Comparison among technical and milled wood lignins through principal component analysis of FTIR spectra

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Co-hydrotreatment of Bio-oil Lignin-rich Fraction and Vegetable Oil

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Pyroliq 2019
Cork, Ireland June 16-20, 2019
Two-Step Hydrotreatment

To ensure economic competitiveness, bio-oil price needs to be a fraction of molasses ($300-400/ton) and petroleum ($200-700/ton). Bio-oil production cost needs to be below $150/t.

In our analysis we used the recommendations made by Lange (2016)

\[
\text{Product cost} \sim \frac{\text{feed Price} + \text{conversion cost}}{\text{yield}}
\]

Feed Price: $150/\text{ton}_{\text{feed}}
Conversion Cost: $200/\text{ton}_{\text{feed}}
Yield: 0.33 \text{ton fuel}/\text{ton}_{\text{feed}}

Product Cost: $1060/\text{ton}_{\text{feed}}
Gasoline market: $700-800/\text{ton}_{\text{feed}}

Bio-oil composition

High oxygen content

High carbon content

Water (19-30 wt. %)

C$_2$-C$_4$ light molecules (10-22 wt. %)

Acetol (5-9 wt. %)

Hydroxyacetaldehyde (1-14 wt. %)

Acetic Acid (2-6 wt. %)

Formic Acid (Less 1 wt. %)

Anhydrosugars (10-20 wt. %)

Levoglucosan

Cellobiosan

Mono-phenols (1-5 wt. %) and mono-furans (around 1 wt. %)

Phenol (0.1 wt. %)

Guaiacol (0.2-0.5 wt. %)

Cresol (0.1-0.4 wt. %)

Syringol (0.4 wt. %)

Eugenol (0.1-0.2 wt. %)

Furfural (0.1-0.2 wt. %)

2(SH)-Furanone (0.2-0.8 wt. %)

Pyrolytic lignin (15-27 wt. %)

Hybrid oligomers (11-18 wt. %)

Humins (3-7 wt. %)
All biomass derived Jet Fuel Production Technologies end-up with a Hydro-deoxygenation step
Overview of Concept Studied

Can the cracking and stabilization step be avoided?

- Bio-oil
  - 1-butanol/water extraction
    - 1-butanol phase
      - (1) hydrocracking
      - (2) rotavap
      - Butanol-rich lights
      - Water-rich lights
        - Sugar-rich “Syrup”
    - Aqueous phase
      - rotavap
      - Reuse the solvent rich fractions

- HEFA Unit
  - Hydrocracking products
    - Cohydrotreatment
      - Vegetable oil
        - Fuels
  - Lignin-rich oil
    - Cohydrotreatment
      - Vegetable oil
        - Fuels
3. Experimental Scheme

Part 1: Bio-oil Fractionation

- Liquid-liquid extraction
- Lignin rich oil + lights
- Rotavap
- Lignin rich oil
- Anhydrosugars + lights

BTG oil (Netherland)

Part 2: Cohydrotreatment of lignin rich oil (LRO) and Canola oil

<table>
<thead>
<tr>
<th>LRO : Canola</th>
<th>LRO : Canola</th>
<th>1-BuOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 : 8</td>
<td>1 : 8</td>
<td>0.5</td>
</tr>
<tr>
<td>1 : 4</td>
<td>1 : 4</td>
<td>0.5</td>
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<tr>
<td>and</td>
<td>and</td>
<td></td>
</tr>
<tr>
<td>1 : 2</td>
<td>1 : 2</td>
<td>0.5</td>
</tr>
<tr>
<td>1 : 1</td>
<td>1 : 1</td>
<td>0.5</td>
</tr>
</tbody>
</table>

- 350°C, 4h, 9.3MPa, 500rpm
- CoMo/Al₂O₃ (C/F=1:50)
- Distillation
- Naphtha
- Kerosene
- Diesel
- Gas oil

*Each hydrotreatment was duplicated.*
## Bio-oil Pyrolytic Lignin Extraction

### Butanol/Water/Bio-oil

<table>
<thead>
<tr>
<th>Ratio</th>
<th>Ratio</th>
<th>Ratio</th>
<th>Ratio</th>
<th>Ratio</th>
<th>Ratio</th>
<th>Ratio</th>
<th>Ratio</th>
<th>Ratio</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>70/20/10</td>
<td>60/20/20</td>
<td>60/30/10</td>
<td>50/40/10</td>
<td>50/30/20</td>
<td>50/20/30</td>
<td>40/50/10</td>
<td>40/40/20</td>
<td>40/30/30</td>
<td>30/60/10</td>
</tr>
<tr>
<td>30/50/20</td>
<td>30/40/30</td>
<td>30/30/40</td>
<td>20/70/10</td>
<td>20/60/20</td>
<td>20/50/30</td>
<td>20/40/40</td>
<td>20/30/50</td>
<td>10/80/10</td>
<td>10/70/20</td>
</tr>
<tr>
<td>10/60/30</td>
<td>10/50/40</td>
<td>10/40/50</td>
<td>70/25/5</td>
<td>65/25/10</td>
<td>60/25/15</td>
<td>55/25/20</td>
<td>50/25/25</td>
<td>45/30/25</td>
<td>40/35/25</td>
</tr>
<tr>
<td>35/35/30</td>
<td>30/35/35</td>
<td>25/40/35</td>
<td>20/45/35</td>
<td>15/50/35</td>
<td>15/55/30</td>
<td>15/60/25</td>
<td>15/65/20</td>
<td>15/70/15</td>
<td>15/75/10</td>
</tr>
</tbody>
</table>

Under each picture, the ratio of butanol/water/bio-oil is indicated, for example, Butanol/Water/Bio-oil: 70/20/10 for the first one on the top left.
Bio-oil Pyrolytic Lignin Extraction

This phase diagram was generated from those pictures shown in the previous slide.

- 2 phases, organic phase on top
- 2 phases, aqueous phase on top
- 1 phase

Water: 46.4 wt. %, BuOH: 40 wt. %, Bio-oil (water free): 13.8 wt. %
Bio-oil Pyrolytic Lignin Extraction

What is the difference between raw bio-oil and the lignin rich oil?

**BTG oil (raw):**

**Lignin-rich oil:**

75 % Pyrolytic lignin + 20% phenolic (GC-detectable)
3. Experimental Scheme

No BuOH

<table>
<thead>
<tr>
<th>LRO</th>
<th>Canola</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8</td>
</tr>
<tr>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

With BuOH

<table>
<thead>
<tr>
<th>LRO</th>
<th>Canola</th>
<th>1-BuOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8</td>
<td>0.5</td>
</tr>
<tr>
<td>1</td>
<td>4</td>
<td>0.5</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>0.5</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Batch reactor setup (Parr)

350°C, 4h, 9.3MPa, 500rpm

CoMo/Al₂O₃ (C/F=1:50)

Hydrotreated oils

H₂ inlet
Stirrer controller
Gas outlet
Heater
Stirrer

Distillation

Naphtha
Kerosene
Diesel
Gas oil
The LRO/Canola blends with and without 1-butanol before and after hydrotreatment

(a) Blends of LRO/Canola with and without 1-butanol

(b) The resulting liquid products from cohydrotreatment

Focus here (top layer)

Naphtha cut (71-182°C)  Kerosene cut (182-260°C)  Diesel cut (260-330°C)
Mass balance on co-hydrotreatment of different blends

![Graph showing mass balance on co-hydrotreatment of different blends. The graph plots the yield of gas, solid, and liquid products against LRO/Canola oil wt ratio for both 'No BuOH' and 'With BuOH' conditions. The data shows a decrease in yield as the LRO/Canola oil wt ratio increases.]
H₂ consumption of cohydrotreatment

Hydrogen consumption decreased with the increase in pyrolytic lignin content
Mass balance on co-hydrotreatment of different blends

The diagram shows the yield of coke (LRO basis) (wt.%) as a function of the LRO/Canola wt ratio. The graph compares the yield with and without BuOH. The yield increases with the LRO/Canola wt ratio, and the presence of BuOH generally results in a higher yield compared to without BuOH.
UV-Fluorescence on all the hydrotreated oils
Van Krevelen plot for LRO, Canola oil, their blends

(yellow zone, ratios with underline, such as 1:8, represent the blends with 1-butanol) and the corresponding hydrotreated oils (green zones). Distinctive line patterns can be associated with specific reactions: (A) hydrogenation, (B) decarbonylation, (C) decarboxylation, (D) direct deoxygenation, (E) dehydration, (F) demethoxylation.
FTIR on the hydrotreated oils

(a) No BuOH

(b) With BuOH
Carbonyl content of the LRO/Canola blends

Before Co-HT
After Co-HT

No BuOH
With BuOH

Carbonyl content (mmol/g oil)

LRO/Canola wt ratio

1:8 1:4 1:2 1:1

1:8 1:4 1:2 1:1
Gaseous products from cohydrotreatment of different blends

(a) Carbon monoxide

(b) Carbon dioxide

(c) Methane

(d) Ethane

(e) Propane

(f) Butane
GC/MS on all the hydrotreated Oils
Yields of n-Paraffinic products
Yields of major Aromatic Products
Product distribution of phenolics after co-hydrotreating LRO/Canola blends

(a) No BuOH

(b) With BuOH

LRO/Canola wt ratio

Mass of Phenols (g)

Phenol, 2-methyl-
Phenol, 2,6-dimethyl-
Phenol, 4-methyl-
Phenol, 3-methyl-
Phenol, 2-ethyl-
Phenol, 2,4-dimethyl-
Phenol, 2-ethyl-5-methyl-
Phenol, 3,4,5-trimethyl-
Phenol, 3-ethyl-5-methyl-
Phenol, 2,4,5-trimethyl-
Phenol, 2,4,6-trimethyl-
Phenol, 2,3,5-trimethyl-
Phenol, 3-propyl-
Hydrocracking and Stabilization
Cracking of LRO:

**Catalyst:** Ni/SiO$_2$-Al$_2$O$_3$

**Solvent used:** Methanol, Butanol

**Temperature:** 200 °C

**Time:** 24 hours

**GC/MS (concentrated by rotavap)**

With Butanol

- Phenols: 6.28
- Alcohol: 3.65
- Ester: 5.83
- Others: 0.43

Dimers or trimers (not GC detectable)
## Product distribution of co-hydrotreatment (after hydrocracking)

<table>
<thead>
<tr>
<th></th>
<th>LRO/Canola=1:4</th>
<th>Cracked LRO* (in MeOH) /Canola=1:4</th>
<th>Cracked LRO* (in BuOH) /Canola=1:4</th>
<th>Canola</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Overall product distribution</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Liquid</td>
<td>76.43 %</td>
<td>80.69 %</td>
<td>80.72 %</td>
<td>84.31 %</td>
</tr>
<tr>
<td>Gas</td>
<td>16.72 %</td>
<td>16.14 %</td>
<td>18.16 %</td>
<td>15.65 %</td>
</tr>
<tr>
<td>Solid</td>
<td>6.85 %</td>
<td>3.18 %</td>
<td>1.13 %</td>
<td>0.04 %</td>
</tr>
<tr>
<td><strong>Distillation cuts of the resulting oils (wt.%)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Naphtha</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>&lt;71 °C</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>71-182°C</td>
<td>20.80</td>
<td>21.69</td>
<td>23.08</td>
<td>17.88</td>
</tr>
<tr>
<td>Kerosene</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diesel</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>260-330 °C</td>
<td>13.16</td>
<td>18.00</td>
<td>19.52</td>
<td>20.67</td>
</tr>
<tr>
<td>330-566 °C</td>
<td>29.61</td>
<td>24.18</td>
<td>20.34</td>
<td>25.37</td>
</tr>
<tr>
<td>Residue</td>
<td>10.91</td>
<td>7.36</td>
<td>7.23</td>
<td>4.44</td>
</tr>
<tr>
<td>Weight loss</td>
<td>10.92</td>
<td>10.51</td>
<td>8.58</td>
<td>9.97</td>
</tr>
<tr>
<td><strong>Coke formation (LRO basis)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LRO basis coke</td>
<td>34.73 %</td>
<td>16.08 %</td>
<td>6.65%</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Cracking and stabilization seems to help the hydro-deoxygenation of lignin rich fraction
Conclusions

1. An important HDO had been achieved for the blends of lignin-rich oil and vegetable oil, resulting in a two-phase liquid product formed with the oil stayed on the top and water at the bottom.

2. By varying the ratio between lignin rich oil and vegetable oil, some phenolics started to be detected when the weight percentage of lignin oil in the blend increased to 1/3 or above.

3. The major components of the hydrotreated oils were paraffinic and aromatic hydrocarbons, with less carbonyl groups than the pristine blends.

4. Adding BuOH into the lignin rich oil resulted in more tetramers and pentamers being produced in the oil which on the other hand mitigated the coke formation in cohydotreatments.

5. Hydrocracking/stabilization is an efficient step to depolymerize the lignin-rich oil which then effectively reduces the coke formation in the HDO step.
Thank you!

Acknowledgements:

- DOE Biomass Technology Office (DE-EE0008505)
- Washington State Department of Ecology
- Federal Aviation Administration
- USDA/NIFA
- WSU-BSE colleagues
QUESTIONS?