil, bio-crude). Bio-oil is a complex mixture of organic compounds containing acids, alcohols, aldehydes, ketones, furans, sugars, amines, amides, esters, ethers, phenols, etc. Free radical and ionic reactions

are considered to be leading reactions in HTL. The dissociation of water increases with an increase in temperature. The ionic product of water (K_w) $10^{-14} \text{ mol}^2/\text{L}^2$ at 25°C increases to $10^{-11} \text{ mol}^2/\text{L}^2$ at 300°C . At HTL conditions (with elevated temperature), mass transfer is improved because of accelerated mass-transfer-limited chemical reactions resulting from the lower viscosity of water. In HTL, water plays an important role as reaction media, helps in the dispersion of biomass, provides hydrogen, and stabilizes radicals. Water inhibits the polymerization of intermediate products, improving the quality and production of bio-oil but at the expense of HC yield [5, 26, 49–51].

The primary conversion of biomass during the HTL comprises three basic reaction mechanisms: depolymerization, decomposition, and recombination. Long-chain biomass polymers are depolymerized and decomposed into shorter-chain compounds. These short-chain compounds are highly reactive and may recombine (repolymerize) to form liquid, gaseous, and solid products. Some bio-oil components could originate from biomass feedstocks, while others could be converted through hydrolysis, depolymerization, decomposition, and recombination of reactive fragments. The important parameters for the depolymerization of long-chain polymer structures to shorter-chain hydrocarbons are temperature and pressure. Depolymerization liquefies macromolecules of biomass by breaking down their physical and chemical components and characteristics. Higher temperatures of the HTL process and desirable physicochemical properties of water help the depolymerization process to overcome the resistance of biomass. Water acts as a catalyst at HTL conditions. The three steps involved in decomposition are dehydration (loss of H_2O molecule), decarboxylation (loss of CO_2 molecule), and deamination (removal of amino acid content). The two mechanisms, dehydration and decarboxylation, facilitate the removal of oxygen from the biomass in the form of H_2O (eliminating the hydroxyl group) and CO_2 (eliminating the carboxyl group), respectively. Biomass macromolecules are hydrolyzed to form monomers and oligomers. When HTL occurs at lower temperatures, biomass undergoes hydrolysis to convert biopolymers into soluble intermediates such as 5-HMF, furfural, amino acids, and fatty acids. The hydrolysis of polysaccharides and proteins begins around 190°C . When temperature increases, subcritical water at HTL conditions breaks down the hydrogen bonds of the cellulose structure to form sugar monomers, which are rapidly degraded by different reactions, including isomerization, dehydration, hydrolysis, reverse aldol defragmentation, rearrangement, and recombination to reactive intermediates. The degradation products, such as furfurals, phenols, organic molecules, glycoaldehydes, and organic acids, are highly soluble in water. Recombination and repolymerization of light MW compounds to yield higher MW compounds occur due to excess oxygen or unavailability of hydrogen molecules [26, 52–55].

Higher temperatures of the HTL process provide the necessary activation energy to decompose lignin in the presence of water. In addition, desirable physicochemical properties, such as low dielectric constant, high ionic product, weak hydrogen bond, and high diffusivity at HTL conditions, catalyze the hydrolysis of biomass breaking down the hydrogen bonds of the cellulose structure to form sugar monomers *via* free radical reactions [56]. Hydrolysis and alkylation reactions rapidly convert lignin fragments into phenolic compounds, including catechols, phenols, guaiacols, etc. The phenolic compounds are then polymerized to form solid residues, which take place at a slower rate than hydrolysis reactions. Unconverted lignin forms char by solid-to-solid conversion [51]. Lignin fragmentation depends on the operating conditions and

reactor design and/or is further converted into H₂, CO, CO₂, CH₄, C₂H₆, and other low MW fragments. HTL process relies on the cleavage of ether or C–C bonds in lignin to form low MW fragments. Competition reactions hydrolysis and cleavage of the ether and C-C bond, demethoxylation, alkylation, and condensation occur during HTL of lignin for phenolic production [50].

The increase in temperature reduces the HC yield. At high temperatures, biomass polymers are degraded, and solid-to-solid conversion necessary for the formation of the HC does not occur or is reduced. The heating rate has been shown to affect the production of HC. Fast heating rates have resulted in higher bio-oil yield and lower HC yield; however, slow heating rates have resulted in a lower bio-oil and higher HC yield. The fast-heating rate significantly increased the reaction temperature, thereby inhibiting the formation of the char [51]. Bio-oil (liquid fraction) is the main product of HTL. The product distribution (gaseous, liquid, and solid) depends on the operating parameters of HTL, including biomass feedstock, temperature, heating rate, residence time, pressure, biomass-to-water ratio (B/W), particle size, and catalyst. The HTL process is endothermic at low temperatures but exothermic at higher temperatures. The advantages of HTL compared to pyrolysis are low operating temperature, high energy efficiency, low gases yield, and low tar yield [52].

The HTL temperature and pressure could impact the reaction directly (activation energy and reaction equilibria) and indirectly (solvent properties). During HTL, cellulose, hemicellulose, and lignin behave differently. Generally, biomass with high cellulose and hemicellulose tends to yield more bio-oil. But there are conflicting views on this. In addition to the three main components, extractives may also affect the yields of bio-oil and HC. Higher bio-oil yields have been obtained from hardwood samples than from softwood. Hardwood contains less lignin than softwood, hence, higher bio-oil yield [49, 50, 57]. Both temperature and lignin contents of wood were shown to have a marked effect on bio-oil yield. Maximum bio-oil production was obtained from wood with low lignin contents [58, 59].

Biomass particle size has negligible to minimal effects on the HTL process as sub/near supercritical water in HTL acts as a good heat transfer medium to overcome the heat transfer limitations, which makes the particle size of biomass a secondary parameter. Excessive biomass feedstock size reduction is not needed. Particle sizes between 4 to 10 mm have been reported as more suitable for the HTL process, which may vary with the operating conditions. No stipulated criteria for particle size selection are available to achieve maximum bio-oil yield during HTL [49, 55, 58].

Although many process parameters can influence the results of the HTL process, generally, it is accepted that temperature is a dominant factor that can alter the yield and properties of bio-oil. It is considered the key process parameter because it has the highest impact, as well as the parameter that can be directly controlled. A temperature range of 260–350°C would be viable for HTL of LCB [49, 52, 55, 58, 60]. Due to the increased fragmentation of biomass at higher temperatures, the effect of temperature on the bio-oil yield is synergetic. Biomass depolymerization occurs when the temperature is sufficiently large enough to overcome the activation energy of bond dissociation. The competing reactions hydrolysis, fragmentation, and repolymerization define the role of temperature during the HTL process. The dominant reaction during the initial stages of HTL is depolymerization. At later stages of HTL, repolymerization becomes active, leading to the formation of HC [49, 58]. Higher HTL temperatures enhance the reaction rates, as well as change the reaction mechanisms. Ionic reactions are favored at lower temperatures; the formation of radicals by homolytic bond breakage is promoted at higher temperatures. A highly

diverse product spectrum usually results in free radical reactions, leading finally to gas formation [49, 61, 62]. Various authors have observed increased bio-oil yields with increasing HTL temperature. Due to reduced bio-oil yield at the maximum operating temperature, various optimum temperatures have been proposed by different authors for various biomasses. The optimum bio-oil yield is considered to occur in a specific temperature range which depends on the properties of biomass feedstock. The reduction of bio-oil yield at high temperatures is due to hydrolysis and repolymerization reactions. It can be assumed that the temperature range of 280–350°C would be suitable for the decomposition of biomass under HTL conditions. Intermediate temperatures usually produce higher bio-oil yields. The peak of bio-oil yield is usually around 300°C with an optimum range of 280–320°C have been reported. The final optimum HTL temperature varies with the biomass type. Temperature increase beyond optimum results in lower bio-oil yield and higher HC yield [49, 52, 55, 58, 60].

The heating rate is still a contentious parameter. Some researchers believe that the bio-oil yield and conversion rate mainly depend on the final temperature; the contribution of the heating rate is negligible. The perception of other researchers is that the heating rate is an important parameter in enhancing the bio-oil yield. The effect of heating rates on the product distributions in HTL is minimal compared to pyrolysis due to the better dissolution and stabilization of fragments in subcritical water. The undesirable breakdown of organic compounds and excessive polymerization of intermediates are reduced at faster heating rates. A positive correlation between heating rates and bio-oil yields has been obtained. Slow heating rates tend to yield more HC due to the increased secondary reactions. Secondary reactions are dominant at very high heating rates and yield more gases. In another study, it was found that the effect of the heating rate depends on the solvent. The heating rate is an important parameter in subcritical water but an optional parameter in supercritical alcohol. Moderate heating rates may be suitable to overcome heat transfer limitations, leading to extensive fragmentation and minimal secondary reactions [49, 52, 53, 58, 60].

The effect of residence time (reaction time) on product distribution during the HTL process has been examined by several researchers. Residence time has been observed to affect biomass conversion, bio-oil yield, and residue yield. Sufficient residence times are required to get high biomass conversions and bio-oil yield. The residence time may characterize the overall biomass conversion and the product compositions. For short residence time, bio-oil yield is lower due to incomplete biomass conversion. Alternatively, if the residence time is too long, the bio-oil may be decomposed and repolymerized, resulting in higher gaseous and solid fractions. A high repolymerization is not conducive to the yield and quality of bio-oil as degradation and repolymerization reactions convert some liquid organic fractions into other compounds. It is essential to inhibit the decomposition of intermediates into lighter products to obtain a higher bio-oil yield. Retention time can be regulated to control further cracking and repolymerization of intermediates. Improved yield and properties of bio-oil have been obtained with increasing residence times. However, a decrease in bio-oil yield has been observed at extended residence times (beyond the threshold limit). The type of biomass, its composition, type of catalysts, and operating conditions define the threshold limit of residence time. Two optimum residence times for maximum bio-oil yield have been reported depending on reaction temperature (120 min at 280°C and 5 min at 375°C), suggesting that shorter residence times are needed at higher reaction temperatures to reduce repolymerization of liquid fraction. In contrast, longer residence times can improve biomass conversion and bio-oil yield at lower reaction temperatures. The products obtained at different residence

times of the same temperature can vary. Therefore, it is important to consider all factors and obtain the optimal residence time and temperature. Generally, bio-oil yield is maximum at optimum residence time, whereas gas yield and biomass conversion continue to increase. Residence time is a key parameter in HTL, which strongly affect the bio-oil yield [49, 50, 52–55, 58, 60].

In the HTL process, pressure is an important parameter for biomass decomposition. It alters the bio-oil yield and supports a single-phase system. HTL uses pressure to maintain a single-phase system and avoid large heat inputs required for phase change. A large heat supply is needed to maintain the temperature of two-phase systems. Pressure increases solvent density and penetrates effectively into larger molecules of biomass, resulting in improved disintegration into smaller fragments. Pressure, once reached supercritical condition, has no significant effect on bio-oil or gas yield. Higher pressures increase the density of the water; it may also cause the local solvent density to increase. This lead to a cage effect around the C–C bonds, which impedes the free radical reactions, inhibits the cleavage of C–C bonds, and ends up in low fragmentations, leading to a decrease in bio-oil yield. Within a specific range, pressure is positively correlated with bio-oil yield, but increasing the pressure above the upper limit shows no noticeable effect [24, 49, 52, 53, 55].

The influence of different solvents (such as subcritical and supercritical alcohols) on the bio-oil yield of LCB has been investigated. Alcohols have lower critical pressures and temperatures than water and significantly milder HTL reaction conditions could be used. Dielectric constants of alcohols are lower than water; hence, relatively high MW intermediates derived from cellulose, hemicelluloses, and lignin are expected to dissolve. Widely employed alcohols for biomass liquefaction have been ethanol and methanol. The biomass/water mass ratio is considered a vital parameter for the HTL process. Different authors have investigated the effect of water density on HTL bio-oil yield. The dilution of reactants, intermediates, and products during the reaction benefit all solvolytic conversions. Cross-reactions are minimized by dilutions and produce a more distinct product spectrum. Cross-reactions due to higher substrate concentrations inevitably lead to undesirable polymerization of the reaction products. Such processes have been observed for the HTL of biomasses. High biomass concentrations were shown to promote HC formation [24, 49, 52, 53, 55].

The lower oxygen and moisture content of HTL bio-oil promotes the higher calorific value and stability. The HTL bio-oil has lower H/C and O/C ratios, indicating a higher energy density than pyrolysis bio-oil. The decrease in the O/C ratio is higher than the H/C ratio indicating that more oxygen is removed as CO₂ or CO during HTL. As a result, HTL produces bio-oil with low oxygen content and improved quality [60].

4.3 Hydrothermal gasification (HTG)

At temperatures between 400 and 600°C and pressures of 23–45 MPa, biomass is primarily converted to a gas fraction (a mixture of non-condensable gases, including H₂, CO, CH₄, and CO₂) in a process known as HTG. It can produce syngas enriched with H₂. The biomass polymers decompose in supercritical water (SCW) above the critical point of water (374°C and 22.1 MPa) with enhanced conversion efficiency. The conversion rate of HTG is typically higher than 80%. The higher reaction temperatures of HTG cause reactions to progress faster, achieving complete decomposition of biomass, a distinctive feature of HTG compared to HTC and HTL. HTC and HTL often produce undesirable by-products that are occasionally dissolved in liquid fraction, and one of the problems of HTC and HTL is the difficulty in by-products

posttreatment. Due to high conversion, only a small amount of organic compounds remain in the liquid fraction of HTG. Consequently, posttreatment of liquid fraction is not required or easily carried out [5, 8, 63].

When water changes from ambient conditions (25°C and 0.1 MPa) to supercritical conditions (400°C and 25 MPa), the properties of water change significantly and exhibit lower density, viscosity, ionic product, and dielectric constant. The dielectric constant at 400°C and 25 MPa is about six. Because of the decrease in the number of hydrogen bonds, water begins to display the behavior of a nonpolar solvent that can completely dissolve many organic compounds, hydrocarbons, and gases (such as CO₂, CH₄, H₂, and N₂). Due to the absence of phase boundaries, many rapid homogeneous reactions involving organic compounds occur at supercritical conditions. Inorganic polar compounds, usually soluble in subcritical water, are insoluble in SCW and easily separated from the reaction products. SCW has low density, low viscosity and exhibits gas-like properties. SCW combines both the dissolution of the liquid phase and the diffusion of the gaseous phase. The advantages of using SCW as the reaction medium in HTG include high diffusion coefficient, enhanced mass transfer, increased solvation properties, single-phase reaction environment in the reactor, and complete miscibility with different organics and gases, and product gas (syngas) does not have tar. It has a high heating value and prevents poisoning of catalyst (if used) and coke formation [6, 26, 49, 63, 64].

Conventional gasification is ineffective for wet biomasses (moisture content >80%), but HTG can be effectively employed when biomass is wet. In conventional gasification, syngas is partially diluted with nitrogen due to partial oxidation using air and contain tar. HTG converts biomass in the presence of water; hence, no dilution of syngas occurs with nitrogen. Syngas from HTG does not contain tars; if produced, they remain in the liquid fraction. HTG produces a high amount of H₂ and a very small amount of CO and char compared to conventional gasification. At low reaction temperatures or when the B/W is too high, HTG encounters a problem with the formation of tarry material. It can cause low gasification efficiency, reactor plugging, or the process water turns dark. At high heating rates, tarry material yield is decreased. This can be explained by assuming ionic reaction during tarry material production and free radical reaction during gasification [5, 8, 63].

During the HTG process, the biomass polymers cellulose and hemicellulose are converted into simple sugars (glucose, fructose, xylose, etc.). Some of the glucose is isomerized to fructose. Fructose produces 5-HMF and furan, which are then converted to alcohols, ketones, and organic acids. Hydrolysis products of small molecules in water are consequently gasified to produce H₂-rich syngas. Simultaneously, glucose and fructose are converted into glyceraldehyde, dihydroxyacetone, etc. Additionally, highly polymerized oligomers produced from the gasified small molecules and some intermediates eventually become liquid products. Phenols that are formed during the reaction are considered to be the final obstacle to complete biomass gasification. Inverse aldol condensation reaction converts xylose (a decomposition product of hemicellulose) to glyceraldehyde and methyl formate, producing propionic acid and acetic acid. Propionic acid and acetic acid are eventually gasified into small molecule gases (H₂ and CO). Propanoic acid may decompose in a second pathway and be gasified to ethane and CO₂. Simultaneously, dehydration of xylose produces furfural, which is decomposed in three proposed pathways. In the first pathway, furfural can be converted into water-soluble humic substances, which are gasified to CO and H₂, or in the second pathway, methyl cyclopentenolone, which is gasified to CO, CH₄, and H₂, or third pathway, gasified directly to CO, H₂, CH₄, and CO₂ [63, 65–67].

At low temperatures ($< 500^{\circ}\text{C}$), biomass tends to produce low concentrations of H_2 in the gaseous fraction along with oil-based liquid fraction. The liquid fraction contains a wide range of products, including acids, phenols, aldehydes, and furfurals. Ions (H^+ and OH^-) from SCW ionization support the cleavage of ring compounds to form simple molecules. At low-temperature HTG of biomass, ions are stable and ionic reactions dominate. In contrast, at high temperatures ($> 500^{\circ}\text{C}$), free radicals are more stable than ions, and free radical mechanisms dominate in HTG of biomass. The gasification temperature and reactants influence free radical concentration. The most difficult biomass component to gasify is lignin. The efficient conversion of lignin in SCW is particularly important for the efficiency of the gasification process. In SCW, Lignin primarily dissociates into phenolics; phenolics decompose into gases [65, 66].

The operating conditions, including biomass characteristics, temperature, pressure, residence time, B/W, and catalyst, strongly influence the performance of HTG. The key parameters that affect the H_2 yield of the HTG process include temperature, pressure, B/W, and residence time. Short residence times are expected to degrade biomass successfully as the rate of hydrolysis and decomposition is relatively fast in the HTG process. For efficient destruction of biomass, residence time optimization is required. A large heat supply is needed to maintain the temperature of two-phase systems. HTG uses pressure to maintain a single-phase system and avoid large heat inputs required for phase change. By maintaining pressure higher than the supercritical pressure, the rate of hydrolysis and biomass dissolution can be controlled, which may enhance favorable reaction pathways for bio-oil or gas yield. In the supercritical region, pressure has a minimal effect on the properties of water. As a result, the effect of pressure on bio-oil or gas yield is minor or negligible [49, 58, 64, 68].

5. Applications of Hydrochar

HC is considered a valuable material for various agricultural, environmental, and industrial applications. The high versatility of HC allows for many applications, including soil amendments in agriculture, solid fuel in power generation, electrode materials in energy storage technologies, adsorbents in contaminant removal, and materials used as sensors and fuel cell catalysts [34]. HC could show different properties based on HT technology, process conditions, and feedstock used. Due to the formation of hydrocarbons on the surface, the surface area and porosity of HC are generally low, hindering its application. High surface area and porosity are vital for contaminant adsorbents and catalysts/catalyst support applications. The physico-chemical properties of HC can be altered and improved through different activations. Chemical activation is achieved by impregnating HC with one or a mixture of chemical agents, followed by an activation process under a nitrogen flow. The most used chemical activating agents for the chemical activation process are potassium hydroxide (KOH), phosphoric acid (H_3PO_4), Zinc chloride (ZnCl_2), sodium hydroxide (NaOH), and potassium carbonate (K_2CO_3) [69]. Biochar has a high degree of carbonization, a highly aromatized carbon structure, lower H/C, and O/C ratios, with a strong anti-decomposition ability (environmentally more stable). But the cost of biochar production was higher. Alternatively, HC has higher H/C and O/C ratios than biochar and is mostly composed of aliphatic hydrocarbons; hence, its environmental stability is lower. The lower H/C and O/C ratios of biochar indicate a higher degree of aromaticity and maturation than HC [70].

Due to low bulk and energy densities, high moisture, and ash contents, untreated biomass is a poor-quality fuel. Biomass is usually pelletized to increase bulk density. But, long-term storage of biomass pellets causes moisture adsorption and biochemical and microbiological activities [71]. Granulated HC showed higher densities. HC densities in the range of 180 to 482% than raw biomass pellets made from four types of biomasses (pine sawdust, coconut fiber, coconut husk, and rice husk) have been obtained. HC pellets showed lower moisture uptake than raw biomass [72]. Consequently, HC has better fuel characteristics compared to biomass. HC needs to meet certain fuel characteristics, including energy density, combustion behavior, grindability, hydrophobicity, and thermal stability, to be effective as a replacement for coal. Its fuel-related characteristics are similar to lignite and can be used in power generation. But the chemical composition is different. HC has a significantly higher amount of volatiles than lignin. Also, the oxygen content of HC is higher than lignite. HC has a similar HHV as lignite. HC could be easily incorporated within existing coal-based processes. During the HTC process O/C ratio of the solid fraction is reduced, leading to increased HHV [28, 32, 37, 69, 73]. A high HHV (20.6–29.2 MJ/kg) of HC has been reported by many researchers as comparable to soft coal (20.93–33.5 MJ/kg) [51, 73, 74]. In addition to increased HHV, HC has lower volatile content (compared to biomass), which ensures better combustion. The low ash melting temperature of biomass makes burning more complicated. Due to the removal of many ash-forming minerals in liquid fraction, HC might have reduced mineral content. As a result, HC can achieve similar ash melting temperature as lignite. Only low-ash HC from certain biomasses (low ash) is suitable for power generation. High ash biomasses include sludge from wastewater treatment plants, agricultural residues, grasses, straws, etc. [28, 32, 37, 73].

The direct use of HC in agricultural and environmental applications might be complicated due to the presence of phenolic and organic acid compounds on the HC surface, which can cause negative plant and microbial responses. Post-treatments, such as composting or anaerobic digestion, can reduce the toxicity of HC and make it suitable for soil application [70]. The factors, such as feedstock used, production process and process conditions, nature of the HC, morphological properties, and nature of the soil (loamy clay, fertile, sandy, or infertile), are important for HC application of crop improvement in the agricultural sector. The application of HC could result in either productive or counterproductive crop yield response. As a result of the low quantity of polar functional groups on the surface of the freshly produced HC, it shows hydrophobicity. However, due to oxidation by interacting with atmospheric oxygen, HC becomes more hydrophilic in nature by creating phenolic and carboxylic functional groups on the surface over time when mixed with soil. The water-holding capacity, cation exchange capacity, and nutrient retention capacity would increase significantly due to these functional groups on the surface [69]. The ability of HC to increase the nutrient supply for plants and decrease leaching losses makes it a good soil amendment to improve soil nutrient retention capacity. HC has a porous structure, low surface area, charged surface, and functional groups, including carbonyl, carboxyl, hydroxyl, and phenolic hydroxyl groups, to remedy the soils contaminated with heavy metals and organic compounds through adsorption [54]. Increased fertility has been achieved by the direct application of HC as a soil amendment, in addition to the formation of stable carbon sinks [75].

Reduced N₂O emission was observed in studying the effect of corn-based HC on the soil. HC was less effective as it is less stable than biochar. However, its production costs are less. Other studies have found that HC reduced N₂O emissions and

contributed to NH_3 , CO_2 , and CH_4 emissions [69, 76]. The nutrient level of HC (especially plant biomass derived) is low; still, it can be used as fertilizer. HC can reduce loss from the surface runoff of fertilizers, enhancing fertilizer use. A decrease in total nitrogen, total phosphorus, nitrate, phosphate, and organic carbon has been reported using fertilizer containing an HC additive. HC addition improved fertilizer runoff and retention. Adding HC to soil could increase nutrient capacity and water retention in soil. Nutrients accumulated in the HC pores are released as needed. Adding HC to soil could change water aggregation, pH, cation, and anion exchange capacity. The addition of HC might improve the water-holding capacity of sandy soils. The colonization of the HC surface by fungi has been observed due to the hydrophobicity of the HC, which had a negative effect on water retention [76].

Increasing levels of HC in soil have been shown to deteriorate the growth of the *Taraxacum* plant. Some studies reported the negative effects of HC caused by nitrogen on crop yields. The absence of nitrogen migration in the first week of HC addition and the slow release of nitrogen with time has resulted in the nonavailability of nitrogen to the plants. Mixing HC into the soil for several weeks before planting has been suggested to overcome this. More research is needed to understand the ecotoxicological properties of HC and evaluate the impact of HC on soils. This will help lower the negative effects of HC in soil improvement for agricultural applications [69].

Energy storage becomes more critical with the increasing use of renewable energy. Carbon-based materials are widely utilized in capacitors. Thus, HC is an attractive material for energy applications. Its properties include surface area, electrical conductivity, tunable pore structure and size, easy accessibility, and strong mechanical properties. These are favorable for applications as supercapacitors and as anode and cathode material for batteries and fuel cells [69, 77, 78]. Due to surface area, polarity, porosity, aromaticity, and stability, HC has gained attention for electrochemical devices such as supercapacitors and batteries. Compared to the lower cycle stability, discharge/charge rate, and higher energy density of rechargeable batteries, HC-based supercapacitors usually exhibit higher cycle stability and power density [69]. Very high capacitance has been reported of HC derived from different sources and activated with KOH at different temperatures. Successful results have been reported of HTC nanospheres as anodes in Li^+ and Na^+ batteries. Their reversible capacity has reached up to 370 mA h/g at a 1C rate, which was better than that of traditional graphite electrodes. In another study, corn straw-based carbon spheres have been used as an anode in Li^+ batteries. The device showed excellent cycle stability with a specific capacity of 577 mA h/g after 100 cycles at 0.2C [77, 78]. Corncobs-based HC having a high surface area has been investigated as a carbon source. Sulfur loaded on HC achieved a discharge capacity of 1600 mA h/g and a reversible capacity of 554 mA h/g after 50 cycles [69]. Walnut shell-derived HC, activated HC/ZnO composites, and activated HC has been investigated for supercapacitors. The specific surface areas of 819 and 1073 m^2/g have been obtained for activated HC/ZnO composite and activated HC, respectively. The specific capacitance of activated HC/ZnO composite was 117.4 F/g at a current density of 0.5 A/g in KOH aqueous solution, which was found to be stable for 1000 cycles [79].

HC can also be used as an adsorbent to remove impurities in aqueous solutions. Depending on the raw material and manufacturing conditions, HC has a wide range of sorption properties [76]. The factors that determine the adsorption efficiency of HC include the specific surface area, pore structure, and surface functional groups. The functional groups on the surface give the HC a high chemical affinity and hydrophobicity, which has good potential adsorption applications [75, 78]. Relative

to biochar, HC has a lower surface area. However, the adsorption capability of the HC is higher than biochar due to the abundance of oxygen-rich functionality and the presence of functional groups such as carbonyl, carboxyl, and hydroxyl groups on the surface [69]. Some of the weaknesses of HC include poor sorption properties compared to other adsorbents, high amounts of volatiles, low pore volume, low surface area, and negative surface charges, which repel negatively charged compounds such as phosphate. Despite the weaknesses, sorption properties for polar and nonpolar contaminants have been confirmed [76, 80]. HC subjected to chemical activation has better properties, which can be done during or after the HTC process. After chemical activation, enhanced sorption of heavy metals has been reported. Lanthanum activation has shown to be effective in phosphate removal as it can neutralize the negative surface charges of the HC. The results showed a maximum absorption of 61.5 mg/pg. [76, 81].

Heavy metal removal using HC has attracted many research interests. Different mechanisms, such as complexation, physical adsorption, precipitation, and electrostatic interactions, can be used to extract heavy metals. The research focused on heavy metal remediation using high-temperature HC has been reported. HC produced at high temperatures has improved surface area, less volatiles, increased ash content, and reduced functional groups. Higher adsorption of Cu by HC (compared to biochar) has been reported due to large quantities of functional groups found in HC. Removal of lead using HC derived from pine wood and rice husk has also been reported. The presence of oxygen functional groups on the HC surface was the primary factor influencing the strong removal capacity of heavy metals [51]. The comparison of the performance of switchgrass-based HC, KOH-activated HC, and activated carbon to remove Cu and Cd from the aqueous solution has shown close to 100% adsorption for Cu and Cd in 24 h by activated HC relative to the HC and activated carbon. The adsorption of lead from an aqueous solution using pinewood and rice husk-derived HC produced by HTL was favored at high temperatures as it is a physical endothermic process [69]. HC has effectively removed Cr (VI) from an aqueous solution. Low pH has been shown to give maximum adsorption efficiency. Pinewood sawdust-derived HC activated with H₂O₂ has been reported to have enhanced adsorption efficiency. The uptake of Pb²⁺ ions was 42 times higher [78, 82].

Adsorption of organic contaminants, including common inflammatory drugs (diclofenac sodium (DCF) and ketoprofen) and fungicides (diphenylamine), have been performed successfully using cellulose-derived carbon spheres. Successful removal of DCF from aqueous samples using KOH-activated HC produced from municipal woody and herbaceous pruning has been demonstrated [78, 82]. Absorption of pharmaceuticals (salicylic acid, flurbiprofen, and DCF) using orange peel-derived HC activated with H₃PO₄ has shown to be effective [83].

HC could serve as an adsorbent for capturing CO₂ to mitigate CO₂ quantities in the atmosphere. HC is economical, but for effective adsorption of CO₂, it needs post-treatments. The CO₂ adsorption potential of HC derived from woody and herbaceous pruning activated with KOH at higher temperatures was tested. The HC showed uptake of 84.5 mg CO₂/g. HC has excellent prospects as a cost-efficient and environmentally friendly material for CO₂ capturing, treating, and monitoring wastewater [78]. Sugarcane bagasse-derived HC and KOH-activated HC have been used to study CO₂ adsorption, which resulted in higher affinity for N₂ and CO₂ at 50°C by activated HC [69]. In another CO₂ adsorption study, silver fir sawdust-derived HC and KOH-activated HC were used in a pressure swing adsorption that resulted in 6.57 mmol/g of CO₂ adsorption at 5 bars with HC. The performance of HC was higher than activated HC and some traditional sorbents [84].

Dye removal by chemical and biological methods is effective, but they produce a lot of by-products. Natural physical adsorbents are environmentally safe, cheap, and abundant and can provide a better solution to this issue [48]. Activated carbon is the widely employed adsorbent for dye removal. The use of activated carbon is limited due to its high cost. HC has proven to be an efficient and economically viable adsorbent for the treatment of dye-contaminated water. Studies have shown that the adsorption performance of HC is most in favor of cationic dyes (methylene blue, rhodamine b, and methyl green) rather than anionic dyes (methyl orange and acid red 1). LCB-derived HC and sewage sludge have shown slightly lower adsorption capacity than commercial activated carbon. The same study reported a higher dye adsorption capacity of HC (128.6 to 160.5 mg/g) compared to biochar (12 to 130 mg/g). HC has been shown more effective in removing cationic dyes such as malachite green (10–40 mg/g) and methylene blue (15–45 mg/g) from the aqueous solution than anionic dye methylene orange (< 6.5 mg/g). HC could be used as an industrial adsorbent and a potential low-cost replacement for activated carbon after undergoing activation [51, 75]. Chemically activated HC could be used as a low-cost adsorbent to remove malachite green [85]. A maximum adsorption capacity of 34.9 mg/g of HC has been achieved in removing methylene blue dye from an aqueous solution using coffee husk-derived HC. In another study, the maximum adsorption capacity was 97 mg/g of HC in removing congo red dye using bamboo-derived HC [69]. A new chitosan-based adsorbent has been synthesized and used to remove methylene blue from wastewater. The adsorbent had outstanding reusability and a maximum adsorption capacity of 215.73 mg/g at 318.15 K based on Langmuir isotherm. Another novel chitosan-based adsorbent has been prepared and tested for methylene blue, methyl orange, and rhodamine B removal. The adsorbent had excellent reusability and ease of separating them from the solution using a magnetic field, and the maximum adsorption capacity for rhodamine B was 191.57 mg/g at 25°C. Carbon-coated polyacrylonitrile nanofibers have been used to adsorb methylene blue, and the adsorption capacity was 153.37 mg/g at room temperature. Even after 5 cycles, adsorption efficiency remained high [48].

Applications of HC in wastewater treatment have been extensively studied. HC has been shown to remove about 55% of gross pollutants from blended (50% of raw +50% of post HTL) wastewater. In the same study, ammonia, COD, nitrate, and phosphate removal efficiencies were 48, 53, 59, and 60%, respectively [21, 51, 86]. Sewage sludge-derived HC and KOH-activated HC has been used to remove orthophosphate (anions) and copper (cations) from wastewater, revealing that 97% of orthophosphates were removed through activated HC at 6 g/L, a higher adsorption capacity than HC [69]. HC is porous, has functional groups, and has a high content of micro- and macronutrients; therefore, it is a highly favorable and suitable environment for microorganisms to grow and can be used as an additive for anaerobic digestion. The addition of HC has been reported to increase methane yield in anaerobic digestion. HC has been shown to increase COD removal capacity in anaerobic digestion [51].

6. Conclusions

LCB, the most abundant biomass, represents a major carbon source. It is a sustainable and eco-friendly alternative renewable energy source. LCB is a complex heterogeneous mixture of three main biopolymers (cellulose, hemicellulose, and lignin) and

a small amount of inorganic compounds and organic extractives. Biomass conversion breaks down the complex structure of biopolymers into smaller molecules. The selection of the biomass conversion process depends on several factors. Thermochemical conversion processes usually offer many advantages, but processes such as pyrolysis, gasification, or combustion, generally require dry biomasses. High moisture content is a major barrier and significantly impacts the biomass conversion process as it requires a large amount of energy to evaporate moisture.

In recent years, more attention has been given to HT processing as a method suitable for processing high moisture content biomass. It converts biomass with high moisture content in the presence of water, eliminating drying, and reducing energy costs. Water has multiple roles in HT conversions as a solvent, reactant, catalyst, and/or catalyst precursor. There are three HT processes, HTC, HTL, and HTG, based on the temperature, pressure, and residence time. The main products of HTC, HTL, and HTG are solid (HC), liquid (bio-oil/water), and gaseous (non-condensable) fractions, respectively. The conversion mechanisms of HTC differ from pyrolysis in that hydrolysis is the determining first step of HTC. Under HT conditions, the onset of carbonization takes place around 180°C.

Hydrolysis initiates the biomass degradation process in HTC as it has the lowest activation energy. Water catalyze and facilitates hydrolysis reactions. Degradation and depolymerization of hydrolyzed products of hemicellulose and cellulose produce a wide range of fragments, oligomers, and monomers; lignin fragments produce phenolic compounds. Subsequent dehydration and decarboxylation reduce oxygen and hydrogen content, leading to condensation reactions. Smaller molecules produced by dehydration and decarboxylation undergo condensation and polymerization, producing larger molecules; further, polymerization and aromatization produce highly aromatized fragments. Condensation and polymerization of these fragments form HC. The intermediate compounds, 5-HMF and furfural, are promising platform chemicals that can produce various chemical products. The process conditions and the biomass feedstock primarily determine the product distribution and characteristics.

The primary conversion mechanisms of HTL are depolymerization, decomposition, and recombination (repolymerization). Long-chain biopolymers undergo depolymerization and decomposition into short chains. Recombination of these highly reactive short-chain molecules produces liquid, gaseous, and solid products. High temperatures and physicochemical properties of water (acts as a catalyst) facilitate the depolymerization process. The three steps of decomposition are dehydration, decarboxylation, and deamination. Subcritical water at HTL conditions breaks down hydrogen bonds to form monomers. These are rapidly degraded to reactive intermediates by isomerization, dehydration, hydrolysis, reverse aldol defragmentation, rearrangement, and recombination. Recombination and repolymerization of short-chain compounds yield long-chain compounds. Under HTG conditions, biopolymers are converted to simple sugars. The simple sugars are gasified in different routes to produce a mixture of gases (CO, H₂, CH₄, and CO₂), the composition of which depends on the conversion route.

Further, research is required to investigate the reaction mechanisms, reaction kinetics and chemistry, integration of processes to make it more energy efficient, uses of process water, environmental implications of liquid and gas fractions, the effect of HC on soil applications, recovery of nutrients, heat transfer, energy, and heat recovery, etc.

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References

- [1] Chandraratne MR, Daful AG. Advances in bioenergy production using fast pyrolysis and hydrothermal processing. In: Samer M, editor. Biomass, Biorefineries and Bioeconomy. London: IntechOpen; 2022. pp. 269-289
- [2] Güleç F, Riesco LMG, Williams O, et al. Hydrothermal conversion of different lignocellulosic biomass feedstocks – Effect of the process conditions on hydrochar structures. *Fuel*. 2021;**302**:121166
- [3] Hodge BK. *Alternative Energy Systems and Applications*. Hoboken, NJ: John Wiley & Sons; 2017
- [4] Carpenter NE. *Chemistry of Sustainable Energy*. Boca Raton, FL: Taylor & Francis; 2014
- [5] Chandraratne MR, Daful AG. Recent advances in thermochemical conversion of biomass. In: Bartoli M, Giorcelli M, editors. *Recent Perspectives in Pyrolysis Research*. London: IntechOpen; 2022. pp. 145-176
- [6] 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. *Renewable and Sustainable Energy Reviews*. 2020;**119**:109546
- [7] Basu P. *Biomass Gasification, Pyrolysis and Torrefaction: Practical Design and Theory*. Second ed. Oxford: Elsevier; 2013
- [8] Daful AG, Chandraratne MR. Biochar production from biomass waste-derived material. In: Hashmi S, Choudhury IA, editors. *Encyclopedia of Renewable and Sustainable Materials*. Oxford: Elsevier; 2020. pp. 370-378
- [9] Daful AG, Chandraratne MR, Loridon M. Recent perspectives in biochar production, characterization and applications. In: Bartoli M, Giorcelli M, editors. *Recent Perspectives in Pyrolysis Research*. London: IntechOpen; 2022. pp. 327-344
- [10] Sanchez J, Curt MD, Robert N, et al. Biomass resources. In: Lago C, Caldés N, Lechón Y, editors. *The Role of Bioenergy in the Emerging Bioeconomy: Resources, Technologies, Sustainability and Policy*. Oxford: Elsevier Inc.; 2019. pp. 25-111
- [11] Dhyani V, Bhaskar T. Pyrolysis of biomass. In: Pandey A, Larroche C, Dussap C-G, et al., editors. *Biofuels: Alternative Feedstocks and Conversion Processes for the Production of Liquid and Gaseous Biofuels*. Oxford: Elsevier; 2019. pp. 217-244
- [12] Wang S, Dai G, Yang H, et al. Lignocellulosic biomass pyrolysis mechanism: A state-of-the-art review. *Progress in Energy and Combustion Science*. 2017;**62**:33-86
- [13] Sannigrahi P, Ragauskas AJ, Tuskan GA. Poplar as a feedstock for biofuels: A review of compositional characteristics. *Biofuels, Bioproducts Biorefining*. 2010;**4**:209-226
- [14] Zheng Y, Shi J, Tu M, et al. Principles and development of Lignocellulosic biomass Pretreatment for biofuels. In: Li Y, Ge X, editors. *Advances in Bioenergy*. Vol. 2. Oxford: Elsevier Inc.; 2017. pp. 1-68
- [15] Agbor VB, Cicek N, Sparling R, et al. Biomass pretreatment: Fundamentals toward application. *Biotechnology Advances*. 2011;**29**:675-685

- [16] Wolf JP. Biomass combustion for power generation: An introduction. In: Rosendahl L, editor. *Biomass Combustion Science, Technology and Engineering*. Cambridge: Woodhead; 2013. pp. 3-8
- [17] Jameel H, Keshwani DR. Thermochemical conversion of biomass to power and fuels. In: Cheng JJ, editor. *Biomass to Renewable Energy Processes*. Boca Raton, FL: Taylor & Francis; 2018. pp. 375-421
- [18] Chen WH, Lin BJ, Lin YY, et al. Progress in biomass torrefaction: Principles, applications and challenges. *Progress in Energy and Combustion Science*. 2021;**82**:100887
- [19] Williams CL, Dahiya A, Porter P. Introduction to bioenergy. In: Dahiya A, editor. *Bioenergy - Biomass to Biofuels*. London: Elsevier; 2015. pp. 5-36
- [20] Adams P, Bridgwater T, Lea-Langton A, et al. Biomass conversion technologies. In: Thornley P, Adams P, editors. *Greenhouse Gas Balance of Bioenergy Systems*. London: Elsevier; 2018. pp. 107-139
- [21] Kambo HS, Dutta A. A comparative review of biochar and hydrochar in terms of production, physicochemical properties and applications. *Renewable and Sustainable Energy Reviews*. 2015;**45**:359-378
- [22] Zhao P, Shen Y, Ge S, et al. Clean solid biofuel production from high moisture content waste biomass employing hydrothermal treatment. *Applied Energy*. 2014;**131**:345-367
- [23] Biller P, Ross AB. Production of biofuels via hydrothermal conversion. In: Luque R, CSK L, Wilson K, et al., editors. *Handbook of Biofuels Production - Processes and Technologies*. Duxford: Elsevier Ltd.; 2016. pp. 509-547
- [24] Moller M, Nilges P, Harnisch F, et al. Subcritical water as reaction environment: Fundamentals of hydrothermal biomass transformation. *ChemSusChem*. 2011;**4**:566-579
- [25] Uematsu M, Frank EU. Static dielectric constant of water and steam. *Journal of Physical and Chemical Reference Data*. 1980;**9**:1291-1306
- [26] Toor SS, Rosendahl L, Rudolf A. Hydrothermal liquefaction of biomass: A review of subcritical water technologies. *Energy*. 2011;**36**:2328-2342
- [27] Krammer P, Vogel H. Hydrolysis of esters in subcritical and supercritical water. *Journal of Supercritical Fluids*. 2000;**16**:189-206
- [28] Kruse A, Dahmen N. Water - a magic solvent for biomass conversion. *Journal of Supercritical Fluids*. 2015;**96**:36-45
- [29] Machmudah S, Diono W, Kanda H, et al. Hydrolysis of biopolymers in near-critical and subcritical water. In: Gonzalez HD, MJG M, editors. *Water Extraction of Bioactive Compounds: From Plants to Drug Development*. Oxford: Elsevier Inc.; 2017. pp. 69-107
- [30] Lachos-Perez D, Torres-Mayanga PC, Abaide ER, et al. Hydrothermal carbonization and liquefaction: Differences, progress, challenges, and opportunities. *Bioresource Technology*. 2022;**343**:126084
- [31] Heidari M, Dutta A, Acharya B, et al. A review of the current knowledge and challenges of hydrothermal carbonization for biomass conversion. *Journal of the Energy Institute*. 2019;**92**:1779-1799
- [32] Titirici MM, Funke A, Kruse A. Hydrothermal carbonization of biomass. In: Pandey A, Bhaskar T, Stöcker M,

et al., editors. *Recent Advances in Thermochemical Conversion of Biomass*. Oxford: Elsevier; 2015. pp. 325-352

[33] Lam PS, Tooyserkani Z, Naimi LJ, et al. Pretreatment and Pelletization of Woody biomass. In: Fang Z, editor. *Pretreatment Techniques for Biofuels and Biorefineries*. Berlin: Springer-Verlag; 2013. pp. 93-116

[34] Paksung N, Pfersich J, Arauzo PJ, et al. Structural effects of cellulose on hydrolysis and carbonization behavior during hydrothermal treatment. *ACS Omega*. 2020;5:12210-12223

[35] Fang J, Zhan L, Ok YS, et al. Minireview of potential applications of hydrochar derived from hydrothermal carbonization of biomass. *Journal of Industrial and Engineering Chemistry*. 2018;57:15-21

[36] Sharma HB, Sarmah AK, Dubey B. Hydrothermal carbonization of renewable waste biomass for solid biofuel production: A discussion on process mechanism, the influence of process parameters, environmental performance and fuel properties of hydrochar. *Renewable and Sustainable Energy Reviews*. 2020;123:109761

[37] Fernández-Sanromán Á, Lama G, Pazos M, et al. Bridging the gap to hydrochar production and its application into frameworks of bioenergy, environmental and biocatalysis areas. *Bioresource Technology*. 2021;320:124399

[38] Titirici MM, White RJ, Falco C, et al. Black perspectives for a green future: Hydrothermal carbons for environment protection and energy storage. *Energy & Environmental Science*. 2012;5:6796-6822

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

[40] Funke A, Ziegler F. Hydrothermal carbonization of biomass: A summary and discussion of chemical mechanisms for process engineering. *Biofuels, Bioproducts Biorefining*. 2010;4:160-177

[41] Shao Y, Ding Y, Dai J, et al. Synthesis of 5-hydroxymethylfurfural from dehydration of biomass-derived glucose and fructose using supported metal catalysts. *Green Synthesis and Catalysis*. 2021;2:187-197

[42] Mathew AK, Abraham A, Mallapureddy KK, et al. Lignocellulosic biorefinery wastes, or resources? In: Bhaskar T, Pandey A, Mohan SV, et al., editors. *Waste Biorefinery: Potential and Perspectives*. Amsterdam: Elsevier B.V.; 2018. pp. 267-297

[43] Lucian M, Volpe M, Gao L, et al. Impact of hydrothermal carbonization conditions on the formation of hydrochars and secondary chars from the organic fraction of municipal solid waste. *Fuel*. 2018;233:257-268

[44] Hitzl M, Corma A, Pomares F, et al. The hydrothermal carbonization (HTC) plant as a decentral biorefinery for wet biomass. *Catalysis Today*. 2015;257:154-159

[45] He C, Zhang Z, Ge C, et al. Synergistic effect of hydrothermal co-carbonization of sewage sludge with fruit and agricultural wastes on hydrochar fuel quality and combustion behavior. *Waste Management*. 2019;100:171-181

[46] Lin Y, Ge Y, Xiao H, et al. Investigation of hydrothermal co-carbonization of waste textile with

- waste wood, waste paper and waste food from typical municipal solid wastes. *Energy*. 2020;**210**:118606
- [47] Ercan B, Alper K, Ucar S, et al. Comparative studies of hydrochars and biochars produced from lignocellulosic biomass via hydrothermal carbonization, torrefaction and pyrolysis. *Journal of the Energy Institute*. 2023;**109**:101298
- [48] Ababneh H, Hameed BH. Chitosan-derived hydrothermally carbonized materials and its applications: A review of recent literature. *International Journal of Biological Macromolecules*. 2021;**186**:314-327
- [49] Singh R, Prakash A, Balagurumurthy B, et al. Hydrothermal liquefaction of biomass. In: Pandey A, Bhaskar T, Stöcker M, et al., editors. *Recent Advances in Thermochemical Conversion of Biomass*. Oxford: Elsevier; 2015. pp. 269-291
- [50] Cao L, Zhang C, Chen H, et al. Hydrothermal liquefaction of agricultural and forestry wastes: State-of-the-art review and future prospects. *Bioresource Technology*. 2017;**245**:1184-1193
- [51] Ponnusamy VK, Nagappan S, Bhosale RR, et al. Review on sustainable production of biochar through hydrothermal liquefaction: Physico-chemical properties and applications. *Bioresource Technology*. 2020;**310**:123414
- [52] Biswas B, Kumar J, Bhaskar T. Advanced hydrothermal liquefaction of biomass for bio-oil production. In: Pandey A, Larroche C, Dussap C-G, et al., editors. *Biofuels: Alternative Feedstocks and Conversion Processes for the Production of Liquid and Gaseous Biofuels*. Oxford: Elsevier Inc.; 2019. pp. 245-266
- [53] Gollakota ARK, Kishore N, Gu S. A review on hydrothermal liquefaction of biomass. *Renewable and Sustainable Energy Reviews*. 2018;**81**:1378-1392
- [54] Fan Y, Hornung U, Dahmen N. Hydrothermal liquefaction of sewage sludge for biofuel application: A review on fundamentals, current challenges and strategies. *Biomass and Bioenergy*. 2022;**165**:106570
- [55] Mishra RK, Kumar V, Kumar P, et al. Hydrothermal liquefaction of biomass for bio-crude production: A review on feedstocks, chemical compositions, operating parameters, reaction kinetics, techno-economic study, and life cycle assessment. *Fuel*. 2022;**316**:123377
- [56] Yiin CL, Bin OE, SSM L, et al. A review on potential of green solvents in hydrothermal liquefaction (HTL) of lignin. *Bioresource Technology*. 2022;**364**:128075
- [57] Bhaskar T, Sera A, Muto A, et al. Hydrothermal upgrading of wood biomass: Influence of the addition of K₂CO₃ and cellulose/lignin ratio. *Fuel*. 2008;**87**:2236-2242
- [58] Akhtar J, Amin NAS. A review on process conditions for optimum bio-oil yield in hydrothermal liquefaction of biomass. *Renewable and Sustainable Energy Reviews*. 2011;**15**:1615-1624
- [59] Zhong C, Wei X. A comparative experimental study on the liquefaction of wood. *Energy*. 2004;**29**:1731-1741
- [60] Fan Q, Fu P, Song C, et al. Valorization of waste biomass through hydrothermal liquefaction: A review with focus on linking hydrothermal factors to products characteristics. *Industrial Crops and Products*. 2023;**191**:116017

- [61] Williams PT, Onwudili J. Composition of products from the supercritical water gasification of glucose: A model biomass compound. *Industrial and Engineering Chemistry Research*. 2005;**44**:8739-8749
- [62] Yoshida T, Oshima Y, Matsumura Y. Gasification of biomass model compounds and real biomass in supercritical water. *Biomass and Bioenergy*. 2004;**26**:71-78
- [63] Matsumura Y. Hydrothermal gasification of biomass. In: Pandey A, Bhaskar T, Stöcker M, et al., editors. *Recent Advances in Thermochemical Conversion of Biomass*. Oxford: Elsevier; 2015. pp. 251-267
- [64] Gemechu ED, Kumar A. The environmental performance of hydrogen production pathways based on renewable sources. In: Ren J, editor. *Renewable Energy Driven Future-Technologies, Modelling, Applications, Sustainability and Policies*. London: Elsevier Inc.; 2021. pp. 375-406
- [65] Wang Q, Zhang X, Cui D, et al. Advances in supercritical water gasification of lignocellulosic biomass for hydrogen production. *Journal of Analytical and Applied Pyrolysis*. 2023;**170**:105934
- [66] Nanda S, Mohammad J, Reddy SN, et al. Pathways of lignocellulosic biomass conversion to renewable fuels. *Biomass Conversion and Biorefinery*. 2014;**4**:157-191
- [67] Goodwin AK, Rorrer GL. Reaction rates for supercritical water gasification of xylose in a micro-tubular reactor. *Chemical Engineering Journal*. 2010;**163**:10-21
- [68] Kersten SRA, Potic B, Prins W, et al. Gasification of model compounds and wood in hot compressed water. *Industrial and Engineering Chemistry Research*. 2006;**45**:4169-4177
- [69] Masoumi S, Borugadda VB, Nanda S, et al. Hydrochar a review on its production technologies. *Catalysts*. 2021;**11**:939
- [70] Masek O. Biochar in thermal and thermochemical biorefineries - production of biochar as a coproduct. In: Luque R, Lin CSKI, Wilson K, et al., editors. *Handbook of Biofuels Production - Processes and Technologies*. Duxford: Elsevier Ltd.; 2016. pp. 655-671
- [71] Lehtikangas P. Storage effects on pelletised sawdust, logging residues and bark. *Biomass and Bioenergy*. 2000;**19**:287-293
- [72] Liu Z, Quek A, Balasubramanian R. Preparation and characterization of fuel pellets from woody biomass, agro-residues and their corresponding hydrochars. *Applied Energy*. 2014;**113**:1315-1322
- [73] Maniscalco MP, Volpe M, Messineo A. Hydrothermal carbonization as a valuable tool for energy and environmental applications: A review. *Energies*. 2020;**13**:4098
- [74] Hoekman SK, Broch A, Robbins C. Hydrothermal carbonization (HTC) of lignocellulosic biomass. *Energy and Fuels*. 2011;**25**:1802-1810
- [75] Nachenius RW, Ronsse F, Venderbosch RH, et al. Biomass Pyrolysis. In: Marin GB, West DH, Li J, et al., editors. *Advances in Chemical Engineering, Chemical Engineering for Renewables Conversion*. Vol. 42. Oxford: Elsevier Inc.; 2013. pp. 75-139
- [76] Czerwińska K, Śliz M, Wilk M. Hydrothermal carbonization process: Fundamentals, main parameter

characteristics and possible applications including an effective method of SARS-CoV-2 mitigation in sewage sludge. A review. *Renewable and Sustainable Energy Reviews*. 2022;**154**:111873

[77] Kruse A, Funke A, Titirici MM. Hydrothermal conversion of biomass to fuels and energetic materials. *Current Opinion in Chemical Biology*. 2013;**17**:515-521

[78] Adolfsson KH, Yadav N, Hakkarainen M. Cellulose-derived hydrothermally carbonized materials and their emerging applications. *Current Opinion in Green and Sustainable Chemistry*. 2020;**23**:18-24

[79] Li Y, Liu X. Activated carbon/ZnO composites prepared using hydrochars as intermediate and their electrochemical performance in supercapacitor. *Materials Chemistry and Physics*. 2014;**148**:380-386

[80] Fang J, Gao B, Chen J, et al. Hydrochars derived from plant biomass under various conditions: Characterization and potential applications and impacts. *Chemical Engineering Journal*. 2015;**267**:253-259

[81] Dai L, Wu B, Tan F, et al. Engineered hydrochar composites for phosphorus removal/recovery: Lanthanum doped hydrochar prepared by hydrothermal carbonization of lanthanum pretreated rice straw. *Bioresource Technology*. 2014;**161**:327-332

[82] Xia Y, Yang T, Zhu N, et al. Enhanced adsorption of Pb(II) onto modified hydrochar: Modeling and mechanism analysis. *Bioresource Technology*. 2019;**288**:121593

[83] Fernandez ME, Ledesma B, Román S, et al. Development and characterization of activated hydrochars from orange peels

as potential adsorbents for emerging organic contaminants. *Bioresource Technology*. 2015;**183**:221-228

[84] Gallucci K, Taglieri L, Papa AA, et al. Non-energy valorization of residual biomasses via HTC : CO₂ capture onto activated Hydrochars. *Applied Sciences*. 2020;**10**:1879

[85] Hammud HH, Shmait A, Hourani N. Removal of malachite green from water using hydrothermally carbonized pine needles. *RSC Advances*. 2015;**5**:7909-7920

[86] Arun J, Varshini P, Prithvinath PK, et al. Enrichment of bio-oil after hydrothermal liquefaction (HTL) of microalgae *C. vulgaris* grown in wastewater: Bio-char and post HTL wastewater utilization studies. *Bioresource Technology*. 2018;**261**:182-187