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Advances in lignin valorization towards bio-based chemicals and fuels: Lignin biorefinery

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Abstract:

Lignin is one of the most promising renewable sources for aromatic hydrocarbons, while effective depolymerization towards its constituent monomers is a particular challenge because of the structural complexity and stability. Intensive research efforts have been

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directed towards exploiting effective valorization of lignin for the production of bio-based platform chemicals and fuels. The present contribution aims to provide a critical review of key advances in the identification of exact lignin structure subjected to various fractionation technologies and demonstrate the key roles of lignin structures in depolymerization for unique functionalized products. Various technologies (e.g., thermocatalytic approaches, photocatalytic conversion, and mechanochemical depolymerization) are reviewed and evaluated in terms of feasibility and potential for further upgrading. Overall, advances in pristine lignin structure analysis and conversion technologies can facilitate recovery and subsequent utilization of lignin towards tailored commodity chemicals and fungible fuels.

Keywords: Circular bioeconomy; Waste to resources; Sustainable development; Waste management/recycling; Bio-based chemicals; Thermocatalytic depolymerization.

1. Introduction

Biomass conversion to valuable chemicals and biofuels is expected to make a significant contribution to the sustainability of energy supply (Chen et al., 2017a; Yu and Tsang, 2017; Petridis & Smith, 2018; Xiong et al., 2019). Lignocellulose is the most abundant form of biomass, mainly composed of varying portions of lignin, hemicellulose, and cellulose depending on biomass types (Shylesh et al., 2017). Over the years, hemicellulose (20-30%) and cellulose (30-40%) have been well studied, and some mature technologies have been industrialized for the production of biofuels and important chemicals from the (hemi)cellulose (Maki-Arvela et al., 2014; Xiong et al., 2017; Cao et al., 2018a). For example, cellulosic ethanol is the key emerging industry for 2nd generation bio-fuel (Yoo et al., 2017a), and our recent studies showcase vegetable/food waste-derived carbohydrates can be upgraded to chemical building blocks (Chen et al., 2017b; Chen et al., 2018; Yang et al., 2019; Yu et al., 2018; Yu et al., 2019).

Lignin, the largest renewable source of aromatics biopolymer on Earth, which accounts to 15 to 40% dry weight in most plants, however, is mostly regarded as a low-value by-product in most biorefinery processes (Cao et al., 2017). One major source of lignin is provided by the pulp and paper manufacturer, where only 5 % of waste lignin has been employed for low-grade fuel for heat and power applications through combustion (Cao et al., 2018b). Efficient lignin valorization from paper processing and biorefinery processes followed by targeted upgrading could significantly increase the economic viability and environmental sustainability (Rahimi et al., 2014; Wu et al., 2018).

The greatest challenge for the lignin-conversion technologies lies in the highly irregular polymeric structure. The complex three-dimensional amorphous polymer consisting of methoxylated phenylpropanoid units are relatively intractable (Li et al., 2015). Valorization of lignin often required organosolvolysis pretreatment of lignocellulosic biomass or enzymatic processing to isolate native lignin followed by hydrogenation/dehydrogenation to produce the desired aromatic products such as monomers, dimers, oligomers and bio-oil (Anderson et al., 2017; Qi & Su, 2014). However, the lignin isolated from different processes is varied in terms of molecular weight, polydispersity, solubility, abundance in functional groups, and type of inter-subunit linkages.

The physiochemical properties and structure difference can change lignin recalcitrance and impact the valorization of lignin. Several researchers articulated the impact of fractionation technologies on the subsequent product recovery, which underlined the key roles and advantages of native lignin with mild modified structure involved in subsequent valorization as well as bio-oil quality and yield (Anderson et al., 2019; Ragauskas et al., 2014). The aromatic monomers yield from direct hydrogenolysis of native lignin in biomass can reach up to 40%-50%, which is 3 to 10 times higher than that of the extracted lignin with the significantly modified structure (Shuai et al., 2016; Shao et al., 2018).

Recent studies have put forward energy-efficient biorefineries for high product yields by thermocatalytic approaches. The catalytic conversion strategies are mainly divided into acid/base catalyzed depolymerization, oxidative/reductive depolymerization, pyrolysis, and gasification (Shao et al., 2017; Wang et al., 2019a; Wang et al., 2019b; Luo et al., 2016). The advances in the catalytic processes have been based on the design of high-performance catalysts (e.g., well-defined and nanosized metal-composed materials) and advanced technologies, such as microwave assisted reaction, hydrothermal liquefaction, photocatalysis, mechanochemical depolymerization (Dabral et al., 2018b; Schutyser et al., 2018b; Sun et al., 2018). However, the poor stability of heterogeneous catalysts and complicated mechanism of homogeneous catalytic reactions need to be further studied. The bio-catalytic process is regarded as an eco-friendly approach for the lignin depolymerization by taking advantage of the mild condition and environmental adaptability (Xu et al., 2018). However, the required specific condition and additional purification have brought difficulties and challenges for industrial production (Zhang et al., 2016). Overall, the previous works have highlighted a broad vision of promising lignin valorization emphasizing fractionation technologies and catalytic conversion.

The importance of native lignin structure in biosynthesis has been gradually recognized, which could govern downstream conversion for value-added chemicals (Anderson et al., 2019; Lancefield et al., 2018; Zaheer & Kempe, 2015). Therefore, this review focuses on the interplay of following important aspects during the course of lignin valorization, where various depolymerization technologies were described in relation to initial lignin structures in order to establish structure-activity relationship in lignin valorization (Fig. 1): (i) lignocellulose fractionation: identification of the exact structure of lignin with various extraction process; (ii) lignin depolymerization: mechanistic understanding and depolymerization technologies towards valuable aromatics and fuels; and (iii) further upgrading towards targeted chemicals.

2. Lignin

2.1 Structure and properties

Lignin is mainly an irregular three-dimensional polymer created by free radical coupling among three monomers, syringyl (S), guaiacyl (G), and p-hydroxyphenyl (H) alcohol, which results in a variety of C-O and C-C linkages (Schutyser et al., 2018b). Unlike hemicellulose, where the biopolymer is relatively easy to be decomposed to pentose and hexose sugars with the typical polymerization degree in the range of 50-300 units, the highly polymerized lignin (up to 10,000 units) generates more rigid structure that is recalcitrant to chemical attack (Sun et al., 2018; Matsagar et al., 2017). The highly complex and unspecified structure of lignin has hampered lignin valorization for a long time. Structural studies revealed that β-O-4 linkage is the most representative linkage in the native lignin, which makes up approximately

50% of total linkages, together with other common bonding patterns including β-5 (1-12%), β-β (5-12%), 5-5 (1-9%), 4-O-5, and β-1 (Li et al., 2015; Pu et al., 2011). Therefore, the cleavage of β-O-4 has been a key for lignin depolymerization strategies.

The structure and composition of lignin largely depend on the source of biomass. For example, softwood lignin contains a high portion of G units (80% - 90%), hardwood lignin has a mixture of G (25%-50%) and S (50%-70%) units, and grass lignin comprises a mixture of G (25-50%), H (10%-25%), S (25-50%) aromatic units (Li et al., 2015). Structural analysis of lignin and identification of nature linkages in lignin are essential for its efficient valorization to renewable fuels, materials or chemicals. Typically, the S/G-rich lignin is favorable to maximize monomer yields in biorefining applications (Rahimi et al., 2014; Shuai et al., 2016) because high S/G ratio can lessen the formation of inactive C-C bonds which leads to undesired condensed lignin during lignin depolymerization (Anderson et al., 2019). The lack of S units and the rich of G units in lignin may predict the abundance of β-O-aryl ether linkages during fractionation, which may undergo fast monomer coupling again.

2.2 Structural characterization

Nevertheless, the precise structures of lignin are also subjected to the fractionation and extraction methods from lignocellulosic biomass. For example, the conventional kraft pulping process can damage lignin structure showing significantly reduced levels of native lignin linkages and increased content of phenolic groups (Lancefield et al., 2018). The lignin structural modification induced by fractionation conditions is an important aspect to be concerned before subsequent valorization to value-added chemicals. The presence of different functionalities and units in lignin, as well as the molecular weight and polydispersity, needs to be analyzed to tailor the lignin valorization. A variety of characterization methods can be applied for different purposes, for instance, gel permeation chromatography (GPC) to determine molecular weights, FTIR spectroscopy to identify functional groups (Anderson et al., 2016). More recently, nuclear magnetic resonance (NMR) spectroscopic techniques such as 1D ^{13}C, ^{31}P spectroscopies and 2D HSQC/HMQC correlation have been extensively used for the elucidation of lignin structure and functionalities (Gioia et al., 2018; Pu et al., 2011). These findings have clearly shown that distinctive lignin structures upon various extraction methods. Even though NMR can elucidate lignin subunit composition and lignin interunit linkage distribution, there is still a lack of effective analysis of intermediate products during the reaction. Advanced *in situ* characterization and theoretical calculation could provide detail understanding of molecular reaction dynamics in the complex biorefineries.

2.3 Solid effect of lignin and catalyst

Poor solubility of lignin inevitably hinders the mass transfer and reaction efficiency during conversion, which also induces the complexity of the liquid-solid multi-phase system. Heterogeneous catalysts such as metal-based catalysts (e.g., Ni, Cu, Fe, and Pt-based catalysts) have been widely adopted for hydrogenation/dehydrogenation of lignin to obtain aromatic monomers in view of their high selectivity and reactivity in cleavage of C-O and C-C bonds (Jongerius et al., 2013; Opris et al., 2017). However, the lack of effective contact between the solid catalyst and the biomass remains an issue, resulting in high energy-consumption mixing and limited conversion. In the current valorization system, employment of appropriate solvents and selection of the desired temperature is the key to overcome this limitation. A classical high temperature over 200 °C together with an organic solvent or under the assistance of acid/base is used to enhance the lignin solubility for subsequent conversion. However, the harsh conditions with high reaction temperature and high reaction pressure (H_2/O_2/N_2) make the active aromatic intermediates of lignin, such as reactive benzylic ketone at C_α position, susceptible to repolymerization and re-condensation (Shuai et al., 2016). Several strategies attempted to block reactive benzylic species to prevent the repolymerization, and the proposed mechanism will be described in detail below. Therefore, lignin depolymerization with a tradeoff between selectivity and activity remains a grand challenge for the production of value-added chemicals.

3. Fractionation

Separation of the desired composition from lignocellulose biomass is the prerequisite of lignin valorization. Extracting a soluble and uncondensed lignin substrate during biomass pretreatment can facilitate the production of lignin monomers and be compatible with other biorefining strategies. Research efforts are underway for: (i) maximal delignification and efficient removal of hemicellulosic fractions; (ii) advanced isolation of lignin in industrial applications for targeted components; and (iii) practical and efficient fractionation to improve biorefinery economic feasibility. Yet, lignin underwent organosolvolysis, enzymatic processing or recovered from pulping and paper industry presents various structures as a result of different fractionation methods, which indicate the potential influence on further valorization.

3.1 Modified lignin

Modified lignin is primarily obtained from pulping industrial processing known as Kraft lignin and sulfite lignin, where the lignocellulosic biomass undergoes harsh treatments of high temperature and strong acid or base to improve product recovery. For the acid sulfite pulping process, the high reaction temperature (120 ^{o}C - 160 ^{o}C) and application of SO_3^{2-} or HSO_3^- under the acidic environment (72% sulfuric acid for extraction of Klason lignin) can significantly destroy the structure of native lignin (Matsagar et al. 2018a). The incorporated sulfonate groups (4% - 8%) in the modified lignin can improve the water solubility. However, the formed sulfonate groups could lead to the poisoning of metal-based catalyst, which may inhibit the catalytic conversion of lignin to produce aromatic chemicals. The pulping process under the base condition is typically named as the Kraft process (Hu et al. 2018). The hydrogen sulfide and hydroxyl anions can break β-O-4 linkages at 160 °C - 180 °C, where repolymerization of C-C bond formation occurs simultaneously (Renders et al., 2016a). The obtained Kraft lignin has a lower molecular weight and enhanced water solubility as a result of decreased content in β-O-4 linkages and increased amount of OH groups, while the exceptionally stable C-C linkages in the modified lignin increase the difficulty to produce related aromatic monomers. Therefore, novel catalytic reaction for the efficient valorization of modified lignin to valuable chemicals and fuels should be developed. The native lignin produced more likely from an experimental scale possesses a higher content of β-O-4 and β-β linkages that favors C-O cleavage.

3.2 Native lignin

Employment of neutral and mild conditions in extraction facilitates the isolation of native lignin. Organic solvents such as alcohols and tetrahydrofuran have been utilized for promising biorefinery fractionation by improving biomass dissolution (Yoo et al., 2017b; Zhang et al., 2016). The high content of alcohol used in lignin extraction could suppress self-condensation and yield high-quality native lignin (Lancefield et al., 2017). NMR HSQC correlation analysis revealed that the native structure can be obtained from n-butanol isolated lignin, making them particularly suitable for depolymerization to aromatic monomers. Compared to the Kraft process, organosolv lignin is more environmental-friendly in terms of generating less amount of acid or base wastes. Ionic liquids have been recently regarded as green solvents to enhance biomass dissolution, which possesses multiple advantages including lower melting points, tunable physical properties, negligible vapor pressure, and outstanding thermal stability (Liu et al., 2016, Matsagar et al. 2018b). These advanced properties can benefit the extraction of native lignin under the mild condition. For example, Prado et al. demonstrated the extraction of native lignin using triethylammonium hydrogen sulfate at 120 °C, which was subjected to oxidative reaction and produced phenolic-rich bio-oil (Prado et al., 2016). Under these mild conditions, the native structure of lignin is protected from re-condensation.

Milled-wood lignin (MWL) is one of the most representative native lignin in the plant cell wall since it is isolated under room temperature in the absence of any strong acid or base species (Yang et al., 2016). The biomass is first ball-milled and then extracted by the mixture of 1,4-dioxane and water (96/4, v/v). The recovery of lignin is mainly associated with ball milling time, where the yield increases from 16 % to 60 % when the ball milling time increases from one day to one week. However, this method mainly focuses on the recovery of lignin, which also includes some compromises like time-consuming and introducing a large number of carbohydrates coupled with the isolated lignin. To obtain a higher purity of native lignin, cellulolytic enzyme lignin (CEL) obtained from MWL or lignin-carbohydrate complex which were treated with cellulolytic enzyme under the mild conditions (pH 4.5-5.0) is most favorable (Yoo et al., 2017b; Zhang et al., 2016). The overall yield of purified lignin can reach up to 50 % with a high content of β-O-4 linkages (84.4 per 100Ar), which depicts a comparative advantage in biorefining applications (Yang et al., 2016).

4. Lignin depolymerization

In this section, we provide the discussion of the catalytic depolymerization, mechanochemistry, photocatalytic, and thermal technologies for the conversion of various types of lignin. An overview of these state-of-the-art methods is shown in Fig. 2. The oxidative depolymerization of lignin mainly exhibited the production of syringaldehyde; and vanillin through oxidative cleavage is one of the oldest methods reported for lignin depolymerization (Sun et al., 2018). The vanillin yield depends on the oxygen concentration and pH of the system. Whereas the reductive depolymerization of lignin usually leads to the formation of aliphatic compounds mainly 4-propylcyclohexanol. The hydrogenation and deoxygenation carried out for birch wood sawdust produce a mixture of C8 and C9 cycloalkanes (Yan et al., 2008). The reductive depolymerization generally uses pure hydrogen gas, hydrogen donor chemicals (such as formic acid, sodium borohydride), or hydrogen donor solvents for the production fuels and bio-oil (Sun et al., 2018; Matsagar et al., 2019). The commercial Pd/C catalyst reported for the lignin fragmentation under ambient hydrogen pressure results in the formation of phenols and ethyl-substituted arenes (Gao et al., 2016). Similarly, the acid/base catalyzed depolymerization of lignin mainly produces bio-oil and phenolic lignin monomers as the main products (Deepa et al., 2014; Chaudhary et al., 2017). Furthermore, thermochemical methods such as pyrolysis and gasification used for lignin biomass leads to the production of bio-oil and syngas. Various methods used for lignin depolymerization shows that the product distribution, the types of lignin monomers produced, and their yields are heavily influenced by the method used for the lignin depolymerization.

Catalytic conversion of lignin for the sustainable utilization of biomass has drawn ever-increasing attention. The key points in the design of the efficient catalytic process is to maximize the value of starting materials while minimizing waste generation and energy consumptions. Summary of advancing catalytic strategies including acid/base catalyzed and oxidative/reductive depolymerization process are shown in Table 1 (Entry 1-4: acid-catalyzed depolymerization; entry 5-8: base-catalyzed depolymerization; entry 9-12: oxidative depolymerization; and entry 13-16: reductive depolymerization). Thus far, reductive depolymerization has primarily been employed for the catalytic conversion of native lignin in high activity and selectivity. However, the high reaction temperature and high pressure (H_2/N_2) required in the reductive reaction may lead to low functionalized aromatics unavoidably. Another important aspect for hydrogenation of lignin is the uncontrolled process in the presence of metal-based catalysts resulting in excessive hydrogenation of the aromatic rings.

In comparison, the oxidative depolymerization involved milder conditions, the attractive advantage is the production of functionalized aromatics that allows facile separation and subsequent valorization.

Most methods for lignin depolymerization still focused on the cleavage of β-O-4 linkage, which makes up about 50% of all linkages in native lignin and has a low bond dissociation 50-70 kcal/mol (Shuai et al., 2018). The cleavage of β-O-4 linkage generated aromatic monomers and reactive intermediates that are prone to subsequent repolymerization, forming bio-oil or biochar. The major challenge in developing efficient conversion of lignin is to prevent interunit C-C coupling by self-condensation and improve aromatic monomers yield. Intensive research efforts have been devoted to preventing repolymerization during lignin conversion. The addition of formaldehyde can block the reactive benzylic positions with a protecting agent during pretreatment, thus effectively preventing lignin condensation (Shuai et al., 2016). The oxidation of the C_α alcohol to a ketone can happen in the presence of formic acid at 110 °C, which yielded more than 60 wt% of aromatics by promoting cleavage of the β-O-4 linkage (Rahimi et al., 2014).

For the most abundant Kraft lignin by-product generated from paper industry byproduct, it contained 11.0 wt% of methoxy groups. The selective utilization of methoxy groups to produce valuable compounds may provide a new method for the comprehensive utilization of lignin resources (Table 1, entry 17-18). Recently, it has been reported that CO and water can react with methoxy group in kraft lignin and organosolv lignin to form acetic acid over $RhCl_3$ catalyst. This reaction was conducted in ionic liquids at a mild reaction temperature (120 °C-140 °C), and 87.5% yield of acetic acid without by-product can be achieved (Mei et al., 2017). In another case, 99% purity of terephthalic acid can be obtained by the de-methoxylation of lignin and the introduction of desired carboxy groups from obtained bio-oils (Song et al., 2019). The selective removal of methoxy in lignin enable the functionalization of complex aromatic chemicals into the target chemicals.

4.1 Acid/Base-catalyzed depolymerization

Dilute aqueous acids (e.g., H_2SO_4, H_3PO_4, and HCl), organic acids (e.g., formic acid) and solid acids (e.g., zeolite, and SiO_2-Al_2O_3 oxides) are known to catalyze depolymerization of lignin or lignocellulose at a mild temperature (Dong et al., 2014; Qu et al., 2015; Nandiwale et al., 2018; Wu et al., 2019). Introduction of dilute acid can improve the degree of delignification without significant structure destruction, and 40% of monomers yield was reached when using H_3PO_4 (Renders et al., 2016a). The proposed acid-catalyzed depolymerization mechanisms have been studied based on the native lignin (Lahive et al., 2016; Shuai et al., 2016). In the presence of solid acid catalysts, the amount of acidic sites over the catalyst surface and the pore structure has a strong impact on lignin deoxygenation. The FTIR and NMR studies identified that high yield (52% - 60%) of aromatic monomers can be attributed to the cleavage of β-O-4 and α-O-4 ether linkages over the solid acid catalysts in the H_2O/CH_3OH (1/5 v/v) solvent mixture (Deepa & Dhepe, 2014).

Base-catalyzed depolymerization can be achieved by using various inexpensive and readily available reagents, such as NaOH, KOH, K_2CO_3, CaO and MgO, which are known to promote delignification by breaking ester linkages combined with enhanced lignin dissolution (Stiefel et al., 2017; Yoo et al., 2017b; Zhang et al., 2018a). Base-catalyzed depolymerization can break down the β-O-4 linkages by two stages, i.e., aerobic oxidation of the Cα alcohol to the carbonyl group, and cleavage of β-O-4 bond followed by aromatic monomers formation (Dabral et al., 2018a; Schutyser et al., 2018b). Under the condition of a strong base, high reaction temperature and long reaction time may theoretically enhance the production of aromatic monomers, while the formation of solid residue also increases due to repolymerization. Severe repolymerization and oligomerization are the main problems in base-catalyzed reaction. In homogeneous reaction, the selectivity and yield of bio-based chemicals are particularly dependent on the reaction temperature, pressure, time, concentration of various base, and substrate/solvent ratio (Qi et al., 2017; Renders et al., 2016a). Regarding solid bases, the strength of basic sites plays an important role in the enhancement of bio-oil and aromatic monomers yield. The enhanced concentration of basic sites over the NaX (Si/Al 1.2/1) catalyst promoted the conversion of alkaline lignin to produce low molecular aromatic products (51% yield) with abundant functional groups (e.g., $-OCH_3$, -CHO, and $-CH_3$ groups) (Chaudhary & Dhepe, 2017).

4.2 Oxidative depolymerization

From a general point of view, oxidative depolymerization of lignin is a valorization strategy that focuses on producing polyfunctional aromatic compounds, ranging from aromatic aldehydes to carboxylic acids, such as vanillin, syringaldehyde, and aromatic acid, which are alternative to fossil fuels derived chemicals. The oxidative cracking reaction includes the cleavage of the β-O-4 bonds, C-C bonds, aromatic rings, or other linkages within the lignin. Homogeneous transition metal complexes, metal oxides, oxygen, and hydrogen peroxide are the most popular oxidative reagents. The presence of NaOH solution and hydrogen peroxide is required to increase the rate of lignin degradation and the yields of phenolic compounds (Dai et al., 2018; Prado et al., 2016). The high percentage of vanillin product was at approximately 350 mg/L under the microwave assisted oxidative reaction by using $Cu(OH)_2$ and Fe_2O_3 catalysts in a $NaOH/H_2O_2$ system (Panyadee et al., 2018). In this regard, the relatively low yield of oxidation of lignin is the major limitation.

Nowadays, most of the studies focus on the oxidation of lignin model compounds. The studies of diaromatic structures can provide a better understanding of the selectivity and activity of monomers in various reaction systems (Lahive et al., 2016). Both β-O-4 linkage and S/G ratios, strongly correlated to lignin structures and properties, have been considered as the key factors for a variety of monomer yields (Yoo et al., 2017a). The model compounds with specific β-O-4 linkage and varying S/G ratio were most commonly reported (Deng et al., 2015). When Co-based catalysts with nitrogen modified carbon support were applied in the oxidation of lignin model compounds, 96% yield of phenol was obtained without oxidative coupling (Luo et al., 2018). The reactivity of copper and vanadium-based catalysts for the oxidation of lignin model compounds were also explored, in which intermediate ketone benzoin methyl ether was formed over the vanadium catalyst and transformed into benzoic acid and methyl benzoate, whereas benzaldehyde and methyl benzoate were produced over the copper catalysts without intermediate formation (Sedai et al., 2011). The development of model compounds studies could provide insight into the reaction mechanism.

In contrast, industrial waste lignin contains mostly interunit C-C bonds, which are formed during biomass pretreatment or pulping processing with strong acids or bases. Higher bond dissociation energies of C-C bonds (75-118 kcal/mol) in comparison to those of C-O linkages (50-70 kcal/mol) poses challenges to lignin depolymerization under mild conditions. Commercial CoS_2 catalyst can break the inactive C-C linkage under reasonably low temperature (250 °C) (Shuai et al., 2018). A representative methylene-linked C-C model dimer achieved 88% yield of mainly two aromatic monomers within 1.5 h (Wang et al., 2016). A two-step strategy for oxidative cleavage of lignin C-C bond to aromatic monomers was employed under oxygen in acetonitrile. The first step was the conversion of β-O-4 alcohol to ketone and the second step was for the active and selective oxygenation of C_β-H. This oxidative process decreased the C_α-C_β (around 100 kJ/mol) bond energy, thus facilitating the cleavage of the C-C bond. Typically, the selectivity and activity based on the lignin model compounds showed extremely high values for producing monomers, which, however, may not be representative considering the high complexity of real lignin. New techniques for the most structurally relevant and well-defined lignin should be developed.

4.3 Reductive depolymerization

Reductive depolymerization is an effective strategy for lignin conversion owing to its excellent selectivity in lignin C-O and C-C bond cleavage (Van den Bosch et al., 2015). The products generated from this method own a high ratio of hydrogen to carbon (H/C), endowing it with great potential to produce bio-fuel. The char formation during lignin hydrogenolysis is relatively minor by reductive stabilization of reactive intermediates (Renders et al., 2016b). For instance, Pd/C catalyzed depolymerization can achieve up to 25 wt% yield of syringol/guaiacol chemicals and suggested no significant loss of activity and selectivity after four cycles (Ouyang et al., 2018). The use of H-donating solvents, such as formic acid, and other stabilizing compounds, such as alcohol, has recently been shown to cleave β-O-4 linkage and stabilize the resulting reactive species *via* reductive pathways (Shao et al., 2018; Wu et al., 2019).

Studies on non-precious-metal-catalyzed depolymerization of lignin are in promising progress. Low-cost nanosized MoOx/CNT for the hydrogenolysis of enzymatic lignin under H_2 atmosphere produced up to 47 wt% aromatic monomers (Xiao et al., 2017). Ni-based catalysts have been widely applied in the industrial catalysis due to its cost-efficient and high activity. For the reductive conversion of lignin, selectively cleavage of β-O-4 in the hydrodeoxygenation process can be promoted over Ni-based catalysts. HBEA zeolite with abundant Brønsted acid sites supported Ni-based catalysts could achieve selective hydrodeoxygenation of organosolv lignin to low molecular weight compounds (Kasakov et al., 2015). The proposed pathway of hydrogenolysis of β-O-4 bonds and aromatic rings to cyclic alcohols over Ni-based catalysts were identified by GC-MS and *in situ* IR analysis. Nevertheless, there are several studies on whether the addition of metal promotor to Ni catalysts has a positive effect on the catalytic activity. Previous studies reported that the “dilution effect” of NiFe alloy effectively reduce Ni particle size, thus providing more active sites for the reaction. Furthermore, the formed Fe^{2+}/Fe^0 redox cycle can contribute to maintaining Ni^0 state to improve the catalytic stability of Ni-based catalysts (Kim et al., 2017; Margossian et al., 2017). Bimetallic Ni-Fe/AC catalyst demonstrated high efficiency in β-O-4 cleavage from lignin model compounds without hydrogenation of aromatic rings. A yield of 39.5 wt% aromatic monomers and 88 % selectivity to propylguaiacol were achieved under H_2

atmosphere when using birch wood sawdust as the lignin substrate (Zhai et al., 2017).

Recently, a chemical reduction of lignin fragments isolated from the lignocellulosic biomass was reported using catalytic upstream biorefining (CUB) processes based on early-stage catalytic conversion of lignin (ECCL) (Rinaldi et al., 2016). This method offered two distinct easily-separable and stable fractions, i.e., highly-aromatic lignin (lignin oil) and holocellulose. The holocellulose can be utilized as a hydrogen source for hydrodeoxygenation (HDO) reaction through gasification. The lignin oil made by HDO reaction consists of aromatics or alkane fuels depending on the reaction conditions (Cao et al., 2018c). The ECCL offered a new way for the efficient deconstruction of lignocellulosic biomass with a high atom economy. The CUB process can be carried out using either inexpensive Rany Ni catalyst or noble metal-supported catalyst, which leads to a reduction of reactive lignin fragments (i.e., reactive functional groups are deactivated) such as reduction of aldehyde functional groups into alcohol.

The product distribution and yields of biomass-based chemicals significantly depend on the biomass type, catalyst type, and reaction conditions of depolymerization. The lignin with higher S-units require less severe reaction conditions so it allows for a higher lignin monomer yield (Rinaldi et al., 2016, Van et al., 2015). A higher number of S-units in lignin would decrease the repolymerization during the reaction. Furthermore, a higher concentration of S-units decreases the relative concentration of G-units, which reduces the complexity of the condensing units in lignin. The CUB based on ECCL is the best example of efficient catalytic delignification of lignin with higher S-unit concentration under less severe reaction conditions, thus it is a promising approach for lignin research in the future.

4.4 Thermal depolymerization

4.4.1 Microwave reaction

Microwave-assisted depolymerization is one of the most attractive techniques for the valorization of biomass owing to its rapid heating rate and energy efficiency (Yu et al., 2017b). Table 2 outlines advantages and disadvantages of various techniques for lignin depolymerization. Microwave irradiation provides heating directly inside the reaction medium *via* efficient hot spots, which are more amenable to produce three high-quality products: bio-oil, gas, and biochar (Fan et al., 2013; Luo et al., 2017; Zhou et al., 2018). Microwave-assisted solvolysis of lignin and other biomass has been widely investigated over suitable catalysts under relatively mild reaction conditions (< 200 °C) (Shao et al., 2017). In comparison with the traditional hydrothermal process, microwave-assisted depolymerization of lignin could give higher bio-oil yield (Zhou et al., 2018). Recently, microwave-assisted depolymerization of alkaline lignin was reported over hydrotalcite-based CuNiAl mixed oxides (Zhou et al., 2018), in which 60% of bio-oil was achieved at 160 ºC within 80 min. The bio-oil contains phenolic monomers such as guaiacol, p-hydroxyacetophenon, hydroxyacetovanillon, and syringaldehyde as the main products. Microwave heating was also used for the isolation of lignin from softwood with dilute H_2SO_4 (Zhou et al., 2017), which offered high lignin yield (82 wt%) and purity (93%) within 10 min at 190 ºC. This illustrates an advantage over conventional thermal treatments that usually take days. For the oxidative degradation of lignin model compounds, microwave irradiation could effectively accelerate the oxidative degradation rate (Pan et al., 2015). However, the scaling up of biorefinery using microwave heating requires further investigation as there are limited application experiences of industrial-scale reaction vessels.

4.4.2 Hydrothermal liquefaction

Hydrothermal liquefaction (HTL) of biomass comprises the thermochemical conversion of a broad range of bio-based materials into a liquid product using water, the greenest solvent, as the reaction media, thus representing a promising and sustainable option for biomass valorization (Qian et al., 2018; Zhang et al., 2019). This process is typically conducted under subcritical conditions: moderate temperatures (150-350 °C) and relatively high pressures (0.5-25 MPa) (Younas et al., 2017). HTL is a thermochemical route allowing the conversion of biomass into bio-oil (Cao et al., 2016). The choice of catalysts and solvents plays a critical role in determining to which degree delignification takes place and to what extent the lignin conversion (Renders et al., 2016a). A base catalyst is often added to enhance the performance of the HTL process. Depolymerization of Kraft lignin in subcritical water by using ZrO_2, K_2CO_3, and KOH as catalysts could yield high percentage of bio-oils (Belkheiri et al., 2018). Subcritical conditions (300-370 °C) were compared with supercritical conditions (390-450 °C) to further investigate the temperature effect on lignin decomposition, in which supercritical conditions tremendously increased the char formation although a higher degree of depolymerization was achieved (Yong & Matsumura, 2013). The HTL is a superior process than pyrolysis because bio-oil produced using the HTL process has relatively low oxygen content (i.e., high energy density bio-oil) than pyrolysis oil. Moreover, HTL can be used for wet biomass, unlike pyrolysis and gasification treatment that requires pre-drying of feedstock.

4.4.3 Pyrolysis and gasification

Pyrolysis and gasification are two of the most commonly used thermochemical methods for the conversion of biomass, lignin, and other residual waste into syngas, bio-oil, and biochar (Beneroso et al., 2017; Lee et al., 2017a; Lee et al., 2017b; You et al., 2017). Pyrolysis is often carried out in a range of 400 ºC to 800 ºC in the absence of oxidizing agents (oxygen or air) or under limited amount of oxygen/air (Yoo et al., 2018). The product distribution is greatly influenced by the temperature and time of pyrolysis. For example, in a slow pyrolysis (low temperature and long residence time) the charcoal yield increases while in fast pyrolysis (high temperature (>800 ºC) and short residence time (< 2 s)) the bio-oil yield increases with many lignin-derived aromatic products. The efficiency of fast pyrolysis reaction is dependent upon reaction temperature, residence time, sweep gas, and flow rate. Microwave-assisted pyrolysis can provide better quality bio-products in shorter timespan compared to conventional pyrolysis (Beneroso et al., 2017). Pyrolysis temperature and microwave irradiation time are the key factors to produce a high yield of bio-oil and low content of biochar (Dai et al., 2017). In pyrolysis the product selectivity is low and separation of product is a challenge, which may limit its practical application for lignin depolymerization.

The gasification provides an alternative for the production of synthetic petroleum from biomass through subsequent conversion of syngas using the Fischer–Tropsch process. Gasification is a thermochemical conversion by partial oxidation under high temperature (> 800 ºC) (Yang et al., 2018). For biomass gasification, using air as oxidizing agent provides the producer gas, while the use of pure oxygen as oxidizing agent provides the syngas. The presence of H_2 and CO in gasification can provide a reductive condition that is favourable for lignin depolymerization. Acid pretreatment helps to break down the highly complex structures of lignin and improve the quality of the bio-oil with high alkyl-phenols content (Duan et al., 2018). However, for the lignin gasification, the production of coke and tar from aromatics is the major problem (Kawamoto et al., 2017), which may require properly designed catalysts to address the issue.

4.5 Photocatalytic depolymerization

Current conversion strategies rely on high-temperature hydrogenation of lignin in presence of various metal-based catalysts. In nature, lignin is produced by photosynthesis and can be depolymerized to chemicals *via* photochemical reaction (Luo et al., 2016). There are few studies on the conversion of native lignin *via* solar energy-driven at room temperature. The β-O-4 linkages in the lignin structure could be cleaved by an electron-hole coupled photo-redox mechanism over the CdS quantum dots, while cellulose/hemicellulose remained almost intact (Wu et al., 2018). Photocatalytic oxidation of lignin model compound is reported by merging visible light photo-redox and Pd catalysis. This dual catalytic method exhibited an efficient oxidation of lignin model compound to high yield of oxidized products under room temperature (Kärkäs et al., 2016). Furthermore, the photocatalytic oxidation-hydrogenolysis of β-O-4 model compounds is reported through dual light wavelength switching strategy for the selective cleavage of the C-O bond (Luo et al., 2016). In this one-pot method, photocatalytic oxidation of α-C–OH bonds occurs over Pd/$ZnIn_2S_4$ while hydrogenolysis of C–O bonds happens over TiO_2–NaOAc. An organo.metallic Ir catalyst could reductively cleave β-O-4 ketones *via* light stimulation (Nguyen et al., 2014). The concept of using solar light energy at room temperature and atmospheric pressure *via* photocatalysis to selectively convert lignin into value-added chemicals represents an innovative route in terms of energy and environmental aspects.

4.6 Mechanochemical depolymerization

Mechanochemical activation generates high energy micro-environment due to the localized pressure and frictional heating provided by the kinetic energy (Muñoz-Batista et al., 2018). In comparison with the conventional thermal depolymerization, the mechanical process can significantly reduce the reaction time, which in turn is conducive to energy and cost savings. For the wet ball milling process, an oxidative approach to lignin depolymerization was used with potassium hydroxide and toluene (Yao et al., 2018). IR and HSQC NMR spectroscopies suggested two-step oxidative depolymerization of Kraft lignin. Meanwhile, mechanochemistry can provide solvent-free condition and unique chemical processes for various reactions. A mechanochemical oxidation and cleavage reaction in lignin β-O-4 model compounds and lignin catalyzed by HO-TEMPO/KBr/Oxone has been developed under milling conditions (Dabral et al., 2018b). A base-assisted ball milling process was also developed for the degradation of lignin (Kleine et al., 2013).

5. Upgrading towards desired chemicals

A variety of useful products can be produced from lignin depolymerization, which includes aromatic monomers, bio-oil, biochar, syngas, heat, and energy. Syngas can be further processed using the Fischer-Tropsch process into methanol, dimethyl ether, and other chemical feedstocks (Sikarwar et al., 2016; Zhang et al., 2018b). Biochar as a secondary product of bioenergy production can be applied in the environmental maintenance, electrochemical or catalytic reactions as the functional support due to its unique chemical structure and properties (Xiong et al., 2017; Zhang et al., 2017; Shaheen et al., 2018; Vikrant et al., 2018). A few of the monomeric compounds obtained from various depolymerization approaches can be applied as such in end-use applications. For instance, vanillin is the most available monoaromatic phenol currently produced at an industrial scale from lignin. Around 20000 tons of vanillin is produced per year, 15% of which coming from lignin (Fache et al., 2015). Thus, vanillin has the potential to be a key renewable aromatic building block. Nonetheless, many depolymerization methods give rise to substituted phenolic compounds that require additional transformation route to marketable chemicals. Low-cost separation and purification of pure compounds from these complex streams are technically challenging, while the obtained quantities of a single compound are generally low. The intensive approach is still needed for selective functionalization and de-functionalization process.

6. Future prospect

Biorefineries of cellulose and hemicellulose fractions from lignocellulose biomass are more mature than lignin biorefinery, while the latter is often regarded as a waste fraction from biorefinery processes. Therefore, a cost-effective integration of lignin biorefinery into the overall lignocellulose biorefinery can significantly enhance value and resource recovery and contribute to economic sustainability in the future. To achieve sustainable and cost-competitive lignin biorefineries, the following prospects for future research needs are underlined within the framework of this review:

(i) Identify the authentic structure of lignin upon various treatment methods. The structure and reactivity of the extracted lignin are probably governed by the biomass types and extraction methods. Further understanding of structure and development of structural characteristics is the key issue for efficient transformation and separation downstream. In addition to 2D-NMR, GPC, FTIR, GC-MS, and LC-MS analytic techniques, density-functional theory, and reaction mechanisms should be further explored.

(ii) Most existing industrial processing conditions, such as Kraft pulping and organosolvolysis methods for the production of bio-ethanol, significantly modify or damage the lignin and lead to a substantial loss of β-O-4 structural units. The main target is to maximally retain the native β-O-4 linkages in lignin and prevent the formation of inactive C-C bonds. Therefore, new fractionation methods that can deliver both high-purity sugars and native lignin streams in biomass separation should be developed.

(iii) The structure-activity relationship between lignin and its valorization products is still inconclusive. Many studies have been performed on pure and simple lignin model compounds such as phenol, guaiacol, and selected compounds with specific β-O-4 linkage, which urges to broaden the applicability of chemocatalytic conversions to more complex compounds and field-related lignin recovered from various industrial applications.

7. Conclusions

Lignin valorization technologies to produce value-added chemicals have attracted a great deal of attention. Lignin is a widely abundant, renewable feedstock comprising aromatic rings from nature. This contribution aims to critically review the state-of-the-art chemical and technical methodologies as well as the latest improvement of advanced analysis techniques and critical factors for efficient lignin depolymerization. This work also highlights the importance of future fractionation process that delivers native lignin, which can provide a competitive advantage for sustainable lignin valorization.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version.

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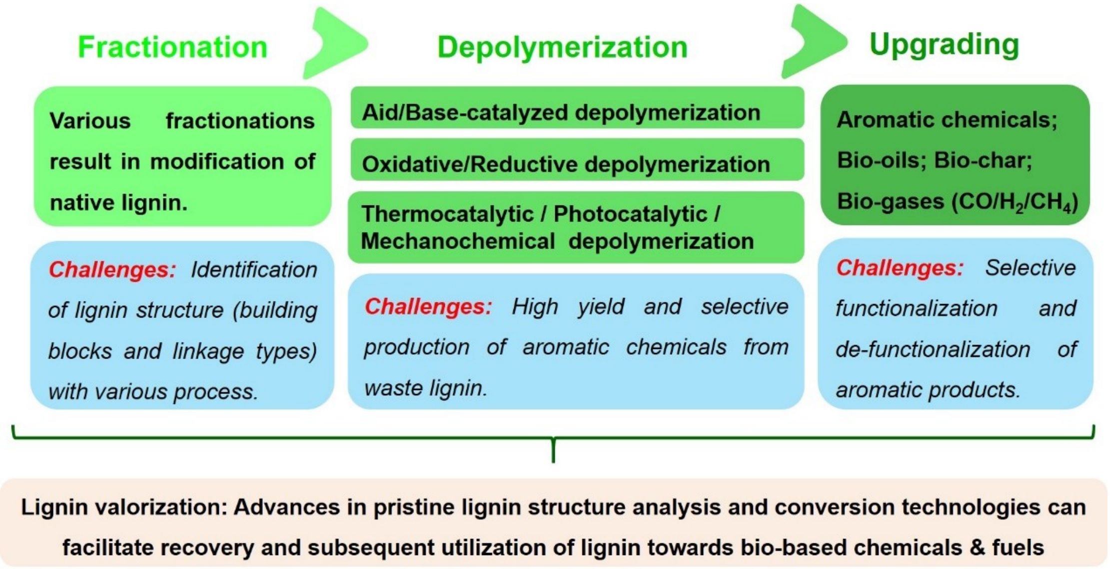

Fig. 1. Overview of lignin valorization.

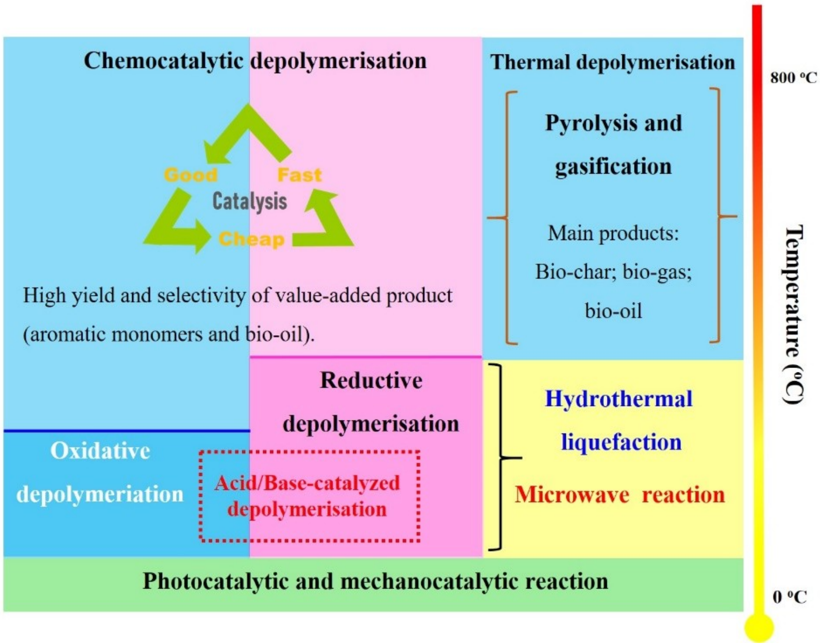

Fig. 2. An overview of depolymerization methodologies of lignin.

Table 1. Summary of various catalytic depolymerization of lignin/biomass

Entry	Substrates	Condition: Solvent; time; temperature and catalysts	Yield: Monomers and bio-oils	Ref.
1	Kraft lignin	Ethanol/1,4-dioxane/ formic acid; 300 °C, 2 h.	Monomers 25.4%; Bio-oils 55%	(Wu et al., 2019)
2	Pulping lignin	Formic acid; 160 °C 30 min.	Bio-oils 54 %	(Dong et al., 2014)
3	Organosolv lignin	Tetralin; 160 °C 30 min; Ni10%AlSBA catalyst.	Bio-oils 17 %	(Toledano et al., 2014)
4	Organosolv lignin	Acetic acid; 250 °C, 5h, N_2; Zr-KIT-5 catalyst.	Monomers 28 wt %	(Nandiwale et al., 2018)
5	Organosolv lignin	H_2O; 180 °C for 8 h Cs_2CO_3 catalyst.	Bio-oils 52-67 wt%	(Dabral et al., 2018a)
6	Alkaline lignin	Ethanol/H_2O; 250 °C, 1 h; NaX (Si/Al = 1.2).	Bio-oils 51 wt%	(Chaudhary & Dhepe, 2017)
7	Alkaline lignin	Ethanol/H_2O; 250 °C, 1 h; Na_2CO_3 catalyst.	Bio-oils 34 wt%	(Chaudhary & Dhepe, 2017)
8	Pulping lignin	Ethanol; 340 °C 4 h, N_2; Cu-Mg-Al mixed oxides.	Monomers 36 wt %	(Huang et al., 2015)
9	Poplar biomass	NaOH solution 175 °C, 30 min, O_2/ He.	Monomers 30 wt%	(Schutyser et al., 2018a)
10	Alkaline lignin	Methanol/formic acid; 160 °C, 30 min.	Bio-oils 72.0 wt% Monomers 6.7 wt%	(Shao et al., 2018)
11	Organosolv lignin	Methanol; 185 °C, 24 h, O_2; Pd/CeO_2 catalyst.	Monomers 8 wt%	(Deng et al., 2015)
12	Organosolv lignin	H_2O; 200 °C, 4 h, O_2; CoFeO mixed oxides.	Monomers 17.8 wt %	(Hdidou et al., 2018)
13	Bamboo biomass	Methanol; 260 °C, 4 h, H_2; Pt/C catalyst.	Monomers 32.2%	(Zhang et al., 2019)
14	Alkaline lignin	Ethanol; 340 °C, 4 h, H_2; $Cu+Ni_2P/SiO_2$ catalyst.	Monomers 53 wt %	(Koranyi et al., 2017)

15	Enzymatic lignin	Methanol; 260 ºC, 4 h, H_2; MoOx/CNT catalyst.	Monomers 47 wt%	(Xiao et al., 2017)
16	Corn stover	Methanol; 200 °C, 24 h; Ni/C catalysts.	Monomers 28 wt%	(Anderson et al., 2016)
17	Corn Stover	Toluene; 320 °C, 2 h, H_2; MoO_x/AC catalyst	De-methoxylation monomers 51 wt%	(Song et al., 2019)
18	Kraft lignin	$HMinBF_4$; 120 °C, 12 h, CO; $RhCl_3$ catalyst.	Acetic acid 87 wt%	(Mei et al., 2017)

Table. 2 Advantages and disadvantages of various techniques for lignin conversion

Techniques	**Advantages**	**Disadvantages**	**Ref.**
Microwave reaction	Rapid heating rate; Energy efficiency; Low temperature and pressure.	Difficulties of scaling up; Uncontrolled heating process; Energy consumption.	(Shao et al., 2018; Zhang et al., 2017)
Hydrothermal liquefaction	Mild reaction condition; Variety of biomass; Large-scale production.	Relatively inefficient convection; Water consumption.	(Lu et al., 2018; Yong & Matsumura, 2013)
Pyrolysis and Gasification	Flexibility of feedstock; Fast rates; High yield.	Harsh temperature; Non-selective conversion.	(Duan et al., 2017; Fan et al., 2018)
Photocatalytic reaction	Definite mild condition; Renewable source of energy.	Design of efficient catalyst; Technological barriers.	(Luo et al., 2016)
Mechanochemical reaction	Fast rates; Solvent-free; Flexibility of feedstock.	Non-selective depolymerization; Process complexity; High energy consumption.	(Yao et al., 2018; Dabral et al., 2018b)