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Downstream Processing Strategies for Lignin-First Biorefinery

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The lignin-first strategy has emerged as one of the most powerful approaches for generating novel platform chemicals from lignin by efficient depolymerization of native lignin. Because of the emergence of this novel depolymerization method and the definition of viable platform chemicals, future focus will soon shift towards innovative downstream processing strategies. Very recently, many interesting approaches have emerged that describe the production of valuable products across the whole value chain, including bulk and fine chemical building blocks, and several concrete examples have been developed for the production of polymers, pharmaceutically relevant compounds, or fuels. This Minireview provides an overview of these recent advances. After a short summary of catalytic systems for obtaining aromatic monomers, a comprehensive discussion on their separation and applications is given. This Minireview will fill the gap in biorefinery between deriving high yields of lignin monomers and tapping into their potential for making valuable consumer products.

1. Introduction

Due to the depletion of the global energy reserves including oil, gas and coal, finding alternative renewable resources became widely recognized.[1] Among all types of renewables, lignocellulosic biomass generated in huge quantities from both agricultural and forestry industry worldwide, represents the most condensed form of energy produced by sunlight.[2–11] Thus it serves as ideal raw material for the construction of future biorefineries that would produce a range of valuable products.[12–14] Over the past few decades, lignin-derived platform chemicals have been defined and significant progress has been made in this area related to the conversion of lignocellulose to valuable chemicals,[15,16] fuels[17,18] as well as functional materials[19] and biorefinery concepts have been established.[9]

Initial biorefinery strategies, have been devoted to the conversion of carbohydrates (hemicellulose and cellulose) to platform chemicals, which then could be further valorized.[20] However, finding efficient strategies for the production of value-added products from lignin, which is a complex, non-uniform aromatic polymer that accounts for nearly one third of whole lignocellulose appeared a bigger challenge and therefore development in this regard was delayed.[21] Especially for paper-making industry, lignin is an unwanted side-product. Thus harsh processing conditions (kraft pulping) need to be applied to solubilize lignin and enhance the quality of cellulose.[22] Under such severe conditions, lignin undergoes considerable modifications yielding a condensed residue that is unsuitable for further depolymerization and application in downstream processes, which is then just burned to generate heat.[23] However, beyond its heating value, lignin reserves significant valorization potential for the production of valuable chemicals and energy density fuels. According to lifecycle assessment, with lignin as feedstock would also have a good impact on greenhouse gas emissions.[12,24]

In the last decade, more and more researches started to focus on better valorization of lignin and at the same time achieve better valorization of all lignocellulose components.[25] Different approaches for separation of high quality lignin under mild conditions or elegant catalytic systems for transformation of lignin to chemicals, fuels as well as materials have emerged.[26–28] Among these promising strategies, the so-called lignin-first biorefinery, which allows for achieving high yield and selectivity of several monophenolic derivatives is considered as one of the most brilliant and well-studied strategies.[29]

Although several great reviews have summarized the recent advances on lignin-first biorefinery, most of them focused on reviewing catalyst design and mechanistic aspects.[28–31] Downstream processing strategies of monomers and methods of separation of aromatic monomers from lignin-first biorefinery have not been reviewed yet. Essentially, a significant gap still exists between deriving well-defined compounds from native lignin via the lignin-first method and utilizing these compounds directly for the production of value-added consumer products. Herein, as shown in Figure 1, we would like to bridge this gap and give a detailed analysis of recently developed processes of

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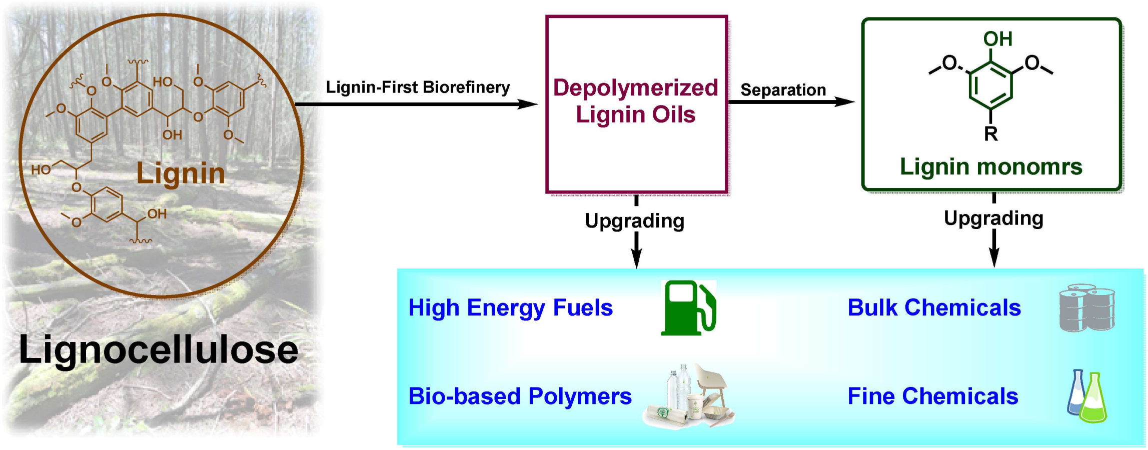

Figure 1. The evolution of lignin-first biorefinery: from lignocellulose to value-added products.

separation and application of lignin monomers derived from lignin-first biorefinery.

2. From Native Lignin to Lignin Monomers via Lignin-First Biorefinery

According to the philosophy "disassemble lignin prior to carbohydrate valorization", the lignin-first strategy embodies the combination of lignocellulose fractionation with integrated lignin depolymerization, typically over a heterogeneous catalyst under reductive atmosphere using H_2 pressure or using hydrogen donor.[29] Since the native lignin can be solvolytically extracted from lignocellulose during this process, it is immediately depolymerized to aromatic monomers before undergoing extensive structural modification to form condensed lignin (Figure 2), therefore this strategy demonstrates high yields and high selectivity of aromatic monomers compared to depolymerization process that use pre-extracted organosolv. lignins.[29]

Recently, different catalytic systems have been developed to reach the theoretical yield and high selectivity of target aromatic monomers. Since several reviews focused on the production of aromatic monomers from lignocellulose and the development of related catalytic methods, here we only give a short summary of the most important findings.[28–31]

Typically, commercially available carbon supported heterogeneous catalysts such as Pd/C[33–37] and Ru/C performed high activity for depolymerization of native lignin and homemade catalysts like Ni/C,[32,38,39] Cu-PMO,[40] ZnPd/C,[34] Beta zeolite[41] and $ZnMoO_4$/MCM-41[42] also achieved high monomer yields. Various lignocellulosic biomass including forestry and agricul-

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Jinling Cheng received her Ph.D. in 2019 in the group of Ben L. Feringa at the University of Groningen, working on the development of new molecular motors and smart materials. In 2019 she joined the group of Avelino Corma at Universitat Politècnica de València for postdoctoral research, where she worked on the application of metal–organic frameworks in biomass conversion. She recently moved to Tsinghua University as a Shuimu Tsinghua Scholar fellow and is working on single atom catalysis.

Katalin Barta received her master's degree at ELTE Budapest and her Ph.D. at RWTH-Aachen under the supervision of Walter Leitner. After postdoctoral research with Peter C. Ford at the University of California, Santa Barbara and Paul T Anastas at Yale University, she started her independent career in 2013 at the Stratingh Institute for Chemistry, University of Groningen. Since 2019, she is Full Professor at the University of Graz.

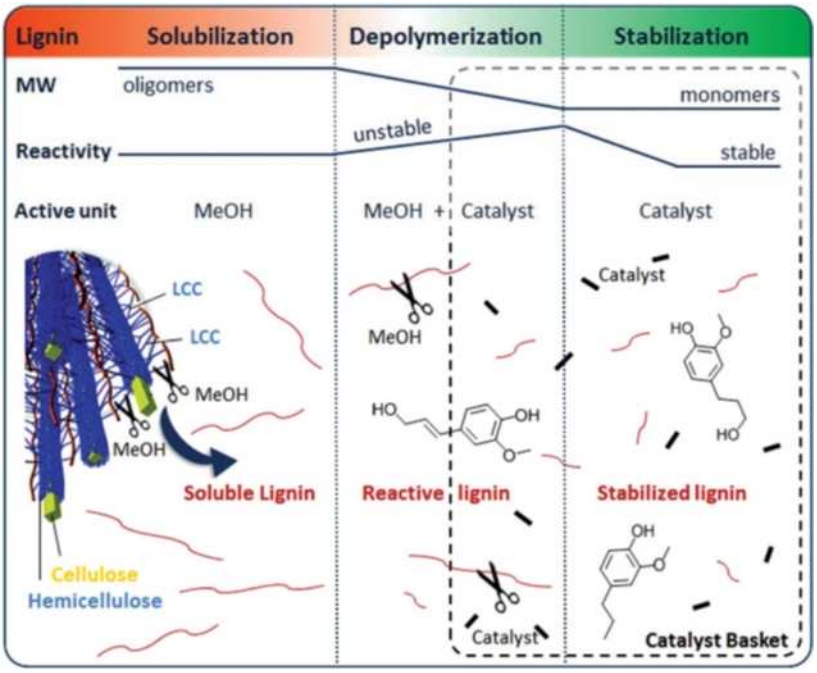

Figure 2. An overview of the lignin-first biorefinery process: from solubilization of native lignin to depolymerization and stabilization of lignin monomers. LCC means the lignin carbohydrate complexes. Adapted with permission from ref. [32]. Copyright 2017, The Royal Society of Chemistry.

tural wastes were investigated. A range of organic solvents,[37] neat or in combination with water were screened.[36] The use of additives (e.g., $Al(OTf)_3$, H_3PO_4) as co-catalyst[43–45] or H_2SO_4 only[46] as catalyst were explored as well for further improving the delignification, monomer yields and the overall efficiency of the process. In addition, the influence of hemicellulose sugars,[47] differences in S/G ratio in native lignin[48] and mass transfer in plant cell walls as well as in particle pores[49] for the overall process have been investigated.

In addition of improving the lignin monomer yields and selectivity, the retention and further application of sugars in the carbohydrate pulp is important. In this case, cascade processes for valorization of the carbohydrate pulp have been carried out. Notable examples are the direct conversion of the carbohydrate fraction to a mixture of alcohols and then upgrading to high energy fuels;[40] treatment with $FeCl_3$ to obtain HMF, levulinic acid and furfural simultaneously;[50] simultaneous saccharification and fermentation to bio-ethanol[32] and enzymatic digestion to glucose.[51]

Efficient separation of the solid catalyst and the delignified carbohydrate pulp mixture has been recognized as a key challenge.[29] To address this, several elegant catalyst separation methods have been developed (Figure 3), including but not limited to the use of magnetically separable catalysts,[52] liquid-liquid extraction for carbon supported catalysts,[37,53] confinement of the catalyst pellets in a microporous catalyst cage[32] or using sieve for the separation of powder catalyst with unconverted sawdust.[50] In the case of Cu-PMO catalyst, catalyst recycling could be integrated with a second stage conversion of carbohydrate pulp (and unreacted lignin residues) to a mixture of aliphatic alcohols in the LignoFlex process.[40]

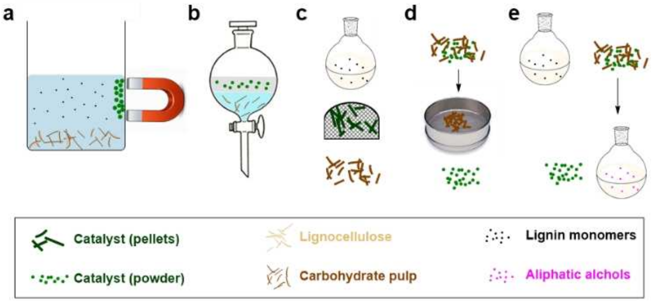

Figure 3. Catalyst recuperation strategies after lignin-first biorefinery. a. Use magnetically separable catalysts. b. Liquid-liquid extraction. c. Utilization of a microporous catalyst cage for physical separation of the catalyst pellets. d. Mesh screening for powder catalyst with unconverted sawdust. e. Integrated second stage conversion of carbohydrate pulp.

Notably, flow-through setups for lignin-first biorefinery were also developed.[54–56] The advantages of flow systems include i) the simple collection of time-resolved data for both lignin extraction and depolymerization; ii) easy control the contact time of catalyst with extracted lignin and extraction time. Minimize the side reactions and condensation could also be achieved in flow system by rapid sampling of the effluent and fast cooling of the final products. More importantly, flow systems allow for facile catalyst separation and enable the study of catalyst activity/stability independently. These contributions showed the possibility of continuous production of lignin monomers and the possibility for realistic industry application of this promising biorefinery approach.

3. Separation Strategies Targeting Isolation of Lignin Monomers

As discussed above, the lignin-first biorefinery provides a promising strategy for depolymerization of lignin, accompanied with a high degree of delignification, high yield and selectivity of lignin monomers and good quality of carbohydrate pulp. Despite these advantages, the phenolic monomer rich lignin oils also contain non-ignorable amount of low molecular weight dimers and higher molecular weight species such as oligomers and unconverted hemicellulose. Therefore, to improve the downstream processing efficiency, it is vitally important to develop efficient technologies for the separation of lignin monomers, and ideally of the other components as well.

Liquid–liquid extraction is one of the most widely used methods for the processing of lignin oils. For example, DCM and water pair could be applied to remove the soluble sugar-derived products.[53] Another similar method used ethyl acetate and water for the isolation of low molecular weight lignin species.[57] Hexane was shown to be a good extraction solvent especially for purification of nonpolar 4-alkylphenolics.[58,59] Instead of separation of lignin oils after depolymerization by liquid-liquid extraction, Sels and co-workers reported the processing of raw lignocellulose in the presence of a hydrogen atmosphere with Ru/C catalyst, in a solvent mixture containing equal amount of n-butanol and water (Figure 4).[60] With this smart co-solvent mixture extraction and depolymerization of both lignin and hemicellulose was carried out simultaneously, and after cooling, the n-butanol phase and aqueous phase separated automatically. This system provides a facile and effective strategy to fast isolation of lignin-derived phenolics (in the n-butanol phase) from hemicellulose-derived polyols (in the aqueous phase).

Membrane filtration, normally operated by semipermeable polymer films has been widely utilized in current industry (e.g., wastewater treatment) due to its high separation efficiency, simple and mild operating conditions.[61] This technology has also been applied for the fractionation and purification of industrial lignin streams, for example a membrane filtration process reported by the company Domsjö could be used for fractionation of lignosulfonates.[62]

Taking advantage of these advances, Rinaldi, Livingston and co-workers[63] exploited the potential of membrane separation for the fractionation of lignin steams produced via Catalytic Upstream Biorefining (CUB) using Raney Ni catalysts and iso-propanol as hydrogen donor. As shown in Figure 5, this two-stage cascade process was conducted to separate and concentrate the lignin stream and resulted in a high molecular weight lignin-rich fraction (dark brown oil) and a low molecular weight monophenol-rich fraction (light yellow solution). Performances of 7 commercial membranes were first critically evaluated for Stage 1 while another 12 membranes are investigated for Stage 2. Moreover, a comprehensive study based on the economic assessment was performed by the authors who successfully demonstrated that membrane filtration would be an economically competitive method while processing one kilogram of dry lignin-phenols product costs only \$0.38.

Distillation is one of the most important separation processes in laboratories and industry, therefore implementing this separation process for the lignin first biorefinery is essential. A distillation protocol aiming for fast purification of the complex monomer-enriched hexane extracted lignin oils was developed by Koelewijn et al.[64] Before setting up the distillation unit, the feasibility of this distillation process was evaluated in terms of relative volatility (α) as well as the distillation resistance (Ω). It was concluded that at a scale of 200–400 $\mathrm{kt_{prod}}$ per year, the recovery cost for 4-propylguaiacol and 4-propylsyringol amounts to about \$85–95 per ton, which is supposed to be economically feasible. Finally, a small-scale continuous distillation unit was set up in cooperation with the company Aspen Plus. The general scheme of this distillation

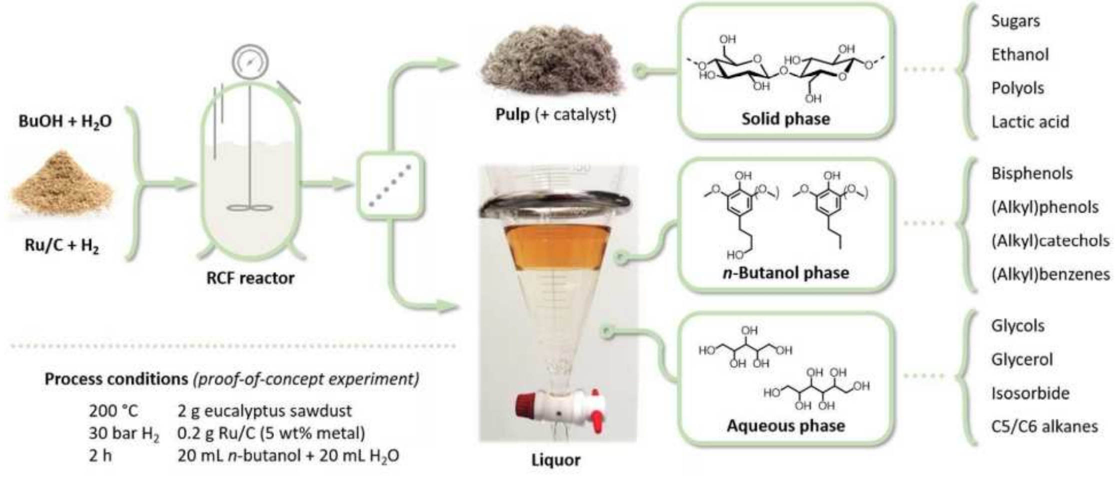

Figure 4. General process of lignin-first biorefinery of raw lignocellulose using butanol/water biphasic system. Adapted with permission from ref. [60]. Copyright 2018, The Royal Society of Chemistry.

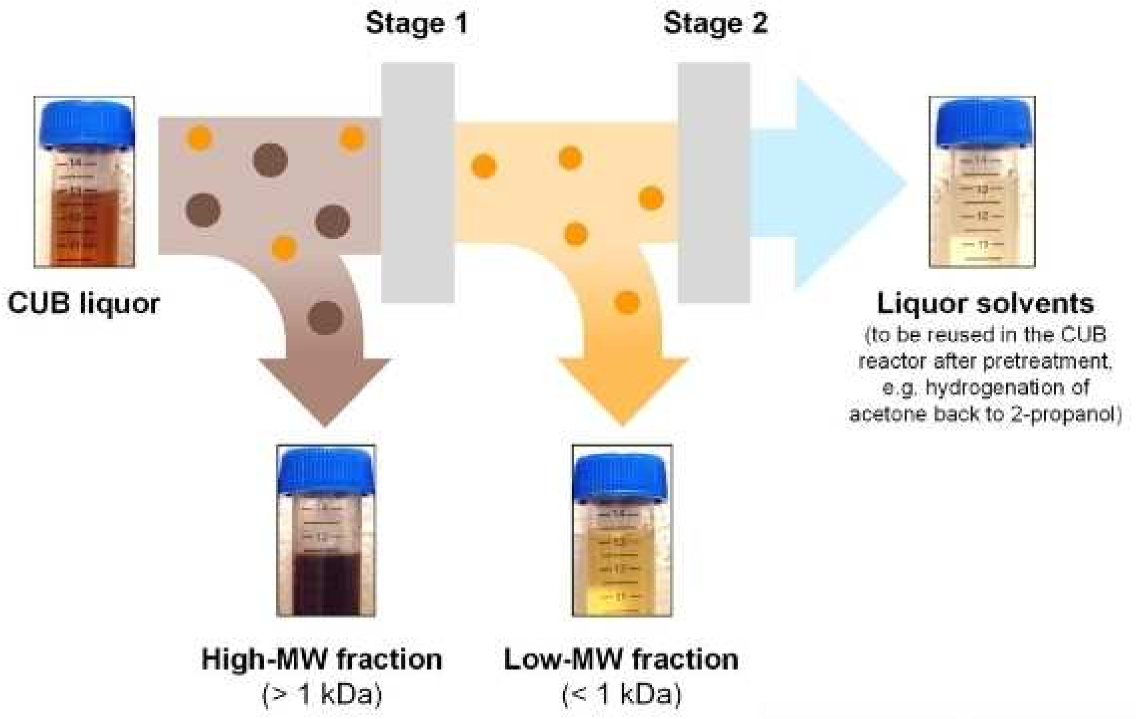

Figure 5. Schematic diagram of a two-stage membrane fractionation process using CUB liquor. Adapted from ref. [63]. Copyright 2019, Wiley-VCH.

unit is shown in Figure 6. In the first atmospheric distillation column n-hexane was removed and then 4-propylguaiacol and 4-propylsyringol were separated after passing through a second vacuum column. A sensitivity analysis together with design optimization revealed a 94.5 wt% recovery yield of 4-propylsyringol with a purity of 98.4 wt% while almost 100% yield of 4-

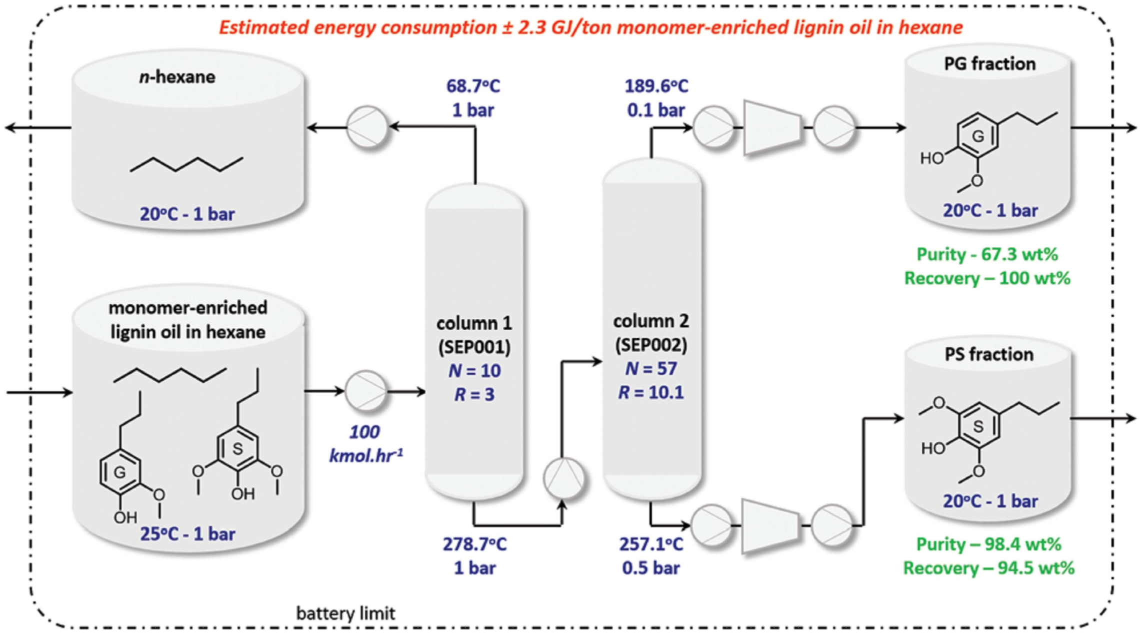

Figure 6. General scheme of down-steam processing of monomer-enriched lignin oil by distillation. Reprinted with permission from ref. [64]. Copyright 2018, The Royal Society of Chemistry.

propylguaiacol was recovered, albeit with lower purity (67.3 %). Considering a low heat duty (2.3 GJ/ton) of feed for this industrial distillation unit, the final recovery cost is estimated only to $112 per ton of product. These results underscored the potential and feasibility of distillation for lignin–first biorefinery.

Taking account of the complexity of produced lignin oils via lignin-first biorefinery, for small scale, laboratory experiments, column chromatography is a method of choice to reliably isolate specific monomers of analytical purity. For example, Barta and co-workers[40] isolated the main product 4-propanolguaiacol (40 mg, 6.9 wt % based on lignin) from a sample obtained upon depolymerization of pine wood (2 g), by flash column chromatography using pentane mixed with ethyl acetate as eluent. Another sample obtained from maple wood (1 g) contained two main components 4-propanolguaiacol (22 mg, 4.2 wt%) and 4-propanolsyringol (31 mg, 6.0 wt%), both could be isolated in excellent yield. Bruggen and Sels reported that for lignin oils from depolymerization of birch wood chips, reagent-grade 4-propylguaiacol (≥98 %) could be also isolated with the yield of 34 wt %.[64]

Although purification by column chromatography could deliver lignin monomers in high purity, the use of large amount of solvent, long operating time and generally small scale make is not ideal for potential industrial application. Finding alternatives that are more efficient, lower in cost and easier to scale up to industry level is essential.

In summary, to date, four conventional separation methods including liquid-liquid extraction, membrane separation, distillation, and column chromatography have been applied for the treatment of lignin monomers derived from lignin-first biorefinery. Liquid-liquid extraction and column chromatography are more suitable for laboratory operation. Membrane separation and distillation as mature industry processes have more potential to be used in industrial production, although more in-depth technoeconomic and environmental analysis needs to be performed.

4. Application of Monomers Produced from Lignin-First Biorefinery

These unique structures of aromatic platform chemicals produced by the lignin-first biorefinery, have initiated new research directions in catalysis especially that focus on (i) selective defunctionalization approaches to bulk chemicals and high energy fuels; (ii) selective functionalization strategies to emerging fine chemicals and polymer building blocks. In the following sections, we will focus on the application of lignin-derived monomers for generating valuable chemicals, fuels and polymer building blocks or renewable polymers.

4.1. Bulk chemicals and fuels

The current petrochemical industry produces bulk chemicals and fuels from crude oil and natural gas. Production of the same or similar chemicals from renewable resources could reduce our dependence on these limited fossil resources and also decrease the environmental impact (e.g., emissions of greenhouse gases) in current chemical processes.[65] Lignin-derived monomers have shown potential to produce aromatic bulk chemicals, like BTX and phenol[22] and due to their high carbon content, making energy density fuels is also a great option.[66]

4.1.1. Phenol

As discussed in Section 2, these alkyl phenolics produced via lignin-first biorefinery are primarily methoxy phenols with an alkyl group (typically propyl). Therefore, to obtain phenol in high yield, selective demethoxylation[67,68] and dealkylation[69,70] (Figure 7) reactions are necessary. In 2016, Sels and co-workers[71] developed the highly efficient catalytic conversion of alkyl phenols into phenol and the associated olefins (e.g., ethylene and propylene) with high selectivity via zeolite catalysts. For the deep understanding of the reaction mechanism, this group then investigated the role of zeolite structure (e.g., acid properties and pore constraint) and influence of steam over various acidic zeolites,[72,73] and found out that ZSM-5 performed the best catalytic activity, which could be attributed to its special shape selectivity effect.

Furthermore, taking advantages of this process, they presented the strategy for complete lignocellulose valorization while using carbohydrate pulp for ethanol production, lignin monomers for phenol and propylene production and the residual phenolic oligomers used as printing ink.[74] This integrated biorefinery process, achieved 78 % of the initial mass of birch wood to be sustainably and economically valorized, lifecycle assessment also estimates a much lower CO_2 footprint compared to similar fossil-based production process. Taking into account the total manufacturing investment, product value, production efficiency and the lower carbon footprint, this process demonstrated a great potential for industry application.[75]

Instead of a two-step process, a single-step protocol from lignin monomers to phenol would be more efficient and highly desired for industry. With 4-propylguaiacol as a model compound, Yan and co-workers[76] first attempted to obtain phenol from lignin-derived monomers. Their approach was to let the two reactions proceed at the same time by physical mixing of two catalysts (Pt/C for demethoxylation and HZSM5 for dealkylation affording phenol) with the yield over 60 % from 4-propylguaiacol. Another example of a single-step process was reported by Hensen and co-workers.[77] In their system, benzene instead of water was used as solvent which prevented the generation of olefins by integrating the demethoxylation and transalkylation reactions to producing cumene, toluene and propylbenzene as co-products at the same time. A high yield of phenol (60 %) was obtained in one step over the mixture of Au/TiO_2 and HZSM-5 catalysts. Recently, this group further improved the phenol yield to 90 mol % by using the MoP/SiO_2 and HZSM-5 in the same system.[78]

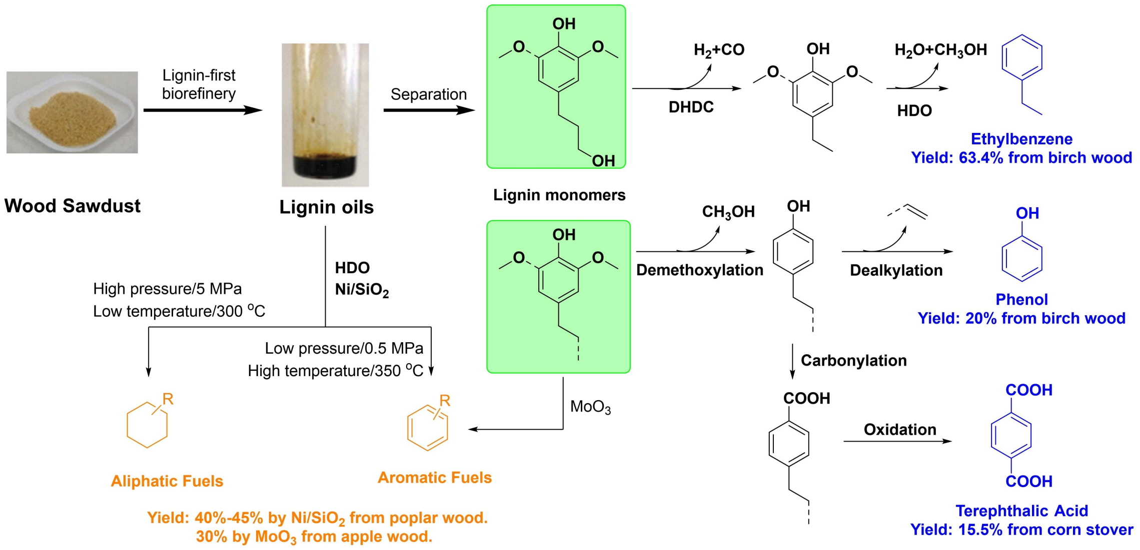

Figure 7. Catalytic processes for producing bulk chemicals and fuels from lignin-first biorefinery-derived lignin oils and lignin monomers. Yield was calculated based on the lignin content in each wood. Inserted figures are adapted with permission from ref. [53]. Copyright 2015, The Royal Society of Chemistry.

4.1.2. Ethylbenzene

Ethylbenzene is an important bulk chemical since it serves as starting material for the production of styrene and polystyrene in the petrochemical industry. Li et al.[79] presented an elegant catalytic strategy to selectively convert lignin-derived 4-propanolphenolics into ethylbenzene by combining dehydrogenative decarbonylation (DHDC) and hydrodeoxygenation (HDO) reactions with a FeO_x-modified Ru/Nb_2O_5 catalyst (Figure 7). After establishing the method on model compounds, it was also successfully applied on lignin oil produced from birch wood. The final yield of ethylbenzene increased from 23.2% over Ru/Nb_2O_5 to as much as 63.4% with $RuFe/Nb_2O_5$ catalyst and the work further elucidated the importance of using Fe as dopant in the removal of phenolic oxygen.

4.1.3. Terephthalic Acid

Previous research for sustainable Terephthalic Acid (TPA) production mainly focus on carbohydrate-derived platform chemicals such as 2–5-dimethylfuran or other furan derivatives via the Diels-Alder reaction with ethylene followed by subsequent dehydration.[80–84] However, catalytic strategies based on lignin-derived aromatic monomers didn't receive much attention. Yan and co-workers[85] recently presented a three steps process for the efficient valorization of lignin oil mixtures derived from corn stover into TPA. As shown in Figure 7, in the first step the lignin oils were catalytically funneled into a mixture of 4-alkylphenols by demethoxylation reaction with supported molybdenum oxide catalysts. This step served to unify the mixture composition towards phenols from both the syringyl and guaiacyl components. In the second step, the first COOH group was introduced by Pd catalyzed carbonylation of the phenol functionality by way of pseudohalogenide formation. The final step further narrowed the mixtures to TPA by oxidation of the alkyl groups. With this system, the overall yields of TPA could reach 15.5 wt%, and more importantly, the desired TPA could be easily isolated in near 100% purity via filtering and then washing with water.

4.1.4. High energy fuels

Valorization of lignin to high energy fuels has been recognized as an important issue[86] and various catalytic systems have been developed in recent years.[87,88] As discussed above, lignin monomers obtained from lignin-first biorefinery contain various low-molecular weight phenolics with a C9 skeleton. This holds the potential of producing jet fuel range aromatic hydrocarbons via HDO reactions.[89,90] In 2018, Fang and co-workers[59] manifested that the low molecular weight monomers in lignin oils can be first extracted by hexane and then converted to aromatic hydrocarbons via HDO over commercial MoO_3 catalyst (Figure 7). After optimization, a 6.9 wt% yield (30 wt % based on the lignin content) of aromatic hydrocarbons was achieved by using dry-apple-wood. A blended sample of these aromatic hydrocarbons with renewable jet fuel produced from waste cooking oil could meet the ASTM standards, especially for the density value (0.805) where conventional jet biofuels always failed because of their high iso-paraffin content.

Another successful example of converting lignin-first biorefinery-derived lignin oils was reported by Rinaldi and co-workers.[91] In their research, lignin oils were catalytically upgraded to aliphatics or aromatics in the presence of a phosphidated Ni/SiO_2 catalyst under reductive atmosphere. Interestingly, as shown in Figure 6, the selectivity towards aromatic or aliphatic hydrocarbons of the final product could be simply regulated by controlling H_2 pressure and temperature. Moreover, as the HDO process is a H_2-intensive approach, employing unconverted pulp as potential H_2 source was also presented in this work, which makes the concept of producing energy-density biofuels via lignin-first biorefinery much more plausible. Recently this group also gave a comprehensive study on the design of Nb_2O_5 supported nickel catalysts.[92]

4.2. Fine chemicals

Fine chemicals, in contrast to bulk chemicals, are manufactured in smaller quantities but hold higher value and are more complex in their structure. Generally, they were used as building blocks for many different products used in our daily life like pharmaceuticals, dyes, fragrances, additives and surfactants.[93] The lignin-derived monomers keep part of the inter structural characteristics of native lignin and abundant functional groups which are ideal building blocks for creating novel atom-economic reaction pathways to certain fine chemicals or creating new types of valuable chemicals.[28]

4.2.1. Indane and its derivatives

In 2019, Wang and co-workers[94] reported the conversion of phenylpropanol structural unit-rich lignin oils into indane and its derivatives with Ru/Nb_2O_5 catalyst decorated with CH_2Cl_2 (Figure 8). Lignin oils contains mainly phenylpropanol structural units were produced via the reductive fractionation of raw lignocellulose over a commercial Pd/C catalyst. Then the produced lignin oils were separated and converted into a mixture of bicyclic aromatic chemicals through an intramolecular cyclization reaction (Figure 8b). Finally, after selective HDO with the same catalyst, indane and its derivatives were formed. Lignin oils generated from different types of lignocellulose were investigated, among which birch-wood lignin oil achieved the highest yield of 23.7 wt%.

4.2.2. Aromatic amines

Aromatic amines play a central role in current industry especially for fine chemicals like dyes, pigments, fertilizers, pesticides, and pharmaceuticals.[95] However, systematic chemocatalytic approaches for the production of amines from lignin or its monomers have not received enough attention partially owing to the complexity and low yield of generated monomers in conventional depolymerization strategies, with the notable exception of vanillin which was earlier subjected to reductive amination.[96,97] Furthermore, phenol to aniline transformations were investigated by multiple groups.[98–100] Another reason for lack of lignin-derived amines were the challenges in the catalytic transformation itself, the difficulties in catalyst design as well as identification of valuable targets.

The first comprehensive study to access various classes of amines from lignin-first depolymerization products was demonstrated in 2018. Inspired by the lignin-first strategy, Barta and co-workers reported the two-step LignoFlex process[40] that could produce 4-propanolguaicol (4PG) as single aromatic intermediate (ca. 90% selectivity) from pine lignocellulose and a mixture of aliphatic alcohols from the remaining solid residues, which also allowed for efficient catalyst recycling. The advantage of the relatively mild (140–220 °C) method is that 4PG could be obtained as main product which in addition to the aromatic –OH also features an aliphatic –OH amenable for further transformation to amines. Regarding the conversion of the phenol moiety (Figure 9), two different strategies were chosen: the first comprised a known oxidation/condensation/rearomatization route which worked especially well for 4PG but also for other substrates derived from this parent compound. The other strategy investigated a Ni catalyzed Buchwald-Hartwig amination using 4-ethylguaiacol derived from 4PG, this approach worked well with several pseudohalogenides to give access to interesting secondary and tertiary aromatic amines. Unsurprisingly, several state-of-the-art catalysts have proven unsuccessful in promoting such transformations, owing to the presence of 1 or 2 methoxy groups on the aromatic ring, which calls for further catalyst development in the future. The

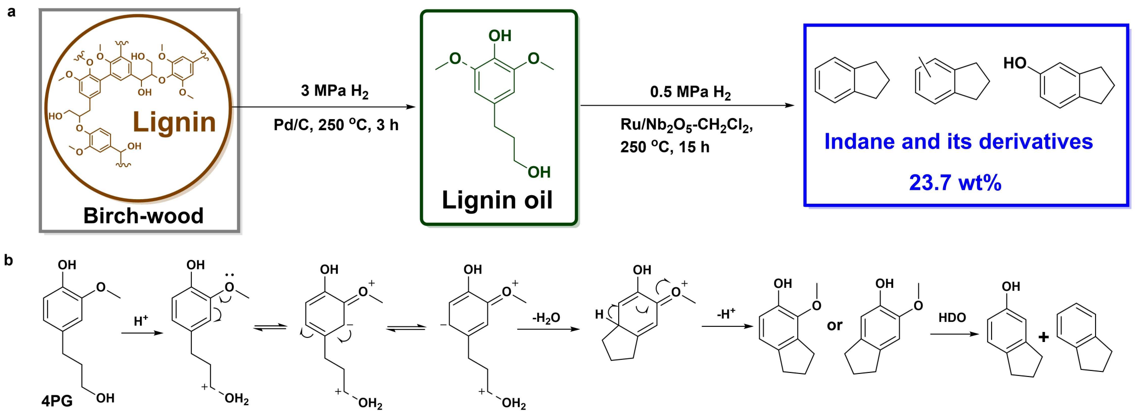

Figure 8. a. General process for converting raw lignocellulose to indane and its derivatives. b. Proposed mechanism for Ru/Nb_2O_5–CH_2Cl_2 catalyzed intramolecular cyclization and HDO.

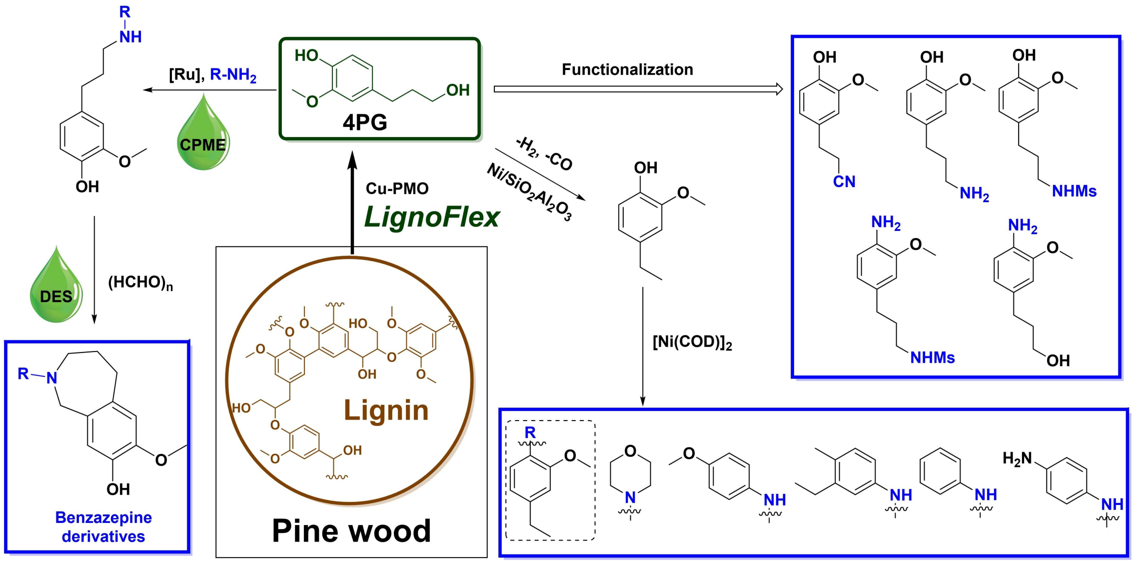

Figure 9. Catalytic strategies for synthesizing aromatic amines from 4-propanolguaiacol produced via LignoFlex process.

corresponding primary amine was obtained in very high selectivity from the nitrile that originated from direct addition of ammonia to 4PG.

In further work, significant progress was made by introducing a highly selective amination methodology using Shvo's catalyst to access a structurally diverse library of secondary amines in the green solvent CPME.[57] Adding another reaction step, the Pictet-Spengler cyclization with formaldehyde afforded a series of tetrahydro-2-benzazepines in deep eutectic solvents. These compound libraries were evaluated for antibacterial and anticancer activities with several promising hits. Benzazepine derivatives are conventionally synthesized from petroleum-derived aromatics in multiple steps, which is generally accompanied by the generation of large quantities of waste. Taking advantage of the structure properties of 4PG, tetrahydro-2-benzazepines could be obtained in three highly selective and waste-free steps, directly from wood. Moreover, this research also found that an ethyl acetate extracted crude mixture could be directly used for the next animation reaction but needed to use more catalyst. Finally, all products could be isolated as pure compound via column chromatography.

Another route for the synthesis of aromatic amines was reported by Maes and co-workers[101] using lignin-derived 4-propylguaiacol (Figure 10). This elegant strategy consists of 4 steps: (i) alkylation of the phenol group; (ii) benzylic oxidation; (iii) Beckmann rearrangement; (iv) amide alcoholysis. To pave the way to an industrial process, the synthesis was performed without any purification steps while workup only required easy-to-operate filtrations and liquid – liquid extractions. As shown in Figure 10, the crude product after concentration and extraction with an organic solvent gave pure 3,4-dimethoxyaniline in 52 % yield upon solvent removal. The final product has potential to be used for the synthesis of actual drug molecules such as anticancer drugs: Prazosin, Alfuzosin, Dox-

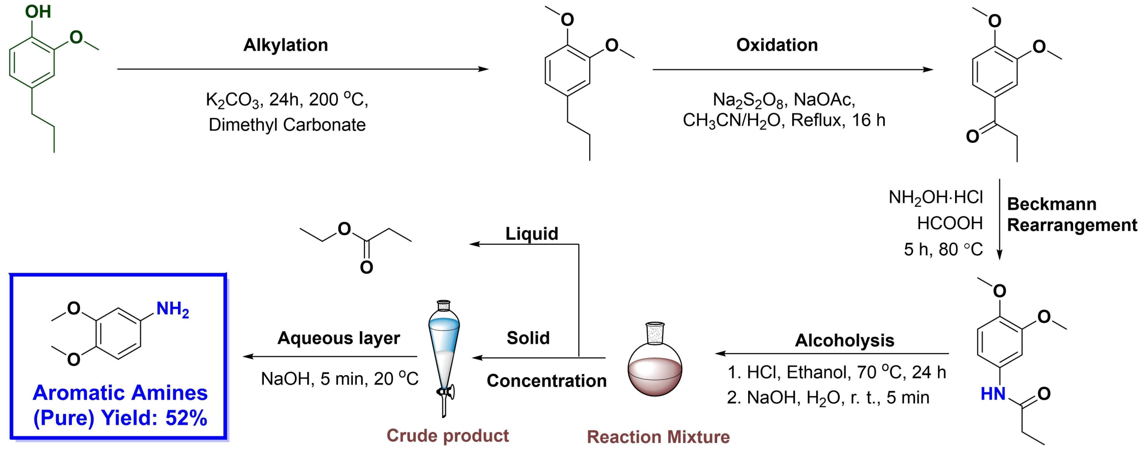

Figure 10. Strategy for 4-alkoxy-3-methoxyaniline synthesis from 4-propylguaiacol.

azosin, Terazosin, Gefitinib, and Erlotinib. During this process, other valuable chemicals alkyl propionates were generated as byproducts that could be used as solvents or flavors. Based on the first pass metrics assessment, they also conclude that this new approach for the synthesis of dialkoxyanilines using "health and safety" substrate, reactants, and reagents, is more step efficient and environmental benign.

4.3. Polymer building blocks and bio-based polymers

Actually, lignin itself has been directly used for bio-based polymer production.[102,103] However, as the properties of the obtained polymer materials strongly depended on the structures of the original lignin, reproducibility of material properties and therefore large scale production processes were key difficulties.[28] Clearly, the utilization of lignin-derived monomers overcomes these limitations, and research groups have moved into this direction especially after higher yield of well-defined aromatic monomers were accessible from the lignin first biorefinery, which have the potential to be produced in large quantity in the future.

As shown in Figure 11, among all lignin-derived monomers, 4-proplyguaiacol is the most widely used substrate for bio-based polymer production. Main routes include the catalytic conversion to caprolactone[104] (precursor for polycaprolactone via ring-opening polymerization) through a sequence of HDO, dehydrogenation and Baeyer–Villiger oxidation; bisphenols via condensation with formaldehyde;[64,105,106] substituted acrylate by functionalization with either acrylate or methacrylate.[58] In addition, 4-propanolguaiacol rich lignin oils also showed potential for bio-based epoxy resins.[107]

4.3.1. Caprolactone

Caprolactone and derivatives are important building blocks for polyesters. Conversion of lignin monomers to caprolactones was reported by Schutyser et al.[104] via a four steps process (Figure 11): (i) Catalytic fractionation of softwood sawdust to 4-alkylguaiacols; (ii) conversion of generated 4-alkylguaiacols into 4-alkylcyclohexanols by selective HDO reactions; (iii) dehydrogenation of 4-alkylcyclohexanols to 4-alkylcyclohexanones by Cu/ZrO_2 catalysts, and finally (iv) Lewis-acidic tin-containing β-zeolite-catalyzed Baeyer-Villiger oxidation of cyclohexanones to corresponding caprolactones, the overall process resulted in yields of caprolactones to 58%. In this four steps process, selective HDO of lignin monomers to alkylated cyclohexanols is the most challenging step as the hydrogenation of aromatic ring normally proceeds under harsh conditions (high temperature and H_2 pressure) with supported noble metal catalyst and generation of by-products is also inevitable. To overcome this major difficulty, a range of home-made supported Ni catalysts were first investigated with guaiacol as model compound at

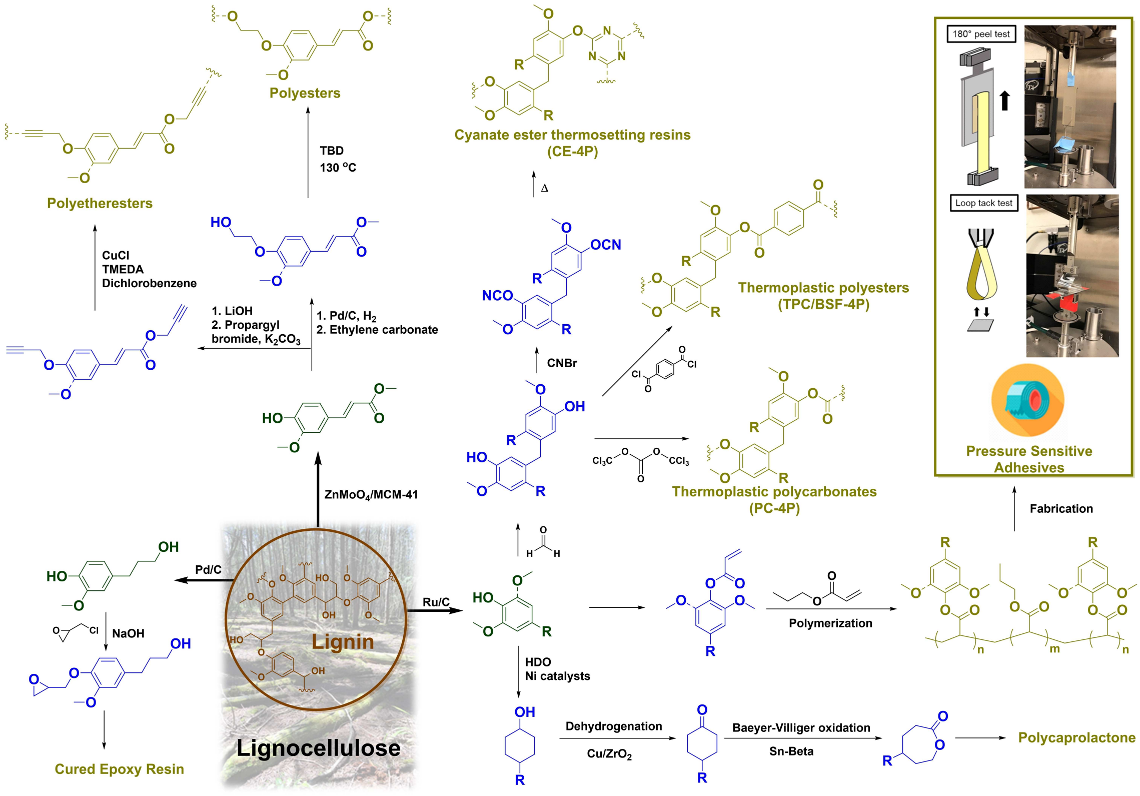

Figure 11. Summary of recent advances on making polymer building blocks or bio-based polymers from produced via lignin-first biorefinery lignin monomers. Inserted figures are adapted with permission from ref. [58]. Copyright 2018, American Chemical Society.

300 °C and 4 MPa H_2. Due to their amphoteric properties, particularly, Ni/ZrO_2 and Ni/CeO_2 delivered the highest cyclohexanol yield (81 %), whereas both basic and acidic supports displayed poor performance. This system is also suitable for softwood-derived guaiacol mixtures, but afforded a slightly lower yield of cyclohexane (73 %). Commercial catalyst including Ru/C, Pd/C and Ni/SiO_2–Al_2O_3 were also evaluated and a good 85 % yield of 4-propylcyclohexanol was obtained with the latter system under 1 MPa H_2, at 250 °C.[108]

4.3.2. Polyesters, polycarbonates and cyanate ester via bisphenols

Conventional synthesis of bisphenols normally starts from nonrenewable aromatic feedstocks and entails huge amount of nonrecycled homogeneous acid catalyst or thermolabile sulfonated resins.[109] Sels and co-workers investigated the potential of zeolites for the synthesis of bisphenols with lignin-derived alkyl phenolics.[106] Their study started with screening of a series of large-pore zeolites in comparison with commercial available sulfonated resins. It was found that the density of Brønsted-acid sites played a key role on the performance of the catalysts and highest conversion and selectivity was obtained by the FAU topology zeolites. After establishing the reaction pathway to bio-based bisphenols, high performance polymers were made (Figure 11). A high-T_g aromatic polyester (TPC/BSF-4P) was first produced by polymerization with terephthaloyl chloride.[64] The final polymer was nearly colorless and high yield of more than 90 % could be reached. The second example was preparing corresponding polycarbonates by reacting the bisphenol precursor with triphosgene.[105] Cyanate ester resins as novel high-performance thermosets have also been synthesized from this bisphenol precursor.[105] It was synthesized via a two steps process, firstly the bisphenol precursor was reacted with cyanogen bromide and following by curing process at high temperature, finally cyanate esters were obtained in excellent yield ($\geq$ 97 %).

4.3.3. Pressure-sensitive adhesives

Pressure-sensitive adhesives (PSAs) is an important polymer material and used frequently in our daily life such as packaging materials, plastic wraps, labels as well as sticky notes. Recently, Epps and co-workers reported the use of 4-propylguaiacol and 4-propylsringol for the development of high-performance PSAs.[58] Initially, the lignin monomers was functionalized with either acrylate/methacrylate groups to generate polymer building blocks. Then a triblock polymer (using n-butyl acrylate as the midblock and functionalized 4-propylsyringol/4-propylguaiacol as the glassy end blocks) was prepared by a scalable reversible addition-fragmentation chain-transfer (RAFT) process. As shown in Figure 11, the resulting PSAs performed excellent adhesion ability to stainless steel. Most importantly, 180° peel forces of this lignin-based polymer could reach up to 4 $N\,cm^{-1}$. A good tack force could reach up to 2.5 $N\,cm^{-1}$. This performance is competitive with commercial Scotch Magic tape and Fisherbrand labeling tape, demonstrating great application potential of this lignin-based polymer material.

4.3.4. Polyetheresters and polyesters through p-hydroxycinnamic derivatives

p-Hydroxycinnamic derivatives has been reported as a versatile building blocks for the construction of polyesters.[110] By employing the zinc molybdate catalyst supported on MCM-41, Song and co-workers[42] reported the efficient depolymerization of corncob lignin, whereby high selectivity of methyl coumarate and methyl ferulate (up to 78 %) was obtained. As shown in Figure 11, they first obtained the bisacetylene compounds through a two-step process including hydrolysis by LiOH, followed by the reaction with propargyl bromide. Finally, the polyetheresters were generated by the oxidative coupling polymerization with CuCl/TMEDA as catalyst in O_2 atmosphere. Instead of using a single compound, a mixture of methyl coumarate: methyl ferulate (1.4 : 1) was used as starting material and the corresponding polymer was obtained in 68 % yield with very good M_w value of 11471 $g\,mol^{-1}$. Another route via hydrogenation, hydroxyethylation and polycondensation afforded a series of aromatic polyesters with molecular weight of 5744–8664 $g\,mol^{-1}$.

4.3.5. Epoxy resins

Epoxy resins are widely used as thermosets due to their good thermal properties and easy combining with other curing agents.[111] Finding renewable resources for the synthesis of bio-based epoxy resins has attracted great attentions using lignin model compounds, such as vanillin and its derivatives.[112,113] Abu-Omar and co-workers reported that lignin and carbohydrate-derived monomers, including 4-methylcatechol, 5-hydroxymethylfurfural (HMF), and furfural could be used to prepare bisphenol-furan type polyphenols and further converted to epoxy networks via glycidylation and curing steps.[114] Recently van de Pas and Torr[107] reported that lignin monomers derived from lignin-first biorefinery were good candidates for the synthesis of bio-based epoxy resins. The starting material used in their research is the lignin oil obtained after reductive depolymerization of pine wood with Pd/C catalyst. The lignin oil was first extracted with dichloromethane and then diethyl ether. Epoxy prepolymers were then produced after reaction with epichlorohydrin. Finally, the prepolymers were cured with diethylenetriamine/isophorone diamine after blending with bisphenol A diglycidyl ether/glycerol diglycidyl ether. The obtained final polymers showed an increase of flexural modulus (up to 52 %) and flexural strength (up to 38 %). More importantly, by using lignin-derived epoxy prepolymers, 25–75 % of the bisphenol A diglycidyl ether could be replaced.

5. Summary and Outlook

In this Minireview, an overview of lignin-first biorefinery approaches that are capable of breaking native lignin into high yields of lignin monomers was first provided. This creative solution enables depolymerization of lignin in its native form into valuable target monomers. Integrated with several efficient separation methods, various aromatic monomers have been isolated. After obtaining these aromatic platform chemicals, producing valuable chemicals, fuels and materials has recently become a topic of great interest. Syntheses of valuable chemicals, including bulk chemicals (e. g., phenol, ethylbenzene and terephthalic acid) and fine chemicals (e. g., indane and various aromatic amines), have been accomplished. High-energy fuels can be directly produced through HDO of the complex lignin oils after depolymerization of native lignin. In addition to chemicals and fuels, making polymer building blocks and bio-based polymers is another important potential application. The unique structure of lignin monomers makes them excellent sources of high-performance polymer materials.

Although great developments have been achieved in recent years, making lignin a conventional feedstock for current industry processes remains a long and uphill journey. Delivering more valuable products and limiting the extra cost of current processes will be the main focus of future lignin-first biorefineries. To this end, more profound insight is desired regarding the following aspects: (i) For the depolymerization of native lignin, decreasing the total process cost, for example, by using cheap catalysts, mild reaction conditions, and easy-to-operate setups is crucial for further industrial-scale production. (ii) Downstream product purification requires more attention, especially for the production of fine chemicals. (iii) Searching for emerging products will be considered a continuous research focus in the near future and the sustainability of the whole synthesis pathway is also worthy of attention. (iv) Lifecycle assessment of the overall process should be carried out and a comprehensive comparison with current petroleum-based processes must be addressed. (v) Future lignin-first biorefinery process design should have a more comprehensive outlook while integrating depolymerization, separation, and utilization into the whole process and developing products that are responsive to market demands.

A decade ago, lignin, with its robust and complex structure, presented a significant challenge to academia, as well as industry. However, with great efforts of researchers worldwide, this “annoying guy” is gradually become our “good friend”. A series of remarkable developments in chemical research have made access to more well-defined chemicals from lignin possible. Therefore, future focus will definitely shift to finding innovative downstream processing strategies to produce valuable chemicals, fuels, polymers, and emerging functional materials. We believe that successful future development of lignin valorization strategies with multidisciplinary collaboration and efforts from both academia and industry will offer exciting prospects for new directions and give us a more sustainable chemical industry.

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Conflict of Interest

The authors declare no conflict of interest.

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