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Review Article

Recent Development in Chemical Depolymerization of Lignin: A Review

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Abstract

This article reviewed recent development of chemical depolymerization of lignins. There were five types of treatment discussed, including base-catalyzed, acid-catalyzed, metallic catalyzed, ionic liquids-assisted, and supercritical fluids-assisted lignin depolymerizations. The methods employed in this research were described, and the important results were marked. Generally, base-catalyzed and acid-catalyzed methods were straightforward, but the selectivity was low. The severe reaction conditions (high pressure, high temperature, and extreme pH) resulted in requirement of specially designed reactors, which led to high costs of facility and handling. Ionic liquids, and supercritical fluids-assisted lignin depolymerizations had high selectivity, but the high costs of ionic liquids recycling and supercritical fluid facility limited their applications on commercial scale biomass treatment. Metallic catalyzed depolymerization had great advantages because of its high selectivity to certain monomeric compounds and much milder reaction condition than base-catalyzed or acid-catalyzed depolymerizations. It would be a great contribution to lignin conversion if appropriate catalysts were synthesized.

1. Introduction

Lignin is a natural resource which exists in woody materials, agricultural residues, and other plant materials (so-called lignocellulosic materials). Lignocellulosic materials consist of 10–30% lignin by weight and 40% by energy [1]. However, it has mainly been used as an energy source in combustion processes, and less than 5% lignin has been used for other purposes nowadays [2]. Because of its high energy content and polymer structure, lignin is considered as a potential renewable resource of chemicals and fuels especially in condition of escalating petroleum price and renewable energy demand. Lignin depolymerization is very promising process which can generate value added products from lignin raw materials. The primary purpose of lignin depolymerization is to convert the complex lignin compound into small molecules for fuels and basic chemicals or oligomers for further application. Considerable amount of research has been done to convert lignin into renewable fuels and chemicals using pyrolysis and gasification methods [3–8]. Pyrolysis refers to the thermal treatment of the biomass or lignin in the absence of oxygen, with or without any catalyst usually at the temperature between 300 and 600°C [3]. The cleavage of OH functional group linked to aliphatic side chain, the breaking of alkyl side chain, aryl ether, and linkage between aromatic rings occur when temperature increases, forming a mixture of phenol, guaiacol, syringol, and catechols. Moreover, the aromatic ring cracking occurs at the temperature above 500°C [9]. However, the process is highly complex and is affected by several factors, including feedstock type, heating rate, and reaction temperature [10]. Gasification represents a process that converts lignocellulosic materials into CO₂, CO, and H₂ at the temperature between 700 and 1000°C. The mixtures of the gases are referred to as “syngas”, which is the only useful product from the process [3]. Biochemical method, such as fungi depolymerization of lignin, was also employed, but it took several weeks for fungi to grow, which made the process have very low efficiency [11, 12]. Compared to pyrolysis and biochemical depolymerization, chemical treatment of lignin has its advantages on both reaction control and high selectivity, which provides great potential in lignin conversion for renewable fuels and chemicals production.

Lignin can be categorized to softwood and hardwood lignins according to their raw biomass sources. Depending on the fractionation methods, lignin can also be categorized to steam explosion, kraft, organosolv, alkaline oxidation, pyrolysis lignins, and so forth [13]. The commonly recognized chemical structure of lignin is exhibited in Figure 1. Ether bond was the target for chemical attacking during chemical conversion processes. Generally, softwood has 45–48 wt.% and hardwood has 60 wt.% of β -O-4 aryl glycerol ether bonds. Softwood has about 5 wt.% and hardwood has 0–2 wt.% of dibenzodioxin 5-5'- α , β -O-4' bonds. In addition, softwood has 3.5–8 wt.% and hardwood has 6–9 wt.% of diphenyl ether 5-O-4' linkages [13, 14]. The differences of these linkages have effects on the depolymerization products from these biomass materials. Moreover, the amounts of some C–C linkages are also varying, such as 5-5 linkage (softwood 19–22 wt.%, hardwood 3–9 wt.%) [14]. All the chemical patterns of ether bonds were marked in circle in Figure 1. Therefore, the reactions of ether cleavage, including α -aryl ether and β -aryl ether, were mainly investigated. Various chemicals were selected with the purpose of breaking the mentioned chemical bonds by which lignin could be depolymerized. Generally, there are five categories of the chemical depolymerization of lignin according to different chemicals applied in the depolymerization process, which includes (1) base-catalyzed, (2) acid-catalyzed, (3) metallic catalyzed, (4) ionic liquids-assisted, and (5) supercritical fluids-assisted lignin depolymerizations.



Figure 1: Common chemical structure of lignin [15].

2. Lignin Depolymerization by Using Different Chemicals

2.1. Base-Catalyzed Lignin Depolymerization

The treatment of lignin using sodium hydroxide aqueous solution at high temperature was straightforward process, from which phenols and phenol derivatives were obtained. Lavoie et al. used softwood and hemp lignin pretreated by steam explosion with 5 wt.% of NaOH aq at the temperature between 300 and 330°C under the pressure ranging from 9 to 13 MPa [16]. There were 26 compounds identified by GC-MS after the reaction, in which guaiacol, catechol, and vanillin were more abundant. Different contents of guaiacol, catechol, and vanillin were obtained mainly because of the different ether linkages proportions in the softwood and hemp lignin. Similar base-catalyzed treatment was carried out for commercial organosolv lignin at 300°C and 25 MPa by Roberts et al. [17]. Syringol, hydroxyacetophenone, and catechol were the major products, but this research found the yield of phenols was increased by adding boric acid in the following treatment of base-catalyzed products. Similar treatment was carried out by Beauchet for treatment of kraft lignin [18]. By optimizing the reaction temperature and time, it was found that pyrocatechol was the most abundant product at 315°C with selectivity up to 25.8%. Toledano et al. provided a different way of base-catalyzed organosolv-processed olive tree pruning lignin depolymerization by using various bases, including KOH, NaOH, Ca(OH)₂, LiOH, and K₂CO₃, in aqueous solution instead of alcohols [19]. Catechol was the most abundant components identified after the lignin was treated by different bases.

In general, base-catalyzed lignin depolymerizations were carried out at temperature above 300°C and a high pressure, from which catechol, syringol, and derivatives were identified to be the most abundant components. The mechanism was the cleavage of the aryl-alkyl bond, which occurred above 270°C. The most abundant aryl-alkyl bond was β -O-4 bond, especially in lignin. Sodium cation helped to form the cation adducts, which catalyzed the formation of six-membered transition on β -O-4 bond during the reaction [17]. Therefore, the concentration of base or the concentration ratio of lignin to base played a very important role in the process. Although base-catalyzed process was simple, it needed to be carried out at high temperature, and the selectivity was still difficult to control. The experiment details of cited literatures are summarized in Table 1.

Table 1: Base-catalyzed lignin depolymerization.

2.2. Acid-Catalyzed Lignin Depolymerization

The application of acid treatment of lignin could be traced back to 1940s. Hewson and Hibbert did a series treatment of maple wood meal using different combination of acids and alcohols, including HCl/ethanol and formic acid/ethylene glycol, with the purpose of separating the lignin into water-soluble and water-insoluble components [40]. A relatively low temperature range of 78 to 200°C used in this research was not high enough to break the complex lignin structure into monomeric compounds for further usage.

Recently, acid-catalyzed method was investigated at a higher temperature range in order to depolymerize lignin [20, 21]. 10 wt.% of formic acid associated with 77 wt.% of ethanol was employed in the reaction with wheat straw lignin by Gasson et al. [20]. A different proportion of formic acid and ethanol solution, which contained 10 wt.% of formic acid and 81 wt.% of ethanol, was used in the reaction with wheat straw lignin but in a CSTR by Forchheim et al. [21]. Methoxyphenol, catechol, and phenol were the major components when the reaction temperature was raised from 360 to 400°C. The maximum yields occurred at reaction time below 200 minutes. Other attempts were carried out using acid/ethanol solution system but associated with metallic catalyst enhancers [23, 24]. These researches were summarized in the section of metallic catalyzed lignin depolymerization.

The acid-catalyzed depolymerization also focused on the cleavage of β -O-4 bond of the lignin, and the reaction was completed in the first 2 to 4 hours of the reaction. Formic acid or other acids provided hydrogen sources in the hydrolysis with the purpose of forming H₃O⁺ on the β -O-4 bond or the cationic aromatic rings. The function of co-catalysts was usually to increase the selectivity. According to the experiments carried out, palladium or platinum did not decrease the activation energy of the depolymerization. In general, acid-catalyzed depolymerization required a harsh reaction condition, which could increase the cost of reaction facility and posthandling. The experiment details of acid-catalyzed lignin depolymerization are summarized in Table 2.

Table 2: Acid-catalyzed lignin depolymerization.

2.3. Metallic Catalyzed Lignin Depolymerization

Metallic catalysts were studied to increase the selectivity of lignin depolymerization. It was reported that the treatment of alcell-derived lignin was carried out in presence of NiCl₂ or FeCl₃ by Hepditch and Thring [41]. But only 2.5 wt.% yield of catechol was obtained at 305°C. More recently, several other attempts showed higher efficiency and selectivity [22–29]. A two-step treatment process was carried out by Yoshikawa et al. in the treatment of kraft lignin [22]. Kraft lignin was treated by Si-Al catalyst in H₂O/butanol medium first, followed by reaction on ZrO₂-Al₂O₃-FeO_x catalyst to increase the total recovery of phenols. The phenols yield was 6.5 to 8.6%, and the conversion of lignin to methoxyphenols was 92–94%. In order to increase the yield of low-molecular weight fraction, 20 wt.% of Pt/C catalyst was used with formic acid and ethanol by Xu et al. in the treatment of organosolv switchgrass lignin [23]. An obvious increase of the guaiacol derivatives yield was observed in presence of metallic enhancer. Another attempt of optimizing the formic acid-catalyzed system was carried out by Liguori and Barth [24]. Pd catalyst and Nafion SAC-13 were used in treatment of both lignin model compounds and spruce dry lignin pretreated by different methods in water medium at 300°C. Guaiacol, pyrocatechol, and resorcinol were isolated, but the yields were all lower than 5 wt.%. The slight difference of the yield of guaiacol, pyrocatechol, and resorcinol is probably because of the different lignin pretreatment methods. Although depolymerization at lower temperature was carried out in presence of Pt and Pd metallic enhancers compared to simple acid-catalyzed

depolymerization mentioned in Section 2.2, no activation energy decrease has been reported. Future research needs to be conducted to clarify the mechanism and function of metallic enhancer in acid-catalyzed lignin depolymerization.

Base- or acid-catalyzed cracking was usually performed at very high temperature (above 300°C) [16–21, 23, 24]. However, efforts were made to decrease the reaction activation energy in order to carry out the lignin depolymerization under mild condition (below 250°C). Research from Song et al. exhibited a method of nickel compound catalyzed depolymerization of lignosulfonate into guaiacols [25]. The nickel catalyst provided a high conversion of above 60% and a high selectivity of 75 to 95% to guaiacols. More importantly, the reaction temperature was decreased to 200°C from around 380°C compared with the pyrolysis process only in presence of acid or base as mentioned in Section 2.2. Another attempt from Song et al. on the treatment of birch wood lignin by nickel catalyst showed a selectivity of above 90% to propanyguaiacol and propenylsyringol and a conversion of more than 50% [26]. Ye et al. reported their work on mild hydrolysis of enzymatic hydrolysis corn stalk lignin between 200 and 250°C [27]. In the presence of Ru/C, Pt/C, or Pd/C catalysts, the maximum yields are 3.1% of 4-ethylphenol and 1.4% of 4-ethylguaiacol. Toledano et al. used metal nanoparticles including nickel, palladium, platinum, and ruthenium supported by mesoporous Al-SBA-15 with the assistance of microwave in the treatment of lignin separated from organosolv olive tree pruning lignin [28]. The results showed that the most abundant product was diethyl phthalate in presence of Ni or Pd catalyst and tetralin solvent. Although the yield was 1.1 wt.%, the reaction temperature was only 140°C, which was lower than 200 to 300°C in other published research. K10 montmorillonite clay ($\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot x\text{H}_2\text{O}$) was applied in the treatment of guaiacyl dehydrogenation oligomers at only 100°C, which led to a degradation of 35 wt.% of the model compounds [29].

By introducing metallic catalysts, the activation energy of the depolymerization was decreased to great extent, which resulted in mild reaction condition. Metallic catalyzing still targeted the C–O and C–C cleavages of the lignin in presence of hydrogen sources like ethanol or water. Nickel or other solid catalysts provided accessible metal sites in the external surface, where the chemical reaction took place in the depolymerization process. This kind of method not only increased the selectivity but decreased the required reaction temperature, which showed great potential. The experiment details of metallic catalyzed lignin depolymerization are summarized in Table 3.

Table 3: Metallic catalyzed lignin depolymerization.

The deactivation issue in metallic catalysts is well known in the biomass pyrolysis. Some of the research to which this article referred mentioned their concern on this point [25–27]. For example, the work done by Song et al. on lignosulfonate depolymerization by using nickel heterogeneous catalyst mentioned that the nickel catalysts helped generate active H species. These active H species combined with nickel sulfides to form H_2S and regenerated Ni(0) site for next catalyzing cycle. This mechanism made the nickel heterogeneous catalysts recyclable [25]. Another research from Song et al. also mentioned that the Ni/C catalysts were recycled 4 times without showing obvious deactivation in birch wood lignin depolymerization [26]. In the work of Ye et al., the Ru/C catalyst was also recycled and showed very good activity [27]. The other research cited in this section did not mention the recycle of catalysts, which made it necessary to study the deactivation of metallic catalysts in the future.

2.4. Ionic Liquids-Assisted Lignin Depolymerization

Ionic liquid was found to be used in separation of lignin and cellulose from raw lignocellulosic materials. Ionic liquids, including 1-butyl-3-methylimidazolium acesulfamate ([BMIM][Ace]) and 1-ethyl-3-methylimidazolium acesulfamate ([EMIM][Ace]), were applied in the treatment of wood powder of *Pinus radiata* lignin by Pinkert et al. [42]. To break the β -O-4 bond under the mild conditions (below 250°C), ionic liquid was also employed in the depolymerization of lignin. The depolymerization of organosolv beech lignin in presence of 1-ethyl-3-methylimidazolium-trifluoromethanesulfonate ([EMIM][CF₃SO₃]) associated with Mn(NO₃)₂ was carried out at 100°C and 8.4 MPa by Stärk et al. [30]. The most important point drawn from their research was that 2,6-dimethoxy-1,4-benzoquinone (DMBQ) was separated as a pure substance in 11.5% overall yield as the final product. Another attempt of [EMIM][CF₃SO₃] associated with Brønsted acid was carried out by Binder et al. in depolymerization of lignin model compound [31]. The reaction was carried out at 200°C, and 11.6 mol% or 7.9 wt.% of guaiacol was obtained from 2-methoxy-4-(2-propenyl)phenol and cleaved 2-phenylethyl phenyl ether, a model for lignin ethers. For both the lignin and the model compounds, ionic liquid associated with ionic salt exhibited high selectivity. Acidic ionic liquid 1-H-3-methylimidazolium chloride [HMIM][Cl] was used in the depolymerization of oak wood lignin at 110 to 150°C by Cox and Ekerdt [32]. The alkyl-aryl ether linkage cleavages were observed in the research. A series of work were done by Jia et al. with the purpose of degrading lignin in various ionic liquids [33–35]. 1-H-3-methylimidazolium chloride was used in depolymerization of both guaiacylglycerol- β -guaiacyl ether and veratrylglycerol- β -guaiacyl ether model compounds to produce guaiacol with the yield of 70% at 150°C [33]. 1-H-3-methylimidazolium chloride with 1,5,7-triazabicyclo[4.4.0]dec-5-ene was used in depolymerization of guaiacylglycerol- β -guaiacyl ether model compounds, from which 40% cleavage of β -O-4 bond was found [34]. The 75% yield of guaiacol was observed in depolymerization of guaiacylglycerol- β -guaiacyl ether model compounds in presence of 1-H-3-methylimidazolium chloride methylsulfate [35].

Currently, it has been proved that some ionic liquids are appropriate solvents for lignin dissolution [43]. Acid associated with ionic liquid, such as Brønsted acid, was believed to be the catalyst which provided the hydrogen sources. However, the high cost of the ionic liquids limited their application on large quantity of lignin depolymerization. The recycle of ionic liquid is very necessary due to its high cost [44]. However, there is difficulty in separation of ionic liquid with lignin-derived molecules because of the π - π interaction between ionic liquid and aromatic moieties [13]. Therefore, the use of ionic liquid in lignin depolymerization may be limited. A summary of ionic liquid-assisted lignin depolymerization is shown in Table 4.

Table 4: Ionic liquids-assisted lignin depolymerization.

2.5. Supercritical Fluids-Assisted Lignin Depolymerization

Supercritical fluid was selected to be the medium for lignin depolymerization. The treatment of kraft- and organosolv-derived lignins using KOH or other bases in supercritical methanol or ethanol was reported in 1990s, indicating that the supercritical liquid had effects on lignin depolymerization [36, 45]. Recently, the use of supercritical fluid on the treatment of lignin attracted researchers' interest again. Supercritical water treatment of alkaline lignin was carried out by Wahyudiono et al. [37]. Under the condition of 300°C and 25–40 MPa, identified products included mainly catechol (28.37 wt.%), phenol (7.53 wt.%), and cresol (11.67 wt.%). Supercritical water associated with *p*-cresol was applied as the medium in treatment of organosolv lignin at the temperature between 350 and 420°C by Takami et al. [38]. 2-(Hydroxy-benzyl)-4-methylphenol (BMP) with a 75 wt.% yield was recovered from the reaction mixtures. Another attempt by Gosselink et al. was using CO₂/acetone/water supercritical fluid to treat organosolv hardwood and wheat straw lignins at the temperature between 300 and 370°C under 10 MPa, from which syringol and guaiacol were obtained [39]. The difference of the yield of some depolymerization products is mainly because of the different linkage contents between hardwood and wheat straw lignin.

Similar to ionic liquid, supercritical fluid was employed as the solvent in the depolymerization system due to its good solubility. Hydrogen sources for the hydrolysis were provided from acid and alcohol. Even though supercritical liquid exhibited high selectivity and convenience on products and solvent separation, the high cost still restricted its development to be a widely used method for lignin conversion. A summary of supercritical fluids-assisted lignin depolymerization is made in Table 5.

Table 5: Supercritical fluids-assisted lignin depolymerization.

3. Summary

Base-catalyzed, acid-catalyzed, metallic catalyzed, ionic liquids-assisted, and supercritical fluids assisted lignin depolymerizations were summarized and compared in this article. In general, base-catalyzed and acid-catalyzed methods required high reaction temperature (above 300°C) and high pressure (10 MPa), which resulted in high costs of facility and handling. High selectivity and conversion are great advantages of ionic liquids- and supercritical fluids-assisted lignin depolymerizations. However, the high cost is the major obstacle to their wide applications. Metallic catalyzed depolymerization had great potential because of its high selectivity to some target products and less severe reaction conditions. Current research on metallic catalyzed depolymerization showed that Ni- and Pt-based catalysts have relatively high conversion of lignin model compounds and high selectivity to certain monomeric products. The development of new transition metal-based catalysts for lignin depolymerization will be the trend in the future as well as the performance of these catalysts on lignin rather than model compounds.

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