Chapter 3
Degradation of Lignin by Depolymerization

Abstract This chapter mainly presents depolymerization of lignin to generate depolymerized lignin or oligomers with smaller molecules and higher reactivity as a potential feedstock for the synthesis of biopolymers. Depolymerization of lignin can be realized with various thermochemical methods including hydrolytic, reductive, and oxidative depolymerization. Possible mechanisms of thermal depolymerization of lignin for the generation of predominant products, and effects of operation factors such as the type of lignin, residence time, reaction temperature, concentration of catalyst, and composition of the reaction media (solvents) on the composition of the resultant products were discussed.

Keywords Depolymerization of lignin · Hydrolytic depolymerization · Reductive depolymerization · Oxidative depolymerization · Depolymerized lignin · Smaller molecules · Higher reactivity

3.1 General Introduction on Lignin Depolymerization

As discussed in the previous chapters, lignin is a macromolecule comprised of three phenyl-propanols i.e., p-hydroxyl-phenyl propanol, guaiacyl-propanol and syringyl-propanol, via primarily ether linkages (e.g., α-O-4, 5-O-4 and β-O-4) as well as some condensed linkage (e.g., 5-5, β-β, β-5 and β-1 linkages) [1, 2]. Lignin thus has great potential as precursors for aromatic (phenolic) chemicals for sustainable production of various bio-based chemicals and materials such as adhesives, polyurethane foams, flocculants and epoxy coating [3].

However, lignin has lower reactivity and high steric hindrance effect due to its large molecular weight and branched structure, which limits the direct use of lignin as chemicals. Several approaches have been taken to enhance reactivity of lignin [4]. One approach is through chemical modification of the chemical structure of lignin, e.g., phenolation or methylolation of lignin could improve the reactivity of lignin in the synthesis of lignin-based phenol formaldehyde resins [4]. The other more effective approach is through depolymerization to generate depolymerized

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lignin (DL) or oligomers with smaller molecules [5]. Using DL, biophenol–formaldehyde (BPF) resins of a phenol substitution ratio up to 75–90% was successfully produced in the authors' lab [5, 6].

Lignin de-polymerization methods mainly include biological method using enzyme and thermal method using heat (such as pyrolysis) and thermochemical methods using heat and chemicals [7–9]. Thermochemical depolymerization of lignin includes hydrolytic depolymerization using water and alkaline catalyst, reductive depolymerization using hydrogen, and oxidative depolymerization of lignin using in the presence of oxygen to produce aromatic aldehydes or carboxylic acids. Among those methods, biological process is a very slow process [1], while pyrolysis operated at 400–800 °C is fast, but lignin pyrolysis resulted in a low oil product yield (20–40 wt%) with high energy consumption in particular for wet feedstocks [2]. Thermochemical depolymerization of lignin operates under milder conditions requiring moderate temperatures (<400 °C) although under elevated pressure (up to 200 bar) commonly employing a catalyst [10].

This chapter focuses on lignin depolymerization via various thermochemical methods, i.e., hydrolytic, reductive and oxidative methods.

3.2 Hydrolytic Depolymerization of Lignin

Hydrolytic depolymerization process is performed in sub- or supercritical water to cleave the ether bonds of lignin in the presence of an acid or an alkaline catalyst, resulting in lower molecular weight oligomers or mono-phenolic compounds. The common operating conditions of lignin hydrolytic depolymerization processes are: in subcritical or supercritical water at 280–400 °C, 20–25 MPa, for a few minutes to few hours, at a water/lignin mass ratio of 2–50 with or without a base or acid catalyst [2, 7, 10]. Hydrothermal degradation of lignin produces various phenols, catechol, guaiacol, and other methoxy phenols through the hydrolysis of ether bonds. Further degradation of methoxy groups can take place, while the benzene ring is stable in this condition, as illustrated in Fig. 3.1 [10]. Additionally, heavier products, i.e., solid residue or char can be produced via the repolymerization/condensation of reaction intermediates at high temperatures and long reaction time during the hydrothermal treatment of lignin. The addition of catalysts such as K_2CO_3, $Ca(OH)_2$, and NaOH in water medium could reduce char formation and catalyze the lignin depolymerization [10]. Another effective way to improve lignin or DL solubility and prevent char formation is using a mixture of water with an organic solvent, e.g., water–ethanol [11, 12], water–methanol [13], water–butanol [14], water–phenol [15–17], water–isopropanol [18], water–acetone [19], and water–formic acid [20], etc. Severe formation of undesired biochar was observed in hydrothermal depolymerization of lignin in water at above 180 °C, and increased dramatically while further increasing temperature [21].

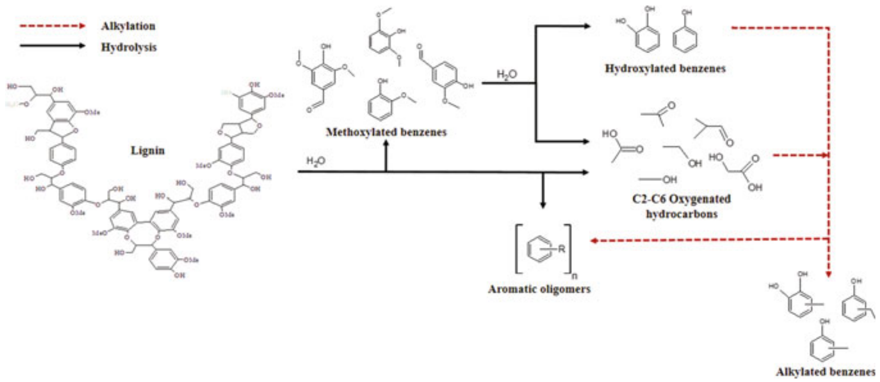

Fig. 3.1 Hydrothermal treatment of lignin, modified from Ref. [10]

To elucidate the mechanism of lignin hydrolytic depolymerization, lignin model compounds such as guaiacol have been investigated. For instance, in a study by Wahyudiono et al. [22], influences of reaction temperature and time were investigated on the product composition in hydrothermal treatment of guaiacol. The degraded products were mainly composed of catechol, phenol, and o-cresol at a maximum yield of 40.73, 14.18, and 4.45 wt%, respectively. With a longer reaction time, the compositions of both guaiacol oligomers (formed by repolymerization/condensation of reaction intermediates) and low molecular weight compound were found to both increase. From the kinetic analysis of the process at varying temperatures, the activation energy of the guaiacol decomposition and the formation of catechol, phenol, and o-cresol was reported to be approx. 39, 21, 65, and 180 kJ/mol, respectively. In a subsequent study by the same authors, catechol as another lignin model compound was hydrothermally treated in near- and supercritical water without any catalyst at temperatures of 643–693 K at various pressures [23]. Formation of phenol from catechol was found to proportionally increase with an increase in the water density. In addition, it was found that the decomposition of catechol followed a first order kinetics. The global rate constant in the range of $(3.0 \sim 11.0) \times 10^{-4}\ \mathrm{min}^{-1}$ and the activation energy was determined to be 50.72 and 38.91 J mol^{-1} in near-critial water and supercritical water, respectively.

As mentioned above, the addition of catalysts such as K_2CO_3, $Ca(OH)_2$, and NaOH in water medium could reduce char formation and catalyze the lignin depolymerization [10]. An alkaline lignin was hydrolytically degraded in hot-compressed water–ethanol mixed solvent system with NaOH as a catalyst and phenol as a capping agent at 220–300 °C by the authors' group [11]. With increasing the reaction time and temperature, the phenol combination rate and the solid residue yield increased due to the repolymerization and crosslinking between the reactive sties of the combined phenol and the side chains of the degraded lignin. The optimum degradation conditions were determined to be: 1 h at 260 °C with the lignin/phenol ratio of 1:1 (w/w), obtaining almost 100% yield of degraded lignin and negligible formation of solid residue (<1 wt%) and gaseous products. The molecular weight of alkaline lignin decreased significantly from $M_w \sim 60{,}000$ g/mol ($M_n \sim 10{,}000$ g/mol) to $M_w \sim 1000$ g/mol ($M_n \sim 450$ g/mol) under the optimum conditions. The base-catalyzed lignin degradation mechanism was proposed for this process. Initially, the phenol-OH groups of lignin were converted into phenolate anions under alkaline condition, followed by several electron migration steps, and a phenolate side chain was eliminated through hydrolytic cleavage of an ether bond to form a quinone intermediate. Then, the quinone intermediate reacted with a sodium phenolate forming a phenol capped product. Simultaneously, OH^- could react with another ether bond to hydrolyze phenol-alkyl ether causing the formation a phenol and alkyl alcohol. The capping reaction between phenol and lignin side chain was limited due to the presence of abundance of water in the reaction media. Mahmood et al. [12] investigated the hydrolytic depolymerization of hydrolysis lignin (HL) in water and water–ethanol mixed solvent at 250 °C for 1 h with 20% (w/v) HL concentration in the presence and absence of catalyst (H_2SO_4 or NaOH). The non-catalyzed process of HL in water–ethanol mixture seemed to be the best condition for depolymerization of lignin with high yield of 70 wt% and low molecular weight of $M_w \sim 1000$ g/mol. Acid catalyzed depolymerization of HL in both media increased the molecular weight of the depolymerized HL, suggesting acid catalyzed repolymerization reactions. Alkaline hydrolysis process of the KL led to a reduction in M_w in water media and an increase in M_w in water–ethanol mixture.

Erdocia et al. [24] investigated on the hydrolytic depolymerization process with three different organosolv lignins (acetosolv, formosolv and acetosolv/formosolv) under alkaline hydrolysis conditions, and the composition of the resultant bio-oil and residual lignin were analyzed by GC-MS, MALDI-TOF and GPC. The highest oil production was obtained from the acetosolv lignin, while depolymerization of formosolv lignin produced bio-oil with the highest content ($\sim 30\%$) of monomeric phenolic compounds such as catechol owing to the lowest M_w of this lignin.

Water–alcohol mixed solvents were commonly used for hydrolytic depolymerization of lignin due to its better performance than the water-alone medium. The role of the presence of an alcohol in the mixed solvent was investigated by Yoshikawa et al. [14], where an organosolv lignin and kraft lignin was subjected to hydrolytic depolymerization using water/butanol (BuOH) mixture (4:1 molar ratio) over silica-alumina at 537–623 K for 2–4 h. Depolymerization of lignin in the water phase over the Lewis acid sites of silica-alumina forms lower molecular weight liquid products such as monomers, dimers, and oligomers. Water/butanol mixture then played an important role in extraction of the depolymerized fragments such as phenolic compounds and carboxylic acids from the water phase into BuOH phase (as illustrated in Fig. 3.2), which prevented the occurring of the repolymerization/condensation reactions of the DL intermediates and hence reduced solid residue (char) formation in the process.

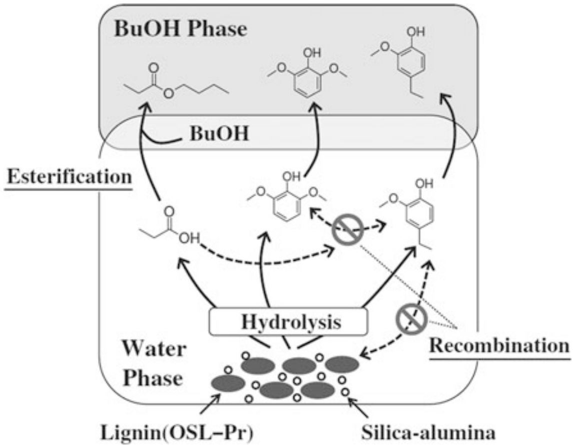

Fig. 3.2 Proposed reaction routes in the depolymerization of lignin using H_2O/BuOH mixed solvent over silica-alumina catalyst, reprinted with permission from Ref. [14]. Copyright (2013) Elsevier

In another similar study [25], hydrolytic depolymerization of various types of lignin was investigated in a novel water–butanol–hexane emulsion using an ionic liquid catalyst ($BSbimHSO_4$). This novel emulsion system was found to intensify the lignin depolymerization, under optimum conditions (0.5 g lignin, 20 mL of n-butanol, 20 mL of H_2O, 2 mL of n-hexane, 3 mmol of $BSbimHSO_4$, 523 K, and 30 min), approx. 90% of bagasse lignin was converted and the yield of desired phenolic compounds was about 30 mg/g, more than three times higher than that without the emulsion (mixed solvents). Hydrolytic depolymerization of other lignins (from rice straw, corn stalk and corncob) at the above optimum conditions led to >90% conversion of lignin, and a total yield of phenolic monomers >40 mg/g for the corn stalk or corncob lignin.

Base-catalyzed hydrolytic depolymerization of kraft lignin was performed in near-critical water (350 °C, 25 MPa) with K_2CO_3 (0.4–2.2 wt%) and water–phenol mixed solvent (approximately 4.1 wt% phenol), where 17% yield of phenolic monomers were obtained [26]. A rapid depolymerization of lignin was also conducted in water–phenol mixture at 400 °C without char formation [16]. After 0.1 h reaction, the molecular weight of lignin reduced from 2100 to 660 g/mol. With further increasing the reaction time to 1 h, the content of low molecular weight fragment increased and the DL showed 99% solubility in THF. The conversion of organosolv lignin was studied in supercritical water with or without phenol at 400 °C and various water densities in the range of 0–0.5 g/cm^3 [15]. Figure 3.3 shows the effects of phenol content in the water–phenol mixed solvents, reaction time and water density on the yield of tetrahydrofuran-insoluble products (TIS products or char). As shown in the Figure, the yield of TIS or char increased with increasing reaction time due to the repolymerization reactions of the reaction intermediates, but the TIS or char yield reduced by increasing the content of phenol in the water–phenol mixture solvent or by raising the water density.

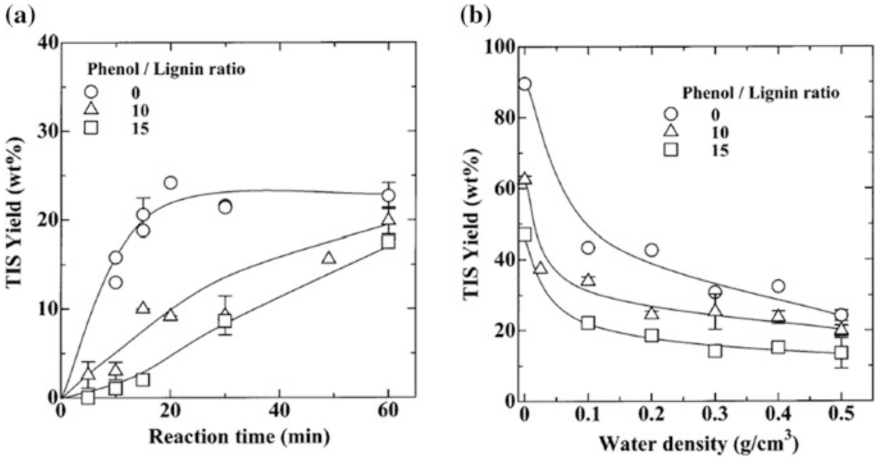

Fig. 3.3 Effects of phenol content (water density of 0.5 g/cm^3) (**a**) and water density (reaction time of 60 min) (**b**) on the TIS or char yield at 400 °C, reprinted with permission from Ref. [15]. Copyright (2003) American Chemical Society

3.3 Reductive Depolymerization of Lignin

Reductive depolymerization of lignin is realized by hydrogenolysis or hydrocracking in the presence of hydrogen and a supported catalyst, such as expensive carbon-supported Pt or Ru catalyst, at temperatures ranging from 300 to 600 °C to rupture the ether bonds of lignin by the addition of hydrogen [7]. The liquid products are mainly composed of volatile hydrocarbons together with phenol and methyl-, ethyl-, and propyl substituted phenol, catechols, and guaiacols [27]. At low temperatures, guaiacols are the dominant product with small amounts of aldehydes. While at high temperatures, the phenols are the more stable compounds with benzene, toluene, and xylene and the formation of char increases as well [27]. In reductive lignin depolymerization processes, hydrogen can be supplied externally in gaseous form [28, 29] or in situ via an active hydrogen donating solvents, such as formic acid [7, 20], 9,10-dihydroanthracene [30], sodium formate [20], and tetralin (1,2,3,4-tetrahydronaphtalene) [31].

3.3.1 Reductive Lignin Depolymerization in Hydrogen Donating Solvents or Reductive Agents

Many studies have demonstrated effective depolymerization of lignin using hydrogen donating solvents as in situ hydrogen source rather than external hydrogen source. Formic acid is an active hydrogen source as it decomposes at elevated temperature to produce hydrogen [32]. For instance, reductive depolymerization of kraft lignin (KL) was performed in an ethanol–water medium with formic acid as an in situ hydrogen donor by Huang et al. [7]. In this study, effects of various parameters such as reaction temperature, reaction time, concentration of formic acid, and ethanol concentration in ethanol–water reaction media were investigated to obtain the optimum reaction conditions. Formic acid decomposes to hydrogen and carbon dioxide at elevated temperature ($HCOOH \rightarrow H_2 + CO_2$). With increasing the concentration of formic acid, the molecular weight and polydispersity index (PDI) and solid residue (SR) reduced, accompanied by an increase in the yield of depolymerization (DL). The experimental results demonstrated that kraft lignin ($M_w \sim 10{,}000$ g/mol) was effectively converted into DL products of $M_w \sim 1270$ g/mol at a high yield of ~90 wt% (solid yield <1 wt%) at the optimum conditions (300 °C, 1 h, ethanol–water (50/50 v/v) and formic acid to lignin mass ratio of 0.7–2.4). The process also had a positive effect in reduction of the sulfur content from 1.5 wt% in the KL to 0.6 wt% in the DL product obtained under the optimum conditions.

Rahimi et al. [20] developed a novel process for depolymerization of oxidized lignin (aspen lignin) under mild conditions in aqueous formic acid with 60 wt% yield of aromatics of a low molecular mass. Oxidation of the C_α alcohol of lignin to a ketone was performed using stochiometric Mn or Cr oxide reagents to promote cleavage of the β-O-4 linkage (Fig. 3.4). While, the depolymerization of unoxidized lignin led to only 7.2 wt% yield of low molecular mass aromatics, depolymerization of oxidized aspen lignin under the formic acid/sodium formate reaction conditions at 110 °C for 24 h led to 52% lignin depolymerization efficiency, producing 19.8 wt% yield of well-known aromatic compounds, mainly syringlyl and guaiacyl-derived diketones, and 4 wt% yield p-hydroxybenzoic acid. The mechanism of cleavage of C–O linkages of the oxidized model compound is illustrated in Fig. 3.5 based on a redox-natural process without net consumption of formic acid.

Feghali et al. [33] reported reductive depolymerization of lignins using hydrosilanes and $B(C_6F_5)_3$ as a reductant and a Lewis acid catalyst, respectively, at ambient pressure and temperature. Hydrosilane contains slightly polar Si–H bonds which can be activated at low temperature to reduce C–O linkages. The Lewis acid catalyst enhances the reduction of a diverse carbonyl derivatives such as ketones, esters, amides, and carbonates. Lignin was converted into a liquid bio-oil with a low oxygen content for motor fuel application via one-step pyrolysis/solvolysis process

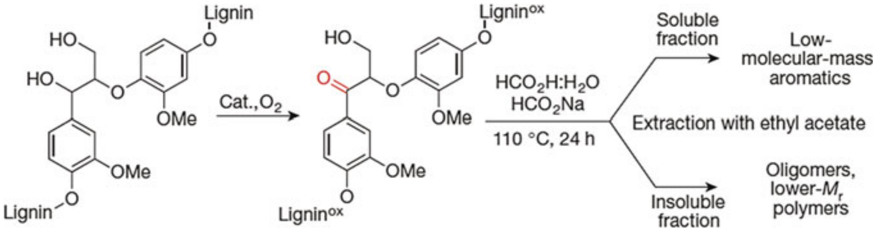

Fig. 3.4 Depolymerization of oxidized aspen lignin using formic acid, reprinted with permission from Ref. [20]. Copyright (2014) Nature Publishing Group

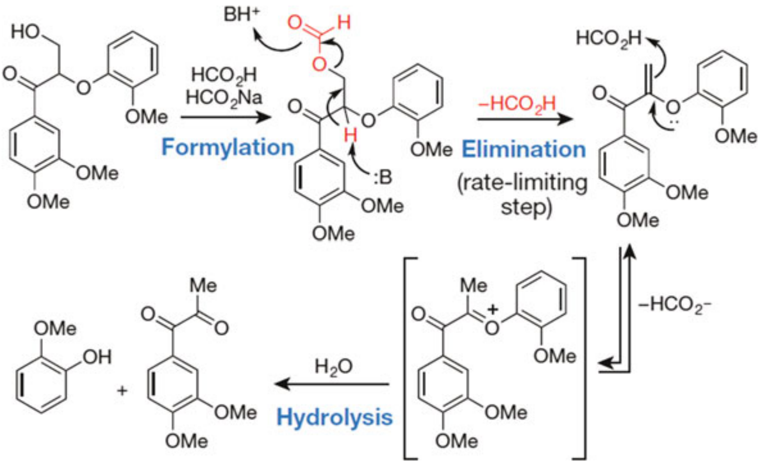

Fig. 3.5 Possible mechanism of cleavage of C–O linkages on the oxidized lignin model compound, reprinted with permission from Ref. [20]. Copyright (2014) Nature Publishing Group

in formic acid/alcohol mixture [34]. In this process, both depolymerization and deoxygenation occurred at the same time. Formic acid was used as a hydrogen source and alcohol acted as a solvent to improve the yield of bio-oil and the H/C (hydrogen to carbon) ratio with small amount of coke formation (5%).

A switchgrass lignin was depolymerized into phenolic monomers using formic acid as hydrogen source, ethanol as a solvent over 20 wt% Pt/C catalyst [35]. It was observed that the reaction time was predominant factor controlling the yield and composition of the DL products. After 4 h reaction, 21 wt% of lignin was converted into phenolic monomers including phenol, p-cresol, guaiacol, p-methylguaiacol, p-ethylguaiacol, p-propylguaiacol, and homovanillyl alcohol. With a longer reaction time (20 h), the yield of liquid-phase reached 76 wt% and the obtained liquid DL products had better quality with reduced O/C molar ratio by 50% and increased H/C molar ratio by 10%. Another similar work was reported by Huang et al. [36] in which supercritical ethanol was used as a hydrogen-donor solvent as well as a capping agent, stabilizing the highly reactive phenolic intermediates by O-alkylating the hydroxyl groups and by C-alkylating the aromatic rings. $CuMgAlO_x$ acted as an inexpensive catalyst. Ethanol was found to be more effective than methanol in depolymerization of lignin.

Organosolv lignins from hardwood and wheat straw were effectively depolymerized in supercritical carbon dioxide/acetone/water mixed solvent medium in the presence of low content of formic acid as hydrogen donor at 300 °C and 100 bar into monomeric aromatic compounds (10–12 wt% yield) [19]. The process is similar to other base-catalyzed lignin depolymerization processes, producing phenolic monomers rich in syringic acid and syringol (at a yield of ∼4 wt%) with wheat straw lignin and organosolv hardwood lignin, respectively.

The so-called Lignin-to-Liquid (LtL) process was reported by Kleinert and Barth [30], where lignin was depolymerized/liquefied to produce monomeric phenolic compounds at 350–400 °C in the presence of formic acid–isopropanol/ethanol mixed solvents. The liquid products were exclusively composed of monoaromatic phenols with several alkylations varying from C_1–C_2 side chains. The yield of the isolated phenolic fraction was as high as 25–35 wt% of the original lignin. Additionally, it was observed that the effects of temperature and residence time on the product yield were negligible.

Tetralin with capability of reversible hydrogenation/dehydrogenation can also be used as a hydrogen donation solvent for the liquefaction of lignin [10]. For instance, Thring et al. [37, 38] investigated conversion of an organosolv (ethylene glycol) hardwood lignin in the presence of tetralin over nickel–tungsten catalyst at temperature of 370–410 °C. Up to 60% of lignin was converted into various phenolic monomers, depending on reaction conditions. At harsh reaction conditions, lignin was mainly degraded into phenol, catechol, and their methyl and ethyl derivatives, while at mild reaction conditions, the dominant products were syringols, guaiacols, aromatic aldehydes, and ketones. The addition of nickel–tungsten heterogeneous catalyst could slightly improve the yield of monomeric phenolic compounds. The effects of tetralin were also studied on liquefaction of kraft lignin with molten $ZnCl_2$-KCl catalyst at 400–700 °C [39]. The results revealed that the addition of tetralin would produce hydrogen radical that can participate in the depolymerization of lignin, forming phenolic monomers (such as p-cresol, m-cresol, o-cresol, phenol, 2,5-xylenol, and 2,6-xylenol). Compared with the neat pyrolysis process, the introducing of 4 mol% tetralin improved the yield of phenolic monomers attained the maximum at 600–650 °C.

3.3.2 *Reductive Lignin Depolymerization in Gaseous Hydrogen*

External hydrogen sources or gaseous hydrogen has been commonly utilized for reductive depolymerization of lignin [10], and the presence of hydrogen contributed to significantly suppress the char formation and alter the yield and composition of the DL products [27]. Heterogeneous metal catalysts (commonly expensive noble metals such as Ru, Pd, Rh, and Pt) have been widely used for promoting hydrogenation/hydrogenolysis reactions in lignin depolymerization with hydrogen through activating hydrogen [10].

A novel two-step process was proposed by Yan et al. [40] for degradation of lignin over noble metal catalyst such as Ru/C, Pd/C, Rh/C, and Pt/C. In the first step, catalytic cleavage of C–O–C linkages in lignin takes place in water or dioxane/water (v/v = 1:1), to produce lignin monomer,dimer and oligomer fragments. In a second step, the formed fragments are undergone hydrogenolysis reactions to transform into C_9 and C_{14}–C_{18} alkanes and methanol byproduct, as illustrated in Fig. 3.6. Over Pt/C catalyst at 200–250 °C with 4 MPa H_2 for 2 h, the

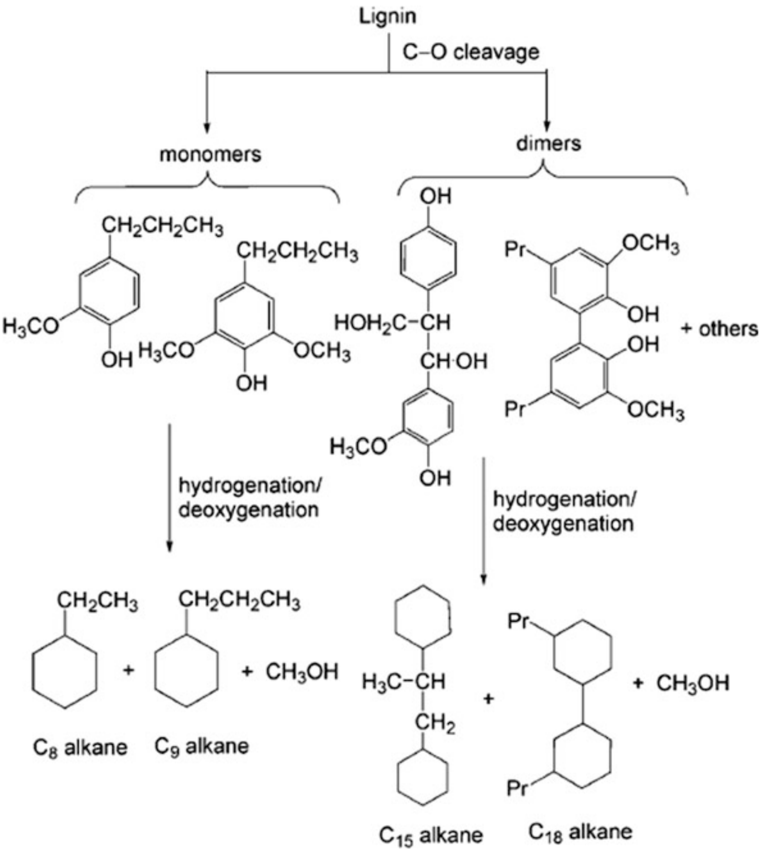

Fig. 3.6 Conversion of lignin into alkanes and methanol by hydrotreatment, reprinted with permission from Ref. [40]. Copyright (2008) John Wiley and Sons

highest yield of monomers and dimers attained 33.6 and 8.7 wt%, respectively, with a total yield of over 42 wt%. Incorporation of H_3PO_4 (0.2 wt%) into the reaction system further enhanced the yields of monomers to 37.9 wt% and dimers to 9.9 wt%. Addition of a co-solvent such as dioxane or ethylene glycol mono ethyl ether could also improve the yields of monomers and dimers.

Reductive depolymerization of organosolv lignin (OL) with gaseous hydrogen was performed by the authors [41]. In this process, OL was dissolved in acetone in the presence of Ru/C as a catalyst and reacted for 1 h at 350 °C at the initial pressure of 100 bar H_2. The resulting viscous liquid product was designated as depolymerized organosolv lignin (DOL) rich in phenolic monomers, and the yield of DOL in this reductive depolymerization process was as high as 85 (±2) wt%. In a similar study, a pyrolytic lignin was undergone hydrotreatment in dodecane solvent for 1 h at 350 °C with 100 bar hydrogen pressure with Ru/C catalyst [31], producing cyclohexanol, alkyl-substituted cyclohexanols, cyclohexanol and linear alkanes that can be used as a fuel additive. The effects of other catalysts such as Ru/ZrO_2/SBA-15 and Ru/SO_4^{2-}/ZrO_2/SBA-15 were examined on the hydrocracking of pyrolytic lignin at 260 °C in supercritical ethanol [42]. A small amount of pyrolytic lignin was converted to coke or tar and the liquid fuel was the predominant product with a high heating value of 34.94 MJ/kg. The liquid product consisted mainly of phenols, guaiacols, anisoles, esters, light ketones, alcohols, and long-chain alkanes, among others.

In addition to the supported noble metal catalysts, molybdenum proved to be an inexpensive but effective catalyst for reductive degradation and hydrotreatment of lignin [43]. In a study by Cheng et al. [44], reductive depolymerization of alkali lignin (AL, $M_w \sim 60{,}000$ g/mol) was investigated in sub/supercritical conditions of water–ethanol (50/50 v/v) and pure ethanol at 200–450 °C under 5 MPa H_2 with or without a catalyst. Various catalysts such as Ni10/Al_2O_3, Ru10/Al_2O_3, Pt10/AC, Ru10/AC, and Ni10/AC, prepared by the incipient wetness impregnation method, were used. Although the addition of the catalyst in either solvent systems had less significant effect on the yield of DLs, the DLs exhibited improved solubility in tetrahydrofuran likely owing to its lower molecular weight. Degradation of AL at 300 °C for 2 h without catalyst in 50/50 v/v water–ethanol mixture produced DL with M_w of $\sim$1000 g/mol at 89 wt% yield. Meier et al. [45] reported a study on catalytic hydropyrolysis of organocell lignin in a semi-continuous reactor, where it was found that oil yield was significantly affected by hydrogen pressure and the total oil yield (middle and light oils) attained over 80 wt% at 400 °C, 14 MPa H_2, for 360 min using inexpensive catalysts, i.e., nickel or chromium oxide supported on alumina/silicate. Nickle-based catalysts demonstrated to be very effective for production of phenolic monomers (such as propylguaiacol and propylsyringol) by reductive depolymerization of a birch wood lignin in an alcohol such as methanol, ethanol, and ethylene glycol under H_2 [46]. The mechanism of lignin degradation in an alcohol solvent was proposed to be through a two-step process. Firstly, lignin thermally decomposes into smaller lignin fragments, and the second step involves the hydrogenolysis cleavage of the fragments into monomer phenols. In addition, NiAu catalyst was found to be an efficient catalyst for hydrogenolysis of organosolv lignin in pure water at a low temperature (170 °C), yielding 14 wt% aromatic monomers [47].

One strategy for reducing the cost of noble metal catalysts may be addition of an inexpensive homogenous catalyst (such as H_2SO_4) as a co-catalyst together with a noble metal catalyst for lignin depolymerization. For instance, Pt/Al_2O_3 and H_2SO_4 as a co-catalyst demonstrated to be effective in reductive depolymerization of lignin in water/ethanol solvent, yielding 17 wt% of monomeric guaiacol-type products, compared to less than 6 wt% yield with the Pt/Al_2O_3 catalyst only. Another strategy for reducing the cost of noble metal catalysts can be addition of an inexpensive metal to a noble metal, to form bimetallic catalysts. For instance, Zhang et al. [48] developed a series of bimetallic catalysts such as NiRu, NiRh, and NiPd and tested them in the hydrogenolysis of lignin in water medium. It was found that NiRu catalyst, composing of 85% Ni and 15% Ru, had a synergistic effect on depolymerization of β-O-4 ether bonds under low temperature (100 °C) and low H_2

pressure (1 bar) owing to the increased concentration of surface metallic atoms, enhancing H_2 and substrate activation. Similarly, other bimetallic catalysts: NiRu and NiPd also exhibited better reactivity and selectivity for the hydrogenolysis of lignin, compared to their single-component counterparts. Tungsten phosphate (WP) based-catalyst was found to be active for hydrogenolysis of alkaline lignin in water–ethanol solvents [49], where doping Fe and Ni into WP/C catalyst, resulted in increased selectivity of phenols formation while the overall yield of phenol reduced.

Other novel inexpensive supported metal catalysts, such as Cu-doped porous metal oxide derived from an easily prepared hydrotalcite precursor [50], activated carbon-supported α-molybdenum Carbide catalyst (α-MoC_{1-x}/AC) [51], and Ni-supported double layered hydrotalcite [52], were reported in the literature for reductive depolymerization of lignin for the production of aromatic monomers at 250–300 °C.

3.4 Oxidative Depolymerization of Lignin

Oxidative depolymerization of lignin is realized by oxidation or oxidative cracking of the lignin macromolecule due to the presence of hydroxyl groups [2, 27]. Various linkages of lignin such as aromatic rings, aryl ether bonds could be cleaved to form phenols, aromatic aldehydes or carboxylic acids, depending on the reaction conditions [2, 53]. Nitrobenzene, hydrogen peroxide, and metal oxides such as CuO, Fe_2O_3 are the most common oxidants for lignin depolymerization [2, 8, 27]. Figure 3.7 shows a proposed mechanism for the oxidative depolymerization of lignin by molecular oxygen as the oxidizing reagent [27].

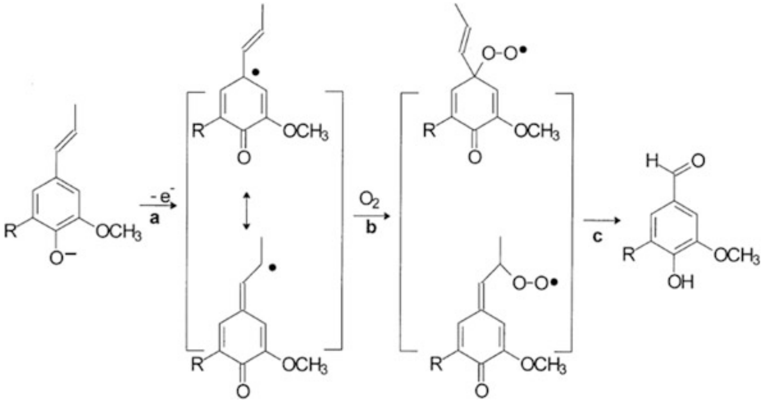

Fig. 3.7 A proposed mechanism for the oxidation of lignin, reprinted with permission from Ref. [27]. Copyright (2000) Elsevier

Oxidative degradation of five types of lignin including pyrolytic lignin, hydrolytic lignin, alkali lignin, sodium lignosulfonate, and calcium lignosulfonate was examined over $H_5PMo_{10}V_2O_{40}$ catalyst using molecular oxygen [54]. Effects of the property of lignin, reaction temperature, reaction time, concentration of catalyst, solvent, and initial O_2 pressure were evaluated. The oxidative depolymerization of pyrolytic lignin produced the best yield of aromatic DL product (over 65 wt% at the optimal conditions). The applied catalyst was recyclable and reused for five times without obvious deactivation.

In another study by Hasegawa et al. [55], hydrothermal oxidation of various types of lignin was performed to produce organic acids in the presence of diluted hydrogen peroxide as an oxidant at 150–200 °C. The mechanism of production of organic acids by hydrothermal oxidation of lignin was proposed and illustrated in Fig. 3.8. The treatment of alkali lignin at 200 °C for 2 min led to production of organic acids, namely formic, acetic and succinic acids, at an overall yield of 0.45 g/g, and the remaining was DL product with M_w >1000 g/mol. While the oxidative depolymerization of organosolv lignin gave the total yield of organic acids of 0.2 g/g and DL product with a smaller M_w ~300 g/mol. Thus, the molecular structure of original lignin played a considerable role in the distribution of the DL products.

Lignin was oxidatively depolymerized by polyoxometalates in the presence of ethanol or methanol as a solvent, and polyoxometalates (POM) such as $H_3PMo_{12}O_{40}$ acted as reversible oxidants and radical scavenger to prevent repolymerization

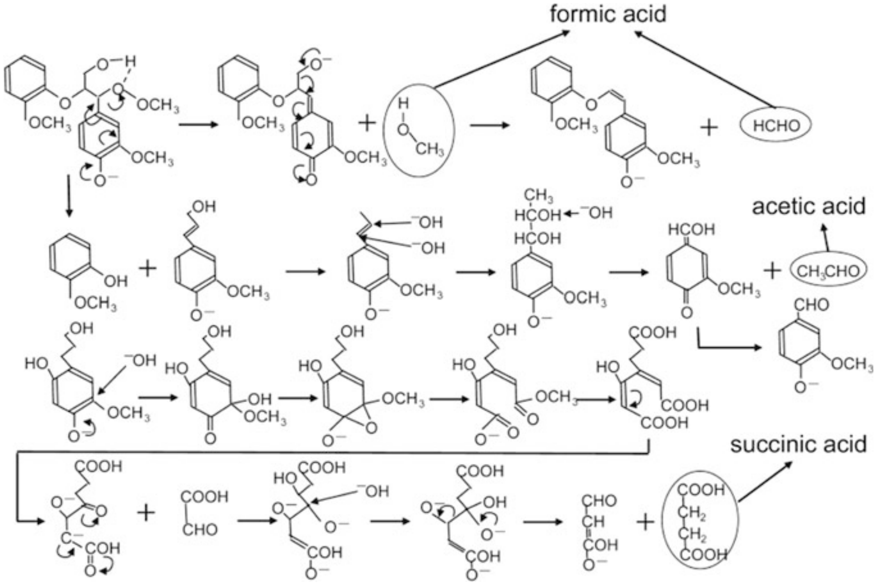

Fig. 3.8 Proposed mechanism for formation of organic acids, reprinted with permission from Ref. [55]. Copyright (2011) American Chemical Society

reactions [56]. The addition of ethanol or methanol into aqueous $H_3PMo_{12}O_{40}$ media greatly improved the production of monomeric compounds by a factor of up to 15. The main species in the obtained products were in vanillin and methyl vanillate (in methanol/water mixed solvent) as well as ethyl vanillate (in ethanol/water mixture). The yields and distribution of vanillin and methyl vanillate products from kraft lignin at 170 °C for 20 min in the presence of methanol–water versus water, POM ($H_3PMo_{12}O_{40}$) versus H_2SO_4, and N_2 versus O_2 atmosphere are comparatively shown in Table 3.1. The results in the Table clearly show that the presence of alcohol, $H_3PMo_{12}O_{40}$ or O_2 atmosphere remarkably enhanced the yields of vanillin and its derivatives. The oxidative depolymerization of kraft lignin at 170 °C for 20 min in the presence of methanol–water (16/4, v/v), $H_3PMo_{12}O_{40}$ and O_2 atmosphere produced a combined yield of vanillin and methyl vanillate at 5.18 wt% in relation to the weight of dry lignin employed.

Various transition metal catalysts in ionic liquids were applied in oxidative depolymerization of beech lignin [57]. $Mn(NO_3)_2$ in 1-ethyl-3-methylimidazolim trifluoromethanesulfonate [EMIMI][CF_3SO_3] was found to be the most effective reaction medium for the lignin oxidation process. Beech lignin was converted into phenol, unsaturated propylaromatics, and aromatic aldehydes at the maximum yield of 66.3% after 24 h reaction at 100 °C in 84×10^5 Pa air. Zakzeski et al. [58] reported the catalytic oxidation of Alcell lignin, soda lignin, and lignin model compounds over several transition metal catalysts in the ionic liquid 1-ethyl-3-methylimidazolium diethylphosphate (EMIM DEP). Under mild conditions, $CoCl_2 \cdot 6H_2O$ in EMIM DEP showed the best performance for the lignin oxidation. The 5-5′, β-O-4, and phenylcoumaran linkages remained unchanged during the oxidation reaction, while benzyl and alcohol functional groups were severely decomposed. A comprehensive study was conducted to elucidate the reactions involved in oxidative conversion of several lignin model compounds:

Table 3.1 Production of vanillin and methyl vanillate from kraft lignin at 170 °C for 20 min, reprinted with permission from Ref. [56]

Acid	Solvent (mL)		pH		Gas	Products (mg)		Yield[a] (%)
	H_2O	MeOH	Start	End		Vanillin	Methyl vanillate	
H_2SO_4	20	0	1.13	0.98	N_2	0.47	0	0.26
POM	20	0	1.13	0.91	N_2	3.35	0	1.84
H_2SO_4	4	16	1.00	1.17	N_2	1.06	0.80	1.01
POM	4	16	1.15	1.27	N_2	1.06	1.3	1.29
H_2SO_4	20	0	1.11	0.95	O_2	2.17	0	1.18
POM	20	0	1.13	0.92	O_2	4.49	0	2.45
H_2SO_4	4	16	1.13	1.28	O_2	2.94	2.12	2.76
POM	4	16	1.13	1.24	O_2	4.99	4.51	5.18

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[a] Combined amount of vanillin and methyl vanillate divided by the weight of dry lignin employed

veratryl alcohol, cinnamyl alcohol, and a model compound with a β-O-4 linkage in the presence of cobalt catalyst and ionic liquids by in situ ATR-IR, Raman, and UV–Vis spectroscopy [59]. Figure 3.9 displays the possible reactions and products from oxidation of each lignin models.

Compared to the above mentioned heterogeneous and homogenous catalytic processes, electrochemical catalysis processes could be efficient for depolymerization of lignin without using any complex organometallic catalysts, hence it could be a cheaper and more environmentally friendly method. For instance, electro-catalytic oxidative depolymerization of an alkali lignin was performed in triethylammonium methansulfonate as a protic ionic liquid (PIL) using anodes coated with oxidation-stable ruthenium–vanadium–titanium a potential ranging from 1.0 to 1.5 V [60]. Lignin was successfully cleaved into a wide range of aromatic fragments including 3-methylfuran, 3-furaldehyde, benzaldehyde, acetovanillone, m-tolualdehyde, guaiacol, 2,6-di-tert-butyl-4-methyl-phenol, diphenylether, 2-methoxy-4-vinylphenil, syringol, and vanillin. The product composition are strongly affected by the applied potential, and with increasing the potential, low molecular weight aromatic compounds became the predominant products in the electro-catalyst process. Figure 3.10 illustrated a possible mechanism of the electro-catalytic oxidative cleavage of the lignin C_{α}–C_{β} bond, involving the formation of H^+ and a proton conducting ionic liquid.

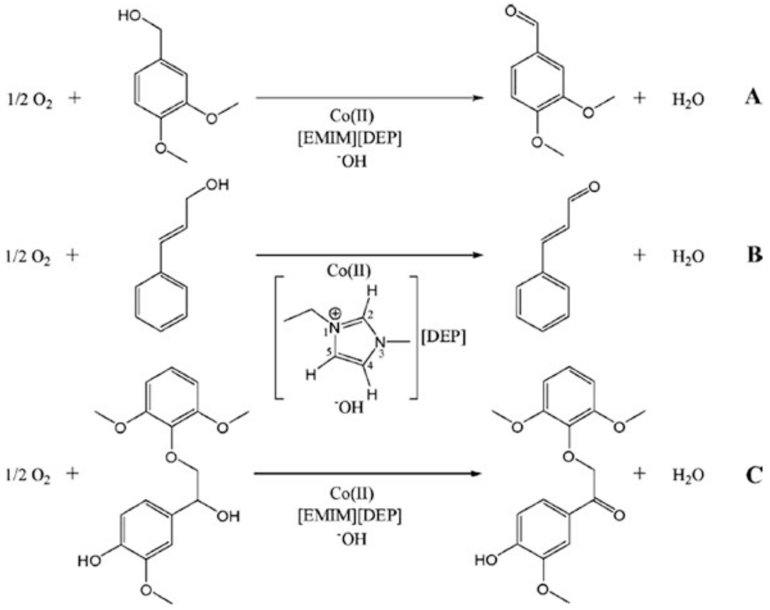

Fig. 3.9 Oxidative conversion of **A** veratryl alcohol to veratraldehyde, **B** cinnamyl alcohol to cinnamaldehyde, and **C** β-O-4 model compound to the corresponding ketone, reprinted with permission from Ref. [59]. Copyright (2011) Royal Society of Chemistry

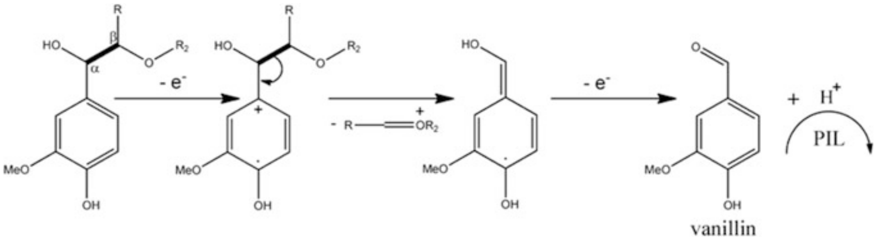

Fig. 3.10 Possible mechanism of the electro-catalytic oxidative cleavage of the lignin C_α–C_β bond, reprinted with permission from Ref. [60]. Copyright (2012) Royal Society of Chemistry

3.5 Summary

Lignin has lower reactivity and high steric hindrance effect due to its large molecular weight and branched structure, which limits the direct use of lignin as chemicals. One approach to enhance reactivity of lignin is through chemical modification of the chemical structure of lignin, e.g., phenolation or methylolation of lignin could improve the reactivity of lignin in the synthesis of lignin-based phenol formaldehyde resins. The other more effective approach is through depolymerization to generate depolymerized lignin (DL) or oligomers with smaller molecules. DL products, with lower molecular weights and less steric hindrance effects and hence higher reactivity, can be used as bioreplacements for phenol, polyols and bisphenol A in the synthesis of phenol–formaldehyde (PF), polyurethane (PU) and epoxy resins.

This chapter focuses on degradation/depolymerization of lignin into value-added chemicals and fuels through thermochemical methods including hydrolytic, reductive, and oxidative depolymerization processes. Hydrolytic depolymerization cleaves the ether linkages of lignin to produce low molecular weight phenolic compounds in sub- or supercritical water under acidic or alkaline condition. Using the mixture of water and organic solvent (such as alcohol, acetone or phenol) could prevent the repolymerization of lignin fragments and improve the stability of phenolic oligomers in hydrolytic treatment. The reductive depolymerization is another thermal treatment of lignin to generate biophenols in the presence of gaseous hydrogen or hydrogen donating solvents (such as formic acid, ethanol, propanol, and tetralin). The char formation could be reduced with increasing the hydrogen content in the reductive depolymerization of lignin. Oxidative depolymerization of lignin is realized by oxidation or oxidative cracking of the lignin macromolecule due to the presence of hydroxyl groups. Various linkages of lignin such as aromatic rings, aryl ether bonds could be cleaved to form phenols, aromatic aldehydes or carboxylic acids, depending on the reaction conditions. Nitrobenzene, hydrogen peroxide, and metal oxides such as CuO and Fe_2O_3 are the most common oxidants for lignin depolymerization. In general, the yield and the product composition of these lignin depolymerization processes are predominantly affected by type of lignin, residence time, reaction temperature, concentration of catalyst, and composition of the solvent as the reaction media.

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