Recent Progress in Biocrude Upgrading and Co-processing

David C. Dayton, Ph. D.
RTI Senior Fellow and Biofuels Director

RTI is an independent, nonprofit institute that provides research, development, and technical services to government and commercial clients worldwide.

Our mission is to improve the human condition by turning knowledge into practice.
Bio-crude Upgrading Overview

Investigate the impact of bio-crude quality in the hydroprocessing step
• Steady-state deoxygenation activity, hydrogen demand, and process severity with bio-crude of various quality (wt%O and chemical composition)
• Long-term operation to determine upgrading catalyst stability and lifetime (500-1000 hrs)
• Refinery integration and co-processing strategies

Simplified RTI HDT Unit Process Flow Diagram

Reactors volume: 350 mL
Catalyst volume: 20 - 250 mL
LHSV - 0.1 to 1.0
Flow rates - 50 to 250 mL/h
Max. design pressure - 3000 psig
Max. design temperature - 450 C
Bio-crude Upgrading Overview

Catalyst Loading, Sulfidation, and HDT Process Conditions
- HDT Catalyst: HaldorTopsoe Bio-Cat
- Catalyst Sulfidation: In-situ with H₂S in H₂ balance.
- Bio-crude flow rate: 50-250 ml/h
- Mass Balance Protocol: Allow at least 48 hours of run time prior to performing mass balance.
- Experiments continue until pressure drop across reactor > 60-100 psig or feed runs out

### Parameters

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Typical Test Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>290 – 350 °C</td>
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<tr>
<td>Pressure</td>
<td>1450-2000 psig</td>
</tr>
<tr>
<td>LHSV</td>
<td>0.125 - 0.5 1/h</td>
</tr>
<tr>
<td>H₂/oil</td>
<td>2000-3300 NL/l</td>
</tr>
</tbody>
</table>

Analysis of Bio-crude and HDT products include:
Elemental Analysis(CHNSO), GC-MS, FTIR, NMR, Carbon Number Distribution, Distillation by ASTM D1160, SG 60/60 by ASTM D4052, Kinematic Viscosity by D445, and Karl Fischer Titration.
Bio-crude Upgrading Overview

Challenges:

- High process severity (T, P, LHSV) is required for bio-crude upgrading
- Bio-crude upgrading is limited by catalyst deactivation
- Poor bio-crude thermal stability (reactivity) causes reactor fouling/plugging.

Bio-crude quality beyond wt% O.
How does bio-crude chemical composition impact upgrading?
## Strategies for Bio-oil/Bio-crude Upgrading

<table>
<thead>
<tr>
<th>Strategy</th>
<th>Process</th>
</tr>
</thead>
</table>
| Pre-processing       | • Ultrafiltration  
                      • Ion exchange  
                      • Chemical modification (esterification, etherification, neutralization) |
| Stabilization        | • Mild hydrotreating  
                      • 200°C, 1500 psig, Ru/C                                               |
| Fractionation        | • Separations (Liquid-Liquid Extraction)  
                      • Distillation (Thermal Stability)                                     |
| Pyrolysis process    | • Catalysts, process conditions, and feedstocks to control chemical composition. Target: ~15 wt% oxygen |
| Co-processing        | • Hydrotreat blends of petroleum refining intermediates and bio-crude (5-50 vol%) to control oxygen and sulfur content |
# Pine CFP Bio-crude Compositions

<table>
<thead>
<tr>
<th>wt.% dry basis</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D*</th>
<th>E</th>
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<tbody>
<tr>
<td>C</td>
<td>72.7</td>
<td>73.1</td>
<td>69.7</td>
<td>76.6</td>
<td>63.7</td>
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<tr>
<td>H</td>
<td>7.1</td>
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<td>7.2</td>
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<td>N</td>
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<td>0.3</td>
<td>0.3</td>
<td>0.5</td>
<td>0.5</td>
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<tr>
<td>O</td>
<td>19.6</td>
<td>19.5</td>
<td>22.8</td>
<td>15.0</td>
<td>29.6</td>
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<tr>
<td>H/C</td>
<td>1.17</td>
<td>1.17</td>
<td>1.24</td>
<td>1.24</td>
<td>1.26</td>
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</table>

### GC-MS Peak Area

- **Unknown**
- **Anhydrosugars**
- **Multifunctional phenols**
- **Monofunctional phenols**
- **PAH**
- **Mono-aromatic**
- **Acids**
- **Furanics**
- **Multifunctional carbonyls**
- **Monofunctional carbonyls**
- **Aliphatic**
Pine Bio-crude Hydrotreating: Feedstock and Process Conditions

Feedstock and Process Conditions:

- **Feed A**: 0.5/h, 1450 psig, T1=290°C, T2=350°C
- **Feed B**: 0.25/h, 2000 psig, T=300°C
- **Feed C**: 0.125/h, 2000 psig, T1=280°C, T2=350°C
- **Feed D**: 0.25/h, 2000 psig, T=300°C
- **Feed E**: 0.35/h, 2000 psig, T=290°C

**Graph Details**:

- **Y-axis**: Density, kg/L
- **X-axis**: Time on Stream, hours
- **Legend**:
  - Open Circles = no ΔP
  - Green line: Feed A, 0.5/h, 1450 psig, T1=290°C, T2=350°C
  - Red line: Feed B, 0.25/h, 2000 psig, T=300°C
  - Yellow line: Feed B, 0.25/h, 2000 psig, T=290°C
  - Blue line: Feed C, 0.125/h, 2000 psig, T1=280°C, T2=350°C
  - Green line: Feed D, 0.25/h, 2000 psig, T=300°C
  - Black line: Feed E, 0.35/h, 2000 psig, T=290°C
  - Orange line: Feed E, 0.35/h, 2000 psig, T=300°C

**Note**: The graph shows the density over time for different feeds and conditions. The legend indicates the specific conditions for each feed.
Bio-crude Separations

- Solvent extraction separates out acids and anhydrosugars.
- Although not detected with GC-MS, oligomers likely end up in the raffinate.

### Solvent Extraction

<table>
<thead>
<tr>
<th></th>
<th>INPUT Mass (kg)</th>
<th>OUTPUT Mass (kg)</th>
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</thead>
<tbody>
<tr>
<td>Bio-crude</td>
<td>26.1</td>
<td>22.6</td>
</tr>
<tr>
<td>Solvent</td>
<td>29.3</td>
<td>32.6</td>
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</table>

### Distillation

<table>
<thead>
<tr>
<th></th>
<th>INPUT Mass (kg)</th>
<th>OUTPUT Mass (kg)</th>
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<tr>
<td>Extract</td>
<td>31.4</td>
<td>24.3</td>
</tr>
<tr>
<td>Solvent</td>
<td>29.3</td>
<td>6.3</td>
</tr>
</tbody>
</table>

### GC-MS Peak Area %

- Unknowns
- Aliphatic hydrocarbons
- Mono-functional phenols
- Furanic compounds
- Mono-functional carbonyls
- Multi-functional carbonyls
- Anhydrosugars
- Acids
- Aromatic hydrocarbons (Mono-, Di-, Poly-)
- Multifunctional phenolics
Solvent Extracted Bio-crude Hydrotreating: Physico-chemical Properties

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<tr>
<td>Catalyst</td>
<td>TK-341</td>
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<tr>
<td>H₂ Flow Rate (sccm)</td>
<td>400</td>
</tr>
<tr>
<td>Feed Rate (g/h)</td>
<td>70-77</td>
</tr>
<tr>
<td>Pressure (psig)</td>
<td>2000</td>
</tr>
<tr>
<td>Average Temperature (°C)</td>
<td>300</td>
</tr>
<tr>
<td>LHSV (h⁻¹)</td>
<td>0.35</td>
</tr>
<tr>
<td>H₂/oil ratio (NL/l)</td>
<td>3300</td>
</tr>
</tbody>
</table>

**Graphs:**
- **Density, kg/L** over time on stream, hours.
- **Carbon (C), Hydrogen (H), Oxygen (O) diff** over time on stream, hours.
12-L RCFP bio-crude produced in 2”FBR over 10 months
Average Hydrogen Consumption: 2.3 wt% Biomass

**Reaction Conditions**
- Catalyst: Mo/Al$_2$O$_3$
- Hydrogen: 80 vol%
- Temperature: 460°C

**Carbon Balance**
- **Aqueous**: 2.5%
- **Organic (C$_4^+$)**: 43.0%
- **Liquid Bio-crude**: 26.4%
- **C4-C6**: 16.6%
- **Gas**: 26.8%
- **Char+Coke**: 30.1%
- **Total**: 102.4%

**Mass Balance**
- **Aqueous**: 27.4%
- **Organic (C$_4^+$)**: 19.6%
- **Liquid Bio-crude**: 15.9%
- **C4-C6**: 3.7%
- **Gas**: 13.1%
- **Char+Coke**: 35.9%
- **Total**: 96.0%

**RCFP Bio-crude Composition (GC-MS Area%)**
- **Unknown**: 3.54%
- **Anhydrosugars**: 22.36%
- **Multifunctional phenols**: 6.58%
- **Monofunctional phenols**: 48.18%
- **PAH**: 10.53%
- **Mono-aromatics**: 1.90%
- **Multifunctional Carbonyls**: 4.95%
- **Monofunctional Carbonyls**:
- **Acids**:
- **Furanics**:
- **Aliphatics**:

**Elemental Properties**
- **Moisture, wt%**: 8.5
- **C wt%, dry**: 73.2
- **H wt%, dry**: 7.3
- **N wt%, dry**: 0.2
- **O (by diff)**: 19.3
RCFP Bio-crude Upgrading: Physico-chemical Properties

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>TK-341</th>
</tr>
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<td>H₂ Flow Rate (sccm)</td>
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<tr>
<td>Feed Rate (g/h)</td>
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<tr>
<td>Pressure (psig)</td>
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<td>Average Temperature (°C)</td>
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<td>LHSV (h⁻¹)</td>
<td>0.31</td>
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<tr>
<td>H₂/oil ratio (NI/l)</td>
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RCFP Bio-crude Upgrading: Hydrotreated Product Compositions

GC-MS Peak Area %

Feed

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<tr>
<th>Time-on-Stream (TOS), hours</th>
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<th>13</th>
<th>25</th>
<th>37</th>
<th>49</th>
<th>61</th>
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<th>97</th>
<th>101</th>
<th>113</th>
<th>125</th>
<th>137</th>
<th>144</th>
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Unknown: 0.0, 0.4, 1.9, 5.6, 6.0, 9.1, 11.8, 16.0, 17.5, 19.1, 20.7, 16.2, 22.1
Olefins: 0, 34.0, 47.0, 40.8, 41.1, 38.4, 36.6, 33.1, 30.7, 24.9, 25.7, 26.1, 23.2
Oxygenates: 23.6, 48.3, 35.6, 27.9, 24.9, 22.3, 18.2, 15.4, 13.4, 12.1, 11.2, 9.8, 8.4
Oxy-Aromatics: 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0
Multifunctional Phenolics: 7.6, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0
Simple Phenols: 0, 13, 25, 37, 49, 61, 85, 97, 101, 113, 125, 137, 144
PAH: 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0
Di-Aromatics: 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0
Mono-Aromatics: 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0
Paraffins: 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0
Naphthenes: 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0
Co-processing Bio-crude with Refinery Intermediates

30% Light Cycle Oil (LC) or Partially Upgraded Bio-crude (CPO) blended with 70% straight run diesel

<table>
<thead>
<tr>
<th>Property</th>
<th>30/70 LC1/LG</th>
<th>30/70 LC2/LG</th>
<th>30/70 CPO1/LG</th>
<th>30/70 CPO2/LG</th>
<th>30/70 CPO3/LG</th>
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</thead>
<tbody>
<tr>
<td>H, wt %</td>
<td>12.46</td>
<td>12.14</td>
<td>12.80</td>
<td>12.58</td>
<td>12.31</td>
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<tr>
<td>O, wt %</td>
<td>-</td>
<td>-</td>
<td>1.26</td>
<td>1.84</td>
<td>2.47</td>
</tr>
<tr>
<td>S, wt %</td>
<td>1.19</td>
<td>1.00</td>
<td>0.828</td>
<td>0.903</td>
<td>0.717</td>
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<tr>
<td>N, ppm</td>
<td>213</td>
<td>433</td>
<td>258</td>
<td>327</td>
<td>377</td>
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<tr>
<td>SG</td>
<td>0.863</td>
<td>0.873</td>
<td>0.861</td>
<td>0.867</td>
<td>0.882</td>
</tr>
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</table>

- No additional pressure drop with CPO
- 6% lower diesel yield from CPO ([O] in feedstock and light and a heavy fractions outside diesel range)
- Lower H₂ consumption for CPO compared to the LCO (HDS vs. HDO)

H₂ pressure: 70 barg
LHSV: 0.4 h⁻¹
H₂/oil ratio: 625 NL/L
Temperature: 330 - 345°C
RCFP Bio-crude Co-processing with Light GasOil

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Unit</th>
<th>LG</th>
<th>RCFP</th>
<th>10/90 RCFP/LG</th>
<th>15/85 RCFP/LG</th>
<th>20/80 RCFP/LG</th>
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</thead>
<tbody>
<tr>
<td>SG at 60/60°F</td>
<td>0.8541</td>
<td>1.005</td>
<td>0.8667</td>
<td>0.8726</td>
<td>0.8782</td>
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<tr>
<td>O wt %</td>
<td>-</td>
<td>9.65</td>
<td>-</td>
<td>-</td>
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<td>-</td>
</tr>
<tr>
<td>S wt %</td>
<td>1.30</td>
<td>0.001</td>
<td>1.14</td>
<td>1.04</td>
<td>1.01</td>
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<tr>
<td>N wt ppm</td>
<td>148</td>
<td>425</td>
<td>165</td>
<td>180</td>
<td>201</td>
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<tr>
<td>H wt %</td>
<td>13.09</td>
<td>8.28</td>
<td>12.59</td>
<td>12.43</td>
<td>12.18</td>
<td></td>
</tr>
</tbody>
</table>

Pressure (Inlet pH₂) 50 – 70 barg (725-1015 psig)
Temperature 340 – 360°C
LSHV 2 h⁻¹
H₂/oil ratio 500 NL/l

> 1000 hours without shut-downs or severe deactivation
Blended feed oxygen in the range 0.9 – 1.9 %wt
Product oxygen ≤6 ppmw
Approximately 89 % of RCFP bio-crude converted to hydrocarbons on weight basis

H₂ consumption (NL/L): 69 vs. 115-134
Feed B, 0.25/h, 2000 psig, T=300°C
Feed D, 0.25/h, 2000 psig, T=300°C
Feed E, 0.35/h, 2000 psig, T=290°C
RCFP Bio-crude, 0.31/h, 2000 psig, T=300°C
SE Bio-crude, 0.35/h, 2000 psig, T=300°C
Conclusions

Commercially-relevant steady-state hydrotreating
- More anyhdro sugars and acids = faster reactor plugging
- Pyrolysis processes for minimizing thermally unstable components
- Separations for removing undesirable components
- Co-processing (50% lower pressure) to minimize impacts of bio-crude composition

Hydrotreating catalyst deactivation
- Mechanism
- Sulfur loss
- Recovery by increasing temperature

Total oxygen content for hydrogen demand

Oxygen speciation for upgrading process performance

Caution: What is not identified with GC/MS that causes additional problems?
Acknowledgements

RTI Biomass Team
- Dr. Ofei Mante
- Dr. Phil Cross
- Joseph Weiner
- Jonathan Peters
- Gary Howe
- Kelly Amato

Haldor Topsøe A/S
- Jostein Gabrielsen
- Nadia Luciw Ammitzboll
- Sylvain Verdier
- Christian Ejersbo Strebel
Pilot-scale (1TPD) *in situ* Catalytic Fast Pyrolysis

- Continuous feed circulating fluidized bed reactor/regenerator
- Pyrolysis temperature: 350-500 ºC
- Regenerator Temperature: 560-640 ºC
- Residence time: 0.5-1.0 s
- Biomass Feed Rate: 35-70 kg/h
- Bio-crude production rate: 20-50 gal/hr

**Laboratory Fluidized Bed Reactor System**

- 2.5” fluidized bed reactor with 4” disengagement zone
- Biomass feeding rate: 2-5 g/min
- Liquid collection: 3 condensers and 1 ESP
- Non-condensable gases analyzed by micro GC
- Liquid product analyzed by Karl Fischer titration, elemental analysis, GC/MS