Partial Depolymerization of Lignin Using Hydrogenolysis over Raney Nickel

Daniel Leong¹, Junna Xin², Jinwen Zhang²
1. Olin College of Engineering, 2. Washington State University
NARA Program, Composite Materials and Engineering Center, Washington State University

1. Introduction

For many years, scientists have been searching for a novel way to create engineering polymers from renewable resources. Lignin, a highly branched amorphous polymer, could be the most promising substance for realizing this goal. Its molecular structure suggests that it could be a valuable source of chemicals. To exploit the wide application of lignin in polymer materials, in this study mild hydrogenolysis over Raney Ni catalyst was successfully performed to convert lignin to polymer units with low molecular weight and high hydroxyl value.

2. Procedure

- Pretreat NARA lignin to remove carbohydrates.
- Charge the pretreated lignin, Raney Ni and 3% NaOH in ethanol/H₂O (v/v, 1/1) to a pressure reactor; Purge the reactor with hydrogen and react for 3.5 h (Figure 2).
- Remove the catalyst using a magnet and filtrate.
- Neutralize the filtrate with hydrochloric acid (Figure 3).
- Collect the product by centrifuge.
- After removing liquid, place remaining solid residue in a freeze dryer (Figure 4). The yield was obtained by M₁/M₀.

3. Results and Discussion

Effect of Temperature on Yield

![Temperature vs Yield Graph]

- Figure 5 showed that 180 °C was the optimal temperature.
- The yield increased with temperatures from 120 to 180 °C. Decreased yield at higher temperatures (200 °C) was due to the formation of more gaseous chemicals (CO, CO₂, CH₄, etc.)

Molecular Weight Analysis

<table>
<thead>
<tr>
<th>Hydrogenolysis Temp.</th>
<th>MW (g/mol)</th>
<th>MN (g/mol)</th>
<th>MW/MN (polydispersity)</th>
</tr>
</thead>
<tbody>
<tr>
<td>120 °C</td>
<td>1388</td>
<td>166</td>
<td>-</td>
</tr>
<tr>
<td>140 °C</td>
<td>2199</td>
<td>523</td>
<td>4.20</td>
</tr>
<tr>
<td>160 °C</td>
<td>3242</td>
<td>891</td>
<td>3.64</td>
</tr>
<tr>
<td>180 °C</td>
<td>2681</td>
<td>610</td>
<td>4.40</td>
</tr>
<tr>
<td>200 °C</td>
<td>1662</td>
<td>458</td>
<td>3.63</td>
</tr>
</tbody>
</table>

- Molecule weight and Molecular number first increased from 120 to 160 °C and then decreased from 160 to 200 °C. MW/MN (3.6-4.4) was relatively low (Table 1).
- Further hydrogenolysis was successfully performed with improving solubility of lignin at high temperatures. Hydrogenolysis under mild conditions effectively broke the bulky structure of lignin into oligomer units with low MW.

4. Conclusion and Future Work

- Hydrogenolysis with Raney Ni was an effective method to partially depolymerize lignin.
- Hydroxyl content was increased by hydrogenolysis and the optimal reaction temperature is 180 °C.
- The partially depolymerized lignin with narrow molecular distribution and increased hydroxyl value is potential feedstock in the preparations of epoxies and polyurethanes.
- Future work could involve using the yield of hydrogenolysis reactions as feedstock for epoxies and polyurethanes.

References

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