

II.B.1 Indirectly Heated Gasification of Biomass to Produce Hydrogen

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

Technical Targets: Biomass Gasification/Pyrolysis Hydrogen Production

Characteristics	2012 Target	2017 Target
Hydrogen Cost (Plant Gate) (\$2005)	\$1.60	\$1.10
Total Capital Investment (\$2005)	\$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 Production section (3.1.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies (HFCIT) Program Multi-Year Research, Development and Demonstration (RD&D) Plan:

- (T) Capital Cost and Efficiency of Biomass Gasification/Pyrolysis Technology
 - t. Indirect steam gasification efficiency
 - u. Capital cost
 - v. 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 experimentally developed gasification data that were used to develop updated gasifier yield and quality estimates. These estimates were

Accomplishments

- Completed parametric steam gasification testing and data reduction and analysis for pine feed:
 - Three temperatures: 750°C, 850°C, 950°C
 - Three steam/biomass ratios: 0.75, 1.25, 2
- Completed multivariate analysis and updated gasifier yield correlations.
- Transferred gasifier correlations to ASPEN.
- Updated the existing H2A model.



Introduction

Through the auspices of DOE's HFCIT Program and based on DOE supported gasification research [1], NREL developed gasifier yield correlations for indirectly heated steam gasification of biomass. These results were used by NREL [2] and others [3] to indicate the feasibility of producing hydrogen and other fuels from biomass. These studies also showed 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 production pathway. Costs developed in the techno-economic modeling effort resulted in estimated hydrogen costs of \$1.77/kg (current) and \$1.52/kg (advanced in 2015).

While these estimates are encouraging, they are based on non-integrated pilot scale data generated by Battelle Columbus Laboratories (BCL) in the 1980s. To give additional credibility to the estimates, additional independent verification testing was required. This project provided:

- Experimental data needed to update gasification yields and gas compositions using the NREL pilot development gasification system.
- Data on contaminants and effectiveness of removal.
- Updated H2A analysis for Program evaluation.

Approach

The NREL 150 kWt (maximum of 30 kg/h biomass throughput) thermochemical pilot development unit (TCPDU), Figure 1, was operated to investigate integrated gasification-hydrogen production to generate a raw syngas using a two-stage gasifier (fluid bed and entrained flow thermal cracker), which is cleaned a) using cyclones for particulate matter and an organic quench for tars, water and ammonia; and b) using cyclones, a fluid bed tar reformer, and an organic quench. During operations with the tar reformer, production of a hydrogen-rich syngas in a

micro-scale pressurized catalytic reactor system under high temperature shift conditions was also evaluated. A molecular beam mass-spectrometer system was used to quantify benzene and tars in the syngas before and after the quench. Permanent gases and sulfur compounds (H_2S and COS) were quantified using gas chromatography and non-dispersive infrared analyses. In combination with experimental material balances, updated correlations of gas yield and quality were developed and new ASPEN simulations performed. Economic analyses using H2A protocols were used to compare results with published information.

Results

The project is divided into three tasks: 1) experimental testing, 2) development of gasifier correlations, and 3) updating of ASPEN model and incorporation into an H2A model. The results section discusses these three tasks.

Task 1: Experimental Testing

In general, a higher steam-to-biomass ratio and a higher thermal cracker temperature yielded a higher hydrogen concentration. The hydrogen concentration

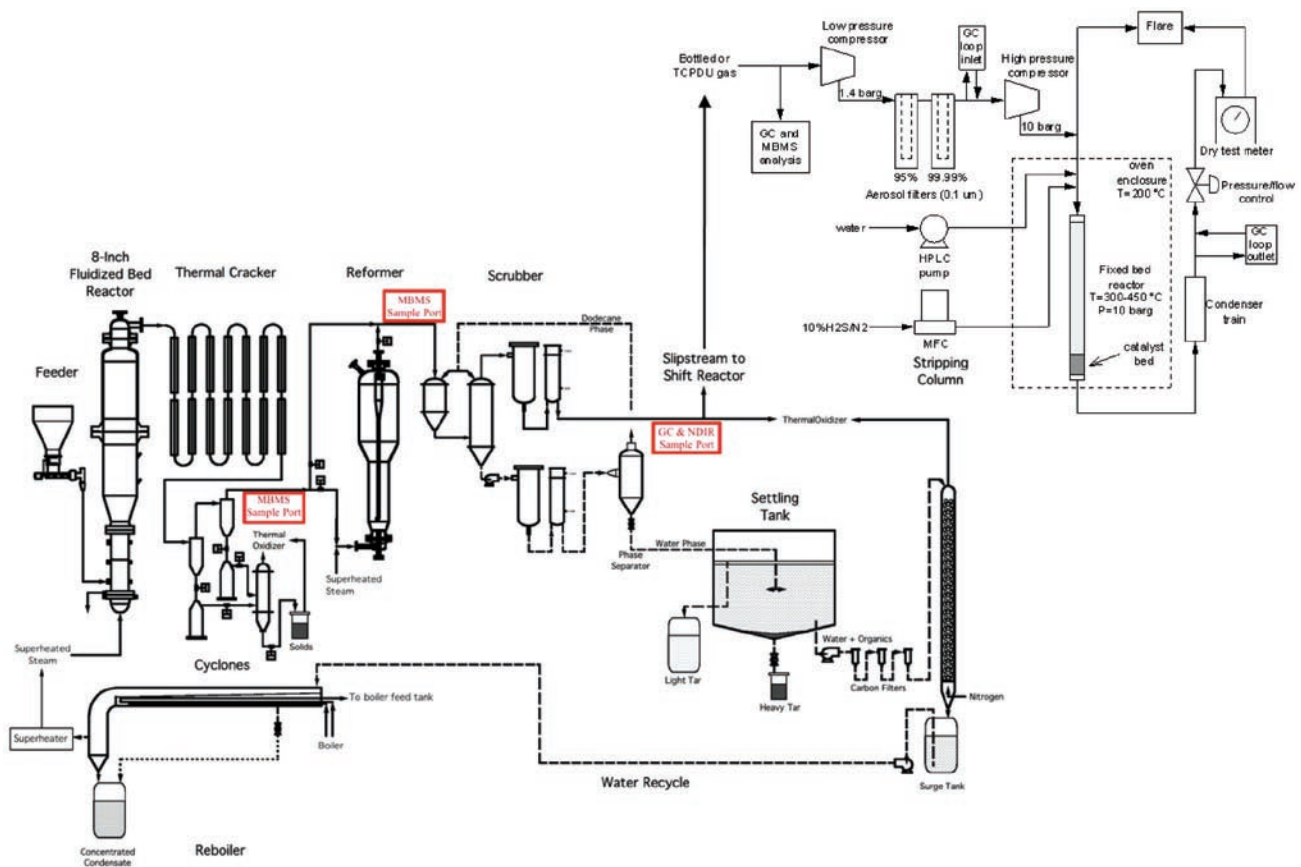


FIGURE 1. NREL Thermochemical Pilot Development Unit

ranged from 26–39% vol (dry, N₂-free) for oak and 35–42% vol for pine gasification. The carbon monoxide concentration ranged from 18–31% vol for oak and 15–23% vol for pine. The H₂/CO ratio for oak varied between 0.9 and 2.1 with an average of 1.2. The H₂/CO ratio for pine varied between 1.5 and 2.7 with an average of 2.0. Overall mass closures of 88–100% during the parametric oak gasification studies and 86–100% during the pine gasification studies were achieved. Qualitative tar measurements were very similar between the two feedstocks.

Shift catalyst tests were first performed using bottled gases with an H₂:CO ratio of 4.2, which is representative of the syngas produced in the TCPDU when the tar reformer is online. A CO conversion of 74% was obtained using a shift reaction temperature of 450°C (842°F), steam-to-H₂ ratio of 5.0, and a gas hourly space velocity of 21,000 h⁻¹. The H₂:CO ratio increased from 4.2 at the inlet to 17 at the outlet. The TCPDU was then used to generate pine-derived syngas at a steam-to-biomass ratio of 2.0 and a thermal cracker temperature of 850°C. Using the same shift reactor conditions as in the bottled gas test, the CO conversion using pine-derived syngas was initially 68%. After 6 hours, the CO conversion decreased to 65%. The H₂:CO ratio increased from 4.2 at the inlet to 14 at the outlet. The change in H₂:CO ratio is shown graphically in Figure 2.

Task 2: Gasifier Correlations

The NREL gasification tests examined the effects of several process variables on the gasifier product yields and compositions (e.g., char production rate, tar rates,

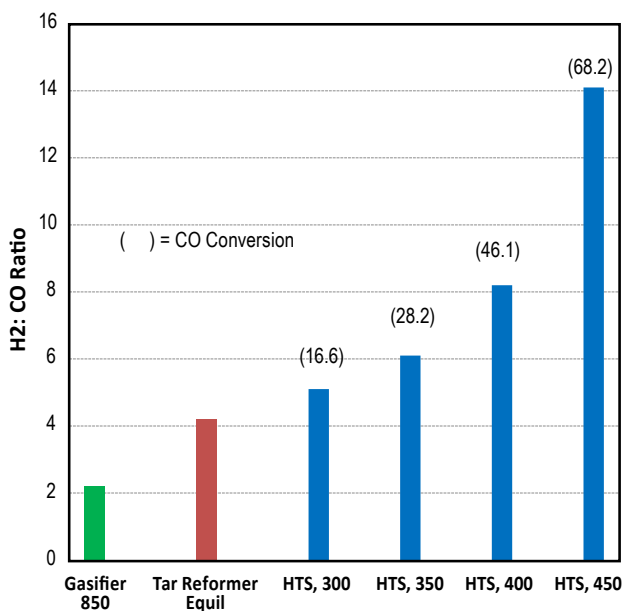


FIGURE 2. H₂:CO Ratios During High Temperature Shift Experiments, Gasification of Pine

and dry gas composition) using oak and pine, plus separate data for wheat straw, Vermont wood, and corn stover.

The data collected during the NREL gasification tests were subjected to a regression analysis using Unscrambler statistical software. The significance of several process variables was first tested. The process variables considered were: 1) proximate analysis, 2) ultimate analysis, 3) ash composition (base ratio, dolomite ratio, Ca content), 4) fluid bed temperature, 5) secondary entrained-flow thermal cracker temperature, 6) steam-to-biomass ratio, and 7) residence time.

The significance testing resulted in 18 significant process variables: five ultimate analysis terms (5), four proximate analysis terms (9), gasification temperature (10), steam to biomass ratio (11), residence time (12), three interactions terms (15), and three squared terms (18). Each output variable was modeled by an equation of the form:

$$Y = a + \sum(b \cdot X + c \cdot X^2), \text{ where}$$

Y = Component Value, [=] mole %, kg/kg feed, or mg/Nm³;
X = Independent Variable

Task 3: Updating of ASPEN Model and Incorporation into H2A

In the model, wood is gasified using an indirectly-heated, entrained-flow gasifier. Indirect heat is supplied by adding hot olivine to the gasifier. After gasification, olivine and char are separated from the syngas using cyclones. The char, mixed with olivine, is then combusted to add heat to the olivine, which is then re-circulated back to the gasifier. Steam is also added to the gasifier to aid in stabilizing the entrained flow of biomass and olivine. The syngas exiting the gasifier then passes through a catalytic tar reformer where hydrocarbons and tars are cracked and reformed with water to increase CO and H₂ yields. The syngas is then cleaned of CO₂ and H₂S. The cleaned syngas then passes through two shift reactors that increase the H₂ to CO ratio. Pressure swing absorption (PSA) is then used to separate hydrogen from the syngas.

The feedstock used for the model is hybrid poplar wood chips delivered at 50 wt% moisture. The capacity of the model is 2,000 bone dry tonnes/day. The model requires a small amount of natural gas, although more will probably be necessary for startup. The majority of steam and electricity necessary to operate the envisioned facility is produced by combusting byproducts.

The 2005 Biomass to Hydrogen Design Report [4] presents a techno-economic analysis for two design cases: a current design case and a goal design case. The current design case assumes tar conversion rates verified experimentally with no regeneration of the tar

reforming catalyst. The current design case also includes a steam-methane reformer, prior to the shift reactors, to convert methane and hydrocarbons to CO and H₂. However, the goal design case assumes higher (goal) tar conversion and includes a tar and methane reforming, catalyst regenerating reactor. As such, the goal design case does not include a steam-methane reformer because conversion of methane and hydrocarbons in the tar reformer is high enough that a steam-methane reformer is not justified.

The new correlations replace the old correlations in the Aspen Plus model presented in the Biomass to Hydrogen Design Report [4]. The new correlations predict a slightly different dry gas composition, although the most significant difference is less char. The new correlations predict 0.10 lb of char per lb of dry feed,

whereas the old correlations predict 0.22 lb of char; consequently, a portion of the raw syngas must be diverted to the char combustor to provide the heat necessary for gasification and drying the incoming biomass. The model predicts 2.6% more final hydrogen product when the new gasifier correlations are used (see Table 1).

HFCIT uses a separate economic evaluation spreadsheet, called H2A, available on the DOE H2A Analysis Web site.

The H2A analysis resulted in a hydrogen cost of \$1.56 per kg in 2005 dollars, using the new correlations, versus \$1.52 using the old correlations. The major process and cost data used in the H2A analysis are summarized in Table 2.

TABLE 1. Coefficients of Determination, BCL and NREL Gasifier Data

Component	New Correlation R ²	Old Correlation R ²	New Correlation R ² _{adj}
Hydrogen	0.81	0.92	0.77
Carbon Monoxide	0.64	0.40	0.59
Carbon Dioxide	0.77	0.42	0.73
Methane	0.81	0.70	0.77
Ethane	0.71	0.85	0.52
Ethylene	0.87	0.88	0.85
Acetylene	0.94	0.72	0.93
Propane	0.90		0.88
Propene	0.92		0.90
1-Butene	0.83		0.82
2-c-Butene	0.73		0.68
Hydrogen Sulfide	0.86		0.82
Benzene	0.93		0.92
Toluene	0.72		0.69
Phenol	0.91		0.89
Cresols	0.89		0.87
Naphthalene	0.92		0.89
Phenanthrene	0.85		0.82
Heavy Tar, MW > 180	0.68		0.65
Total Tar, MW > 78	0.82	0.89	0.79
Char	0.78	0.66	0.72
Nitrogen Free Dry Gas Yield	0.87	0.94	0.85

TABLE 2. Comparison of Existing and New H₂A Correlations

	BCL Gasifier	NREL Gasifier
Biomass Usage, kg dry biomass per kg H ₂	11.99	11.68
Electricity Usage, kWh per kg H ₂	1.48	0.95
Natural Gas Usage, Nm ³ per kg H ₂	0.38	0.63
Cooling Water Usage, gal per kg H ₂	2.37	2.46
Process Water Usage, gal per kg H ₂	1.60	2.23
Total Capital Costs, 2005 Dollars	\$155.3 million	\$156.0 million
Annual Fixed Operating Costs, 2005 Dollars	\$10.1 million	\$10.2 million
Annual Variable Operating Costs, 2005 Dollars	\$43.7 million	\$47.5 million
Selling Price, 2005 Dollars per kg H ₂	\$1.52	\$1.56

Conclusions and Future Direction

- 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 (pine) and temperature range (up to 950°C) were used.
- The data from the Fiscal Year 2008 oak test campaign and the 2009 pine 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. Eighteen variables were determined to be significant, including feed ultimate analysis, thermal cracker temperature, steam-to-biomass ratio, and residence time.
- Slip stream high temperature shift experiments were performed using TCPDU product gas. Carbon monoxide conversions comparable to reported results for commercial systems were obtained.
- The results of the regression analysis were incorporated into an existing ASPEN simulation. The simulation model was optimized and capital and operating costs updated.
- The ASPEN model yields, capital costs, and operating costs were used to update the existing H₂A model for a \$60/ton feed. The H₂A analysis resulted in a hydrogen cost of \$1.56 per kg in 2005 dollars, using the new correlations, versus \$1.52 using the old correlations. The conclusion reached was that although the NREL gasifier correlation gave different gas yield because of lower char yield, the integrated process heat requirements and

downstream unit operations (tar reformer, shift reactors, hydrogen separation) resulted in overall process yields and hydrogen costs, thus verifying the earlier results.

Additional modeling work is planned to be completed in Calendar Year 2009 evaluating the feasibility of using PSA tail gas to improve the performance of a sulfur getter that would be located before the tar reformer.

FY 2009 Publications/Presentations

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