Goals

• Determine economically feasible technologies for production of biomass followed by production of biomass-derived syngas used for:
  – Renewable power generation
  – Liquid fuel production
Quad Chart Overview

Timeline

• Project start date - 2010
• Project end date - 2013
• 80% complete

Budget

• Funded in FY10
• $1.5 million
• $281k cost share

Barriers

• Barriers addressed
  – Bt-A Biomass Fractionation
  – Gt-C High Temperature Gas Production from Biomass
  – Gt-G Fuel Synthesis and Upgrading
  – Gt-K Gaseous Intermediates Process Integration

Partners

• Project conducted at Auburn University
• Collaboration with Rentech
Project Overview

• Overall Objectives
  – Determine economic constraints associated with harvesting forest biomass from southern pine and hardwood plantations.
  – Refine techniques for biomass fractionation and conversion into forms suitable for trade in commodity markets.
  – Develop process simulation models for biomass gasification and gas conditioning.
  – Develop models of Fischer-Tropsch synthesis processes.
Approach

Continuation of Previous Project

– Models used to evaluate logistics (harvest and transport) systems for young plantations of southern pine and hardwood

– Experimental methods used to identify preprocessing methods to convert biomass into relatively uniform products of cellulose, hemicellulose, and lignin.

– Models developed and validated for biomass gasification, tar formation, and syngas composition using experimental data from a bubbling-bed fluidized-bed reactor.

– Models developed and validated for supercritical phase Fischer-Tropsch conversion of synthesis gases into fuels and chemicals using experimental FT data and gasification modeling results.
Auburn Gasification Platforms

- **Bench-scale**
  - (~1 kg/hr)
  - Bubbling bed

- **Pilot-scale**
  - (1 ton/day)
  - Bubbling bed

- **Pilot-scale**
  - (0.5 ton/day)
  - Mobile Downdraft CHP
Gasification Research

Objectives

• Understand the effect of biomass properties on syngas quality and contaminants (e.g. tar, H\textsubscript{2}S).

• Understand the fate of contaminants in gasification with different oxidizing media.

• Determine appropriate syngas conditioning and cleanup strategies for subsequent FT synthesis.

Approach:

• Perform gasification studies on different biomass species (e.g. pine, eucalyptus, poplar, and switchgrass) and build process models to predict gasifier performance.
Gasification Research

Bench-scale Gasifier Specifications

- Pressure: atmospheric
- Temperature: 600, 700, 800°C
- Feed rate: ≤ 0.85 kg/h
- Biomass particle size: ~ 850 µm
- Moisture content: ~ 10% (wb)
- Analysis systems:
  - NDIR based gas analyzer (online)
    - CO, CO₂, CH₄, H₂, O₂
  - HP GC (offline)
    - H₂S
  - FTIR based gas analyzer (online)
    - CO, CO₂, NH₃, HCN, HCl
  - Impinger train for tar analysis (offline)
Syngas Composition
Example Results

Typical syngas composition profile from southern pine gasification with $O_2$ as oxidant and $N_2$ as fluidization gas.

- **Syngas Composition, vol %**
  - $O_2$: 0.7, 0.0
  - CO: 15.8, 12.1
  - $CO_2$: 8.0, 8.1
  - CH$_4$: 4.2, 3.0
  - H$_2$: 11.2, 9.0
  - N$_2$: 60.1, 67.7

- **Contaminants, ppm**
  - NH$_3$: 421.5, 797.6
  - HCN: 40.9, 63.5
  - HCl: 0.9, 0.9
  - H$_2$S: 31.5, 25.4

Pine gasification at 700°C from using bench-scale gasifier

<table>
<thead>
<tr>
<th>ER</th>
<th>0.19</th>
<th>0.28</th>
</tr>
</thead>
<tbody>
<tr>
<td>Syngas Composition, vol %</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$O_2$</td>
<td>0.7</td>
<td>0.0</td>
</tr>
<tr>
<td>CO</td>
<td>15.8</td>
<td>12.1</td>
</tr>
<tr>
<td>$CO_2$</td>
<td>8.0</td>
<td>8.1</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>4.2</td>
<td>3.0</td>
</tr>
<tr>
<td>H$_2$</td>
<td>11.2</td>
<td>9.0</td>
</tr>
<tr>
<td>N$_2$</td>
<td>60.1</td>
<td>67.7</td>
</tr>
</tbody>
</table>

Contaminants, ppm

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_3$</td>
<td>421.5</td>
<td>797.6</td>
</tr>
<tr>
<td>HCN</td>
<td>40.9</td>
<td>63.5</td>
</tr>
<tr>
<td>HCl</td>
<td>0.9</td>
<td>0.9</td>
</tr>
<tr>
<td>H$_2$S</td>
<td>31.5</td>
<td>25.4</td>
</tr>
</tbody>
</table>
Fischer-Tropsch Synthesis (Gas Phase)
FTS Product Distribution

Extremely low sulfur, nitrogen

Selectivity(%) vs Carbon Number

- Gasoline Range
- Diesel Range
- Wax Range
- Jet Fuel Range
FTS (Supercritical Phase)

Setup: Syngas

Reactions:
- Fixed Bed Reactor
- Product Purification

Products:
- Wax
- Diesel
- Light Hydrocarbons
- Recycled Gasoline

Catalyst: Catalyst Particle
Benefits of Supercritical FTS

- Suppressed CH$_4$ and CO$_2$ formation
- Increased olefin selectivity at higher carbon numbers
- Improved activity maintenance
- Decreased Adiabatic Temperature Rise
- Higher activity and enhanced diesel and wax selectivity

![Graph showing weight fraction of various products]

T = 240 °C, P$_{syngas}$ = 20 bar, P$_t$ = 65 bar in SCH
P$_t$ = 20 bar in gas phase
FTS Research

Objectives

• Synthesize and characterize Fe-based Fischer-Tropsch Synthesis (FTS) catalysts suitable for use with biomass-derived syngas

• Compare gas-phase, slurry-phase, and supercritical phase FTS with syngas obtained from biomass gasification

• Quantify the effect of syngas composition and contaminant levels on FTS performance
  – Characterize this performance relative to syngas conversion, product selectivity, and yield of fuel-range hydrocarbons
FTS Liquid Product Functionality -v- Carbon Number

CO Conversion = 45%

- 100 Fe : 10 Zn : 1 Cu : 2 K (by mol) catalyst, T = 240°C, P = 17.5 bar, H₂ / CO = 1.65
**SCF-FTS Liquid Product Functionality -v- Carbon Number**

CO Conversion = 45%

- **100 Fe : 10 Zn : 1 Cu : 2 K (by mol) catalyst**
- **T = 240°C, P = 79 bar, H₂ / CO = 1.65, media = hexanes, media rate = 1 mL/min per 50 SCCM**
Modeling Research

Objectives

• Optimize gasification-FTS system design using process integration techniques for thermal management and resource conservation.

Approach

• Models developed using commercial process simulation software.

• Models augmented with customized units for specific equipment, (not be readily available in commercial simulators).

• Models developed in collaboration with other researchers to enable synergistic feedback of design changes identified by simulation to guide targeted validation experiments.
Model Formulation

• **Simulation Input**
  - Proximate and ultimate analysis used as simulation input
  - Aspen Plus® process simulation software
  - Gibbs Free Energy minimization approach

• **Initial Analyses**
  - Analyze impacts of increased oxygen (air) content
  - Determining optimal air-to-fuel ratio for each feedstock
  - Examine effects of varying gasifier pressure
  - Steam injection to augment synthesis gas production
Gas Phase FTS Model
Model Specification

• Fischer-Tropsch Reactor
  – Based on ARGE reactor (Ruhrchemie and Lurgi)
  – 2050 tubes, 5 cm ID and 12 m length (48.3 m³)
  – Recycle of tail gas (ca. 1/3)
  – Production requires 70.5 gmole CO/sec
  – CO consumption 1.46 gmole CO/m³-sec
  – Heat of Rxn = 170,000 J/gmole CO
  – Volumetric heat generation= 248 kW/m³
  – Packed bed thermal conductivity= 4.49 W/m-K
  – $\Delta T_{max} = \frac{S_e R^2}{4k}$, $\Delta T_{max} = 8.6K$ (average)
Supercritical Phase FTS Model
FTS System Comparison

Fuels Production Analysis

<table>
<thead>
<tr>
<th></th>
<th>Syngas (kmol/hr)</th>
<th>Gasoline (kg/hr)</th>
<th>JPS (kg/hr)</th>
<th>Total Fuel (kg/hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>D1</td>
<td>D2</td>
<td>Total</td>
</tr>
<tr>
<td>Gas-Phase FTS</td>
<td>1524</td>
<td>882</td>
<td>526</td>
<td>1348</td>
</tr>
<tr>
<td>Same Syngas Feed</td>
<td>1524</td>
<td>608</td>
<td>1318</td>
<td>1826</td>
</tr>
<tr>
<td>Same Fuel Product</td>
<td>1122</td>
<td>374</td>
<td>974</td>
<td>1348</td>
</tr>
<tr>
<td>(based on gasoline)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Same Fuel Product</td>
<td>1259</td>
<td>420</td>
<td>1090</td>
<td>1510</td>
</tr>
<tr>
<td>(based on total</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>product)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Supercritical Phase FTS Model

SCF-FTS is about 20% more expensive than Gas-Phase with the same syngas molar feed rate, but produces about 50% more fuel!
Process Integration

• Heat Exchanger Network Design
  – Based on conventional pinch analysis methods
  – Performed using AspenTech HX-Net™
  – Multiple network configurations generated
  – Default setup attempts minimizing total annualized cost based on utility use and equipment size
FTS System Comparisons

• **Gas Phase FTS**$^a$
  - 900°C adiabatic temperature rise
  - 180 reactor modules

• **Supercritical Phase FTS**$^{a,b}$
  - 30°C adiabatic temperature rise
  - 6 reactor modules

\[a\] 50% Conversion with a 5°C allowable temperature rise

\[b\] Hexane media with 3.5 mol media per mol syngas
# FTS System Comparison

<table>
<thead>
<tr>
<th></th>
<th>ARGE</th>
<th>SCAR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of Reactors in Series</td>
<td>1</td>
<td>6</td>
</tr>
<tr>
<td>Number of Tubes</td>
<td>2050</td>
<td>1</td>
</tr>
<tr>
<td>Tube Diameter (m)</td>
<td>0.05</td>
<td>2.3</td>
</tr>
<tr>
<td>Tube Length (m)</td>
<td>12</td>
<td>2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>SCAR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of Heat Exchangers in Series</td>
<td>6</td>
</tr>
<tr>
<td>Number of Tubes</td>
<td>128</td>
</tr>
<tr>
<td>Tube Diameter (m)</td>
<td>0.062</td>
</tr>
<tr>
<td>Tube Length (m)</td>
<td>9.74</td>
</tr>
</tbody>
</table>
# FTS System Comparison

<table>
<thead>
<tr>
<th></th>
<th>ARGE</th>
<th>ARGE Modified for SCF-FTS</th>
<th>SCAR (Single Reactor)</th>
<th>SCAR (Multi-Reactor)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of Reactors</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>6</td>
</tr>
<tr>
<td>Pressure (bar)</td>
<td>45</td>
<td>200</td>
<td>200</td>
<td>200</td>
</tr>
<tr>
<td>Reactor Volume (m$^3$)</td>
<td>48</td>
<td>48</td>
<td>48</td>
<td>8</td>
</tr>
<tr>
<td>Adiabatic Temperature Rise (K)</td>
<td>N/A</td>
<td>N/A</td>
<td>5</td>
<td>30</td>
</tr>
<tr>
<td>Surface Area per Reactor (m$^2$)</td>
<td>3864</td>
<td>3864</td>
<td>85.4</td>
<td>14.2</td>
</tr>
<tr>
<td>Reactor Cost</td>
<td>$2,700,000</td>
<td>$5,500,000</td>
<td>$240,000</td>
<td>$40,000</td>
</tr>
<tr>
<td>Number of Heat Exchangers</td>
<td>N/A</td>
<td>N/A</td>
<td>1</td>
<td>6</td>
</tr>
<tr>
<td>Surface area per HX (m$^2$)</td>
<td>N/A</td>
<td>N/A</td>
<td>825</td>
<td>241</td>
</tr>
<tr>
<td>Cost per HX</td>
<td>N/A</td>
<td>N/A</td>
<td>$1,160,000</td>
<td>$340,000</td>
</tr>
<tr>
<td>Equipment Cost</td>
<td>$2,700,000</td>
<td>$5,500,000</td>
<td>$1,400,000</td>
<td>$2,300,000</td>
</tr>
<tr>
<td>Equipment Cost ($/BPD)</td>
<td>$3,000</td>
<td>$6,000</td>
<td>$1,600</td>
<td>$2,500</td>
</tr>
</tbody>
</table>
Technical and economic feasibility of biomass-to-liquid systems will be improved through:

• Enhanced understanding of the relation between biomass physicochemical properties and syngas quality (Tt-C).

• Enhanced understanding of the relation between biomass gasification conditions and feedstock properties on syngas quality (Tt-F).

• Enhanced fuel selectivity and productivity using SCFTS (Tt-G).

• Expanded understanding of the performance of FT catalysts using biomass derived syngas (Tt-H).
Critical Success Factors

- Developing information and models that will accurately predict syngas composition from biomass characteristics and gasifier operating parameters.
- Refining models that predict the overall technical and economic feasibility of gasification and SC FTS systems.
- Using models to successfully demonstrate the cost effectiveness of SC FTS and its potential ability to match the scale of biorefineries with biomass logistics systems.
Future Work

• Continue biomass gasification studies with broader range of feedstocks.

• Test FT catalysts with biomass syngas produced from southern pine.

• Update feedstock definition to match materials used in gasification studies and validate models using experimental gasification data.

• Combine gasification models with FTS models to evaluate optimal integration and recycle scenarios.
Summary

• Gasification testing using bubbling bed gasification systems was used to expand our understanding of gasification of southern pine.

• Model development is underway to predict gasification performance based on biomass composition and operating parameters.

• Supercritical phase Fischer-Tropsch synthesis has been tested extensively at bench scales.
  1) Suppressed CH\textsubscript{4} and CO\textsubscript{2} formation
  2) Increased olefin selectivity at higher carbon numbers
  3) Improved activity maintenance
  4) Decreased Adiabatic Temperature Rise
  5) Higher activity and enhanced diesel and wax selectivity

• Process modeling shows that production of liquid fuels and chemicals through supercritical FTS can be more cost effective than traditional gas-phase FTS.
Additional Slides
Publications

- Rui Xu, Ph.D., December 2012, Auburn University Ph.D. Dissertation: Synthesis of Methanol and Higher Alcohols from Syngas over K Prompted Cu Based Catalyst in Supercritical Solvent
Publications


Presentations

- Narendra Sadhwani, Sushil Adhikari and Mario M Eden, 2012. Effect of temperature and oxidizing medium on tar formation in southern pine gasification will be presented at Annual International Meeting of American Institute of Chemical Engineers (AIChE), October 28- November 2, Pittsburgh, PA.
Presentations


• R. Xie*, M. Tu (2012) Identification of Nucleophilic Reactions in Detoxification of Phenolic Model Compounds for Bioethanol Fermentation. AIChE Meeting October 28-November 2, poster presentation, Pittsburgh, PA


