Advanced Thermochemical Conversion of Biomass to Biofuels and Bioproducts

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  - Biofuels Technology Options
  - Thermochemical Biomass Conversion

- Catalytic Biomass Pyrolysis Technology Development
  - Fundamental Studies
  - Laboratory-scale process development
  - Pilot-scale process development

- Bio-crude Processing and Upgrading
  - Hydroprocessing for Biofuels
  - Separation and purification

- Bioproducts Development
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  - Grant Funding

- Contract Research Organizations
  - Niche expertise
  - Client-driven
  - Contract funding

- Industry R&D
  - Industry-specific expertise
  - Market-driven
  - Internal or venture capital funding

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NEW PRODUCTS

Licensing
Joint Development
Cost Share Partnership

Sale
Spin-out
Client exclusive

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Energy Research
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Environmental Sciences
International Development
Social Policy
Health
Education & Workforce Development

Flexible and Creative Business Relationships with Clients
Research to Impact, In Partnership with Leaders in Academia, Industry & Government
Development of step-out technologies requires integration of process and materials innovation with understanding of process scale-up.
Thermochemical Conversion Process Severity

**Gasification**
- Thermal conversion (partial oxidation) of biomass at elevated temperature and reducing conditions to produce primarily CO, CO₂, and H₂ as products

**Pyrolysis**
- Thermal conversion (decomposition) of biomass in the absence of oxygen
- In the biomass community, this commonly refers to lower temperature thermal processes producing liquids as the primary product

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**Primary technical challenge for renewable hydrocarbon fuels**

**Biomass** – \( CH_{1.8}O_{0.5}N_{0.2} \)

**Gasoline** – \( CH_2 \)
Pyrolysis Pathways for Advanced Biofuels

- **Fast Pyrolysis**
- **Catalytic Fast Pyrolysis**
- **Hydropyrolysis**
- **RCFP**

**Heat**

- Biomass
- **Fast Pyrolysis**
- **Catalytic Fast Pyrolysis**
- **Hydropyrolysis**

**Upgrading**

- Catalyst Added
- **H₂ Added**

**Product Quality (wt% O) vs. Yield**

**Carbon Conversion Efficiency in C₄⁺ organics (% of feedstock Carbon)**

**Oxygen Content (Wt% of Bio-crude)**

- CFP
- HYP
- RCFP
Biomass Pyrolysis Fundamentals - MicroPyrolyzer-GC/MS

Fundamental research to support technology development
- Dual microreactors for in situ or ex situ catalytic pyrolysis studies
- Fundamental chemical understanding of biomass pyrolysis processes

Efficiently screen catalysts and process conditions with real biomass
- Rapidly (30 min) characterize small (1 mg) samples
- Good mass balance (>90%)
- Excellent reproducibility (s.d.< 2~3%)

0.5mg pine - 500ºC pyrolysis
20mg MoO₃ catalyst - 450ºC
75 ml/min H₂ flow
- 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
Catalytic Biomass Pyrolysis Scale-up

Understand the effect of operating parameters on product yields and quality
- Pyrolysis temperature (350-500 ºC); Regenerator Temperature (560-640 ºC)
- Residence time (0.5-1.0 s)
- Biomass Feed Rate: 35-70 kg/h
- Catalyst circulation rate (catalyst to biomass ratio)
- Type of biomass

Continuous, long-term operation
- Validate bio-crude yields and quality
- Demonstrate catalyst stability and durability
- Gain operational experience
- Collect engineering design data for scale-up

Produce bio-crude for Upgrading Technology Development and Bioproducts Separations
# Waste to Energy - Biosolids Pyrolysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>Elemental Analysis*</th>
<th>Proximate Analysis*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>Milorganite</td>
<td>34.2</td>
<td>5.2</td>
</tr>
<tr>
<td>Dried Sewage Sludge**</td>
<td>36.9</td>
<td>5.7</td>
</tr>
<tr>
<td>Fecal sludge</td>
<td>47.5</td>
<td>6.8</td>
</tr>
<tr>
<td>Loblolly Pine</td>
<td>45.4</td>
<td>6.3</td>
</tr>
<tr>
<td>Corn Stover</td>
<td>44.0</td>
<td>5.9</td>
</tr>
</tbody>
</table>

*as received basis; ** secondary sludge after anaerobic digester in WWTP

Milorganite™ is a commercial fertilizer produced by Milwaukee Metropolitan Sewage District

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Milorganite</th>
<th>Sludge*</th>
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</thead>
<tbody>
<tr>
<td>Elemental analysis (wt%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>69.5</td>
<td>73.0</td>
</tr>
<tr>
<td>H</td>
<td>8.5</td>
<td>8.8</td>
</tr>
<tr>
<td>N</td>
<td>10.0</td>
<td>11.1</td>
</tr>
<tr>
<td>O</td>
<td>12.0</td>
<td>7.0</td>
</tr>
<tr>
<td>GC/MS analysis (peak area %)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>aliphatics</td>
<td>9.1</td>
<td>15.3</td>
</tr>
<tr>
<td>aldehydes/ketones</td>
<td>1.7</td>
<td>3.9</td>
</tr>
<tr>
<td>acids</td>
<td>0.7</td>
<td>0.1</td>
</tr>
<tr>
<td>Monoaromatics</td>
<td>18.5</td>
<td>18.1</td>
</tr>
<tr>
<td>PAHs</td>
<td>22.2</td>
<td>8.8</td>
</tr>
<tr>
<td>phenols</td>
<td>9.0</td>
<td>3.5</td>
</tr>
<tr>
<td>Nitrogen compounds</td>
<td>38.0</td>
<td>48.4</td>
</tr>
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</table>

High nitrogen content is a challenge for biocrude upgrading but a potential for bioproduct recovery.
Bio-crude Upgrading - Hydrotreating

UNIT OPERATIONS
- Oil feed system including pumps and flow control
- Gas feed system
- Reactor system
- Separator system
- Gas and liquid sampling system

Reactor volume - 350 mL
Catalyst volume - 20 to 250 mL
Design temperature: 450°C
Max. operating temperature: 430°C
Max. operating pressure: 170 bar (2500 psig)

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)
- Long-term unattended operation to determine upgrading catalyst stability and lifetime (500-1000 hrs)
- Refinery integration and co-processing strategies

Challenges: Reactor plugging, process severity correlated to bio-crude composition
Effect of Hydrotreating Conditions

<table>
<thead>
<tr>
<th>Condition</th>
<th>Experiment-1</th>
<th>Experiment-2</th>
<th>Experiment-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (bar)</td>
<td>100</td>
<td>138</td>
<td>138</td>
</tr>
<tr>
<td>Average temperature (°C)</td>
<td>350</td>
<td>300</td>
<td>290</td>
</tr>
<tr>
<td>LHSV (h⁻¹)</td>
<td>0.5</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>H₂/oil ratio (NL/l)</td>
<td>2000</td>
<td>3000</td>
<td>3300</td>
</tr>
<tr>
<td>Catalyst dilution (Vol %)</td>
<td>40</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>TOS (h)</td>
<td>16</td>
<td>103</td>
<td>365</td>
</tr>
</tbody>
</table>

Inherent functionalized nature of biomass offers unique opportunity for the production of bio-based oxygen-containing chemicals that are not easily synthesized from petroleum feedstocks.

- Mixed phenolic fraction has commercial potential as a feedstock for value-added bioproducts with price points based on current markets.
- Preliminary TEA indicates MP yield and product price have largest economic impact. Biofuel production cost can be reduced by 30%.
- Strategic separations and chemistries can be used to expand into multiple markets with defined technical requirements for product quality and purity.
- Remaining biocrude fractions can be upgraded into biofuels.
Methoxyphenols as Bioproducts

RTI CFP Technology produces partially deoxygenated, thermally stable biocrude that contains useful methoxyphenols (MPs) such as eugenol, isoeugenol, dihydroeugenol, and guaiacols (methyl-, and ethyl-).

**Yield/Selectivity of MPs**

<table>
<thead>
<tr>
<th>Partially deoxygenated biocrude</th>
<th>GC-MS Analysis (wt.% dry basis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Major Chemical Components</td>
<td></td>
</tr>
<tr>
<td>Levoglucosan</td>
<td>11.40</td>
</tr>
<tr>
<td>Isoeugenols</td>
<td>10.55</td>
</tr>
<tr>
<td>Furfural</td>
<td>6.94</td>
</tr>
<tr>
<td>Hydroxy Ketones</td>
<td>4.00</td>
</tr>
<tr>
<td>Guaiacols</td>
<td>3.75</td>
</tr>
<tr>
<td>Acetic Acid</td>
<td>2.18</td>
</tr>
<tr>
<td>Alkylated Benzenediols</td>
<td>1.72</td>
</tr>
<tr>
<td>Vanillin and phenolic aldehydes</td>
<td>0.82</td>
</tr>
<tr>
<td>Cyclopentanones, Hydroxy</td>
<td>0.74</td>
</tr>
<tr>
<td>Benzenediols</td>
<td>0.72</td>
</tr>
<tr>
<td>Eugenol</td>
<td>0.68</td>
</tr>
<tr>
<td>2(5H) Furanone</td>
<td>0.63</td>
</tr>
<tr>
<td>Propanoic acid, 2-oxo-, methyl ester</td>
<td>0.48</td>
</tr>
<tr>
<td>Furans</td>
<td>0.41</td>
</tr>
<tr>
<td>Cyclopentanones</td>
<td>0.36</td>
</tr>
</tbody>
</table>

- Relatively high methoxyphenol concentration in biocrude (9-15 wt.%).
- Process conditions and feedstock can be adjusted to maximize MP production.
- Oxygenates attract higher market price (> $2/kg) than hydrocarbons (BTX) made from biomass.
- Building blocks for other products with simpler and cheaper synthetic routes compared to using petroleum precursors.

Feedstock for many applications with large market sizes. Purity and quality can be tailored to end use applications.
Development and Optimization of an efficient and economical separation strategy for MPs recovery from biocrude

**Technical Approach for Separations**

**Distillation**
- High residue formation
- Limited by boiling point
- Low purity

**Solvent Extraction**
- Non-selective
- High solvent use
- Precipitate formation in alkaline extraction
- Low recovery

**Adsorption Chromatography**
- Large solvent volumes
- High rate of media exhaustion
- Many stages

**Approach**
- Evaluate distillation, solvent extraction, and adsorption chromatography
- Modify selected methods to address biocrude separation challenges
- Identify a hybrid strategy to enhance separation efficiency and bioproduct purity.

**Critical Technical Goals**
- Develop and demonstrate an efficient (≥ 75wt%), cost competitive separation strategy to obtain high purity (≥ 90%) MPs.
- Demonstrate process scalability
Bench-top Separation Strategy Development

Three Separation Strategies
- Isolation-Concentration
- Isolation-Purification
- Isolation-Concentration-Purification

Technical Targets

<table>
<thead>
<tr>
<th>Separation Metrics</th>
<th>Proposed Target</th>
<th>Achieved Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>Overall Efficiency, %</td>
<td>85</td>
<td>75</td>
</tr>
<tr>
<td>Product Purity, wt%</td>
<td>90</td>
<td>95</td>
</tr>
<tr>
<td>Residual Losses, wt%</td>
<td>15</td>
<td>0</td>
</tr>
</tbody>
</table>

**Isolation:** Selective aromatic solvent (toluene) extraction for separating MPs from biocrude followed by distillation to obtain a fraction boiling within 180 and 320 °C. 45-50 wt% concentration of the MPs at overall recovery efficiency of 78-99 %.

**Concentration:** Alkaline extraction of recovered distillate exploiting differences in pKa of the various phenolics and compounds in the isolated MP-rich fraction. Alkaline extraction at pH 11.5 was optimal for concentrating the MP-fraction with more than 90% efficiency. A product containing up to 86 wt% MPs can be recovered.

**Purification:** Gradient elution method over silica gel to separate targeted MPs from other phenolic components. Bio-product with 97 wt% MPs with 85-97% recovery efficiency.
Demonstrate an advanced biofuels technology that integrates a catalytic biomass pyrolysis step and a hydroprocessing step to produce infrastructure compatible biofuels. Improve the economic viability of this process by recovering high-value bio-products.

- **Scale-up CFP process to pilot-scale to validate catalyst performance and bio-crude yields and quality**
  1) Optimize the catalytic biomass pyrolysis process (1TPD) to maximize high-quality bio-crude production (< 20 wt% O and > 40% carbon recovery)
  2) Improve bio-crude thermal stability

- **Design, build and operate a pilot-scale hydroprocessing unit to upgrade bio-crude intermediates**
  1) Evaluate the impact of bio-crude quality on the hydroprocessing step
  2) Evaluate co-processing opportunities
  3) Evaluate hydrogen demand of the integrated process
  4) Maximize biofuels yield

- **Develop and optimize a hybrid separation method to recover high-value methoxyphenols(MPs) from biocrude.**
  1) Leverage catalytic biomass pyrolysis to produce a thermally stable biocrude with narrow product slate.
  2) Tailor separation approach to the physicochemical properties of the biocrude.
  3) Adapt a hybrid separation strategy for extraction, concentration and purification of MPs
Continuing Challenges

- **Technical barriers**
  - Improve biofuel yields
  - Maximize carbon efficiency
  - Minimize hydrogen consumption
  - Feedstock quality vs. technology robustness

- **Economics: How do we become cost competitive? ($3/gge)**
  - Tax credits and subsidies (short term)
  - Reduce CAPEX – optimize scale
  - Leverage integration opportunities
  - Reduce feedstock costs
  - High value co-products

- **Sustainability**
  - GHG emissions reduction
  - Waste-to-energy
  - Direct and indirect land use changes
  - Water consumption (feedstock and process)

- **Market acceptance**
  - Early adopters: commercial aviation industry and military
  - Blendstocks and fuel properties
  - Infrastructure compatibility
Acknowledgements

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

Industry Partners
- Kim Knudsen
- Glen Hytoft
- Jostein Gabrielsen
- Nadia Luciw Ammitzboll
- Jeppe Kristensen
- Sylvain Verdier

Funding Agencies
- ARPA-E
- U.S. Department of Energy
- Bioenergy Technologies Office
- Haldor Topsoe
- Arkema
- AECOM
- Veolia
- Phillips 66