Biomass-Derived Hydrogen from a Thermally Ballasted Gasifier

DOE Hydrogen Program Contractors’ Review Meeting
May 18-21, 2003

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Objective

• Develop hydrogen production system based on thermal gasification of switchgrass
Relevance

- If successful, this project would provide a renewable source of hydrogen from biomass
Approach Outline

• Develop subsystems for the hydrogen production system:
  – Indirectly heated gasifier
  – Gas cleaning process
  – Gas conditioning system
  – Trace gas contaminant measurements

• Testing performed at two scales:
  – Pilot plants (5 tpd) for gasifier and gas cleaning system
  – Slip stream for gas conditioning system
Approach: Indirectly heated gasifier

- Conventional fluidized bed gasification
  - Combustion and pyrolysis occur simultaneously in a single reactor
    - Exothermic combustion provides heat
    - Endothermic pyrolysis produces light gases and hydrocarbons
  - Products of combustion dilute product gas
- Indirectly heated gasification
  - Combustion and pyrolysis processes are separated (usually spatially)
  - No nitrogen dilution of product gas
  - Energy must be transported to the pyrolysis reactions
Approach: Indirectly heated gasifier

Combustion and Pyrolysis are Temporally Separated in the Ballasted Gasifier System
Approach: Indirectly heated gasifier

• Thermal ballast is high temperature phase-change material
  – Lithium fluoride sealed in stainless steel tubes which are immersed in fluidized bed
  – Thermal ballast consists of an array of 48 tubes
• Air fluidizes the bed during combustion
• Steam fluidizes the bed during pyrolysis
• Gasifier temperature varies between 922 K to 1172 K
Approach: Gas Conditioning

- Particulate removal
  - Required to prevent blinding of catalytic beds
  - Evaluating moving bed granular filter
- Trace contaminate removal using sorbent injection
  - $\text{H}_2\text{S}$ and $\text{HCl}$ removal to avoid poisoning of catalytic beds
  - Also removes some heavy tar
- Ammonia and tar removal
  - Steam reforming
- Water gas shift
  - Increases H$_2$ and removes CO
Approach: Gas Conditioning

- Guard bed for trace contaminant removal
  - Fixed bed of dolomite
- Steam reformer
  - Nickel catalysts
- High temperature water gas shift
  - Iron based catalyst
- Low temperature water-gas shift
  - Copper based catalyst

The four reactors are identical in construction.
Approach: Gas Analysis

- Hot gas isokinetic sampling of *particulate matter*
- Impinger train using dichloromethane used for quantitative *tar* analysis
- Micro GC for periodic, *comprehensive gas* analysis
- Non-dispersive IR (CO, CO$_2$), thermal conductivity (H$_2$), and electrochemical (O$_2$) for *continuous gas* monitoring
- Quantitative methods developed for *trace contaminants*
  - NH$_3$ – collection in acid solution and analyzed at a commercial lab
  - H$_2$S – Draeger tubes and GC
## Project Timeline (FY 03)

<table>
<thead>
<tr>
<th>Task</th>
<th>Description</th>
<th>Qtr 1</th>
<th>Qtr 2</th>
<th>Qtr 3</th>
<th>Qtr 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Task 1</td>
<td>Design and construct multi-contaminant control system based on sorbent injection.</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Task 2</td>
<td>Improve trace contaminant instrumentation.</td>
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<tr>
<td>Task 3</td>
<td>Evaluate effectiveness of multi-contaminant control system.</td>
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<tr>
<td>Task 4</td>
<td>Evaluate catalytic reactors for removal of tar and ammonia and enriching hydrogen</td>
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<tr>
<td>Task 5</td>
<td>Identification of appropriate separation technology to purify hydrogen.</td>
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<tr>
<td>Task 6</td>
<td>Thermal System and Cost Estimation Analysis</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Task 7</td>
<td>Project administration and reports</td>
<td></td>
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</tr>
</tbody>
</table>

- **Milestone**
- **Work performed**
- **Work remaining**
Accomplishments/Progress
Multi-contaminant Control

- Established ability of pilot-scale moving bed granular filter to remove fly ash
  - Efficiencies exceeding 90%
- Must keep velocity in downcomer ($U_D$) below the minimum fluidization velocity ($U_{mf}$) of the granular media in the filter to keep efficiency high
Accomplishments/Progress
Trace Contaminant Instrumentation

Temperatures: Sample lines upstream from the tar condenser are at 450°C. Sample lines downstream from the tar condenser are at 110-120°C.
Accomplishments/Progress
Ammonia Sampling Procedure

Quartz Thimble Filters (450°C)

Pressure Cooker (100°C)

Impingers in ice bath (2 acid impingers followed by a silica gel impinger)

Hot Plate

Condensation coil and canister of glass wool remove heavy tars without condensing H2O

Filters remove ash without condensing tars

Highly efficient collection of NH3 with <2% breakthrough from first impinger

Pump
### Accomplishments/Progress

**Gas Conditioning: Tar Cracking**

#### Operating Conditions of Tar Cracking System

<table>
<thead>
<tr>
<th>Parameter</th>
<th>ICI 46-1</th>
<th>Z409</th>
<th>RZ409</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcined dolomite</td>
<td>120ml (132 g)</td>
<td>120ml (132 g)</td>
<td>120ml (132 g)</td>
</tr>
<tr>
<td>Ni-Based Catalyst</td>
<td>20 ml (22.3 g)</td>
<td>20 ml (23.2 g)</td>
<td>20 ml (23.1 g)</td>
</tr>
<tr>
<td>Inert material mixed with catalyst</td>
<td>20 ml (15.3 g)</td>
<td>20 ml (15.2 g)</td>
<td>20 ml (15.4 g)</td>
</tr>
<tr>
<td>Pretreatment of catalyst</td>
<td>No reduction</td>
<td>No reduction</td>
<td>Reduced by manufacturer</td>
</tr>
<tr>
<td>Guard bed temperature ($T_{GB}$)</td>
<td>650°C</td>
<td>650°C</td>
<td>650°C</td>
</tr>
<tr>
<td>Steam reformer temperature ($T_{CR}$)</td>
<td>740 - 820°C</td>
<td>740 - 820°C</td>
<td>740 - 820°C</td>
</tr>
<tr>
<td>Space Velocity (SV)</td>
<td>1500 – 6000 h⁻¹</td>
<td>1500 – 6000 h⁻¹</td>
<td>1500 – 6000 h⁻¹</td>
</tr>
<tr>
<td>Operating time</td>
<td>12 hrs</td>
<td>18 hrs</td>
<td>18 hrs</td>
</tr>
</tbody>
</table>
Accomplishments/Progress
Gas Conditioning: Tar Cracking

• Typical heavy tar levels in producer gas: 10 - 20 g/m³
• All three metal catalysts proved effective
  – Greater than 99% destruction of heavy tar
  – Hydrogen increased by 6-11 vol-% (dry basis)
• Parametric effects:
  – Increasing space velocity had little effect
  – Increasing temperature boosted H₂ and reduced light hydrocarbons
• Results consistent with tar destruction controlled by chemical kinetics
• Catalysts showed evidence of increasing pore size, which could lead to deactivation
• Evidence of coking and sulfur accumulation on metal catalysts
Accomplishments/Progress
Gas Conditioning: Steam Reforming & Water Gas Shift

Operating Conditions of Tar Cracking System

<table>
<thead>
<tr>
<th>Items</th>
<th>GB</th>
<th>TR</th>
<th>HTS</th>
<th>LTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp. of Central cat. Bed °C</td>
<td>650</td>
<td>800</td>
<td>400</td>
<td>200</td>
</tr>
<tr>
<td>SV(h⁻¹)</td>
<td></td>
<td>3000</td>
<td>1500</td>
<td>1200</td>
</tr>
<tr>
<td>Catalyst</td>
<td>Calcined dolomite</td>
<td>ICI 46-1</td>
<td>Fr-Cr based LB</td>
<td>Cu-Zn-Al based B202</td>
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<tr>
<td>Catalyst volume (ml)</td>
<td>200</td>
<td>60</td>
<td>120</td>
<td>150</td>
</tr>
<tr>
<td>Inert material (ml)</td>
<td>0/20</td>
<td>20/20</td>
<td>20/50</td>
<td>25/50</td>
</tr>
<tr>
<td>Gas Composition (%-vol)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂</td>
<td>8.5</td>
<td>19.44</td>
<td>23.7</td>
<td>27.1</td>
</tr>
<tr>
<td>CO</td>
<td>14.5</td>
<td>8.9</td>
<td>1.37</td>
<td>0.18</td>
</tr>
<tr>
<td>CO₂</td>
<td>18.1</td>
<td>20.1</td>
<td>26.8</td>
<td>27.2</td>
</tr>
<tr>
<td>CH₄</td>
<td>4.3</td>
<td>3.5</td>
<td>3.4</td>
<td>3.1</td>
</tr>
<tr>
<td>C₂H₄</td>
<td>1.5</td>
<td>0.27</td>
<td>0.31</td>
<td>0.13</td>
</tr>
<tr>
<td>Tar content (g/Nm³)</td>
<td>19.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

*Volume of inert material above and below catalyst layer respectively
Accomplishments/Progress
Gas Conditioning: Steam Reforming & Water Gas Shift

Air-blown gasification of switchgrass (ballast system not operated)

<table>
<thead>
<tr>
<th>Gas constituent</th>
<th>Raw gas</th>
<th>Steam reformer*</th>
<th>High temperature shift reactor*</th>
<th>Low temperature shift reactor*</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂ (vol-%)</td>
<td>8.5</td>
<td>19.4</td>
<td>23.7</td>
<td>27.1</td>
</tr>
<tr>
<td>CO (vol-%)</td>
<td>14.5</td>
<td>8.9</td>
<td>1.4</td>
<td>0.18</td>
</tr>
<tr>
<td>CO₂ (vol-%)</td>
<td>18.1</td>
<td>20.1</td>
<td>26.8</td>
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<td>4.3</td>
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<td>3.1</td>
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</table>

*Concentration exiting the reactor
Accomplishments/Progress
Trace Gas Sampling

H\textsubscript{2}S Measured from Gasification of Waste Seed Corn

- H\textsubscript{2}S levels (Drager tubes) were consistently 190-220 ppm over a 5-hr period
- H\textsubscript{2}S concentrations were 50-70\% lower than what would be expected if ALL the sulfur remained in the gas phase
- Limestone added to the fluidized bed reactor to suppress agglomeration is the likely reason for sulfur retention
Accomplishments/Progress
Trace Gas Sampling

NH₃ Measured from Gasification of Waste Seed Corn

• NH₃ levels were about 5000 ppm; results from duplicate sample runs were within 3% of one another

• Injection of NH₃ into producer gas yielded gas stream measurements within 5% of expected values
Accomplishments/Progress
Separation Technology

- Identification of a combined water-gas shift/CO₂ removal system
- Builds upon engineered materials developed at ISU
  - Core-in-shell concept developed for gas sorption
  - Nickel catalyst in shell to promote steam reforming of methane
- This new task will explore copper and iron catalysts in shell for water-gas shift reactions

\[
\text{CaO} + \text{CO}_2 \rightarrow \text{CaCO}_3
\]
Accomplishments/Progress
Thermal System Analysis

- Computer simulation of ballasted reactor during cooling with steam
- Phase change material plays significant role in increasing time to cool the reactor
Accomplishments/Progress
Thermal System Analysis

- Experimental data for pyrolysis phase of cycle
  - H$_2$ and CO$_2$ decrease, CO increases
  - Micro-GC data consistent with the CEM data
Interactions & Collaborations

• Energy Products of Idaho
  – Licensing technology on moving bed granular filter for control of particulate matter

• Community Power Corporation
  – Investigating use of moving bed granular filter for multi-contaminant control

• University of Victoria, University of British Columbia & National Renewable Energy Center
  – Coauthored paper on hydrogen from biomass (under review by the Int. J. Hydrogen Energy)

• Zhengzhou University, China
  – Visiting scientist working on gas conditioning catalysts
Future Plans

• Testing of multi-contaminant control system (limestone injection upstream of moving bed granular filter)
• Evaluating combined water-gas shift/CO$_2$ sorption concept
• Operate ballast system with gas conditioning system
Responses to FY 02 Panelist

<table>
<thead>
<tr>
<th>Reviewer Comment</th>
<th>Investigator’s Response</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gasification of switchgrass is not economical…</td>
<td>The ultimate advantage of hydrogen energy is replacement of polluting fossil fuels. Thus, biomass is the ultimate fuel even if not cost-effective by current economic measures.</td>
</tr>
<tr>
<td>Project is heavy on analytical methods and light on technical results…</td>
<td>The first year of the project was devoted to building equipment and establishing analytical methods. Significant data was collected on all phases of the project during the second year.</td>
</tr>
</tbody>
</table>
Acknowledgements

• Collaborators in this study include Jerod Smeenk, Andy Suby, Glenn Norton, Ruiqin Zhang, Ming Xu, Nate Brown, and Colin Brue

• This work was performed at the Iowa Energy Center’s BECON facility

• This work was funded by the U.S. Department of Energy’s Hydrogen Energy Program with cost-sharing from the Iowa Energy Center and Iowa State University