Co-processing bio-oil in a petroleum refinery is an attractive option to decrease the cost of upgrading pyrolysis oil to transportation fuels. However, the oil would need to fulfill several criteria, among others:

1. The acidity of the bio-oil must be reduced from the typical TAN (total acid number) value of over 100 to about 15 if bio-oil is blended in ratio 1:8.
2. The bio-oil must be miscible with hydrocarbons.
3. The bio-oil must be highly volatile so that it is amenable to fractional distillation.

The lignin fraction of pyrolysis oil has a lower oxygen and acid content than whole bio-oil and could give better properties than the whole oil. We produced pyrolytic lignin by adding water to pyrolysis oil, and hydrotreated the pyrolytic lignin fractions with the goal of producing bio-oil that fulfills the above criteria.

### Semi-Batch Autoclave

![Semi-Batch Autoclave Diagram](image)

**Water-Separated Pyrolytic Lignin**

Acid number of lignins separated with various amounts of water. Acidity decreases with increased dilution and improved screening of large batches.

### Catalysts Employed

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Composition</th>
<th>Manufacturer</th>
<th>Pretreatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>Ni-Mo/Al2O3</td>
<td>Grace Davison</td>
<td>Milled, screened to 35-57 μm, presulfided</td>
</tr>
<tr>
<td>Pt</td>
<td>5% Pt on char</td>
<td>Johnson Matthey</td>
<td>Heated to final operating T in H2</td>
</tr>
<tr>
<td>Pd</td>
<td>5% Pd on activated C</td>
<td>Johnson Matthey</td>
<td>Heated to final operating T in H2</td>
</tr>
</tbody>
</table>

### Oxygen Content

Oxygen content for total organic product with all catalysts:

- Ni,1,L: 69.4 ± 1.7, 5.1 ± 0.1, 1.8 ± 0.1, 3.2 ± 0.3
- Ni,1,M: 70.3 ± 0.9, 5.8 ± 0.5, 1.3 ± 0.0, 3.6 ± 0.4
- Ni,3,H: 67.0 ± 0.3, 6.5 ± 0.1, 1.5 ± 0.0, 4.6 ± 0.5

Platinum yields higher coke and CO2. Palladium yields higher methane.

### Carbon Distribution

- Platinum yields higher coke and CO2. Palladium yields higher methane.

### Less Acid Than Whole Oil

Acid number of hydrogenated products from pyrolytic lignin much lower than that of products from whole oil at similar conditions.

### Conclusions

The hydrotreating of pyrolytic lignin was studied over NiMo, Pt and Pd catalysts. 55% conversion of the carbon in the biomass pyrolysis lignin to a low-oxygen (<8%), low-ash, low-metal, hydrocarbon-miscible liquid product can be achieved. This was possible with all three catalysts at the most severe condition (400 °C, 2450 psig) and with platinum at somewhat less severe conditions.

The results suggest that hydrotreating of the organic fraction (pyrolytic lignin) is a technically feasible strategy for producing a refinery intermediate, and oil with better properties (lower O and lower TAN) than for hydrotreating of the whole oil can be produced at equivalent conditions.

**Loss on Ignition**

- Ni: 0.2 ± 0.0
- Pt: 3.1 ± 0.1
- Pd: 3.2 ± 0.1

**C3 NMR shows high conversion to aliphatics with residual phenolics**

Analysis of residue samples remaining in reactor at end of experiment.