Solvolysis of Lignosulfonate Catalyzed by Supported NiMo

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Publication date:
2017

Document Version
Peer reviewed version

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Citation (APA):
Solvolysis of Lignosulfonate Catalyzed by Supported NiMo

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Introduction
Lignin is the most abundant aromatic compound on Earth. Lignin is mostly burned as a low quality fuel in pulp mills and biorefineries. Lignosulfonate is a byproduct from sulfite pulping, mainly produced by the company Borregaard [1]. Extraction of higher value products from lignosulfonate is of interest, which is rarely addressed in literature. Amongst different methods, solvothermal conversion assisted by a heterogeneous catalyst is a promising method for conversion of lignin. However, the sulfur in the structure of lignosulfonate deactivates most of the heterogeneous catalysts by sulfur deposition. Conversion of lignosulfonate to liquefied products using sulfur tolerant hydro treating catalysts is investigated in this work.

Materials and Methods
Spruce based sodium lignosulfonate (Na-LS, Mw= 6700) and ammonium lignosulfonate (NH4-LS, Mw= 46500), provided by Borregaard, were used as lignin source. Na-LS is further ion-exchanged to proton-lignosulfonate (H-LS). The sulfur content of Na-LS and NH4-LS are 2.7 and 7 wt%, respectively. Non-catalytic and catalytic experiments with a g: 10 g: 100 ml at 25 barg initial H2 pressure and 3 h reaction time.

Results and Discussion
The results of the conversion of lignosulfonate on NiMo catalyst are presented in Table 1. The oil yields are calculated based on the dry and ash free lignin. The results show that the oil yield increased by addition of catalyst; the yield of bio-oil from conversion of H-LS at 260 °C doubled from 13 to 27 wt%. Increased lignin depolymerization was observed in both non-catalytic and catalytic experiments with increasing temperature: Considering conversion of lignosulfonate at 315 °C, an oil yield of 24 wt% was observed in non-catalytic test, while an oil yield of 62 wt% was obtained by introducing the catalyst. The higher oil yields over NiMo catalyst compared to non-catalytic tests might be due to the suppression of repolymerization reactions involving reactive in situ degraded compounds over catalytic active sites. Methyl substituted phenols constitute the main identified compounds in the oil fraction of H-LS conversion. The C/O ratio doubled to 4.0, which confirms deoxygenation activity of the catalyst.

Table 1 Results of the catalytic experiments with NiMo. Catalyst: lignin: solvent ratio of 1:10 g: 100 ml at 25 barg initial H2 pressure and 3 h reaction time

<table>
<thead>
<tr>
<th>Lignosulfonate</th>
<th>Catalyst</th>
<th>T [°C]</th>
<th>Oil yield wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-LS</td>
<td>Non-catalytic</td>
<td>260</td>
<td>13</td>
</tr>
<tr>
<td>H-LS</td>
<td>Non-catalytic</td>
<td>315</td>
<td>24</td>
</tr>
<tr>
<td>H-LS</td>
<td>NiMo (Non-presulfided)</td>
<td>260</td>
<td>27</td>
</tr>
<tr>
<td>H-LS</td>
<td>NiMo (Non-presulfided)</td>
<td>315</td>
<td>62</td>
</tr>
<tr>
<td>NH4-LS</td>
<td>NiMo (Non-presulfided)</td>
<td>260</td>
<td>21</td>
</tr>
<tr>
<td>NH4-LS</td>
<td>NiMo (Presulfided)</td>
<td>315</td>
<td>34</td>
</tr>
<tr>
<td>NH4-LS</td>
<td>NiMo (Presulfided)</td>
<td>315</td>
<td>37</td>
</tr>
</tbody>
</table>

No significant effect is observed by presulfidation of catalyst for conversion of NH4-LS: 21 and 20 wt% oil is obtained by conversion of NH4-LS at 260 °C over non-presulfided and presulfided NiMo catalysts. The oil yield from conversion of NH4-LS at 315 °C increased slightly from 34 wt% over non-presulfided catalyst to 37 wt% over sulfided catalyst. Therefore, it can be speculated that presulfidation of NiMo for conversion of lignosulfonate may not be required, presumably due to the successful activation of catalyst by the sulfur content of lignosulfonate. Work is ongoing to verify this hypothesis.

Significance
Good catalytic activity of NiMo catalyst for conversion of sulfonated lignin to liquid products is presented in this work, which may assist the introduction of novel uses of lignin.

References