Indirectly Heated Biomass Gasification

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June 12, 2008

PD 29

Overview

Timeline

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

Budget

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

Barriers

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

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

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).

DOE (2007). “Hydrogen, Fuel Cells & Infrastructure Program Multi-Year Research and Demonstration Program,” p 3.1-1.

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

Milestones

Month/Year	Milestone
Jun-08	Complete initial gasification and hydrogen production testing
Jun-08	Complete initial ASPEN modeling and H2A modeling
Sep-08	Complete parametric gasification/shift reaction testing for two biomass feeds
Sep-08	Complete ASPEN model update and revised H2A estimate

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
  - H_2S removal
  - High temperature shift
  - Membrane separation (option)

Process Modeling

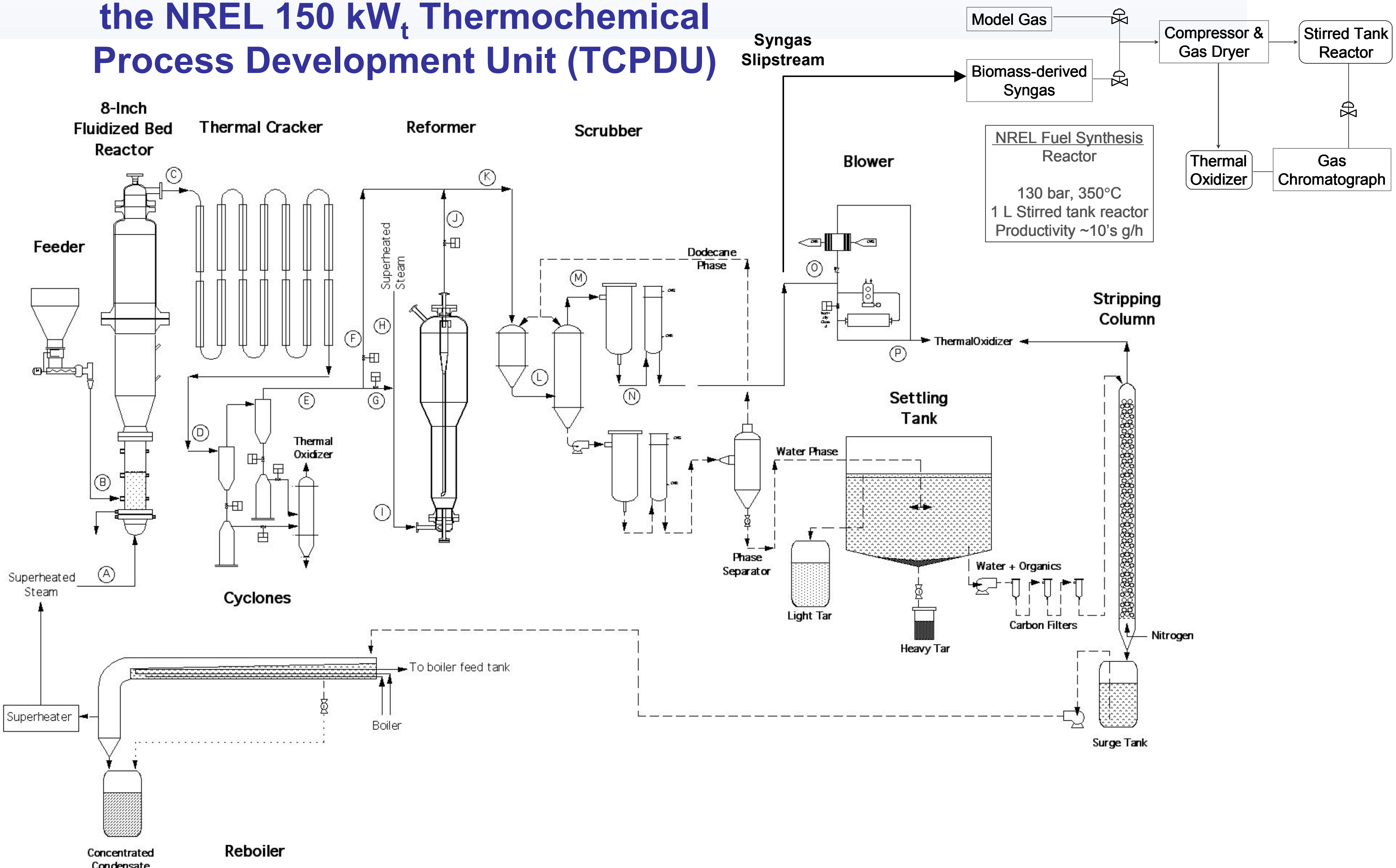
- Gasifier Correlation
  - Parametric data
  - Multivariate analysis (Unscrambler)
- ASPEN Analysis
  - ASPEN gasifier correlation FORTRAN block
  - ASPEN H2 integrated plant analysis
- EXCEL Summaries
- Comparison with 2005 Model

Economic Modeling

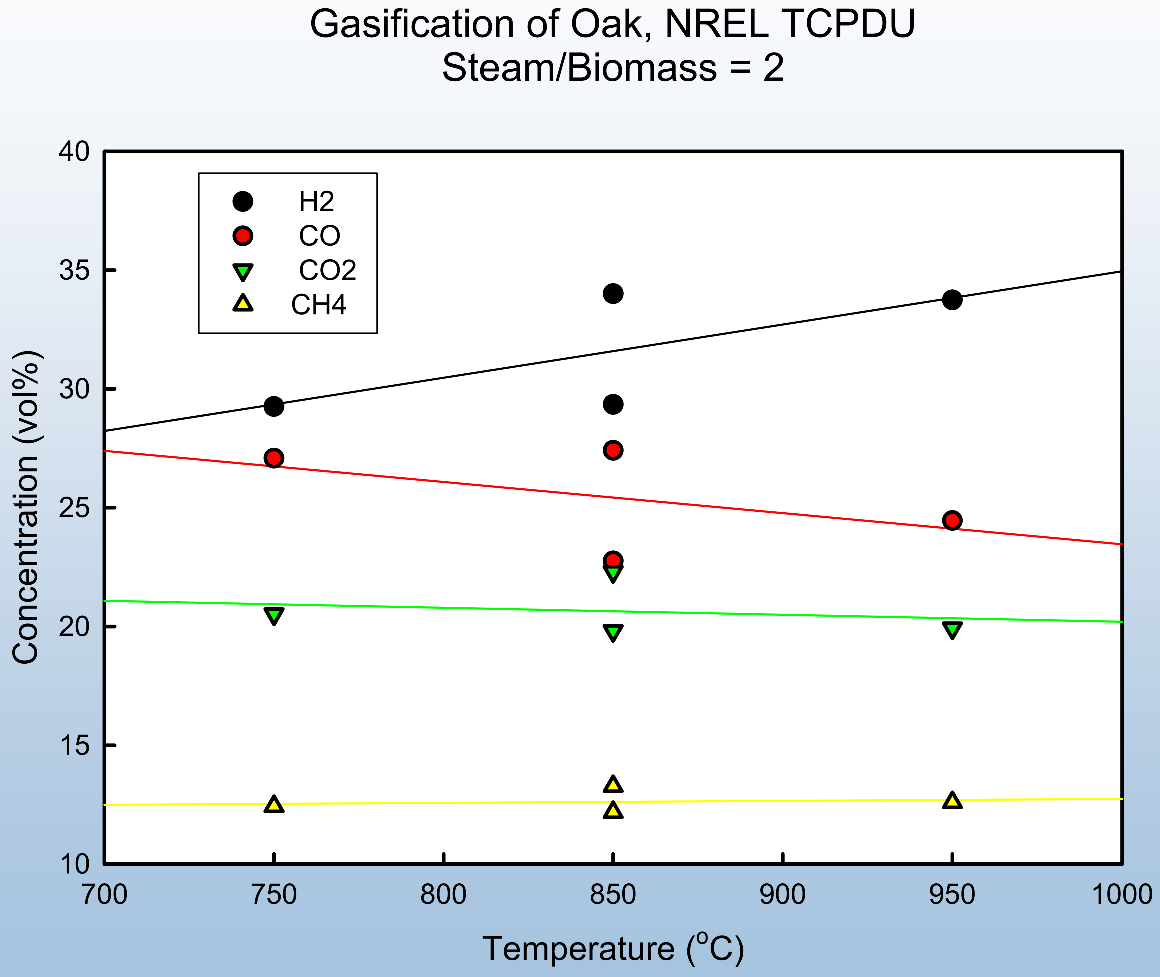
- Import of Process Modeling Results into H2A
- Comparison with Previous Results

Experimental System

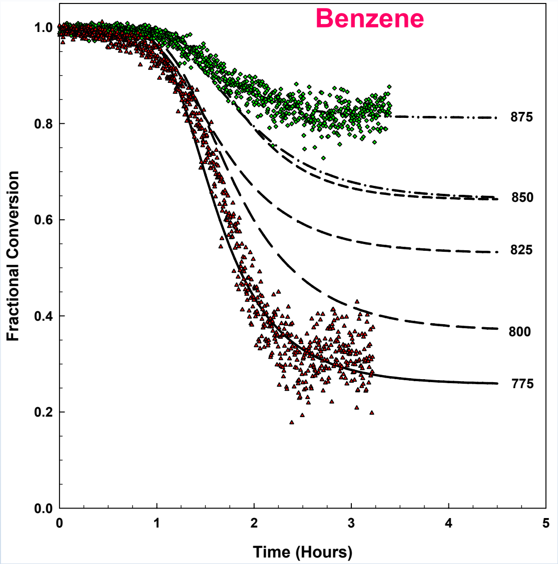
The gasification testing is being performed in the NREL 150 kW$_t$ Thermochemical Process Development Unit (TCPDU)



Typical Gasification Results



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

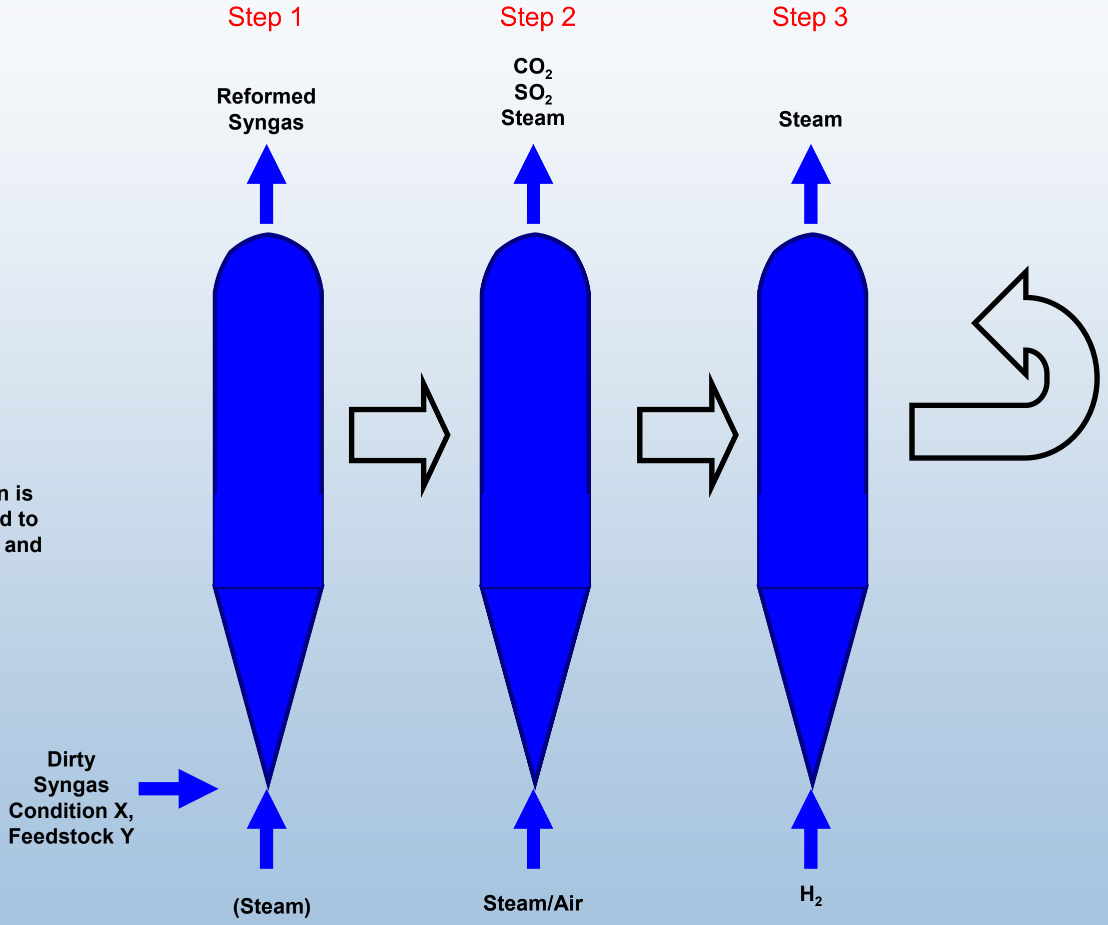
$$k\tau a = \ln\left[\frac{X_A}{1-X_A}\right]$$

1st order deactivation w residual activity

$$a = a_{s1} + (1-a_{s1})e^{-\psi^{*}_{d1}t}$$

……

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



Step 1

Reformed Syngas

Step 2

CO_2
SO_2
Steam

Step 3

Steam

Dirty Syngas Condition X, Feedstock Y

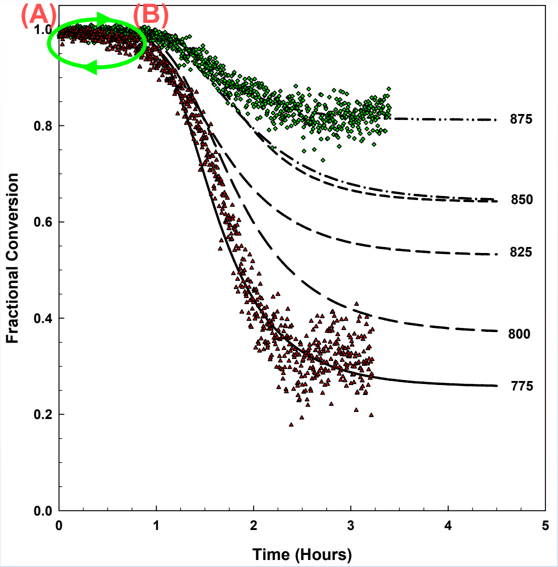
(Steam)

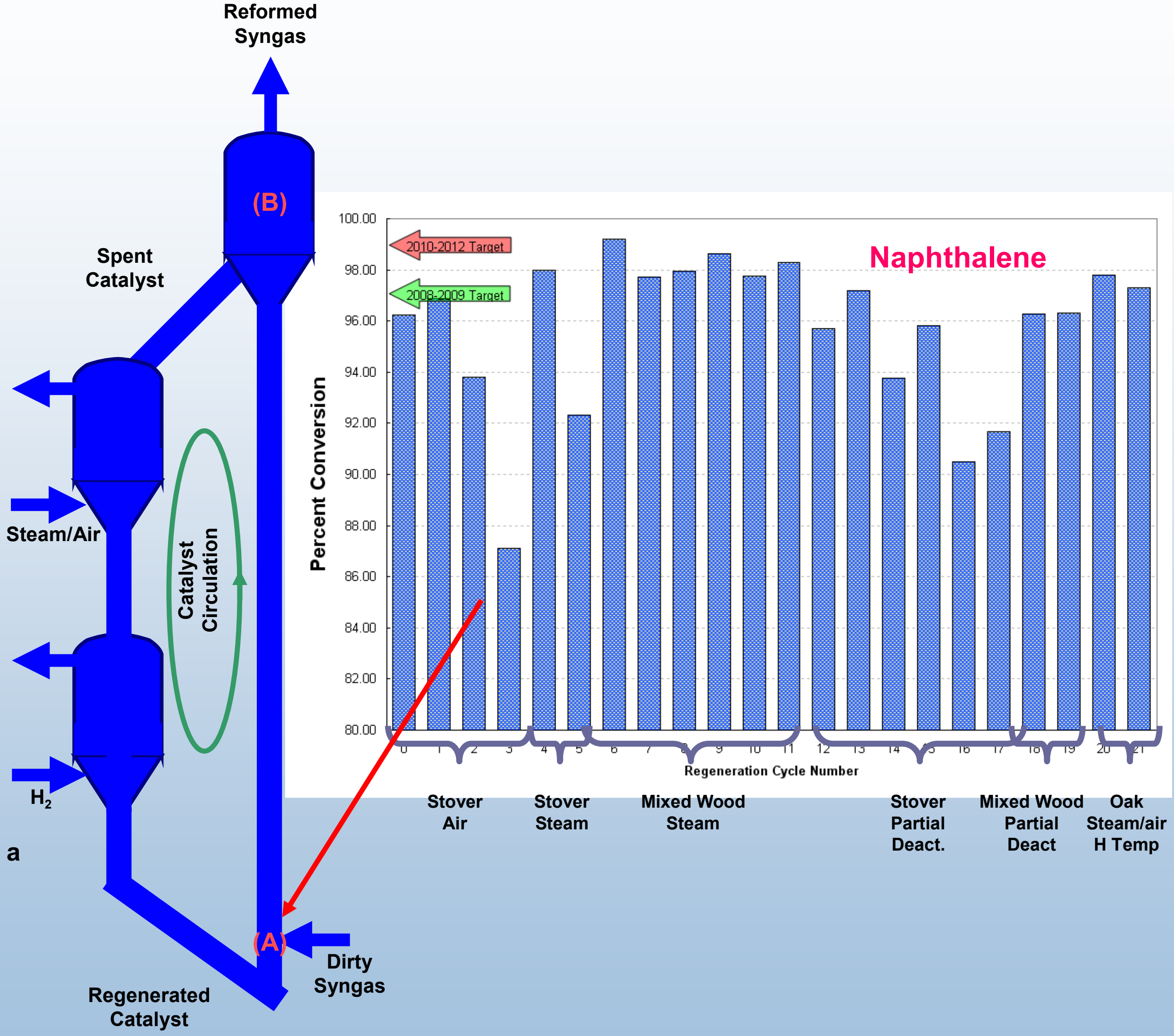
Steam/Air

H_2

Bain, R. L., D. C. Dayton, D. L. Carpenter, S. R. Czernik, C. J. Feik, R. J. French, K. A. Magrini-Bair and S. D. Phillips (2005). “An Evaluation of Catalyst Deactivation During Catalytic Steam Reforming of Biomass-Derived Syngas,” *I&ECR*, 44, p 7945-7956.

Tar Reforming Experiments





Tar /light hydrocarbon reforming is performed in a semi-batch fluid-bed reactor with multiple regenerations of a nickel/alkali catalyst

Gasifier / Reformer Performance

Oak Gasification: NREL TCPDU, Nov-Dec 2007

Run Order:	4	5	13	14
Run Code:	97095	InDe1	97095b	InDe2
	OK_HY_97095	OK_NREL32b_InDe1	OK_HY_97095b	OK_NREL32b_InDe2
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	
N2	0.00	0.00	0.00	
He (tracer)	1.86	1.07	1.69	
C2H6	0.00	0.00	0.00	
C2H4	2.12	0.17	1.66	
C2H2	0.01	0.00	0.03	
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	0.02	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)	reformer in	reformer out (initial)	reformer in	reformer o
benzene	7785	280	6874	
toluene	393	0	326	
phenol	46	29	39	
cresols	0	0	0	
naphthalene	2383	42	1834	
phenanthrene	792	0	535	
"other tar" (as 128)	2157	0	1691	0
"heavy tar" (as 178)	1417	0	824	0
"total tar" (minus 78)	7188	72	5250	52

		initial conv.*			sample time (min)
	InDe#	methane	benzene	naphthalene	methane
OK_NREL32b	1	50.3%	95.4%	97.8%	9
11/07-12/07	2	56.0%	95.6%	97.3%	8
S:B=2					
R500=700					
TC=950					
R600=900					

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
  - Bain, R.L. (1992). " Material and energy balances for methanol from biomass using biomass gasifiers," 136 pp, NREL Report No. TP-510-17098.
- 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 (H_2).
- Data are analyzed and regression analysis conducted using Unscrambler software.

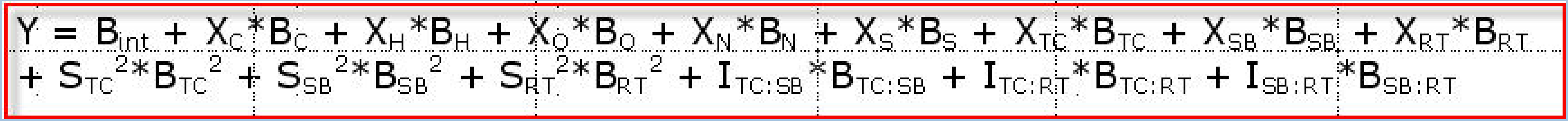
New Correlation: Significant Variables

- 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
  - TC^2
  - SB^2
  - RT^2

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



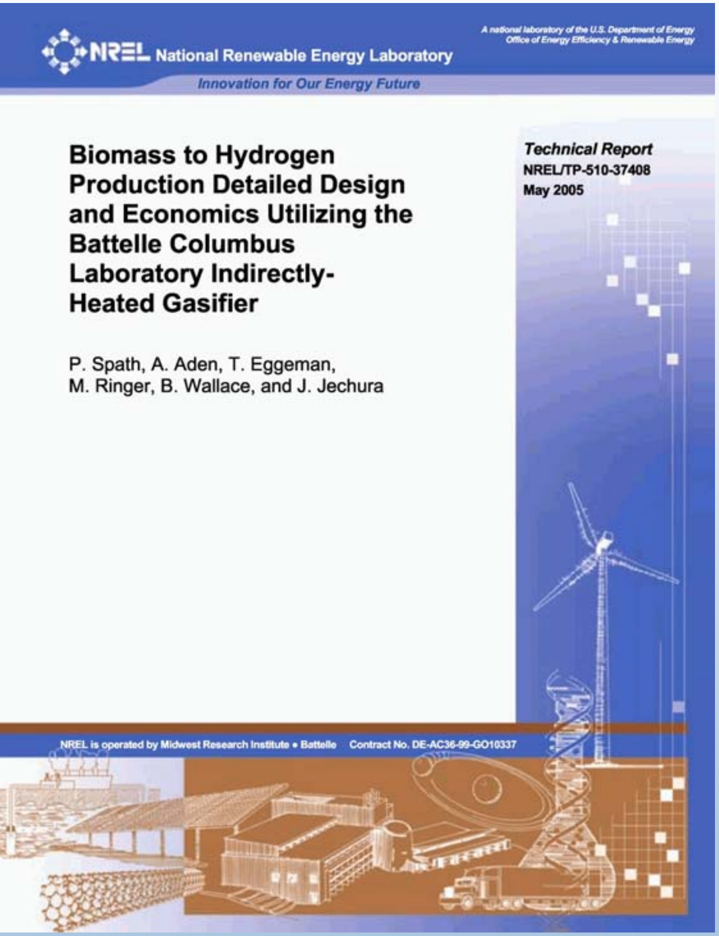
$$Y = B_{int} + X_C{*}B_C + X_H{*}B_H + X_O{*}B_O + X_N{*}B_N + X_S{*}B_S + X_{TC}{*}B_{TC} + X_{SB}{*}B_{SB} + X_{RT}{*}B_{RT} + S_{TC}{}^2{*}B_{TC}{}^2 + S_{SB}{}^2{*}B_{SB}{}^2 + S_{RT}{}^2{*}B_{RT}{}^2 + I_{TC:SB}{*}B_{TC:SB} + I_{TC:RT}{*}B_{TC:RT} + I_{SB:RT}{*}B_{SB:RT}$$

Comparison of Current and New Correlations

Component	New R^2	Current R^2
1-Butene	0.88	
2-c-Butene	0.71	
2-t-Butene	0.71	
Carbon Dioxide	0.81	0.42
Carbon Monoxide	0.73	0.40
Ethane	0.72	0.85
Ethylene	0.96	0.88
Acetylene	0.96	0.72
Hydrogen	0.81	0.92
Methane	0.84	0.70
Propane	0.90	
Propene	0.95	
Hydrogen Sulfide	0.85	

Component	New R^2	Current R^2
Benzene	0.97	
Toluene	0.83	
Phenol	0.93	
Cresols	0.94	
Naphthalene	0.98	
Phenanthrene	0.98	
Heavy Tar, MW > 180	0.55	
Total Tar, MW > 78	0.77	0.89
Char	0.74	0.66
NF Dry Gas Flowrate	0.98	0.94

Update of ASPEN and Economic Models



NREL National Renewable Energy Laboratory

A national laboratory of the U.S. Department of Energy
Office of Energy Efficiency & Renewable Energy

Innovation for Our Energy Future

Biomass to Hydrogen Production Detailed Design and Economics Utilizing the Battelle Columbus Laboratory Indirectly-Heated Gasifier

P. Spath, A. Aden, T. Eggeman,
M. Ringer, B. Wallace, and J. Jechura

Technical Report
NREL/TP-510-37408
May 2005

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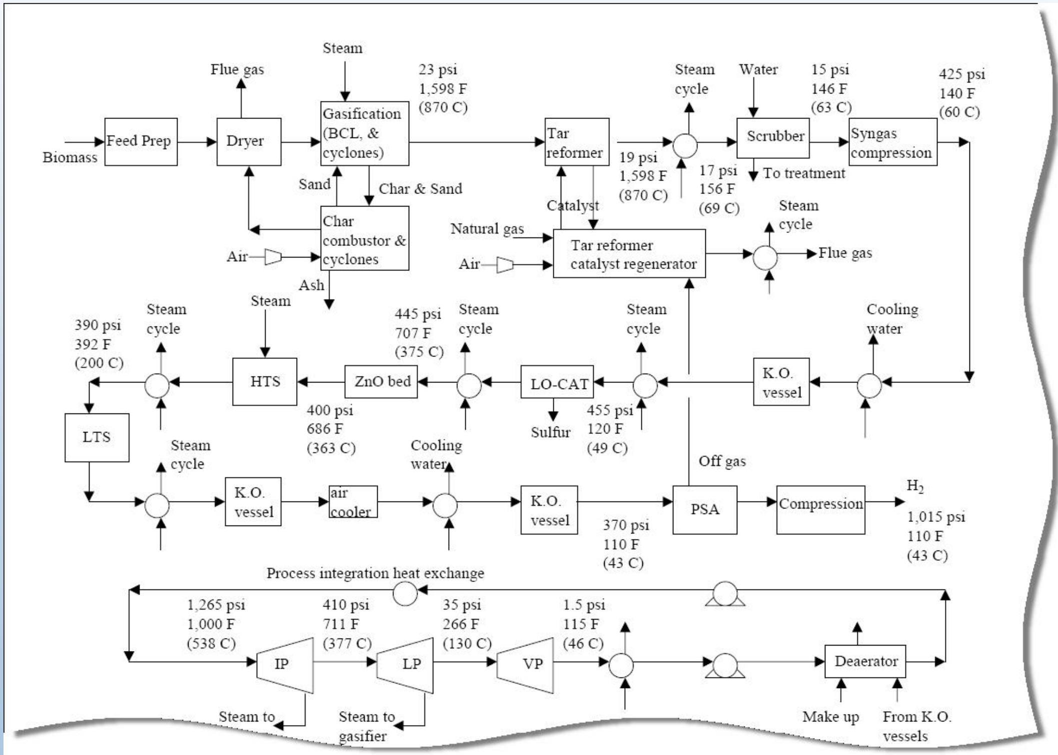
Objective: Update existing ASPEN model using updated gas yield composition correlations



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_2S 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
    - Spath, P.; Aden, A.; Eggeman, T.; Ringer, M.; Wallace, B.; Jechura, J. (2005). Biomass to Hydrogen Production Detailed Design and Economics Utilizing the Battelle Columbus Laboratory Indirectly-Heated Gasifier. 161 pp.; NREL Report No. TP-510-37408.

- 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 efficency, 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 gasifer / reformer campaign completed; initial update of gasifier correlation complete

Future Work: Complete gasifier / reformer / shift reactor testing

Complete technical modeling

Complete H2A economics