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Hydrothermal carbonization and liquefaction for sustainable production of hydrochar and aromatics

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Abstract

Sustainable biorefinery depends on the development of efficient processes to convert locally abundant, energy-rich renewable biomass into fuels, chemicals, and materials. Hydrothermal processing has emerged as an attractive approach for wet biomass conversion with less environmental burden. Although considerable efforts have been made in sustainable biorefinery by unitizing innovative technologies at a laboratory scale, its scaling-up is still impeded by the biomass heterogeneity. This article critically reviews the recent advances in hydrothermal carbonization and liquefaction technologies for the sustainable production of hydrochar and aromatics from different biomass wastes. Three main aspects, including lignocellulose-/lignin-rich feedstock, operating conditions, and design of liquid/solid catalysts, are critically reviewed and discussed to understand the reaction mechanisms and system designs for increasing the yields of aromatics and improving the properties of hydrochar. The latest knowledge and technological advances demonstrate the importance of identifying the physical and chemical properties of feedstock. The science-informed design of hydrothermal technology and optimization of operational parameters with reference to the biomass properties are crucial for the selective production of value-added chemicals and multifunctional hydrochar. This review identifies current limitations and offers original perspectives for advancing hydrothermal processing of biomass towards carbon-efficient resource utilization and circular economy in future applications.

Keywords

Biomass valorization; Lignocellulose; Sustainable biorefinery; Platform chemicals, Waste management; Engineered biochar/hydrochar.

Abbreviation

HTC: hydrothermal carbonization

HTL: hydrothermal liquefaction

HTG: hydrothermal gasification

GHG: greenhouse gas

HMF: hydroxymethylfurfural

HHV: higher heating value

H: *p*-hydroxyphenyl

G: guaiacyl

S: syringyl

*p*CA: p-coumarate

FA: ferulic acid

HDO: hydrodeoxygenation

XPS: X-ray photoelectron spectroscopy

FTIR: Fourier transform infrared spectrometer

NMR: nuclear magnetic resonance spectroscopy

LC-MS: liquid chromatography-mass spectrometry

GC-MS: gas chromatography-mass spectrometry

1. Introduction

Developing sustainable production of fuels, materials, and valuable chemicals from renewable feedstock have received considerable attention due to the rapid transition from fossil

fuel [1]. Biomass is a renewable organic material including wood, wood processing waste, yard and garden waste, energy crop, algae, and municipal solid waste, etc. [2]. Lignocellulosic biomass, such as woody waste and agricultural residues, is the most abundant resource with an estimated annual global production of approximately 170 billion tons, and the utilization of these renewable resources ensures a more sustainable society [3]. In terms of environmental protection, using lignocellulosic biomass could effectively abate greenhouse gases (GHGs) emissions, contributing to the mitigation of climate change by carbon sequestration [4].

Lignocellulosic biomass mainly consists of cellulose, hemicellulose, lignin, and extracts [5]. Most of the frontier biofuel production strategies focused on the conversion of hemicellulose and cellulose [6, 7]. These precursors are the promising sources for producing lignocellulose-derived sugars and valuable chemicals such as bioethanol, hydroxymethylfurfural (HMF), furfural, and levulinic acid [8-12]. Nowadays, large amounts of lignocellulosic biomass are processed in the pulp and paper industry which generates around 150-180 million tons of technical lignin as industrial byproduct every year [13]. Lignin is one of the most abundant sources of sustainable aromatics on the planet, but it is generally underutilized in these cellulosic projects and mostly burned as fuel due to the challenges associated with its recalcitrance and inherent heterogeneity [14, 15]. The variability of biomass composition would result in products with different physicochemical properties and energy values. The societal drive for a sustainable future highlights the recognition of lignin depolymerization into aromatics (e.g., aromatic monomers, dimers, and low-molecular-weight oligomers), which could improve the overall economic feasibility and sustainability metrics of biorefinery [16-18]. To achieve sustainable production, not only the biomass feedstock but also the process

conditions should be carefully designed and tuned to obtain the desirable products.

Lignocellulosic biomass, though abundant in reserve for bioenergy production, has its own drawbacks due to high moisture, bulk volume, and low heating value [19, 20]. Hydrothermal processing is an effective and advanced technology that can directly convert carbon-rich feedstock without prior drying step. This process is endothermic and usually carried out under subcritical or supercritical water conditions, where the feedstock is fractionated into valuable constituents through hydrolysis, depolymerization, and condensation [21]. Water is one of the greenest solvents, and it can simultaneously act as a reactant and a suitable medium for acid-catalyzed reactions to break down the biomass into small fractions by the high concentration of H^+ ions generated from subcritical water [21, 22]. Hydrothermal carbonization (HTC), hydrothermal liquefaction (HTL), and hydrothermal gasification (HTG) are involved in the processes for the selective production of carbonized solids (i.e., hydrochar), liquid bio-oils, and fuel gases depending on the operating temperatures [23, 24]. HTC is conducted at temperatures between 180 °C and 250 °C and produces hydrochar with properties similar to brown coal [25, 26]. The cellulose and hemicellulose fractions of lignocellulosic biomass can be largely degraded into monomeric chains during the HTC process, whereas the lignin component is mildly modified because of its recalcitrance. With increasing reaction temperatures, the lignin-rich solid residues could be completely converted into liquid biofuel during the HTL process at 250-370 °C and be gasified during the HTG process (370-750 °C) [27-29]. Thus, these routes could realize various design of products with pre-defined properties and whole-biomass valorization by an integrated process.

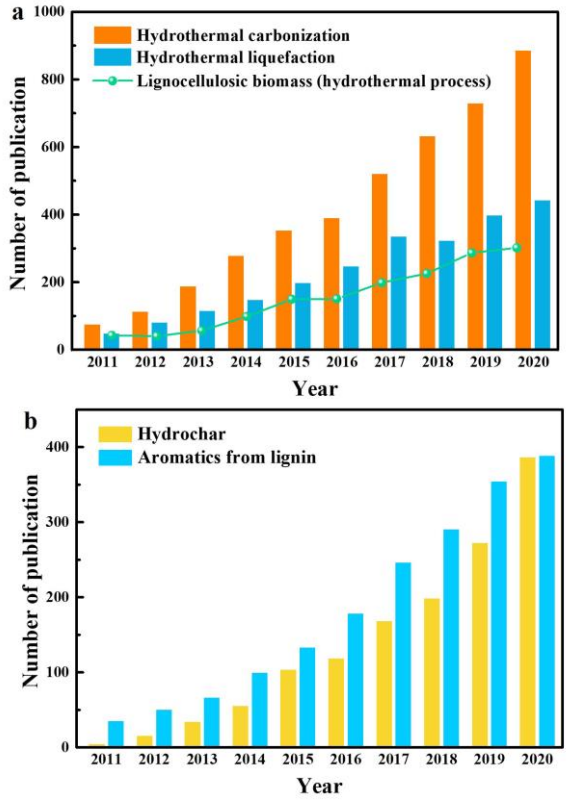

Fig. 1. Number of publications related to (a) hydrothermal technologies and (b) hydrochar and aromatics from 2011 to 2020 (according to Web of Science™).

By far, HTC and HTL have been particularly popular for the processing of biomass into value-added products at low to intermediate temperatures, *e.g.*, sustainable carbon-rich materials produced by HTC process, high selective production of aromatic monomers from HTL of lignin-rich feedstock, and novel catalytic approaches for HTL of algae towards biofuel production [30-33]. The number of publications related to hydrothermal processes between 2011 and 2020 (according to Web of Science™) is shown in Fig. 1a. In particular, the interest in the production of hydrochar and aromatics has significantly increased because hydrochar can be a source of low-cost fuel energy replacing fossil fuels and lignin-rich feedstock offers significant valorization potential beyond its heating value for lignocellulose refining (Fig. 1b). Hydrothermal processing of lignocellulose-/lignin-rich feedstock presents an economically

attractive and environmentally friendly approach for sustainable biorefinery. However, several fundamental and technical questions related to the variability in biomass, operating parameters, and efficient catalysis need to be addressed in the hydrothermal processing of biomass into desired products and commercialization of biofuels and bioproducts [34].

An overview of hydrothermal processing and its fundamentals as well as crucial issues of hydrothermal conversion have been discussed above and reviewed in previous studies [23, 24, 31]. With regard to different hydrothermal routes, it is even more important to critically review the advantages and challenges faced in the selective production of target products (*e.g.*, hydrochar and aromatics), because the chemical conversion reactions and physical/chemical challenges will differ when treating various types of biomass feedstock. HTC process is the main subject of biorefinery research for producing solid hydrochar with different structures and properties [35, 36]. The key factors including reaction temperature, time, pressure, loading ratio, and use of catalyst can directly alter the reaction pathways and modify hydrochar for different applications [20]. Hydrochar with a high energy density can be applied for energy storage while it can also serve as a sustainable carbon material for environmental remediation and catalysis [37-39]. HTL of lignin-rich feedstock can produce aromatic products with properties similar to petroleum-derived counterparts. The influences of operating parameters on the selective conversion of lignin have been widely studied to provide practical guidance, metrics, and methods [40, 41]. Recent studies have highlighted that the selective production of targeted aromatics would be determined by the inherent properties of lignin-rich feedstock [42-44]. Traditionally, most studies focus on the optimization of reaction parameters to tune the yields and qualities of biofuel and bioproducts. Nevertheless, the critical impacts of feedstock

properties are often overlooked, which should be considered at the earliest stage to achieve high-efficiency conversion. In-depth understanding with advanced analysis of feedstock variability is essential for developing better production methods and understanding multiple reaction mechanisms involved in the hydrothermal processes. In this case, extensive efforts are still required to identify the correlations and interactions among feedstock properties and targeted products.

We review the HTC of lignocellulose and HTL of lignin-rich feedstock for tailoring the selective production of multifunctional hydrochar and aromatics with the aim to provide a holistic and critical view on how the biomass variability, operational parameters, and catalyst fundamentally affect its valorization. The key contributions of this work are to: (a) present the important inherent properties of lignocellulosic biomass and physiochemical properties of their derived hydrochar/aromatics; (b) evaluate the critical impacts of feedstock characteristics, operating parameters, and use of catalysts on the yield and selective production of target products; (c) illustrate the reaction mechanisms during the HTC and HTL processes when using different lignocellulose-/lignin-rich feedstock with the optimized reaction parameters; (d) identify the current limitations related to the scale-up of hydrothermal processes and provide guidelines for sustainable biorefinery towards resource-efficient utilization in the future.

2. Lignocellulosic biomass and hydrothermal process

This section briefly summarizes the typical characteristics of lignocellulosic biomass and key factors involved in HTC and HTL processes for the production of hydrochar and aromatics.

2.1. Composition of lignocellulosic biomass

Lignocellulosic biomass, such as grass, agricultural fibers, and wood-based residues, is a

promising alternative source for biorefinery due to its surplus availability and cost - effectiveness [45-47]. The major components of lignocellulosic biomass are cellulose, hemicellulose, lignin, and extractives (proteins and inorganic compounds) [5]. Cellulose is the most abundant polysaccharide in nature (making up 40-50% of dry weight of lignocellulose), mainly consisting of D-glucopyranose units linked by β-glycosidic bonds, as shown in **Fig. 2** [48, 49]. Hemicellulose is an amorphous biopolymer consisting of pentoses and hexoses other than glucose, accounting for 30-50% of lignocellulose [50, 51]. Lignin (10-30%) is an amorphous tridimensional polymer mainly composed of three types of building blocks: *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) units [52, 53]. These monolignols are linked through several types of C-O (*e.g.*, β-O-4, α-O-4, and 4-O-5) and C-C (*e.g.*, β-β, β-5, and 5-5) bonds during lignin biosynthesis [54]. In its native state, labile β-O-4 linkage is the most abundant and its cleavage shares the potential of producing aromatic monomer with a high yield. In addition, the extractives such as proteins and inorganic compounds are also present in small amounts [55].

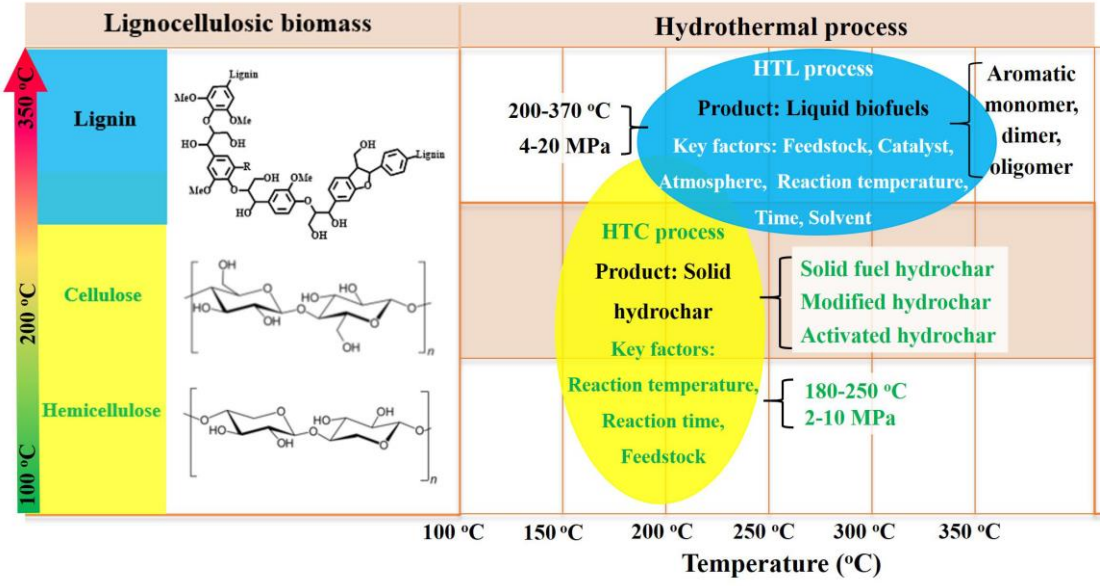

Fig. 2. Structural formula of lignocellulosic biomass and key factors in hydrothermal processes.

Chemical composition analysis of various lignocelluloses is a tool to explain the feedstock variability. Table 1 highlights the relative amounts of cellulose, hemicellulose, and lignin in several typical lignocellulosic biomass [56-58]. Cellulose and hemicellulose are particularly abundant in the grass biomass. Woody and nutshell wastes contain high contents of lignin that, for example, makes up 43.9% of dry weight of walnut shell. Biomass variability results in different chemical and physical properties, such as elemental compositions, higher heating value (HHV), contents of fixed carbon and volatile matter. Downstream conversion needs to consider these properties to take full advantage of biomass resources.

Table 1. Chemical compositions of the typical biomass [50-52].

Feedstock		Cellulose	Hemicellulose	Lignin
Hardwood	Poplar	42.1%	37.3%	24.8%
	Birch	41.7%	34.7%	21.9%
	Oak	40.4%	35.9%	24.1%
	Eucalyptus	39.0%	24.0%	29.0%
Softwood	Pine	42.1%	31.4%	20.4%
	Spruce	34.4%	29.8%	29.9%
Grass	Corn cob	33.3%	31.2%	16.2%
	Corn stover	51.2%	30.7%	14.4%
	Switchgrass	37.0%	26.0%	17.0%
Others	Endocarps	37.0%	25.4%	32.7%
	Almond shell	23.6%	27.6%	31.6%
	Walnut shell	13.4%	10.4%	43.9%

2.2. Hydrothermal carbonization for hydrochar production

Biomass typically contains a relatively high content of oxygen. It is an important object to increase the energy density of biofuel by removing oxygen from biomass *via* dehydration or

decarboxylation reactions [59]. HTC is an environment-friendly technology to convert lignocellulosic biomass to solid biofuel. This process is typically conducted at low temperatures ranging from 180 ºC to 250 ºC and under 2-10 MPa, as shown in **Fig. 2**. Due to the high ionization of water, the acidic and basic nature of water can accelerate the carbonization process of biomass feedstock [21]. In general, substrates undergo hydrolysis, dehydration, decarboxylation, repolymerization, and condensation/aromatization in the HTC process [60, 61]. As a result, hydrochar with a high energy density can achieve comparable properties to brown coal. Moreover, HTC also provides hydrochar as a carbon-rich material with tunable structure through various controlled chemical processes. The advantages of HTC process are listed in **Table 2**. However, technological difficulties may be encountered during the reactions at a high solid loading rate, such as high energy consumption and rate-limiting heat and mass transfer.

Table 2. Advantages and disadvantages of different hydrothermal processes.

Process	Key Factors	Advantages	Disadvantages
HTC process	Feedstock; Operating parameters	Variable wet feedstock; Mild reaction condition; Multifunctional hydrochar	Low heat-transfer coefficient; Low selectivity; Multiple reaction pathways
HTL process (Lignin-rich feedstocks)	Lignin structure; Catalytic systems; Operating parameters	Moderate temperature; Selective production; Wide range of aromatic products	High pressure; Solid effect of feedstock; Uncontrolled condensation; Complex products

Many studies have established practices for hydrochar production and demonstrated that multiple types of feedstock, operation parameters, and subsequent modification or activation can alter hydrochar properties such as HHV, surface morphology, and textural structure [62,

63]. Typically, cellulose and hemicellulose undergo degradation at a considerably lower temperature. The yields of hydrochar are lower at a higher reaction temperature due to the enhanced hydrolysis and degradation of carbohydrate-rich feedstock with a larger amount of small fragments dissolved in the liquid phase. In contrast, the decomposition of lignin-rich feedstock into soluble products is hindered due to higher reaction temperature required [64]. Therefore, the hydrothermal reaction conditions should be selected based on the chemical compositions of feedstock to obtain hydrochar with desired properties.

2.3. Hydrothermal liquefaction for aromatics production

Lignin is an irregular three-dimensional biopolymer that is hardly degraded during the HTC process. With a higher temperature, the HTL process (200-370 ^{o}C, 4-20 MPa) can convert the lignin-rich feedstock from the solid phase to valuable bio-oils such as aromatic monomer, dimer, and oligomer (**Fig. 2**) [65, 66]. The lignin-rich feedstock in the high ionization of water is subjected to hydrolysis and depolymerization *via* the selective cleavage of β-O-4 linkages into small fragments in the presence of catalysts [67, 68]. Water properties differ at different temperatures and influence the HTL process. Specifically, H^+ and OH^- derived from water dissociation at high temperatures can act as the homogeneous acid/base catalysts, whereas the solubility of solid substrate reduces due to the decrease in water density [21, 69]. Therefore, the feedstock/water ratio should be optimized based on the dissolution capacity of water at various reaction temperatures. Different from the key factors involved in HTC process (*e.g.,* temperature and feedstock compositions), catalytic system is regarded as a key component enabling lignin conversion in the HTL process, as listed in **Table 2**. Reductive and oxidative approaches have been extensively studied for the selective production of desired products.

Moreover, catalytic systems with a high pressure of hydrogen or nitrogen can be explored to further improve the production of aromatics. Nevertheless, the high-pressure requirement for the HTL process may also present a major technical challenge for scaling up due to the safety consideration and capital-intensive equipment requirement.

Various types of lignin feedstock (*e.g.,* wood, agro-waste, and technical lignin) have been widely used for producing desired aromatic products. Initial structure of lignin varies and it can govern the selective production of targeted aromatics. Native structure of lignin can be altered easily by harsh pretreatments that cause the cleavage of β-O-4 linkages along with the formation of stable C-C bonds, adding to the structural complexity of lignin [68]. Typically, the modified lignin through extraction or pretreatment exhibited a limited yield of aromatics because the depolymerization and condensation of lignin fragments are concomitant. To achieve efficient valorization of lignin-rich feedstock, it is essential to improve the lignin quality with less complexity and prevent its repolymerization and formation of recalcitrant structures. Furthermore, understanding the mechanisms of depolymerization and condensation of lignin-derived intermediates is an effective strategy towards aromatics production with a higher yield.

3. Hydrothermal carbonization

3.1. Biomass feedstock

Feedstock plays a significant role in the product yield, surface functional groups, textural structure, chemical composition, and surface morphology of hydrochar. The effects of feedstock on producing multifunctional hydrochar are reviewed in **Table 3**. The high content of lignin typically leads to an increase in the yield and thermal stability of hydrochar [70, 71].

Hydrochar derived from carbohydrate-rich feedstock has abundant hydroxyl groups and enrichment of aromatic carbons [71]. Previous studies compared the differences in the yield and redox capacity among Zn-loaded lignin-, cellulose-, and D-xylose-derived hydrochar. The addition of Zn(II) could increase the redox capacity of lignin-derived hydrochar due to the presence of phenolic hydroxyl and surface active -COOH groups [72]. These functional groups are the essential active sites for wastewater treatment by adsorption/degradation of various pollutants. The hydrochar surface properties are correlated to the compositions of biomass feedstock. Hydrochar produced from spruce sawdust and wheat were more acidic than those produced from canola straw and non-lignocellulosic feedstock [73]. The CO_2 released from lignocellulosic biomass could form carbonic acid, resulting in an acidic condition during HTC process. The depolymerization of lignin-rich feedstock could produce abundant phenol-derived products, which may also affect the acidity of hydrochar.

Pretreatment of raw feedstock also impact the hydrochar properties. Intensive grinding of feedstock is an effective strategy to increase the specific surface area of the resultant hydrochar, and subsequent activation can produce a potential carbon material for high-performance supercapacitor [62]. HTC of corn stalk before and after anaerobic digestion were employed to investigate the influence of pretreatment on the quality of solid fuel [74]. The results showed that anaerobic digestion activated amorphous cellulose and increased the carbon content and HHV of produced hydrochar, whereas the content of mineral constituents decreased due to leaching in anaerobic digestion.

In the HTC process, cellulose, glucose, fructose, and lignin extracts, etc., could be used to produce spherical carbon-based materials by self-assembly [75-78]. The specific structures of

hydrochar have been applied in the preparation of catalysts or high-performance carbon-rich materials for water purification and energy storage. HTC of enzymatic lignin at 160 ºC for 12 h produced highly regular spherical aggregates *via* π-π interaction of lignin fragments [76], while higher reaction temperature promoted the cleavage of β-O-4 linkages and dehydration reaction, resulting in a decreased content of carboxyl groups. Wang et al. [79] reported glucose as a promising carbon source that can be used to prepare hollow carbonaceous materials with abundant active sites, which showed a superior electrochemical performance. Zhang et al. [80] used fructose as a carbon source for the preparation of mesoporous support by using P123 and F127 as soft templates through a hydrothermal reaction at 180 ºC for 24 h. Its high specific surface area contributed to the high dispersion of Ru-based catalysts with porous structures. Overall, the starting feedstock is of significance for selectively producing the targeted carbon materials with specific structures and functionalities via the HTC process.

Table 3. Effects of feedstock selection and process conditions on HTC process.

Feedstock	Conditions	Key Findings	Ref.
Sunflower stalk	230 ºC, 24 h, 2/40 (w/v)	Grinding of feedstock (8000 mesh) contributed to an obvious increase in specific surface area of the hydrochar (720 m^2/g). This material was further activated by KOH to increase its surface area (1505 m^2/g), and showed high electrochemical storage capacity for high-performance supercapacitor.	[62]
Wood	220 °C, 1 h; 20/80 (w/v)	Lignin-rich woody biomass was used to produce activated carbon for adsorption *via* the HTC process and two-step chemical activation with KOH. The functional groups, surface area, and pore size distribution are strongly related to the HTL process and feedstock.	[70]
Canola straw, Wheat straw, Sawdust	180-300 °C, 1/8 (w/v)	Feedstock type (lignocellulosic and non-lignocellulosic feedstock) and HTC temperature affected the elemental compositions and biofuel properties of hydrochar. The hydrochar from lignocellulosic biomass at 240 and 300 ºC had a low content of ash and resembled high-volatile bituminous coal.	[73]

Lignin	300-390 °C	The low surface area of lignin-derived hydrochar was activated with KOH to yield carbon-based material with a high surface area of 3235 m^2/g and pore volume of 1.77 cm^3/g, which displayed a good hydrogen uptake of 6.2 wt% at -196 °C and 2 MPa.	[77]
Kraft lignin	240 °C, 22 h, $H_2SO_4/FeCl_2$, 10/100 (w/w)	Homogeneous acid catalyst (H_2SO_4) promoted the degradation of lignin-rich biomass through the cleavage of carbon side chains and β-O-4 linkages, resulting in a higher yield of solid hydrochar with a more stable structure.	[64]
Lignin, Cellulose, D-xylose,	240 ºC, 4 h, $ZnSO_4$, 10/50 (w/v)	The hydrochar yields from cellulose, D-xylose, and lignin showed an increased trend with the values of 33.9%, 36.0%, and 45.3%, respectively. Zn(II) catalyst significantly altered the redox capacity of lignin-derived hydrochar by inhibiting the decomposition of phenolic hydroxyl group, which could be used for reductive degradation of toxic organics.	[72]
Cellulose	200 °C, 48 h, $Al(OTf)_3$, 1.5/20 (w/v)	Acidic $Al(OTf)_3$ catalyst promoted the degradation of cellulose, and its derived hydrochar showed a spherical morphology with a diameter of 300-600 nm.	[78]
Glucose	180 °C, 8 h, 8/80 (w/v)	HTC of glucose produced uniform carbon nanospheres, which were then calcined under NH_3 atmosphere and activated by CO_2 to form N-doped carbon nanospheres with high specific surface area (2813 m^2/g) for electrocatalytic oxygen reduction.	[75]
Fructose	180 °C, 24 h, 2/70 (w/v)	The mesoporous carbon supports were prepared by using P123 and F127 as the composite templates and fructose as the carbon source *via* HTC process. High specific surface area of carbon-based support provided abundant active sites for heterogeneous catalysis.	[80]

3.2. Operating conditions

3.2.1. Reaction temperature

HTC temperature is a critical factor that directly affects the hydrolysis of biomass feedstock as well as the degradation and carbonization of newly formed intermediates for the production of hydrochar. In general, a gradual increase in C content and a corresponding loss of H and O contents occurred when increasing the reaction temperature through the enhanced deoxygenation and dehydration reactions, as shown in **Table 4** [25, 26, 81]. For instance, Cuevas et al. [58] investigated the short-time HTC of olive endocarps to identify the hydrochar

properties with different reaction temperatures. High HTC temperatures would facilitate free radical generation and promote biomass degradation, whereas the yield of hydrochar decreased. Keiller et al. [82] employed 200 °C, 230 °C, and 260 °C to investigate the changes in functional groups and compositions of hydrochar from saltbush. At 260 °C, the decarboxylation reaction of cellulose resulted in the loss of C=O carbonyl groups and the formation of formic acid and CO_2. The contents of hemicellulose, cellulose, and lignin in Saltbush declined from 21%, 24%, and 28% to 0%, 6%, and 17%, respectively. These results confirmed that the high temperature could effectively promote the degradation of carbohydrate-rich feedstock. By contrast, lignin only partly hydrolyzed and a large proportion of insoluble lignin remained in hydrochar. HTC of raw food waste (76% moisture content), containing vegetables, fruits, and staple food, resulted in a low yield of hydrochar with only 7% at 200 °C and 5% at 300 °C [83]. The yields of hydrochar from dried food waste ranged 44-53.1% at 160-200 °C for 5 h, with an energy densification of 5.5-7.3 [84].

Table 4. Characterization of various biomasses and their derived hydrochar.

Feedstock	Conditions	C	H	O	FC	Ash	HHV	Yield	Ref.
Endocarps	Raw	49.65	6.83	42.68	13.06	0.71	18.78	-	[58]
	175 ºC, 0-10 min	49.12	6.73	43.73	13.32	0.28	20.50	97	[58]
	200 ºC, 0-10 min	49.34	6.67	43.64	14.22	0.21	20.88	85	[58]
	225 ºC, 0-10 min	51.77	6.68	41.26	18.23	0.2	21.90	61	[58]
Corn cob	Raw	43.1	5.8	44.6	17.2	4.2	17.2	-	[58]
	190 ºC, 1.5 h	46.7	5.5	43.9	19.2	3.7	18.1	66	[81]
	250 ºC, 1.5 h	65.0	4.6	24.5	44.3	6.4	25.5	45	[81]
	310 ºC, 1.5 h	67.7	4.5	20.9	51.6	6.3	26.6	38	[81]
	370 ºC, 1.5 h	70.3	4.3	17.8	65.8	7.0	27.6	33	[81]
Corn stover	Raw	45.12	5.77	45.19	17.15	3.51	17.8	-	[25]
	180 ºC, 4 h	48.05	5.34	43.85	19.57	2.40	18.4	68	[25]
	200 ºC, 4 h	50.10	5.26	43.85	24.18	2.38	19.1	62	[25]
	220 ºC, 4 h	62.64	5.21	28.95	38.75	2.79	24.9	51	[25]

	220 ºC, 2 h	61.21	5.22	30.61	29.62	2.58	24.3	56	[25]
	220 ºC, 12 h	67.36	5.01	24.26	49.78	2.97	26.8	50	[25]
Mallow	Raw	44.9	6.02	46.78	5.62	1.97	17.8	-	[25]
	180 ºC, 1 h	49.7	5.77	42.72	9.75	1.40	19.7	66	[26]
	200 ºC, 1 h	52.5	5.78	40.21	14.42	1.05	20.9	61	[26]
	220 ºC, 1 h	54.5	5.67	38.39	16.04	1.05	21.7	56	[26]
Canola straw	Raw	48.6	4.9	39.9	2.6	5.6	18.5		[73]
	180 ºC, 4 h	53.2	5.2	32.9	10.8	8.1	21.2	61	[73]
	240 ºC, 4 h	68.1	5.5	18.5	11.7	5.6	28.2	43	[73]
	300 ºC, 4 h	72.0	5.1	13.9	30.3	7.2	29.6	26	[73]
Olive tree	Raw	49.98	6.45	37.67	26.6	3.86	21.2		[85]
	200 ºC, 1 h	55.43	6.15	29.78	31.99	6.59	23.4	82	[85]
	250 ºC, 1 h	60.29	5.87	23.41	38.63	7.97	25.4	66	[85]
	300 ºC, 1 h	63.39	5.01	18.58	56.74	9.97	26.0	51	[85]
	350 ºC, 1 h	64.40	5.02	15.88	64.71	11.95	26.5	39	[85]
Vineyard	Raw	47.14	6.46	43.25	30.2	2.0	23.9		[85]
	200 ºC, 1 h	51.86	5.77	38.50	32.19	3.09	20.9	82	[85]
	250 ºC, 1 h	58.78	5.28	30.81	43.39	3.62	23.5	63	[85]
	300 ºC, 1 h	65.78	4.22	23.05	67.85	5.37	25.4	42	[85]
	350 ºC, 1 h	72.35	4.03	13.99	73.22	7.91	28.4	37	[85]
Food waste	Raw	39.00	7.32	47.68	14.48	6.41	15.0		[83]
(76%	200 ºC, 1 h	62.83	7.25	24.88	30.34	4.52	20.81	7	[83]
moisture)	250 ºC, 1 h	68.10	7.09	20.09	45.41	3.11	28.89	6	[83]
	300 ºC, 1 h	73.00	7.01	17.09	47.43	2.21	31.00	5	[83]
Food waste	Raw	52.0	6.9	38.1	5.0	1.8	15.1		[84]
(dried)	160 ºC, 5 h	51.5	7.0	31.1	1.7	5.9	23.3	52	[84]
	180 ºC, 5 h	61.4	6.6	24.6	2	0.9	29.5	44	[84]

Raw: biomass feedstock; Weight content of O was calculated by difference (O% = 100% - ash% - C% - H% - N% - S%).

3.2.2. Reaction time

Reaction time also influences the chemical, morphological, and structural properties of hydrochar. Prolonged reaction time could result in continuous hydrolysis and simultaneous polymerization of degraded fragments, forming the secondary char with a complex structure.

297 The increases in HHV and content of fixed carbon due to the removal of oxygen from biomass
298 feedstock are listed in **Table 4** [26, 58, 81]. Johnson et al. [86] found that the yields of hydrochar
299 decreased from 55% to 35% from 3 h to 7 h while the HHV value steadily increased from
300 200 °C (11.4 MJ/Kg) and approximately doubled at 250 °C (24.9 MJ/Kg). Zhang et al. [25]
301 revealed that a longer reaction time resulted in the decrease of hydrochar yields and H/C (0.76-
302 1.33) and O/C (0.19-0.68) ratios due to the dehydration and decarboxylation reactions.
303 Regarding the effects of time on morphological properties of hydrochar, increasing the reaction
304 time from 4 h to 24 h could strongly destruct the initial structure of corn stover and accelerate
305 the formation of nanospheres and microfiber at high reaction severity. Similar results were
306 reported by Zhang et al. [63], in which the long reaction time obviously destroyed the fiber
307 structure of wheat straw and produced carbon microspheres after HTC process.

308 **3.3. Catalyst**

309 Various catalysts were explored to develop the multifunctional hydrochar materials by a
310 controlled chemical process. In general, the modification using acids such as H_2SO_4, H_3PO_4,
311 and organic acids facilitated the establishment of high surface area and porous structure of
312 hydrochar [87, 88]. Acid-assisted HTC was conducted to produce functionalized carbon-based
313 catalysts [87], in which Kraft lignin feedstock was carbonized and sulfonated with the H_2SO_4
314 catalyst at 180 °C for 12 h. An increase in acidic groups over the surface of lignin-derived
315 hydrochar catalyst was detected, and these oxygenated groups were supposed as the active sites
316 to promote the dehydration of fructose. Xu et al. [88] reported that acids could drive the self-
317 assembly of F127 micelles and pentose into the stable structure and contributed to the
318 formation of hydrochar at a low temperature. The hydrochar yield is also affected by the

promoted hydrolysis of feedstock with acidic catalyst. Simsir et al. [78] reported that the yields of hydrochar from both cellulose and glucose were reduced by the addition of acidic $Al(OTf)_3$ catalyst, while the yield increased in the presence of alkaline catalysts because of the inhibition of secondary char formation.

Biomass loaded with different concentrations of metal salts (Fe^{3+}, Ni^{2+}, Cu^{2+}, or Zn^{2+}) have also been explored to modify the surface and structure of hydrochar for pollutant degradation, catalysis, and energy storage [89, 90]. Zhu et al. [91] activated the forestry waste by zinc chloride ($ZnCl_2$) for producing hydrochar with a high porosity. The condensation of aromatics and removal of tar were promoted in the presence of $ZnCl_2$ catalyst, and the addition of K_2CO_3 further broadened microporosity distribution of the resultant hydrochar. The promotional effect of Zn^{2+} on surface groups was investigated by Ma et al. [72], who found the decline in carboxyl groups and the increase in phenolic hydroxyl groups in the Zn-loaded hydrochar. The difference was attributed to metal adsorption that hindered the subsequent dehydration reaction of phenolic hydroxyl groups. Li et al. [92] reported richer oxygenated groups, higher carbon content (up to 64%), and improved specific surface area, average pore size, and pore volume by subsequent HCl washing that removed $ZnCl_2$ from the channels of Zn-modified bamboo hydrochar. Xu et al. [93] similarly improved the porosity of bamboo hydrochar by the addition of $Fe_2(SO_4)_3$ in the HTC process while retaining the spherical morphology. The Fe-decorated carbon sphere could be a potential electrode material for high-performance supercapacitor application. In addition, mineral ash as catalysts play an important role in the yield and quality of hydrochar [94, 95]. The yield of hydrochar derived from Scenedesmus with a high ash content is lower than that from the de-ashed feedstock, indicative of the catalytic hydrolysis of

biomass due to ash content [95]. Nevertheless, feedstock de-ashing by acid washing could enrich the carbon content and enhance the quality of hydrochar as a solid fuel.

3.4. Reaction pathway

Reaction pathways in the HTC process can be categorized into three steps: hydrolysis, decomposition, and carbonization/polymerization of degraded products, as shown in **Fig. 3** [96-98]. Firstly, lignocellulosic biomass is hydrolyzed to small soluble fragments and key intermediates in the liquid phase. The solution pH value decreases due to the formation of organic acids and phenolic chemicals. Secondly, the degraded fragments, including monomers (*e.g.,* glucose, xylose, 5-HMF, furfural, and their derived products) and oligomers undergo dehydration and polymerization, and the insoluble phase precipitates slowly from the liquid phase. As a result, the hydrochar is formed through the final step of aromatization reaction along with decarboxylation reaction. This process is adequate for hemicellulose, cellulose, and soluble lignin. The predominant mechanism differs when using different types of feedstock that contain variable contents of cellulose, hemicellulose, and lignin. For instance, hemicellulose-rich feedstock has a low degree of polymerization as compared to cellulose and lignin-rich feedstock. At low temperatures, hydrolysis of hemicellulose mainly generates xylo-oligomers. When increasing the reaction temperature up to 180 ºC, monomeric xylose and furfural resulting from dehydration of pentoses were the key intermediates accountable for the formation of insoluble secondary char through the polymerization reaction.

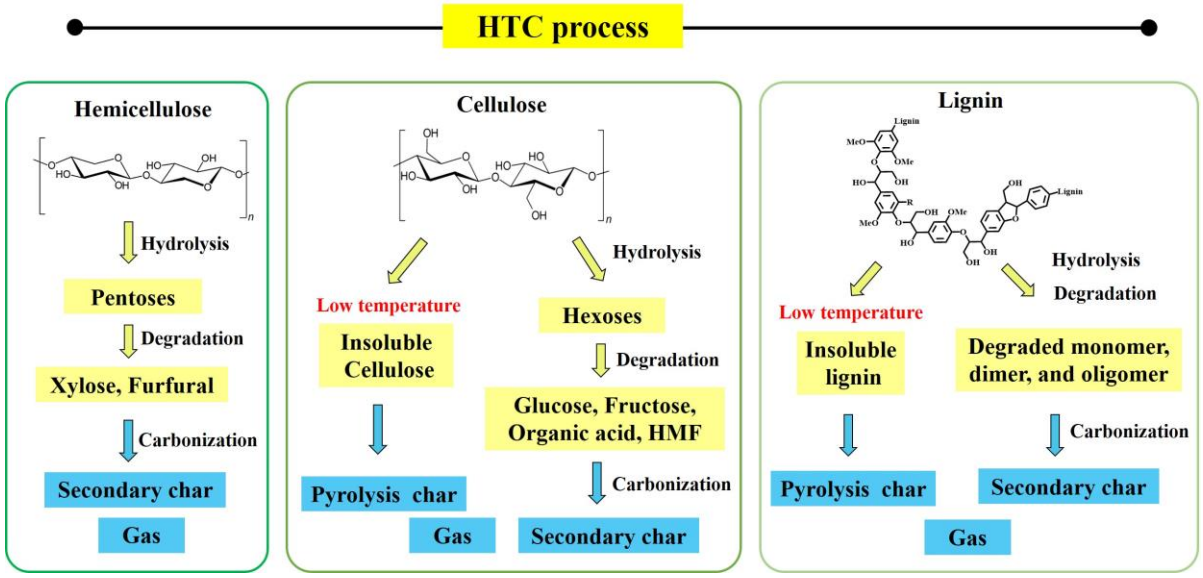

Fig. 3. Reaction pathways of HTC process.

The mechanisms proposed for HTC processing of cellulose-rich and lignin-rich feedstock include two pathways, *i.e.*, soluble pathway and insoluble pathway, which depend on the reaction temperature. In general, cellulose can be degraded into soluble fragments above 200 ºC, while it is partly subjected to hydrolysis at a low temperature [99]. The soluble products (*e.g.,* glucose oligomers, glucose, and fructose) from cellulose subsequently undergo a series of reactions, including isomerization, dehydration, and fragmentation into active intermediates such as HMF and organic acids. These reactive products can be polymerized and condensed to form the secondary char. The insoluble parts are subjected to a pyrolysis-like reaction at a low reaction temperature [99]. As lignin is an amorphous heteropolymer with a low solubility in water, the hydrolysis of lignin into soluble fragments (*e.g.,* aromatic monomer, dimer and oligomer) is the critical limiting factor for the formation of secondary char [64]. The majority of insoluble lignin are subjected to mild dehydration and decarboxylation reactions and then remain as the pyrolysis char [72], as shown in **Fig. 3**.

3.5. Properties and applications of hydrochar

The key characteristics and possible applications of multifunctional hydrochar from HTC of various feedstock are illustrated in **Fig. 4**. The proximate and ultimate analysis of hydrochar is necessary to ensure an efficient utilization of hydrochar as a solid biofuel. The proximate analysis includes volatile matter, ash, and fixed carbon. The O/C and H/C ratios, as well as yields of hydrochar, can illustrate the degree of carbonization of biomass feedstock with variable reaction severities. Typically, Van Krevelen diagram that is used to illustrate the H/C and O/C ratios can indicate the degree of dehydration and decarboxylation reactions and provide a direct comparison between raw feedstock and its derived hydrochar [100, 101], which is exemplified in **Fig. 5a**. The HHV is directly related to the contents of C, O, N, S, and ash [60]. Increasing reaction severity usually results in a higher percentage of fixed carbon and a decrease in the contents of ash and O, thus improving the HHV of hydrochar.

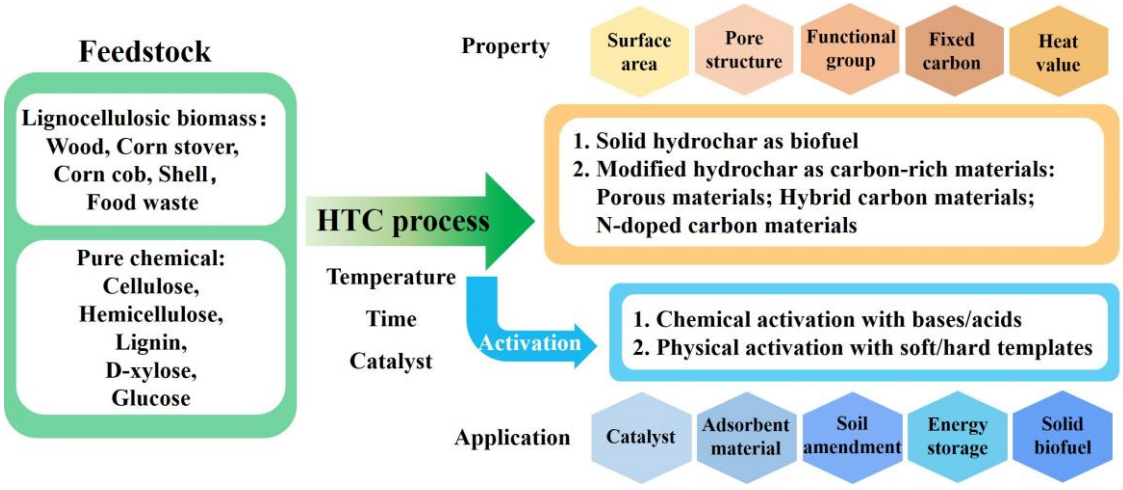

Fig. 4. HTC of various feedstock to produce multifunctional hydrochar.

Advanced structure analysis enables a comprehensive understanding of hydrochar properties after different treatments. The physicochemical changes are often assayed by using FTIR, NMR, and XPS (**Fig. 5b-e**) [102-104]. FTIR is widely used to identify the surface functional

groups (*e.g.,* C=C bonds, -OCH_3, and -OH groups) and reveal the evolution of structural characteristics under different HTC conditions [105]. NMR is employed to provide valuable quantitative data for surface functionality analysis [106], and 2D NMR provides detailed information about the intermolecular linkages and aromatic structures existing in the complex lignin feedstock [107, 108]. XPS reveals the chemical environment of hydrochar surface. Two prominent peaks in C (C1s) and O (O1s) are usually investigated in XPS spectra to determine the functional groups on the hydrochar surface [109]. The surface morphology and textural properties of hydrochar are significantly affected by biomass feedstock and carbonization temperature. The morphology changes and structural evolutions are generally evaluated by SEM and BET analyses for the specific surface area and pore size distribution. The above physicochemical properties provide fundamental information of the material characteristics for the rational design of the multi-functionality of hydrochar.

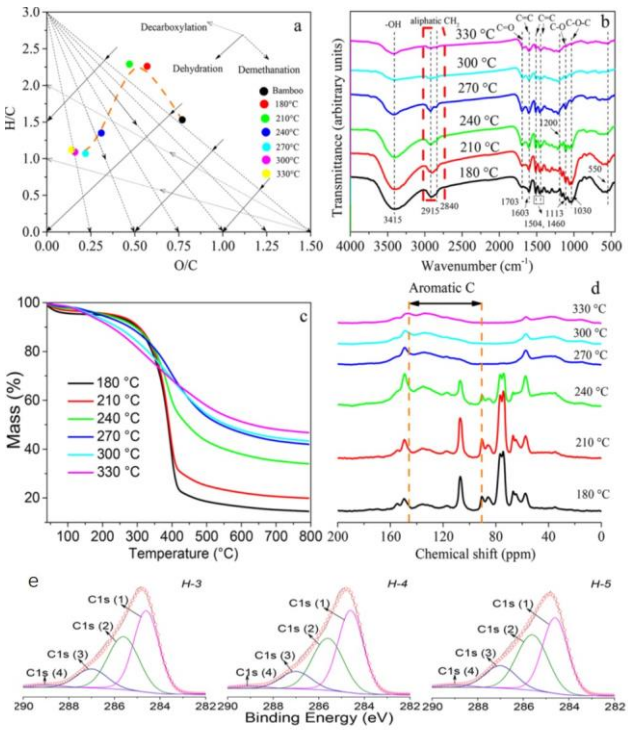

Fig. 5. (a) H/C and O/C atomic ratios in Van Krevelen diagram, (b) FTIR spectra, (c)

thermograms, (d) solid-state ^{13}C NMR spectra, and (e) XPS spectra of hydrochar [100, 101].

However, the low surface area and underdeveloped porosity of hydrochar may hinder its diverse utilization. To address this limitation, a range of strategies have been investigated for improving its physicochemical properties and morphologies, such as the incorporation of heteroatom, hierarchical porosity customization, and introduction of surface defects to expand their applications [110-112]. For example, a two-stage HTC and chemical activation technology method was applied to prepare activated hydrochar with large surface areas and enriched pore structures [113]. Chemical activation with acids, bases, and metal salts was explored to increase the surface area and porosity of hydrochar. Activation using KOH was conducive to establishing pore structures, exposing more active sites and oxygen-containing functional groups, and boosting the potential application of hydrochar in energy storage, pollutant adsorption, and catalysis, as listed in **Table 5**. For instance, activation of lignin-derived hydrochar by KOH could generate carbon-based materials with a high surface area up to 3235 m^2/g that served as a superior sorbent for hydrogen storage [77]. The high content of undegraded lignin made hydrochar richer in oxygenated functional groups that could be the active sites for pollutant adsorption and degradation [70].

Furthermore, physical activation by using CO_2 or the use of soft template can effectively enlarge the pore size of hydrochar [75, 114]. The CO_2 activation of hydrochar can also significantly increase the specific surface area due to the carbon loss by incomplete carbonization process ($C + CO_2 \rightarrow 2CO$) [75]. In the latest studies, heteroatom doping has been a major research subject to improve the physiochemical properties of hydrochar [115]. Nitrogen-doped carbon materials showed a remarkable performance in many applications such

as pollutant adsorption, gas storage/separation, and catalytic reaction [39, 115]. The blending of lignocellulosic biomass with nitrogen-rich materials (*e.g.,* protein, urea, Spirulina) in the HTC process can effectively improve the nitrogen doping level and introduce structural nitrogen into the resultant hydrochar [111, 112]. Besides, food waste and yard waste could be mixed in the HTC process for the solid biofuel production, and the HHV increased to 27.6 MJ/kg at 220 ºC for 1 h [116]. Microwave-assisted HTC of corn stalk at 230 ºC also produced solid biofuel with a high energy density [117]. Overall, modification/activation approaches are critical to improve the performance of hydrochar-based carbon materials.

Table 5. Modification and application of hydrochar.

Modification approaches	**Properties**	**Applications**	**Ref.**
Chemical activation by KOH	High specific surface area	High-performance supercapacitor	[62]
Co-HTC of lignin with protein and chemical activation by KOH	Hierarchical pore structure; High specific surface area; Nitrogen doping	High-performance supercapacitor	[112]
Physical activation by CO_2 and modification by NH_3	High specific surface area; Nitrogen doping	Electrocatalytic oxygen reduction	[75]
Physical activation and use of soft template (P123 and F127)	High specific surface area; Porous structure	Ru-loaded carbon catalyst for xylose conversion	[114]
H_2SO_4-catalyzed HTC	Acidic groups	Meatal-free catalyst for fructose conversion	[87]
Impregnation of Al on hydrochar	Al-hydrochar with oxygenated functional group	Al-hydrochar catalyst for glucose isomerization	[115]
Co-HTC of leaves and Spirulina and activation by $ZnCl_2/CO_2$	High specific surface area; Nitrogen doping; Ultra-micropores	CO_2 adsorption	[111]

Chemical activation by KOH	High specific surface area	Gas storage	[77]
Co-HTC of food waste with yard waste	High energy density; High mass density	Solid biofuel	[116]
Microwave-assisted HTC	High energy density	Solid biofuel	[117]
Urea-assisted HTC and chemical activation by KOH	High specific surface area; Porous structure; Nitrogen doping	Pollutant adsorption	[39]
Acid-catalyzed HTC	Oxygen-rich functional groups	Organics adsorption	[110]
Zn(II)-catalyzed HTC	Oxygenated functional groups	Organics degradation	[72]

4. Hydrothermal liquefaction

For the HTL process of lignin-rich feedstock, selective production of aromatics depends on the lignin source, specific reaction parameters, and catalysts used. The key factors involved in lignin pretreatment are the biomass source and the pretreatment conditions that influence the initial structure of lignin and govern its subsequent conversion. The lignin structure and catalytic systems are the vital factors in the HTL process (**Fig. 6**). We first discuss the lignin feedstock and its importance for the selective production, as well as the associated implications for scale-up process. We then discuss the operating parameters and various catalysts developed for the HTL process of lignin to specific aromatics.

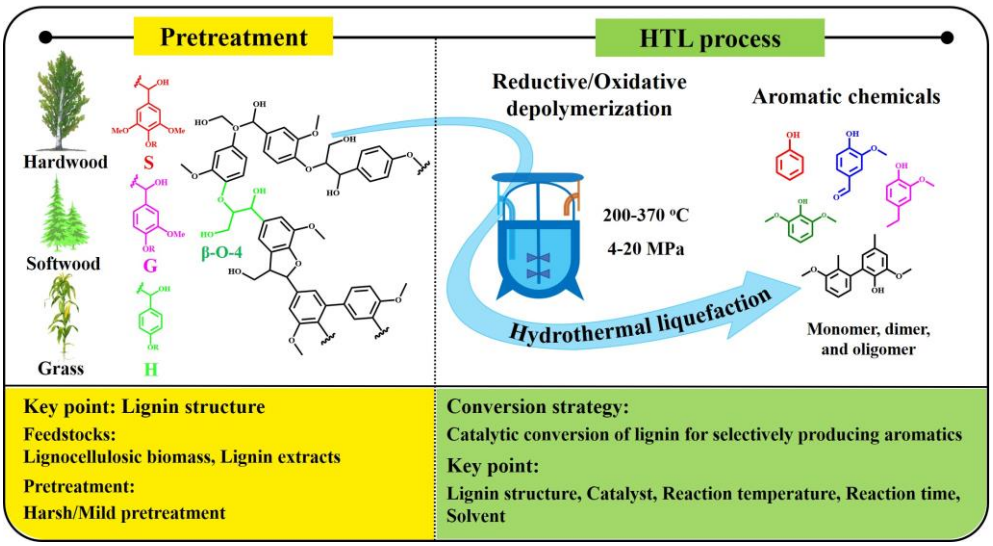

Fig. 6. HTL of lignin-rich feedstock for production of aromatics.

4.1. Feedstock

4.1.1. Native lignin in lignocellulosic biomass

Lignocellulosic biomass and lignin extract involved in the HTL process are reviewed for the aromatics production (**Table 6**). Reductive catalytic fractionation (RCF) has been explored for the conversion of native lignin in lignocellulose, and the well-preserved carbohydrates are suitable for further processing [118, 119]. High degree of delignification and high yields of aromatic monomers could be achieved in RCF of lignocellulosic biomass [120]. However, this strategy also resulted in the degradation or modification of carbohydrates, posing a fundamental challenge in selective conversion process. The biomass variability adds to the problems associated with structural complexity of lignin and its derived products. Various analyses such as element analysis, FTIR, 2D NMR, and SEM have been used to characterize the chemical, morphological, and structural properties of lignin sources. Specially, 2D HSQC NMR is used to elucidate the initial structure of lignin in terms of S:G:H ratio and interunit linkage distribution. Gel permeation chromatography can be used to analyze the molecular

463 weight distribution of lignin feedstock and its derived bio-oil. With the improved understanding
464 of complex characteristics of lignin, it has been recognized in recent studies that its structure
465 differs markedly owing to different biomass sources and pretreatment methods.

466 Lignin derived from softwood, hardwood, and grass possess different contents of S, G, and
467 H units that are typically cross-linked through C-O and C-C bonds [43], as shown in **Fig. 7**.
468 The S/G-rich lignin in hardwood is rich in β-O-4 linkage that is related to high-yield production
469 of aromatic monomers [68]. Lignin in grass is mainly composed of S-G-H-type units, whereas
470 lignin in softwood is mainly composed of G units that often lead to the formation of stable β-β
471 and 5-5 linkages [121]. Because of the high content of G units, softwood lignin can be a
472 potential feedstock for high selective production of G-type aromatics. Vanillin, as a building
473 block for the chemical industry, has been produced from the oxidative conversion of softwood
474 by using alkaline catalysts [122, 123]. With the recent development, monolignol p-coumarate
475 (*p*CA) and ferulic acid (FA) moieties that are cross-linking agents between carbohydrates and
476 lignin were detected in the fast-growing biomass, such as corn stalk and wheat straw [124-126].
477 Due to its unique structure, several studies investigated the reactivity of *p*CA for the selective
478 production of target aromatics [127, 128]. Lignin source is a crucial factor determining the
479 native structures of lignin and the properties of resulting products. It is essential to scrutinize
480 the structural variability of lignin feedstock and elucidate the key characteristics of lignin
481 sources, β-O-4 linkage, and S:G:H ratio for designing an effective biorefinery strategy.

482 **Table 6.** Experimental investigation on the HTL of various lignin-rich feedstock.

Feedstock	Conditions	Catalyst	Key Findings	Ref.
Pine	160 °C, 1 h, 1 MPa O_2	NaOH	**Baes-catalyzed oxidation:** Oxidative conversion of various lignocelluloses (*e.g.*, pine, eucalyptus, grass, and bagasse	[121]

			waste) could produce both aromatics and cellulose. Pine gave a high yield of vanillin (21.1 wt%) and low-molecular oligo-phenolics (56.7%).	
Alkaline lignin	250 °C, 1 h, N_2	Solid bases	**Base-catalyzed reaction:** Reaction temperature, time, and pressure could affect HTL of alkaline lignin over various solid bases. A high yield of low-molecular-weight products was obtained over basic NaX catalyst at 250 °C for 1 h.	[129]
Kraft lignin	200 °C, 30 min, 1.5 MPa O_2	NaOH	**Baes-catalyzed oxidation:** The yields of organic acids and the contents of phenolic monomers, dimers, and trimers (<1 kDa) increased with the increase in oxygen pressure and temperature.	[130]
Organosolv lignin	300 °C, 80 min, 9 MPa	NaOH	**Baes-catalyzed oxidation:** HTL of different organosolv lignin from olive tree was investigated. Acetosolv lignin gave the highest yield of bio-oil (18.48 wt%), while formosolv lignin enabled a high yield of phenolic monomers (28.2%) in the bio-oil.	[131]
Bagasse lignin	260 °C, 15 min, N_2	Acidic ionic liquid	**Acid-catalyzed reaction:** HTL of sugarcane bagasse lignin using $[C_4H_8SO_3Hmim]HSO_4$ achieved 65% of delignification and yielded 13.5% of aromatic monomers, including phenol, guaiacol, and 4-ethylphenol.	[132]
Alkali lignin	160 °C, 7 min, 1 MPa O_2	NaOH, $CuSO_4$	**Oxidation:** The cleavage of C-O and C-C bonds in lignin was promoted in the presence of Cu^{2+} to yield aromatic aldehydes and ketones. At high pH, depolymerization and condensation reactions occurred simultaneously and shared the reactive intermediates.	[133]
Dealkaline lignin	250 °C, 30 min, 0.7 MPa N_2	Solid acids	**Reduction:** HTL process with various solid acid catalysts could convert different types of lignins into aromatic monomers under an inert atmosphere. Depolymerization of dealkaline lignin over the SiO_2-Al_2O_3 catalyst achieved a high yield of phenolic monomers (60%).	[65]
Birch lignin	250 °C, 20 h,	Ru/Nb_2O_5	**Reduction:** HTL of lignin over a Ru/Nb_2O_5 catalyst produced a high yield	[134]

0.7 MPa H_2	of liquid hydrocarbons (35.5 wt%) with high selectivity of 71 wt% for arenes.

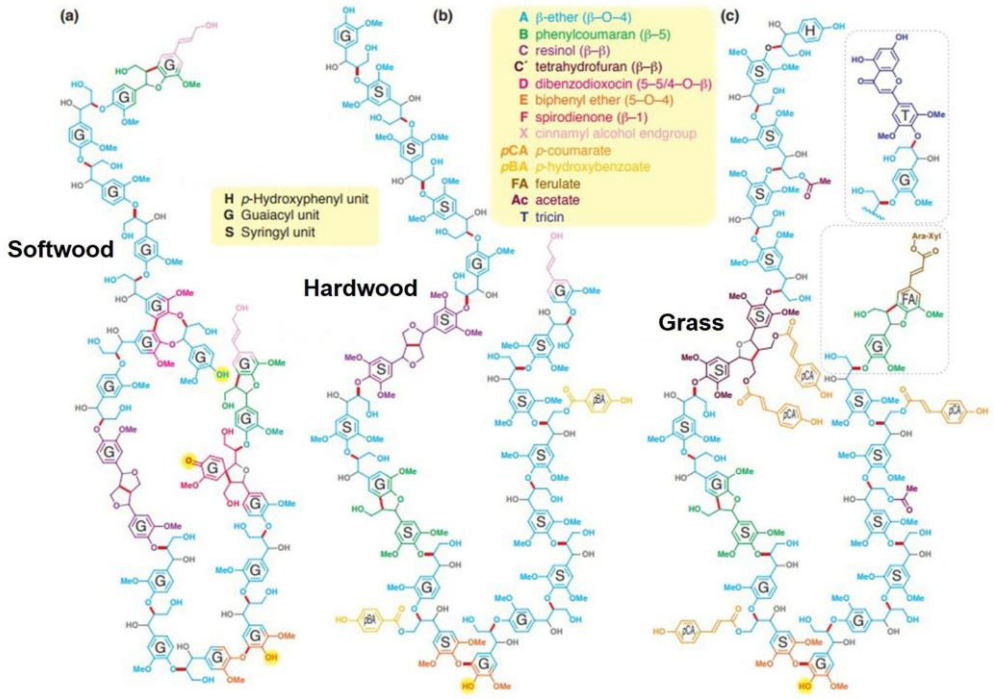

Fig. 7. Lignin structures in softwood, hardwood, and softwood [43].

4.1.2. Lignin extracts

Selective lignin extraction from initial lignocelluloses could produce high-purity lignin extracts. Wide-ranging pretreatments have been developed by using acids, bases, and organic solvents. The harsh pretreatment can alter the H/G/S ratios and reduce the degree of polymerization in order to remove lignin from biomass [53]. Studies on lignin extraction have demonstrated that the lignin extracts containing variable aromatic rings and side chains are more complex than their original structures [69, 135]. By far, the most common extraction approaches are organosolv methods that employ an organic solvent for delignification. Organosolv pretreatment can liberate lignin from biomass by cleaving ether and ester bonds and forming C-OH groups with a mildly modified structure of lignin [136, 137]. Typical thermal pretreatments such as hydrothermal liquefaction and steam explosion focus on the

497 production of monomeric carbohydrates and lead to the formation of more recalcitrant lignin
498 polymer. High-severity conditions using a strong acid/base similarly result in undesirable
499 condensation of lignin, and the recovered low-quality lignin is not suitable for subsequent
500 depolymerization. For example, Kraft lignin subjected to alkaline pretreatment in the pulp and
501 paper industry typically possesses a lower content of β-O-4 linkages but high contents of C-C
502 bonds and phenolic hydroxyl groups due to the cleavage of C-O bonds [69]. This process makes
503 the lignin recalcitrant for subsequent conversion. The microwave-assisted HTL of Kraft lignin
504 also gave low yields of aromatic monomers and bio-oils [53].

505 **4.2. Operating conditions**

506 **4.2.1. Operating parameters in reductive systems**

507 High oxygen content is one of the most significant barriers to biomass conversion into ideal
508 liquid biofuel. Hydrodeoxygenation (HDO) reaction can produce de-functional aromatics such
509 as arenes and phenolics from the lignin-rich feedstock. However, high-severity conditions
510 simultaneously facilitate the production of cycloalkanes through HDO reaction [80, 134, 138].
511 Shao et al. [134] explored the selective production of arenes *via* HDO of lignin over a
512 Ru/Nb_2O_5 catalyst at 250 ºC for 10 h. Four phenolic monomers (total G-/S-type monomer
513 yields of 7.7 wt%) were obtained together with arenes and cycloalkane-based hydrocarbons
514 (total yields of 9.7 wt%). Hydrocarbon yields of 35.5 wt% with a selectivity of 71 wt% for
515 arenes was obtained after 20 h. This study suggested that birch lignin could be firstly
516 depolymerized to phenolic monomers *via* the cleavage of β-O-4 linkages, and the formed
517 phenolic monomers were sequentially converted to arenes and cycloalkanes by HDO over the
518 Ru/Nb_2O_5 catalyst. The promotional effect of high reaction temperatures on the cleavage of

519 $C_{aromatic}$-OH bonds over the Ru/Nb_2O_5 catalyst was also demonstrated by using lignin model
520 compounds.

521 Various reaction conditions were optimized by Liu et al. [120] through RCF of eucalyptus
522 to selectively produce phenolic compounds over the Ni@ZIF-8 catalyst. Lower reaction
523 temperature (or performing the reaction under the N_2 atmosphere) sharply reduced monomer
524 yields along with a significant drop in the delignification degree. Chaudhary et al. [129]
525 investigated the effects of reaction time, temperature, and pressure on the base-catalyzed
526 depolymerization of lignin into low-molecular-weight aromatics. Maximum yield (51%) of
527 low-molecular-weight products was achieved at 250 °C after 1 h, but the yields started
528 declining with a decrease in temperature or a longer reaction time. At high temperatures, the
529 decline in monomer yields might be not only associated with the temperature effect but also
530 affected by the pressure changes. Increasing the reaction pressure by 0.3 MPa of N_2 at a fixed
531 temperature promoted the lignin depolymerization towards high-yield aromatics production.
532 Zhang et al. [80] found that the hydrogenation of benzene to cyclohexane occurred when the
533 H_2 pressure was over 1 MPa, implying the direct deoxygenation and deep HDO reactions
534 become more dominant at higher severity.

535 **4.2.2. Operating parameters in oxidative systems**

536 For oxidative systems, the major challenge for the selective production of aromatics is to
537 overcome stronger oxidation or condensation of reactive products [130, 139, 140]. High
538 temperatures or O_2 pressures could increase the yields of phenol-derived chemicals, and
539 organic acids such as formic and acetic acids resulted probably from HTL of Kraft lignin [130].
540 At a high temperature, lignin depolymerization becomes more complex as the secondary

reactions occur, and the condensation of reactive intermediates leads to the formation of stable C-C bonds. The study of microwave-assisted wood degradation highlighted the strong influence of reaction temperature on vanillin production [123]. High temperatures significantly promoted lignin conversion and enabled high yields of vanillin and vanillic acid. The yields of vanillic acids decreased when the reaction temperature was higher than 200 °C, implying that the oxidation of vanillin was hindered and the condensation became more dominant at high severity. Vanillin yields were hardly affected by a longer reaction time.

Previous studies also investigated the influence of O_2 pressure on the product yields. A higher O_2 pressure enabled lignin depolymerization into aromatic monomers at a lower temperature (120 °C) [139]. Nonaromatic carboxylic acids were formed as the secondary breakdown products from subsequent oxidation of lignin-derived aromatics under severe conditions. High reaction pressures could suppress the formation of oligomers more significantly than monomers [140, 141]. The negative effect of pressure on the monomer yields was ascribed to the solvent-cage effect from the high density of water under high pressures, resulting in stronger intermolecular interactions and limited diffusion of soluble reactants [21, 22]. Therefore, the reaction pathways in subcritical water would change with the increase of water density under high pressures. Hafezisefat et al. [140] investigated the oxidative cracking with O_2 to convert lignin into phenolic monomers by using various solvents to increase the oxygen solubility. They reported that increasing O_2 pressure from 50 psi (0.34 MPa) to 300 psi (2.07 MPa) could improve the yields of vanillin and syringaldehyde from 6.0 wt% to 10.5 wt%. Meanwhile, deep oxidation of aromatic aldehydes was promoted with the formation of corresponding aromatic acids. In addition, enhanced water density at high pressures might

result in higher dissolution capacity to dissolve more organic compounds but with limited diffusion ability [23].

4.3. Catalysts

4.3.1. Homogeneous catalysts

The HTL process of lignin has been widely studied using various homogeneous bases (*e.g.*, NaOH, KOH, and Na_2CO_3), metal salts (*e.g.*, $CuSO_4$, $CuCl_2$, and $MnCl_2$), water-soluble metal complexes, and ionic liquids (ILs) [131, 133, 141-143]. Experimental investigations on the base-catalyzed depolymerization of various lignin-rich feedstock *via* HTL process are listed in **Table 6**. Erdocia et al. [131] performed HTL of lignin in a 4 wt% of NaOH solution and investigated the influence of different organosolv lignin on the oil production. Lignin extracted from acetosolv pulping gave the highest bio-oil yields of 18.5%. In addition to the cleavage of β-O-4 linkage, the dealkylation of side chains occurred along with the formation of phenol, cresols and catechol. Oxidative depolymerization of Kraft lignin was investigated by Abdelaziz et al. [130], in which low-molecular-weight chemicals, mainly consisting of aromatic monomers and carboxylic acids, were produced at high O_2 pressures. Zhu et al. [121] reported efficient delignification of softwood, hardwood, and grass for the selective production of vanillin and cellulose by oxidative biorefining in a 7.5 wt% of NaOH solution. Under the optimal condition, 90% of lignin could be converted into aromatics. Various operating conditions were explored by Roberts et al. [141] to elucidate the detailed mechanisms of base-catalyzed depolymerization. The presence of Na^+ could react with lignin and form cation adducts and then polarize β-O-4 linkages, leading to the heterolytic cleavage of C-O bonds and the release of monomers.

In addition to homogeneous bases for lignin liquefaction, the acid-catalyzed strategy has attracted extensive attention due to simultaneous delignification and conversion of lignocellulosic biomass in this process [144-146]. Dilute aqueous acids such as H_2SO_4, H_3PO_4, and organic acids could promote hydrolysis and delignification of lignocelluloses, resulting in the formation of soluble lignin fragments that were subsequently converted into aromatics [147]. The latest studies reported that small organic acids, such as formic acid and acetic acid, could act as *in situ* hydrogen donors, thus reducing the demand for external hydrogen to upgrade lignin [148, 149]. A novel acidic IL as a homogeneous catalyst was explored by Long et al. [132, 150] for lignocellulosic biomass conversion. The results demonstrated that acidic IL possessed excellent cleavage capability of C-O bonds and particularly promoted the degradation of G- and S-lignin due to the formation of cooperative IL pair with G-/S-type units in the lignin structure.

4.3.2. Heterogeneous catalysts

Heterogeneous catalysts such as metals, metal oxides, and carbon-based materials have been explored in the HTL process for their easy separation and recovery [53, 120, 138]. A wide range of support (*e.g.,* Nb_2O_5, ZrO_2, Al_2O_3, TiO_2, HZSM-5, and activated carbon) were used to prepare Ru-based catalysts and tested for HTL of organosolv birch lignin [134]. The yield of C_7-C_9 hydrocarbons over the Ru/Nb_2O_5 catalyst was 35.5 wt% with a high selectivity of 71 wt% for arenes. The other catalysts showed a decrease in both yields of C_7-C_9 hydrocarbons and selectivity of arenes. Over the Ru/Al_2O_3 catalysts, the yields of C_7-C_9 products decreased to 18.3 wt%. The C_7-C_9 arenes were not detected when using the Ru/C catalyst. This work highlighted the synergy between the Ru and Nb_2O_5 species that enabled simultaneous

607 depolymerization and hydrogenolysis of organosolv lignin *via* the selective cleavage of β-O-4
608 linkages in lignin and $C_{aromatic}$-OH bonds in phenolic monomers. Accordingly, Zhang et al. [80]
609 prepared Ru/Nb_2O_5-MC (micro-mesoporous carbon) catalyst with the enhanced pore structure
610 to further improve its catalytic activity. The hydrophobic MC and hydrophilic Nb_2O_5
611 contributed to the formation and stabilization of Pickering emulsions in the biphasic process,
612 where the selective cleavage of $C_{aromatic}$-OH bonds could occur.

613 A variety of heterogeneous catalysts based on non-precious metals (*e.g.,* Co, Ni, Cu, and Fe)
614 have been widely explored [27, 150, 151]. Different mesoporous zeolites supported metal
615 catalyst (Ni/MCM, Al/MCM-41, and Ni-Al/MCM-41) were explored in the HTL of Kraft
616 lignin [27]. The maximum bio-oil yield of 44.3 wt% was obtained in the presence of Ni-
617 Al/MCM-41 catalyst. The high carbon contents of bio-oils were obtained as 84.2%, 81.4%, and
618 80.3% using water, ethanol, and methanol as solvents, respectively, indicating the promotion
619 of oil deoxygenation over Ni-based catalysts. For the oxidative reaction, Cu-based catalyst
620 exhibited excellent activity in the dehydrogenation of biomass feedstock [152-154]. The
621 coexistence of Cu^+ and Cu^0 provided a high activity and played different roles in O_2-rich and
622 H_2-rich streams. Feng et al. [155] demonstrated the Cu^+-Cu^0 bicomponent CuNPs@ZIF-8
623 catalyst contributed to the high activity for selective hydrogenation of HMF. The aldehyde
624 could be adsorbed by the electron-deficient Cu^+ species while H_2 could be dissociated at Cu^0
625 via hydrogen spillover effect to achieve efficient hydrogenation. The promotional effect of the
626 coexistence of Cu^+ and Cu^0 in the CuO/BCN catalyst was reported in the oxidative conversion
627 of lignin [53]. The strong metal-support interaction contributed to the cleavage of C-O bonds
628 through dehydrogenation reaction. Various solid acid catalysts (*e.g.*, H-USY, H-ZSM-5, H-

BEA, and K10 clay) could assist the cleavage of ether bonds and the removal of functional groups such as hydroxyl, carboxyl, and methoxy groups [65]. Typical basic zeolites, such as NaX, NaP, and KLTL, were explored for improving the lignin depolymerization and the NaX catalyst under the lower reaction temperature gave the best oil yield (51%) at 250 °C for 1 h [129].

4.4. Fundamental mechanisms

Based on the latest studies [156-159], the reaction pathways for HTL of native lignin within β-O-4 structures are illustrated in **Fig. 8**. The conversion of native lignin aimed to cleave C-O bonds in β-O-4 motifs. (1) In general, C_α-OH undergoes hydrogenolysis in β-O-4 linkages. (2) The oxidation C_α-OH to C_α=O through dehydrogenation reaction can lower the dissociation energy of C_β-O bond from 247.9 to 161.1 kJ mol^{-1} but lead to notably higher dissociation energy of C_α-C_β (294.2 kJ mol^{-1}), making it harder to be cleaved [159]. (3) The newly formed C_α ketone undergoes dehydration reaction to generate an enol ether intermediate, and the weakened C_β-O bond can be cleaved by hydrolysis or hydrogenolysis, thus releasing small and degraded fragments.

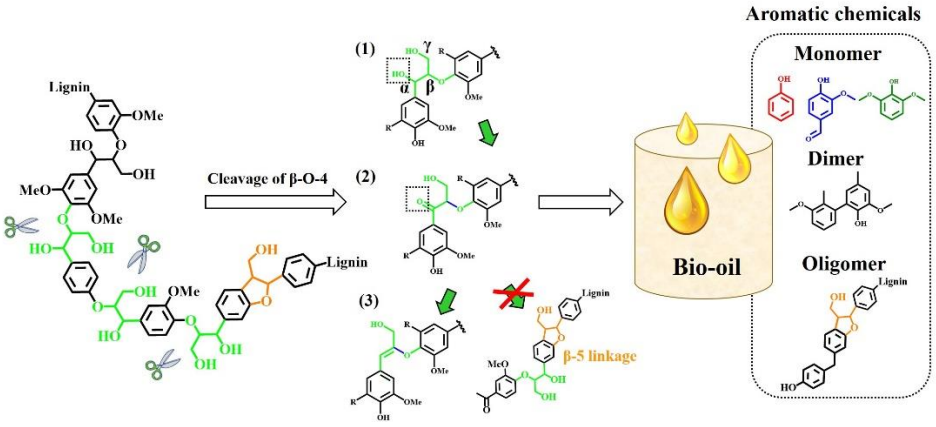

Fig. 8. Pathways for the cleavage of β-O-4 linkages into aromatics.

Native lignin and its extract typically undergo a series of chemical reactions, including hydrolysis, cleavage, and condensation during its biosynthesis and chemical fractionation, resulting in various contents of C-O and C-C bonds in their structures. For example, Kraft lignin structures recovered from the pulp industry was tremendously modified, which significantly limited the monomer yield due to the formation of robust C-C bonds by alkaline pretreatment [160]. For native lignin, several studies investigated the protection strategies by using formic acid or formaldehyde to stabilize the highly reactive intermediates and inhibit the formation of C-C bonds [157, 158]. However, lignin extracts have existed a large amount of C-C bonds in the structures. The selective cleavage of C-C bonds using effective catalysts was studied to provide new insights into lignin valorization with broad applicability. Stein et al. [161] reported that Ru-based complexes exhibited a high selectivity in the cleavage of C-C bonds in 1,3-dilignol model compounds. Dong et al. [162] explored the catalytic cleavage of both interunit C-C and C-O bonds over the $Ru/NbOPO_4$ catalyst. The abundant Brønsted acid sites in the phosphate-based catalyst can protonate the benzene rings in the 5-5 C–C bonds in biphenyl, as a lignin model compound, and thus facilitate the cleavage of C-C bonds.

5. Techno-economic assessment

Recent studies have conducted techno-economic assessment (TEA) for the production of biofuel and bio-products from lignocellulosic biomass [163, 164]. For the HTC process of yard waste, process models were developed for two different HTC plant configurations that included flash separators (case A) and heat exchangers (case B). In terms of costs, the price for case A was $3.3 per GJ more than that in case B, but case A was preferable in terms of energy production [165]. For case B, increasing plant capacity from 9.6 to 960 tons per day

668 significantly decreased the cost of production from $47.2 to $4 per GJ. The TEA results of
669 HTC of food waste mixed with coal revealed that the break-even costs would be $60.26, $62.24,
670 and $69.90 per ton for handling food waste, coal, and mixture of food waste and coal,
671 respectively. The costs associated with raw feedstock collection and transportation were crucial
672 factors that significantly affected the corresponding break-even costs [166]. Mahmood et al.
673 [167] identified the key factors affecting profitability of hydrochar production from food waste
674 (2000 tons per day) based on the TEA results. The sensitivity analysis revealed that both bio-
675 oil yield and cost of enzyme for pretreatment had a significant impact on the selling price of
676 hydrochar, and the minimum selling price of products from non-enzyme pretreated ($30 per
677 ton) is less than half of the market price ($85.68 per ton). The results from TEA of HTC of
678 green waste showed that the hydrochar product could economically compete with fossil-
679 derived biofuel in an optimal context [168]. Besides, the potential for reducing GHG emissions
680 was evident compared with the processing of fossil sources [4]. Nevertheless, there is still a
681 large potential for cost saving by reducing the costs related to the transformation and full
682 utilization of selected biomass feedstock and its residue and byproducts.

683 For the HTL process of lignocellulosic biomass, Liao et al. [16] designed a process model
684 to perform a TEA study for converting 1000 kg of birch wood into 653 kg of carbohydrate pulp,
685 64 kg of lignin oligomers, 42 kg of phenol, and 20 kg of propylene. The cost of feedstock (birch
686 wood, €158 per ton) showed the highest contribution to the manufacturing costs, whereas the
687 cost of recyclable catalysts could be negligible. Furthermore, shorter reaction time and higher
688 substrate loading ratio were considered to be essential factors for improving the profitability of
689 the process, which required the design of a more efficient HTL reactor. Vanillin production

690 from Kraft lignin was the only established HTL process to valorize the lignin waste from paper
691 pulp and produce valuable chemicals [169]. In terms of the economic aspect, the optimal
692 process conditions were the concentration of 30 g/L of lignin feedstock with low operating
693 temperature at 130 °C and oxygen partial pressure of 0.5 MPa, then the payback period for the
694 investment would be 6.2 years. Additional TEA of the HTL of oil from lignin for the BTEX
695 (benzene, toluene, ethylbenzene, and xylenes) production of 65-70 million liters per year was
696 explored [170]. The results showed that the minimum selling price of BTEX was between $1.65
697 and $2.00 per liter. Further research efforts are required for reducing the oxygen content of bio-
698 oil through HDO reaction and decreasing the HTL operating costs in order to render biofuel
699 products more economically competitive with fossil-based fuels in the market.

700 **6. Challenges and perspectives**

701 The hydrothermal processing of lignocellulosic biomass into fuels and value-added products
702 has received renewed emphasis thanks to recent advances and better understanding of the
703 complex characteristics of feedstock variability, reaction mechanisms and pathways, and
704 properties of target products and byproducts. Although considerable efforts have been made in
705 fundamental research and technology development at a laboratory scale, inherent challenges
706 associated with biomass heterogeneity still impede its large-scale implementation. HTC
707 process has been industrialized for selected biomass, but HTL process is yet to be
708 commercialized due to the technological challenges (*e.g.*, high pressure and harsh chemical
709 environment). The major challenges and future perspectives are discussed as follows:

710 **6.1. Challenges**

711 (1) Various types of biomass contain a wide diversity in compositions and chemical

712 structures of cellulose, hemicellulose, and lignin, as described in Section 2. The interactions
713 among these components and process severities differ in the hydrothermal process, resulting in
714 less-efficient conversion and simultaneous production of mixed products. Subsequent efforts
715 required for separation and purification of mixed products would be crucial for achieving cost-
716 effective and sustainable biorefinery towards industrial-scale implementation.

717 (2) Selection of lignocellulose biomass is a crucial factor associated with both chemical and
718 physical challenges in HTL and HTC processes. The impact of chemical aspects, including
719 compositions, structures, and properties of biomass feedstock, and technological parameters
720 such as reaction temperature, ramping and holding time, and heat and mass transfer rate, etc.,
721 have to be extensively studied for a holistic understanding. Some less-investigated physical
722 parameters of biomass feedstock (particle size, mass density, mechanical strength. etc.) and
723 economic issues (reactor design, liquid-to-solid ratio, mixing regime, catalyst stability/recovery,
724 product separation/purification, etc.) play crucial roles in the scale-up of the hydrothermal
725 process. They are currently less explored and the information gaps between the laboratory and
726 industry scales should be addressed.

727 (3) Lignin-derived bio-oil typically contains abundant aromatic monomers associated with
728 the cleavage of β-O-4 linkages. Besides lignin monomers, the remaining fractions include
729 dimers and oligomers derived from C-C bond-linked units or repolymerization of reactive
730 monomeric intermediates. Using GC-MS and LC-MS can only identify and quantify monomers
731 and dimers, whereas the analysis of oligomers in the liquid phase still poses a technical
732 challenge.

733 (4) Hydrochar is a temperature-sensitive material, and its characteristics can be greatly

altered when subjected to high reaction temperatures. Increasing the hydrothermal temperature will form a parallel network of varying reaction pathways of degradation of different components in lignocellulosic biomass. As a result, monosaccharides, polysaccharides, organic acids, and humins are simultaneously formed. The fate and value-added utilization of the polysaccharides and humins have been little explored [170]. Improved analytics are required for obtaining new insights into the reaction mechanisms and pathways for hydrochar customization and broader application.

(5) The transformation of minor species (*e.g.,* N, P, Si, K, Na, Mg, and Ca) is often ignored in the HTC process. These inorganic species can affect (or catalyze) the formation pathways of hydrochar and the distribution of products/by-products. A significant quantity of wastewater (process water) that is rich in organic compounds should be recycled as much as possible and carefully treated before final discharge. For example, a few recent studies have used the process water for anaerobic digestion to produce biogas afterwards.

6.2 Future perspectives

To overcome the technological challenges, future studies should elucidate the crosslinking influences of biomass variability on the production of biofuels/bioproducts and develop product-oriented solutions to address the heterogeneity of lignocellulosic biomass. Advanced characterization of the molecular structures and properties of oligomers can improve the holistic design of downstream valorization strategies. It is imperative to standardize the feedstock provision (*e.g.*, characterization protocols and material specifications) and develop reaction models and process flow designs that consider the biomass compositions and determine the hydrothermal temperature, time, loading, mixing, solvent, pressure, and catalyst

required to accomplish the selective conversion. Rational selection of various types of lignocellulosic biomass should be based on our deep understanding of the properties of raw feedstock and targeted biofuels/bioproducts.

Homogeneous and heterogeneous catalysis is of paramount significance for high-efficiency energy production and chemical transformation. Their applicability and limitations in the hydrothermal process are discussed in Sections 3&4 and summarized in **Table 7**. Homogeneous catalysis has been extensively investigated. The main drawback is that mineral acids can cause equipment corrosion, catalyst wastage, wastewater treatment, and environmental impacts. Heterogeneous reactions depend on the properties of biomass feedstock, operating temperature, and atmosphere of the reaction system, etc. Understanding and tailoring the chemical states of the solid catalysts and conversion pathways of substrates with the assistance of *in situ* characterization and advanced material synthesis can put us in a better position to design more energy-efficient catalytic systems. New development in catalyst design (*e.g.*, highly selective and recyclable catalysts) and heterogeneous systems can foster the innovation and broad application of sustainable engineering solutions. Overall, cost-effective and eco-friendly engineering designs of catalytic hydrothermal process require our concerted efforts in the future studies on fundamental research extending the frontiers of knowledge.

Table 7. Applicability and limitations of homogeneous and heterogeneous catalysis for sustainable conversion of lignocellulosic biomass.

Reaction	**Key Factors**	**Applicability**	**Limitations**
Homogeneous catalysis	Active species, Solvent system,	High activity, Solvent effect,	Equipment corrosion, Difficult separation,

	Temperature, Reactor design	Uniform dispersion, Various biomass feedstock	Poor reusability, Low selectivity
Heterogeneous catalysis	Biomass feedstock, Particle size, Temperature, Atmosphere	Easy separation, Well-defined structure, Multiple active sites, High selectivity	Low hydrothermal stability, Limited contact with feedstock, Low active atom utilization

The keys to the implementation of hydrothermal technologies on a larger scale are related to economics, performance, and environmental footprints. Economics is critical for biofuel as it has already been proven to exhibit similar performance and greater environmental friendliness compared with petroleum-derived counterparts. Continued development of fundamental and translational research as well as further establishment of worldwide bio-based economy will be vital for the scale-up hydrothermal processes. All of the above rely on our effective and interdisciplinary collaboration in the future.

7. Conclusions

Hydrothermal treatment of biomass has been extensively studied as a biorefinery technology for producing solid hydrochar and liquid bio-oil with high chemical functionality. In this critical review, we articulate the key factors (*e.g.,* feedstock variability, reaction temperature, time, and catalyst) that determine the nature and properties of solid and liquid biofuel in the HTC and HTL processes. In particular, we critically review the influences of feedstock compositions and chemical structures on the selective production of value-added chemicals and multifunctional hydrochar. Temperature is a crucial parameter to determine the degree of carbonization and liquefaction. Catalysis plays a key role in governing the physicochemical properties of hydrochar, improving the product yields, and facilitating the selective production

of aromatics. The hydrochar with desirable functionalization can enable broad applications in catalysis, energy storage, and environmental fields. A wide range of aromatics from HTL of lignin-rich feedstock with homogeneous or heterogeneous catalysts can closely resemble petroleum-derived fuels. The state-of-the-art developments, current challenges, and future perspectives of hydrothermal processes presented in this review will advance our fundamental knowledge of sustainable chemistry for maximizing the carbon-efficient valorization of biomass resources towards bio-based circular economy.

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References

[1] Zimmerman JB, Anastas PT, Erythropel HC, Leitner W. Designing for a green chemistry future. Science 2020;367:397-400.

[2] Mirmohamadsadeghi S, Karimi K, Azarbaijani R, Parsa Yeganeh L, Angelidaki I, Nizami A-S, Bhat R, Dashora K, Vijay VK, Aghbashlo M, Gupta VK, Tabatabaei M. Pretreatment of lignocelluloses for enhanced biogas production: A review on influencing mechanisms and the importance of microbial diversity. Renew Sustain Energy Rev 2021;135:110173.

[3] Petridis L, Smith JC. Molecular-level driving forces in lignocellulosic biomass deconstruction for bioenergy. Nature Rev Chem 2018;2:382-389.

[4] Yang Y, Tilman, D. Soil and root carbon storage is key to climate benefits of bioenergy crops. Biofuel Res J 2020;7:1143-1148.

[5] Yu, IKM, Chen H, Abeln F, Auta H, Fan J, Budarin VL, Clark JH, Parsons S, Chuck CJ, Zhang S. Chemicals from lignocellulosic biomass: A critical comparison between biochemical, microwave and thermochemical conversion methods. Crit Rev Environ Sci Technol 2020;51:1479.

[6] Usmani Z, Sharma M, Karpichev Y, Pandey A, Chander Kuhad R, Bhat R, Punia R, Aghbashlo M, Tabatabaei M, Gupta VK. Advancement in valorization technologies to improve utilization of bio-based waste in bioeconomy context. Renew Sustain Energy Rev 2020;131:109965.

[7] Liu W, You, W Sun W, Yang W, Korde A, Gong Y, Deng Y, Ambient-pressure and low-temperature upgrading of lignin bio-oil to hydrocarbons using a hydrogen buffer catalytic system. Nature Energy 2020;5:759-767.

[8] Zhang XG, Wilson K, Lee AF, Heterogeneously Catalyzed Hydrothermal Processing of C_5-C_6 Sugars. Chem Rev 2016;116:12328-12368.

[9] Chen SS, Maneerung T, Tsang DCW, Ok YS, Wang C-H, Valorization of biomass to hydroxymethylfurfural, levulinic acid, and fatty acid methyl ester by heterogeneous catalysts. Chem Eng J 2017;328:246-273.

[10] Yu IKM, Tsang DCW, Yip ACK, Hunt AJ, Sherwood J, Shang J, Song H, Ok YS, Poon CS. Propylene carbonate and γ-valerolactone as green solvents enhance Sn(iv)-catalysed hydroxymethylfurfural (HMF) production from bread waste. Green Chem 2018;20:2064.

[11] Chen SS, Cao Y, Tsang DCW, Tessonnier J-P, Shang J, Hou D, Shen Z, Zhang S, Ok YS, Wu KCW. Effective Dispersion of MgO Nanostructure on Biochar Support as a Basic Catalyst for Glucose Isomerization. ACS Sustainable Chem Eng 2020, 8, (18), 6990-7001.

[12] Yu IKM, Xiong X, Tsang DCW, Wang L, Hunt AJ, Song H, Shang J, Ok YS, Poon CS. Aluminium-biochar composites as sustainable heterogeneous catalysts for glucose isomerization in a biorefinery. Green Chem 2019;21:1267-1281.

[13] Hu J, Zhang Q, Lee DJ. Kraft lignin biorefinery: A perspective. Bioresour Technol 2018;247:1181-1183.

[14] Abu-Omar MM, Barta K, Beckham GT, Luterbacher JS, Ralph J, Rinaldi R, Román-Leshkov Y, Samec JSM, Sels BF, Wang F, Guidelines for performing lignin-first biorefining. Energy Environ Sci 2021;14:262-292.

[15] Wu X, Fan X, Xie S, Lin J, Cheng J, Zhang Q, Chen L, Wang Y. Solar energy-driven lignin-first approach to full utilization of lignocellulosic biomass under mild conditions. Nature Catal 2018;1:772-780.

[16] Liao YH; Koelewijn SF, Bossche GVD, Aelst JV, Bosch SVD, Renders T, Navare T, Nicolaï T, Aelst VK, Maarten M, Matsushima H, Thevelein JM, Acker KV, Lagrain B, Verboekend D, Sels BF. A sustainable wood biorefinery for low–carbon footprint chemicals production. Science 2020;367:1385-1390.

[17] Liu B, Rajagopal D, Life-cycle energy and climate benefits of energy recovery from wastes and biomass residues in the United States. Nature Energy 2019;4:700-708.

[18] Linger JG, Vardon DR, Guarnieri MT, Karp EM, Hunsinger GB, Franden MA, Johnson CW, Chupka G, Strathmann TJ, Pienkos PT, Beckham GT. Lignin valorization through integrated biological funneling and chemical catalysis. Proc Natl Acad Sci 2014;111:12013.

[19] Martinez CLM, Sermyagina E, Saari J, Jesus MSD, Vakkilainen EK. Hydrothermal carbonization of lignocellulosic agro-forest based biomass residues. Biomass Bioenergy 2021;147:106004.

[20] 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. Renew Sustain Energy Rev 2020;123:109761.

[21] Yang C, Wang S, Yang J, Xu D, Li Y, Li J, Zhang Y, Hydrothermal liquefaction and gasification of biomass and model compounds: a review. Green Chem 2020;22:8210-8232.

[22] Zhao Z, Bababrik R, Xue W, Li Y, Briggs NM, Nguyen D-T, Nguyen U, Crossley SP, Wang S, Wang B, Resasco DE. Solvent-mediated charge separation drives alternative hydrogenation path of furanics in liquid water. Nat Catal 2019;2:431-436.

[23] Gu X, Martinez-Fernandez JS, Pang N, Fu X, Chen S, Recent development of hydrothermal liquefaction for algal biorefinery. Renew Sustain Energy Rev 2020;121:109707.

[24] Tekin K, Karagöz S, Bektaş S. A review of hydrothermal biomass processing. Renew Sustain Energy Rev 2014;40:673-687.

[25] Zhang Y, Jiang Q, Xie W, Wang Y, Kang J, Effects of temperature, time and acidity of hydrothermal carbonization on the hydrochar properties and nitrogen recovery from corn stover. Biomass and Bioenergy 2019;122:175-182.

[26] Śliz M, Wilk M. A comprehensive investigation of hydrothermal carbonization Energy potential of hydrochar derived from Virginia mallow. Renew Energ 2020;156:942-950.

[27] Feng L, Li X, Wang Z, Liu B. Catalytic hydrothermal liquefaction of lignin for production of aromatic hydrocarbon over metal supported mesoporous catalyst. Bioresour Technol 2021;323:124569.

[28] Watson J, Wang T, Si B, Chen W-T, Aierzhati A, Zhang Y, Valorization of hydrothermal liquefaction aqueous phase: pathways towards commercial viability. Prog Energy Combust Sci 2020;77:100819.

[29] Sikarwar VS, Zhao M, Clough P, Yao J, Zhong X, Memon MZ, Shah N, Anthony EJ, Fennell PS, An overview of advances in biomass gasification. Energy Environ Sci 2016;9: 2939-2977.

[30] Roy P, Dutta A, Gallant J. Evaluation of the life cycle of hydrothermally carbonized biomass for energy and horticulture application. Renew Sustain Energy Rev Reviews 2020;132:110046.

[31] Nicolae SA, Au H, Modugno P, Luo H, Szego AE, Qiao M, Li L, Yin W, Heeres HJ, Berge N, Titirici MM. Recent advances in hydrothermal carbonisation: from tailored carbon materials and biochemicals to applications and bioenergy. Green Chem 2020;22:4747-4800.

[32] Galadima A, Muraza O. Hydrothermal liquefaction of algae and bio-oil upgrading into liquid fuels: Role of heterogeneous catalysts, Renew Sustain Energy Rev 2018;81: 1037-1048.

[33] Meng Q, Yan J, Wu R, Liu H, Sun Y, Wu N, Xiang J, Zheng L, Zhang J, Han B, Sustainable production of benzene from lignin. Nat Commun 2021;12:4534.

[34] Yan J, Oyedeji O, Leal JH, Donohoe BS, Semelsberger TA, Li C, Hoover AN, Webb E, Bose EA, Zeng Y, Williams L, Schaller KD, Sun N. Ray AE, Tanjore D. Characterizing Variability in Lignocellulosic Biomass: A Review. ACS Sustainable Chem Eng 2020;8:8059.

[35] Kunkes EL, Simonetti DA, West RM, Serrano-Ruiz JC, Gartner CA, Dumesic JA. Catalytic Conversion of Biomass to Monofunctional Hydrocarbons and Targeted Liquid-Fuel Classes. Science 2008;322:417.

[36] Zhao X, Zhou H, Sikarwar VS, Zhao M, Park AHA, Fennell PS, Shen L, Fan LS. Biomass-based chemical looping technologies: the good, the bad and the future. Energy Environ Sci 2017;10:1885-1910.

[37] Ren S, Usman M, Tsang DCW, O-Thong S, Angelidaki I, Zhu X, Zhang S, Luo G. Hydrochar-Facilitated Anaerobic Digestion: Evidence for Direct Interspecies Electron Transfer Mediated through Surface Oxygen-Containing Functional Groups. Environ Sci Technol 2020;54:5755-5766.

[38] Zhu X, Liu Y, Luo G, Qian F, Zhang S, Chen J. Facile fabrication of magnetic carbon composites from hydrochar via simultaneous activation and magnetization for triclosan adsorption. Environ Sci Technol 2014;48:5840-8.

[39] Xiao K, Liu H, Li Y, Yang G, Yao H. Excellent performance of porous carbon from urea-assisted hydrochar of orange peel for toluene and iodine adsorption. Chem Eng J 2020;382:122997.

[40] Matsagar BM, Wang ZY, Sakdaronnarong C, Chen SS, Tsang DCW, Wu KCW. Effect of Solvent, Role of Formic Acid and Rh/C Catalyst for the Efficient Liquefaction of Lignin. ChemCatChem 2019;11:4604-4616.

[41] Changi SM, Faeth JL, Mo N, Savage PE. Hydrothermal Reactions of Biomolecules Relevant for Microalgae Liquefaction. Ind Eng Chem Res 2015;54:1733-11758.

[42] Anderson EM, Stone ML, Katahira R, Reed M, Muchero W, Ramirez KJ, Beckham GT, Roman-Leshkov Y. Differences in S/G ratio in natural poplar variants do not predict

catalytic depolymerization monomer yields. Nat Commun 2019;10:2033.

[43] Ralph J, Lapierre C, Boerjan W. Lignin structure and its engineering. Curr Opin Biotechnol 2019;56:240-249.

[44] Yoo CG, Dumitrache A, Muchero W, Natzke J, Akinosho H, Li M, Sykes RW, Brown SD, Davison B, Tuskan GA, Pu Y, Ragauskas AJ. Significance of Lignin S/G Ratio in Biomass Recalcitrance of Populus trichocarpa Variants for Bioethanol Production. ACS Sustain Chem Eng 2017;6:2162-2168.

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

[46] Chen WH, Lin BJ, Lin YY, Chu,YS, Ubando AT, Show PL, Ong HC, Chang JS, Ho SH, Culaba AB, Pétrissans A, Pétrissans M. Progress in biomass torrefaction: Principles, applications and challenges. Prog Energy Combust Sci 2021;82:100887.

[47] Tursi, A. A review on biomass: importance, chemistry, classification, and conversion. Biofuel Res J 2019;6:962.

[48] Zheng M, Pang J, Sun R, Wang A, Zhang T. Selectivity Control for Cellulose to Diols: Dancing on Eggs. ACS Catal 2017;7:1939-1954.

[49] Fan J, Shuttleworth PS, Gronnow M, Breeden SW, Clark JH, Macquarrie DJ, Budarin VL. Influence of Density on Microwave Pyrolysis of Cellulose. ACS Sustain Chem Eng 2018; 6:2916-2920.

[50] Zhou X, Li W, Mabon R, Broadbelt LJ. A mechanistic model of fast pyrolysis of hemicellulose. Energy Environ Sci 2018;1:1240-1260.

[51] Chen Z, Reznicek WD, Wan C. Aqueous Choline Chloride: A Novel Solvent for Switchgrass Fractionation and Subsequent Hemicellulose Conversion into Furfural. ACS Sustain Chem Eng 2018;6:6910-6919.

[52] Liu X, Bouxin FP, Fan J, Budarin VL, Hu C, Clark JH. Microwave-assisted catalytic depolymerization of lignin from birch sawdust to produce phenolic monomers utilizing a hydrogen-free strategy. J Hazard Mater 2021;402:123490.

[53] Cao Y, Chen SS, Tsang DCW, Clark JH, Budarin VL, Hu C, Wu KCW, Zhang S. Microwave-assisted depolymerization of various types of waste lignins over two-

963 dimensional CuO/BCN catalysts. Green Chem 2020;22:725-736.
964 [54] Wong SS, Shu R, Zhang J, Liu H, Yan N. Downstream processing of lignin derived
965 feedstock into end products. Chem Soc Rev 2020;49:5510-5560.
966 [55] Guo H, Zhang B, Qi Z, Li C, Ji J, Dai T, Wang A, Zhang T. Valorization of Lignin to
967 Simple Phenolic Compounds over Tungsten Carbide: Impact of Lignin Structure.
968 ChemSusChem 2017;10:523-532.
969 [56] Ragauskas AJ, Beckham GT, Biddy MJ, Chandra R, Chen F, Davis MF, Davison BH,
970 Dixon RA, Gilna P, Keller M, Langan P, Naskar AK, Saddler JN, Tschaplinski TJ,
971 Tuskan GA, Wyman CE. Lignin valorization: improving lignin processing in the
972 biorefinery. Science 2014;344:1246843.
973 [57] Bueren JBD, Héroguel F, Wegmann C, Dick GR, Luterbacher JS. Aldehyde-Assisted
974 Fractionation Enhances Lignin Valorization in Endocarp Waste Biomass. ACS Sustain
975 Chem Eng 2020;8:16737-16745.
976 [58] Cuevas M, Martinez Cartas ML, Sanchez S. Effect of Short-Time Hydrothermal
977 Carbonization on the Properties of Hydrochars Prepared from Olive-Fruit Endocarps.
978 Energy Fuels 2018;33:313-322.
979 [59] Poerschmann J, Weiner B, Koehler R, Kopinke FD. Hydrothermal Carbonization of
980 Glucose, Fructose, and Xylose-Identification of Organic Products with Medium
981 Molecular Masses. ACS Sustain Chem Eng 2017;5:6420-6428.
982 [60] Lu X, Ma X, Chen X. Co-hydrothermal carbonization of sewage sludge and
983 lignocellulosic biomass: Fuel properties and heavy metal transformation behaviour of
984 hydrochars. Energy 2021;221:119896.
985 [61] Li L, Wang Y, Xu J, Flora JRV, Hoque S, Berge ND. Quantifying the sensitivity of
986 feedstock properties and process conditions on hydrochar yield. Bioresource
987 Technology 2018;262:284-293.
988 [62] Wang X, Yun S, Fang W, Zhang C, Liang X, Lei Z, Liu Z. Layer-Stacking Activated
989 Carbon Derived from Sunflower Stalk as Electrode Materials for High-Performance
990 Supercapacitors. ACS Sustain Chem Eng 2018;6:11397-11407.
991 [63] Zhang X, Li Y, Wang M, Han L, Liu X. Effects of Hydrothermal Carbonization

Conditions on the Combustion and Kinetics of Wheat Straw Hydrochar Pellets and Efficiency Improvement Analyses. Energy Fuels 2019;34:587-598.

[64] Wikberg H, Ohra-aho T, Pileidis F, Titirici MM, Structural and Morphological Changes in Kraft Lignin during Hydrothermal Carbonization. ACS Sustain Chem Eng 2015;3:2737-2745.

[65] Deepa AK, Dhepe PL, Lignin Depolymerization into Aromatic Monomers over Solid Acid Catalysts. ACS Catal 2014;5:365-379.

[66] Li H, Song G. Ru-Catalyzed Hydrogenolysis of Lignin: Base-Dependent Tunability of Monomeric Phenols and Mechanistic Study. ACS Catal 2019;9:4054-4064.

[67] Zhang JW, Lu GP, Cai C. Self-hydrogen transfer hydrogenolysis of β-O-4 linkages in lignin catalyzed by MIL-100(Fe) supported Pd-Ni BMNPs. Green Chem 2017;19:4538-4543.

[68] Cao Y, Chen SS, Zhang S, Ok YS, Matsagar BM, Wu KC, Tsang DCW. Advances in lignin valorization towards bio-based chemicals and fuels: Lignin biorefinery. Bioresour Technol 2019;291:121878.

[69] Cao Y, Zhang C, Tsang DCW, Fan J, Clark JH, Zhang S, Hydrothermal Liquefaction of Lignin to Aromatic Chemicals: Impact of Lignin Structure. Ind Eng Chem Res 2020;59:16957-16969.

[70] Correa CR, Stollovsky M, Hehr T, Rauscher Y, Rolli B, Kruse A. Influence of the Carbonization Process on Activated Carbon Properties from Lignin and Lignin-Rich Biomasses. ACS Sustain Chem Eng 2017;5:8222-8233.

[71] Liu C, Li N, Peng L, Zhong W, Mao L, Yin D. Hydrothermal Carbonization of Renewable Natural Plants as Superior Metal-Free Catalysts for Aerobic Oxidative Coupling of Amines to Imines. ACS Sustain Chem Eng 2020; 8:11404-11412.

[72] Mai D, Wen R, Cao W, Yuan B, Liu Y, Liu Q, Qian G. Effect of Heavy Metal (Zn) on Redox Property of Hydrochar Produced from Lignin, Cellulose, and d-Xylose. ACS Sustainable Chem Eng 2017;5:3499-3508.

[73] Nzediegwu C, Naeth MA, Chang SX. Carbonization temperature and feedstock type interactively affect chemical, fuel, and surface properties of hydrochars. Bioresour

Technol 2021;330:124976.

[74] Zhang D, Wang F, Shen X, Yi W, Li Z, Li Y, Tian C. Comparison study on fuel properties of hydrochars produced from corn stalk and corn stalk digestate. Energy 2018;165:527-536.

[75] Gu D, Ma R, Zhou Y, Wang F, Yan K, Liu Q, Wang J. Synthesis of Nitrogen-Doped Porous Carbon Spheres with Improved Porosity toward the Electrocatalytic Oxygen Reduction. ACS Sustain Chem Eng 2017;5:11105-11116.

[76] Wang H, Xiong F, Tan Y, Yang J, Qing Y, Chu F, Wu Y. Preparation and Formation Mechanism of Covalent-Noncovalent Forces Stabilizing Lignin Nanospheres and Their Application in Superhydrophobic and Carbon Materials. ACS Sustain Chem Eng 2021;9:3811-3820.

[77] Sangchoom W, Mokaya R. Valorization of Lignin Waste: Carbons from Hydrothermal Carbonization of Renewable Lignin as Superior Sorbents for CO_2 and Hydrogen Storage. ACS Sustain Chem Eng 2015;3:1658-1667.

[78] Simsir H, Eltugral N, Karagoz S. Effects of Acidic and Alkaline Metal Triflates on the Hydrothermal Carbonization of Glucose and Cellulose. Energy Fuels 2019;33:7473-7479.

[79] Wang J, Luo X, Young C, Kim J, Kaneti YV, You J, Kang YM, Yamauchi Y, Wu KCW. A Glucose-Assisted Hydrothermal Reaction for Directly Transforming Metal-Organic Frameworks into Hollow Carbonaceous Materials. Chem Mater 2018;30:4401-4408.

[80] Zhang C, Jia C, Cao Y, Yao Y, Xie S, Zhang S, Lin H. Water-assisted selective hydrodeoxygenation of phenol to benzene over the Ru composite catalyst in the biphasic process. Green Chem 2019;21:1668-1679.

[81] Zhang L, Wang Q, Wang B, Yang G, Lucia LA, Chen J. Hydrothermal Carbonization of Corncob Residues for Hydrochar Production. Energy Fuels 2015;29:872-876.

[82] Keiller BG, Muhlack R, Burton RA, Eyk PJV. Biochemical Compositional Analysis and Kinetic Modeling of Hydrothermal Carbonization of Australian Saltbush. Energy Fuels 2019;33:12469-12479.

[83] Saqib NU, Baroutian S, Sarmah AK. Physicochemical, structural and combustion

characterization of food waste hydrochar obtained by hydrothermal carbonization. Bioresour Technol 2018;266:357.

[84] Gupta D, Mahajani SM, Garg A. Investigation on hydrochar and macromolecules recovery opportunities from food waste after hydrothermal carbonization. Sci Total Environ 2020;749:142294.

[85] Duman G, Balmuk G, Cay H, Kantarli IC, Yanik J. Comparative Evaluation of Torrefaction and Hydrothermal Carbonization: Effect on Fuel Properties and Combustion Behavior of Agricultural Wastes. Energy Fuels 2020;34:11175-11185.

[86] Johnson S, Faradilla RHF, Venditti RA, Lucia L, Hakovirta M. Hydrothermal Carbonization of Nanofibrillated Cellulose: A Pioneering Model Study Demonstrating the Effect of Size on Final Material Qualities. ACS Sustain Chem Eng 2020;8:1823-1830.

[87] Nunes RS, Tudino TC, Vieira LM, Mandelli D, Carvalho WA. Rational production of highly acidic sulfonated carbons from kraft lignins employing a fractionation process combined with acid-assisted hydrothermal carbonization. Bioresour Technol 2020;303:122882.

[88] Xu F, Chen Y, Tang M, Wang H, Deng J, Wang Y. Acid Induced Self-Assembly Strategy to Synthesize Ordered Mesoporous Carbons from Biomass. ACS Sustain Chem Eng 2016;4:4473-4479.

[89] Fang G, Liu C, Gao J, Dionysiou DD, Zhou D. Manipulation of persistent free radicals in biochar to activate persulfate for contaminant degradation. Environ Sci Technol 2015;49:5645-53.

[90] He X, Zhang T, Xue Q, Zhou Y, Wang H, Bolan NS, Jiang R, Tsang DCW. Enhanced adsorption of Cu(II) and Zn(II) from aqueous solution by polyethyleneimine modified straw hydrochar. Sci Total Environ 2021;778: 146116.

[91] Zhu X, Liu Y, Qian F, Zhou C, Zhang S, Chen J. Role of Hydrochar Properties on the Porosity of Hydrochar-based Porous Carbon for Their Sustainable Application. ACS Sustain Chem Eng 2015;3:833-840.

[92] Li F, Zimmerman AR, Hu X, Yu Z, Huang J, Gao B. One-pot synthesis and

characterization of engineered hydrochar by hydrothermal carbonization of biomass with $ZnCl_2$. Chemosphere 2020;254:126866.

[93] Xu Z, Zhang X, Li K, Lin H, Qian X, Sheng K. Green Synthesis of Fe-Decorated Carbon Sphere/Nanosheet Derived from Bamboo for High-Performance Supercapacitor Application. Energy Fuels 2020;35:827-838.

[94] Wang L, Skjevrak G, Hustad JE, Skreiberg Ø. Investigation of Biomass Ash Sintering Characteristics and the Effect of Additives. Energy Fuels 2013;28:208.

[95] Liu H, Chen Y, Yang H, Gentili FG, Söderlind U, Wang X, Zhang W, Chen H. Hydrothermal carbonization of natural microalgae containing a high ash content. Fuel 2019;249:441.

[96] Jung D, Zimmermann M, Kruse A. Hydrothermal Carbonization of Fructose: Growth Mechanism and Kinetic Model. ACS Sustain Chem Eng 2018;6:13877-13887.

[97] Shi N, Liu Q, He X, Wang G, Chen N, Peng J, Ma L. Molecular Structure and Formation Mechanism of Hydrochar from Hydrothermal Carbonization of Carbohydrates. Energy Fuels 2019;33:9904-9915.

[98] He Q, Yu Y, Wang J, Suo X, Liu Y. Kinetic Study of the Hydrothermal Carbonization Reaction of Glucose and Its Product Structures. Ind Eng Chem Res 2021;60:4552-4561.

[99] Zhang J, An Y, Borrion A, He W, Wang N, Chen Y, Li G. Process characteristics for microwave assisted hydrothermal carbonization of cellulose. Bioresour Technol 2018;259: 91-98.

[100] Zhu X, Liu Y, Qian F, Lei Z, Zhang Z, Zhang S, Chen J, Ren ZJ. Demethanation Trend of Hydrochar Induced by Organic Solvent Washing and Its Influence on Hydrochar Activation. Environ Sci Technol 2017;51:10756.

[101] Hao S, Zhu X, Liu Y, Qian F, Fang Z, Shi Q, Zhang S, Chen J, Ren ZJ. Production Temperature Effects on the Structure of Hydrochar-Derived Dissolved Organic Matter and Associated Toxicity. Environ Sci Technol 2018;52:7486.

[102] Zhang Z, Jia B, Liu L, Zhao Y, Wu H, Qin M, Han K, Wang WA, Xi K, Zhang L, Qi G, Qu X, Kumar RV. Hollow Multihole Carbon Bowls: A Stress-Release Structure Design for High-Stability and High-Volumetric-Capacity Potassium-Ion Batteries. ACS Nano

2019;13:11363-11371.

[103] Peng L, Liang Y, Huang J, Xing L, Zheng M. Mixed-Biomass Wastes Derived Hierarchically Porous Carbons for High-Performance Electrochemical Energy Storage. ACS Sustainable Chem. Eng. 2019;7:10393-10402.

[104] Jing S, Zhao Y, Sun R-C, Zhong L, Peng X. Facile and High-Yield Synthesis of Carbon Quantum Dots from Biomass-Derived Carbons at Mild Condition. ACS Sustain Chem Eng 2019;7:7833-7843.

[105] Qi W, He C, Wang Q, Liu S, Yu Q, Wang W, Leksawasdi N, Wang C, Yuan Z. Carbon-Based Solid Acid Pretreatment in Corncob Saccharification: Specific Xylose Production and Efficient Enzymatic Hydrolysis. ACS Sustain Chem Eng 2018;6:3640-3648.

[106] Lahive CW, Deuss PJ, Lancefield CS, Sun Z, Cordes DB, Young CM, Tran F, Slawin AM, Vries JGD, Kamer PC, Westwood NJ, Barta K. Advanced Model Compounds for Understanding Acid-Catalyzed Lignin Depolymerization: Identification of Renewable Aromatics and a Lignin-Derived Solvent. J Am Chem Soc 2016;138:8900-8911.

[107] Qi S, Wang G, Sun H, Wang L, Liu Q, Ma G, Parvez AM, Si C. Using Lignin Monomer As a Novel Capping Agent for Efficient Acid-Catalyzed Depolymerization of High Molecular Weight Lignin to Improve Its Antioxidant Activity. ACS Sustain Chem Eng 2020;8:9104-9114.

[108] Wang S, Gao W, Li H, Xiao LP, Sun RC, Song G. Selective Fragmentation of Biorefinery Corncob Lignin into p-Hydroxycinnamic Esters with a Supported Zinc Molybdate Catalyst. ChemSusChem 2018;11:2114-2123.

[109] Chen W, Zhang G, Li D, Ma S, Wang B, Jiang X. Preparation of Nitrogen-Doped Porous Carbon from Waste Polyurethane Foam by Hydrothermal Carbonization for H_2S Adsorption. Ind Eng Chem Res 2020;59:7447-7456.

[110] Li Y, Meas A, Shan S, Yang R, Gai X, Wang H, Tsend N. Hydrochars from bamboo sawdust through acid assisted and two-stage hydrothermal carbonization for removal of two organics from aqueous solution. Bioresour Technol 2018;251:257-264.

[111] Balou S, Babak SE, Priye A. Synergistic Effect of Nitrogen Doping and Ultra-

Microporosity on the Performance of Biomass and Microalgae-Derived Activated Carbons for CO_2 Capture. ACS Appl Mater Interfaces 2020;12:42711-42722.

[112] Zhang L, You T, Zhou T, Zhou X, Xu F. Interconnected Hierarchical Porous Carbon from Lignin-Derived Byproducts of Bioethanol Production for Ultra-High Performance Supercapacitors. ACS Appl Mater Interfaces 2016;8:13918-13925.

[113] Tu W, Liu Y, Xie Z, Chen M, Ma L, Du G, Zhu M. A novel activation-hydrochar via hydrothermal carbonization and KOH activation of sewage sludge and coconut shell for biomass wastes: Preparation, characterization and adsorption properties. J Colloid Interface Sci 2021;593:390-407.

[114] Zhou N, Zhang C, Cao Y, Zhan J, Fan J, Clark JH, Zhang S. Conversion of xylose into furfural over MC-SnOx and NaCl catalysts in a biphasic system. J. Clean Prod 2021;311:127780.

[115] Liu J, Zhang X, Yang L, Danhassan UA, Zhang S, Yang M, Sheng K, Zhang X. Glucose isomerization catalyzed by swollen cellulose derived aluminum-hydrochar. Sci Total Environ 2021;777:146037.

[116] Sharma HB, Dubey BK. Co-hydrothermal carbonization of food waste with yard waste for solid biofuel production: Hydrochar characterization and its pelletization. Waste Manage 2020;118:521.

[117] Shao Y, Tan H, Shen D, Zhou Y, Jin Z, Zhou D, Lu W, Long Y. Synthesis of improved hydrochar by microwave hydrothermal carbonization of green waste. Fuel 2020;266:117146.

[118] Chen X, Zhang K, Xiao LP, Sun RC, Song G. Total utilization of lignin and carbohydrates in Eucalyptus grandis: an integrated biorefinery strategy towards phenolics, levulinic acid, and furfural. Biotechnol Biofuels 2020;13:2.

[119] Zhang K, Li H, Xiao LP, Wang B, Sun RC, Song G. Sequential utilization of bamboo biomass through reductive catalytic fractionation of lignin. Bioresour Technol 2019;285:121335.

[120] Liu X, Li H, Xiao L-P, Sun R-C, Song G. Chemodivergent hydrogenolysis of eucalyptus lignin with Ni@ZIF-8 catalyst. Green Chem 2019;21:1498-1504.

[121] Zhu Y, Liao Y, Lv W, Liu J, Song X, Chen L, Wang C, Sels BF, Ma L. Complementing Vanillin and Cellulose Production by Oxidation of Lignocellulose with Stirring Control. ACS Sustain Chem Eng 2020;8:2361-2374.

[122] Fache M, Boutevin B, Caillol S. Vanillin Production from Lignin and Its Use as a Renewable Chemical. ACS Sustain Chem Eng 2015;4:35-46.

[123] Qu C, Kaneko M, Kashimura K, Tanaka K, Ozawa S, Watanabe T. Direct Production of Vanillin from Wood Particles by Copper Oxide-Peroxide Reaction Promoted by Electric and Magnetic Fields of Microwaves. ACS Sustain Chem Eng 2017;5:11551-11557.

[124] Hilgers R, Kabel MA, Vincken JP. Reactivity of p-Coumaroyl Groups in Lignin upon Laccase and Laccase/HBT Treatments. ACS Sustain Chem Eng 2020;8:8723-8731.

[125] Erven GV, Wang J, Sun P, Waard PD, Putten JVD, Frissen GE, Gosselink RJA, Zinovyev G, Potthast A, Berkel WJHV, Kabel MA. Structural Motifs of Wheat Straw Lignin Differ in Susceptibility to Degradation by the White-Rot Fungus Ceriporiopsis subvermispora. ACS Sustain Chem Eng 2019;7:20032-20042.

[126] Peng C, Chen Q, Guo H, Hu G, Li C, Wen J, Wang H, Zhang T, Zhao ZK, Sun R, Xie H. Effects of Extraction Methods on Structure and Valorization of Corn Stover Lignin by a Pd/C Catalyst. ChemCatChem 2017;9:1135-1143.

[127] Ralph J, Hatfield RD, Quideau S, Helm RF, Grabber JH, Jung HJG. Pathway of p-Coumaric Acid Incorporation into Maize Lignin As Revealed by NMR. J Am Chem Soc 1994;116:9448-9456.

[128] Timokhin VI, Regner M, Motagamwala AH, Sener C, Karlen SD, Dumesic JA, Ralph J. Production of p-Coumaric Acid from Corn GVL-Lignin. ACS Sustain Chem Eng 2020;8:17427-17438.

[129] Chaudhary R, Dhepe PL. Solid base catalyzed depolymerization of lignin into low molecular weight products. Green Chem 2017;19:778-788.

[130] Abdelaziz OY, Ravi K, Mittermeier F, Meier S, Riisager A, Lidén G, Hulteberg CP. Oxidative Depolymerization of Kraft Lignin for Microbial Conversion. ACS Sustain Chem Eng 2019;7:11640-11652.

[131] Erdocia X, Prado R, Corcuera MÁ, Labidi J. Base catalyzed depolymerization of lignin: Influence of organosolv lignin nature. Biomass Bioenergy 2014;66:379-386.

[132] Long J, Lou W, Wang L, Yin B, Li X. $[C_4H_8SO_3Hmim]HSO_4$ as an efficient catalyst for direct liquefaction of bagasse lignin: Decomposition properties of the inner structural units. Chem Eng Sci 2015;122:24-33.

[133] Phongpreecha T, Hool NC, Stoklosa RJ, Klett AS, Foster CE, Bhalla A, Holmes D, Thies MC, Hodge DB. Predicting lignin depolymerization yields from quantifiable properties using fractionated biorefinery lignins. Green Chem 2017;19:5131-5143.

[134] Shao Y, Xia Q, Dong L, Liu X, Han X, Parker SF, Cheng Y, Daemen LL, Ramirez-Cuesta AJ, Yang S, Wang Y. Selective production of arenes via direct lignin upgrading over a niobium-based catalyst. Nat Commun 2017;8:16104.

[135] Dong C, Meng X, Yeung CS, Tse HY, Ragauskas AJ, Leu SY. Diol pretreatment to fractionate a reactive lignin in lignocellulosic biomass biorefineries. Green Chem 2019;21:2788-2800.

[136] Wang G, Liu X, Yang B, Si C, Parvez AM, Jang J, Ni Y. Using Green γ-Valerolactone/Water Solvent To Decrease Lignin Heterogeneity by Gradient Precipitation. ACS Sustain Chem Eng 2019;7:10112-10120.

[137] Li YJ, Li HY, Cao XF, Sun SN, Sun RC. Understanding the Distribution and Structural Feature of Eucalyptus Lignin Isolated by γ-Valerolactone/Water/Acid System. ACS Sustain Chem Eng 2018;6:12124-12131.

[138] Wu K, Wang W, Guo H, Yang Y, Huang Y, Li W, Li C. Engineering Co Nanoparticles Supported on Defect MoS_2–x for Mild Deoxygenation of Lignin-Derived Phenols to Arenes. ACS Energy Lett 2020;5:1330-1336.

[139] Zhu Y, Liu J, Liao Y, Lv W, Ma L, Wang C. Degradation of Vanillin During Lignin Valorization Under Alkaline Oxidation. Top Curr Chem 2018;376:29.

[140] Hafezisefat P, Lindstrom JK, Brown RC, Qi L. Non-catalytic oxidative depolymerization of lignin in perfluorodecalin to produce phenolic monomers. Green Chem 2020;22:6567-6578.

[141] Roberts VM, Stein V, Reiner T, Lemonidou A, Li X, Lercher JA. Towards quantitative

catalytic lignin depolymerization. Chemistry 2011;17:5939-48.

[142] Renders T, Schutyser W, Van den Bosch S, Koelewijn S-F, Vangeel T, Courtin CM, Sels BF. Influence of Acidic (H_3PO_4) and Alkaline (NaOH) Additives on the Catalytic Reductive Fractionation of Lignocellulose. ACS Catal 2016;6:2055-2066.

[143] Liu Y, Li C, Miao W, Tang W, Xue D, Li C, Zhang B, Xiao J, Wang A, Zhang T, Wang C, Mild Redox-Neutral Depolymerization of Lignin with a Binuclear Rh Complex in Water. ACS Catal 2019;9:4441-4447.

[144] Mellmer MA, Sanpitakseree C, Demir B, Ma K, Elliott WA, Bai P, Johnson RL, Walker TW, Shanks BH, Rioux RM, Neurock M, Dumesic JA. Effects of chloride ions in acid-catalyzed biomass dehydration reactions in polar aprotic solvents. Nat Commun 2019;10:1132.

[145] Mellmer MA, Sener C, Gallo JM, Luterbacher JS, Alonso DM, Dumesic JA. Solvent effects in acid-catalyzed biomass conversion reactions. Angew Chem Int Ed Engl 2014;53:11872-11875.

[146] Xue B, Yang Y, Zhu M, Sun Y, Li X. Lewis acid-catalyzed biphasic 2-methyltetrahydrofuran/H_2O pretreatment of lignocelluloses to enhance cellulose enzymatic hydrolysis and lignin valorization. Bioresour Technol 2018;270:55-61.

[147] Zhao B, Hu Y, Gao J, Zhao G, Ray MB, Xu CC. Recent Advances in Hydroliquefaction of Biomass for Bio-oil Production Using In Situ Hydrogen Donors. Ind Eng Chem Res 2020;59:16987-17007.

[148] Hwang KR, Choi IH, Choi HY, Han JS, Lee KH, Lee JS. Bio fuel production from crude Jatropha oil; addition effect of formic acid as an in-situ hydrogen source. Fuel 2016;174:107-113.

[149] Li Y, Cai Z, Liao M, Long J, Zhao W, Chen Y, Li X. Catalytic depolymerization of organosolv sugarcane bagasse lignin in cooperative ionic liquid pairs. Catal Today 2017;298:168-174.

[150] Zhai Y, Li C, Xu G, Ma Y, Liu X, Zhang Y. Depolymerization of lignin via a non-precious Ni–Fe alloy catalyst supported on activated carbon. Green Chem 2017;19:1895-1903.

[151] Nam DH, Taitt BJ, Choi KS. Copper-Based Catalytic Anodes To Produce 2,5-Furandicarboxylic Acid, a Biomass-Derived Alternative to Terephthalic Acid. ACS Catal 2018;8:1197-1206.

[152] Xiao G, Montgomery JRD, Lancefield CS, Panovic I, Westwood NJ. Copper-Mediated Conversion of Complex Ethers to Esters: Enabling Biopolymer Depolymerisation under Mild Conditions. Chemistry 2020;26:12397-12402.

[153] Mottweiler J, Puche M, Rauber C, Schmidt T, Concepcion P, Corma A, Bolm C. Copper- and Vanadium-Catalyzed Oxidative Cleavage of Lignin using Dioxygen. ChemSusChem 2015;8:2106-13.

[154] Feng Y, Yan G, Wang T, Jia W, Zeng X, Sperry J, Sun Y, Tang X, Lei T, Lin L. Cu^{1}–Cu^{0} bicomponent CuNPs@ZIF-8 for highly selective hydrogenation of biomass derived 5-hydroxymethylfurfural. Green Chem 2019;21:4319-4323.

[155] Li H, Song G. Paving the Way for the Lignin Hydrogenolysis Mechanism by Deuterium-Incorporated β-O-4 Mimics. ACS Catalysis 2020;10:12229-12238.

[156] Rahimi A, Ulbrich A, Coon JJ, Stahl SS. Formic-acid-induced depolymerization of oxidized lignin to aromatics. Nature 2014;515:249-52.

[157] Shuai L, Amiri MT, Questell-Santiago YM, Heroguel F, Li Y, Kim H, Meilan R, Chapple C, Ralph J, Luterbacher JS. Formaldehyde stabilization facilitates lignin monomer production during biomass depolymerization. Science 2016;354:329.

[158] Wang M, Lu J, Zhang X, Li L, Li H, Luo N, Wang F. Two-Step, Catalytic C-C Bond Oxidative Cleavage Process Converts Lignin Models and Extracts to Aromatic Acids. ACS Catal 2016;6:6086-6090.

[159] Shuai L, Saha B. Towards high-yield lignin monomer production. Green Chem 2017;19:3752-3758.

[160] Stein TV, Hartog TD, Buendia J, Stoychev S, Mottweiler J, Bolm C, Klankermayer J, Leitner W. Ruthenium-catalyzed C-C bond cleavage in lignin model substrates. Angew Chem Int Ed Engl 2015;54:5859-63.

[161] Dong L, Lin L, Han X, Si X, Liu X, Guo Y, Lu F, Rudić S, Parker SF, Yang S, Wang Y.k Breaking the Limit of Lignin Monomer Production via Cleavage of Interunit

Carbon-Carbon Linkages. Chem 2019;5:1521-1536.

[162] Scown CD, Baral NR, Yang M, Vora N, Huntington T. Technoeconomic analysis for biofuels and bioproducts. Curr Opin Biotechnol 2021;67:58.

[163] Klein-Marcuschamer D, Simmons BA, Blanch HW. Techno-economic analysis of a lignocellulosic ethanol biorefinery with ionic liquid pre-treatment. Biofuels Bioprod Biorefin 2011;5:562.

[164] Akbari M, Oyedun AO, Kumar A. Comparative energy and techno-economic analyses of two different configurations for hydrothermal carbonization of yard waste. Bioresour Technol Rep 2019;7:100210.

[165] Mazumder S, Saha P, McGaughy K, Saba A, Reza MT. Technoeconomic analysis of co-hydrothermal carbonization of coal waste and food waste. Biomass Conv Biorefin 2020, DOI:10.1007/s13399-020-00817-8 10.1007/s13399-020-00817-8.

[166] Mahmood R, Parshetti GK, Balasubramanian R. Energy, exergy and techno-economic analyses of hydrothermal oxidation of food waste to produce hydro-char and bio-oil. Energy 2016;102:187.

[167] Zeymer M, Meisel K, Clemens A, Klemm M. Technical, Economic, and Environmental Assessment of the Hydrothermal Carbonization of Green Waste. Chem Eng Technol 2017;40:260.

[168] Khwanjaisakun N, Amornraksa S, Simasatitkul L, Charoensuppanimit P, Assabumrungrat S. Techno-economic analysis of vanillin production from Kraft lignin: Feasibility study of lignin valorization. Bioresour Technol 2020;299:122559.

[169] Funkenbusch LT, Mullins ME, Vamling L, Belkhieri T, Srettiwat N, Winjobi O, Shonnard DR, Rogers TN. Technoeconomic assessment of hydrothermal liquefaction oil from lignin with catalytic upgrading for renewable fuel and chemical production. WIREs Energy Environ 2019;8:e319.

[170] Xiong X, Yu IKM, Dutta S, Masek O, Tsang DCW. Valorization of humins from food waste biorefinery for synthesis of biochar-supported Lewis acid catalysts. Sci Total Environ 2021; 775:145851.