Catalytic hydroprocessing of ground cottonseeds in a cottonseed oil and i-octane solvent to produce renewable diesel

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Background and motivation
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• Hydrotreatment of HTL bio-oil (two-step process)

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Background and motivation

• Aim
  – Determine if renewable diesel can be directly produced from dry biomass
  – Maximize renewable diesel yield

• Objectives
  – Biomass loading
  – Effect of solvent
  – Effect of temperature
Experimental setup

Vessel
Volume = 350 cm$^3$

GC analysis
Catalyst activation

- 6 g NiMo catalyst
- N₂ purge
- H₂S pressure: 5 MPa
- Temperature: 400°C (6°C/min)
- Residence time: 1 hr

Reaction

- Depressurisation
- Cooled down
- Solvent added (syringe)
- Dry biomass added (5 wt%, 10 wt%, 15 wt%)
- N₂ purge
- H₂ pressure: 9 MPa
- Temperature: 350-410°C (6°C/min)
- Residence time: 1 hr
Pure cottonseed oil (9 MPa, 410°C)

- Saturation of double bonds
- Cracking of triglycerides
- Decarboxylation and decarbonylation

Cottonseed oil as solvent (9 MPa, 410°C)

- Less saturation of double bonds
- Decarboxylation and decarbonylation
Iso-octane as solvent (9 MPa, 410°C)

- No unsaturated fatty acids present
- Hydrodeoxygenation

Reaction pathway

- Reaction pathways
  - Decarboxylation
  - Decarbonylation
  - Hydrodeoxygenation

\[
\frac{C_{n+1}}{C_n} < 1
\]

\[
\frac{C_{n+1}}{C_n} > 1
\]
**Reaction pathway**

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Solvent</th>
<th>C_{16}:C_{17}</th>
<th>C_{16}:C_{15}</th>
</tr>
</thead>
<tbody>
<tr>
<td>350</td>
<td>Cottonseed oil</td>
<td>0.86</td>
<td>0.98</td>
</tr>
<tr>
<td>390</td>
<td></td>
<td>0.70</td>
<td>1.04</td>
</tr>
<tr>
<td>410</td>
<td></td>
<td>0.49</td>
<td>0.56</td>
</tr>
<tr>
<td>350</td>
<td>Iso-octane</td>
<td>1.73</td>
<td>1.86</td>
</tr>
<tr>
<td>370</td>
<td></td>
<td>1.71</td>
<td>1.79</td>
</tr>
<tr>
<td>390</td>
<td></td>
<td>1.75</td>
<td>1.83</td>
</tr>
<tr>
<td>410</td>
<td></td>
<td>1.79</td>
<td>1.95</td>
</tr>
</tbody>
</table>

**Reaction pathway**

![Bar chart showing wt% of liquid product for pure cottonseed, iso-octane solvent, and cottonseed oil solvent.](chart.png)
### Liquid and char yields

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Cotton seed oil solvent</th>
<th>i-octane solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Liquid yield</td>
<td>Solid yield</td>
</tr>
<tr>
<td>350</td>
<td>72%</td>
<td>9%</td>
</tr>
<tr>
<td>370</td>
<td>70%</td>
<td>7%</td>
</tr>
<tr>
<td>390</td>
<td>82%</td>
<td>2%</td>
</tr>
<tr>
<td>410</td>
<td>76%</td>
<td>1%</td>
</tr>
</tbody>
</table>

### Liquid yield

![Graph showing liquid yield vs reaction temperature for Cottonseed oil solvent and Iso octane solvent](image-url)
Biomass loading: Cottonseed oil

Liquid composition (9 MPa, 410°C)
Results and discussion

Results and discussion: iso-octane
Conclusion

- Liquid phase is indeed renewable diesel
- Possible to produce renewable diesel from dry biomass
- Maximum liquid yield at 390°C, 10 wt%