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From technical lignin to wood lignin: an evaluation of two approaches for lignin valorization

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From Technical Lignin to Wood Lignin: An Evaluation of Two Approaches for Lignin Valorization

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INTRODUCTION

1.1 GENERAL INTRODUCTION

In the 20th century, the industrial and social development was highly dependent on the fossil resources and related technologies. For example, based on refinery and petrochemical technologies, we can convert crude oil into energy, fuel and various chemicals which are indispensable in our modern society. Nevertheless, due to various factors, the dominating role of fossil resources in energy and chemical supply is being challenged and a transition to more sustainable feedstocks is underway in the 21st century. First of all, it is obvious that the fossil resources are not unlimited and not sustainable in mankind scale although new reserves of crude oil, coal and natural gas and the development of more efficient technologies might prolong the exhaustion time. Furthermore, the enormous consumption of fossil resources brought about severe environmental issues. For example, according to the Fifth Assessment Report of Intergovernmental Panel on Climate Change (IPCC), the CO$_2$ released by usage of fossil resources is the primary greenhouse gas that triggered the global warming.\footnote{1} The plastics based on petrochemistry also created another great environmental challenge since synthetic plastics cannot be degraded easily and will stay in the environment for a long time. Last but not least, energy security is also an argument for such transition from fossil resources to other alternative resources. Because of uneven distribution of global fossil resources and complexed international geopolitical reasons, the price of crude oil fluctuated dramatically in the past decades and is hard to predict in the future.

In order to tackle with the problems caused by fossil fuel, renewable resources represent an excellent alternative and gain more popularity and importance in recent years. Among other renewable energy sources, e.g. solar, hydraulic, wind and geothermal, biomass is a promising alternative for fossil resource which not only can be converted to energy and fuels but also to chemicals. Several governments in the world have set ambitious goals for energy and chemical
production from biomass. The US Department of Energy declared to replace 30% of liquid petroleum-based fuels by biofuels and to produce 25% of industrial organic chemicals from bio-derived chemicals by 2025.\(^2\) The European Union has set a mandatory target of 20% renewable energy’s share in energy consumption by 2020.\(^3\) All of these ambitious goals triggered and intensified the interest in development of new technology for biomass conversion in both academia and industry.

### 1.2 BIOREFINERY

A biorefinery is a facility that integrates biomass conversion process and equipment to produce fuels, power, heat and valued added chemicals from biomass.\(^4\) The concept of biorefinery is analogous to today’s petroleum refinery yet there are marked differences between these two processes regarding feedstock composition and processing strategies and technologies. A comparison of refinery and biorefinery is showed in Fig. 1.1. From a chemical viewpoint, a major difference between these two feedstocks is that there are more oxygen functionalities in biomass. Consequently, oxygen removal steps are necessary in order to get fuels from biomass.

![Fig. 1.1 Comparative processing for fuel and chemical production from petroleum and biomass](image_url)
Apparently, the feedstock for biorefinery is biomass. Nevertheless, biomass is a rather general concept which is composed of various components with variable chemical and physical properties such as carbohydrates, fatty acids, lignin and other functionalized molecules. Moreover, biomass can be classified into two generations. The first generation consists of edible biomass, e.g. crops, starch, sugarcane fats and so on and they compete with food production. Given the increasing worldwide population pressure, the usage of food to produce fuel and chemical cannot be justified completely. So the second generation of biomass, which is non-edible and is able to grow at non-arable land, is gaining more and more popularity in research.

The future for biorefinery seems very promising, but successful commercialization examples are still limited. The most important example of biomass conversion is bio-ethanol production by fermentation of sugars using edible corn and wheat as feedstock. Some important chemicals, e.g. 1,3-propanediol and succinic acid, also can be obtained from sugars by fermentation or catalytic reaction. Besides carbohydrate case, there are few valorization examples of lignin as well. For example, the Norwegian biorefinery company, Borregaard, can produce vanillin from lignin which is extensively used in food and perfume industry because of its flavor.6,7

1.3 LIGNOCELLULOSIC BIOMASS

Lignocellulose is a composite material synthesized by plant cell and gives plant structural rigidity and protection against environmental damages. Fig. 1.2 shows the schematic representation of spatial arrangement of lignocellulose. Lignocellulose mainly consists of cellulose, hemicellulose and lignin which in total account for ca. 90% of dry matter of plant. In addition to the above three major components, lignocellulose also contains smaller amounts of pectin, inorganic compounds, proteins and extractives, such as lipids and waxes, which also have potential values.8 According to its origin, lignocellulose can be divided into three categories, i.e. softwood-, hardwood- and grass lignocellulose. Lignocellulose from different feedstocks has different composition and properties. Table 1.1 shows the composition of some lignocellulose species.
Table. 1.1 Composition of different types of biomass feedstocks (wt%)\textsuperscript{10}

<table>
<thead>
<tr>
<th>Feedstocks</th>
<th>Cellulose</th>
<th>Hemicellulose</th>
<th>Lignin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Miscanthus</td>
<td>24-33</td>
<td>45-52</td>
<td>9-13</td>
</tr>
<tr>
<td>Switchgrass</td>
<td>26-33</td>
<td>32-37</td>
<td>17-18</td>
</tr>
<tr>
<td>Corn Stover</td>
<td>31</td>
<td>37</td>
<td>18</td>
</tr>
<tr>
<td>Poplar</td>
<td>16-22</td>
<td>42-48</td>
<td>21-27</td>
</tr>
<tr>
<td>Eucalyptus</td>
<td>24-28</td>
<td>39-46</td>
<td>29-32</td>
</tr>
<tr>
<td>Pine</td>
<td>23</td>
<td>46</td>
<td>28</td>
</tr>
</tbody>
</table>

1.3.1 Cellulose and Hemicellulose

Cellulose and hemicellulose are both polysaccharides but different in building units, degree of polymerization (DP) and morphology. Cellulose is the most abundant biopolymer on earth consisting solely of glucose units linked by 1-4 $\beta$ glycosidic bonds.\textsuperscript{11} It is a linear polymer with a DP can be 10000 or higher.\textsuperscript{12} A prominent feature of cellulose is its extensive intramolecular and intermolecular hydrogen bonds. Through these hydrogen bonds, numerous linear cellulose strands are packed into crystalline fibrils.\textsuperscript{13} Such highly ordered packing of cellulose contributes to its insolubility in water and other common solvents despite the fact that glucose is water-soluble.
In contrast to cellulose, hemicellulose is amorphous and made from several hexose and pentose sugars, such as xylose, mannose, arabinose and galactose. It has a smaller DP around 100-200 and can be a branched conformation and substituted with other functionalities, such as acetyl and methyl groups\textsuperscript{14}. It has been suggested that such hydrophobic substitution groups can enhance its affinity to lignin which aids cohesion between the three major lignocellulosic components\textsuperscript{15}. Moreover, compared with highly crystalline cellulose, hemicellulose is more easily depolymerized and converted to valuable products such as bioethanol and furfural due to its lower DP and non-crystalline feature.

1.3.2  Lignin

Lignin is a three-dimensional amorphous polymer synthesized by plants via radical polymerization of substituted phenyl propylene units. It is one of the major components of lignocellulosic biomass, consisting 15-30\% of the dry weight and approximately 40\% of the energy content\textsuperscript{15}. In plants, lignin serves as glue in lignocellulose and provides plant structural integrity, water-proofing property and resilience to various environmental attacking\textsuperscript{16}. Nevertheless, it is worth mentioning here that what we call as lignin or native lignin refers to a class of phenolic biopolymers, rather than to a well-defined biopolymer, like cellulose and hemicellulose.

1.3.2.1  Composition and Structure of Lignin

A schematic representation of lignin molecule is showed in Fig. 1.4. Lignin is built up from three monolignols: p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol as depicted in Fig. 1.5. The three building units also can be denoted as H, G and S units. The three monolignols are linked via various C-O-C (ether) and C-C bonds. More specifically, C-O-C

![Fig. 1.3 Typical monosaccharides in cellulose and hemicellulose](image-url)
Fig. 1.4 Representative fragment of hardwood lignin

Fig. 1.5 Three main monolignols in lignin

linkages including β-O-4, α-O-4 and 4-O-5 bonds and C-C linkages including β-5, β-1, β-β and 5-5 bonds. Based on linkage type, 45-48% in native lignin are β-O-4 bonds and 12% are β-5 bonds. Fig 1.6 shows some typical linkage patterns in lignin.

Fig. 1.6 Four typical linkages in lignin
1.3.2.2 Lignin Isolation

Lignocellulosic biomass is a complex composite interconnected via different physical and chemical linkages, so isolation of lignin is not only crucial but also challenging in a biorefinery. An ideal isolation technology should not only take technical factors into account, such as purity and solubility, but also economic and environmental factors. There are a number of isolation methods available for lignin isolation nowadays, some of them are listed in Table 1.2. Among them, Kraft process and Sulfite pulping process are the two major industrial processes, especially in paper and pulp industry. Nevertheless, Kraft lignin or lignosulfonate seems not to be the ideal feedstock for further lignin valorization due to their irreversible structural changes during processing and due to the potential poisoning effect of their sulfur content.

1.3.2.3 The Role of Lignin in Biorefinery

Compared to the easy utilization of (hemi-)cellulose in bioethanol production, the efficient valorization of lignin is still very limited. It is estimated that only about 2 % of the lignin available from pulp and paper industry are currently used commercially with the remainder simply burned as low value fuel.\(^{23}\) So in order to achieve an integrated biorefinery, i.e. utilizing all components of lignocellulose, and to make biorefinery more economically viable, it is imperative to develop new technologies to obtain fuel and chemical from lignin.

Given the foreseeable enormous production of underutilized lignin in nearby future and its unique chemistry structure, lignin is considered as an unawakened giant in future biorefinery. Currently, the pulp and paper industry produces proximately 130 million tons of Kraft lignin annually.\(^{24}\) Notably, due to the predicted growth in second-generation bio-ethanol production, lignin produced as by-product expects to increase rapidly. Furthermore, the unique role of lignin in future biorefinery also lies in its unique structure. Lignin is the only large volume available feedstock for renewable aromatics production.\(^{25}\) Because of its richness in functionalities, lignin is an attractive candidate for fine chemical production and vanillin production is such a current example. At last, an interesting argument was made recently
Table 1.2 Comparison of different Lignin pretreatment methods

<table>
<thead>
<tr>
<th>Solution method</th>
<th>Lignin name</th>
<th>Typical process</th>
<th>Characteristics</th>
<th>Nature of disruption</th>
<th>Dissolved species</th>
</tr>
</thead>
<tbody>
<tr>
<td>Klason method</td>
<td>Klason lignin</td>
<td>72% sulfuric acid</td>
<td>Extensive structure change, hardwood lignin is partly dissolved.</td>
<td>Chemical pretreatment</td>
<td>(Hemi-) cellulose</td>
</tr>
<tr>
<td>Kraft process</td>
<td>Kraft lignin</td>
<td>Na$_2$S/NaOH</td>
<td>Highly modified, partially fragmented.</td>
<td>Chemical pretreatment</td>
<td>Lignin</td>
</tr>
<tr>
<td>Sulfite pulping process</td>
<td>Lignosulfonate</td>
<td>Extract lignin from waste liquor of the sulfate pulping process of soft wood.</td>
<td>Highly modified, high average molecular weights, cleavage of ether linkages, loss of methoxyl groups and formation of new C–C bonds.</td>
<td>Chemical pretreatment</td>
<td>Lignin</td>
</tr>
<tr>
<td>Bjöckman process</td>
<td>Milled wood lignin (MWL)</td>
<td>Ball milling, then extracted by aqueous dioxane.</td>
<td>Most similar to the native structure, possible depolymerization due to extensive milling</td>
<td>Physical pretreatment</td>
<td>Lignin</td>
</tr>
<tr>
<td>Organosolv process</td>
<td>Organojolv lignin</td>
<td>Using organic solvents to extract lignin.</td>
<td>Mild conditions, results in more unaltered lignin, solvent could be recovered by distillation.</td>
<td>Solvent fraction</td>
<td>Lignin</td>
</tr>
<tr>
<td>Enzyme process</td>
<td>Cellulolytic enzyme lignin (CEL)</td>
<td>Hydrolysis of cellulose, leave lignin as a residue.</td>
<td>Low structure change, bears less phenolic hydroxyl groups than MWL</td>
<td>Biological process</td>
<td>(Hemi-) cellulose</td>
</tr>
<tr>
<td>Soda pulping process</td>
<td>Soda lignin</td>
<td>Concentrated NaOH, addition of delignification agent</td>
<td>Sulfur free, high purity</td>
<td>Chemical pretreatment</td>
<td>Lignin</td>
</tr>
<tr>
<td>Ionic Liquid pretreatment</td>
<td>Ionic liquid lignin</td>
<td>Stepwise precipitation or selective extraction</td>
<td>Tunable strategy, low structure change, more uniform molar mass distribution compared to those of Kraft lignin.</td>
<td>Solvent fraction</td>
<td>Lignin</td>
</tr>
<tr>
<td>Stream explosion process</td>
<td>Steam explosion lignin</td>
<td>High temperature steam explosion of fibers.</td>
<td>Require little or no chemical input, short treatment time, low energy requirement, changes of certain functional groups.</td>
<td>Physical pretreatment</td>
<td>Lignin</td>
</tr>
</tbody>
</table>
associated with the advent of shale gas production.\textsuperscript{26} If shale gas becomes the game changer in future energy market, it is predicted that there will be a shortage in aromatics production considering the technical challenging of conversion of shale gas into aromatics and then lignin becomes the most obvious feedstock for sustainable aromatics production.

1.4 LIGNIN VALORIZATION REVIEW

Over the past several decades, there is an extensive research aiming to produce value-added chemicals, alternative fuel and platform compounds from lignin due to its important role in lignocellulose biorefinery. On the one hand, lignin can either be directly or chemically modified to renewable materials, such as bio-dispersant, wood panel products, emulsifier, polyurethane foams, automotive brakes and epoxy resins.\textsuperscript{27-28} On the other hand, depolymerization of lignin into value-added products seems to be a more promising approach to valorize lignin. Various strategies aiming to achieve effective depolymerization of lignin have been developed up to now, either in neutral condition, or with the aid of oxidant or reductant. Figure 1.7 is a brief summary of major available lignin depolymerization approaches adapted from a recent published review.\textsuperscript{21}

\textbf{Fig. 1.7} A summary of approaches for lignin depolymerization
Among all these depolymerization methods, liquid phase reforming, gasification and pyrolysis are performed in relatively high temperature and can be done without catalyst. Herein, the main focus is on the other four catalytic depolymerization methods with the aid of catalyst, i.e. base catalyzed depolymerization, acid catalyzed depolymerization, oxidation and hydroprocessing. Those four catalytic processes will be discussed in detail, in particular hydroprocessing, in the following sub-sections according to the type of approach.

1.4.1 Base-catalyzed depolymerization

During base-catalyzed depolymerization, cleavage of ether bonds, including β-O-4 bonds is the dominant reaction. The bases can be either inorganic bases, such as NaOH, KOH, CsOH, or other organic bases. Toledano et. al. screened different inorganic bases, i.e. NaOH, KOH, LiOH, Ca(OH)$_2$ and K$_2$CO$_3$, at pH 14 for depolymerization of Organosolv processed olive tree pruning lignin in water. The authors concluded that NaOH promoted the formation of monomers more efficiently than other base catalysts. For using of organic base as a catalyst, Song and his co-workers developed a novel strategy to transfer lignocellulose into monomeric molecules catalyzed by organic acid and organic base. The organic base they used was tetramethylammonium hydroxide and it was proved that that organic base can catalyze depolymerization of lignin in such a catalytic system.

A major problem of base-catalyzed depolymerization of lignin is the simultaneous repolymerization of reactive intermediates during depolymerization. It was suggested that both depolymerization and repolymerization take place simultaneously and share the same intermediate states. Therefore, decreasing the rate of depolymerization during reaction is a key issue to enhance monomer yield. In order to tackle with that problem, many strategies have been proposed. For example, Lercher and his co-workers used boric acid to capture the reactive species during NaOH-catalyzed lignin depolymerization and such capping agent can improve phenolic monomer yield. It was claimed that boric acid can form ester by reacting with phenols and then prevent undesired condensation reaction. Besides using different capping agents to avoid repolymerization, it was showed that hydrogen donor solvent, such as formic acid, can also effectively suppress repolymerization.
1.4.2 Acid-catalyzed depolymerization

Originally, mineral acid was used to isolate lignin from lignocellulosic feedstock rather than to depolymerize lignin into valuable monomers. Nevertheless, various types of acid, such as mineral acid, Lewis acid, solid acid, organic acid and acidic ionic liquid were tested for hydrolysis of lignin or lignin model compounds recently. Similar with base-catalyzed depolymerization, the breaking of weaker ether linkages is also the main reaction during acid-catalyzed lignin depolymerization.

Adler and his co-workers reported the first example of mineral acid promoted hydrolysis of Björkmn lignin.\textsuperscript{34} Afterwards, there were some attempts to depolymerize lignin using common Lewis acid, such as metal chloride. For instance, Hepditch and Thring investigated depolymerization of Alcell-derived lignin in the presence of NiCl\textsubscript{2} and FeCl\textsubscript{3} in water medium. They found that the highest conversion, 30\% and 26\% from NiCl\textsubscript{2} and FeCl\textsubscript{3}, respectively, were attained at the reaction conditions of 305 °C and 1 h reaction time.\textsuperscript{35} Recently, zeolite was employed in lignin depolymerization as well. For example, Deepa and Dhepe reported that a very high yield (60\%) of value-added aromatic monomer was achieved using bare solid acid catalysts below 250 °C.\textsuperscript{36}

Another interesting alternative approach in literature is to using acidic ionic liquid as both solvent and catalyst. Ionic liquid is able to readily dissolve lignin even lignocellulose under mild condition so it may convert raw biomass directly without pretreatment. Ekerdt and his co-workers demonstrated that two lignin model compounds, \textit{e.t.} guaiacylglycerol-β-guaiacyl ether and veratrylglycerol-β-guaiacyl ether, can be effectively depolymerized in 1-H-3-methylimidazolium chloride ionic liquid at 150 °C, yielding higher than 70\% of guaiacol as the main product.\textsuperscript{38} Besides model compound experiments, real lignin depolymerization in ionic liquid was also reported. Argyropoulos and his co-workers reported that acid pretreatment of raw wood in ionic liquid [Amin]Cl resulted in conversion of lignin to phenols as well as hydrolysis of cellulose and hemicellullose.\textsuperscript{39}

At last, even though different kinds of acids were utilized in lignin depolymerization, most acid-catalyzed methods also face severe recondensation problem similar with base-catalyzed situation. Consequently, effort to mitigate or avoid such undesired side reaction was made in
literature. For instance, Barta et al. demonstrated an elegant strategy to largely suppress undesired recondensation by capturing the unstable compounds with diols and by in situ conversion of reactive intermediates.\textsuperscript{40}

1.4.3 Oxidative depolymerization

The products of oxidative depolymerization of lignin are polyfunctional aromatic monomers, such as vanillin, syringaldehyde, 4-hydroxybenzaldehyde, muconic acid and so on. Some common oxidants for lignin depolymerization are chlorine, chlorine dioxide, oxygen, hydrogen peroxide, ozone and peroxy acid.\textsuperscript{41} The catalysts used for oxidative approach can be divided into three categories: (1) organometallics, (2) inorganic metal-based catalysts and (3) organocatalysts. In the following section, several typical catalysts from each category will be presented, with focus on lignin model compound oxidation in particular.

Among all kinds of organometallics, methyltrioxo rhenium (MTO) is one of the simplest compounds that can be used for catalytic activation of oxidizing species. Crestini and his coworkers have done a systematic research on MTO-catalyzed lignin oxidation reaction recently and they found out that MTO/H\textsubscript{2}O\textsubscript{2} catalytic system was the most efficient one. It was reported that MTO/H\textsubscript{2}O\textsubscript{2} can be employed for oxidation of lignin model compounds and three technical lignins.\textsuperscript{42} Furthermore, cobalt salen (N,N–bis(salicylidene)ethylenediamine) is another interesting organometallic catalyst for lignin oxidation because it is cheap, stable in aqueous media and easy to synthesize.\textsuperscript{43} Liu et al. reported that Co(salen) complex can catalyze number of reactions of lignin model polymer, including C\textsubscript{α}-alcohol oxidation, C\textsubscript{α}–C\textsubscript{β} side chain cleavage, demethoxylation, aromatic ring cleavage and β-O-4 cleavage in water with molecular oxygen and hydrogen peroxide as oxidants. \textsuperscript{44}

\begin{figure}
\centering
\subfigure[Structure of MTO]{
\includegraphics[width=0.3\textwidth]{mto.png}
\label{fig:mto}}
\hspace{1cm}
\subfigure[Structure of Co(salen)]{
\includegraphics[width=0.3\textwidth]{cosalen.png}
\label{fig:cosalen}}
\caption{Structure of MTO and Co(salen)}
\end{figure}
For inorganic metal-based catalysts, there are several options available as well, such as single metal ion, metal oxides, composite metal oxides and polyoxometalate (POM). For example, cupric oxide (CuO) is long known as an effective catalyst for lignin oxidative conversion and used as a quantantive analysis of lignin in different plants. Polyoxometalate is another promising metal-based catalyst for lignin oxidation. POMs are structurally diverse anionic clusters consisting of d⁰ metal cations and oxygen anions arranged in MO₆ octahedral units. Weinstock and co-workers observed a high reactivity between PMOs ([Al₅VW₁₁O₄₀]⁶⁻ and Na₅[SiVW₁₁O₄₀]) and phenolic-type lignin model compounds at room temperature in a aqueous phase aerobic oxidation condition.

Fig. 1.10 Catalytic mechanism of aerobic oxidation of lignin with PMOs

At last, organocatalysts received increasing attention in scientific community in the last few years because of their high selectivity and catalytic efficiency in many reactions. Considering its great catalysis potential, there were many works aiming to use organocatalysts for lignin oxidation and 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) is the most investigated one. For example, Stahl and co-workers have developed a catalysis system consisting of TEMPO, HNO₃ and HCl and they showed that lignin model compound, benzylic alcohol, can be selectively aerobic oxidized and an extension to natural lignin has also been demonstrated.
1.4.4 Hydroprocessing

Hydroprocessing refers to reduction of feedstock by hydrogen. It is the most efficient way to convert lignin to valuable compounds, such as phenols, BTX and alkanes. There are many reactions during hydroprocessing, e.g. hydrogenation, hydrogenolysis, hydrodeoxygenation and hydroalkylation. In the following section, a short introduction of lignin hydroprocessing will be given in the order of catalyst type, i.e. monometallic catalyst, bimetallic catalyst and bifunctional catalyst.

Ni-based catalysts were longtime used for lignin hydroprocessing in research and the earliest record can be tracked back to 1940s. In recent years, Lercher and co-workers reported a novel Ni/SiO$_2$ catalyst for selective cleavage of lignin-derived aromatic ethers at 120 °C in presence of 6 bar H$_2$ in aqueous phase. Meanwhile, Sergeev and Hartwig have made great progress on homogenous nickel complex catalyzed hydrogenolysis of diaryl ethers. Such catalyst was suitable for a wide range of ether substrates and high monomer yield was achieved under 0.1 MPa H$_2$ at around 100 °C. Moreover, depolymerization of real lignin using Ni-based catalysts has been reported as well. Xu and co-workers studied the valorization of native birch wood lignin into monomeric phenols over nickel-based catalysts. The results showed that lignin can be selectively converted to two main phenolic monomers with total selectivity > 90% at a lignin conversion of about 50%.

The platinum-group metals (PGMs) are another promising candidates for lignin processing. Due to their high hydrogen transfer ability, PGMs can depolymerize raw or pretreated lignin more easily than Ni-based catalysts. For example, Chang et al. demonstrated that corn stalk
lignin with different ratio of H, G and S units can be selectively valorized to 4-ethylphenol and 4-ethylguaiacol, with 65 vol.% ethanol/water as solvent, 5% Ru/C, Pd/C and Pt/C as catalysts.\textsuperscript{52} Suckling and co-workers investigated the Pd/C-catalyzed hydrogenolysis of in-situ and isolated lignin from \textit{Pinus radiata} wood and they found out that lignin can be converted into solvent-soluble oils composed of monomeric, dimeric, and oligomeric products in high yields, up to 89\% of the original lignin.\textsuperscript{53} Nevertheless, also because of their high reactivity, there is a hidden drawback of using PGMs for lignin hydroprocessing \textit{i.e.} other concurrent H-related reactions may occur during hydrogenolysis, such as hydrogenation of arenes which is an undesired reaction if BTX are the target products.

Hydrodeoxygenation (HDO) is a hydrogenolysis process to remove oxygen from oxygen containing compounds and it is regarded as the most efficient approach for bio-oil upgrading. The Mo-based catalysts are traditional catalysts for HDO reaction. Smith and co-workers studied the hydrogenation of 4-methylphenol over unsupported, low-surface-area MoS\textsubscript{2}, MoO\textsubscript{2}, MoO\textsubscript{3} and MoP catalysts.\textsuperscript{54} The results showed that the catalyst turnover frequency (TOF) based on CO uptake decreased in the order of MoP > MoS\textsubscript{2} > MoO\textsubscript{2} > MoO\textsubscript{3}. It was also reported that other transitional sulfides have been applied in HDO of lignin model compounds recently. For example, Rinaldi \textit{et al.} reported that monocrystalline FeS\textsubscript{2} supported on SBA-15, aerosil SiO\textsubscript{2}, activated carbon or Al\textsubscript{2}O\textsubscript{3} is a precursor of highly active catalyst for HDO of dibenzyl ether into toluene.\textsuperscript{55} XRD and XPS analysis indicated that a fresh surface, formed upon the chemical transformation of FeS\textsubscript{2} into Fe\textsubscript{1-x}S is the real active species for conversion of dibenzyl. At last, HDO reaction on real lignin feedstocks are also studied in literature. Li and co-workers examined the production of phenols from alkaline lignin over activated carbon supported tungsten phosphide in a hot compressed water-ethanol mixed solvent, resulting in the highest overall phenols yield of 67.0 mg/g lignin.\textsuperscript{56}

It was well documented in the literature that adding a second metal to monometallic catalyst can enhance catalytic activity and tailor product selectivity in many reactions. A classic example of bimetallic catalyst is Co or Ni promoted Mo-based HDO catalyst. Studies showed that there was a significant improvement in HDO rate over Co or Ni promoted Mo catalyst than only sulfide Mo catalyst.\textsuperscript{57-58} Zhang and co-workers reported a direct catalytic conversion of
raw woody biomass into two groups of chemicals over a carbon supported Ni-W\textsubscript{2}C catalyst in which lignin component was converted into monophenols with a yield of 46.5\%.\textsuperscript{59} Interestingly, the results indicated a synergistic effect between Ni and W\textsubscript{2}C catalysts. Recently, it was reported that organosolv lignin can be depolymerized to aromatic monomers at 170 °C in water using Ni-based bimetallic catalysts, such as NiAu.\textsuperscript{60} In the following works from the same group, Zhang and co-workers demonstrated that a series of NiM (M = Ru, Rh and Pd) bimetallic catalysts can also depolymerize lignin model compounds and organosolv lignin under mild conditions (100–130 °C, 10 bar H\textsubscript{2}).\textsuperscript{61}

Bifunctional catalyst, consisting of metal and acid catalysts, was also developed for lignin valorization in order to improve catalytic performance. Zhao and Lercher investigated the kinetics of dual-functional system Pd/C and H\textsubscript{3}PO\textsubscript{4} on the catalytic hydrodeoxygenation of phenol and substituted phenols.\textsuperscript{62} The systematic kinetic study revealed that both catalysts were indispensable and the acid-catalyzed steps determined the overall HDO reaction. Abu-Omar and co-workers introduced Zn(II) into Pd-based catalyst and they reported that the bifunctional catalyst was far more effective than sole Pd/C for cleavage of β-O-4 bonds and remarkably, the aromaticity of feedstocks was maintained during hydroprocessing.\textsuperscript{63} In addition to homogenous Brönsted and Lewis acids, solid Brönsted acids were also investigated in bifunctional catalysts for lignin hydrodeoxygenation. Zhao and Lercher reported that the combination of Pd/C and HZSM-5 showed an extremely high selectivity in removing oxygen-containing groups of lignin-derived phenolic products via a cascade metal-acid catalyzed cleavage of C-O bonds.\textsuperscript{64} Ma and co-workers developed a novel strategy for efficient lignin depolymerization and char elimination using Ru/C-NaOH bifunctional catalyst, resulting in 13 % phenolic monomers, 6 % aliphatic alcohol and less than 14 % residual solid.\textsuperscript{65}

1.5 SCOPE OF THE REPORT

The goal of this master graduation project is to convert lignin into valuable lower molecular weight products, such as benzene, toluene, xylene (BTX) and phenolic monomers. The focus is on improving monomer yield and selectivity by means of synthesizing new catalysts, addition of promoter, optimizing reaction conditions, etc.
Chapter 2 discusses the depolymerization of P1000 lignin in supercritical ethanol using mixed oxide catalysts. The effect of atmosphere, solvent and catalyst type on monomer yield and selectivity were explored. Besides that, the recyclability of three mixed oxide catalysts was tested and a detailed investigation of catalyst deactivation was done. Chapter 3 describes a novel one-pot approach to obtain phenolic monomers directly from lignocellulose via tandem catalysis using Pd/C and metal triflate as catalyst. At first, the promotion effect of metal triflate was demonstrated using scotch pine as feedstock. Afterwards, type of feedstock, reaction temperature and type of metal triflate were screened in order to obtain a better catalytic performance. At last, a detailed study of product composition and properties was carried out combined with several model compound experiments with the aim to elucidate the specific role of Pd/C and metal triflate during catalytic reaction. At the end, the main results of this master graduation project are summarized and a brief comparison of two catalytic approaches in chapter 2 and 3 is made.
1.6 REFERENCES


CHAPTER 2

Reductive Depolymerization of Lignin in Supercritical Ethanol
Using Mixed Metal Oxide Catalyst

2.1 INTRODUCTION

Lignin is one of the three main constituents of plant cell wall consisting 15-30% of the dry weight and approximately 40% of the energy content.\(^1\) It is also considered as the only large amount available source for aromatics production.\(^2\) Nevertheless, due to its recalcitrant nature, efficient depolymerization and valorization of lignin is still in its primitive stage. In current practice, most of lignin is burned as low value fuel to produce process steam and electricity,

Early example to depolymerize lignin is by pyrolysis or base-catalyzed depolymerization (BCD).\(^3\)-\(^4\) The bio-oil derived from such a process contains high amounts of water and oxygen, and is relatively unstable and prone to repolymerization.\(^5\) As a result, a following (hydro)-deoxygenation step is necessary to upgrade the obtained bio-oil to higher quality fuel-grade products. Alternatively, it will be interesting if lignin can be depolymerized and (hydro)-deoxygenated in one step in a reductive atmosphere, either by molecular hydrogen or by hydrogen-donor solvent. Several attempts were made in such a direction in the literature. For example, it was reported that switch grass lignin can be converted into phenolic products by Pt catalyst using formic acid as hydrogen-donor solvent.\(^6\) Ford and co-workers successfully depolymerized lignin into monomeric products using Cu-doped porous metal oxides with or without H\(_2\).\(^7\)-\(^9\) Recently, Huang \textit{et al.} reported a new depolymerization approach in which soda lignin was depolymerized in supercritical ethanol using Cu-doped porous metal oxides catalyst, yielding 23 wt% monomer without char formation.\(^10\)

In Huang’s report, the Cu-doped porous metal oxides catalyst was prepared by calcination of corresponding layered double hydroxides (LDH). Layered double hydroxide consists of octahedral brucite-like layers, charge-balancing anions and interlayer water molecules as
depicted in Fig. 2.1. The host layer is positively charged because of the substitution of divalent metal ions ($M^{2+}$) by trivalent ones ($M^{3+}$). The structure is stabilized by electrostatic interactions between the brucite-like layers and the anions as well as by hydrogen bonds among hydroxyl slabs, interlayer water molecules and anions. Furthermore, supercritical ethanol was chosen as solvent for reaction due to several reasons. At first, ethanol can act as hydrogen-donor solvent at elevated temperature to reductive depolymerize lignin. Secondly, it was reported that ethanol can act as capping agent and formaldehyde scavenger via esterification and Guerbet reaction, suppressing repolymerization and char formation. At last, in contrast to normal liquid phase, supercritical phase, i.e. a state at a temperature and pressure exceeding its critical temperature and pressure, may provide extra advantages to lignin depolymerization, e.g. elimination of gas-liquid and liquid-liquid mass transfer resistances, enhancement of diffusion rate and heat transfer etc.

In this chapter, we continued Huang’s work on reductive depolymerization of lignin in supercritical ethanol using mixed metal oxide catalyst and examined further other factors affecting overall catalytic performance. The investigated factors were atmosphere, solvent, catalyst type, lignin type and catalyst reusability.
2.2 EXPERIMENTAL SECTION

2.2.1 CHEMICALS AND MATERIALS

Protobind 1000 alkali lignin was purchased from GreenValue. It was produced by soda pulping of wheat straw (sulfur-free lignin with less than 4 wt% carbohydrate and less than 2 wt% ash). Organosolv. lignin and enzymatic lignin (with 10 wt% carbohydrate) were obtained from Adenstedt, Germany. Extra-dry absolute methanol and ethanol were purchased from Biosolve. All commercial chemicals were analytical reagents and were used without further purification.

2.2.2 SYNTHESIS OF MIXED METAL OXIDE CATALYST

The Cu-doped mixed oxide catalysts were prepared by calcination of corresponding layered double hydroxides (LDH). The catalyst was denoted as Cu$_y$MgM(X) where $y$ refers to the copper loading as weight percent and $x$ indicates the M$^{2+}$/M$^{3+}$ ratio. The table below shows the recipe for three different mixed oxide catalysts used in the experiments.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Cu$_{20}$MgAl(4)</th>
<th>Cu$_{20}$MgCe(4)</th>
<th>Cu$_{20}$MgZr(4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$_{20}$MgMO$_4$</td>
<td>0.010</td>
<td>0.010</td>
<td>0.010</td>
</tr>
<tr>
<td>Mg(NO$_3$)$_2$·6H$_2$O</td>
<td>0.065</td>
<td>0.056</td>
<td>0.060</td>
</tr>
<tr>
<td>Al(NO$_3$)$_3$·9H$_2$O</td>
<td>0.020</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Cu(NO$_3$)$_2$·2.5H$_2$O</td>
<td>0.015</td>
<td>0.024</td>
<td>0.020</td>
</tr>
<tr>
<td>Na$_2$CO$_3$</td>
<td>0.024</td>
<td>0.024</td>
<td>0.024</td>
</tr>
<tr>
<td>NaOH</td>
<td>0.220</td>
<td>0.220</td>
<td>0.220</td>
</tr>
<tr>
<td>Ce(NO$_3$)$_3$·6H$_2$O</td>
<td>N/A</td>
<td>0.020</td>
<td>N/A</td>
</tr>
<tr>
<td>ZrO(NO$_3$)$_2$·xH$_2$O</td>
<td>N/A</td>
<td>N/A</td>
<td>0.020</td>
</tr>
</tbody>
</table>

The mixed oxide catalyst was prepared by a co-precipitation method followed by calcination. For example, Cu$_{20}$MgCe(4) catalyst was prepared via the following way: certain amount of Mg(NO$_3$)$_2$·6H$_2$O, Al(NO$_3$)$_3$·9H$_2$O and Cu(NO$_3$)$_2$·2.5H$_2$O as showed in the recipe were dissolved in 100 ml de-ionized water. That solution, along with 100 ml of NaOH solution,
was slowly added (1 drop/sec) through 100 ml dropping funnels to 150 ml of Na₂CO₃ solution in a 500 ml beaker at 60 °C with vigorous stirring, while keeping the pH of the slurry at 10. When addition was complete after ca. 45 min, the mile-like light-blue slurry was aged at 60 °C under stirring for 24 h. The precipitate was filtered and washed with distilled water until the filtrate reached a pH of 7. The solid was dried overnight at 110 °C, and grinded and sieved to a particle size below 125 μm. The hydrotalcite-like precursor was calcined with a heating rate of 2 °C/min from 40 °C to 460 °C and kept at that temperature for 6 h in static air.

2.2.3 EXPERIMENTAL SETUP AND PROCEDURE

Experimental Setup: The catalytic depolymerization experiments were carried out in 100 ml stainless steel Parr batch autoclave, equipped with thermocouple, pressure gauge and back-pressure regulator and heated by oven, as showed in Figure 2.2.

![Catalytic depolymerization setup](image)

Fig. 2.2 Catalytic depolymerization setup

Catalytic Reaction: In a typical run of lignin catalytic depolymerization reaction, the autoclave was charged with a suspension of 0.5 g catalyst and 1.0 g lignin in 40 ml ethanol. The reactor was sealed and purged with nitrogen several times to remove oxygen. After leaking testing, the pressure was set to 10 bar and the reaction mixture was heated to 380 °C under continuous stirring at 500 rpm within 1 h. After the reaction, the heating oven was removed
and the reactor was cooled down to room temperature by water bath. After cooling down, the final temperature and pressure of the reactor were recorded.

**Products Analysis Procedure:** The products analysis begins with gas phase products analysis. Gas phase products were collected from autoclave and analyzed by Gas-Solid Chromatography (GSC) before it was opened. Collected gas products were sent to an Interscience Compact Gas Chromatography system, equipped with a Molsieve 5 Å and Porabond Q column each with a Thermal Conductivity Detector (TCD) and a Al₂O₃/KCl column with a Flame Ionization Detector (FID). The identification and quantification of gas products were done by using a gas cylinder containing known quantities of permanent gases.

Following this, the autoclave was adjusted to pressure of 1 bar before opened to the ambient air. A work-up procedure developed by Huang *et al.* was applied to the product mixture inside the autoclave as showed in Figure 2.3 (the numbers between brackets refer to the steps in Figure 2.3). First, 30 μl *n*-dodecane internal standard was added to the solution. An aliquot of 1 ml was taken from the reaction mixture and directly analyzed by GC-MS without dilution following filtration with a 0.45 μm syringe filter (1). The remaining mixture was collected and combined with solution obtained from washing the autoclave with ethanol (2). The combined mixture was subsequently subjected to filtration and the filter cake was washed with ethanol several times (3). The filtrate was brought to 30 ml by blowing the reaction mixture with air at room temperature, followed by acidification with adding 15 ml of 0.1 M HCl solution (final pH=1) (4), and 50 ml deionized water to precipitate unconverted lignin and high molecular-weight lignin fragments (5). After aging for about 30 min, the resulting mixture was filtrated over a 0.45μm filter membrane (6). The filter cake was retrieved by washing with THF (7). The solid residue from step (3) was washed with excess of THF in order to retrieve the unconverted lignin adsorbed on catalyst (8). The lignin residue was obtained by combing the two THF solutions and removing THF by rotary evaporation at 60 °C. The resulting filter cake was regarded as a mixture of catalyst and repolymerization products which are denoted as THF-insoluble. In order to determine the exact amount of THF-insoluble, thermo gravimetric analysis (TGA) was further applied (9).
2.2.4 CHARACTERIZATION

**Lignin Products Analysis:** The liquid phase products were analyzed by a Shimadzu 2000 GC-MS system equipped with a RTX–1701 column (60 m × 0.25 mm × 0.25 μm) and a flame ionization detector (FID) together with a mass spectrometer (MS) detector. Identification of products was achieved based on a research of the MS spectra with the NIST11 and NIS11s MS libraries. These products were further divided into four groups, namely hydrogenated cyclics (-o (oxygen free)), hydrogenated cyclics (+o (oxygen containing)), aromatics (-o) and aromatics (+o), according to the nature of ring and functional groups. All the quantitative analysis of liquid phase product was based on 1D GC-FID. Experimentally determined weight response factors of cyclohexane (1.221), cyclohexanone (0.992), ethyl benzene (1.103) and ethyl guaiacol (0.803) were used for these four groups related to \( n \)-dodecane as internal standard. The yield of lignin monomers and lignin residue were calculated by following equations (1)-(3).

\[
\text{Yield of monomers (wt\%) = } \frac{\text{weight of monomers (calculated from GC−FID)}}{\text{weight of starting P1000 lignin}} \times 100\% \quad (1)
\]

\[
\text{Yield of THF−soluble (wt\%) = } \frac{\text{weight of THF−soluble LR}}{\text{weight of starting P1000 lignin}} \times 100\% \quad (2)
\]

\[
\text{Yield of THF−insoluble (wt\%) = } \frac{\text{weight of THF−insoluble LR}}{\text{weight of starting P1000 lignin}} \times 100\% \quad (3)
\]

**Thermo Gravimetric Analysis:** The THF-insoluble lignin residue formed during reaction was determined by thermo gravimetric analysis (TGA) on TG/DSC \(_1\) STAR system of Mettler Toledo. The temperature was increased to 750 °C at the rate of 5 °C/min under flowing air (50 ml/min). The weight loss between 150°C and 600 °C was considered as total THF-insoluble lignin residue content.

**Catalyst Characterization:** Powder X-ray diffraction (XRD) was measured on a Bruker Endeavour D2 with Cu K\(\alpha\) irradiation (40 kV and 30 mA). They were recorded with 0.02° steps over the 5-80° angular range with 0.2s counting time per step. Elemental analysis was done by ICP-OES on a Spectro Ciros ICP optical emission spectrometer with axial plasma
Fig. 2.3 Work-up procedure of reaction product mixture from lignin reaction

1. 1ml sample for GC-MS analysis
2. Washing autoclave with ethanol
3. Filtration (washing the filter cake with ethanol)
4. Acidification (15 ml of 0.1 M HCl to pH=1)
5. Addition of de-ionized water (50 ml)
6. Aging and filtration (0.45 μm filter membrane)
7. Aging lignin residue (dissolving the filter cake with THF)
viewing, samples were digested in an equivolumetric mixture of distilled water and concentrated sulfuric acid. Surface area and porosity of catalyst were determined by nitrogen physisorption technique by Micromeritics TrisStar II Gas Sorption Analyzer. The sample was degassed at 250 °C for 5 h before measurement. The specific surface area, pore volume and pore diameter were calculated automatically from nitrogen physisorption using Brunauer, Emmett and Teller (BET) theory. The distribution and strength of basic sites in catalyst were determined by CO$_2$ temperature programmed desorption (CO$_2$-TPD) by a home-built reactor system. After the catalyst was pretreated at 460 °C for 1 h under He stream (50 ml/min), it was cooled down to 100 °C and then CO$_2$ was introduced for adsorption for 0.5 h. Afterwards, the catalyst was swept with He for 1 h to remove the physisorbed CO$_2$ from catalyst surface and then the temperature was increased linearly with a rate of 10 °C/min in He flow. During heating period, the signal of CO$_2$ (m/e=44) was recorded by online mass spectrometer (Quadrupole Mass Spectrometer, Balzers TPG-300). The amount of CO$_2$ was quantified by a calibration curve which was established by thermal decomposition of certain amounts of NaHCO$_3$.

**Gel Permeation Chromatography (GPC):** GPC analysis was performed by using a Shimadzu apparatus equipped with two columns in series (Mixed-C and Mixed-D, polymer laboratory) and a UV-Vis detector at 254 nm. The columns were calibrated with polystyrene standards. Analysis was carried out at 25 °C using THF as eluent with a flow rate of 1 ml/min. For lignin residue analysis, the sample was prepared at a concentration of 2 mg/ml. All the samples were filtered using 0.45 μm filter membrane prior to injection.

### 2.3 RESULTS AND DISCUSSION

Various cyclic and linear products were produced after reaction and an exemplary lignin monomer distribution is showed in the following figure. The cyclic products were classified into four categories: hydrogenated cyclics (-o), hydrogenated cyclics (+o), aromatics (-o) and aromatics (+o) and all of them were alkylated with methyl and/or ethyl groups with different degree. Besides lignin-derived cyclic products, a wide range of linear products (mainly higher alkyl alcohols and esters) were produced as well. These products were formed by conversion of ethanol solvent via Guerbet reaction and oxidative esterification catalyzed by Cu$_{20}$MgAl(4).
catalyst. Such conversion of ethanol to linear products was confirmed by control reaction without lignin under the same conditions.

2.3.1 Effect of Atmosphere

We firstly investigated the catalytic performance of Cu_{20}MgAl(4) in four different atmospheres. The initial idea of using H\textsubscript{2} is to enhance hydrogenolysis, CO to improve H\textsubscript{2} production and water removal through the water-gas-shift reaction and CO\textsubscript{2} to reduce char content/carbon deposits.

The catalytic results are listed in Table 2.2. Due to the extensive alkylation during reaction, the total yield of experiment with catalyst was over 100%. The results show that H\textsubscript{2} could not enhance monomer yield significantly compared with N\textsubscript{2} which indicates that the initial 10 bar H\textsubscript{2} did not have much effect on hydrogenolysis. On the other hands, CO or CO\textsubscript{2} had a negative effect on monomer yield. The negative effect of CO may result from interaction between CO and Lewis acid sites of catalyst and such Lewis acid sites are responsible for alkylation of lignin fragments which can hinder repolymerization.\textsuperscript{13} The negative effect of CO\textsubscript{2} may result from interaction of CO\textsubscript{2} and basic sites of catalyst and such base sites are the active sites for
dehydrogenation of ethanol which in turn provides active hydrogen species for hydrogenolysis.\textsuperscript{13}

Table 2.2 Lignin monomer yield, lignin residue and total yield of catalytic lignin depolymerization in different atmosphere conditions\textsuperscript{[a]}

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Atmosphere</th>
<th>Monomers</th>
<th>THF-soluble</th>
<th>THF-insoluble (TGA)</th>
<th>Total yield</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>&lt; 400 °C</td>
<td>&gt; 400 °C</td>
<td>(%)</td>
</tr>
<tr>
<td>1</td>
<td>Cu\textsubscript{20}MgAl(4)</td>
<td>N\textsubscript{2}</td>
<td>31</td>
<td>68</td>
<td>14.1</td>
<td>9.6</td>
</tr>
<tr>
<td>2</td>
<td>Cu\textsubscript{20}MgAl(4)</td>
<td>H\textsubscript{2}</td>
<td>32</td>
<td>62</td>
<td>13.3</td>
<td>8.9</td>
</tr>
<tr>
<td>3</td>
<td>Cu\textsubscript{20}MgAl(4)</td>
<td>CO</td>
<td>28</td>
<td>59</td>
<td>11.9</td>
<td>7.2</td>
</tr>
<tr>
<td>4</td>
<td>Cu\textsubscript{20}MgAl(4)</td>
<td>CO\textsubscript{2}</td>
<td>27</td>
<td>79</td>
<td>6.9</td>
<td>14.7</td>
</tr>
<tr>
<td>5</td>
<td>Blank</td>
<td>N\textsubscript{2}</td>
<td>3</td>
<td>28</td>
<td>2.3</td>
<td>17.9</td>
</tr>
</tbody>
</table>

\textsuperscript{[a]} Reaction condition: 1g P1000 lignin, 0.5 g catalyst, 40 ml ethanol, T = 380 °C, P = 10 bar, Time = 4 h.

The formation of heavier residue molecule due to higher degree of repolymerization under CO and CO\textsubscript{2} atmosphere is further confirmed by TGA and GPC data. As shown in TGA curves of THF-insoluble residue (Fig. 2.5), the CO\textsubscript{2} curve shifts to higher temperature, which indicates that more high molecular weight products formed during the reaction. In GPC chromatograms of THF-soluble residue (Fig. 2.6), there are more high molecular weight products in CO case compared with N\textsubscript{2} which implies more repolymerization. Surprisingly, the chromatogram of CO\textsubscript{2} shows a smaller molecular weight distribution compared with N\textsubscript{2} (Fig. 2.6). That observation, we cannot fully understand now but one possible explanation is that the original high molecular weight products in THF-soluble residue may be converted into THF-insoluble residue during the reaction.

![Fig. 2.5 TGA curves of four THF-insoluble residues](image1)

![Fig. 2.6 GPC chromatograms of the THF-soluble for different atmosphere](image2)
The monomer distributions under four atmospheric conditions are shown in Fig. 2.7. More hydrogenated cyclicity (+o) products are in nitrogen and hydrogen. However, except for that difference, no other significant differences in monomer selectivity can be observed in the four different atmospheres. In other words, the effect of initial 10 bar gas atmosphere on lignin catalytic depolymerization was quite limited considering the final high temperature and high pressure reaction conditions.

**Fig. 2.7** Lignin monomer distribution under four atmosphere conditions

### 2.3.2 Effect of Solvent

The effect of solvent on catalytic lignin depolymerization was examined in four alcoholic solvents, *i.e.* methanol, ethanol, 1-propanol and 1-butanol. The results are showed in Table 2.3. The reaction of methanol was stopped at 3 h because of the high pressure due to the fast decomposition of methanol. We can see from the results that the best monomer yield was achieved in ethanol followed by methanol and the monomer yields in 1-propanol and 1-butanol were much lower compared with ethanol.

One possible reason for such a difference may relate to how facile is the dehydrogenation of the solvent under reaction condition. The amount of hydrogen evolved from these four solvents are calculated in Table 2.4. However, these data indicates that there is no relation between monomer yield and solvent dehydrogenation ability. As we can see in Table 2.4, hydrogen production was almost the same for ethanol and 1-propanol but monomer yield for
those two solvents was largely different (Table 2.3). Moreover, much less hydrogen was produced from methanol than 1-propanol yet more monomer produced in methanol instead.

Table 2.3 Monomer yield, lignin residue and total yield of catalytic lignin depolymerization in different solvent\[a\]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Solvent</th>
<th>Time (h)</th>
<th>Monomers</th>
<th>THF-soluble</th>
<th>THF-insoluble (TGA)</th>
<th>Total yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cu(_{20})MgAl(4)</td>
<td>methanol</td>
<td>3</td>
<td>19</td>
<td>6</td>
<td>7</td>
<td>57</td>
</tr>
<tr>
<td>2</td>
<td>Cu(_{20})MgAl(4)</td>
<td>ethanol</td>
<td>4</td>
<td>34</td>
<td>77</td>
<td>12</td>
<td>9</td>
</tr>
<tr>
<td>3</td>
<td>Cu(_{20})MgAl(4)</td>
<td>1-propanol</td>
<td>4</td>
<td>8</td>
<td>65</td>
<td>13</td>
<td>4</td>
</tr>
<tr>
<td>4</td>
<td>Cu(_{20})MgAl(4)</td>
<td>1-butanol</td>
<td>4</td>
<td>6</td>
<td>65</td>
<td>11</td>
<td>4</td>
</tr>
</tbody>
</table>

[a] Reaction conditions: 1g P1000 lignin, 0.5 g catalyst, 40 ml solvent, T=380°C, P (N\(_2\)) = 10 bar

Alternatively, other explanation can be suggested in terms of repolymerization for such solvent effect. For the methanol case, the monomer yield was low because formaldehyde could be produced from methanol by dehydrogenation which can induce repolymerization of reactive lignin fragments. Such suggestion is consistent with TGA and GPC results in the following. According to the TGA curves (Fig. 2.8), there is relatively more higher molecular-weight THF-insoluble residue in methanol than in the other three solvents. In the GPC results, the methanol curve shifts to higher molecular weight region. The reason for lower monomer yields for 1-propanol and 1-butanol is that they are less effective for alkylation, etherification and Guerbet reactions because of their longer chain length.\(^{17}\) It was reported that those three reactions can hinder repolymerization of the phenolic monomers formed during lignin disassembly.\(^{13}\) The high degree of repolymerization in 1-propanol and 1-butanol is evidenced by GPC data of THF-soluble residue (Fig. 2.9). The molecular weight distribution of 1-propanol and 1-butanol shifts to higher molecular weight compared with ethanol.
The monomer distribution in different alcoholic solvents is presented in the following figure. Firstly of all, there is a big difference in monomer selectivity between methanol and ethanol. In methanol almost all the monomers were phenolic products with only little hydrogenated monomers. On the contrary, considerable amount of monomers for each product category were produced in ethanol. At last, the major monomers produced in 1-propanol and 1-butanol were belong to hydrogenated cyclics (-o) and aromatics (+o) yet the amount of products were much less than the ethanol case.
2.3.3 Effect of catalyst type and catalyst reusability

In this section, we replaced Al content in Cu$_{20}$MgAl(4) with Zr and Ce to prepare two new catalysts, *i.e.* Cu$_{20}$MgZr(4) and Cu$_{20}$MgCe(4), aiming to improve the catalyst stability. Table 2.5 shows the catalytic performance and recyclability of those three catalysts. The monomer yield data indicates Cu$_{20}$MgZr(4) and Cu$_{20}$MgCe(4) were inferior to Cu$_{20}$MgAl(4) for lignin depolymerization. Furthermore, the monomer yield of all three recycled catalysts decreased significantly compared with fresh catalysts.

Table 2.5 Monomer yield, lignin residue and total yield of catalytic lignin depolymerization with Cu$_{20}$MgAl(4), Cu$_{20}$MgZr(4) and Cu$_{20}$MgCe(4) catalysts $^{[a]}$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Monomers</th>
<th>THF-soluble</th>
<th>THF-insoluble (TGA)</th>
<th>Total Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>&lt; 400 °C</td>
<td>&gt; 400 °C</td>
</tr>
<tr>
<td>1</td>
<td>Cu$_{20}$MgAl(4)</td>
<td>33</td>
<td>77</td>
<td>12</td>
<td>9</td>
</tr>
<tr>
<td>2</td>
<td>Cu$_{20}$MgAl(4)</td>
<td>13</td>
<td>35</td>
<td>8</td>
<td>5</td>
</tr>
<tr>
<td>3</td>
<td>Cu$_{20}$MgZr(4)</td>
<td>22</td>
<td>50</td>
<td>13</td>
<td>6</td>
</tr>
<tr>
<td>4</td>
<td>Cu$_{20}$MgZr(4)</td>
<td>9</td>
<td>53</td>
<td>8</td>
<td>4</td>
</tr>
<tr>
<td>5</td>
<td>Cu$_{20}$MgCe(4)</td>
<td>29</td>
<td>72</td>
<td>7</td>
<td>3</td>
</tr>
<tr>
<td>6</td>
<td>Cu$_{20}$MgCe(4)</td>
<td>16</td>
<td>57</td>
<td>5</td>
<td>3</td>
</tr>
</tbody>
</table>

$^{[a]}$ Reaction conditions: 1g P1000 lignin, 0.5 g catalyst, 40 ml ethanol, T = 380 °C, P (N$_2$) = 10 bar, reaction time = 4 h.

$^{[b]}$ Catalyst recyclability experiments

The monomer distribution of Cu$_{20}$MgAl(4), Cu$_{20}$MgZr(4) and Cu$_{20}$MgCe(4) catalysts is shown in Fig. 2.10. We can see that Cu$_{20}$MgZr(4) has a lower aromatics yield compared with Cu$_{20}$MgAl(4) and Cu$_{20}$MgCe(4) has a higher selectivity towards hydrogenated cyclics (-o) compared with Cu$_{20}$MgAl(4). The monomer distribution of fresh and spent catalysts is presented in Fig. 2.11. It can be seen the yields of hydrogenated cyclics (-o), hydrogenated (+o), aromatic (-o) and aromatics (+o) decreased simultaneously for all three recycled catalysts.
In order to better understand the different catalytic performance of the three catalysts and deactivation of these catalysts, we carried out XRD, BET, CO$_2$-TPD and ICP measurements.
for both fresh and spent catalysts. The results are presented in the following tables and figures.

It is noted that the recycled catalysts were obtained by recalcinating the catalysts at 500 °C for 6 h following reaction.

Table 2.6 Textural properties and elemental composition of fresh Cu$_{20}$MgAl(4), Cu$_{20}$MgZr(4), Cu$_{20}$MgCe(4) and recycled Cu$_{20}$MgAl(4) catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$S_{BET}$ (m$^2$/g)</th>
<th>$V^a$ (cm$^3$/g)</th>
<th>$D_b$ (nm)</th>
<th>Cu$^c$ (mg)</th>
<th>Mg$^c$ (mg)</th>
<th>Al$^c$ (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$_{20}$MgAl(4) fresh</td>
<td>167</td>
<td>0.72</td>
<td>16.7</td>
<td>81.7</td>
<td>141.5</td>
<td>45.7</td>
</tr>
<tr>
<td>Cu$_{20}$MgZr(4) fresh</td>
<td>105</td>
<td>0.58</td>
<td>18.2</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Cu$_{20}$MgCe(4) fresh</td>
<td>95</td>
<td>0.58</td>
<td>20.6</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Cu$_{20}$MgAl(4) recycled</td>
<td>123</td>
<td>0.35</td>
<td>7.8</td>
<td>60.3</td>
<td>98.9</td>
<td>44.3</td>
</tr>
</tbody>
</table>

a. average pore volume; b. average pore diameter c. elemental mass calculation is based on 0.5g fresh catalyst.

Table 2.7 Basic properties of fresh Cu$_{20}$MgAl(4), Cu$_{20}$MgZr(4), Cu$_{20}$MgCe(4) and recycled Cu$_{20}$MgAl(4) catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>CO$_2$ desorption peaks (area %)</th>
<th>Total basic sites (mmol CO$_2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>weak</td>
<td>medium</td>
</tr>
<tr>
<td>Cu$_{20}$MgAl(4) fresh</td>
<td>28</td>
<td>41</td>
</tr>
<tr>
<td>Cu$_{20}$MgZr(4) fresh</td>
<td>25</td>
<td>41</td>
</tr>
<tr>
<td>Cu$_{20}$MgCe(4) fresh</td>
<td>28</td>
<td>38</td>
</tr>
<tr>
<td>Cu$_{20}$MgAl(4) recycled</td>
<td>35</td>
<td>42</td>
</tr>
</tbody>
</table>

Fig. 2.13 CO$_2$-TPD profiles of three fresh mixed oxide catalysts

Fig. 2.14 CO$_2$-TPD profiles of fresh and recycled Cu$_{20}$MgAl(4)
At first, we compare three fresh mixed oxide catalysts. Cu$_{20}$MgAl(4) catalyst has the largest surface area followed by Cu$_{20}$MgZr(4) According to textual properties from nitrogen physisorption (Table 2.6). From CO$_2$-TPD measurement (Table 2.7), all the three catalysts have the same total basic site density. Such observation is not surprising since basic sites of those three catalysts are derived from Mg content and the initial Mg content in these catalysts are almost the same as showed in the preparation recipe. Nevertheless, there is a difference in basic site distribution in the three fresh catalysts (Table 2.7). Cu$_{20}$MgAl(4) and Cu$_{20}$MgCe(4) catalysts have more weak basic sites which corresponds to basic surface OH$^{-}$ groups and such surface OH$^{-}$ is thought to be the active site during lignin depolymerization. So combined textual and basic properties data, we suggest that the better catalytic performance of Cu$_{20}$MgAl(4) is due to its large surface area and relatively more surface OH$^{-}$ weak basic sites.

We also studied the deactivation of catalysts using Cu$_{20}$MgAl(4) as an example. At first, we can see from the composition data (Table 2.6) that there is a significant loss in Cu and Mg contents in the recycled catalyst. Moreover, according to the XRD patterns (Fig. 2.15), CuAl$_2$O$_4$ spinel phase was formed after reaction and this spinel phase was stable and another new CuO phase was formed after recalcination of the catalyst. Meanwhile, the surface area

![XRD patterns of fresh and recycled Cu$_{20}$MgAl(4) and Cu$_{20}$MgAl(4) after reaction](image-url)
(Table 2.6) and total basic site density (Table 2.7) decreased greatly in the recycled catalyst compare with the fresh one. In summary, all the above data indicate that the deactivation of Cu20MgAl(4) is originated from loss in Cu and Mg contents during reaction condition which further leads to formation of new phases and decreasing in surface area and basic site density.

2.3.4 Effect of Lignin Type

In order to study the influence of lignin type on depolymerization, we tested P1000, enzymatic and organosolv lignins in the catalytic reaction. The results indicate that these three lignins show very different depolymerization performances (Table 2.8). Enzymatic lignin showed a higher and organosolv lignin showed a much lower monomer yield than the P1000 lignin. The monomer distribution of these three lignins is showed in Fig. 2.15. We suggest that such a big difference in reactivity among these lignins is due to structural change caused by the isolation process. Enzymatic lignin is obtained in a mild condition using enzyme and such lignin would maintain more chemical structure in native lignin. On the contrary, the organosolv and P1000 lignins are obtained in a more severe isolation conditions, such as at high reaction temperature, in the presence of a base and so on. During such process, readily cleavable ether linkages may be broken accompanied by forming new C-C linkages, resulting a more recalcitrant structure than native lignin.

Table 2.8 Monomer yield, lignin residue and total yield of catalytic lignin depolymerization with P1000 lignin, enzymatic lignin and organosolv lignin[^a]

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Lignin Type</th>
<th>Time (h)</th>
<th>Monomers</th>
<th>THF-soluble</th>
<th>THF-insoluble (TGA)</th>
<th>Total Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu20MgAl(2)</td>
<td>organosolv</td>
<td>4</td>
<td>11</td>
<td>95</td>
<td>8</td>
<td>4</td>
</tr>
<tr>
<td>Cu20MgAl(2)</td>
<td>enzymatic</td>
<td>4</td>
<td>39</td>
<td>41</td>
<td>6</td>
<td>3</td>
</tr>
<tr>
<td>Cu20MgAl(2)</td>
<td>P1000</td>
<td>4</td>
<td>30</td>
<td>68</td>
<td>5</td>
<td>2</td>
</tr>
</tbody>
</table>

[^a]: Reaction conditions: 1g lignin feedstock, 0.5 g catalyst, 40 ml ethanol, T = 340 °C, P (N2) = 10 bar

Furthermore, we carried out GPC measurements of acetylated enzymatic lignin, organosolv lignin and THF-soluble residue of enzymatic and organosolv lignins. The reason for choosing these two lignins is that they were produced from the same wheat chaff feedstock. It is noted that acetylating enzymatic lignin is to improve its solubility. The experimental results
are listed in Fig. 2.16. There is a huge difference between the molecular weight distribution of these two lignins. For enzymatic lignin, the THF-soluble residue shifts to lower molecular weights and the situation in organosolv lignin is just the opposite: the THF-soluble residue shifts to higher molecular weights. Such an observation is consistent with the catalytic activity results and indicates that enzyme lignin is prone to depolymerization during reaction and it is more difficult to depolymerize organosolv lignin.

**Fig. 2.16** Monomer distribution of P1000 lignin, enzymatic lignin and organosolv lignin

**Fig. 2.17** GPC chromatograms obtained from organosolv lignin and enzymatic lignin
2.4 CONCLUSIONS

In summary, we investigated the catalytic depolymerization of P1000 lignin in supercritical ethanol using mixed oxide catalyst in this chapter. The results show that various valuable lignin monomer products with good yield can be obtained after catalytic reaction, such as BTX. Furthermore, we examined the effect of atmosphere, solvent, catalyst type and lignin type on depolymerization and we found that:

- Significant positive effect on monomer yield using H₂ instead of N₂ initial atmosphere was not found and there were less monomers produced using CO or CO₂ gases as initial atmosphere which may result from partial blocking of active site on catalyst surface by CO or CO₂.
- For the case of solvent effect, the best monomer yield was achieved in ethanol. On the other hand, methanol, 1-propanol and 1-butanol were inferior solvents for P1000 lignin depolymerization due to higher degree of repolymerization of lignin fragments during reaction.
- Replacement of Al content with Zr and Ce in mixed oxide catalyst did not result in better catalytic performance and neither of these three catalysts can recover its original catalytic activity after recycling.
- The deactivation of Cu₂₀MgAl(4) catalyst is due the loss of Mg and Cu content during reaction which further leads to smaller surface area and less basic sites in the catalyst.
- Different lignin feedstocks have apparently different catalytic results. In the three lignins we examined in this chapter, we found that enzymatic lignin was easier to depolymerize than P1000 lignin yet organosolv lignin was more difficult for such a transformation.
2.5 REFERENCES


CHAPTER 3

One-step Delignification and Hydrogenolysis of Lignin into Value-added Phenolic Monomers from Lignocellulose

3.1 INTRODUCTION

Lignocellulosic biomass is a composite material synthesized by plant cells which is made up mainly from polymeric cellulose, hemicellulose and lignin. The utilization of the carbohydrate fraction has been well demonstrated in traditional pulp and paper industry, as well as in the bio-ethanol production in recent bio-refinery processes. Both of these processes will deliver lignin as by-stream which yet receives little attention. Given that large amount of lignin is available and due to its interesting chemical structure, conversion of lignin into valued-added products is highly imperative and important by which the economics of bio-refinery could be further improved.

Indeed, there are increasing enthusiasm and effort in scientific community to valorize technical lignin nowadays. Nevertheless, efficient depolymerization of technical lignin usually requires harsh conditions (e.g. 300-500 °C) and the monomer selectivity is often problematic where a complex product mixture is obtained after depolymerization. Such a non-selective mixture severally hinders the further down-stream upgrading of monomer products. One reason for such difficulty in technical lignin valorization lies in its intrinsic incompatibility with depolymerization methods. On the one hand, there are impurities in technical lignin, e.g. sulfur content, which may poison catalysts. On the other hand, unwanted irreversible structure alteration will occur during technical lignin production. For example, during Kraft lignin production, some readily cleavable ether linkages are broken accompanied by forming new C-C linkages, resulting a more recalcitrant structure than native lignin.\textsuperscript{1-2} Therefore, proper pretreatment to activate lignin is a key issue for efficient lignin valorization. For example, Stahl et. al. reported a novel approach to depolymerize lignin by a two-step method in which lignin
was oxidized first followed by a redox-neutral bond cleavage step mediated by formate and formic acid at mild conditions.\textsuperscript{3} The author claimed that the pre-oxidation step can effectively activate lignin molecule, making it more susceptible to depolymerization. Fig. 3.1 shows the general procedure and chemical reactions during such a two-step depolymerization strategy.\textsuperscript{4}

![Fig. 3.1 Two-step lignin depolymerization strategy\textsuperscript{4}](image)

Alternatively, combining lignin pretreatment with depolymerization in one pot is another promising strategy to achieve high lignin valorization performance because it can avoid recondensation of reactive intermediate lignin fragments to a great extent. Indeed, there are some recent reports in literature employing such an approach. Xu \textit{et al.} studied the conversion of native birch wood lignin into monomeric phenols over nickel-based catalysts, resulting a lignin conversion of about 50%.\textsuperscript{5} Sels and co-workers reported that birch sawdust was efficiently delignified through simultaneous solvolysis and catalytic hydrogenolysis in the presence of Ru/C in methanol under a H\textsubscript{2} atmosphere at elevated temperature, resulting in a carbohydrate pulp and lignin oil.\textsuperscript{6} Ferrini and Rinaldi developed a new lignin isolation method in the presence of Raney Ni in 2-propanol/H\textsubscript{2}O mixed solvent. The resulting non-pyrolytic lignin oil was highly susceptible to further hydrodeoxygenation.\textsuperscript{7} Similarly, Abu Omar \textit{et al.} reported a bimetallic Zn/Pd/C catalyst that directly converted lignin from lignocellulosic biomass into two methoxyphenol products in methanol solvent. A monomer yield of 52 wt% was obtained after reaction at 225 °C for 12h, using birch hardwood as feedstock.\textsuperscript{8}

Following previous works on such one-pot catalytic approach, we investigated a tandem catalytic system in this chapter where lignin was firstly disassembled from wood sawdust
catalyzed by a homogenous metal triflate catalyst and then the soluble lignin fragments were simultaneously depolymerized via a hydrogenolysis step catalyzed by a heterogeneous metal catalyst (e.g. Pd/C) in the presence of H₂. The choice of metal triflate here is due to its several advantages over other traditional Lewis acid catalysts, such as AlCl₃ and ZnCl₂. First of all, the most characteristic feature of metal triflates is that they are stable and work as Lewis acid in water medium and can be reused after reaction. Next to that, metal triflate is still active in the coexistence of many Lewis bases containing nitrogen, oxygen, phosphorus and sulfur atoms. In this chapter, the experiments focus on screening of lignocellulose source, temperature and metal triflate to get the best catalysis performance. In addition, the transformation of lignocellulose feedstock was characterized in detail via various techniques and several model compound experiments were carried out as well aiming to elucidate the specific roles of metal triflate and Pd/C in such catalysis system.

### 3.2 EXPERIMENTAL SECTION

#### 3.2.1 CHEMICALS AND MATERIALS

Protobind 1000 alkali lignin was purchased from GreenValue. It was produced by soda pulping of wheat straw (sulfur-free lignin with less than 4 wt% carbohydrate and less than 2 wt% ash). Scotch pine and oak biomass were obtained from Istanbul Technical University, Turkey. Wheat chaff biomass was obtained from Adenstedt, Germany. Birch and poplar biomass were obtained from Energy Research Center of Netherlands (ECN). Extra-dry absolute methanol was purchased from Biosolve. All commercial chemicals were analytical reagents and were used without further purification.

#### 3.2.2 EXPERIMENTAL SETUP AND PROCEDURE

**Experimental Setup:** The same 100 ml Parr autoclaves as in chapter 2 were used for lignocellulose feedstock catalytic depolymerization reactions in this chapter.

**Feedstock Pretreatment:** The feedstock was firstly ball milled to small particles and then sieved into three particle sizes, *i.e.* smaller than 150 μm, between 150 μm and 300 μm and
bigger than 300 μm. The feedstock particles with particle size between 150 μm and 300 μm were selected for further soxhlet extraction in which the feedstock was extracted consecutively with water and ethanol to remove non-structural contents. After soxhlet extraction, the feedstock particles were dried at 105 °C overnight for catalytic reaction.

**Catalytic Reaction:** In a typical run of catalytic lignocellulose depolymerization reaction with metal triflate, the autoclave was charged with a suspension of 2.0 g feedstock, 200 mg Pd/C (5 wt% Pd loading), 0.0322 mmol metal triflate and 30 μl n-dodecane internal standard in 40 ml methanol. The reactor was sealed and purged with nitrogen and hydrogen several times sequentially. After leak testing, the hydrogen pressure was set to 30 bar and the reaction mixture was heated to reaction temperature under continuous stirring at 500 rpm within 0.5 h. In order to monitor the whole reaction process, several liquid samples (about 0.4 ml for each) were taken out from autoclave for direct GC-MS measurement by a special sampling loop. After reaction, the heating oven was removed and the reactor was cooled down to room temperature by water bath.

For model compound experiments, 12 ml mini-autoclave was used for reaction. For each model compound, four experiments with different catalyst combination were done, i.e. without catalyst, with Yb triflate, with Pd/C (5 wt% Pd loading) and with Yb triflate and Pd/C (5 wt% Pd loading). In a typical run with both Yb triflate and Pd/C, 50 mg model compound, 10 mg Pd/C, 5 mg Yb triflate and 30 μl n-dodecane internal standard were added to 5 ml methanol. Then the mini-autoclave was sealed and checked for possible leaking. After leaking check, the mini-autoclave was heated to 160 °C and maintained at that temperature for 2 h (glyceryl trioleate model compound is an exception, the reaction time for it is 1h). After reaction, an aliquot of 1 ml was taken from reaction mixture and directly analyzed by GC-MS without dilution following filtration with a 0.45 μm syringe filter. The model compound conversion was based on 1D GC-FID using experimentally determined weight relative response factors to n-dodecane.

For Yb triflate recyclability experiment, the reaction mixture was treated as shown in Fig. 3.2. As a result, most of Yb triflate would be in the water-soluble sugar solution after treatment. Then the obtained solution was rotary evaporated to remove water under vacuum. The resulting
solid residue was re-dissolved in 40 ml methanol and subjected to a new experiment under the same conditions.

**Lignocellulose Products Analysis Procedure:** The products analysis begun with gas phase products analysis. Gas phase products were collected from the autoclave before it was opened and analyzed by Gas-Solid Chromatography (GSC). Collected gas products were sent to an Interscience Compact Gas Chromatography system, equipped with a Molysieve 5 Å and Porabond Q column each with a Thermal Conductivity Detector (TCD), and a Al₂O₃/KCl column with a Flame Ionization Detector (FID). The identification and quantification of gas products were done by using a gas cylinder containing known quantities of permanent gases.

Then the autoclave was adjusted to pressure of 1 bar before was opened to ambient air. A work-up procedure was developed for the analysis of both liquid products and solid residue as showed in Fig. 3.2. At first, the remaining mixture was collected and combined with solution obtained from washing the autoclave with methanol. Then the collected reaction mixture was filtered and separated into liquid phase and solid residue. For liquid phase, the methanol was removed by rotary evaporation and the remaining “product oil” was extracted by water and ethyl acetate three times to obtain water phase (mainly consisting of sugar products) and ethyl acetate phase (mainly consisting of lignin products). For the carbohydrate and Pd/C solid residue, a standard total sugar determination procedure was applied to determine the content and composition of carbohydrate residue.

![Fig. 3.2 Work-up procedure of reaction product mixture from lignocellulose reaction](image-url)
3.2.3 CHARACTERIZATION

**GC-MS:** The liquid phase products were analyzed by a Shimadzu 2000 GC-MS system equipped with a RTX–1701 column (60 m×0.25 mm×0.25 μm) and a flame ionization detector (FID) together with a mass spectrometer detector. For lignin monomers, the peak identification of products was achieved based on a research of the MS spectra with the NIST11 and NIS11s MS libraries. For methylated monosaccharides, the peak identification was achieved by comparing retention time with standard methylated monosaccharides. All the quantitative analyses of liquid phase product were based in 1D GC-FID. Experimentally determined weight relative response factors were used for calculation related to n-dodecane as the internal standard. The yields of lignin monomers and methylated sugar and the mass balance are calculated using following equations.

\[
\text{Yield of monomers (wt%) = } \frac{\text{weight of monomers}}{\text{weight of starting feedstock} \times \text{lignin weight percentage in feedstock}} \times 100\%
\]

\[
\text{Yield of methylated sugars (wt%) = } \frac{\text{weight of methylated sugars}}{\text{weight of starting feedstock}} \times 100\%
\]

\[
\text{Mass balance(wt%) = } \frac{\text{weight of residue + weight of methylated sugars + weight of monomers}}{\text{weight of starting feedstock}} \times 100\%
\]

**Gel permeation chromatography (GPC):** GPC analyses were performed by using a Shimadzu apparatus equipped with two columns in series (Mixed-C and Mixed-D, polymer laboratories) and a UV-Vis detector at 254 nm. The column was calibrated with polystyrene standards. Analyses were carried out at 25 °C using THF as eluent with flow rate of 1 ml/min. For the lignin residue analysis, the sample was prepared at a concentration of 2 mg/ml. All samples were filtered using 0.45 μm filter membrane prior to injection.

**1H-13C HSQC NMR Analysis:** All NMR spectra were recorded using a Varian 400 MHz spectrometer. The samples were dissolved in DMSO-d6. 1H-13C HSQC NMR spectra were obtained using the phase sensitive Crisis gc2HSQC program. The spectral widths were 5000 Hz and 20000 Hz for the 1H- and 13C-dimensions, respectively. Normally, 1.5 s relaxation delay, the number of scans was 16, and 256 time increments were recorded in the 13C dimension. Data processing was performed using the MestReNova software. The residual DMSO solvent peak
was used as an internal reference. The assignment of the cross-peaks were made by comparison with literature data and standard compounds which contain the same functional groups.\textsuperscript{10-11}

3.3 RESULTS AND DISCUSSION

3.3.1 Promoting Effect of Yb-triflate

The promoting effect of Yb triflate was firstly demonstrated using scotch pine as feedstock. The results are summarized in Table 3.1 and Fig. 3.3. It is clear that combining Pd/C and Yb triflate can greatly enhance depolymerization of lignin of scotch pine. For example, the maximum yield was reached only at the reaction time of 1h if both Pd/C and Yb triflate were used. Moreover, there was much less residue left if Yb triflate was added which implies that Yb triflate can catalyze the release of lignin and hemicellulose from lignocellulose during reaction. The mass balance was less than 100 \% is due to the existence of lignin dimers, oligomers and sugar dimers, oligomers which cannot be identified in GC-MS. The residue in blank experiment was less than 2 g because slow release of lignin and hemicellulose by alcoholsysis.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst(s)</th>
<th>residue (mg)</th>
<th>Lignin Monomer Yield (wt%)</th>
<th>Methylated C5 &amp; C6 sugars (mg)</th>
<th>Mass Balance (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Blank</td>
<td>1780</td>
<td>5 (27 mg)</td>
<td>0</td>
<td>90</td>
</tr>
<tr>
<td>2</td>
<td>Pd/C</td>
<td>1780</td>
<td>17 (95 mg)</td>
<td>0</td>
<td>94</td>
</tr>
<tr>
<td>3</td>
<td>Yb-triflate</td>
<td>1240</td>
<td>1 (3 mg)</td>
<td>496</td>
<td>87</td>
</tr>
<tr>
<td>4</td>
<td>Pd/C+Yb-triflate</td>
<td>1260</td>
<td>24 (133 mg)</td>
<td>517</td>
<td>95</td>
</tr>
</tbody>
</table>

[a] The weight percentage of lignin content in scotch pine is 27 wt\%.\textsuperscript{6}

[b] Reaction conditions: 40 ml methanol, P (H\textsubscript{2}) = 30 bar, Temperature=180 °C Reaction time=6 h
Fig. 3.3 Monomer yield evolution of Scotch pine over time in methanol

The chromatogram of products mixture obtained after reaction using both Pd/C and Yb triflate is shown in Fig 3.4. There are three major monomer products which are derived from G type lignin unit in scotch pine feedstock. Such monomer composition is reasonable since scotch pine is softwood and mainly consists of G units.

Fig. 3.4 Chromatogram of mixture obtained after reaction using Pd/C and Yb triflate

3.3.2 Effect of Feedstock

In this section, different lignocellulose feedstocks were tested, including hardwood (birch, oak and poplar), softwood (scotch pine), grass (wheat chaff) and P1000 lignin. The results are showed in Table 3.2 and Fig. 3.5. These data show that Yb triflate has a positive effect on monomer yield for scotch pine, poplar, oak and birch but such effect does not exist on wheat chaff and P1000 lignin. The highest monomer yield was achieved with birch as feedstock. Based on that observation, we decided to use birch as feedstock for further experiments.
Table 3.2 Monomer yield of different feedstocks in methanol\[^a\]

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Catalyst(s)</th>
<th>Reaction Time (h)</th>
<th>Temperature (°C)</th>
<th>residue (g)</th>
<th>Monomer Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scotch</td>
<td>Pd/C</td>
<td>2</td>
<td>200</td>
<td>1.78</td>
<td>17</td>
</tr>
<tr>
<td>Pine</td>
<td>Pd/C+Yb-triflate</td>
<td>2</td>
<td>200</td>
<td>1.26</td>
<td>24</td>
</tr>
<tr>
<td>Polar</td>
<td>Pd/C</td>
<td>2</td>
<td>200</td>
<td>1.69</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>Pd/C+Yb-triflate</td>
<td>2</td>
<td>200</td>
<td>1.55</td>
<td>41</td>
</tr>
<tr>
<td>Oak</td>
<td>Pd/C</td>
<td>2</td>
<td>200</td>
<td>1.33</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td>Pd/C+Yb-triflate</td>
<td>2</td>
<td>200</td>
<td>0.64</td>
<td>48</td>
</tr>
<tr>
<td>Birch</td>
<td>Pd/C</td>
<td>2</td>
<td>200</td>
<td>1.56</td>
<td>39</td>
</tr>
<tr>
<td></td>
<td>Pd/C+Yb-triflate</td>
<td>2</td>
<td>200</td>
<td>1.08</td>
<td>54</td>
</tr>
<tr>
<td>Wheat chaff</td>
<td>Pd/C</td>
<td>2</td>
<td>200</td>
<td>1.77</td>
<td>7</td>
</tr>
<tr>
<td>P1000 lignin[^b]</td>
<td>Pd/C+Yb-triflate</td>
<td>2</td>
<td>200</td>
<td>N/A</td>
<td>3</td>
</tr>
</tbody>
</table>

\[^a\] The weight percentages of lignin content in scotch pine, poplar and birch are 27 wt\%, 21 wt\%, and 19 wt\%.\[^6\] The weight percentage of lignin content in oak (26 wt\%) and wheat chaff (21 wt\%) were experimentally determined by Klason lignin method.

\[^b\] For P1000 lignin experiment, the amount of feedstock is 1 g instead of 2 g.
**Fig. 3.5** Monomer yield evolution over time in methanol of (a) polar, (b) oak, (c) birch (d) wheat chaff and (e) P1000 lignin

The chromatograms of birch and wheat chaff catalyzed by Pd/C and Yb triflate are shown in Fig. 3.6. There are six major products in the birch case of which three are derived from G type units and the other three are derived from S type units. It should be noted that the above six products were also identified in other two hardwood biomass (poplar and oak) yet with a slightly different ratio of S-derived products to G-derived products. Also six products can be identified in the wheat chaff case with much less yield than in birch and monomers derived from all H, G, and S type lignin units can be found (Fig. 3.6).

**Fig. 3.6** Chromatograms of mixture obtained from (a) birch and (b) wheat chaff
Combing the monomer yield data and GC-MS chromatograms of different feedstocks, we suggest that hardwood lignin rich in S units is generally more suitable for valorization using Pd/C and Yb triflate as catalyst in methanol than softwood and grass lignins. Similar suggestion was also put forward in a recent publication using Ru/C as catalyst.\textsuperscript{6}

3.3.3 Effect of Temperature

We investigated the catalytic depolymerization of birch lignocellulose at different temperatures using Pd/C and Yb triflate in this section. The results shown in Table 3.3 indicate that temperature plays an important role in this catalytic reaction. With increasing temperature, the monomer yield increased and the residue weight decreased. Less residue is produced at higher temperature means that more hemicellulose and lignin were released from the feedstock which is consistent with the fact that more lignin monomers and methylated C5 sugars were produced at higher temperature. The reason for equal monomer yield at 200 °C and 220 °C is that both temperatures were high enough to fully convert almost all lignin content in birch at reaction time of 2 h. The smaller mass balance at higher temperature is due to the existence of more lignin and sugar dimers and oligomers.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Temperature (°C)</th>
<th>Residue (mg)</th>
<th>Lignin monomer yield (wt %)</th>
<th>Methylated C5 sugar (mg)</th>
<th>Mass balance (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>160</td>
<td>1650</td>
<td>31 (119 mg)</td>
<td>125</td>
<td>94</td>
</tr>
<tr>
<td>2</td>
<td>180</td>
<td>1360</td>
<td>51 (194 mg)</td>
<td>255</td>
<td>90</td>
</tr>
<tr>
<td>3</td>
<td>200</td>
<td>1080</td>
<td>54 (207 mg)</td>
<td>497</td>
<td>89</td>
</tr>
<tr>
<td>4</td>
<td>220</td>
<td>940</td>
<td>54 (205 mg)</td>
<td>508</td>
<td>83</td>
</tr>
</tbody>
</table>

[a] The weight percentage of lignin content in birch is 19 wt\%.\textsuperscript{6}
[b] Reaction conditions: 40 ml methanol, P (H\textsubscript{2}) = 30 bar, Reaction time=2 h

The monomer yield evolution over time at different reaction temperatures is shown in Fig. 3.7. Quite surprisingly, the maximum monomer yield was reached at 220 °C even during the heating-up period, \textit{i.e.} at the reaction time of 0 h. Also more methylated C5 sugar produced at 200 °C and 220 °C which suggests that more hemicellulose was depolymerized at higher temperature. On the other hand, lignin depolymerization was relatively slow at 160 °C as the
monomer yield at 2 h was only about half of the maximum yield. Based on the observations above, we decided to choose 180 °C as reaction temperature for further experiments due to moderate monomer yield and good sugar retention at this temperature.

![Graph showing monomer yield evolution over time in methanol at different temperature](image)

**Fig. 3.7** Monomer yield evolution over time in methanol at different temperature

### 3.3.4 Effect of Different Metal Triflates

We further examined the promoting effect of different metal triflates and two common Lewis acids, *i.e.* AlCl$_3$ and ZnCl$_2$. The results are summarized in Table 3.4. First of all, all metal triflates, either divalent or trivalent or tetravalent, have a significant promoting effect on lignin monomer yield and Al triflate led to the highest monomer yield. Furthermore, if we compare different metal triflates, a general trend can be observed: the smaller the size and the higher the positive charge of the metal cation, the stronger the promoting effect. Such observation indicates that the promoting effect of metal triflate is related to Lewis acidity of its metal cation. At last, the results show that metal triflate has a stronger promoting effect than common metal chloride Lewis acid. A possible reason for such a difference is that metal chloride is less stable in reaction condition, especially in the presence of water.
Table 3.4 Yield of residue, lignin monomer, sugar and mass balance of birch in methanol with different Lewis acid catalysts\(^{[a-b]}\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Metal.</th>
<th>Residue yield (mg)</th>
<th>Lignin monomer yield (wt %)</th>
<th>Methylated C5 sugar (mg)</th>
<th>Mass balance (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ni(II)</td>
<td>1340</td>
<td>46 (174 mg)</td>
<td>235</td>
<td>87</td>
</tr>
<tr>
<td>2</td>
<td>Cu(II)</td>
<td>1360</td>
<td>42 (161 mg)</td>
<td>192</td>
<td>86</td>
</tr>
<tr>
<td>3</td>
<td>Sc(III)</td>
<td>1250</td>
<td>48 (184 mg)</td>
<td>331</td>
<td>88</td>
</tr>
<tr>
<td>4</td>
<td>Yb(III)</td>
<td>1360</td>
<td>51 (194 mg)</td>
<td>255</td>
<td>90</td>
</tr>
<tr>
<td>5</td>
<td>La(III)</td>
<td>1390</td>
<td>44 (169 mg)</td>
<td>243</td>
<td>90</td>
</tr>
<tr>
<td>6</td>
<td>Al(III)</td>
<td>1190</td>
<td>55 (208 mg)</td>
<td>490</td>
<td>94</td>
</tr>
<tr>
<td>7</td>
<td>Hf(IV)</td>
<td>1110</td>
<td>51 (193 mg)</td>
<td>478</td>
<td>89</td>
</tr>
<tr>
<td>8</td>
<td>ZnCl2</td>
<td>1690</td>
<td>28 (107 mg)</td>
<td>30</td>
<td>91</td>
</tr>
<tr>
<td>9</td>
<td>AlCl3</td>
<td>1540</td>
<td>35 (133 mg)</td>
<td>67</td>
<td>87</td>
</tr>
<tr>
<td>10</td>
<td>Blank</td>
<td>1790</td>
<td>16 (62 mg)</td>
<td>5</td>
<td>93</td>
</tr>
</tbody>
</table>

\(^{[a]}\) The weight percentage of lignin content in birch is 19 wt%.\(^6\)

\(^{[b]}\) Reaction conditions: 40 ml methanol, P (H\(_2\)) = 30 bar, Temperature = 180 °C, Reaction time=2 h

### 3.3.5 Detailed Investigation of Birch Catalytic Depolymerization

In order to understand the depolymerization process better, we carried out four experiments with different catalyst combinations. The photos of solutions after reaction are shown in Fig. 3.8 and the catalytic results are presented in Table 3.5. The two solutions without Pd/C are yellow in color which may result from the undepolymerized lignin fragments. Furthermore, similar to results of scotch pine at 200 °C, much less residue was left and more methylated sugars were produced if Yb triflate was added. At last, unlike in the case of scotch pine, Pd/C can also catalyze the depolymerization of hemicellulose in the case of birch to some degree as proved by data gained with sole Pd/C catalyst.

---

**Fig. 3.8** Product mixtures after reaction of different catalyst combinations.
From left to right: blank, Pd/C, Yb triflate, Pd/C and Yb triflate
Table 3.5 Yield of residue, lignin monomer, sugar and mass balance of birch with different catalyst combination[a-b]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Residue (mg)</th>
<th>Lignin monomer yield (wt %)</th>
<th>Methylated C5 sugar (mg)</th>
<th>Mass balance (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Blank</td>
<td>1810</td>
<td>6 (22 mg)</td>
<td>0</td>
<td>92</td>
</tr>
<tr>
<td>2</td>
<td>Yb-triflate</td>
<td>1410</td>
<td>9 (34 mg)</td>
<td>146</td>
<td>80</td>
</tr>
<tr>
<td>3</td>
<td>Pd/C</td>
<td>1790</td>
<td>16 (62 mg)</td>
<td>5</td>
<td>93</td>
</tr>
<tr>
<td>4</td>
<td>Pd/C+Yb-triflate</td>
<td>1360</td>
<td>51 (194 mg)</td>
<td>255</td>
<td>90</td>
</tr>
</tbody>
</table>

[a] The weight percentage of lignin content in birch is 19 wt%.
[b] Reaction conditions: 40 ml methanol, P (H₂) = 30 bar, Temperature = 180 °C, Reaction time=2 h

We extracted lignin products from the full products mixture using ethyl acetate with the aim to characterize them in more details. We can see in Fig. 3.9 that almost all peaks in the chromatogram after extraction are lignin monomers. We further characterized these lignin products by means of GPC and HSQC NMR.

We can see the molecular weight distribution of lignin products in the GPC chromatograms (Fig. 3.10). The most important observation is that there are many oligomeric products in the chromatograms of blank and Yb triflate experiments in the absence of Pd/C catalyst. Such observation implies that it is Pd/C that catalyzes the depolymerization of lignin. Furthermore,
some oligomers also present in the experiment of Pd/C + Yb triflate and the presence of such oligomers is due to the strong C-C linkage in lignin which cannot be broken by Pd/C. The lowest amount of oligomers can be found in the mixture using Pd/C catalyst because less lignin was released in the absence of Yb triflate.

We can get more information about chemical structure changes in the lignin product mixture from the 2D HSQC NMR results (Fig. 3.11). Signals of common lignin linkages, such as β-O-4 and β-β, and double bonds can be found in Figs 3.11 a and c without using Pd/C catalyst. These signals disappear when Pd/C catalyst is present (Figs. 3.11 b and d), which implies that Pd/C can break lignin linkages and saturate double bonds during the reaction. Furthermore, if we compare spectra of a with b, we observe that linkage signals disappear in the presence of Pd/C. Such observation suggests that releasing of lignin from lignocellulose is the rate-limiting step during catalytic reaction since there should be lignin linkage signals in spectrum b if breaking linkages would be a slow reaction step. At last, the spectra of blank and Yb triflate samples are very similar and such observation suggests the sole Yb triflate has little impact on lignin structural changes.

![Fig. 3.10 GPC of the lignin products mixture obtained from reactions catalyzed by blank, Pd/C, Yb triflate, and Pd/C and Yb triflate in methanol.](image)
3.3.6 The Catalytic Role of Pd/C and Metal Triflate

In this section, we intend to give a picture on lignocellulose depolymerization and elucidate the specific roles of Pd/C and metal triflate during the reaction based on the above presented results and on further model compound experiments. Since depolymerization of lignocellulose is a rather complex process, we simplify it into three stages which are releasing of lignin and hemicellulose, depolymerization of hemicellulose and depolymerization of lignin.

For the first stage, the residue data in Table 3.1 and Table 3.5 shows that experiment with only Yb triflate results much less residue than blank experiment but experiment with only Pd/C catalyst results almost the same amount of residue as blank experiment. These observations imply that it is the metal triflate that catalyzes the releasing of lignin and hemicellulose. Moreover, also as suggested in Fig. 3.11, the releasing step is the rate limiting step. So the
origin of promoting effect of metal triflate on lignin monomer yield is that it can facilitate releasing of lignin. In order to further confirm such an argument, two model compound experiments were carried out using glyceryl trioleate and phenyl glycoside which mimic ester and ether linkages between lignin and carbohydrates. The reason for choice of those two model compounds is that they can represent two common linkages in carbohydrate complex. The results are presented in Fig. 3.12 and 3.13. In both cases, Yb triflate can efficiently break the ester and ether linkages in model compounds but Pd/C cannot do it. Such model compounds results are consistent with the results of experiments with real lignocellulose.

![Fig. 3.12 Yield of products of glyceryl trioleate with four catalyst combination](image1)

![Fig. 3.13 Yield of products of phenyl glycoside with four catalyst combination](image2)
For the hemicellulose depolymerization, Yb triflate plays a role in this stage as indicated by the experiments with sole Yb triflate in section 3.3.1 and 3.3.5 in which much methylated sugars are produced. For the role of Pd/C in this stage, the results of scotch pine and birch were different. After adding Pd/C the yield of methylated sugar did not increase significantly but it increased in the case of birch. We explain this difference by assuming that the effect of Pd/C on hemicellulose depolymerization is dependent on the properties of hemicellulose, such as degree of polymerization (DP), composition, etc. We think that heterogeneous Pd/C catalyst cannot facilitate depolymerization of hemicellulose with large DP because of access limitations but it can catalyze depolymerization of small hemicellulose fragments. In order to investigate the effect of Pd/C on depolymerization of small sugar molecules, we carried out an experiment with cellulbiose as model compound. Both chromatograms of only Pd/C and only Yb triflate show peaks of methylated sugar products by breaking the glycosidic bond in cellulbiose. This model compound results indicates that Pd/C catalyst can catalyze depolymerization of small sugar molecule.

![Figure 3.14](image)

**Fig. 3.14** GC chromatograms of products of cellulbiose with Pd/C and Yb triflate

The experimental data with only Pd/C (section 3.3.1 and 3.3.5) indicates that Pd/C can convert lignin into monomers in which certain amount of lignin monomer are produced. It is not clarified yet, if Yb triflate plays a role in lignin depolymerization, such as synergistic effect with Pd/C. If we compare the experiments of single Pd/C with combined Yb triflate and Pd/C,
there is a significant increasing in monomer yield. Obviously, such observation can be explained by the fact that Yb triflate can catalyze releasing of lignin from lignocellulose, but is it the only reason or more specifically is there synergy effect between Pd/C and Yb triflate in lignin depolymerization.

In order to answer this question, we carried out experiments using solution with real lignin fragments and with model compound. The lignin fragments were obtained by catalytic depolymerization of birch with sole Yb triflate and the resulting products mixture was extracted by ethyl acetate followed by rotary evaporation. The lignin fragments were redissolved in 80 ml methanol before reaction and 40 ml methanol solution of lignin fragments was used for each reaction. The reaction results are listed in table 3.5. It can be seen very well from those data that both reaction have the same monomer yield evolution profile over time. Furthermore, we used benzyl phenyl ether (BPE) as lignin model compound for experiment and the results are showed in Fig. 3.15. It is Pd/C shown in Fig. 3.15 that Pd/C catalyzes the breaking the ether bond in BPE and there is no difference in total monomer yield in experiments with Pd/C and Pd/C + Yb triflate. At last, the monomer yield evolution profile of P1000 lignin in Fig. 3.5 shows that adding Yb triflate does not improve monomer yield compared with only Pd/C catalyst.

Table 3.5 Lignin monomer yield from extracted lignin fragments$^{[a-b]}$

<table>
<thead>
<tr>
<th>catalyst</th>
<th>Lignin monomer yield at different reaction time (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0h</td>
</tr>
<tr>
<td>Pd/C</td>
<td>9</td>
</tr>
<tr>
<td>Pd/C and Yb triflate</td>
<td>9</td>
</tr>
</tbody>
</table>

$^{[a]}$ The weight percentage of lignin content in birch is 19 wt% and lignin monomer yield is based on initial 2 g birch feedstock.

$^{[b]}$ Reaction conditions: 40 ml methanol, P (H$_2$)=30 bar, Temperature = 180 °C, Reaction time=2h

Base on all results above, we suggest that there is no obvious synergistic effect between Pd/C and Yb triflate in lignin depolymerization. But it should be noted that such suggestion is not conclusive as we can see from the results in Table 3.5 and Fig. 3.12 that monomer yields in both experiments with Pd/C and Pd/C + Yb triflate reach the maximum yield due to fast
hydrogenolysis during reaction. So further experiments at lower temperature are needed to finally confirm the synergistic effect between Pd/C and Yb triflate.

3.3.7 Yb triflate Recyclability and Effect of Atmosphere

At last, some additional experiments were carried out to examine the recyclability of Yb triflate and the effect of atmosphere. The catalytic results are presented in Table 3.6. Replacement of H₂ with N₂ results much less lignin monomer production which points out the important role of H₂ in lignin hydrolysis. Yet it is interesting to note that considerable amount of lignin monomers were still produced. We think that those monomers were produced by in situ produced H₂ from methanol catalyzed by Pd/C. In addition, more residue and less methylated sugar were produced in nitrogen atmosphere and such observation again agrees with our previous argument of Pd/C’s role in hemicellulose depolymerization. For the recycled Yb triflate experiment, the monomer yield reached 76 % of original yield by fresh Yb triflate. For the origin of such decrease in activity, catalyst deactivation is one possible reason. Nevertheless, we consider a more likely reason is the loss of Yb triflate during recycling procedure because it was really difficulty experimentally to recycle little amount of Yb triflate (20 mg in this case) by simple evaporation and extraction.
Table 3.6 Yield of residue, lignin monomer, sugar and mass balance of birch with nitrogen atmosphere and recycled Yb triflate\[^{[a-b]}\]

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Atmosphere</th>
<th>Residue (mg)</th>
<th>Monomer yield (wt %)</th>
<th>Methylated C5 sugar (mg)</th>
<th>Mass balance (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/C+Yb triflate</td>
<td>H(_2)</td>
<td>1360</td>
<td>51 (194 mg)</td>
<td>255</td>
<td>90</td>
</tr>
<tr>
<td>Pd/C+Yb triflate</td>
<td>N(_2)</td>
<td>1470</td>
<td>19 (72 mg)</td>
<td>106</td>
<td>82</td>
</tr>
<tr>
<td>Pd/C+recycled Yb triflate</td>
<td>H(_2)</td>
<td>1550</td>
<td>39 (149 mg)</td>
<td>206</td>
<td>95</td>
</tr>
</tbody>
</table>

\[^{[a]}\] The weight percentage of lignin content in birch is 19 wt\%
\[^{[b]}\] Reaction conditions: 40 ml methanol, P = 30 bar, Temperature = 180 °C, Reaction time=2 h

3.4 CONCLUSIONS

In this chapter we investigated a novel lignin depolymerization approach, \textit{i.e.} one-step delignification and hydrogenolysis from raw lignocellulose. We observed that adding metal triflate to Pd/C catalyst can enhance monomer production enormously. Then we further screened influence of feedstock origin, temperature, metal triflate type on the overall catalytic performance and we found out that:

- Significant promoting effect of metal triflate was observed in softwood and hardwood feedstock but not observed in grass lignin and technical lignin.
- Temperature plays a crucial role in lignocellulose depolymerization. At higher temperature (200 °C and 220 °C) maximum lignin yield was reached at very short time in the expense of significant loss of hemicellulose. At lower temperature (160 °C), the production of lignin monomer was relatively low.
- All the metal triflates examined in this chapter have a great promoting effect on lignocellulose conversion and metal triflate was superior to common metal chloride Lewis acid.

Moreover, four well-designed experiments with birch as feedstock and some model compound experiments were done combined with a detailed characterization of lignin products with aim to shed light on the specific role of metal triflate and Pd/C in this catalytic system. Based on the results from above mentioned experiments, we suggested that:

- The releasing of lignin from lignocellulose is the rate-limiting step for Pd/C catalyzed lignocellulose depolymerization. The origin of promoting effect of metal triflate is that it can facilitate releasing of lignin and hemicellulose. One step further, metal triflate
can catalyze the breaking of common ether and ester linkages between lignin and carbohydrate.

- Apart from the role in accelerating the releasing of lignin, metal triflate also plays a role in hemicellulose depolymerization. For the Pd/C catalyst, the experimental results indicate that it catalyzes the depolymerization of released lignin fragments and the depolymerization of hemicellulose to some extent. At last, no apparent synergistic effect is found between metal triflate and Pd/C in lignin depolymerization.

Finally, two additional factors were examined, *i.e.* atmosphere and Yb triflate recyclability. The results imply that catalytic depolymerization was less efficient than that in N\textsubscript{2} and the recycled Yb triflate can recover to 76 % of its initial monomer yield.
3.5 REFERENCES


SUMMARY

Given the fact that there is an increasing demand for sustainable energy and chemical production nowadays, research of utilizing alternative feedstocks to fossil resources is becoming more and more important. Among all possible feedstocks, biomass presents to be a promising candidate which can not only be converted into fuel but also chemical. Nevertheless, lignin, one of the major components of biomass, is underutilized due to its recalcitrant physicochemical nature. Traditional lignin depolymerization approach starts with technical lignin which is readily available from industry. On the other hand, production of lignin monomers directly from wood lignin appears to be another interesting approach for lignin valorization as evidenced by several recent reports. In this graduation project, we investigated both two lignin valorization strategies with the aim to evaluate their potential role in future biorefinery.

In chapter 2, we tested the depolymerization of technical lignin using mixed oxide catalyst in supercritical condition. The factors of atmosphere, solvent, catalyst type and lignin type were examined further in order to achieve the optimized catalytic performance. The results show that many valuable monomers (such as BTX and hydrogenated cyclics) can be obtained via this approach after reaction. In chapter 3, we tested the depolymerization of raw lignocellulose in reductive atmosphere at relatively lower temperature. We found out that lignin monomers with high yield and selectivity were produced via this approach after reaction. Furthermore, mechanism study revealed that adding metal triflate to reaction can greatly enhance overall reaction activity because it can catalyze lignin and hemicellulose release from lignocellulose during reaction.

At last some advantages and disadvantages of above two lignin depolymerization approaches are listed in Table 1. Base on such comparison, we suggest here that lignin valorization directly from raw lignocellulosic feedstock is the a promising approach compared with from technical lignin.
Table 1. A brief comparison of lignin valorization with technical lignin and wood lignin.

<table>
<thead>
<tr>
<th>Lignin Type</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Technical Lignin</td>
<td>• One step reaction, BTX products</td>
<td>• Harsh reaction condition (High Temp. and Pressure)</td>
</tr>
<tr>
<td></td>
<td>• Without using H₂</td>
<td>• Ethanol consumption</td>
</tr>
<tr>
<td></td>
<td>• Cheap catalyst</td>
<td>• Catalyst deactivation</td>
</tr>
<tr>
<td></td>
<td>• Flow reactor might be possible</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• High monomers yield possible (lignin + ethanol)</td>
<td></td>
</tr>
<tr>
<td>Wood lignin</td>
<td>• Cheap feedstock and solvent</td>
<td>• Flow reactor is difficult</td>
</tr>
<tr>
<td></td>
<td>• Much milder reaction condition</td>
<td>• 2nd upgrading process needed</td>
</tr>
<tr>
<td></td>
<td>• High selectivity</td>
<td>• Limited production capacity (15 -30 wt% lignin content)</td>
</tr>
<tr>
<td></td>
<td>• Commercial catalyst</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Easy product separation</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Catalyst expected to be stable</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Easier to scale up</td>
<td></td>
</tr>
</tbody>
</table>
ACKNOWLEDGEMENTS

First of all, I would like give my sincere gratitude to Prof. Hensen for accepting me to do my graduation project in the Inorganic Material Chemistry group. I also like to thank you for your critical discussions and valuable suggestions during our meetings and for giving me the opportunity to attend CHAINS and NCCC conferences from which I really broadened my horizon in catalysis. Next, I would like to give my thanks to my project supervisor, Xiaoming, who provided continuous guidance during this project. Without your all kinds of help, it would be impossible for me to finish this graduate project. You taught me how to operate with autoclave to run reaction, how to characterize catalysts and products by various techniques and how to analyze and present experimental results in a scientific way.

The next person I would like to thank is Tamás. Thanks so much for reviewing my graduation project and I think my graduation project would be full of grammatical mistakes and Chinglish without your kindly help. You effort definitely makes my report much more readable and professional. I also would like to give my gratitude to Olivia for the contribution to this project. Most of the wood lignin samples were prepared by you which really facilitates the progress of this project a lot. My thanks also will be given to other members in the lignin group. You are all helpful and considerate to me during this project, such as fixing GC-MS machine and sharing autoclaves.

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