Sustainable pathways to chemicals and fuels from lignocellulose via catalytic cleavage and coupling reactions
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Catalytic Two Steps Conversion of Lignocellulose to Alkanes

Efficient methodologies for converting lignocellulose to liquid fuels have potential to reduce the rapid depletion of fossil fuels and carbon dioxide emissions. Herein, I described a two-step process that is able to completely convert pinewood lignocellulose to alkanes. The first step involves the conversion of raw woody biomass (lignocellulose) to alcohols using a solid base catalyst - copper doped porous metal oxide (Cu-PMO), in supercritical methanol (sc-MeOH). The second step involves the hydrodeoxygenation (HDO) of the resulting alcohols to alkanes performed by using a solid acid catalyst together with Pd/C in dodecane. A number of solid acid catalysts were tested and both HZSM-5 and Nafion performed a similar degree of efficiency. At 180 °C, the product mixture from the first step could be fully converted to alkanes with chain length of 5 to 10. This simple process opens a new, two step method for conversion of lignocellulose to alkanes with high selectivity.

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### 7.1 Introduction

With the decreasing oil reserves and concerns toward global warming due to CO₂ emission, it is vital to move on to more sustainable fuel sources. The conversion of biomass to fuels would mean the acquisition of a fossil fuel replacement that is both CO₂ neutral and renewable as it can be extracted from plant material. Lignocellulosic biomass, which are non-edible and normally by-products of agricultural production, would be a favorable renewable material to be used in fuel production.

![Figure 7.1 General strategies for catalytic conversion of lignocellulose to alkanes.](image)

The development of highly selective and energy efficient methods for the quantitative conversion of lignocellulosic biomass to alkanes has been a hot subject of much research in the past decades and one of the grand challenges for modern catalytic chemistry. The strategy as shown in Figure 7.1 is typically comprised of several types of transformations: i) Pretreatment to separate each component of lignocellulose; ii) Direct conversion of the lignin, cellulose or hemicellulose to alkanes via HDO reactions; iii) conversion of the separated components to a liquid phase platform chemicals or mixture of various simple chemicals, which means partial removal of oxygen of starting material; and iv) catalytic upgrading of this platform chemicals to the final hydrocarbon fuel by controlled C–C coupling reactions and removal of the remaining oxygen functionality.

For example, isolated lignin after pretreatment can be used as a fuel precursor and converted to cycloalkanes with Ni catalysts via cascade HDO reaction. Hydroxymethylfurfural (HMF) which derived from cellulose can be converted to linear C₉ or C₁₅ alkanes by aldol-condensation over solid base catalysts followed by dehydration/hydrogenation reaction over bifunctional catalysts. Cyclopentanone derived from hemicellulose in agriculture wastes and forest residues can be
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converted to a high-density bicyclic C_{10} hydrocarbon liquid fuel by the combination of solvent-free aldol condensation and one-step hydrodeoxygenation (HDO) reaction.\(^{10}\) It can be also used as coupling agent for the production of jet fuel range alkanes via aldol condensation with butanal\(^{11}\) or 2-methylfuran\(^{12}\). However, in most of the processes, lignocellulose is first separated to its single component by energy intensive pre-treatment process\(^{13,14}\) and only a part of this material is used. As a result direct conversion of raw lignocellulose into fuels would be an ideal process.

Recently, several elegant processes have been developed for direct conversion of lignocellulose to fuels. Xia et al. described the direct hydrodeoxygenation of raw woods into liquid alkanes over a multifunctional Pt/NbOPO\(_4\) catalyst.\(^{15}\) Liu et al. reported the efficient conversion of raw biomass into gasoline alkanes and monophenols and related hydrocarbons over layered LiTaMoO\(_6\) and Ru/C in aqueous phosphoric acid medium.\(^{16}\) However in both of these processes, lignocellulose is not fully converted and the left solid residue makes the separation of catalyst really challenging. Another disadvantage of existing processes is the use of noble metal catalysts which definitely would increase the total input for further industry applications.

Copper doped porous metal oxides (Cu-PMOs) as described in previous chapters containing only earth abundant metals and can be prepared based on very simple procedure. In 2011, Ford and coworkers have found that this catalyst can be used a solid base catalyst for depolymerization of lignocellulose in supercritical methanol.\(^{17}\) Little or no char is formed in this process, which means lignocellulose is fully converted and the solid catalyst can be easily separated and reused. The major liquid product is a mixture of C2-C6 and C9 aliphatic alcohols and methylated derivatives.

This process sounds promising, but several questions related to product analysis and further application remained open. For example, the detail composition of obtained products and the relationship between catalyst composition and product distribution are not clear. Alcohols can be directly used as fuels but normally have low heating values compared to alkanes.\(^{18}\)

Considering this process, the conversion of the alcohols to alkanes has not been accomplished yet, despite the fact that such process is quite ideally suited for a potentially highly efficiently and very simple two step lignocellulose conversion to alkanes. Several catalytic systems have been developed for efficient conversion of alcohols to alkanes\(^{19-22}\) and one simple solution would be the combination of a solid acid and hydrogenation catalyst\(^{23,24}\). Lercher and co-workers\(^{23}\) reported that the combination of Pd/C and HZSM-5 showed an extremely high selectivity in removing oxygen-containing groups of lignin derived phenolic monomers. Approximately 90% cycloalkanes were produced from various substituted phenols in the presence of HZSM-5 and Pd/C at 160 °C. Inspired by this work, we now would like to test if this system could efficiently convert the alcohol mixtures from depolymerization of lignocellulose to alkanes.
Therefore, our goal here is to first investigate the relationship between catalyst composition and product distributions. This needs to provide significantly deeper insight into the compositions of produced alcohol mixtures. Furthermore I would like to explore the possibility and feasibility of upgrading obtained alcohols to alkanes. Finally, a two-step process from lignocellulose to alkanes would be established as shown in Scheme 7.1 which includes the depolymerization of raw lignocellulose to alcohols with Cu-PMO catalyst (step 1) and HDO of produced alcohols to alkanes by the combination of Pd/C and solid acid catalyst.

Scheme 7.1 Process for complete conversion of lignocellulose to alkanes.

7.2 Results and discussion

The Cu-PMO catalysts with different copper content were obtained by calcining the prepared hydrotalcite (HTC) precursors at 460 °C based on previous literature\textsuperscript{25}. The composition of each catalyst (Table 7.1) was found to be in very good agreement with the theoretically expected values, indicating good incorporation of the metal ions into the parent hydrotalcite structures. The formation of the double-layered structure during HTC synthesis was confirmed by powder XRD measurements (Figure 7.1a). After calcination, the HTC structure was transformed into an amorphous mixed-oxide composition (Figure 7.1b). The broad peaks at 37°, 43° and at 63° indicate the formation of spinels MgAlO\textsubscript{2} and CuAlO\textsubscript{2}.

Table 7.1 Composition of prepared Cu-PMO catalysts determined by elemental analysis.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Element content (wt %)</th>
<th>Theoretical composition</th>
<th>Experimental composition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu</td>
<td>Mg</td>
<td>Al</td>
</tr>
<tr>
<td>Cu5-PMO</td>
<td>4.4</td>
<td>31.15</td>
<td>12.4</td>
</tr>
<tr>
<td>Cu10-PMO</td>
<td>8.45</td>
<td>27.85</td>
<td>11.8</td>
</tr>
<tr>
<td>Cu20-PMO</td>
<td>16.25</td>
<td>24.35</td>
<td>11.35</td>
</tr>
</tbody>
</table>
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Figure 7.1 XRD images of prepared hydrotalcite precursors and obtained PMO catalysts.

The catalysts were used in the depolymerization of pine lignocellulose at 300-320 °C, in supercritical methanol based on the procedure described by the Ford group. Notably, during this catalytic processing the reducing equivalents needed for the depolymerization process originate from a part of the solvent upon its reforming. During this reaction most of the lignocellulose (wood sawdust) was converted to liquid products and this enabled the easy separation and of the catalyst.

Figure 7.2 GC-MS of depolymerization products from pinewood lignocellulose using Cu20-PMO in sc-MeOH (Green=confirmed with the use of authentic standard, Blue=similarity index above 90%, Red=similarity index between 70% and 90%)

I attempted to take a closer look into the composition of the product mixture, since previously a holistic evaluation of the product mixture was given by the Ford group, indicating the majority of products being aliphatic alcohols. Indeed, the results found here were in very good agreement with those obtained previously by Ford and coworkers. The
liquid product fractions were analyzed in detail by GC-MS (Figure 7.2). As shown in Figure 7.2, most of products are alcohols with small amount of ethers and esters also detected.

![Diagram showing product distributions](image-url)

**Figure 7.3** Conversion and distribution of products after sc-MeOH reaction from different substrates with different catalysts. Reaction conditions: Substrate 100 mg, catalyst 100 mg, methanol 3 mL, 310 °C, 6 h. a. conversion determined by gravimetric analysis.

The results of products distributions as function of catalyst composition was summarized in Figure 7.3, which clearly shows that the conversion of raw lignocellulose (from 89% to 97%) and selectivity of alcohols (from 39% to 73%) increased with the increase of copper content. This is very likely due to different extent of methanol reforming producing different total pressure of the mixture, which should influence the extent of depolymerization. At the same time, products with chain length of more than 7 decreased slightly with the increase of copper content – this is also attributed to hydrogenolysis processes being more pronounced with more copper content, while Cu5-PMO should behave more like a classical hydrotalcite, promoting possible aldol condensation steps that lead to chain elongation.

Isolated lignin and pure cellulose were also reacted under the same reaction conditions with Cu20-PMO catalyst to evaluate the products obtained from these starting materials. When pure cellulose was used as starting material, the generated product mixtures had similar distributions as that of pine lignocellulose (Figure 7.3). Aliphatic alcohols were obtained as main products with 75% selectivity. Depolymerization of isolated organosolv lignin gave also good conversion of around 90% and alcohols were obtained as the main products with selectivity of 65%. The results were consistent with previous reports by Ford and co-workers.17,26 All these results performed that the sc-MeOH medium provides conditions suitable for solubilizing both cellulose and lignin. Depolymerization of the solubilized cellulose and lignin could be carried out by Cu20-PMO catalyst efficiently. In summary, the catalyst with 20% copper content (Cu20-PMO) gave the best activity and selectivity and able
to fully convert lignocellulose to alcohols with good yield. The following research was based on the products produced with Cu20-PMO catalysts.

Since the product mixtures obtained upon catalytic conversion of pine lignocellulose in sc-MeOH using Cu-PMO, consisted of mainly alcohols, the next, deoxygenation HDO step was studied. First, suitable model compound mixtures were used to discern the optimal catalyst and catalytic conditions for the HDO reaction. We have selected the combination of solid acid and hydrogenation catalyst which have previously shown high efficiency for HDO of lignin derived phenolics.23,24 Different solid acid (e.g. Nafion, HZSM-5, USY-600, ZrO2 and Nb2O5) and temperature (140-180 °C) are tested in order to get the best yield of alkanes.

**Scheme 7.2** Reaction pathways in the hydrodeoxygenation of cyclohexanol.

First, cyclohexanol was identified as suitable model substrate and different solid acids were compared at the same reaction condition (140 °C, 4 h, 10 bar H2). As shown in Scheme 7.2, the reaction starts with an acid catalysed dehydration to yield the corresponding olefin, followed by a C=C hydrogenation by Pd/C. In this way an alcohol can be converted to an alkane in one-pot.

**Table 7.2** Conversion of cyclohexanol using different solid acid catalysts with Pd/C.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solid acid</th>
<th>Conversion %</th>
<th>Selectivity %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cyclohexane</td>
</tr>
<tr>
<td>1</td>
<td>HZSM-5</td>
<td>99</td>
<td>93</td>
</tr>
<tr>
<td>2</td>
<td>USY-600</td>
<td>99</td>
<td>100</td>
</tr>
<tr>
<td>3</td>
<td>ZrO2</td>
<td>8</td>
<td>100</td>
</tr>
<tr>
<td>4</td>
<td>Nb2O5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>Nafion</td>
<td>99</td>
<td>99</td>
</tr>
</tbody>
</table>

Reaction condition: 0.1 mL cyclohexanol, 50 mg solid acid, 10 mg Pd/C, 140 °C, 4 h, 10 bar H2.

As can be seen from the results in Table 7.2, the two zeolites (HZSM-5 and USY-600) as well as Nafion were found to be promising candidates for the conversion of cyclohexanol, giving full substrate conversion at 140 °C after 4 hours. Next, a mixture of primary and secondary alcohols was investigated (Figure 7.4a) and here more differences were seen. HZSM-5 performed the best promoting effect at 140 °C with almost full conversion of all alcohols and the increase of temperature had very little difference aside from the removal of most ether at 180 °C. Other two solid acids showed lower conversion at 140 °C especially for primary alcohols, but almost full conversion could be achieved at higher temperature (160 °C and 180 °C). To further investigate the formation of ethers and the difficulty of converting primary alcohols, another mixture containing only primary alcohols (Figure 7.4b) was prepared and investigated at the same reaction condition. As shown in Figure 7.4b,
conversions of primary alcohol mixtures were quite low in all these three catalytic systems at 140 °C. Therefore, the temperature was then increased to 160 and 180 °C. Indeed the conversion increased dramatically for all substrate mixtures; however, the mixture with USY-600 as solid acid gave a substantial amount of ethers as by-product. HZSM-5 and Nafion gave almost the same results at 180 °C, and the yield of alcohols accounted for 86% and 85% respectively.

**Figure 7.4** Product distribution upon conversion of alcohol model compounds (a. alcohol mixture 1 and b. alcohol mixture 2) using different solid acid catalysts. Reaction conditions: 0.128 mL alcohol mixture 1 or 0.138 mL alcohol mix 2, 50 mg solid acid catalyst, 10 mg Pd/C, 4 h, 10 bar H2.

Since HZSM-5 and Nafion both performed very well on the model mixtures and give similar results at 180 °C, they were both selected for the following tests for the upgrading of lignocellulose derived products to alkanes. The products of depolymerization of pine lignocellulose, cellulose and pine organosolv lignin with Cu20-PMO were used as starting
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materials. As the presence of methanol would hamper reactivity of further HDO reaction, dodecane was added first to the product solution and methanol was subsequently removed through evaporation. The dodecane solution, containing most of the products, was then used for the further upgrading to alkanes. As can be seen in Figure 7.5, the product mixture from pine lignocellulose could be converted to alkanes in high yield with both HZSM-5 and Nafion as solid acid catalyst. However, a bit more by-products were formed when using cellulose and pine organosolv lignin derived product mixture as substrate. The possible reasons could be: i) there are more primary alcohols in the products from cellulose which may result in more esters after reaction as shown previously; ii) the higher content of aromatic monomers, dimers and oligomers from depolymerization of pine organosolv lignin may adsorb on the surface of solid acid catalysts and decreased the activity for further HDO reactions.

The products obtained upon HDO were analyzed in detail by GC-MS, and contained mainly alkanes. As shown in Figure 7.6, both acyclic alkanes (mainly from cellulose and hemicellulose part) and cycloalkanes (mainly from lignin part) were identified. The chain length of the obtained alkanes ranged from 5 to 10. Using Nafion as solid acid catalyst resulted in higher selectivity (26% vs 12%) of long chain alkanes (> 8) as shown in the pie chart of Figure 7.6. This could be explained by the larger pore size of Nafion (> 10 nm) than HZSM-5 (< 1 nm).27 And HZSM-5 is also a good cracking catalyst,28 the obtained alkanes may further converted to other short chain alkanes by HZSM5.

7.3 Conclusions
In summary, we have developed a two-step process that can simply convert lignocellulose solids to liquid alkanes. This process is based on the unique reactivity of Cu-PMO catalysts for complete conversion of lignocellulose to small molecules first developed by Ford’s group,
and then the obtained products were upgraded to alkanes by HDO reaction with the combination of Pd/C and solid acid catalysts.

Cu-PMO catalysts with different copper content performed different activity and the full conversion of pinewood sawdust were achieved by Cu20-PMO catalyst. The obtained product mixtures are detailed analyzed by GC-MS. The Cu20-PMO catalyst also performed well for depolymerization of pure cellulose and organosolv lignin and produce alcohols as main products as well. Screening of different solid acid found that Nafion and HZSM-5 gave the best synergistic effects on the production of alkanes. The product mixture from step 1 by depolymerization of pine lignocellulose could be upgraded to alkanes with around 85% selectivity.

Although this two-step process could convert raw lignocellulose to alkanes, several challenges still need to be solved for further industry applications. For example, some alkanes with chain length less than 5 would be too volatized to be used as fuels and also hard to be quantified. The solvent change from methanol to dodecane between step 1 and step 2 may lose some compounds and takes a lot of energy. Finally, Pd/C is a noble metal catalyst; it would be nice to use non-noble metal catalyst like Ni or Co in order to reduce the total cost of this process.

7.4 Experimental procedures

7.4.1 Preparation of the Cu-PMO catalysts
The HTC (hydrotalcite) catalyst precursor was prepared by co-precipitation. In a typical procedure, a solution containing AlCl₃·6H₂O (12.07 g, 0.05 mol), Cu(NO₃)₂·2.5H₂O (6.98 g, 0.03 mol) and MgCl₂·6H₂O (24.40 g, 0.12 mol) in deionized water (0.2 L) was added to a solution containing Na₂CO₃ (5.30 g, 0.05 mol) in water (0.3 L) at 60 °C under vigorous stirring. The pH was kept between 9 and 10 by addition of small portions of a 1 M solution of NaOH. The mixture was vigorously stirred at 60 °C for 72 h. After cooling to room temperature, the light blue solid was filtered and re-suspended in a 2 M solution of Na₂CO₃ (5.30 g, 0.05 mol) in water (0.3 L) at 60 °C under vigorous stirring. The mixture was vigorously stirred at 60 °C for 72 h. After cooling to room temperature, the light blue solid was filtered and re-suspended in a 2 M solution of Na₂CO₃ (0.3 L) and stirred for overnight at 40 °C. The solids were filtered and washed with deionized water until chloride free. After drying the solid for 6 h at 100 °C, 15.07 g of the hydrotalcite (HTC) was obtained. 4 g of obtained hydrotalcite was then calcined at 460 °C for 24 h in air and yielded 2.5 g of Cu20-PMO catalyst.

The catalyst prepared in this procedure is a porous metal oxide (PMO), denoted as Cu20-PMO, which indicates that in a 3:1 Mg/Al hydrotalcite precursor 20% of the Mg²⁺ ions were replaced with Cu²⁺ ions. Other catalysts with different Cu content were prepared in the same procedure but using different amounts of Cu(NO₃)₂·2.5H₂O and MgCl₂·6H₂O salt and named as Cu5-PMO and Cu10-PMO respectively.
7.4.2 Extraction of lignin from pine lignocellulose
Extraction of lignin from pine lignocellulose was carried out in a 500 mL autoclave with an overhead stirrer and temperature controller. Typically the reactor was charged with 30 g of pine lignocellulose, 250 mL of methanol at room temperature. The reactor was sealed and stirred for 24 h at 170 °C. During the reaction 25 bar of autogenous pressure was developed. After completion of the reaction, the reactor was cooled down to room temperature. The reaction mixture was collected in a 1000 mL beaker by rinsing the reactor several times with methanol and then filtered. The solids were washed with methanol and the combined solution was concentrated to 100 mL by rotary evaporator and precipitated with ice-cold water and then stirred overnight. The mixture was then centrifuged and the solids (Lignin) were collected by decanting the solutions which contained hemicelluloses. The crude lignin was then dried under vacuum. 0.66 g organosolv lignin was then obtained.

7.4.3 Catalytic conversion of pine lignocellulose
Pinewood sawdust (100 mg) and Cu-PMO catalysts (100 mg) was added to a 10 mL Swagelok stainless steel microreactor with 3 mL methanol. The reaction vessel is placed in a heating block at 310 °C for 6h. After reaction the reactor was quickly cooled down in an ice-water bath. The contents of the reaction vessel were transferred to a centrifuge tube and the solid is separated. The liquid layer was collected in a round bottom flask and the solid was washed twice with methanol. All liquid products are combined and methanol is removed in the rotatory evaporator until approximately 5 mL liquid is left. The products are then identified by GC-MS.

7.4.4 HDO of model compounds
Cyclohexanol (0.1 mL) or alcohol mixture 1 (0.128 mL, see Table S1) or alcohol mixture 2 (0.136 mL, see Table S2) is added to a reaction vessel with 50 mg solid acid catalyst and 10 mg Pd/C in 3mL dodecane. The reaction vessel is placed in the endeavor reactor and purged with N₂ for 3 times. Then the reactor was filled with H₂ (10 bar) and heated to desired temperature. After the reaction the reaction solution is transferred to a GC vial by filtration over celite and cotton in a glass pipette. The products were then analyzed by GC-MS and GC-FID.

2.4.5 HDO of product mixtures from depolymerization of pine lignocellulose
Dodecane was first added to the methanol solution containing all the products from Step 1. Then methanol is evaporated by rotary evaporator and leave a dodecane solution contain most of the products from step 1. The dodecane solution was then transferred to reaction vessel with 50 mg solid acid catalyst and 10 mg Pd/C. The reaction vessel is placed in the endeavor reactor and purged with N₂ for 3 times. Then the reactor was filled with H₂ (10 bar) and heated to desired temperature. After the reaction the reaction solution is transferred to a GC vial by filtration over celite and cotton in a glass pipette. The products were then analyzed by GC-MS and GC-FID.
7.5 References