Oxygen-Blown Gasification and Fixed-Bed Fischer–Tropsch Synthesis of Coal and Biomass

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Joshua Strege
What Is the EERC?

- Founded in 1951 as a U.S. Bureau of Mines laboratory to study lignite gasification.
- Defederalized in 1983 and became a part of the University of North Dakota.
- Has expanded into all fossil fuels, renewables, pollution prevention, environmental remediation, water, hydrogen, and materials research.
What Is the EERC?

• Work through partnerships with federal and state government as well as numerous commercial clients
• $236 million contract portfolio in FY09
• Clientele:
  – Governmental: 93
  – Academia: 52
  – International Market: 142
  – Private Corporations: 798
Project Overview

• Multiyear U.S. Department of Energy (DOE) National Energy Technology Laboratory (NETL) agreement.

• First year – $750,000 through DOE NETL, $950,000 total to study distributed coal-to-liquid (CTL) and biomass-to-liquid (BTL) scenarios.

• Membership in Brigham Young University (BYU) Fischer–Tropsch (FT) Consortium offers FT reactor design and cheap, available catalyst formulations.

• Concept in first year was to demonstrate small-scale production of FT liquids for potential distributed systems.
Why FT? 50 Years of EERC Experience in Gasification

Chronology of Gasification Research, Development, and Demonstration (RD&D) at the EERC

Annular Externally Heated Retort Slagging Fixed-Bed Gasifier Mild Gasification Biomass Microgasifier
Transport Reactor Development Unit Catalytic Gasification/SOFC Entrained-Flow Gasifier
Why FT?
EERC Fuel-Upgrading Capabilities

- $4.7MM Defense Advanced Research Projects Agency (DARPA) project
  - Experience, reactors for hydrotreating vegetable oils to green diesel and jet fuel
- Numerous feeds, including various crop oils, fatty acids, and waste greases
- Preliminary testing of FT liquids
- Marrying gasifier technology, catalyst development with upgrading gives full FT technology package
First-Year Project Plan

• Coal is Powder River Basin (PRB) and lignite; biomass is torrefied, leached, or raw.
  – Best available gasifier at the EERC is bench-scale fluid-bed gasifier (FBG).
• Gasify coal and coal–biomass blends.
• Perform limited warm-gas cleanup to remove particulate, $\text{H}_2\text{S}$, $\text{H}_2\text{O}$, and condensables.
• Examine performance of FT catalysts.
Catalyst Source

• Commercial FT catalyst vendors very protective.
  – Difficult to obtain catalyst samples early in project.
• The EERC developed an iron-based FT catalyst based on open literature for preliminary testing.
• Membership in BYU consortium offers proven catalyst formulations that could be used in distributed systems.
• The EERC has since established partnership with commercial catalyst vendor for second year of project.
First-Year Developments

• Design and construction of FBG, FT reactor
• Tested PRB, lignite, and biomass (straight and blended)
• AspenPlus™ coal-to-liquids model
• Catalyst-processing equipment
• Fe-based FT catalyst formulation
• Product upgrading
FBG Reactor Design

- 2–9-kg/hr feed rate
  - K-Tron feeder provides real-time feed rate.
- Syngas recycle
- O$_2$-blown
- Up to 70 bar
- 840°C at maximum pressure
- Full-stream warm-syngas cleanup
The EERC’s Other CTL Option

• FBG shares feed system, cleanup train, FT reactor with bench-scale entrained-flow gasifier (EFG).
  – Allows high degree of flexibility in feedstock and operating conditions.
• The EERC also has in-house fuel preparation if need arises for switching from FBG to EFG.
  – 4-tph coal crusher
  – 1-tph pulverizer (-200 or 325 mesh)
  – 5-tph classifier (3/4 in. down to 325 mesh)
  – Steam dryer
  – Various processing equipment for biomass
FT Reactor Design

- Skid-mounted, modular design
- Design from BYU
- Two Dowtherm-cooled packed-bed FT reactors
  - Space and modules for expansion to four beds
- Syngas preheat
- Both gas and FT liquid recycle
FT Reactor Design

- 1-lph nominal production rate with all beds running
- 2.5-cm i.d., 3-m-tall reactors (2x, room for 4x)
- 2-kg catalyst required
- Multiple thermocouples throughout each bed length, plus independent inlet and outlet temperatures for each stream and unit operation
Catalyst

- Supported iron-based catalyst was developed under a separate project.
- Previously tested at lab-scale.
Biomass Pretreatment

• Biomass treated by leaching.
  – Reduces troublesome ash components including alkali and chlorine.
• One sample of olive pits further treated by torrefaction.
  – Torrefaction produces a char material similar to coal.
  – Reduces transportation costs, makes cofeeding easier.
• All samples blended 30% with PRB coal and cofed.
## Coal and Biomass Analyses

<table>
<thead>
<tr>
<th></th>
<th>PRB Antelope Coal</th>
<th>ND Lignite</th>
<th>Leached Olive Pits</th>
<th>Torrefied Olive Pits</th>
<th>Leached DDGS</th>
<th>Leached Switchgrass</th>
<th>DDGS</th>
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## Coal and Biomass Ash Analyses

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<th>PRB Antelope Coal</th>
<th>ND Lignite</th>
<th>Leached Olive Pits</th>
<th>Torrefied Olive Pits</th>
<th>Leached DDGS</th>
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<td>8/28 1:00</td>
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Biomass Cofeeding
Biomass-Cofeeding Conclusions

• Biomass cofeeding did not affect FT product.
• Leaching sufficient to limit agglomeration.
• Torrefaction allowed higher bed temperatures.
• Untreated biomass (DDGS) led to rapid agglomeration and temperature divergence.
# Average FT Run Conditions

<table>
<thead>
<tr>
<th></th>
<th>1&lt;sup&gt;st&lt;/sup&gt; Test</th>
<th>2&lt;sup&gt;nd&lt;/sup&gt; Test</th>
<th>3&lt;sup&gt;rd&lt;/sup&gt; Test</th>
<th>4&lt;sup&gt;th&lt;/sup&gt; Test</th>
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<tr>
<td><strong>Pressure, bar</strong></td>
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<td><strong>Syngas, slpm</strong></td>
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<td>25</td>
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<tr>
<td><strong>Recycle, slpm</strong></td>
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<td>176</td>
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<td><strong>H&lt;sub&gt;2&lt;/sub&gt;</strong></td>
<td>IN 28.3</td>
<td>OUT 13.3</td>
<td>IN 13.8</td>
<td>OUT 7.1</td>
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<tr>
<td></td>
<td>OUT 7.1</td>
<td></td>
<td></td>
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</tr>
<tr>
<td><strong>CO</strong></td>
<td>IN 15.9</td>
<td>OUT 8.3</td>
<td>IN 8.6</td>
<td>OUT 4.3</td>
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<tr>
<td><strong>CO&lt;sub&gt;2&lt;/sub&gt;</strong></td>
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<td>OUT 45.1</td>
<td>IN 20.5</td>
<td>OUT 23.2</td>
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<td><strong>Conversion, %</strong></td>
<td>CO 61</td>
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<td>H&lt;sub&gt;2&lt;/sub&gt; 52</td>
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<td></td>
<td></td>
<td></td>
<td>CO 24</td>
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<td>CO 49</td>
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<td><strong>Selectivity to Light Gas, %</strong></td>
<td>CO 18</td>
<td>H&lt;sub&gt;2&lt;/sub&gt; 24</td>
<td>CO 32</td>
<td>H&lt;sub&gt;2&lt;/sub&gt; 28</td>
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<tr>
<td><strong>Liquid Product, kg/hr</strong></td>
<td>0.12</td>
<td>0.064</td>
<td>0.043</td>
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<tr>
<td><strong>Organic:Aqueous Ratio, kg/kg</strong></td>
<td>0.18</td>
<td>0.097</td>
<td>0.062</td>
<td>0.066</td>
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<tr>
<td><strong>Aqueous TOC, mg/L</strong></td>
<td>7880</td>
<td>7950</td>
<td>16,100</td>
<td>25,500</td>
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</table>
Notes from First Test

• Mass balance across FT reactor 71%.
  – 14% of product HC; remainder water (8 g/L TOC).
  – Much of this error due to different calibration of inlet and outlet gas-metering devices – 73% on N₂.

• Some mass loss is due to light HC.
  – Samples depressurized into ice-cooled pot.
  – When samples were depressurized, they bubbled in the drain line and formed foam.
  – This indicates rapid evaporation of light products that condensed at pressure.
  – Similarity of mass balance during syngas or N₂ feed suggests mass loss to evaporation is small.
Product Properties – First Test

CO Conversion = 61%
Selectivity to Light Gas = 18%
Notes from Second Test

• Product was collected into ice-cooled pot in first test but at room temperature in later tests.
  – This is a primary reason for lower organic:aqueous ratio in products after first test.

• Second test went smoothly, although product was accidentally destroyed.

• Second test conducted at higher space velocity and higher N₂ dilution (~50%) than first test, resulting in poorer conversion and lighter product.
Ambient Air Temperatures

Test

Air Temperature, °C

-20 -10 0 10 20 30 40

1 2 3 4
Notes from Third Test

- Cold weather caused significant system upsets, frequent shutdowns during third test.
  - Problem areas heated to solve problem.
- High CO$_2$ in syngas and FT recycle gas.
  - Rapid FT catalyst deactivation
  - Very poor conversion
  - High light gas production
  - High water-soluble content (i.e., alcohols)
- Cofeeding treated biomass with lignite actually improved gasifier performance.
Product Properties – Third Test

CO Conversion = 24%
Selectivity to Light Gas = 32%
Notes from Fourth Test

- Attempt was made to regenerate catalyst under hot CO prior to fourth test.
  - Operating conditions similar to first test, but product quality similar to third test.
  - Catalyst activity does not seem to have fully recovered.

- Heating cold lines after third test caused gasifier tars to carry through to FT reactor.
  - Heating did not fully stabilize gasifier operation, as agglomeration formed early in fourth test and affected fluid-bed operation for duration of test.
Product Properties – Fourth Test

CO Conversion = 49%
Selectivity to Light Gas = 28%
GC–MS Product Breakdown

![GC-MS Product Breakdown Chart](chart.png)
FT Reactor Conclusions

• Two-stage warm-gas cleanup reduced syngas sulfur to nondetectable levels.
• Packed-bed FT reactor design feasible with high recycle, low single-pass conversion.
• Critical to capture tars from gasifier – catalyst not easily regenerated after tar exposure.
  – Also capture tars to avoid plugging, as catalyst activity does not recover after rapid shutdown.
• High CO$_2$ detrimental to iron-based catalyst.
  – For small-scale packed-bed FT reactor, may need to use cobalt-based catalyst or develop effective warm-gas CO$_2$ sorbents.
Hydrotreating

- Used coal-derived product from first test.
- Treated over commercial hydrotreating catalyst.
- No aqueous phase observed after hydrotreating.
  - FT product from lab-scale testing deoxygenated to hydrocarbons and water.
- Also no readily discernable change in GC–MS.
  - Insignificant olefin saturation
- Karl Fischer analysis showed very low water content.
- Results suggest very little oxygen in FT product.
- Hydrotreated product distilled into two fractions.
- Heavier fraction suitable for upgrading to jet and diesel; major peak at C10, extends to C30+.
- Lighter naphtha fraction potential gasoline feedstock; major peak at C7, only traces above C11.
Isomerization

- Heavy product isomerized over commercial catalyst.
- Product distilled to yield naphtha, jet fuel, diesel.
- FT product did not sufficiently isomerize for jet fuel.
  - Note that FT product not pure: some gasifier tars.
  - Demonstrates potential need for catalysts, processes specific to FT products.

Jet Fuel
Freeze Point = -45°C

Isomerized Heavy Fraction
67% Isomerization
Future Work

• Second year – Develop process-specific FT and fuel-upgrading catalysts.
  – Catalyst partner working with EERC to develop catalysts for commercialization.

• Third year – Demonstrate warm-gas cleanup train suitable for long-term operation.
  – Critical for small-scale gasifiers.
  – Compare to performance of cold-gas cleanup.
  – To date, the EERC has demonstrated only short-term FT operation with warm-gas cleanup.
Possible Future Work

• Require cost share from outside U.S. federal government.
• Further catalyst development.
• Connect FT reactor to other gasifiers.
  – Coupling FT skid to off-site gasifiers for testing syngas online.
• Mixed alcohol synthesis at high pressure (70+ bar).
• Develop technoeconomic models.
• Produce gallon-scale quantities of fungible fuel.
Contact Information

Energy & Environmental Research Center
University of North Dakota
15 North 23rd Street, Stop 9018
Grand Forks, North Dakota 58202-9018

World Wide Web: www.undeerc.org
Telephone No. (701) 777-5000
Fax No. (701) 777-5181

Josh Strege
Research Engineer
(701) 777-3252
jstrege@undeerc.org