

Review

Lignin-First Biorefinery for Converting Lignocellulosic Biomass into Fuels and Chemicals

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Abstract: Driven by the excessive consumption of fossil resources and environmental pollution concerns, a large amount of biorefinery research efforts have been made for converting lignocellulosic biomass into fuels and chemicals. Recently, a strategy termed “lignin-first,” which allows for realizing high-yield and high-selectivity aromatic monomers, is regarded as one of the best prospective strategies. This review summarizes recent research advances in lignin-first biorefinery, starting from the raw lignocellulose through lignin-first processing and moving to downstream processing pathways for intermediate compounds. In particular, for the core purpose of producing liquid fuels, the corresponding downstream processing strategies are discussed in detail. These are based on the structural properties of the intermediates derived from lignin-first biorefinery, including the catalytic conversion of lignin and its derivatives (aqueous phase system and pyrolysis system) and the cascade utilization of carbohydrate residues (fermentation, pyrolysis, and hydrothermal liquefaction). We conclude with current problems and potential solutions, as well as future perspectives on lignin-first biorefinery, which may provide the basis and reference for the efficient utilization of lignocellulosic biomass.

Keywords: lignocellulosic biomass; lignin-first biorefinery; lignin and its derivatives; carbohydrate; fuels and chemicals



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1. Introduction

Given the limited fossil-energy reserve on the planet and concerns over anthropogenic climate change, seeking alternative renewable resources has become widely recognized [1]. Lignocellulosic biomass is a renewable and non-food organic material that is considered to be a good alternative carbon source [2]. Lignocellulosic biomass is composed of three constitutive components: cellulose, hemicellulose, and lignin [3,4], which harbors great potential for the sustainable production of fuels and chemicals [5]. However, unlocking this potential requires innovative biorefining methods that can overcome the complexity of the wood fiber structure and allow the three main components to take full advantage of their value [6].

Conventional biorefineries have been geared towards optimal carbohydrate valorization. Due to the harsh reaction conditions, native lignin is prone to undergoing condensation reactions to form the industry lignin that is chemically stubborn and inappropriate for further conversion in downstream processes [7,8]. This lignin is always treated as waste and then just burned for heat [9]. As lignin has a natural aromatic ring structure, it is increasingly being recognized that it is foolish to ignore its potential value [10,11]. With the worldwide emphasis on sustainable development and the rise of the biomass chemical industry, making full use of lignocellulose—especially the efficient catalytic conversion of lignin—has attracted the extensive attention of scientists [12]. Researchers are pursuing more comprehensive strategies for biomass utilization, and much of the motivation is driven by techno-economic analyses and life cycle assessments, which indicate that lignin valorization is able to improve the economic benefits and environmental benefits of overall biorefinery [13,14].

A new strategy has emerged in recent decades named “lignin-first,” in which the subsequent availability of the lignin fraction, together with the carbohydrate preservation, is considered upfront when dealing with biomass raw materials [15]. Abu-Omar and colleagues define “lignin-first” as an active stabilization approach that liberates lignin from the natural lignocellulose biomass and prevents condensation reactions through either catalysis or protection-group chemistry [16]. The lignin-first strategy is considered to be one of the most well-studied prospective strategies, which allows for the realization of a high selectivity and high yield of phenolic monomers [17].

So far, several methods have been reported. The corresponding chemical-reactions mechanism is illustrated in Figure 1. The most common method comprises solvent-based lignin extraction from lignocellulosic biomass feedstock in the presence of a metal catalyst under a reductive atmosphere. The most typical metal catalysts contain Pt, Pd, Rh, Ru, and Ni on activated C or Al₂O₃ supports [18,19]. This method is termed “reductive catalytic fractionation,” and is less time-consuming and has a high lignin conversion rate. Lignin derivatives obtained through catalytic depolymerization are present in the liquid phase, thus facilitating direct hydrodeoxygenation for the production of value-added hydrocarbon fuels and chemicals [20]. This approach mitigates the issue of lignin degradation, which is frequently encountered during traditional lignin-isolation techniques [21]. Moreover, the other active stabilization methods during biomass fractionation comprise the appropriate use of protection-group chemistry. Alcohols have been used in lignocellulosic biomass fractionation for nearly a century. However, it is only in recent years that certain advantages of their use in the lignin extraction process have become clear. During lignin extraction, benzylic carbocation ion intermediates can be intercepted by an alcohol that acts as an external nucleophilic reagent to produce ethers [22]. Additionally, reactive intermediates may be protected as acetals by using small molecules such as aldehydes and ethylene glycol. Thus, chemically stabilized lignin is extracted and enables further depolymerization and transformation [23,24]. This method physically separates the biomass-fractionation and lignin-depolymerization operations and is therefore more flexible and has better controllability. Nevertheless, the addition of small-molecule protection reagents may lead to adverse environmental impacts, which consequently need to be considered in a comprehensive manner.

In recent years, with the establishment and improvement of lignin-first biorefinery, the research hotspots in this direction will gradually shift towards downstream processing strategies which efficiently integrate the utilization of lignin-degradation products and carbohydrate residues. Novel catalytic methodologies have been pursued for a long time to achieve better valorization of lignin and its derivatives for the production of hydrocarbon fuels and chemicals [25–27]. In addition, cascade processes have been carried out for the valorization of carbohydrate residues. Notable examples include the direct conversion of carbohydrates to mixed alcohols, followed by upgrading to fuel-range alkanes [28]; treatment with FeCl₃ to obtain furfural, 5-hydroxymethylfurfural, and levulinic acid simultaneously [29]; and saccharification and fermentation to produce bio-ethanol [30]. The efficient separation of the delignified pulp and the solid catalyst mixture has been considered to be a critical challenge. Therefore, a rational design of multifunctional catalysts for the direct catalytic upgrading of solid-residue mixtures (carbohydrate and catalyst) is a potentially viable solution.

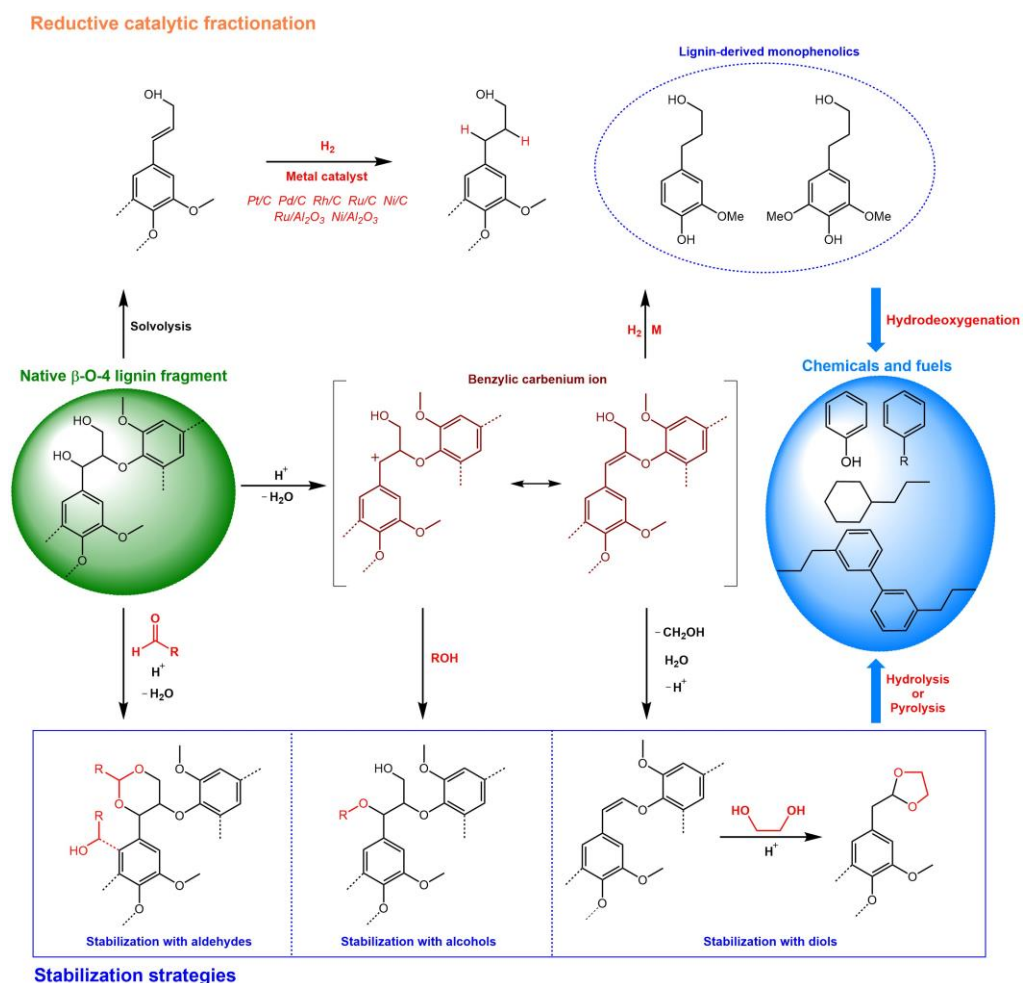


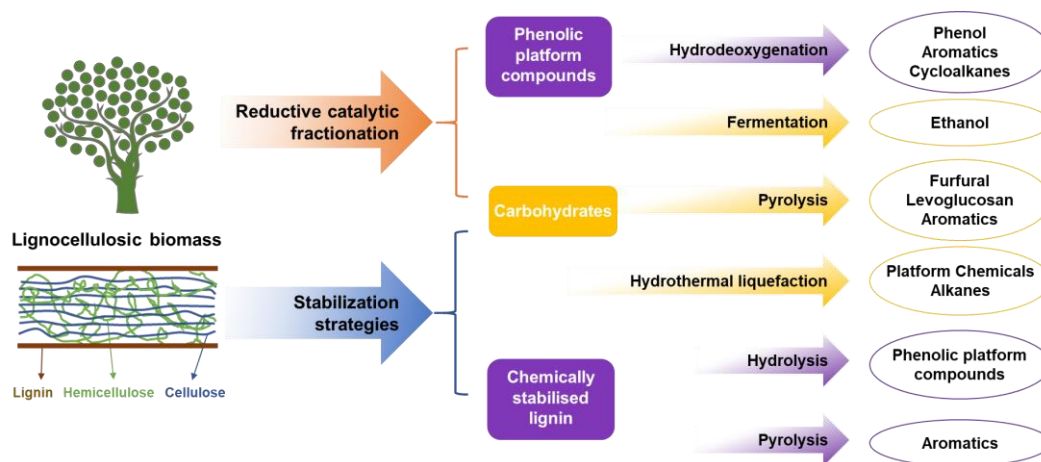
Figure 1. The chemical-reaction mechanism of lignin-first biorefinery using solvolysis and the catalytic stabilization of reactive intermediates to stable products or protection-group chemistry and subsequent upgrading.

As is shown in Table 1, several notable reviews have summarized the recent advances in lignin-first biorefinery. However, most of these reviews focused on the lignin fractions unilaterally, and the fate of the carbohydrates has rarely been considered to date. Thus, this review provides a detailed overview of recent research advances in lignin-first biorefinery, highlighting the effects of catalyst, solvent, and reactor configurations and functional group protection reagents on lignin monomer and carbohydrate yields. Subsequently, we classify intermediate products in detail and summarize high-value utilization strategies for all lignocellulose components, respectively, including the catalytic conversion pathways of lignin fractions in the aqueous phase and pyrolysis systems, as well as the applications of different technology pathways in the conversion of carbohydrate residues such as fermentation, pyrolysis, and hydrothermal liquefaction.

Table 1. Summary of notable works previously published that are relevant to lignin-first biorefinery.

Year	Key Focus	Reference
2017	Fractionation methods that implement active stabilization mechanisms; techno-economic considerations.	[17]
2019	Elementary reductive catalytic fractionation steps; recent innovations such as flow-through operation and synergy with feedstock engineering.	[31]
2020	The kinetics of lignin and polysaccharide depolymerization; the strategies for chemical functionalization.	[32]
2020	Chronological overview of the development of the “lignin-first” approach with the inclusion of reductive catalytic depolymerization of all lignocellulosic components.	[15]
2020	Downstream processing strategies of lignin monomers; methods of separation of aromatic monomers from lignin-first biorefinery.	[33]
2020	The fundamental catalytic reactions relevant to lignin-first biorefinery approach; the further transformations of lignin-derived monolignols and phenolics into value-added products.	[34]
2021	A set of guidelines for analyzing critical data from lignin-first approaches, including feedstock preparation and characterization, reactor design, catalyst efficiency, mass balances, and product yields.	[16]
Newest	The effects of catalyst, solvent, reactor configurations and functional group protection reagents on intermediate products; downstream processing strategies for lignin as well as carbohydrate fractions.	-

In order to improve the overall efficiency of the resource use of biomass, novel routes for all components derived from lignocellulosic-biomass hierarchical utilization are proposed based on lignin-first strategies (Figure 2), which provide new ideas for the efficient conversion of lignocellulosic biomass into fuels and chemicals. Furthermore, we discuss associated technical challenges and future directions of lignin-first biorefinery.

**Figure 2.** Complete conversion of all lignocellulose components yielding fuels and chemicals based on the lignin-first strategy.

2. Overview of Lignin-First Biorefinery

Conventional lignocellulosic-biomass-utilization strategies have difficulty in avoiding the undesirable condensation of reactive intermediates during biomass deconstruction, which poses fundamental challenges for commercial applications. Lignin-first biorefinery inhibits the condensation of reactive intermediates either by selectively catalyzing the conversion of these intermediates to stable derivatives or by avoiding their formation by functionalizing natural structures or intermediates [32]. This strategy has attracted wide attention from researchers since it was proposed. In the past few years, the global biomass-conversion community has continuously published new studies in this area. This section introduces the research progress made by domestic and foreign research groups in this sphere in detail, and also analyzes the existing problems and solutions for this strategy.

2.1. Reductive Catalytic Fractionation (RCF)

One of the most effective strategies is the direct hydrogenolysis of native lignin in lignocellulosic biomass; that is, a stable, low-Mw lignin oil (phenolic monomers, dimers, and small oligomers) can be obtained through tandem lignin depolymerization and stabilization [17]. This methodology is now termed reductive catalytic fractionation (RCF) [35], also known as catalytic upstream biorefining (CUB) or early-stage catalytic conversion of lignin (ECCL) via H-transfer reactions for the process using 2-PrOH as an H-donor [36,37]. We have introduced the recent progress on RCF and discussed the influences of catalysts, solvents, and reactor configurations in terms of yield of phenolic monomers, degree of delignification, and retention of carbohydrate pulps. In Table 2, selected reaction systems that achieve high-monomer yields are generalized.

Table 2. Reductive catalytic fractionation of biomass feedstock.

Feedstock	Catalyst	Solvent	Monomer Yield	Sugar Retention	Year ^{Ref}
Miscanthus	Ni/C	Methanol	68 wt%	86 wt%	2016 [38]
Corn Stover	Ni/C	Methanol	24.5 wt%	76 wt%	2016 [39]
Flax Shive	Ru/C	Ethanol	9.5 wt%	Glucan 67.2 wt%	2020 [40]
Spruce	Ru/C	Ethanol	30 wt%	Glucan 84.4 wt%	2022 [41]
Bamboo	Pd/C	Methanol	32.2 wt%	Glucan 73.4 wt% Xylan 57.4 wt%	2019 [42]
Eucalyptus	Pd/C	Methanol	49.8 wt%	Glucan 82.5 wt% Xylan 67.8 wt%	2020 [29]
Poplar	Pd/C	Methanol/ H ₂ O (7:3)	43.5 wt%	66.7 wt%	2016 [43]
	Zn/Pd/C	Methanol	54 wt%	79 wt%	2015 [44]
Birch	Ru/C	Methanol	51.5% (C-Yield)	81% (C-Yield)	2015 [35]
	Pd/C	Methanol	49.3% (C-Yield)	89% (C-Yield)	2015 [45]
	Pd/C	Water	43.8 wt%	55 wt%	2016 [46]
	Pd/C	Ethanol/ H ₂ O (1:1)	36% (C-Yield)	84.4 wt%	2016 [47]
	Ni/Al ₂ O ₃ ^a	Methanol	36 wt%	84.9 wt%	2017 [30]
	Pd/C+H ₃ PO ₄ ^b	Methanol/ H ₂ O (7:3)	37 wt%	56 wt%	2017 [48]

^a Ni/Al₂O₃ pellets in catalyst cage. ^b Reaction operated in a flow-through reactor.

2.1.1. Role of the Catalyst Used

A general understanding of the RCF processes has been established through mechanistic studies, which can be summarized in three basic steps: lignin extraction, which entirely depends on the solvent; solvolytic depolymerization and catalytic hydrogenolysis; and stabilization, which is controlled by a heterogeneous, redox-active catalyst [31]. Since the

hydrogenolysis of C–O bonds is metal-dependent, the type and yield of products can be controlled by selecting an appropriate metal [18]. Heterogeneous metals have been shown to catalyze lignin depolymerization efficiently, including Pt, Pd, Rh, and Ru, as well as Ni, which is abundant on Earth [19,38,45,49].

Sels and colleagues presented the RCF of birch with a Ru/C catalyst, in which the lignin fraction was degraded to a propyl-substituted phenol compound with a monomer yield of 52%. Cellulose retention reached 95%, while hemicellulose retention was only 47% among the carbohydrates, which were converted into C2–C6 sugar polyol products in the subsequent hydrolysis reaction [35]. Furthermore, Pd/C and Ru/C catalysts were compared under identical conditions. As expected, the lignin product yields were similar for the two catalysts. However, the chemical structures of the products were quite different, and the Pd/C catalyst had a higher selectivity for lignin monomers rich in hydroxyl groups and a higher retention of carbohydrate residues [45].

Luo et al. have shown that Pd/Zn synergistic catalysis is relevant to lignin conversion in terms of the cleavage of β -O-4 linkages and the follow-up hydrodeoxygenation [50]. Furthermore, when different types of biomass feedstocks were treated with Zn/Pd/C, the native lignin was converted into two main products: dihydroeugenol and 2,6-dimethoxy-4-propylphenol, with lignin monomer yields ranging from 40% to 54% [44]. Further mechanistic studies revealed a synergistic effect between Pd/C and Zn^{II} ; it was proposed that the addition of Zn^{II} can activate and promote the removal of $\text{C}_\gamma\text{-OH}$ from the β -O-4 bond [51].

From the perspective of industrial applications, the development of low-cost and highly available catalysts is imperative. Song et al. presented a selective hydrogenolysis of natural lignin fractions from birch wood to dihydroeugenol, 2,6-dimethoxy-4-propylphenol, and a small amount of propenyl-substituted phenols using a Ni/C catalyst [52]. Interestingly, the Fe-doped bimetallic catalyst showed stronger hydroxyl removal when compared to the Ni/C catalyst, and the monomer product distribution changed from PG-OH and PS-OH to PG and PS [53]. Li et al. developed a new Ni- W_2C /AC bimetallic catalyst and found that there was a synergistic effect between the Ni and W_2C , which could significantly promote the formation of lignin-derived monomers. Carbohydrates were further converted into ethylene glycol and other diol products. This catalyst can be widely used in birch, poplar, pine, beech, and other raw materials [54].

2.1.2. Influence of Solvents

In the process of the direct catalytic treatment of lignocellulosic biomass, solvent decomposition can cut the lignin–carbohydrate complex (LCC) between lignin and hemicellulose, realizing lignin stripping from the biomass substrates. Subsequently, the β -O-4 linkage bond in the lignin structure is broken under solvent decomposition. Soluble lignin fragments are then generated, which make further contact with the catalyst surface and complete the subsequent activation of the β -O-4 linkage bond into a single-molecule compound. Solvents play an important role in the delignification of biomass and lignin depolymerization, affecting the yield of aromatic monomers as well as the retention of carbohydrate pulps [55,56].

Sels et al. investigated the effects of different solvents on the RCF of birch wood. It was found that the higher the polarity of the solvent, the higher the degree of delignification. This was because highly polar solvents can better complete the dissolution of the wood fiber structure and make the solvents more accessible to lignin; among them, methanol and ethylene glycol showed the highest efficiencies for delignification. From the distribution of lignin degradation products in a Pd/C catalytic system, with the increase of solvent polarity, the monomers and dimers of degradation products increased, while the oligomer products significantly decreased, indicating that highly polar solvents can also accelerate the degradation of the lignin oligomer into monomers and dimers [46]. A techno-economic analysis of the RCF process using different solvents was carried out by Beckham et al., who replaced the solvent in the methanol-case with ethylene glycol. Due to the lower

vapor pressure of ethylene glycol, the overall reactor pressure was reduced substantially. Generally, lower pressure during RCF results in lower capital costs. On the other hand, ethylene glycol has a higher cost and higher energy consumption for solvent recovery than methanol. Overall, on the basis of supporting the sale of bioethanol at USD 2.50 per gallon of gasoline equivalent, the methanol case has a higher MSP–monomer fraction at USD 3.63 per kg, while the ethylene glycol case has a lower MSP–monomer fraction at USD 3.07 per kg [14].

Sels and colleagues further investigated the effects of different alcohol/water-mixing solvent systems on the RCF, and their results showed that the addition of moderate amounts of water significantly enhanced the extraction efficiency of lignin. However, too much water resulted in a lower degree of delignification [43]. Chen et al. also confirmed the positive effect of adding water on the yield of lignin monomers [57]. It should be noted that, if pure water is used as the medium while the lignin fraction is efficiently separated and degraded, the carbohydrate fraction also undergoes hydrolysis reactions and almost all of the hemicellulose and about 20% of the cellulose are removed [46]. Similar solvent-polarity effects can also be observed in other catalytic systems. When water replaced methanol as the solvent in the case of the Ru/C system, not only did the yield of phenol monomer decrease from 52% to 25%, but the carbohydrate fraction was also degraded into soluble polyols [35]. A plausible explanation for this is the autoionization of water into H^+ acid ions under high temperature conditions, which can catalyze the hydrolysis of carbohydrate [58]. In addition, the redeposition of dissolved lignin on the surface of lignocellulosic fibers should be considered when water is used as the solvent [59]. Above all, a pure water system may not be suitable for the current direct catalytic reduction process of biomass feedstocks.

2.1.3. Flow-Through Reactors

The new strategy of reductive catalytic fractionation has been proposed to depolymerize and stabilize lignin by mixing metal catalysts and biomass; however, this usually results in the catalyst not being recovered. Thus, flow-through systems for lignin-first biorefinery were developed (Figure 3). In 2017, two research teams introduced flow-through reactors for the RCF process, in which the biomass and catalyst were separated by filling into two different beds. The solvent was passed through the heated biomass bed to extract and partially depolymerize the lignin polymer. Then a liquid mixture of dissolved lignin fragments flowed through the catalyst bed for further depolymerization and stabilization of active intermediates [48,60].

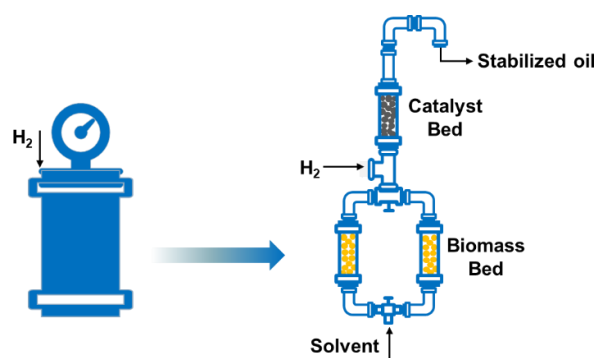


Figure 3. The evolution of reactor configurations for reductive catalytic fractionation.

However, flow-through systems also have certain limitations. For example, they require harsh reaction conditions in order to realize efficient delignification and stabilization, which significantly increases reactor costs [14]. Generally, the solvent consumption is high, because this design may increase the time taken by solvent-extracted lignin fragments to reach the catalyst bed, and partial lignin may undergo an irreversible condensation reaction, resulting in a decrease in the final phenolic-monomer yield and selectivity. Therefore,

kinetic issues such as adequate mass transfer between active lignin fragments and the catalyst need to be considered [48,60–62].

Beckham and colleagues demonstrated that the lignin oil obtained from the flow-through system could be stored for a long time without compromising subsequent hydrogenolysis activity, but the unusually high ratio of solvent to biomass made it difficult to implement on an industrial scale [63]. In 2021, the team found that solvent usage exhibits a significant effect on the GWP; with the methanol solvent loading reducing from a 9 L/dry kg biomass to a 4 L/dry kg biomass, the GWP reduces from 0.079 kg CO₂-eq/kg to a −1.078 kg CO₂-eq/kg lignin fraction [14]. On this basis, a multiple flow-reduction catalytic fractionation strategy has been proposed, which successfully reduced the solvent–biomass ratio to 1.9 L/kg with no significant decline of lignin oil quality found in the case of catalyst overload. This strategy greatly reduces the energy demand and operation cost of solvent recovery, which has a good development prospect [64].

2.2. Stabilization Strategies

Given that the effective extraction of lignin with a high purity and less-condensed structure from lignocellulosic biomass is crucial for lignin valorization, various biomass-fractionation technologies have been developed [65]. Extraction with supercritical fluid using CO₂ in a supercritical condition is generally applied, which can enhance the accessibility of biomass and reduce the pretreatment temperature [66]. Moreover, organosolv pretreatment is considered one of the most promising methods for biomass fractionation. The organic media can realize a higher lignin extraction efficiency thanks to its higher lignin solubility when compared to water [67]. In Table 3, selected extraction systems which achieve high-lignin isolated yields are generalized.

Table 3. Solvent- or co-solvent-assisted lignin extraction from biomass feedstock.

Feedstock	Conditions	Organic Media	Isolated Lignin ^a	Year ^{Ref}
Hemp Hurds	165 °C 20 min	Methanol H ₂ SO ₄ aqueous solution	75 wt%	2014 [68]
Switchgrass	180 °C 60 min	Ethanol H ₂ SO ₄ aqueous solution	60.5 wt%	2012 [69]
Poplar	160 °C 30 min	Methanol H ₂ SO ₄ aqueous solution Formaldehyde	64 wt%	2018 [70]
Walnut	170 °C 30 min	Methanol H ₂ SO ₄ aqueous solution Formaldehyde	50 wt%	2021 [71]
	120 °C 150 min	1-butanol H ₂ SO ₄ aqueous solution	85 wt%	2021 [72]
Birch	85 °C 180 min	Formaldehyde 1,4-dioxane Hydrochloric acid	116 wt%	2019 [73]
	95 °C 210 min	Propionaldehyde 1,4-dioxane Hydrochloric acid	89 wt%	2019 [73]

^a Lignin isolated yields are calculated based on the theoretical amount of lignin in feedstock.

The theoretical maximum yield of lignin depolymerization to monomers is approximately the square of the cleavable interunit ether bond (β-O-4) content [6]. Therefore, the retention of the reactive β-O-4 bond is one of the means to realize lignin valorization [21].

Alcohols can act as external nucleophiles to capture benzyl carbocation intermediates and form ether at the α -position of the β -O-4 bond, which further inhibits the condensation reaction [22,32]. Lancefield et al. found that most of the β -O-4 bonds were retained in bioethanol- and biobutanol-extracted lignin [74]. Zhu et al. found that higher yields of monomers were obtained by the depolymerization of benzyl alcohol after microwave-assisted methylation, which meant that etherification improved the reactivity of the β -O-4 bond [75]. Deuss and colleagues reported the semi-continuous extraction of high β -O-4 content lignin with butanol in a flow-through system, thereby reducing the difficulty of further catalytic depolymerization [72]. However, when compared to reductive catalytic fractionation, the alcohol-etherification approach usually produces a lower yield of phenolic monomers owing to inefficient lignin extraction and incomplete intermediate capture [32].

In 2015, Barta and colleagues proposed the addition of ethylene glycol as a functional group protector to produce a stable G/S-C2-glycol acetal (1,3-dioxolane) structure through its combination with the acidolysis reaction intermediate, thus improving the yield of aromatic monomers [23,76]. On this basis, De Santi et al. used the green solvent dimethyl carbonate (DMC) to replace 1, 4-dioxane and toluene; meanwhile, sulfuric acid was used to replace the expensive iron (III) trifluoromethanesulfonate ($\text{Fe}(\text{OTf})_3$). The monomer yield reached 9 wt% when pine was used as raw material [77].

In 2016, Luterbacher and colleagues reported the addition of formaldehyde to organic solvent processing to avoid repolymerization during lignin extraction. This method takes advantage of the functional group protection of formaldehyde: formaldehyde reacts with α -OH and γ -OH on the side-chain of lignin to form a stable 1, 3-dioxane structure through acylation, which inhibits the formation of benzyl carbocation. At the same time, the electron-rich positions on the aromatic ring (usually the positions ortho or para to methoxyl groups) are easily replaced with protonated-formaldehyde electrophilic aromatics to form a hydroxyl methyl group, which further blocks the polycondensation reaction site [24]. Recently, the team demonstrated that the extracted lignin was able to achieve steady-state, continuous depolymerization with a Ni/C catalyst in a flow-through system, in which the yield of 45% monophenol was achieved and maintained for 125 h [78].

In 2018, Abu-Omar and colleagues used a solvent mixture of methanol and dilute sulfuric acid with a small amount of formaldehyde to extract lignin. Over 68% of the lignin in poplar was extracted and depolymerized by the Ni/C catalyst, resulting in three major phenolic monomers: isoeugenol, 4-propenyl eugenol, and guaiacol, with a total yield of 63% [70]. This extraction method is also applicable to walnut-shell biomass. Compared to ethanol, methanol—as a stronger nucleophilic reagent—is more effective in protecting carbocation intermediates [71].

In summary, the method of using alcohols or aldehydes to stabilize lignin intermediates is basically compatible with the established organic solvent pulping method. Compared to the RCF process, its biggest advantage is that it can separate the biomass fractionation from the subsequent depolymerization step so that the two steps can be optimized independently and the depolymerization is more flexible. Therefore, only the solvent and reaction conditions need to be adjusted [32].

3. Downstream Value-Added Terminal Products

Several reviews have summed up recent research progress on lignin-first strategies. However, most of them were only concerned with the catalytic system design and reaction mechanism studies. There was little discussion on the downstream-integrated utilization strategies of lignin degradation products and carbohydrate residues from lignin-first biorefinery [16,18]. In order to improve the overall benefits of lignin-first biorefinery, it is necessary to develop technological pathways for the comprehensive, efficient use of these compounds to produce liquid fuels and chemicals, which is crucial for the further development of lignin-first biorefinery in the future. Recent research results relevant to biomass valorization for the production of biofuels and chemicals are summarized in Table 4. The

main strategies through hydrothermal liquefaction, pyrolysis, and fermentation are examined and further discussed.

Table 4. Comparison of different technology pathways.

Pathways	Description	Feedstock	Conditions	Key Products	Ref
Hydrothermal liquefaction	The reaction of biomass in hot-compressed or sub-/supercritical water or solvent.	2-methoxy-4-propylphenol	•Pt/C 400 °C •H-ZSM-5 350 °C	Phenol~60%	[79]
		3-(4-hydroxyphenyl)propanol	RuFe/Nb ₂ O ₅ 250 °C	Ethylbenzene~78.5%	[25]
		RCF lignin oil	Mo ₂ C 350–375 °C	C9-C12~56% C14-C20~11.9%	[80]
		Organosolv oak lignin	Pd/C 180 °C	4-n-propyl syringol /guaiacol~25%	[81]
		Birch lignin	Ru/Nb ₂ O ₅ 250 °C	C7–C9 hydrocarbons~35.5%	[82]
		Carbohydrates	FeCl ₃ 200 °C	Furfural~55% Levulinic acid~76%	[38]
		Microcrystalline cellulose	•Tungstosilicic acid •Ru/C 210 °C	C5-C6 alkane~60%	[83]
		Microalgae	330 °C	Bio-oil~45.7%	[84]
Pyrolysis	The light, small molecules are converted to oily products through homogeneous reactions in the gas phase.	Organosolv poplar lignin	HZSM-5 600 °C	Aromatic hydrocarbons ~3.57%	[85]
		Enzymatic hydrolysis lignin	Nb ₂ O ₅ 650 °C	Aromatic hydrocarbons ~11.2%	[27]
		Microcrystalline cellulose	500 °C	Hydrocarbons~6.5%	[86]
		Nannochloropsis sp.	HZSM-5 400 °C	Aromatic hydrocarbons ~48.60% (32.7 MJ/kg)	[87]
		Microalgae	600 °C	Bio-oil~21.9%	[84]
Fermentation	The heterogeneous biochemical process which is catalyzed by enzymes.	RCF pulp	•Accelerase trio enzyme mixture •GSE16-T18-HAA1 * yeast suspension •Commercial enzyme solution	Ethanol~73% of the maximum theoretical yield	[30]
		Organosolv beech pulp	Cellic® CTec2 •Saccharomyces cerevisiae strain Ethanol Red® •Commercial Cellulase	Ethanol~83% of the maximum theoretical yield	[88]
		Jute	•Beta-glucosidase enzymes •Saccharomyces cerevisiae JRC6	Ethanol~77.73%	[89]
		Microalgae	•Endoglucanase •β-glucosidase •Amylases	Ethanol~87.6% of the theoretical yield	[90]

* A genetically modified yeast strain, which has been engineered for fermentation of both C6 and C5 sugars into bio-ethanol in non-detoxified lignocellulose hydrolysates.

3.1. Lignin and Its Derivatives

Lignin-first biorefinery achieves the separation of lignin fractions through the solvent-depolymerization method. Recently, with the continuous establishment and improvement of various new catalytic systems, the research hotspots in this area will be gradually shifted to the downstream conversion process, including the efficient conversion of lignin and its derivatives. In this section, lignin degradation products are classified into two types according to their structural characteristics. One type includes fragmented small molecules

obtained from the RCF process, while the other type is retained as macromolecules with modified functional groups. Both of these types are good feedstocks for the production of liquid fuels and valuable chemicals. In the following sections, the specific catalytic conversion pathways of the above components will be discussed in detail (Figure 4), and the key breakthrough directions for subsequent research will be foreseen.

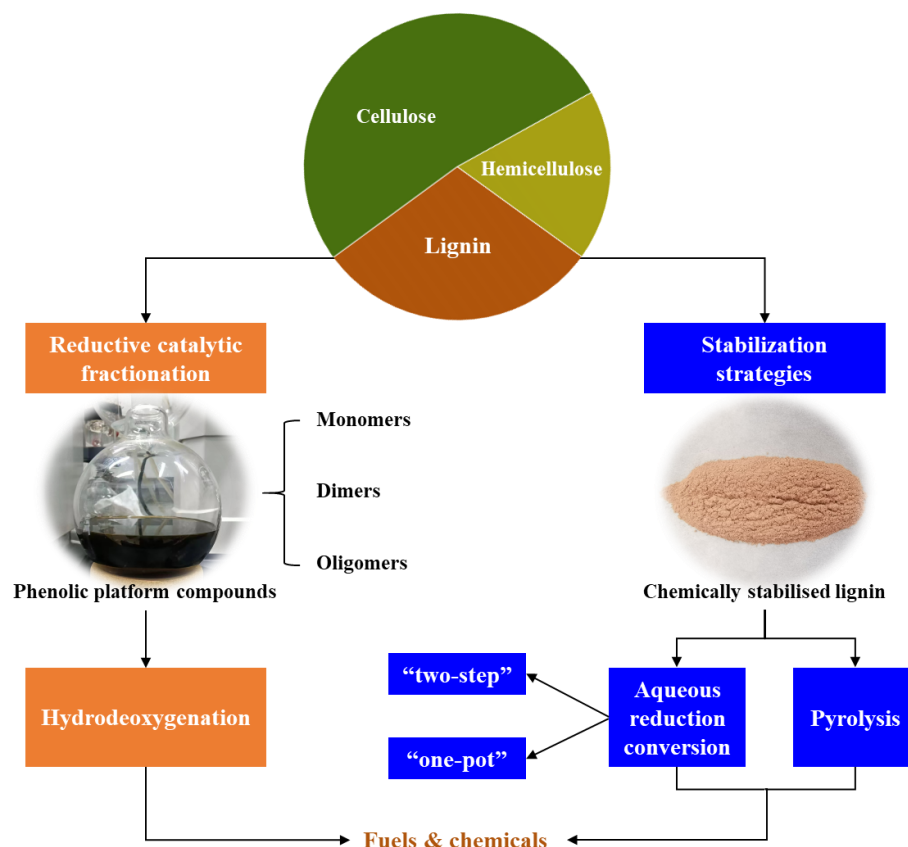


Figure 4. The subsequent conversion pathways of different lignin degradation products derived from lignin-first biorefinery.

3.1.1. Phenolic Platform Compounds

A typical RCF process extracts lignin from biomass by solvation and simultaneous catalytic depolymerization, after which an oxygenated, aromatic oil consisting of about 50 wt% phenolic monomer and about 50 wt% C-C-linked dimer and larger oligomers is obtained [91]. Lignin degradation products can be separated into different components for further use or can be used whole for added value.

Phenolic monomer platform compounds obtained from lignin-first biorefinery retain the unique methoxyphenol structural unit of lignin, and these platform compounds can be obtained by the selective breaking of C-O and C-C bonds to obtain bulk chemicals with simpler structures, such as phenol and monocyclic aromatic hydrocarbons [12,25,92]. Verboekend et al. pioneered the development of a two-step catalytic conversion system for the highly selective conversion of alkyl phenolic compounds to phenols and olefins through a molecular sieve catalyst [93]. Obviously, one-step conversion from a lignin-derived monomer to phenol is much more efficient and better-suited for industrial production compared to the two-step process. Zhang et al. catalyzed demethoxylation and dealkylation reactions simultaneously through a physical mixture of Pt/C and HZSM-5 with phenol yields of up to 60% [79]. Our previous studies have shown that a physical mixture of Nb₂O₅ and Ru/C can realize the complete deoxygenation of complex phenol-monomer platform mixtures (dihydroeugenol, isoeugenol, and 4-allyl-2,6-dimethoxyphenol) to propyl cyclohexane and propyl benzene [94]. Li et al. combined dehydrodecarbonylation and

hydrodeoxygenation reactions with a FeO_x -modified $\text{Ru}/\text{Nb}_2\text{O}_5$ catalyst and selectively converted 4-n-propanol-based phenolic compounds into ethylbenzene (Figure 5) [25]. Considering the high cost of precious metals in industrial applications, the study on cheap transition metals (Cu, Fe, Co, and Ni) has become a hotspot. At present, $\text{Cu}/\gamma\text{-Al}_2\text{O}_3$, Fe/SiO_2 , $\text{Co}_1@\text{NC}(\text{SBA})$, and Ni/SiO_2 catalysts have been proven to have positive effects on the hydrodeoxygenation [95–98].

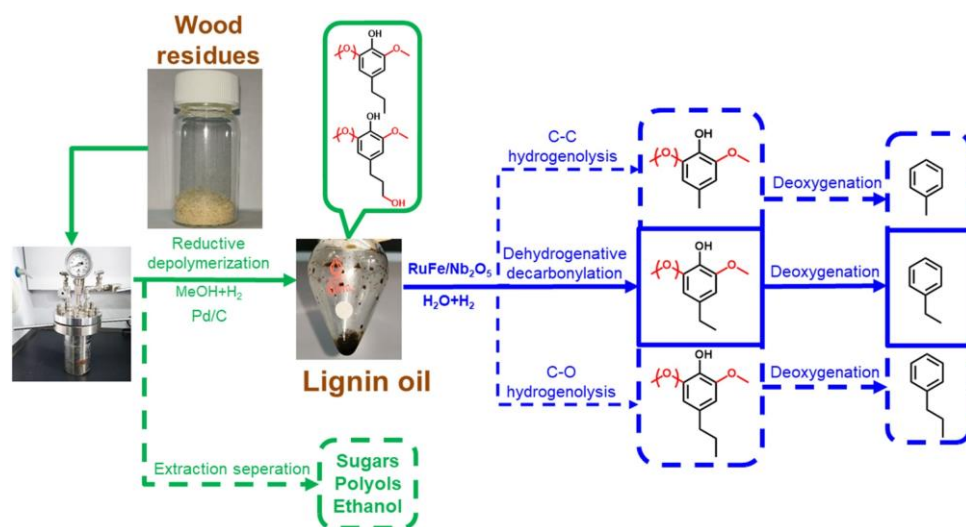


Figure 5. Procedure for the production of ethylbenzene from the lignin fraction of wood residues [25].

The complete deoxygenation of RCF oil will produce a mixture rich in alkylated aromatic hydrocarbons, which have great potential to produce bio-jet fuel [99]. Rinaldi and colleagues presented a new approach using a $\text{Ni}/\text{Nb}_2\text{O}_5$ catalyst for the hydrodeoxygenation of RCF oil. Despite obtaining products with O/C and H/C ratios of 0.006 and 1.8, respectively, recycling tests of the catalyst showed that it was severely deactivated after the first run. This proves that the condensation reaction of oligomers will also occur in RCF oil under reducing conditions, and coking will lead to catalyst deactivation [100]. Cao et al. successfully converted RCF oil from a lignin-first biorefinery process into liquid fuel. Firstly, the lignin in poplar was degraded preferentially using commercial Raney nickel to obtain RCF oil, followed by the catalytic upgrading of the lignin to aliphatic or aromatic compounds using phosphorus-modified Ni/SiO_2 catalysts. Notably, the selectivity of the final products to aromatic or aliphatic hydrocarbons can be simply modulated by the hydrogen pressure and temperature. The lignin degradation products were completely converted into saturated alkanes at 300 °C and 5 MPa H_2 , while the aromatic, hydrocarbon-dominated liquid fuels were obtained at 350 °C and 0.5 MPa H_2 . In addition, since the HDO reaction requires a large amount of hydrogen, it is also proposed to use unconverted cellulose as a source of hydrogen, making the strategy of producing high-energy-density fuels through lignin-first degradation process more reasonable [101]. L. Stone et al. successfully achieved the production of sustainable aviation fuel (SAF)-range aromatics through the hydrodeoxygenation of poplar RCF oil in a flow-through reactor with an aromatic selectivity of up to 87.5%, due to the selectivity of the Mo_2C catalyst to cleave C-O bonds while maintaining the integrity of the C-C bond of the lignin substrates [80].

3.1.2. Chemically Stabilized Lignin

During lignin extraction, benzyl carbocation intermediates can be stabilized by etherification and acetal functionalization, which can inhibit undesirable condensations [32]. Since lignin's β -ether bonds are partially conserved, chemically stabilized lignin can be further selectively depolymerized into monomers through chemo-catalytic methods. More importantly, the resulting monomer yield is much higher than that of conventional industrial lignin [24]. Obviously, the depolymerization products can be further converted into hydrocarbons by the hydrodeoxygenation strategies of phenolic platform compounds described in the upper section. In addition, powerful catalysts should be developed to produce liquid fuels and chemicals directly from lignin [102], which is mainly focused on aqueous phase systems and pyrolysis systems in recent studies [103].

There are two main types of lignin-aqueous-reduction conversion processes. One is based on a two-step reaction ("two-step method") where depolymerization is performed and followed by de-functionalization or functional group modification to obtain the target products [20,104–108]. The other is based on a one-step reaction ("one-pot method") where the target products are obtained by direct conversion [109–113]. Regarding the aspect of product yield, the "two-step method" is expected to achieve 30–50% carbon efficiency; however, the direct conversion of lignin to fully deoxygenated hydrocarbon products by the "one-pot method" is generally only a 10–30 wt% yield [53,112,114–116]. The "two-step method" has better controllability for the distribution of target products and is more flexible. The "one-pot method" increases the complexity of the entire reaction system, and the matching of catalyst and intermediate product interactions at different stages needs to be considered during the conversion process, thus increasing the difficulty of effective regulation. However, this method can directly obtain the target hydrocarbon mixture in the same batch of reaction, and the operation process is simpler and more convenient.

In addition, pyrolysis is a simple and rapid pathway to decomposing lignin into smaller fragments [117–120]. Catalytic fast pyrolysis (CFP) is the most efficient method to produce low-carbon aromatics and has attracted great interest from scholars [121,122]. Zeolite catalysts are commonly used in the catalytic pyrolysis of lignin, and can produce hydrocarbons suitable for gasoline blending [123,124]. It is generally believed that this type of catalyst plays two main roles in lignin pyrolysis. One is that its acidic sites can promote the depolymerization and deoxygenation of lignin to form the target hydrocarbon products, and the other is that it has the appropriate pore size to improve the selectivity of the target products through the shape-selective effect. However, the current problems of zeolite catalysts are mainly its low yield of liquid products and the rapid carbon deposition and deactivation of catalysts. The acid-active site can be adjusted by introducing metal loading or changing the pore structure and distribution, so as to delay the deactivation of catalyst [119,120,125]. However, zeolite catalysts have poor hydrothermal stability. For example, the Si-O-Si bond structure of a HY molecular sieve is easily dissolved under water vapor, leading to the loss of the catalyst [126]. Therefore, the introduction of novel catalysts that are resistant to carbon deposition and that have hydrothermal stability is of crucial importance for the lignin catalytic pyrolysis system. In recent years, metal oxide catalysts have also been used in CFP systems to optimize the pyrolysis product distribution. Hernando et al. studied the effect of ZrO_2 doped with zeolite molecular sieves on the concentration and distribution of Brønsted and Lewis acids. It was found that the modified catalyst reduced secondary reactions and promoted the conversion of preliminary pyrolysis products [127]. Moreover, our previous studies have demonstrated that a Nb_2O_5 catalyst was effective in promoting the removal of oxygenated functional groups from lignin and inhibiting the formation of polycyclic aromatic hydrocarbons [27].

3.2. Carbohydrate

Although the lignin-first strategy was proposed with the primary goal of realizing lignin valorization, this pretreatment method will inevitably have irreversible impacts on the structure and downstream transformation of cellulose and hemicellulose [36]. Currently, most studies on lignin-first biorefinery still focus on the isolation and conversion of lignin components, and the fate of carbohydrate derivatives has been rarely explored [16,128]. However, as the lignin-first strategy moves toward industrial applications, the fate of these secondary products will become increasingly important in order to achieve all components' hierarchical utilization and improve the overall resource-utilization efficiency of biomass. In fact, the basic units of carbohydrate residues (cellulose and hemicellulose) are C5 and C6 sugars, which are relatively simple in structure and can be converted into liquid fuels and platform chemicals through biochemical, pyrolysis, and hydrothermal liquefaction processes [44].

3.2.1. Fermentation

Most commonly, carbohydrates can be hydrolyzed and fermented to produce fuel ethanol, which is a comparatively cleaner fuel with high octane and fuel-extension properties. Recently, an increasing number of countries are using an ethanol–petrol blend as transportation fuel to reduce the environmental pollution caused by vehicle emissions [129].

Enzymatic saccharification is a heterogeneous biochemical process in which carbohydrate hydrolysis is catalyzed by enzymes [130]. In general, cellulose hydrolysis is governed by many factors, such as cellulose accessibility, crystallinity index, lignin and hemicellulose content, and inhibitors. Therefore, the efficiency of enzymatic hydrolysis depends on the combined action of several related factors [131]. The lignin-first strategy is able to achieve a high degree of delignification, which greatly increases the accessibility to enzymatic hydrolysis and breaks the recalcitrance of biomass [24,132–134]. Generally, the delignification degree can be effectively improved by appropriately extending the pretreatment time and increasing the pretreatment temperature. Noteworthy, the higher the cellulose content in the carbohydrate residue, the more conducive it will be to the subsequent enzymatic hydrolysis [46,135]. Inevitably, the crystal structure and fiber morphology of the solid residues after lignin-first pretreatment may also be affected to some extent, and the loose structure is more conducive to the binding of enzymes to cellulose [135]. There are obvious differences in the morphology of carbohydrate residues obtained by different pretreatment methods (Figure 6). The surface of organosolv pulps is fibrous and porous, while the CUB pulps present a more compact surface [36].

However, the feasibility of implementing this technology pathway varies for different lignin-first strategies. Zhang et al. found that the residual catalyst could inhibit the downstream enzymatic hydrolysis and fermentation of carbohydrates from the reduction catalytic fractionation process [136]. To solve the problem of difficulty in catalyst recovery, one option is to use ferromagnetic catalysts, such as Ni/C or RANEY®Ni catalysts, which can be magnetically separated from the carbohydrate pulp after the reaction and have good reusability [36,52,137]. Using a sieve for the separation is also a viable means [42,132]. In addition, a smart reactor design can avoid the above problem by using a microporous catalyst cage or flow-through reactors. These can achieve physical isolation of biomass feedstock and catalyst, effectively promoting catalyst recovery and clean pulp production [30,47,60]. Sels and colleagues successfully performed multiple catalyst-recovery experiments and simultaneous saccharification fermentation of highly delignified pulp (93% glucose and 83% xylose retention) with ethanol yields of up to 73% by using a catalyst cage [30].

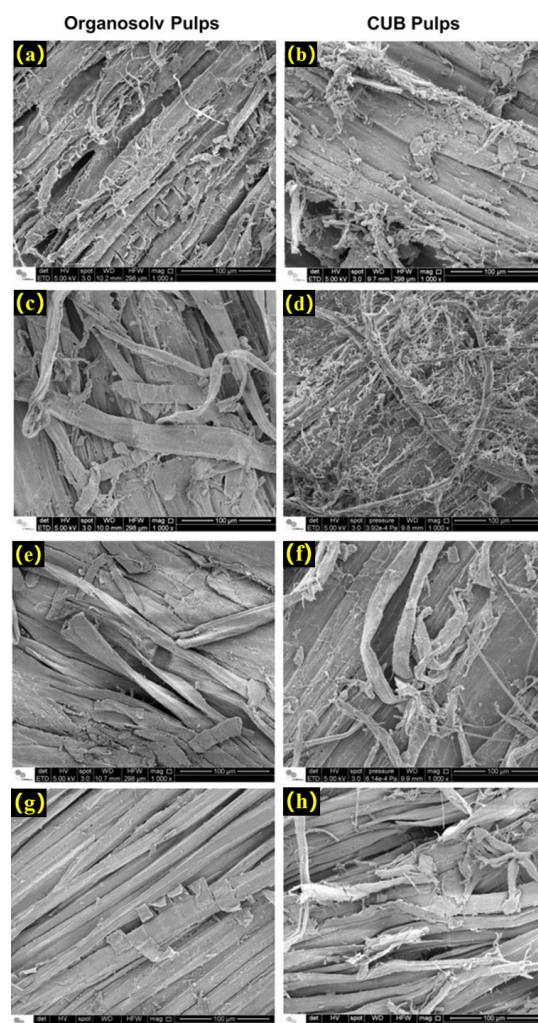


Figure 6. FESEM images of organosolv pulps and CUP pulps: (a,b) were obtained at 160, (c,d) at 180, (e,f) at 200, and (g,h) at 220 °C [36].

3.2.2. Pyrolysis

Rapid pyrolysis is one of the direct liquefaction technologies of biomass and has been favored by many researchers due to its advantages of rapid and high-volume processing of biomass feedstocks with high oil yields [138,139]. However, crude bio-oil has a high water content, low calorific value, high acidity, and high viscosity, amongst other characteristics, which limits its application in automotive or aerospace power machinery [140]. In order to improve the quality of bio-oil and even to produce liquid hydrocarbons directly from lignocellulosic biomass, many catalytic-assisted pyrolysis processes have been investigated [141,142]. Generally speaking, it is easier to convert and utilize the lighter components of crude bio-oil, which are mainly derived from cellulose and hemicellulose, while the hydrodeoxygenation of monophenols or phenolic oligomers derived from lignin fraction is much more difficult [143,144]. The lignin-first strategy puts the conversion of the lignin fraction upstream when processing biomass feedstock, which provides a novel solution to the current dilemma of difficult bio-oil refining. Meanwhile, the carbohydrate residues can be further converted to liquid fuels and chemicals through pyrolysis technology.

Theoretically, the lignin-first biorefinery process mainly converts the lignin fraction to oil while preserving most of the carbohydrate fraction as a solid. Parsell et al. found that the rapid pyrolysis behavior of carbohydrate residues after lignin-first pretreatment is closer to that of pure cellulose, which yields a similar product distribution. This is in sharp

contrast to the highly complex mixtures obtained after rapid pyrolysis of raw biomass [44]. Indeed, the morphological structure and crystallinity of the carbohydrate residues derived from lignin-first biorefinery differ from that of the original holocellulose, which may largely affect their downstream applications. Limited studies have found that the lignin-first pretreatment may lead to partial breakage of cellulose chains, which can aggravate the production of pyrolytic char to a certain extent. It is worth noting that the catalyst used in upstream treatment will affect the pyrolysis behavior of holocellulose. When compared to Ru/C holocellulose, the char yield from RANEY[®]Ni holocellulose was higher, which indicates that the RANEY[®]Ni catalyst breaks cellulose chains more severely during the related RCF process [145].

The main chemical reactions involved in the catalytic pyrolysis of cellulose include deoxygenation, cleavage, aromatization, ketonization, aldol condensation, hydrogenation, and reforming [146,147]. Currently, catalysts commonly used in cellulose-catalytic pyrolysis studies include alkali metals, alkaline earth metals, metal oxides, zeolite molecular sieves, etc. [148,149]. The reaction path can be selectively optimized to improve the quality of pyrolysis products by adjusting the structural properties of the catalysts and changing the reaction conditions. In addition, the participation of hydrogen gas has many advantages when compared to the inert atmosphere. On one hand, reducing hydrogen gas generates hydrogen radicals, which react with volatile fractions released from biomass. In the presence of a catalyst, the reaction is more likely to remove oxygen in the form of H₂O, CO, and CO₂ in order to produce hydrocarbons. On the other hand, the hydrogen radicals generated in the reaction can stabilize the active intermediates and avoid the polymerization reaction, thus alleviating the coking deactivation of the catalyst [150]. Li et al. investigated the reaction mechanism during hydrolysis of cellulose (Figure 7), and the introduction of hydrogen gas promoted the degree of thermal decomposition of cellulose and increased the H/C ratio of the liquid products at 3 MPa of H₂ from 1.4 to 1.9 [86]. Due to the complexity of hemicellulose and its cross-linking with other biomass components, it is extremely challenging to obtain natural hemicellulose from biomass. This has led to most of the relevant pyrolysis studies revolving around model compounds [151,152]. Hemicellulose is another abundant polysaccharide in biomass, which can be expected to have a similar pyrolytic reaction mechanism to cellulose [153]. However, the pyrolysis temperature of hemicellulose is usually lower than that of cellulose [154]. Under the same conditions, the yield of aromatic hydrocarbons obtained from hemicellulose by the catalytic pyrolysis over HZSM-5 is lower than that of cellulose, and the relatively high temperature is more conducive to the formation of aromatic hydrocarbons [155].

3.2.3. Hydrothermal Liquefaction

Hydrothermal liquefaction is another direct-liquefaction technology of biomass, which generally refers to the reaction of biomass in hot-compressed or sub-/supercritical water or solvent to obtain bio-crude oil. Generally, the reaction temperature of hydrothermal liquefaction is in the range of 250–450 °C and the pressure is between 5–20 MPa. The biomass feedstock does not require baking and can be directly used in the reaction [156]. When compared to the pyrolysis, the low operating temperature, high efficiency, and low tar yield of hydrothermal liquefaction has prompted researchers to focus on its process [157]. The product distribution obtained from biomass liquefaction mainly depends on the lignin content in the biomass feedstock. Generally speaking, the higher the lignin content in the raw material, the lower the conversion rate and oil yield will be. This is due to the fact that a higher lignin content is prone to more severe condensation and repolymerization reactions [158]. However, the lignin-first strategy can effectively avoid the problem of undesirable condensation between components that exist in a one-pot conversion of biomass through cascade utilization. As a result, the difficulty of reaction regulation is greatly reduced. While a high yield of lignin monomer is achieved, the carbohydrate residues are also easier to convert into platform chemicals and liquid fuels by liquid phase catalysis.

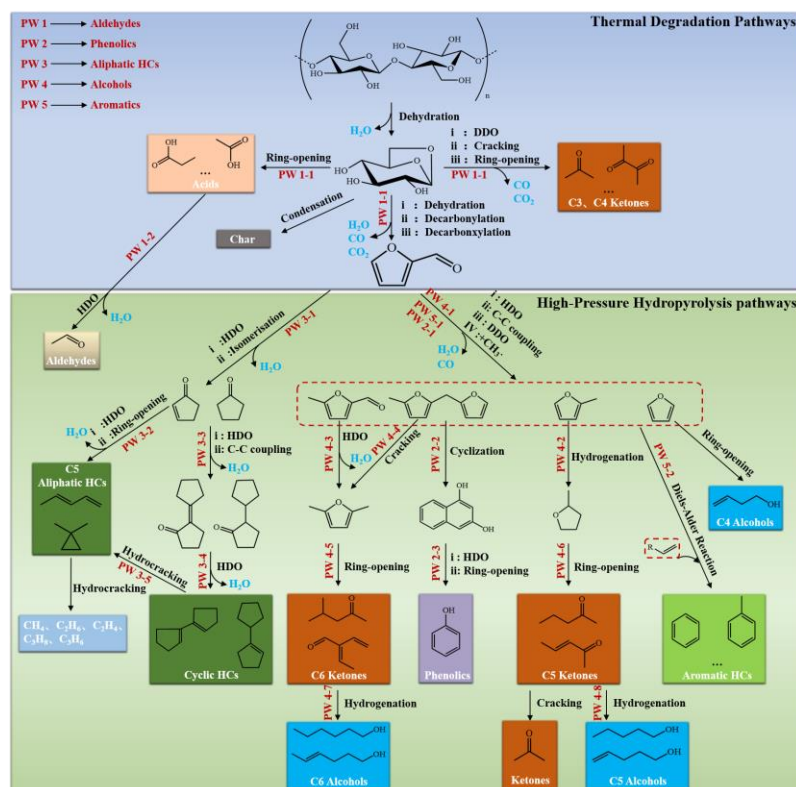


Figure 7. Possible reaction mechanisms involved in the formation of various products during the fast pyrolysis of cellulose [86].

During the lignin-first pretreatment process, carbohydrates are retained as solid residues after the removal of the lignin fraction, which can be subsequently converted into platform chemicals (hydroxymethyl furfural, levulinic acid, formic acid, etc.) using earth-abundant Lewis acid catalysts such as FeCl_3 . In this process, the whole components of biomass are effectively utilized, and 55% of the total available biomass is converted into high-value-added products [38]. Catalyst recovery is a challenge in the RCF process of lignocellulosic biomass. Based on this, Guo et al. designed an acid-free reaction system consisting of THF and concentrated seawater, in which solid residues rich in (hemi)cellulose can be converted into 5-hydroxymethylfurfural and furfural. Moreover, the effective separation of the Pd/C catalyst can be achieved easily [159]. Sun et al. designed a catalytic strategy in which lignocellulose biomass was fully converted. At the core of the strategy was the flexible use of the copper-doped, porous, non-noble metal-oxide catalyst ($\text{Cu}_{20}\text{-PMO}$) in two distinct steps. First, the lignin fraction was decomposed into monomeric platform compounds (mainly aromatic alcohols) in a mild methanol system while the cellulose and hemicellulose components existed in the form of solid residues. Next, the unreacted lignocellulose residues could be easily separated from the liquid phase and directly converted to aliphatic alcohol platform compounds in the supercritical methanol system. Thereby, the catalyst could be readily recycled. The complex mixtures of aliphatic alcohols could be further converted to liquid fuels via fatty-chain elongation and hydrodeoxygenation [28].

The direct catalytic conversion of carbohydrates to aviation fuels is a huge challenge. Once directly hydrodeoxygenated, they can only produce short-chain alkanes [83,160]. New C-C bonds must be established between the depolymerization intermediates to produce aviation fuels with suitable carbon numbers. Existing studies on the topic are usually focused on converting sugars into platform chemicals with active functional groups, such as 5-hydroxymethylfurfural (5-HMF), furfural (HMF), angelica lactone (AL), levulinic acid (LA), and γ -valerolactone (GVL), etc. [161–163]. Various platform chemicals undergo carbon chain growth through aldol-condensation, hydroxyalkylation/alkylation (HAA),

pinacolic coupling, oligomerization reaction, self-coupling reaction, etc., and are finally converted into aviation liquid fuels along with hydrodeoxygenation (HDO), ring opening, and a series of other reactions (Figure 8) [162,164,165].

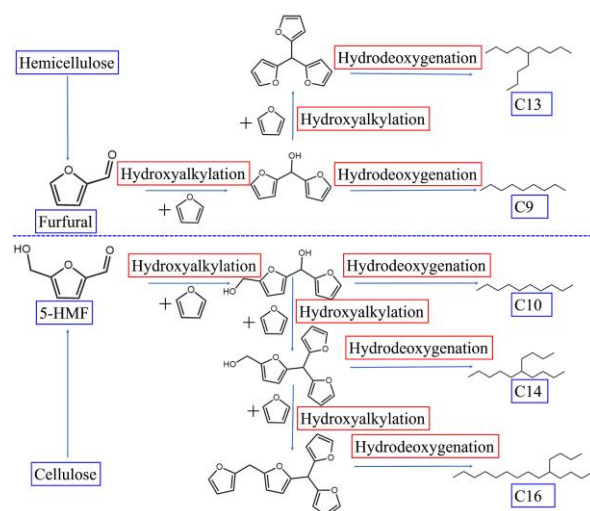


Figure 8. Production of aviation fuels from carbohydrate-derived furanic intermediates via hydroxyalkylation/alkylation (HAA) and hydrodeoxygenation (HDO) reactions [162].

4. Summary and Prospect

In this mini-review, a comprehensive overview of lignin-first strategies that are capable of breaking native lignin into high-yield phenolic monomers is first presented. The core of this strategy is to inhibit the irreversible polycondensation reaction of lignin components so as to obtain more value from lignin. Currently, most research is focused on stabilization chemistry, catalyst-materials development, or the catalytic process, and the fate of carbohydrates has been little explored to date. However, before industrialization, it is necessary to establish complete, hierarchical utilization routes for all components of biomass. As was described in detail in Section 3, this review discusses the downstream conversion pathways of both lignin degradation products and carbohydrate residues to produce fuels and chemicals.

In recent years, although multiple achievements have been realized in lignin-first biorefinery, from the point of scaled applications there are still many challenges. Subsequent research needs to make breakthroughs in the following directions: (i) Applicability of biomass feedstock. To solve this problem, more widely applicable reaction systems need to be developed; (ii) In the selection of solvents, the yield of lignin monomers and carbohydrates should be considered comprehensively, and the cost of solvent recovery should also be measured; (iii) Catalyst cost and reusability. On one hand, it is necessary to develop new reaction systems based on non-precious metals or trace precious metals to replace the current noble-metal heterogeneous catalysts. On the other hand, effective removal of catalysts from pulp to improve catalyst recyclability is essential to move towards a true upgrade effort. In addition, it is important to develop carriers with high thermal and oxidative stability, such as SiC, which can be regenerated simply by calcination [99], and (iv) The design of the lignin-first strategy should be considered from a more macro perspective, through a life-cycle assessment (LCA), and a techno-economic analysis (TEA) of the overall utilization process ought to be carried out.

Lignin has presented a significant challenge for both academia and industry due to its stubborn and complex structure. A series of innovative achievements in the lignin-first sphere have made access to liquid fuels and value-added chemicals from lignin easier. In fact, our team has been working on building new systems to convert lignin into hydrocarbon fuels. Moreover, future research focus will gradually shift to seeking creative methods for all lignocellulosic components, as well as a diversification of product portfolio. With increasing

national requirements for energy conservation and emission reduction, it is imperative to improve the sustainability of the process. More importantly, industrial implementation of the lignin-first strategy needs to be economically viable to compete with conventional refineries. Therefore, optimizing the overall process to produce fuels and chemicals in a more economical and environmentally friendly way will undoubtedly become a future research hotspot in this sphere. Through close multidisciplinary cooperation and the efforts of both academia and industry, the successful development of a lignin-first biorefinery will provide exciting prospects for the new directions of biomass liquefaction, which will produce fuels and valuable chemicals in a more sustainable way.

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