Indirectly Heated Biomass Gasification

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PD 29

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Overview

Timeline

- Project start date: July 2007
- Project end date: September 2008
- Percent complete: 33%

Barriers

- Barriers
  - Gasification efficiency
  - Capital intensity
  - Improved tar removal/reforming catalysts

- Targets
  - $1.60 / gge hydrogen in 2012
  - $1.10 / gge hydrogen in 2017

Budget

- Total project funding - $1,100,000
- Funding received in FY07 - $500,000
- Funding for FY08 - $600,000

Partners

- Collaboration with the DOE Office of the Biomass Program sponsored research at NREL
  - Gasification & tar reforming
MYPP Objective

By 2012, reduce the cost of hydrogen produced from biomass gasification to $1.60 / gge at the plant gate (<$3.30 / gge delivered).

By 2017, reduce the cost of hydrogen produced from biomass gasification to $1.10 / gge at the plant gate ($2.10 / gge delivered).

Objective and Key Outcomes

Objective:
To experimentally update the technical & economic performance of an integrated biomass gasification-based hydrogen production process based on steam gasification

- Steam gasification
- Gas cleanup: tar & light hydrocarbon reforming
- Hydrogen sulfide removal
- Shift reaction
- Hydrogen separation

• Key Outcomes Expected:
  - Production of clean syngas
  - Production of high-purity hydrogen
  - Development of updated yield and gas quality correlations
  - Development of updated technoeconomic model
<table>
<thead>
<tr>
<th>Month/Year</th>
<th>Milestone</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jun-08</td>
<td>Complete initial gasification and hydrogen production testing</td>
</tr>
<tr>
<td>Jun-08</td>
<td>Complete initial ASPEN modeling and H2A modeling</td>
</tr>
<tr>
<td>Sep-08</td>
<td>Complete parametric gasification/shift reaction testing for two biomass feeds</td>
</tr>
<tr>
<td>Sep-08</td>
<td>Complete ASPEN model update and revised H2A estimate</td>
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Approach

Data Generation

- Parametric Gasification Testing
  - Performed using indirect steam gasifier
  - 2 feeds (oak, pine)
  - 3 temperatures (750, 850, 950°C)
  - 3 steam/biomass ratios
  - 20 kg/h biomass

- Tar reformer testing at a selected condition

- Slip-stream syngas processing at a selected condition
  - H₂S removal
  - High temperature shift
  - Membrane separation (option)

Process Modeling

- Gasifier Correlation
  - Parametric data
  - Multivariate analysis (Unscrambler)

- ASPEN Analysis
  - ASPEN gasifier correlation FORTRAN block
  - ASPEN H₂ integrated plant analysis

- EXCEL Summaries

- Comparison with 2005 Model

Economic Modeling

- Import of Process Modeling Results into H₂A

- Comparison with Previous Results
Experimental System

The gasification testing is being performed in the NREL 150 kW\textsubscript{t} Thermochemical Process Development Unit (TCPDU)
Typical Gasification Results

Gasification of Oak, NREL TCPDU
Steam/Biomass = 2

![Graph showing typical gasification results with concentration vs. temperature for H2, CO, CO2, and CH4.](Image)
Tar Reforming Experiments

For catalyst evaluation experiments complete deactivation is permitted to gain insights about chemical mechanisms and to estimate reforming and deactivation kinetic rate constants and activation energies.

1st order reaction

\[ k \tau a = \ln \left( \frac{X_A}{1 - X_A} \right) \]

1st order deactivation w residual activity

\[ a = a_{s1} + (1 - a_{s1})e^{-\psi_{d1}t} \]

\[ X_A = \frac{e^{k \tau (a_{s1} + (1-a_{s1})e^{-\psi t})}}{1 + e^{k \tau (a_{s1} + (1-a_{s1})e^{-\psi t})}} \]

Tar Reforming Experiments

Tar /light hydrocarbon reforming is performed in a semi-batch fluid-bed reactor with multiple regenerations of a nickel/alkali catalyst.
### Oak Gasification: NREL TCPDU, Nov-Dec 2007

<table>
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<tr>
<th>Run Order</th>
<th>Run Code</th>
<th>OK_HY 97095</th>
<th>OK_NREL32b</th>
<th>OK_HY 97095b</th>
<th>OK_NREL32b</th>
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<tr>
<td>4</td>
<td>97095</td>
<td>33.74</td>
<td>50.46</td>
<td>39.15</td>
<td>49.91</td>
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<tr>
<td>5</td>
<td>InDe1</td>
<td>24.45</td>
<td>12.18</td>
<td>18.37</td>
<td>13.95</td>
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<tr>
<td>13</td>
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<td>19.93</td>
<td>23.64</td>
<td>23.45</td>
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<tr>
<td>14</td>
<td>InDe2</td>
<td>12.59</td>
<td>4.62</td>
<td>11.06</td>
<td></td>
</tr>
</tbody>
</table>

**H2** 33.74 50.46 39.15 49.91
**CO** 24.45 12.18 18.37 13.95
**CO2** 19.93 23.64 23.45
**CH4** 12.59 4.62 11.06 5.84
**N2** 0.00 0.00 0.00
**He (tracer)** 1.86 1.07 1.69
**C2H6** 0.00 0.00 0.00
**C2H4** 0.00 0.00 0.00
**C2H2** 0.00 0.00 0.00
**C3H8** 1.25 0.07 0.99
**C3H6** 0.00 0.00 0.00
**1-C4H8** 0.00 0.00 0.00
**2-cis-C4H8** 0.00 0.00 0.00
**2-trans-C4H8** 0.00 0.00 0.00
**COS** 0.0000 0.0000 0.0291
**H2S** 0.0058 0.0006 0.0040
**Closure** 95.99 92.21 96.42

**tar (mg/Nm3-wet)**

<table>
<thead>
<tr>
<th>benzene</th>
<th>reformer in</th>
<th>reformer out (initial)</th>
<th>reformer in</th>
<th>reformer out</th>
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<tr>
<td>7785</td>
<td>280</td>
<td>6874</td>
<td></td>
<td></td>
</tr>
<tr>
<td>393</td>
<td>0</td>
<td>326</td>
<td></td>
<td></td>
</tr>
<tr>
<td>46</td>
<td>29</td>
<td>39</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2383</td>
<td>42</td>
<td>1834</td>
<td></td>
<td></td>
</tr>
<tr>
<td>792</td>
<td>0</td>
<td>535</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2157</td>
<td>0</td>
<td>1691</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1417</td>
<td>0</td>
<td>824</td>
<td></td>
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</tr>
<tr>
<td>2158</td>
<td>72</td>
<td>5250</td>
<td></td>
<td></td>
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</tbody>
</table>

**"other tar" (as 128)**
**"heavy tar" (as 178)**
**"total tar" (minus 78)**

<table>
<thead>
<tr>
<th>InDe#</th>
<th>initial conv.*</th>
<th>sample time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OK_NREL32b</td>
<td>methane</td>
<td>benzene</td>
</tr>
<tr>
<td>11/07-12/07</td>
<td>1</td>
<td>50.3%</td>
</tr>
<tr>
<td>S:B=2</td>
<td>R500=700</td>
<td>TC=950</td>
</tr>
</tbody>
</table>

**Detailed gas and tar analyses are used to estimate both initial and reformed product gas composition, and percent conversions of components during reforming.**
Updated Gasifier Correlations

- Current correlation based on 1980s data with yield only a function of temperature

- Updated correlation to predict more components and tars in the product gas.

- Updated correlation to consider the feed composition and additional process variables.

- Updated correlation to use original data and recent data from the NREL TCPDU for corn stover, switchgrass, wheat straw, Vermont wood, and oak (H₂).

- Data are analyzed and regression analysis conducted using Unscrambler software.
New Correlation: Significant Variables

- **Ultimate Analysis**
  - Moisture

- **Ash**
  - Carbon
  - Hydrogen
  - Oxygen
  - Nitrogen
  - Sulfur
  - Chlorine

- **Process Variables**
  - Thermal Cracker Temperature (TC)
  - Steam to Biomass Ratio (SB)
  - Thermal Cracker Residence Time (RT)

- **Squared Effects**
  - TC²
  - SB²
  - RT²

- **Interaction Effects**
  - TC*SB
  - TC*RT
  - SB*RT

\[ Y = B_{\text{int}} + B_C X_C + B_H X_H + B_O X_O + B_N X_N + B_S X_S + B_{\text{TC}} X_{\text{TC}} + B_{\text{SB}} X_{\text{SB}} + B_{\text{RT}} X_{\text{RT}} + B_{\text{TC}^2} X_{\text{TC}^2} + B_{\text{SB}^2} X_{\text{SB}^2} + B_{\text{RT}^2} X_{\text{RT}^2} + B_{\text{TC} \cdot \text{SB}} X_{\text{TC} \cdot \text{SB}} + B_{\text{TC} \cdot \text{RT}} X_{\text{TC} \cdot \text{RT}} + B_{\text{SB} \cdot \text{RT}} X_{\text{SB} \cdot \text{RT}} \]
## Comparison of Current and New Correlations

<table>
<thead>
<tr>
<th>Component</th>
<th>New $R^2$</th>
<th>Current $R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Butene</td>
<td>0.88</td>
<td></td>
</tr>
<tr>
<td>2-c-Butene</td>
<td>0.71</td>
<td></td>
</tr>
<tr>
<td>2-t-Butene</td>
<td>0.71</td>
<td></td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>0.81</td>
<td>0.42</td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td>0.73</td>
<td>0.40</td>
</tr>
<tr>
<td>Ethane</td>
<td>0.72</td>
<td>0.85</td>
</tr>
<tr>
<td>Ethylene</td>
<td>0.96</td>
<td>0.88</td>
</tr>
<tr>
<td>Acetylene</td>
<td>0.96</td>
<td>0.72</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>0.81</td>
<td>0.92</td>
</tr>
<tr>
<td>Methane</td>
<td>0.84</td>
<td>0.70</td>
</tr>
<tr>
<td>Propane</td>
<td>0.90</td>
<td></td>
</tr>
<tr>
<td>Propene</td>
<td>0.95</td>
<td></td>
</tr>
<tr>
<td>Hydrogen Sulfide</td>
<td>0.85</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Component</th>
<th>New $R^2$</th>
<th>Current $R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>0.97</td>
<td></td>
</tr>
<tr>
<td>Toluene</td>
<td>0.83</td>
<td></td>
</tr>
<tr>
<td>Phenol</td>
<td>0.93</td>
<td></td>
</tr>
<tr>
<td>Cresols</td>
<td>0.94</td>
<td></td>
</tr>
<tr>
<td>Naphthalene</td>
<td>0.98</td>
<td></td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>0.98</td>
<td></td>
</tr>
<tr>
<td>Heavy Tar, MW &gt; 180</td>
<td>0.55</td>
<td></td>
</tr>
<tr>
<td>Total Tar, MW &gt; 78</td>
<td>0.77</td>
<td>0.89</td>
</tr>
<tr>
<td>Char</td>
<td>0.74</td>
<td>0.66</td>
</tr>
<tr>
<td>NF Dry Gas Flowrate</td>
<td>0.98</td>
<td>0.94</td>
</tr>
</tbody>
</table>
Update of ASPEN and Economic Models

Objective: Update existing ASPEN model using updated gas yield composition correlations

Link to Model and Report:
http://devafdc.nrel.gov/biogeneral/Aspen_Models/
FY08 Future Work

• Data Generation
  – Parametric gasification testing with pine
  – Tar reformer testing (one condition, new catalyst)
  – Slip-stream syngas testing
    • H$_2$S removal (Sud Chemie proprietary sulfur getter)
    • High temperature shift (Sud Chemie proprietary shift catalyst)
    • Membrane separation (option)

• Process Modeling
  – Multivariate analysis – incorporate pine data
  – ASPEN analysis
    • http://devafdc.nrel.gov/biogeneral/Aspen_Models
  – EXCEL process summaries
  – Comparison with 2005 ASPEN model

• Import Updated Model into H2A Model

• Go / No-Go Decision
## Project Summary

**Relevance:**
Answer questions about 2012 ($1.60 / gge) and 2017 ($1.10 / gge) MYPP objectives for hydrogen produced from biomass gasification. Address efficiency, capital intensity, and reforming barriers.

**Approach:**
A three phase approach is being used: 1) gasification, reforming, and shift reaction testing to produce a clean hydrogen-rich syngas, 2) material and energy balance modeling using updated gasifier correlation and ASPEN, and 3) updated H2A economic estimates.

**Technical Progress:**
One gasifier / reformer campaign completed; initial update of gasifier correlation complete.

**Future Work:**
Complete gasifier / reformer / shift reactor testing
Complete technical modeling
Complete H2A economics