Catalytic Processes in Biomass Gasification and Pyrolysis

David C. Dayton, Director of Biofuels
RTI International
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Established in 1958 as collaboration between state government, area universities, and business leaders

Mission: to improve the human condition by turning knowledge into practice

Revenues >$750MM with 13% average annual growth over the last 10 years.

>4,200 professionals in >40 countries

High-quality scientific staff with tremendous breadth

>130 different academic disciplines

Notable Achievements:
- Taxol® and Camptothecin™
- Cochlear ear implants
- Wind shear avoidance system
CET develops advanced energy technologies to address some of the world’s great energy challenges.

Leading-edge expertise in:
- Advanced materials development
  - Catalysts
  - Membranes
  - CO₂ solvents
- Process engineering & design
- Scale-up & field testing

Industries served by CET:
- Power
- Fuels & Chemicals
- Gas Processing
- Transportation
- Cement
Center for Energy Technology

Energy R&D within CET

Program Areas

Advanced Gasification
- Syngas cleanup/conditioning
- Substitute natural gas production
- Hydrogen production (Chemical Looping)

Biomass & Biofuels
- Biomass gasification
- Syngas cleanup/conditioning
- Pyrolysis to biocrude and conventional fuels

Fuels and Chemicals
- Syngas to fuels and chemicals
- Hydrocarbon desulfurization

Carbon Capture & Reuse
- Post-combustion CO₂ capture
- Pre-combustion CO₂ capture
- CO₂ reuse for fuels chemicals

Core Competencies
- Catalyst & Sorbent Development
- Membrane Development
- Reaction Engineering
- Process Engineering & Design
- Bench-scale & Prototype Testing
- Techno-Economic Evaluations

Feedstocks
- Biomass
- Coal
- NG
- HCs

(Catalytic) Pyrolysis
- Gasification
- Reforming
- Partial Oxidation
- Catalytic Upgrading

Gasification
- Cleanup and Conditioning
- CO₂ Capture
- CO₂ Utilization

Catalytic Conversion
- Fuels
- Chemicals

Power
Catalytic Processes in Biomass Gasification

- **Feed Processing & Handling**
- **Biomass Gasification**
- **Syngas Cleanup**
- **Syngas Conditioning**
- **Catalytic Fuel Synthesis**
- **Next Generation Biofuels**

**In-bed catalysts**
- Tar cracking
- Methanation (SNG)

**Tar Conversion**
- Tar cracking
- Tar reforming

**Heteroatoms**
- Sulfur sorbents
- NH$_3$ decomposition
- HCN removal
- HCl scrubbing

**Metals capture**
- Alkali, Hg, As

**Water Gas Shift**
- High temp shift
- Low temp shift
- Sour shift

**Guard beds**
- Sulfur sorbents
- NH$_3$ decomposition
- HCN removal
- HCl scrubbing
Syngas Utilization

**Clean Syngas**

H₂, CO, CO₂

**Building Blocks for Fuels and Chemicals**

**Chemicals**

- **Steam Iron Process**
  \[
  \text{Fe}_3\text{O}_4 + \text{CO} \rightarrow 3\text{FeO} + \text{CO}_2 \\
  3\text{FeO} + \text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + \text{H}_2
  \]
  Hydrogen

- **Methanol Synthesis**
  \[
  \text{CO} + 2\text{H}_2 \rightarrow \text{CH}_3\text{OH} \\
  \text{CO}_2 + 3\text{H}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O} \\
  \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2
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- **Methanation**
  \[
  \text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O} 
  \]
  Methane (SNG)

- **Mixed Alcohol Synthesis**
  \[
  2\text{nH}_2 + \text{nCO} \rightarrow \text{C}_n\text{H}_{2n+1}\text{OH} + (n-1)\text{H}_2\text{O} 
  \]
  Ethanol and Gasoline Additive

- **Fischer-Tropsch Synthesis**
  \[
  2\text{nH}_2 + \text{nCO} \rightarrow (-\text{CH}_2-) + \text{nH}_2\text{O} 
  \]
  Gasoline and Diesel

- **Dimethyl Ether Synthesis**
  \[
  2\text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O} 
  \]
  LPG and Diesel Fuel

**Transportation Fuels**

- **Steam Iron Process**
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  Hydrogen

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Tar Cracking Process Development at RTI

**Technical Goals**
- Reduce syngas cleanup process complexity
- Validate technology with biomass-derived syngas

**Economic Target**
- Reduce syngas cleanup/conditioning capital and operating costs to achieve biofuel production cost goals

**Process Advantages**
- Thermally efficient
- Cleaner and reduced-volume water product
- Process intensification (i.e., fewer unit operations)

**Technical Targets**
- Tar < 0.1 g/Nm³
- NH₃ < 10 ppm
- H₂S < 100 ppb
- HCl < 10 ppb
Technology Development Approach

**Catalyst Development**
- Productivity
- Attrition resistance
- Stability

**Process Development**
- Reaction kinetics
- Integration strategy

**Catalyst Development**
- Catalyst scale-up

**Process Development**
- Reactor scale-up
- Process modeling and design
- Detailed engineering
- Continuous operation
- Performance evaluation
- Pilot-plant testing
Tar cracking catalyst screening
- Use sorbent for sulfur removal
- FCC has promising tar cracking activity

Biomass Gasification Testing
- Successful operation of integrated biomass gasification system (gasifier, feeder, filter)
- Syngas quality (composition, HHV) sensitive to steam flow and O\textsubscript{2} addition

Tar cracking reactor design, fabrication, and installation complete
Integrated Testing just starting
What are the target bio-crude physical properties and the desired chemical composition that make it valuable as an intermediate for fuels and chemicals production?
**Proposed Technology:** A novel process that uses multi-functional catalysts to control biomass pyrolysis chemistry to produce a cost-effective refinery-compatible hydrocarbon intermediate.

**Technology Development Approach**

- **Catalyst Development**
  - Catalyst Synthesis
  - Catalyst Characterization: BET, TPR, Surface Analysis
  - Model Compound Testing
  - Bench-scale Catalytic Pyrolysis
  - Proof-of-concept
  - Identify key parameters for reactor design
    - Deoxygenation
    - Regeneration
    - Coke yields/Energy efficiency
    - Oxidation and reduction rates

- **Process Development**
  - Oxygen Rejection
  - Reactor design/prototypes
  - Real Biomass Testing
  - Yields: Gas, Bio-crude, Char/Coke
  - Hydrogen demand
  - Bio-crude Analysis and Quality
  - Process Modeling: Heat and Material Balances

- **Scale-up and Commercialization**

Focus on technology scale-up from the beginning.
Catalytic Microreactor Test System

Reaction Conditions:
- Temperature: 300-500°C
- Catalyst loading: 5 g
- Liquid feed rate: 0.02-0.05 ml/min.
- Carrier feed rate: 50 ml/min.
- LHSV: 0.1 h⁻¹
- GHSV: 1831 h⁻¹

- Convenient & effective approach to understanding complex reaction chemistries
- Enables fast & relevant screening of catalysts
- Helps develop understanding of deoxygenation pathways (mechanism)
- Provide insights for catalyst optimization and development of novel catalyst composition
Catalytic Biomass Pyrolysis Proof-of-Concept

- Catalytic pyrolysis studies in micro-fluidized bed reactor
- Rapid catalyst screening
- Biomass injected directly into fluidized catalyst bed
- Mass closures > 90%
- On-line gas analysis
- Liquid and solid product collection and analysis
RTI’S Bench-Scale Pyrolysis System

Biomass Pyrolysis – Vapor Phase Upgrading

Biomass feed rate: 100-350 g/h
Carrier gas: 2-20 SLPM N₂
Residence time: 0.3-5 s
Temperature: 350-900 °C
Mass closure - >95 wt%
  On-line microGC gas analysis
  Liquid yield: 50-70 wt%
  Char yield: 5-15 wt%

Bio-oil Collection
  Heat Exchanger (~13° C)
  Condensation Train (dry ice impingers)
  Electrostatic Precipitator

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Gas yields increase with temperature
- Hydrogen yields with catalyst are much higher than baseline (useful in process for regeneration)
- \( \text{CO}_2/\text{CO} \) increases with temperature

Coke deposits on the catalyst and at the entrance to the upgrading reactor

Bio-crude phase separates
- Water content increases with temperature (more cracking and dehydration)
- Light fraction also increases with temperature
- Water content of heavy fraction relatively constant

<table>
<thead>
<tr>
<th>Liquid Yield (g)</th>
<th>Baseline</th>
<th>400° C</th>
<th>450° C</th>
<th>500° C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total</td>
<td>389 (22%)</td>
<td>16.8 (31%)</td>
<td>13.2 (42%)</td>
<td>21.3 (44%)</td>
</tr>
<tr>
<td>Light Fraction</td>
<td>na</td>
<td>8.2 (49%)</td>
<td>7.8 (62%)</td>
<td>12.7 (67%)</td>
</tr>
<tr>
<td>Heavy Fraction</td>
<td>na</td>
<td>8.6 (14%)</td>
<td>5.4 (12%)</td>
<td>8.6 (10%)</td>
</tr>
</tbody>
</table>
Acknowledgments

- RTI Team in CET
- Industrial and University Partners
- Funding from the U.S Department of Energy (Office of Biomass Programs and ARPA-E)

Turning Knowledge into Practice
Lab-Scale → Bench-Scale → Pilot-Scale → Demonstration-Scale
Some Perspectives on RTI

- We are one of the world’s leading research institutes
  - Exceptional depth and a continuously evolving knowledge base
  - Unique ability to create high-performing teams to solve the most complex problems

- We are an applied research organization
  - Little basic research or true consultancy
  - Dependant upon competitively awarded contracts

- We are an institute, not a university
  - 100% professional, dedicated staff
  - Experienced project managers, many from industry

- We are a non-profit organization
  - Very conducive to true “win-win” scenarios
  - Independent, objective work on complex scientific challenges
  - We have a pragmatic, flexible approach to IP

- We have a diverse client base
  - Extensive network of relationships with industrial, academic, and government clients.
  - When appropriate, we can provide access to mission oriented federal programs
Catalytic Processes in Biomass Gasification

Feed Processing & Handling -> Biomass Gasification -> Syngas Cleanup -> Syngas Conditioning -> Catalytic Fuel Synthesis -> Next Generation Biofuels

- In-bed catalysts
  - Tar cracking
  - Methanation (SNG)
- Tars Removal
  - Tar cracking
  - Tar reforming
- Heteroatoms
  - Sulfur sorbents
  - NH₃ decomposition
  - HCN removal
  - HCl scrubbing
- Metals capture
  - Hg, As, alkali

Syngas CO + H₂

- Fischer-Tropsch
- Water Gas Shift
  - High temp shift
  - Low temp shift
  - Sour shift
- Guard beds
  - Sulfur sorbents
  - NH₃ decomposition
  - HCN removal
  - HCl scrubbing

Ethanol

- Homologation with CO + H₂
  - CuCo-Based
  - MoS₂-Based
- Zeolite
- Al₂O₃/Zeolite/HPA

Methanol CH₃OH

- Oxosynthesis
  - Co, Rh
- CuZnO-Based
- CuCo-Based
- MoS₂-Based

- Formaldehyde
- Acetic Acid
- Methyl Acetate

Diesel Waxes
- Gasoline Olefins

Gasoline Olefins
- Diesel Waxes
- Gasoline Olefins

Aldehydes
- Alcohols
- Mixed Alcohols

DME CH₃OCH₃
- HPA/Zeolite
- Methyl Acetate