Catalytic Biomass Pyrolysis Studies at Pilot-Scale

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Ofei Mante, D. Dayton, D. Barbee, M. Carpenter, L. Shumaker, K. Wang, and J. Peters
**Objective:** Demonstrate an advanced biofuels technology that integrates a catalytic biomass pyrolysis step and a hydroprocessing step to produce infrastructure compatible biofuels.

Technical goals are to:
1) optimize the catalytic biomass pyrolysis process (1 tonne/day) to achieve high degree of deoxygenation, while maximizing the bio-crude production
2) improve bio-crude thermal stability
3) evaluate the impact of bio-crude quality in the hydroprocessing step
4) minimize hydrogen demand of the integrated process
5) maximize biofuels yields.

**Feedstocks**
- Loblolly Pine
- Hybrid Poplar
- Corn Stover
- Switchgrass

**Catalytic Biomass Pyrolysis**
- Proof of Concept (1" dia fluidized bed)
  - RTI (ARPA-E)
- Bench-scale (1 TPD)
  - RTI (BETO)

**Hydroprocessing**
- Proof of Concept (1-L upgrading)
  - P66 (ARPA-E)
- Bench-scale (350-mL integrated)
  - Haldor Topsøe (BETO)

**Advanced Biofuels**
- Gasoline, Diesel, Jet Fuel
Increasing biocrude yield while decreasing oxygen content is a major challenge.
Objective:
- Demonstrate steady-state operation for at least 12 consecutive hours to evaluate process conditions on biocrude yield and quality.

Feedstocks:

<table>
<thead>
<tr>
<th>Biomass</th>
<th>Particle Size</th>
<th>Moisture wt%</th>
<th>Elemental composition (as-received), wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Carbon</td>
</tr>
<tr>
<td>Loblolly pine</td>
<td>2 mm top size</td>
<td>15.0</td>
<td>47.4</td>
</tr>
<tr>
<td>Red Oak</td>
<td>&lt; 2 mm</td>
<td>10.0</td>
<td>45.5</td>
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</tbody>
</table>

Catalyst:
- Non-zeolite alumina based catalyst with nominal 70 μm particle size

CFP Conditions:
- Biomass Feed Rate: 35-70 kg/h
- Pyrolysis Temperature: 425-600 °C
- Regenerator Temperature: 560 - 640 °C
- Mixing Zone N₂ flowrate: 75 – 550 scfh
- Mixing Zone Residence time: 0.5 – 2 s
RTI’s 1TPD Catalytic Biomass Pyrolysis Unit

Front View

- Biomass Hopper
- Biomass Conveyer Screw
- Regenerator
- Reactor
- Biomass Feeder
- Controls Cabinet
CFP Process:

Start-up Procedure:
- Electric heating to 350 °C
- Increase gas flows to initiate solids circulation
- Diesel injection in regenerator to reach desired mixing zone temperature
- Discontinue diesel injection and commence biomass feeding
- Feed biomass continuously for 12 hours
- Stop biomass feeding and shutdown

Analysis:
- CFP product gases and regenerator off gases are analyzed online by micro-GCs
- Liquids and solids are routinely sampled to determine mass and carbon balances.
- Characterization of liquid samples
  - Moisture, Density, Viscosity
  - CHNOS
  - GC-MS
  - $^{13}$C-NMR
<table>
<thead>
<tr>
<th>Run Code</th>
<th>Biomass feed rate (kg/h)</th>
<th>Mixing zone Temp. (°C)</th>
<th>Riser Temp. (°C)</th>
<th>Mixing zone N₂ flow rate (scfh)</th>
<th>Mixing zone residence time (s)</th>
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</thead>
<tbody>
<tr>
<td>13703-37</td>
<td>45.6</td>
<td>424.3</td>
<td>421.7</td>
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<td>13703-52</td>
<td>50.9</td>
<td>576.0</td>
<td>583.5</td>
<td>513</td>
<td>0.75</td>
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<td>445</td>
<td>1.00</td>
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<td>544</td>
<td>0.79</td>
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<td>546</td>
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<td>478.1</td>
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<td>1.86</td>
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</table>
Pilot Plant Operation - Reactor Temperature Profile

Temperature, °C

Time on stream (hours)
Steady-state (6-10 h) yields of biocrude for CFP of loblolly pine using alumina catalyst at 425 °C was around 40-45 gal/ton.

Steady-state yields of biocrude for CFP of loblolly pine using alumina catalyst at 465 °C was around 50 gal/ton.
Results - Biocrude Composition

Peak Area, %

CFP Temperature, °C

- 425 °C
- 465 °C
- 485 °C
- 520 °C
- 575 °C

Other
Aliphatic
Furans
Acids
Phenol, mono
Phenol, multi
Carbonyls, mono
Mono-Aromatic
Sugar
Carbonyls, multi
PAH
**Results - Biocrude Physico-Chemical Properties**

<table>
<thead>
<tr>
<th>CFP liquid products*</th>
<th>Density, g/cm³</th>
<th>Kinematic viscosity, cSt</th>
<th>Carbon, wt%</th>
<th>Hydrogen, wt%</th>
<th>Nitrogen, wt%</th>
<th>Oxygen, wt%</th>
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<tbody>
<tr>
<td>Light-biocrude</td>
<td>1.018</td>
<td>4.1</td>
<td>80.3</td>
<td>8.1</td>
<td>0.077</td>
<td>11.5</td>
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<tr>
<td>Heavy-biocrude</td>
<td>1.162</td>
<td>154</td>
<td>70.9</td>
<td>6.6</td>
<td>0.108</td>
<td>22.4</td>
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</tbody>
</table>

* From CFP of loblolly pine at 520 °C

**Carbon distribution**

**Distillation Temperature (°C)**

- Light Biocrude
- Heavy Biocrude

**Weight %**

- Gas Oil
- Middle Distillate
- Naphtha
<table>
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<tr>
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</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>424</td>
<td>528</td>
<td>576</td>
<td>465</td>
<td>494</td>
<td>433</td>
<td>461</td>
<td>520</td>
<td>521</td>
<td>514</td>
<td>489</td>
</tr>
<tr>
<td>Bio-oil (Organic), %</td>
<td>10.3</td>
<td>10.4</td>
<td>7.4</td>
<td>17.9</td>
<td>14.1</td>
<td>17.4</td>
<td>6.7</td>
<td>-</td>
<td>5.8</td>
<td>7.2</td>
<td>13.9</td>
</tr>
<tr>
<td>Bio-oil (Aqueous), %</td>
<td>17.2</td>
<td>12.9</td>
<td>9.3</td>
<td>23.1</td>
<td>13.3</td>
<td>9.9</td>
<td>10.2</td>
<td>15.3</td>
<td>19.8</td>
<td>14.6</td>
<td>10.1</td>
</tr>
<tr>
<td><strong>Total Liquid, %</strong></td>
<td><strong>27.5</strong></td>
<td><strong>23.3</strong></td>
<td><strong>16.7</strong></td>
<td><strong>41</strong></td>
<td><strong>27.4</strong></td>
<td><strong>27.3</strong></td>
<td><strong>16.9</strong></td>
<td><strong>15.3</strong></td>
<td><strong>25.6</strong></td>
<td><strong>21.8</strong></td>
<td><strong>24</strong></td>
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<tr>
<td>Pyrolysis Gas, %</td>
<td>6.7</td>
<td>21.8</td>
<td>13.8</td>
<td>7.8</td>
<td>7.3</td>
<td>4.6</td>
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<td>10.9</td>
<td>9.4</td>
<td>10.7</td>
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<tr>
<td>Solid/Regen Gas, %</td>
<td>48.8</td>
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<tr>
<td><strong>Carbon Balance</strong></td>
<td><strong>82.9</strong></td>
<td><strong>97.4</strong></td>
<td><strong>62.6</strong></td>
<td><strong>100.3</strong></td>
<td><strong>82.6</strong></td>
<td><strong>87.9</strong></td>
<td><strong>76.0</strong></td>
<td><strong>80.0</strong></td>
<td><strong>84.3</strong></td>
<td><strong>80.7</strong></td>
<td><strong>67.6</strong></td>
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</table>
Results - Parametric Effects (Alumina, loblolly pine)

Main Effects Plot for Organic Yield

- Mixing Zone Temperature, °C
- Mixing zone residence time, s
- Dry biomass feedrate, kg/h

Carbon, %

<table>
<thead>
<tr>
<th>Mixing Zone Temperature, °C</th>
<th>Mixing zone residence time, s</th>
<th>Dry biomass feedrate, kg/h</th>
</tr>
</thead>
<tbody>
<tr>
<td>424.3</td>
<td>0.8</td>
<td>35.5</td>
</tr>
<tr>
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</tr>
<tr>
<td>576.0</td>
<td>1.9</td>
<td>54.6</td>
</tr>
</tbody>
</table>
Main Effects Plot for Total liquid yield

- Mixing Zone Temperature, °C
- Mixing zone residence time, s
- Dry biomass feedrate, kg/h

Carbon, %
Results - Parametric Effects (Alumina, loblolly pine)
Results - Yields Summary

- Bio-crude (organic) Yield, wt%
- Oxygen content (wt% of bo-crude)

- Bench-scale published data
- RTI Bench-Scale Data
- RTI Pilot-Plant Data

- Target
Summary

- Catalytic biomass pyrolysis in a 1”-dia fluidized bed reactor
- 20 wt% oxygen content with 42% energy recovery
- 1 TPD unit operational for more than Three years
  - 4 catalysts tested; 5 feedstocks – loblolly pine, hybrid poplar, corn stover, hardwood pellets, red oak
  - 12 h Parametric Studies
    - Temperature was the most influential factor.
    - Short residence times reduced biomass devolatilization.
    - Moderate temperatures (450 \(\leq T < 500\) \(^{\circ}\)C) favored higher yields.
    - Anhydrosugars are cracked at higher temperature > 500 °C, and formation of simple phenols, catechols, and PAH increases.
    - Steady-state yield analysis varied between 38 and 50 gallons/dry ton of biomass.
  - Extended Operations
    - Completed 30 and 20 hours of steady-state operation.
    - Over 200-gal of loblolly pine bio-crude produced for upgrading.
- Preliminary techno-economic analysis complete
  - See other presentations by Dr. Sylvain Verdier in Session 2.2:Pyrolysis and Dr. Ofei Mante in Session 3.2: Upgrading
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Kelly Amato
Michael Carpenter