

## II.D.1 Indirectly Heated Gasification of Biomass to Produce Hydrogen

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will be used in an updated ASPEN material and energy balance simulation of an integrated biomass to hydrogen process. Yield and capital/operating cost estimates resulting from the simulation will be used to update the H2A model for the process. This project will address the following DOE technical targets outlined in Table 3.1.8 of the HFC&IT Multi-Year RD&D Plan:

Technical Targets: Biomass Gasification/Pyrolysis Hydrogen Production

Characteristics	2012 Target \$2005	2017 Target \$2005
Hydrogen Cost (Plant Gate)	\$1.60	\$1.10
Total Capital Investment	\$150M	\$110M
Energy Efficiency (LHV)	43%	60%

LHV - lower heating value

### Objectives

Verify the technical and economic performance of an integrated biomass steam gasification-based hydrogen production process that includes steam gasification, tar and light hydrocarbon reforming, hydrogen sulfide removal, shift reaction, and hydrogen separation.

- Parametric gasification of two biomass feedstocks
- Gas cleanliness verification with slip stream hydrogen sulfide removal and high temperature shift
- Update of gas yield correlations
- Update of ASPEN process simulation model
- Update of H2A techno-economic model

### Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section (3.1.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies (HFC&IT) Program Multi-Year Research, Development and Demonstration (RD&D) Plan:

- (T) Capital Cost and Efficiency of Biomass Gasification/Pyrolysis Technology
- Indirect steam gasification efficiency
  - Capital cost
  - Tar/light hydrocarbon reforming

### Technical Targets

This project is directed at the verification of the technical and economic performance of a hydrogen production process using integrated biomass steam gasification. The project will experimentally develop gasification data that will be used to develop updated gasifier yield and quality estimates. These estimates

### Accomplishments

- Completed parametric steam gasification testing and data reduction/analysis for oak feed.
  - Three temperatures: 750°, 850°, 950°C
  - Three steam/biomass ratios: 0.75, 1.25, 2
- Completed multivariate analysis and updated gasifier yield correlations
- Transferred gasifier correlations to ASPEN



### Introduction

Through the auspices of the DOE Hydrogen Program and based on DOE supported gasification research [1] NREL has developed gasifier yield correlations for indirectly heated steam gasification of biomass. These results have been used by NREL [2] and others [3] to indicate the feasibility of producing hydrogen and other fuels from biomass. These studies have also shown the benefits of catalytically converting high-molecular weight contaminants (tars) and light hydrocarbons (e.g., methane, ethane) in one unit operation. These early efforts were used by NREL to develop detailed ASPEN models and associated economic models [4] that in turn were used to provide yield, capital cost, and operating cost data for use in H2A. These models and analyses indicate that hydrogen production from biomass may be a viable alternative. Costs developed in the techno-economic modeling effort have resulted in estimated hydrogen costs of \$1.77/kg (current) and \$1.47/kg (advanced in 2015). While these estimates are encouraging, they are based on

non-integrated pilot scale data generated by Battelle Columbus Laboratories in the 1980s. To give additional credibility to the estimates, additional testing is required. This project is providing:

- Experimental data needed to confirm gasification yields and gas compositions
- Data on contaminants and effectiveness of removal
- Updated H<sub>2</sub>A analysis for Program evaluation

## Approach

The NREL 150 kWt (maximum of 30 kg/h biomass throughput) thermochemical pilot development unit (TCPDU) is being operated to investigate integrated gasification-hydrogen production to: A) generate a raw syngas that is cleaned using a two-stage gasifier (fluid bed and entrained flow thermal cracker), cyclones for particulate matter and an organic quench for tars, water and ammonia; B) produce a clean sulfur-free syngas on a syngas slipstream using a zinc oxide bed; and C) demonstrate production of a hydrogen-rich syngas in a micro-scale pressurized catalytic reactor system. A molecular beam mass-spectrometer system is used to quantify benzene and tars in the syngas before and after the quench. Permanent gases and sulfur compounds (H<sub>2</sub>S and COS) are quantified using gas chromatography and non-dispersive infrared analyses. In combination with experimental material balances, updated correlations of gas yield and quality are developed and new ASPEN simulations performed. Economic analyses using H<sub>2</sub>A protocols are used to compare results with published information. A process design will be completed and equipment ordered for a two-stage shift system and hydrogen separation. Operation of the shift/membrane train will provide the Program with actual integrated operation data to support simulation results.

## Results

The project is divided into four tasks: 1) experimental testing, 2) development of gasifier correlations, 3) updating of ASPEN model and incorporation into a H<sub>2</sub>A model, and 4) design, costing, and possible evaluation of a hydrogen separation unit. The results section discusses these four tasks.

### Task1: Experimental Testing

The TCPDU is a 30 kg/h pilot unit (see Figure 1) which is used for gasification and pyrolysis experimentation. The system configuration for this project is a two-stage gasifier where the first stage is an electrically-heated fluid-bed reactor and the second stage is an entrained flow reactor. After the gasifier, two cyclones remove particulate matter. Other contaminants—benzene, tars, water, and ammonia—are removed in a liquid spray quench system. A zinc oxide

bed is used to remove H<sub>2</sub>S from a slip stream of the clean gas. The sulfur-free gas is used as feed to a slip-stream catalytic reactor system capable of operation in either fixed-bed or stirred-tank mode at pressures up to 13.9 MPa and temperatures up to 650°C. In the catalytic reactor system a high-temperature shift catalyst is used to demonstrate the cleanliness of the syngas and to demonstrate the first stage of a shift/pressure swing adsorption operation. Typical conditions are 2.75 MPa and 385±25°C. Two feeds have been selected for evaluation; a hard wood (oak) and a soft wood (pine).

A parametric gasification campaign was completed using oak as the feedstock. The parametric gasification tests were performed looking at steam/biomass ratio (0.75, 1.25, and 2.0) and entrained-flow reactor temperature (750°, 850°, and 950°C). Material balances were developed based on molecular beam mass spectrometer, gas chromatograph, and nondispersive infrared analyses. A representative plot of major gas components for a steam/biomass ratio of 2 is given in Figure 2 and hydrogen to carbon monoxide ratio is given in Figure 3.

### Task 2: Gasifier Correlations

The gasifier data generated in this project for oak (plus gasifier data developed previously for the DOE Biomass Program for corn stover, Vermont mixed wood, and wheat straw) were used to develop new empirical correlations for indirect steam gasification. Because of a lack of residence time and char data, the yield data from the Battelle pilot testing were not included. The earlier parametric studies consisted of 23 statistically designed experimental conditions for the purpose of examining the effects of process variables on the product gas composition (dry gas composition, tar rates, char production rate, etc.). The following process variables were adjusted in the experiments:



FIGURE 1. NREL Thermochemical Pilot Development Unit

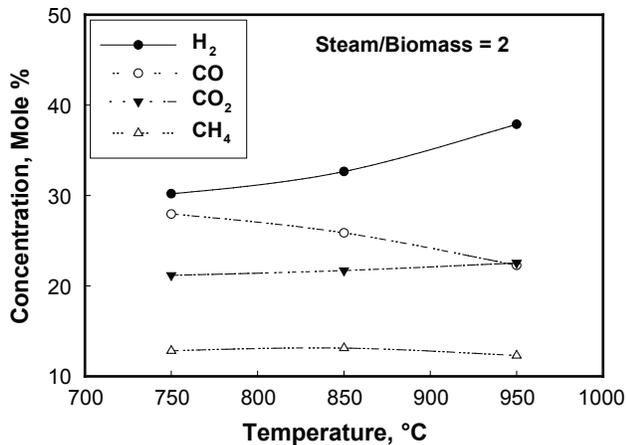


FIGURE 2. Representative Gas Concentrations, Indirect Gasification of Oak

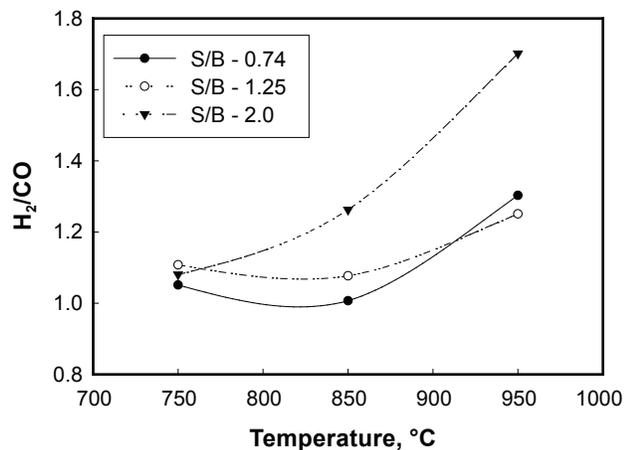


FIGURE 3. Hydrogen/Carbon Monoxide Ratio, Indirect Gasification of Oak

- Feedstock: wheat straw, Vermont wood, and corn stover
- Fluid bed temperature: 600°, 650°, and 710°C
- Secondary thermal cracker temperature: 600°, 650°, 750°, and 875°C
- Steam to biomass ratio: 1, 0.5, and 0.33

The effects of the adjusted process variables were measured in the following product rates and compositions: nitrogen flow rate, gas composition (hydrogen, carbon dioxide, carbon monoxide, methane, C2-C5 hydrocarbons, carbonyl sulfide, and hydrogen sulfide), benzene, toluene, phenol, cresols, naphthalene, phenanthrene, total tars, and char. The TCPDU data were subjected to a regression analysis using Unscrambler statistical software. The significance of several process variables was first tested. The process variables considered were:

- Proximate analysis
- Ultimate analysis

- Ash composition (base ratio, dolomite ratio, calcium content)
- Fluid bed temperature
- Secondary thermal cracker temperature
- Steam to biomass ratio
- Residence time

In addition to the process variables listed above, interactions between most of the process variables as well as squared effects of the processes variables were also tested for significance. All of the process variables were determined to be significant for at least a few of the output variables, and none were determined to significantly affect all output variables although several process variables were found to be significant more often than others. The process variables that were most often significant, as well as generally the most significant in terms of the highest degree of significance were:

- Ultimate analysis (carbon, hydrogen, nitrogen, sulfur, oxygen)
- Thermal cracker temperature
- Steam to biomass ratio
- Residence time
- Interactions between thermal cracker temperature, steam to biomass ratio, and residence time
- Squared effects of thermal cracker temperature, steam to biomass ratio, and residence time

The significance testing resulted in 14 significant process variables: five ultimate analysis terms, thermal cracker temperature, steam-to-biomass ratio, residence time, three interactions terms, and three squared terms. After significant effects were determined, a separate regression analysis was run in Unscrambler for each of the output variables (product rates and compositions). The results of the regression analyses were a set of equations that predict the product rates and compositions as a function of the input process variables. Coefficients of determination ( $R^2$ ) for product composition are given in Table 1.

### Task 3: Updating of ASPEN model and Incorporation into H2A

The regression equations have been translated into ASPEN and the ASPEN model is being modified to optimize convergence criteria.

### Task 4: Design, Cost, and Evaluation of Hydrogen Separation System

This task has not started because data have not been collected on gas composition exiting the slip-stream shift reactor system.

**TABLE 1.** Coefficients of Determination, Indirect Biomass Gasification

Component	Units	New R <sup>2</sup>	BCL R <sup>2</sup>
1-Butene	mole %	0.880	
2-c-Butene	mole %	0.712	
2-t-Butene	mole %	0.713	
Carbon Dioxide	mole %	0.812	0.417
Carbon Monoxide	mole %	0.730	0.397
Ethane	mole %	0.716	0.852
Ethene, Ethylene	mole %	0.958	0.876
Ethyne, Acetylene	mole %	0.964	0.717
Helium	mole %	0.846	
Hydrogen	mole %	0.807	0.918
Methane	mole %	0.846	0.693
Propane	mole %	0.901	
Propene	mole %	0.954	
Carbonyl Sulfide	ppmv/lb dry wood	0.497	
Hydrogen Sulfide	ppmv/lb dry wood	0.850	
benzene	lb/lb dry wood	0.971	
toluene	lb/lb dry wood	0.833	
phenol	lb/lb dry wood	0.932	
cresols	lb/lb dry wood	0.942	
naphthalene	lb/lb dry wood	0.978	
phenanthrene	lb/lb dry wood	0.976	
"other tar"	lb/lb dry wood	0.939	
"heavy tar"	lb/lb dry wood	0.549	
total (>78)	lb/lb dry wood	0.767	0.999
Char	lb/lb dry wood	0.740	0.655

## Conclusions and Future Directions

- A parametric gasification test campaign was completed using the NREL 150 kWt TCPDU, investigating the effects of temperature and steam to biomass ratio on yields and gas composition. During the test a new feed (oak) and temperature range (up to 950°C) was used.
- The data from the oak test campaign, plus data generated by NREL for the DOE Biomass Program for wheat straw, Vermont mixed wood, and corn stover were analyzed by multivariate analysis using Unscrambler. Fourteen variables were determined to be significant, including feed ultimate analysis, thermal cracker temperature, steam-to-biomass ratio, and residence time.
- The results of the regression analysis were incorporated into an existing ASPEN simulation.
- A second parametric gasification test campaign will be completed using another new feed (pine). During this test campaign a slip stream with sulfur removal and high temperature shift will be evaluated. Both the sulfur getter and shift catalysts are proprietary commercial formulations.

- The gas compositions from the shift reactor will be used to evaluate options for hydrogen separation, and a system will be designed and costed. A decision will be made on proceeding with purchase of a hydrogen separation system.
- The results of the second parametric test will be used to further update the regression results and the ASPEN simulation. ASPEN Icarus Process Evaluator will be used to update capital and operating costs. These data will be used in H2A to determine updated costs.

## FY 2008 Publications/Presentations

1. Bain, R. L. "Hydrogen Program First Quarter, FY08 Report; Project 3.13: Gasification of Biomass to Produce Hydrogen, January 2008.
2. Bain, R. L. "Hydrogen Program Second Quarter, FY08, Report; Project 3.13: Gasification of Biomass to Produce Hydrogen, January 2008.
3. Bain, R. L. "Indirectly Heated Biomass Gasification," HFCIT Merit Review Presentation PD29, <http://www.hydrogen.energy.gov/>, June 12, 2008.

## References

1. Feldman, H.F.; Paisley, M.A.; Applebaum, H.R.; Taylor, D.R. *Conversion of Forest Residues to a Methane-Rich Gas in a High-Throughput Gasifier*. PNL-6570/DE88-013138. City, State: Work Performed by Battelle Columbus Laboratory, Columbus, OH. Richland, WA: Pacific Northwest Laboratory, May 1988.
2. Wyman, C.E.; Bain, R.L.; Hinman, N.D.; Stevens, D.J. "Ethanol and Methanol from Cellulosic Materials," Chapter 21. ed. TB Johansson, et al. *Renewable Energy: Sources for Fuels and Electricity*, Washington, DC. Island Press, 1993.
3. Hamelinck, C.N.; Faaij, A.P.C. *Future Prospects for production of methanol and hydrogen from Biomass.*, NMS-E-2001-49. Utrecht, the Netherlands: Utrecht University, September 2001.
4. Spath, P.; Aden, A.; Eggeman, T.; Ringer, M.; Wallace, B.; Jechura, J. *Biomass to Hydrogen Production Detailed Design and economics Utilizing the Battelle Columbus Laboratory Indirectly-Heated Gasifier*. NREL/TP-510-37408. Golden, CO: National Renewable Energy Laboratory, May 2005.