



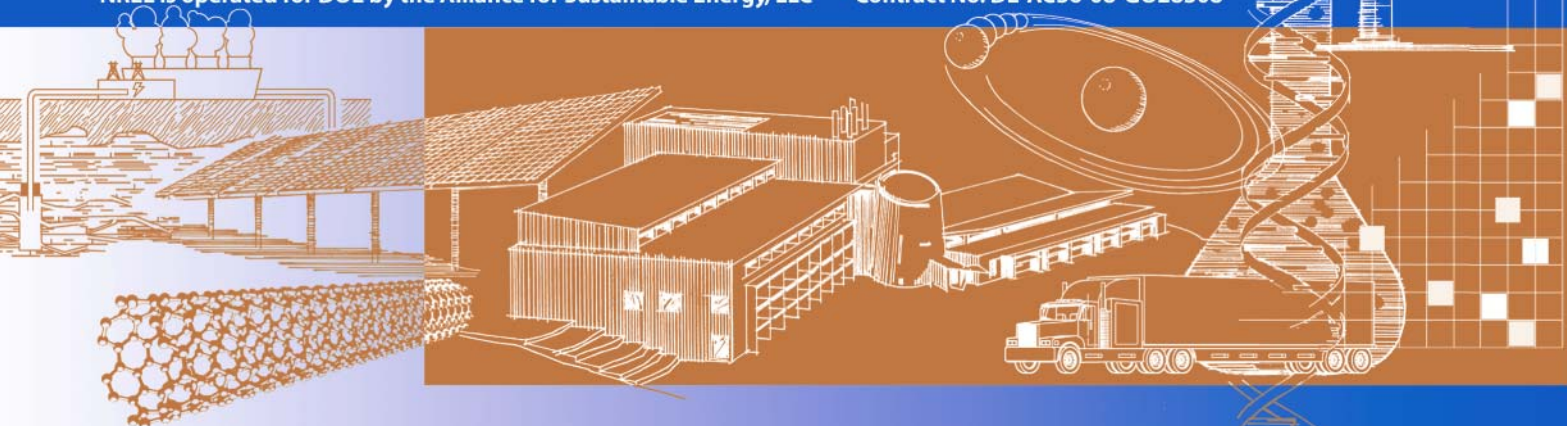
Parametric Gasification of Oak and Pine Feedstocks Using the TCPDU and Slipstream Water-Gas Shift Catalysis

Jason Hrdlicka, Calvin Feik, Danny Carpenter, and Marc Pomeroy

Technical Report
NREL/TP-510-44557
December 2008

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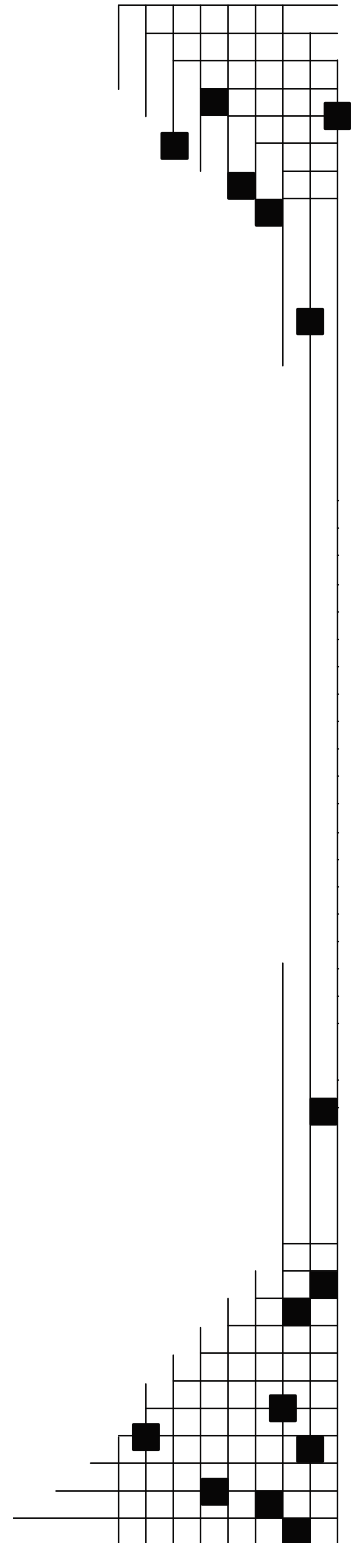


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Prepared under Task No. H2713B13

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Executive Summary

The goal of the Gasification of Biomass to Hydrogen project is to experimentally verify the technical and economic performance of an integrated biomass gasification-based hydrogen production process based on steam gasification. Through the auspices of the Department of Energy (DOE) Hydrogen Program, the National Renewable Energy Laboratory (NREL) has developed techno-economic models and analyses that have indicated that hydrogen production from biomass may be a viable approach. Costs developed in the techno-economic modeling effort have been used in H2A (DOE's Hydrogen Analysis project) modeling and have resulted in estimated hydrogen costs of \$1.77/kg (current) and \$1.47/kg (advanced in 2015).

To experimentally verify this work, NREL's Thermochemical Process Development Unit (TCPDU) was used. The TCPDU is an integrated system of unit operations designed to investigate biomass thermochemical conversion to gaseous and liquid fuels and chemicals. The TCPDU has a biomass throughput range of 10–30 kg/hr. The TCPDU's capabilities include gasification/pyrolysis, solid separation, full-stream methane and tar reforming, liquid scrubbing, and slipstream water-gas shift catalysis. Analytical instrumentation, including continuous non-dispersive infrared analyzers, gas chromatographs, and molecular beam mass spectrometry, measures gas and tar compositions at various steps in the process.

A comprehensive experimental design of tests was developed to explore variations in the biomass-derived product gas composition as a function of a range of process conditions. Oak and pine were used as feedstocks for this project. Product gas composition (H_2 , CO, CO_2 , CH_4 , C_2H_2 , C_2H_4 , C_2H_6 , C3s, and C4s), tar composition, and tar concentration were measured, and carbon conversion and material balances were determined for a total of nine process conditions established by varying thermal cracker temperatures (750°C, 850°C, and 950°C) and steam-to-biomass ratio (0.74, 1.25, and 2.00 for oak; 0.81, 1.25, and 2.00 for pine). For the slipstream water-gas shift catalysis, a commercial sulfided cobalt/molybdenum catalyst was used. The Full Stream Reformer (FSR), with an NREL-developed, nickel-based catalyst (NREL56), was used during water-gas shift fixed-bed reactor testing to maximize H_2 production.

In general, results from this study show that a higher steam-to-biomass ratio and a higher thermal cracker temperature yielded a higher hydrogen concentration. The hydrogen concentration ranged from 26%–39% vol. (dry, N_2 -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 H_2 -CO ratio for oak varied between 0.9 and 2.1 with an average of 1.2. The H_2 -CO ratio for pine varied between 1.5 and 2.7 with an average of 2.0. Overall mass closures of 88%–100% were achieved during the parametric oak gasification studies and 86%–100% for pine gasification studies. Qualitative tar measurements were very similar between the two feedstocks.

The shift catalyst was tested using bottled gases with an H_2 -CO ratio of 4.2, which is representative of the syngas produced in the TCPDU when the FSR is on-line. CO conversion of 74% was obtained using a shift reaction temperature of 450°C (842°F), steam-to- H_2 ratio of 5.0, and a gas hourly space velocity (GHSV) of 21,000. The H_2 -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 (1562°F). Using the same shift-reactor conditions as in the bottled-gas test, the CO conversion using pine-derived syngas

was initially 68%. After six hours, the CO conversion decreased to 65%. The H₂-CO ratio increased from 4.2 at the inlet to 14 at the outlet. The shift catalyst was not tested with oak-derived syngas.

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1 Introduction

The goal of the Gasification of Biomass to Hydrogen project is to experimentally verify the technical and economic performance of an integrated biomass gasification-based hydrogen production process based on steam gasification. Through the auspices of the Department of Energy (DOE) Hydrogen Program, the National Renewable Energy Laboratory (NREL) has developed techno-economic models and analyses that have indicated that hydrogen production from biomass may be a viable alternative to fossil fuel based hydrogen production. Costs developed in the techno-economic modeling effort have been used in H2A (DOE's Hydrogen Analysis project) modeling and 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 (BCL) in the 1980s. To give additional credibility to the estimates, integrated testing is required. This project has provided data needed to confirm gasification yields and gas compositions, has provided experimental hydrogen-yield data, and will provide updated techno-economic information for program evaluation efforts.

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 (methane, ethane, etc.) in one unit operation. These early efforts were used by NREL to develop detailed ASPEN models and accompanying economic models[4] that were used to provide yield, capital cost, and operating cost data for use in H2A.

The BCL Process Development Unit (PDU) was used to gather basic gasification-yield data under steam gasification conditions. The major components of the systems were the gasifier/heater, cyclones for solids separation, and a water scrubber for removal of tars. To further support the yields expected from a steam gasifier, a comparison of data from the BCL gasifier and the large FERCO gasifier in Vermont was made in 1995.[5] Gas yields and compositions were comparable. Tar sampling was not performed independently of the scrubber. In later efforts the NREL transportable molecular-beam mass spectrometer was used to independently measure tars, both at the Battelle PDU and at the NREL PDU. These measurements have been used to estimate tar yields in updated yield correlations. Very low contaminant levels are allowable in shift reactors and steam methane reformers.[6] Tars, ammonia, and halide levels must be less than 0.1 mg/Nm³ for fuels synthesis.[7]

Typical CO conversion in a natural gas-ammonia plant in a high-temperature, water-gas shift reactor is reported as 76%.[8] There have been some recent attempts to produce hydrogen from biomass-derived syngas using water-gas shift catalysts. Brown et al.[9] generated biomass-derived syngas using a ballasted gasifier, steam reformer, and two-stage water-gas shift reactor system. They were able to achieve 83% CO conversion in the high-temperature shift reactor and 98% conversion in the overall two-stage process. Haryanto et al.[10] looked at ultra high-temperature (>500°C) water-gas shift catalysts to increase overall process efficiency using bottled gas. They produced initial CO conversions of 40% for Ir on alumina, 50% for Pt-Ce on alumina and Rh-Pt-Ce on alumina, and 80% for Rh-Ce on alumina.

2 Experimental Procedures

2.1 TCPDU Process Description

The Thermochemical Process Development Unit (TCPDU) is an integrated system of unit operations designed to investigate biomass thermochemical conversion to gaseous and liquid fuels and chemicals. The individual unit operations were designed to permit multiple equipment configurations. The ability to reconfigure the TCPDU permits operation over a wide range of conditions from pyrolysis to gasification and facilitates the evaluation of various processes and feedstocks for multiple users. The TCPDU also enables study of catalytic upgrading of pyrolysis vapors and raw syngas conditioning, depending on research needs.

Extensive instrumentation for Supervisory Control and Data Acquisition (SCADA) is used to continuously monitor process streams at key locations. This monitoring assures operators that mass closure is obtained before and during analytical measurements of performance tests. State-of-the-art analytical equipment has also been integrated into the TCPDU to determine product composition at various points in the process. The SCADA and analytical equipment are linked to enable data integration into a single database-management system.

The feeding system consists of a loss-in-weight feeder with a 450 L hopper (200 kg capacity) that meters pelletized biomass through two purged rotary valves, then into a crusher that grinds the material to less than 2-mm particle size, and finally through a third rotary valve. The rotary valves isolate the process from the feeding system before the feed drops into a 22-mm diameter screw, which augers the feed into the gasifier at a rate between 5 and 30 kg/hr (11 and 66 lb/hr).

The first reactor in the process is an electrically heated fluidized bed reactor that is 20.3 cm (8 in.) in diameter with a freeboard that is 40.6 cm (16 in.) in diameter. The bed zone is 76.6 cm (34 in.) high. The freeboard zone is 170.2 cm (67 in.) high connected by a frustrum that is 29.2 cm (11.5 in.) high. The total reactor volume is 260 L (9.10 ft³) after accounting for the volume displaced by the olivine used in the bed. The bubbling bed is fluidized with either superheated steam for gasification experiments or preheated nitrogen for pyrolysis experiments. The minimum steam flow rate to maintain fluidization of olivine ($\rho = 1.73 \text{ g/mL}$) is 10 kg/hr (22 lb/hr) to maintain a superficial gas velocity of 25 cm/s (0.8 ft/s). Typical steam flow rates are varied between 10 and 30 kg/hr (22 and 66 lb/hr), depending on biomass feed rate and desired gas composition. For gasification, a steam-to-biomass ratio between 0.5 and 3 is desired.

In the process configuration for gasification, as shown in Figure 1, gas, entrained char, and bed material flows from the reactor through a pipe that is 3.81 cm (1.5 in) in diameter and into a thermal cracker. The thermal cracker is 26 m (85 ft) long by 3.81 cm (1.5 in.) diameter tubular reactor with 11 independently controlled, electrically heated zones. The volume of the thermal cracker is approximately 28 L (1.0 ft³).

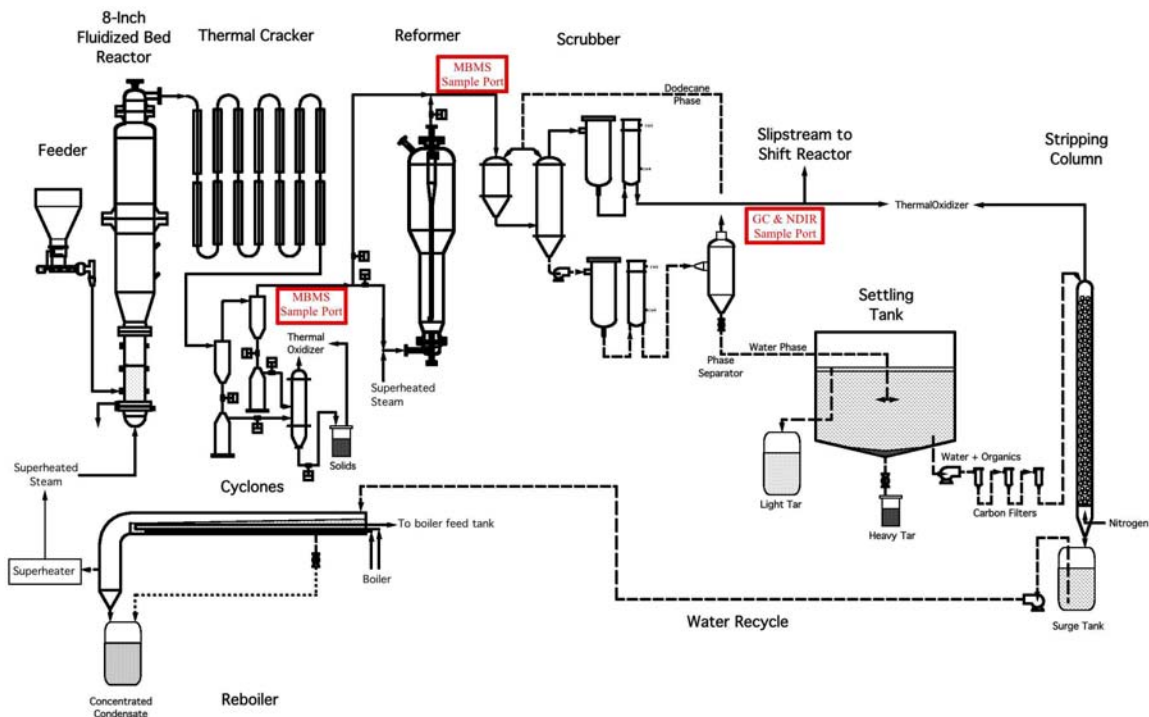


Figure 1: Process flow sheet for NREL's Thermochemical Process Development Unit (TCPDU). The full stream tar reforming (FSR) reactor shown was on-line during the shift catalyst tests. MBMS sampling is performed before and after the FSR reactor as well as after the scrubber.

Downstream of the thermal cracker are two cyclone separators in series with barrels measuring 10.2 cm (4 in) and 7.6 cm (3 in.) in diameter, respectively. The design collection efficiency of each cyclone is 95% with an overall design collection efficiency of 99.7%. Captured solids removed by the cyclones are collected in char pots below the cyclones. The char pots are emptied automatically, according to a programmable schedule, into an intermediate vessel where the char is cooled using nitrogen gas. The cooling vessel is operated like a lock hopper. After the char has cooled, it is transferred to a collection vessel that sits on an electronic scale to acquire mass data. Discrete char samples can be collected at this point for analysis, or bulk char can be accumulated and collected for further analysis or disposal.

The gas leaving the cyclones moves quickly through the remaining 3.81 cm (1.5 in.) diameter pipe to the scrubber system. The volume of the piping between the cyclones and the scrubber is about 7.1 L (0.25 ft³). Heated sample ports are available in this section of pipe for removing process gas or vapors and directing it to on-line analytical equipment for compositional analysis.

The condensation operation consists of a conical vessel (25.4 cm to 5.08 cm taper) for mixing hot gases with cooling liquid followed by a vessel that is 25.4 cm (10 in.) in diameter with nozzles in the top to spray in cooling liquid. Dodecane cools the process gas. Dodecane easily separates from the condensed steam and assists with tar removal from the process gas stream. The dodecane flow rate is about 114 L/min (30 gal/min). This rate is sufficiently high to keep the dodecane from heating significantly as it contacts the hot gases and vapors entering the condensation vessels. The warm dodecane and condensed steam are pumped through a two

micron filter to remove residual particulate not collected by the cyclonic separators. The liquid then cools using a shell and tube heat exchanger and proceeds to a phase separator. The dodecane rises to the top of the phase separator and reenters to the scrubber. The condensed water and tar flow out the bottom of the phase separator to the settling tank.

Condensed steam is pumped from the middle or water phase of the settling tank through a series of filters and into a stripping column where nitrogen removes light hydrocarbons. The stripped gases and nitrogen are directed to the thermal oxidizer (flare) for destruction. The water is then pumped back to a vessel where saturated steam at 850 kPag (125 psig) flowing through internal coils vaporizes the re-circulated water for process steam. Small amounts (ppm levels) of phenol, cresol, and naphthalene as detected by TMBMS sampling also return to the process. The concentrated “brine” in the reboiler is occasionally purged and disposed of as waste.

Gas exiting the scrubber typically contains residual particulate not collected in the cyclones or scrubber and aerosols that form as the gas cools in the scrubber. Entrained particles or droplets exiting the second scrubber vessel are removed by filters with a nominal two-micron filtration size. These filters collect 1–3 kg/hr of material, most of which is entrained dodecane. The process gas cools further in another shell and tube heat exchanger. After a slipstream is removed for analytical sampling and for the shift catalyst reactor, the process gas is sent to the thermal oxidizer (flare) where it is combusted at 650°C (1202°F).

2.2 Full Stream Tar Reformer

The Full Stream Reformer (FSR) shown in Figure 1 and detailed in the Full Stream Reformer flow sheet in Figure 2 is an electrically heated fluidized bed reactor that is 35.6 cm (14 in.) in diameter with a freeboard that is 61 cm (24 in.) in diameter. The total FSR volume is 448 L (15.8 ft³) without any catalyst. The vessel consists of an inlet gas plenum, a fluidized bed section, and a freeboard. The plenum that is 33 cm (13 in.) high and 26.7 cm (10.5 in.) in diameter has a tangential gas inlet and is flanged to the bottom of the bed section. The gas distribution plate is welded to the top of the plenum and contains sixty-two 3.2 mm holes in concentric circles. The bed section is composed of an 18 cm (7 in.) high conical transition above the distributor and a pipe that is 92 cm (36.25 in.) high. The 100 cm (39 in.) high freeboard is connected to the bed section by a conical reducer that is 30.5 cm (12 in.) high. The FSR is mounted to a support stand at the bed to freeboard transition cone. The electrical bed heaters are supported by the plenum flange, and the freeboard heaters are supported by the vessel supports.

The electric heaters are controlled using a cascaded proportional-integral-derivative (PID) control strategy. The highest temperature measured of the bottom three bed thermocouples and the heater surface temperature is used for the cascaded control. The vessel pressure is measured using a nitrogen-purged port on the freeboard to minimize catalyst plugging of the pressure lines.

The catalyst is loaded into the vessel using a container connected to the catalyst fill port. Small samples may be taken from the bed during operation using a drain valve mounted in the center of the gas distributor. A cooling chamber on the bottom of the drain port allows hot samples to be collected safely for analysis. The same drain valve is used to drain the catalyst when the vessel is cool.

Process gas from the gasification system mixes with superheated steam or nitrogen in an eductor. The combined gas heats further to at or near bed temperatures in the 6.7 m (22 ft) long, electrically heated preheater. The reformed gas exits the FSR via an internal cyclone that is 11.4 cm (4.5 in.) in diameter. The cyclone collects entrained solids from the catalyst bed and returns them to the bed through a dip leg that is 4 cm (1.5 in.) in diameter.

Catalyst regeneration requires the catalyst first to be oxidized to remove coke and other contaminants (e.g., sulfur). During catalyst oxidation, the FSR is isolated from the gasification process and fluidized by steam. Air may be introduced to the FSR just before the plenum for complete catalyst oxidation. Catalyst reduction occurs in the same manner except with the catalyst fluidized by nitrogen and hydrogen introduced to the plenum. The reforming catalyst is an NREL-developed, nickel-based catalyst. The current formulation is referred to as NREL56.

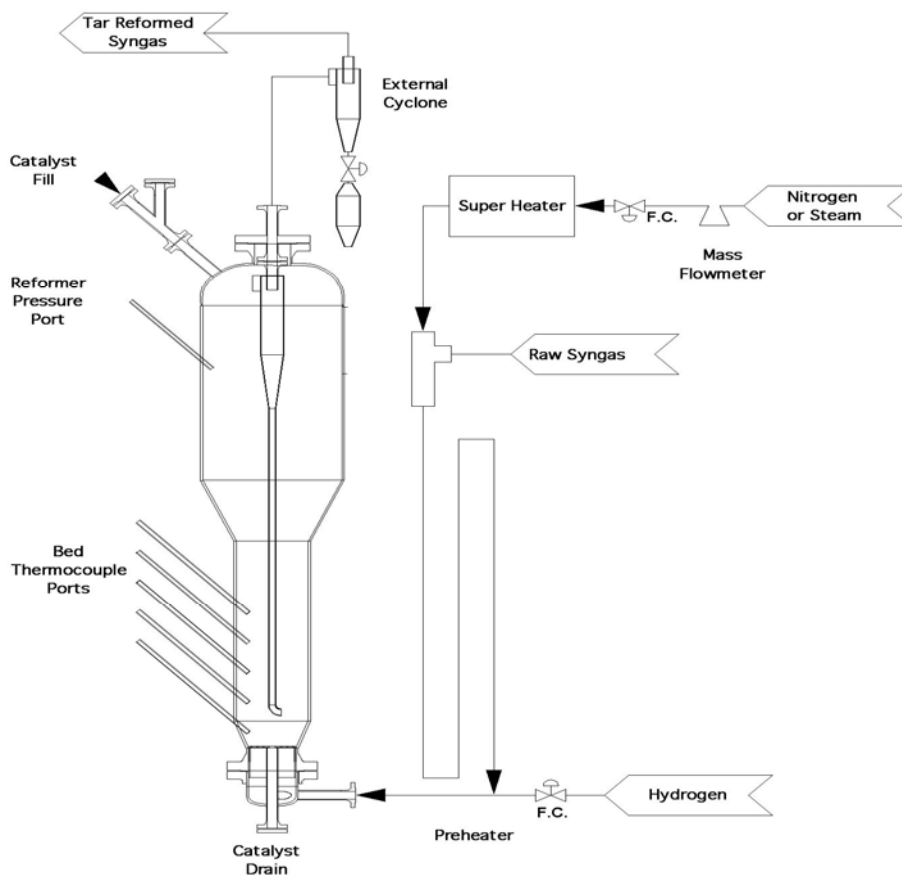


Figure 2: Process flow sheet for the Full Stream Reformer (FSR)

2.3 Fixed Bed Reactor Process Description

Located in NREL's Thermochemical Users Facility (TCUF), the BTRS, Jr. (Autoclave Engineers) and its associated equipment is a bench-scale fixed bed reactor system capable of handling reaction temperatures up to 650°C (1202°F) and pressures up to 200 barg (2900 psig). This system will be used to house the shift catalyst during this testing. Figure 3 shows a

schematic of the reactor system. The high-pressure compressor is a lubrication-free, three-stage piston design. It has a maximum output capacity of 7.5 slm (16 scfh, 0.5 Nm³/h) at 152 barg (2200 psig). Reaching its maximum volumetric output requires a small, low-pressure gas booster pump to bring the inlet pressure up to 1.7 barg (25 psig). The low-pressure booster pump is a PTFE diaphragm design with a stainless-steel pump head, which is rated at an output of 15 slm (30 scfh, 0.9 Nm³/h) at 1.7 barg (25 psig) and a maximum output of 7 slm (15 scfh, 0.4 Nm³/h) at 3.4 barg (50 psig). The gas is filtered for 0.1 μm aerosols and particulate before entering the high pressure compressor.

Prior to entering the high-pressure compressor, the gas travels through a GC loop for analysis. All of the gas sent through this loop returns to the process to provide an accurate measurement of flow. The gas is then heated to 200°C (392°F) in an enclosed oven before entering the packed bed reactor where the gas is heated to the desired reaction temperature. Steam is added to the reactor by pumping water into the oven enclosure using an HPLC pump. The water evaporates in a heated coil before mixing with syngas. Depending on the hydrogen sulfide (H₂S) concentration in the syngas, additional H₂S may need to be added. Hydrogen sulfide is added directly at the inlet of the reactor using a mass-flow controller.

The packed bed reactor is a stainless-steel (A-286) tube that is 431.8 mm (17.0 in.) in length and has an inner diameter of 13.1 mm (0.52 in.). The reactor was loaded with 10 mL (8.8 g) of catalyst at the outlet end. The catalyst occupied about 76 mm (3.0 in.) of the reactor, and the remaining length of the reactor was filled with glass wool for support and glass beads for heat transfer.

After exiting the reactor, the gas passes through a condenser train consisting of two condensers using an ethylene glycol and water mixture (50:50) to cool the gas and steam to about 5°C (41°F). A knockout vessel follows the condensers to remove the condensed steam. The cooled, moisture-free gas travels through a GC loop for analysis. All of the gas that passes through this loop returns to the process to provide an accurate measurement of flow. A diaphragm valve measures the flow, and a dry test meter measures the gas-flow rate. The gas then travels to the thermal oxidizer (flare).

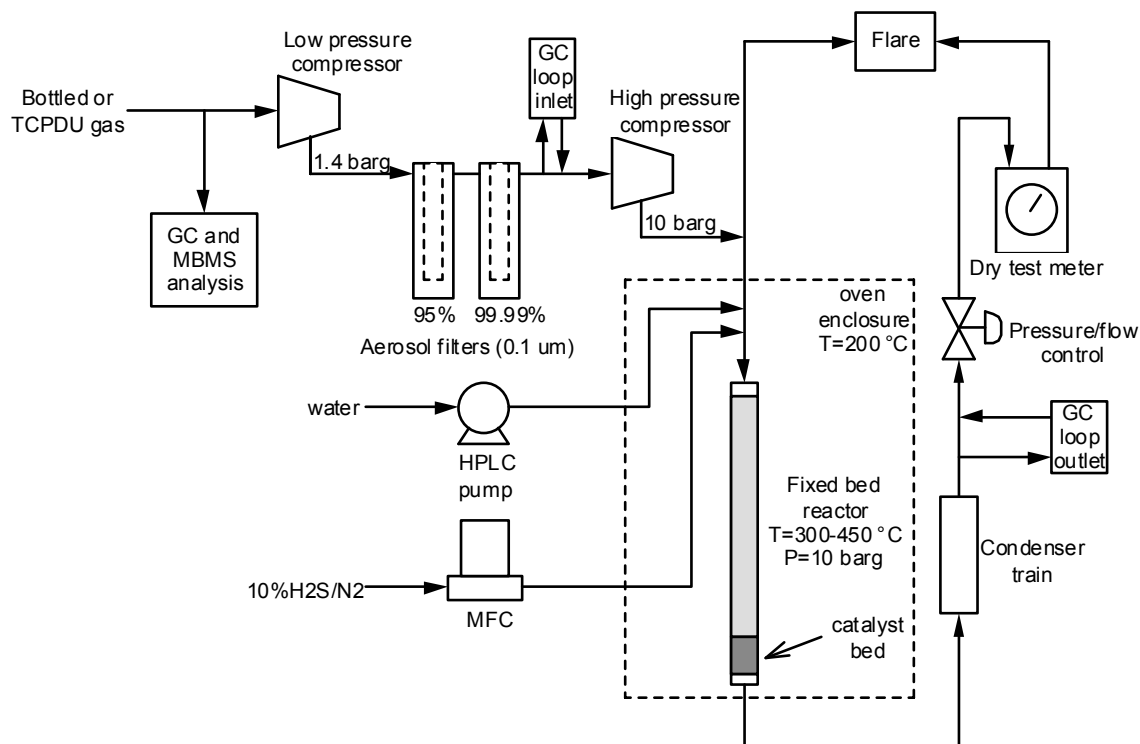


Figure 3: Schematic of fixed bed reactor system (BTRS, Jr.)

2.4 Analytical Gas Sampling

Extensive analytical instrumentation is available to determine gas composition at the exit of the TCPDU scrubbing system. Prior to analysis, however, the gas must be conditioned further before it is introduced to the instruments. A slipstream of the process gas is removed at the exit of the scrubbing system and compressed to 70 ± 10 kPa (10.2 ± 1.5 psig) in a Teflon diaphragm pump. The compressed gas then passes through a cold-finger condenser to remove excess moisture and any semi-volatile compounds (e.g., naphthalene, phenol) that might have bypassed the main process scrubber. The conditioned gas then passes to a pressure letdown valve, and the pressure reduces to 30 ± 2 kPa (4.3 ± 0.3 psig) before supplying the analytical instruments. To preserve the integrity of this sample slipstream in the analytical system, the gas comes in contact only with Sulfinert-passivated stainless steel (Restek, Bellefonte, CA) or Teflon surfaces.

With steam and other condensable vapors removed from the product gas stream, compositions can be measured with three on-line, continuous, non-dispersive infrared (NDIR) chemical analyzers to monitor CO, CO₂, and CH₄: a thermal conductivity H₂ analyzer; a paramagnetic O₂ analyzer; and a four-channel, rapid-analysis gas chromatograph that cycles every three minutes to measure permanent gases and hydrocarbons (C₂s through C₄s and benzene).

The analytical equipment includes:

- California Analytical Instruments (CAI) Model 100P Paramagnetic Oxygen Analyzer with a range of 0–25 vol. %.

- Methane is measured with a CAI Model 100, NDIR Analyzer with a range of 0–50 vol. %. Carbon dioxide and carbon monoxide are measured with a CAI Model 200, NDIR Analyzer with a range of both analytes of 0–50 vol. %.
- NOVA H2 thermal conductivity analyzer with a range of 0–50 vol. % and analog inputs for %CO, %CH4 and %CO₂ to correct the hydrogen value.
- A Varian Inc. CP4900 Quad Micro Gas Chromatograph (μGC) with thermal conductivity detectors (TCD). It is a four-channel, on-line, gas chromatograph with a cycle time of three minutes. A 10-m MoleSieve-5A column with an argon carrier is used to determine H₂, O₂, N₂, CH₄, and CO. Helium can also be determined when added as an internal standard. A 10-m PoraPlot Q column with a helium carrier is used to determine CO₂ and C₂H₂. Ethane and ethene co-elute on this column and can be measured as a composite peak. A 10-m Alumina (sodium modified) column with a helium carrier is used to determine C₂H₄, C₂H₆, C₃H₆, and C₃H₈. This column can also determine higher paraffins and olefins, but for this use, the methodology has been optimized for the C2 and C3 hydrocarbons. A 4-m methyl-silicone column with an argon carrier is used to determine C4 paraffins and olefins as well as benzene.
- A second Varian μGC is used to duplicate some of these data points above but is also used for sulfur analysis. A 10-m Porabond Q column with a helium carrier is used to determine H₂S and COS using a TCD as well as a tandem Differential Mobility Detector (DMD).

Calibration gases to calibrate the on-line instrumentation and the two gas chromatographs are made by using two premixed, certified, commercial gas mixtures dynamically mixed on-line to generate the intermediate concentrations needed to calibrate across the experimental range. Divided between the premixed standards are all of the major gas components (H₂, CO, CO₂, CH₄, C₂s, C₃s and C₄s) expected in the product gas. In addition, there are mass-flow controllers to add nitrogen and helium to the mixed-gas standards for dilution and internal standard. The on-line gas analyzers are typically calibrated at their zero point using a mixture of nitrogen with 1% helium (the internal standard used in the process), and the span is adjusted with a gas mixture that closely approximates the gas composition under typical gasification conditions. The microchannel GC calibrates across a nine-point calibration curve that spans the range from 99% nitrogen to the highest concentrations found in the premixed commercial gas mixtures. The Sulfur μGC for sulfur measurements is calibrated using a standard mixture of H₂S in nitrogen and COS in argon, which is then mixed with the other commercial gas calibration mixtures to calibrate the instrument at three levels.

Each of the on-line instruments has an output of a 4–20 mA signal that is proportional to the analyte concentration. This signal is captured by an OPTO22 SCADA system and is recorded every minute to a log file on the system control computer. The GCs are both controlled by Varian Galaxie software running on a separate data-acquisition computer. The CP4900 microGCs are cycled every three minutes, and the data are immediately transferred by a custom Excel macro to a spreadsheet. The spreadsheet displays a running graph of the concentration of all of the major gas components so operators can assess the stability of the process continuously.

2.5 Hot Gas Sampling—Tar Measurements

2.5.1 TMBMS Instrument

A transportable molecular-beam mass spectrometer (TMBMS) was used to provide continuous, on-line chemical analysis of hot product vapors from indirect gasification. The instrument, developed at NREL, is a useful tool for monitoring high-temperature thermochemical processes. The tool allows direct, real-time sampling of hot process vapors, providing a time-resolved account of the wet-gas composition. More information on the instrument can be found elsewhere.[11] A brief description follows.

For these tests, a hot slipstream of the product gas from the TCPDU was conducted to the TMBMS through heat-traced and insulated 0.95 cm (0.375 in.) stainless-steel transfer lines maintained at 450°C (842°F). This temperature was hot enough to prevent condensation losses in the sampling system, yet sufficiently cool to minimize further thermal decomposition of the sampled tars. A heated sampling manifold filtered particulates and controlled the temperature, pressure, and flow of the sampled gases (see Figure 4). The gas-sampling system operated in “flow-by” mode, flowing approximately 3.5 standard liters per minute, of which the sampling orifice extracted roughly 10%. The unused gas passed through a condensation system to remove condensed steam and tars prior to the downstream metering system.

A molecular beam forms as the gases are extracted through a 300 μm diameter orifice into the first stage of a three-stage, differentially pumped vacuum system. The nature of this free-jet expansion quenches chemical reactions and inhibits condensation by rapidly decreasing the internal energy of the sampled gases. The central core of this expansion becomes a molecular beam upon passing through a conical skimmer located at the entrance to the second stage of the vacuum system. The beam then enters the third stage where components are ionized and mass analyzed by a quadrupole mass spectrometer. Mass spectra are generated according to the measured signal intensity as a function of the molecular weight of the ions.

The TMBMS is equipped with a heated sampling manifold and an OPTO22 (Temecula, CA) control system that allows it to interface with and monitor a variety of chemical process streams. Ten integrated temperature-control loops maintain sample line temperatures. The TCPDU process control system controls additional heaters for the sampling lines. Two mass-flow controllers introduce inert gases for sample dilution, liquid standard injections, and internal standards. Additional mass flow meters provide nitrogen purges to prevent line plugging and accumulation of process gases. Flow and pressure control valves operate in tandem to deliver a constant flow of gas at a constant pressure to the sampling orifice. OPTO stores values from these auxiliary channels electronically and uses them for data reduction.

The mass spectrometer and spectral data collection were automated using a PC-based data-acquisition and control system manufactured by Extrel CMS (Pittsburgh, PA). Mass spectra were recorded for $m/z=3$ to $m/z=400$ along with auxiliary pressure data at a rate of 36 scans/min with one-minute averages stored.

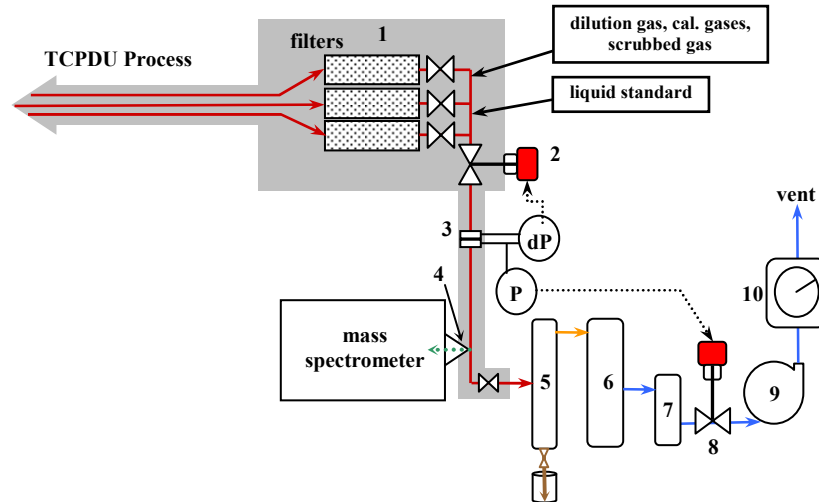


Figure 4: Schematic of TMBMS gas sampling system: (1) sampling manifold; (2) flow-control valve; (3) orifice-plate flow meter; (4) sampling orifice; (5) condenser; (6) chilled impingers with cotton wool; (7) coalescing filter; (8) pressure control valve; (9) sample pump; (10) dry test meter. Shaded areas maintained at 450°C.

2.5.2 Tar Calibration

The raw TMBMS mass spectra represent semi-quantitative, relative intensities for all species measured and detected. For the present parametric gasification studies, absolute tar concentrations in the product gas are desired for input into techno-economic models under development. Several factors, however, affect the instrument's response non-uniformly to different chemical species. Absolute concentration data for selected tar species were achieved by carefully controlled injections of a liquid calibration standard containing benzene, toluene, phenol, cresol, naphthalene and phenanthrene dissolved in methanol. To avoid uncertainty due to sample matrix effects (e.g., bulk gas composition), the two-level standard is introduced as a standard addition while sampling raw process gas. Using high-pressure, liquid-chromatography (HPLC) pumps, the standard was injected into the sample line through a heated stainless-steel capillary downstream of the shut-off valves (see Figure 4). The liquid was vaporized upon entry into the sampling oven, giving rise to the changes in gas-phase concentration shown in Table 1. The weight loss of standard in the reservoir was recorded with a balance to determine the liquid feed rate.

Table 1: Nominal composition of liquid calibration standard for tar species

Species	Molecular Weight	Standard Liquid Concentration (wt%)	Std. Nominal Change in Concentration (mg/Nm ³)		Response Factor (counts per mg/L-actual)	R ² from Calibration Curve
			Low level	High level		
Methanol	32	73.09	<i>Low level</i>	<i>High level</i>		
Benzene	78	8.73	3810	7980	5.246 x 10 ⁷	0.9995
Toluene	92	7.92	3450	7240	4.910 x 10 ⁷	0.9992
Phenol	94	4.08	1780	3730	3.073 x 10 ⁷	0.9971
Cresol	108	1.79	780	1640	4.190 x 10 ⁷	0.9984
Naphthalene	128	3.36	1460	3070	9.934 x 10 ⁷	0.9999
Phenanthrene	178	1.03	448	940	1.015 x 10 ⁸	0.9995

Using the signal observed in the raw gas and during the standard injections, a three-point calibration curve was generated for each species in the standard. The response factors were derived from the slopes of the linear least-squares fits to the calibration data. Figure 5 shows the TMBMS response at specific molecular weights for each calibrated tar species from the liquid injection calibrations along with the linear least-squares fit (dashed lines).

The mass spectrometer has proven to have a stable response to tar species across the spectrum, provided the sample matrix does not change significantly. Because large variations in gas composition are inherent in these parametric studies, and because conducting a liquid tar standard at each condition is prohibitively time consuming, additional steps were taken to ensure accurate calibrations. The liquid tar calibration was performed two to three times during each weeklong series of experiments. In addition, the instrument's response to argon, added at a constant molar flow as a tracer gas in the TCPDU, was gauged at each discrete condition by carrying out a separate argon calibration. The tar response factors were then adjusted per condition for any changes observed in the argon response factors.

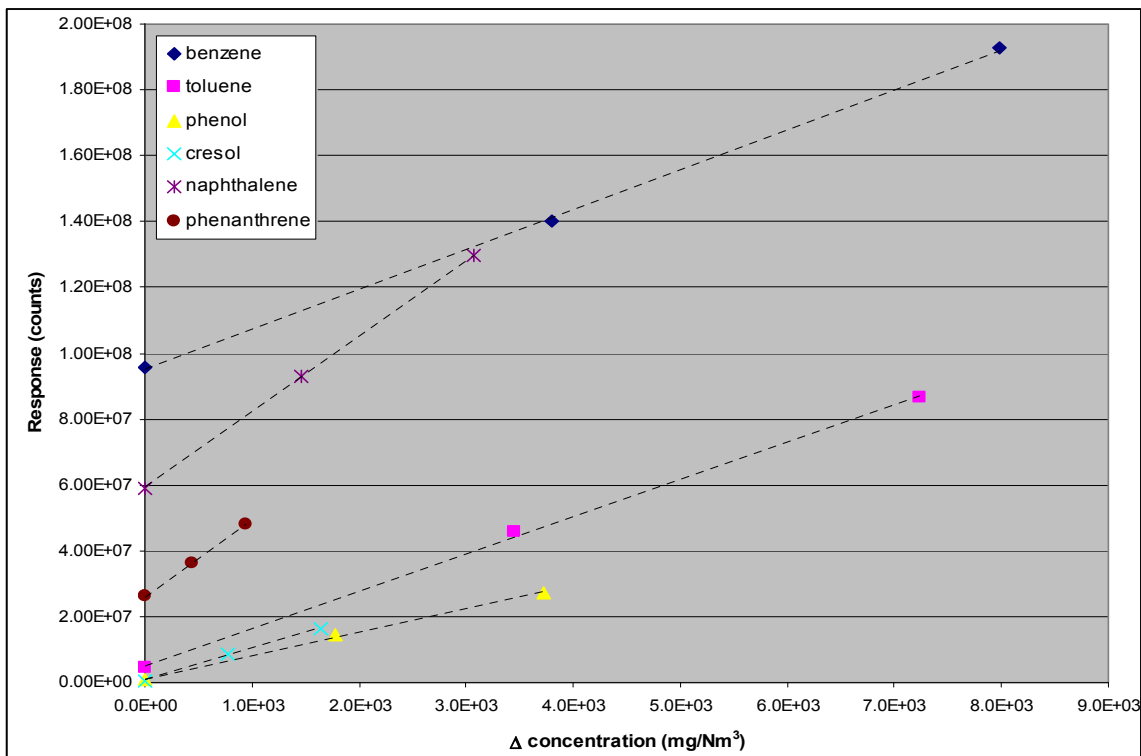


Figure 5: Response curves from liquid standard injections for the TMBMS for various tar species. Dashed lines represent linear least-squares fits to the data

2.6 Water-Gas Shift Catalyst

A commercial high-temperature, water-gas shift catalyst employed of cobalt and molybdenum active metals supported on high purity, activated alumina extrusions was used. The catalyst was received as 3 mm-diameter extrusions. The extrusions were hand crushed and sieved to a size of -14/+35 (0.5–1.4 mm). The bulk density of the sieved particles is 0.88 g/mL. This catalyst is a sulfided catalyst and requires an operating sulfur concentration of at least 30 ppmv. The catalyst was shipped in the oxidized form and was presulfided before exposure to syngas. The sulfidation procedure consisted of exposing the catalyst to 5 wt% H₂S in nitrogen at an initial temperature of 204°C (400°F) and gradually ramping up the temperature to a final value of 316°C (600°F). The sulfidation procedure was complete once the inlet and outlet sulfur concentrations were equal.

2.7 Experimental Test Matrix

A comprehensive experimental design was developed to explore variations in the biomass-derived product gas composition as a function of a statistically robust range of process conditions. Product gas composition (H₂, CO, CO₂, CH₄, C₂H₂, C₂H₄, C₂H₆, C₃s, and C₄s), tar composition and concentration, carbon conversion, and material balances were determined at a total of nine process conditions established by varying thermal cracker temperature (750°C, 850°C, and 950°C) and steam-to-biomass ratio (0.74, 1.25, and 2.00 for oak; 0.81, 1.25, and 2.00 for pine). The range of oak and pine gasification conditions attainable in NREL's TCPDU are summarized in Table 2 and Table 3, respectively.

Material balances and on-line gas compositions determined by GC were determined in real time for all process conditions throughout the experimental campaign. On-line tar analysis by molecular beam mass spectrometry was also performed. Random grab samples of the pelletized oak and pine feed were taken, and selected char samples were isolated during each steady-state condition and were submitted for proximate, ultimate, and elemental ash analyses.

Of the two process variables, thermal cracker temperature is easier to change and has less impact on overall process stability and steady-state operation. The thermal cracker temperature was never lower than the bed temperature. Varying the steam-to-biomass ratio can be achieved in several ways. The steam rate and the biomass-feed rate both can be varied independently between 10 and 30 kg/hr (22 and 66 lb/hr) within the limitations of maintaining fluidization in the reactor and heat conduction to the bed.

From a steady-state process perspective, changing the steam-to-biomass ratio impacts the environment directly in the 8-in. fluidized bed reactor, specifically the dynamic accumulation and removal of unconverted carbon and ash, collectively referred to as char. During operation, large char particles accumulate in the reactor until a steady-state level is reached. The char particles leave the reactor once they become entrained in the exit gas. Entrainment occurs either when the particles become small enough to be carried by the gas or when larger particles enter into a region of higher velocity gas near the reactor outlet. For larger particles, this occurs more frequently as the char level in the bed increases in height. The rate at which the level increases is a function of the feed material density, size, shape, carbon conversion and feed-ash content. Consequently, a truly representative char sample associated with a given process condition is difficult to obtain when the bed conditions are changed during an experimental period.

Table 2: Summary of parametric oak gasification process conditions

Date/Time Started	Date/Time Completed	ID	Biomass (kg/hr)	Steam (kg/hr)	S:B	Bed Temp (°C)	TC Temp (°C)
11/20/2007 12:45	11/20/2007 14:41	OK_HY_97095	10.1	20.2	2.00	700	950
11/28/2007 13:22	11/28/2007 16:22	OK_HY_97085	10.1	20.2	2.00	700	850
11/28/2007 17:35	11/28/2007 20:35	OK_HY_97075	10.1	20.2	2.00	700	750
11/29/2007 13:40	11/29/2007 16:47	OK_HY_77075	18.6	13.8	0.74	700	750
11/29/2007 18:32	11/29/2007 21:32	OK_HY_77085	18.6	13.8	0.74	700	850
11/30/2007 11:41	11/30/2007 15:00	OK_HY_77095	18.6	13.8	0.74	700	950
12/4/2007 13:20	12/4/2007 14:44	OK_HY_97095b	10.1	20.2	2.00	700	950
12/12/2007 11:56	12/12/2007 14:57	OK_HY_87095	13.85	17.3	1.25	700	950
12/12/2007 16:15	12/12/2007 19:20	OK_HY_87085	13.85	17.3	1.25	700	850
12/13/2007 13:30	12/13/2007 16:32	OK_HY_87075	13.85	17.3	1.25	700	750
12/14/2007 11:45	12/14/2007 14:50	OK_HY_77085b	18.6	13.8	0.74	700	850
12/17/2007 11:55	12/17/2007 15:20	OK_HY_97085b	10.1	20.2	2.00	700	850
12/18/2007 13:24	12/18/2007 16:25	OK_HY_87085b	13.85	17.3	1.25	700	850

Table 3: Summary of parametric pine gasification process conditions

Date/Time Started	Date/Time Completed	ID	Biomass (kg/hr)	Steam (kg/hr)	S:B	Bed Temp (°C)	TC Temp (°C)
8/26/2008 13:47	8/26/2008 16:50	PI_HY_97095	10.1	20.2	2.00	700	950
8/27/2008 12:39	8/27/2008 16:11	PI_HY_97085	10.1	20.2	2.00	700	850
8/28/2008 14:27	8/28/2008 17:27	PI_HY_97075	10.1	20.2	2.00	700	750
9/2/2008 13:45	9/2/2008 16:48	PI_HY_77075	17.5	14.2	0.81	700	750
9/3/2008 12:28	9/3/2008 15:45	PI_HY_77085	17.5	14.2	0.81	700	850
9/4/2008 12:24	9/4/2008 15:40	PI_HY_77095	17.5	14.2	0.81	700	950
9/5/2008 13:45	9/5/2008 16:50	PI_HY_87095	13.85	17.3	1.25	700	950
9/8/2008 13:00	9/8/2008 16:00	PI_HY_87085	13.85	17.3	1.25	700	850
9/9/2008 14:00	9/9/2008 17:23	PI_HY_87075	13.85	17.3	1.25	700	750
9/11/2008 14:00	9/11/2008 17:03	PI_HY_97085b	10.1	20.2	2.00	700	850

Because of the wide range of char particle sizes and the variety of mechanisms determining the size and shape of the particles, those particles captured in the char cyclones likely have a wide, unknown time history in the reactor. Changes in operating conditions also affect the particle history and the steady-state char level. Higher throughputs of gases and biomass (especially gases) will lower the steady-state level of char. When changing from a relatively low velocity to a higher velocity, the apparent char yield appears to increase due to the increased entrainment of char. Decreasing the gas rate has the opposite effect. The only method to determine the char yield directly from measurements of char versus time is waiting for the reactor to reach steady-state char level at each set of operating conditions. Depending on conditions, this can take up to several hours after each change.

2.8 Solid Sample Analyses—Feed and Char Residues

The proximate, ultimate, and elemental ash analyses for the oak and pine-grab samples are presented in Table 4. The proximate and ultimate analyses of the two wood feedstocks are very similar. The ash chemistry of oak and pine is also very similar with the exception of calcium and magnesium content. Oak ash has more calcium, and pine ash has more magnesium. Appendix A contains the proximate, ultimate, and elemental ash analyses for each of the char samples collected.

To minimize the time averaging of the char sampling method, relatively small char samples were collected during each steady-state operating period. Typically, char removed from the process is collected in a plastic bag that lines a 113-L (30 gal) char drum. These bags can hold up to 17 kg of char that accumulates over time as about 500 g of char is blown down every 10 to 15 minutes. Steady-state conditions were usually designated once the gas compositions were stable and after a char blow-down event. During the steady-state sampling period, the char sample removed from the char pots was diverted to a one-gallon container and collected. This collection provided a representative sample of the char that escaped the gasifier during a relatively short time period. It should also be noted that because of char accumulation in the fluidized bed reactor, char captured by the cyclones at any given time could have evolved from biomass fed hours earlier.

Table 4: Proximate, ultimate, and elemental ash analysis for oak and pine feed samples

	Oak	Pine
<i>Proximate Analysis (wt% as received)</i>		
Moisture	5.81	7.55
Ash	0.53	0.30
Volatile Matter	79.05	79.86
Fixed C	14.61	12.29
HHV (Btu/lb)	7993	8263
<i>Ultimate Analysis (wt% as received)</i>		
C	48.55	49.67
H	5.11	6.11
N	0.05	0.06
O (by difference)	39.92	36.29
S	0.03	0.02
Cl	0.01	0.01
Moisture	5.81	7.55
Ash	0.53	0.30
<i>Elemental Ash Analysis (wt% of ash as oxide)</i>		
SiO ₂	3.82	5.39
Al ₂ O ₃	0.91	1.54
TiO ₂	0.04	0.06
Fe ₂ O ₃	0.71	2.02
CaO	42.40	29.00
MgO	2.02	10.50
Na ₂ O	0.43	0.39
K ₂ O	18.90	18.90
P ₂ O ₅	2.62	5.24
SO ₃	2.63	3.26
Cl	0.03	0.17
CO ₂	24.47	21.27

3 Experimental Results

The parametric oak gasification experiments were conducted during November and December 2007, and the parametric pine gasification experiments were conducted during August and September 2008. Prior to each set of experiments, the fluidized bed reactor was loaded with a fresh charge of olivine, and initial system check-out and preparation was performed.

3.1 GC Gas Sampling Results

Complete raw gas compositions are measured every four minutes, and data export continuously to a spreadsheet for data manipulation. Helium was added to the front end of the TCPDU as an internal standard to correct changes in gas-flow rate through the process. Nitrogen is added at several points in the process as a purge gas. For reporting purposes, all gas compositions measured with the GC are reported on a dry basis. The average gas compositions measured during each process condition during oak and pine gasification are presented in Table 5 and Table 6, respectively. Random conditions were performed twice to obtain replicates. These conditions have a “b” in the run ID.

Table 5: Summary of dry, nitrogen-free gas composition for parametric oak tests

Run ID	77075	77085	77085b	77095	87075	87085	87085b	87095	97075	97085	97085b	97095	97095b
S:B ratio	0.74	0.74	0.74	0.74	1.25	1.25	1.25	1.25	2.00	2.00	2.00	2.00	2.00
TC Temp (°C)	750	850	850	950	750	850	850	950	750	850	850	950	950
Gas (%vol.)													
H ₂	29.14	30.45	26.70	32.35	29.74	29.38	30.17	32.01	29.26	29.35	34.01	33.74	39.15
CO	27.73	26.05	30.76	24.83	26.85	26.98	28.34	25.59	27.08	27.41	22.76	24.45	18.37
CO ₂	21.30	21.55	19.52	21.57	21.50	20.33	20.55	20.31	20.51	19.81	22.30	19.93	23.45
CH ₄	13.03	13.74	15.05	14.01	13.04	13.67	14.06	13.60	12.42	13.27	12.17	12.59	11.06
He (tracer)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C ₂ H ₆	1.24	1.17	1.29	1.12	1.68	1.58	0.57	1.48	2.22	2.13	1.95	1.86	1.69
C ₂ H ₄	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C ₂ H ₂	3.03	3.61	4.05	2.29	3.03	3.63	3.75	2.12	3.11	3.69	3.09	2.12	1.66
C ₃ H ₈	1.47	0.59	0.56	0.09	1.31	0.50	0.50	0.06	1.17	0.46	0.40	0.01	0.03
C ₃ H ₆	0.14	0.33	0.41	1.12	0.15	0.41	0.42	1.22	0.19	0.48	0.39	1.25	0.99
1-C ₄ H ₈	0.54	0.08	0.10	0.01	0.45	0.08	0.08	0.00	0.47	0.10	0.07	0.00	0.00
2-cis-C ₄ H ₈	0.25	0.07	0.06	0.03	0.21	0.06	0.06	0.04	0.19	0.04	0.04	0.00	0.00
2-trans-C ₄ H ₈	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
COS (ppmv)	0	0	0	0	0	0	0	0	0	0	0	0	0
H ₂ S (ppmv)	0	48	54	51	0	52	51	51	0	59	48	58	40
Closure (%)	97.9	97.7	98.5	97.5	98.0	96.6	98.5	96.4	96.9	96.8	97.2	96.0	96.4
H ₂ :CO ratio	1.1	1.2	0.9	1.3	1.1	1.1	1.1	1.3	1.1	1.1	1.5	1.4	2.1

In general, higher steam-to-biomass ratio and higher thermal cracker temperature yields a higher hydrogen concentration. The hydrogen concentration ranged from 26%–39% for oak and 35%–42% for pine gasification. The carbon monoxide concentration ranged from 18%–31% for oak and 15%–23% 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. The carbon dioxide concentration ranged from 19%–23% for oak and 21%–25% for pine. The water-gas shift catalyst requires sulfur to maintain activity so the H₂S concentration in the syngas is also

important. For oak, the H₂S concentration was 40–60 ppmv. For pine, the H₂S concentration was 20–30 ppmv. These concentrations were observed when the thermal cracker temperature was either 850°C (1562°F) or 950°C (1742°F). At a thermal cracker temperature of 750°C (1382°F), the H₂S concentration was 0 ppmv because the sulfur remains bound with tar and char at lower temperatures.

Table 6: Summary of dry, nitrogen-free gas composition for parametric pine tests

Run ID	77075	77085	77095	87075	87085	87095	97075	97085	97085b	97095
S:B ratio	0.81	0.81	0.81	1.25	1.25	1.25	2.00	2.00	2.00	2.00
TC Temp (°C)	750	850	950	750	850	950	750	850	850	950
Gas (%vol.)										
H ₂	35.59	35.49	37.87	39.08	39.94	40.53	35.29	35.18	42.11	37.53
CO	18.93	17.95	20.45	17.68	16.40	17.69	23.44	20.58	15.34	19.94
CO ₂	24.26	23.90	23.35	24.13	24.74	23.57	22.10	21.49	24.98	20.80
CH ₄	12.09	12.80	15.04	10.12	10.87	11.39	13.29	12.30	9.80	12.29
He (tracer)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C ₂ H ₆	0.88	0.82	0.74	0.97	0.88	0.82	1.63	1.55	1.17	1.40
C ₂ H ₄	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C ₂ H ₂	2.92	3.72	0.07	2.41	3.02	0.05	3.06	0.49	2.71	2.05
C ₃ H ₈	1.51	0.63	0.00	1.13	0.53	0.00	1.18	0.02	0.44	0.05
C ₃ H ₆	0.12	0.34	1.03	0.12	0.13	0.00	0.18	0.45	0.28	1.34
1-C ₄ H ₈	0.56	0.10	0.00	0.40	0.07	0.56	0.46	0.10	0.06	0.00
2-cis-C ₄ H ₈	0.24	0.06	0.03	0.17	0.00	0.00	0.06	0.00	0.00	0.00
2-trans-C ₄ H ₈	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
COS (ppmv)	0	0	0	0	0	0	0	0	0	0
H ₂ S (ppmv)	0	31	30	0	23	25	0	26	20	20
Closure (%)	97.1	95.8	98.6	96.2	96.6	94.6	101.5	92.2	96.9	95.4
H ₂ :CO ratio	1.9	2.0	1.9	2.2	2.4	2.3	1.5	1.7	2.7	1.9

3.2 Mass Spectral Results—Tar Concentrations

3.2.1 Raw Syngas

The raw gas from indirect oak and pine gasification contained the familiar slate of tar compounds typically observed. Figure 6 shows a series of time-averaged mass spectra taken during the 97075, 97085, and 97095 steady-state conditions for pine gasification, showing the effect of thermal cracker temperature on the product slate. Predominant peaks in all three plots include methane ($m/z=16$), benzene ($m/z=78$) and naphthalene ($m/z=128$). Other peaks observed in the spectra, typical of those encountered in previous biomass gasification studies, are identified in the inset of the figure, and Table 7 gives a list of tar compounds with their molecular formulas. As expected for these conditions, the spectrum is comprised largely of tertiary tar compounds, characterized by the polycyclic, aromatic hydrocarbon series of peaks, along with some alkylated, aromatic derivatives (e.g., toluene, indene, methylnaphthalenes) and secondary tars (e.g., phenolics). Notable omissions from the spectrum include water ($m/z=18$), carbon monoxide/N₂ ($m/z=28$), and carbon dioxide ($m/z=44$), which were not scanned to avoid saturating the detector.

Table 7: Molecular weight and identification of common hydrocarbons detected in corn stover gasification product gases with the TMBMS

Molecular Weight	Formula	Chemical Name(s)
15,16	CH ₄	methane
26	C ₂ H ₂	acetylene
78	C ₆ H ₆	benzene
91,92	C ₇ H ₈	toluene
94	C ₆ H ₆ O	phenol
104	C ₈ H ₈	styrene
106	C ₈ H ₁₀	(m-, o-, p-) xylene
108	C ₇ H ₈ O	(m-, o-, p-) cresol
116	C ₉ H ₈	indene
118	C ₉ H ₁₀	indan
128	C ₁₀ H ₈	naphthalene
142	C ₁₁ H ₁₀	(1-, 2-) methylnaphthalene
152	C ₁₂ H ₈	acenaphthylene
154	C ₁₂ H ₁₀	acenaphthene
166	C ₁₃ H ₁₀	fluorene
178	C ₁₄ H ₁₀	anthracene, phenanthrene
192	C ₁₅ H ₁₂	(methyl-) anthracenes/phenanthrenes
202	C ₁₆ H ₁₀	pyrene/fluoranthene
216	C ₁₇ H ₁₂	methylpyrenes/benzofluorenes
228	C ₁₈ H ₁₂	chrysene, benz[a]anthracene, ...
242	C ₁₉ H ₁₄	methylchrysenes, methylbenz[a]anthracenes
252	C ₂₀ H ₁₂	perylene, benzo[a]pyrene,
266	C ₂₁ H ₁₄	dibenz[a,k]anthracene,
278	C ₂₂ H ₁₄	dibenz[a,h]anthracene,
302	C ₂₄ H ₁₄	dibenzochrysenes, etc.
352	C ₂₈ H ₁₆	dibenzoperylene, etc.

At these process conditions, the raw gas spectra from the two feedstocks were qualitatively very similar. As seen in Figure 6, an increase in the severity of thermal cracking resulted in a decrease of secondary tar species as the methyl and hydroxyl groups characteristic of secondary tar species were cleaved from the aromatic structures. Table 8 shows the tar concentrations in the raw oak- and pine-derived product gas, as measured by the TMBMS for the six quantified species. Also included are estimations of “other tars” and “heavy tars.” These quantities were derived by applying the response factors for naphthalene and phenanthrene to the mass spectral summations m/z 80–176 (“other tars”) and m/z 180–400 (“heavy tars”), respectively. These values are typical of those measured during previous studies under the same conditions.

Table 8 indicates that oak gasification yielded somewhat more tar than the pine gasification. This difference is consistent with the GC results that show a noticeable increase of methane and other hydrocarbons during oak gasification. Tar concentration data from all parametric conditions are tabulated in Appendix C.

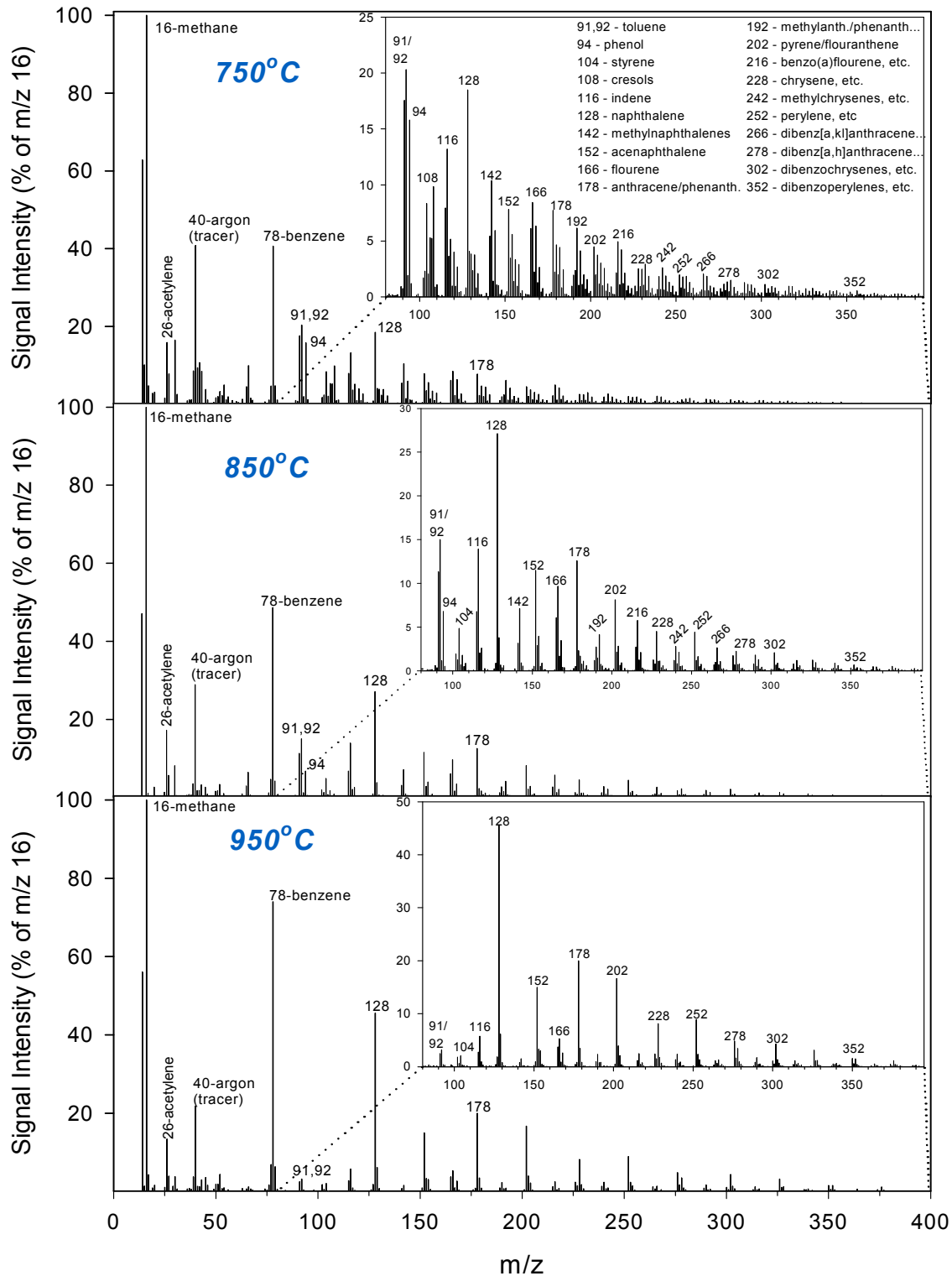


Figure 6: Time-averaged pine gasification mass spectra collected during steady-state conditions 97075, 97085, and 97095 corresponding to thermal cracker temperatures of 750°C, 850°C, and 950°C, respectively. Steam:biomass = 2:1, 8" fluidized bed = 700°C

Table 8: Comparison of tar concentrations in raw oak- and pine-derived syngas for quantified species representative of conditions established for 97085

Species	m/z	Tar Concentrations (mg/Nm ³ - wet basis)	
		oak	pine
Benzene	78	4860	4690
Toluene	92	1510	1540
Phenol	94	690	1090
Cresol	108	100	100
Naphthalene	128	1250	1310
Phenanthrene	178	390	570
“other tar” ^(a)	80-176	2900	3190
“heavy tar” ^(b)	180-400	2930	3590
Total (>m/z 78)		9770	11380

^(a)Summation of mass spectral peak intensities (m/z 80–176)—response for naphthalene used, ^(b)Summation of mass spectral peak intensities (m/z 180–400)—response for phenanthrene used

3.2.2 Reformed and Scrubbed Syngas

For the shift experiments, the raw syngas was first catalytically reformed to convert the tar contaminants into additional H₂ and CO. The reformed gas was then quenched with cold dodecane in the scrubbing system as an additional cleaning step before being fed into the shift reactor. Post-reformer syngas monitoring with the TMBMS was conducted during this portion of the test, including monitoring of the dry, quenched gas. Figure 7 shows a mass spectral comparison of the raw, reformed, and scrubbed syngas sampled during condition 97085. The TMBMS samples the gas “as is,” including any steam. Compared to the first two plots, the mass spectral components in the “post-quench” plot of Figure 7 therefore appear enhanced (by roughly a factor of two) due to the removal of steam from the sampled gas. As seen in Figure 7, some components remained in the dry gas after scrubbing—notably, toluene (m/z 91,92), styrene (m/z 104), indene (m/z 116), and naphthalene (m/z 128). All of these species, except naphthalene, appear to have increased, an indication that there may be some holdup of these components in the scrubbing system. Also of note is the appearance of a trace dodecane peak at m/z 170, indicating that some of the quench liquid carried over as vapor from the scrubbing system.

Table 9 summarizes the quantified species observed in the raw, reformed, and scrubbed gas during a shift experiment.

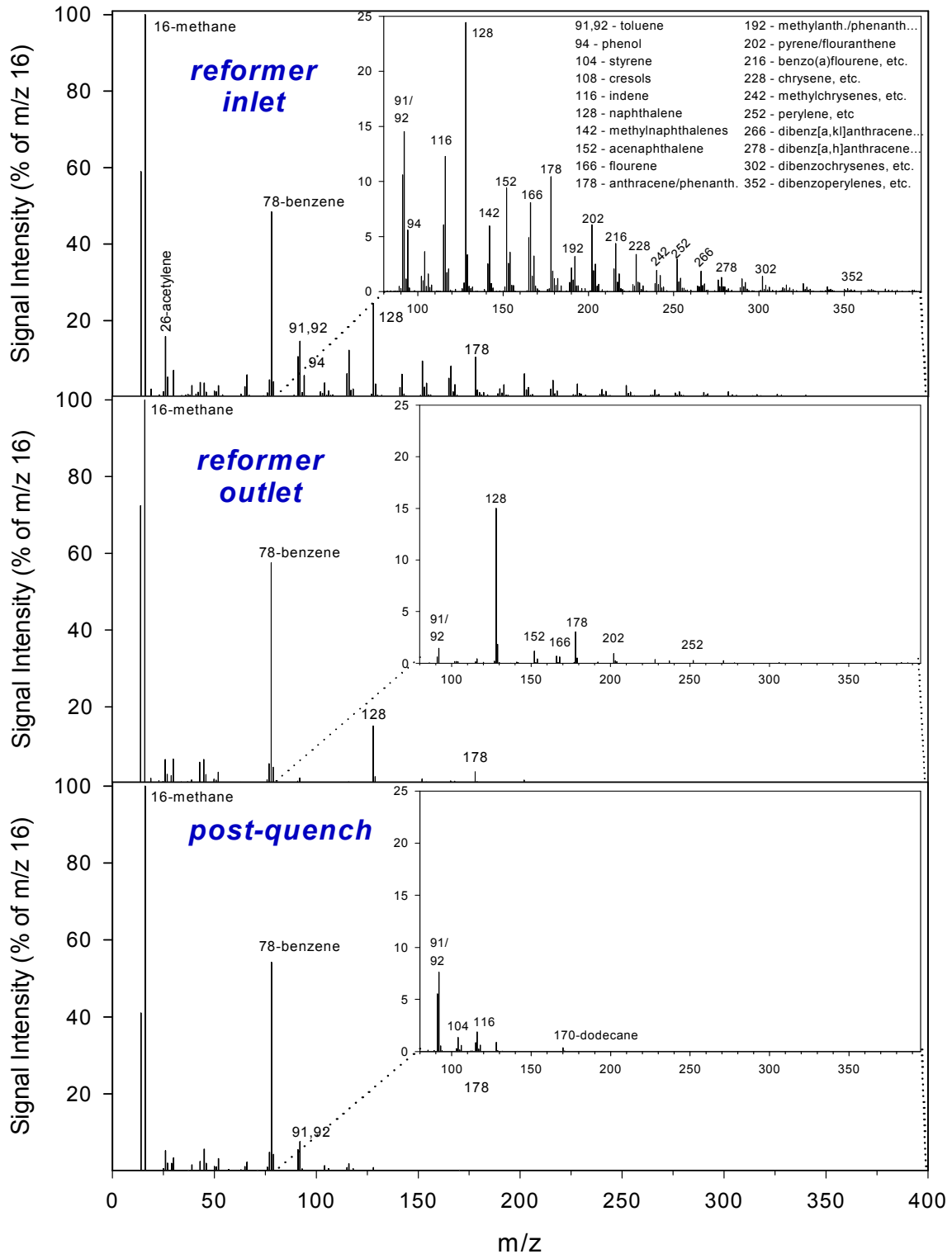


Figure 7: Time-averaged mass spectra showing components of raw, reformed, and scrubbed syngas during steady-state condition PI_HY_97850

Table 9: Average concentrations (mg/Nm³-dry basis) of pine-derived tars in raw, reformed, and scrubbed gas

Species	m/z	Tar Concentrations (mg/Nm ³ – dry basis)		
		Raw gas	Reformed gas	Scrubbed gas
Benzene	78	11170	7880	11720
Toluene	92	3650	230	1770
Phenol	94	2200	60	30
Cresol	108	180	–	–
Naphthalene	128	2980	1090	110
Phenanthrene	178	1240	230	–
“other tar” ^(a)	80-176	6300	240	530
“heavy tar” ^(b)	180-400	6270	120	–
Total (>m/z 78)		22830	1960	2430

^(a)Summation of mass spectral peak intensities (m/z 80–176)—response for naphthalene used, ^(b)Summation of mass spectral peak intensities (m/z 180–400)—response for phenanthrene used

3.3 Shift Catalyst Performance

Bottled gas was first used to test the performance of the high-temperature, water-gas shift catalyst. Table 10 shows the results of the bottled-gas test using an H₂-CO ratio of 1.0. The inlet gas composition was about 48% CO and 48% H₂ on a nitrogen-free basis. There was no CO₂ or CH₄ added in this test to try to maximize CO conversion. The highest CO conversion, 91%, was achieved using a reaction temperature of 450°C (842°F) and a gas hourly space velocity (GHSV) of 21,000. A higher steam flow rate also increases the CO conversion. When the H₂O-H₂ ratio was increased from 4.4 to 5.6, the CO conversion increased from 31% to 37%. The most important parameters are temperature and space velocity.

Table 11 shows the results of the bottled-gas test using an H₂-CO ratio of 4.2, which is more representative of the syngas produced in the TCPDU when the steam reformer is on-line. Carbon dioxide was also added at a concentration of 27%. Methane is also a major syngas component but was unavailable for this test. Similar to the previous test, the highest CO conversion, 74%, was obtained using a temperature of 450°C (842°F) and a GHSV of 21,000.

Table 10: Bottled-gas test results using an H₂-CO ratio of 1.0, no CO₂

Temp (C)	GHSV	H ₂ S (ppmv)	H ₂ O:H ₂	H ₂ O:CO	CO (vol. %)	H ₂ (vol. %)	CO ₂ (vol. %)	CH ₄ (vol. %)	CO conv	H ₂ /CO
					48.3	47.8	0.0	0	-	1.0
			reactor inlet composition							
300	39200	100	4.4	4.4	42.6	49.8	4.5	0	11.7%	1.2
350	39200	100	4.4	4.4	33.3	52.6	10.3	0	31.1%	1.6
350	45200	100	5.6	5.6	30.2	53.8	12.0	0	37.4%	1.8
400	45200	100	5.6	5.6	20.4	57.1	18.5	0	57.7%	2.8
450	45200	100	5.6	5.6	16.1	59.2	21.9	0	66.7%	3.7
450	45200	300	5.6	5.6	18.5	58.7	20.3	0	61.6%	3.2
450	21500	300	7.5	7.5	4.0	63.6	29.6	0	91.7%	15.9

Table 11: Bottled-gas test results using an H₂-CO ratio of 4.2, 27 vol% CO₂

Temp (C)	GHSV	H ₂ S (ppmv)	H ₂ O:H ₂	H ₂ O:CO	CO (vol. %)	H ₂ (vol. %)	CO ₂ (vol. %)	CH ₄ (vol. %)	CO conv	H ₂ /CO
					13.4	55.8	27.3	0	-	4.2
			reactor inlet composition							
300	20800	200	5.1	21.5	10.5	57.5	28.7	0	21.6%	5.5
350	20800	200	5.1	21.5	7.9	58.0	30.5	0	41.1%	7.3
400	20800	200	5.1	21.5	5.4	59.0	32.2	0	59.4%	10.9
450	20800	200	5.1	21.5	3.5	59.8	33.3	0	74.0%	17.1
450	41600	200	5.1	21.5	6.6	58.7	31.3	0	50.9%	8.9

The bottled-gas test showed that high-temperature, high steam-to-syngas ratio, and low space velocity increased the CO conversion. Table 12 shows the results from the shift catalyst tests using biomass-derived syngas generated by the TCPDU. For this test, the TCPDU was operated using a high steam-to-biomass ratio (2.0) and middle thermal cracker temperature (850°C). In addition, the FSR was brought on-line to reform methane and tars to increase the H₂ yield. Similar to the bottled-gas tests, maximum CO conversion was obtained at 450°C (842°F) and a GHSV of 20,000. The reaction temperature was increased from 300°C (572°F) to 450°C (842°F) and held for six hours. Initially, the CO conversion was 68% and decreased to 65% after six hours. The initial CO conversion during the actual syngas test (68%) is close to the CO conversion obtained during the bottled syngas test (74%). After the six-hour test, the steam flow reduced, and CO conversion remained relatively high at 61%.

Table 12: TCPDU-gas test results with an H₂-CO ratio of 4.2 using pine feedstock

Temp (C)	GHSV	H ₂ S (ppmv)	H ₂ O:H ₂	H ₂ O:CO	CO (vol. %)	H ₂ (vol. %)	CO ₂ (vol. %)	CH ₄ (vol. %)	CO conv	H ₂ /CO
					12.2	50.9	26.0	7.3	-	4.2
					reactor inlet composition					
300	20000	200	4.8	20.4	10.2	52.4	27.5	7.3	16.6%	5.1
350	20000	200	4.8	20.4	8.7	53.1	28.4	7.3	28.2%	6.1
400	20000	200	4.8	20.4	6.6	53.8	30.0	7.0	46.1%	8.2
450	20000	200	4.8	20.4	3.9	54.8	31.7	7.0	68.2% at 0 hr	14.1
450	20000	200	4.8	20.4	4.1	54.7	31.7	7.0	66.2% at 3 hr	13.3
450	20000	200	4.8	20.4	4.2	54.6	31.6	7.0	65.1% at 6 hr	13.0
450	14700	200	2.9	12.2	4.7	54.2	31.4	7.0	61.1%	11.5

3.4 Material and Element Balances

Overall mass closures of 94% ± 4% (mean ± standard deviation) were achieved during the parametric oak gasification studies and 93% ± 4% for pine gasification. Overall closure was obtained by accurately measuring all solid-, vapor-, and gas-phase inputs and combining the analytical measurements of gas composition, char yields, and liquid accumulation rates to determine the outputs. Appendix B contains the overall and elemental balance for each condition. Carbon balances were 89% ± 8% for oak and 96% ± 9% for pine gasification. The hydrogen balances were 103% ± 3% for oak and 102% ± 3% for pine gasification. The oxygen balances were 102% ± 3% for oak and 105% ± 4% for pine gasification.

The char accumulation in the fluidized bed and actual char yields are difficult to measure directly because steam-to-biomass ratio changes on a regular basis. The weight of the solids collected in the cyclones is measured in semi-continuous batches and includes oak or pine char and any bed material (olivine) carried over out of the reactor. A true char yield can be established if a steady-state accumulation of char in the reactor has been reached and the bed conditions are stable so the bed material carryover is constant. The level of char in the reactor reaches steady-state only for a given condition after at least several hours. Process upsets and changes in biomass feed rate or steam rate can all impact the char accumulation rate or the level of char in the reactor.

4 Conclusions

Parametric gasification tests were performed in NREL's TCPDU using oak and pine feedstocks. The parameters of interest were steam-to-biomass ratio and thermal cracker temperature. Generally, a higher steam-to-biomass ratio and a higher thermal cracker temperature increased H₂ production. Oak gasification yielded slightly more tar than pine gasification, which is consistent with GC results that show an increase of methane and other hydrocarbons during oak gasification. A slipstream fixed bed reactor was used to house a water-gas shift catalyst to increase H₂ production further. Bottled syngas tests yielded CO conversion of 74% at a reaction temperature of 450°C, an H₂O-H₂ ratio of five, and GHSV of 20,000. Pine-derived syngas using a high steam-to-biomass ratio (2.0), middle thermal cracker temperature (850°C), and full-stream reforming yielded an initial CO conversion of 68% using the same shift-reactor conditions for the bottled syngas test above. CO conversion decreased to 65% after six hours of testing the shift catalyst on pine-derived syngas. The shift catalyst was not tested with oak-derived syngas.

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Appendix A—Char Analysis

Table 13: Char analysis for oak samples

Sample ID	OK_77075	OK_77085	OK_77085b	OK_77095	OK_87075	OK_87085
Sample Date Taken	11/29/07	11/29/07	12/14/07	11/30/07	12/13/07	12/12/07
Sample Date Received	12/3/07	12/3/07	12/20/07	12/3/07	12/20/07	12/20/07
Sample Date Report	12/21/07	12/21/07	1/11/08	12/21/07	1/11/08	1/11/08
Loss on drying, %	0.64	0.33	0.38	0.17	0.7	0.51
Carbon, %	83.94	69.41	84.86	77.76	83.54	83.47
Hydrogen, %	1.43	0.99	1.29	1.04	1.24	1.2
Nitrogen, %	0.33	0.29	0.09	0.35	0.08	0.07
Oxygen, % (by diff)	0	0	4.33	0	4.41	0.86
Sulfur, %	0	0	0.01	0.01	0.02	0.01
Chlorine, %	0.009	0.005	0	0.005	0	0
Ash, %	14.83	30	9.04	22.44	10.1	10.88
Volatile matter, %	5.93	4.2	8.56	5.08	5.66	4.88
Fixed carbon, %	78.6	65.47	82.02	72.31	83.63	83.73
HHV, Btu/lb	12773	10394	13137	11646	12876	12790
Ash Al, %	0.96	0.87	0.49	1.01	0.45	0.51
Ash Ca, %	16.4	5.49	27.5	7.98	22.3	21
Ash Fe, %	6.36	7.92	4.36	7.34	5.36	5.35
Ash Mg, %	32.5	44.9	21.8	40.8	30.6	29.2
Ash P, %	1.04	0.39	1.64	0.57	1.3	1.29
Ash K, %	6.38	2.39	11.3	3.76	9.16	8.78
Ash Si, %	30.38	38.39	22.26	35.8	27.52	27.38
Ash Na, %	0.28	0.11	0.48	0.12	0.42	0.24
Ash S, %	0.38	0.18	0.52	0.07	0.57	0.43
Ash Ti, %	0.04	0.04	0.04	0.04	0.00	0.04
Ash Cl, %	0.03	0.01	0.00	0.04	0.00	0.00
Ash CO ₂ , %	4.17	1.15	6.45	3.03	5.31	5.67
Ash fusion temps, °F (those reported as 2700 are actually >2700)						
Initial- O*	2555	2700	2512	2700	2609	2567
Softening- O*	2579	2700	2236	2700	2610	2609
Hemispherical- O*	2583	2700	2557	2700	2611	2618
Fluid- O*	2600	2700	2700	2700	2612	2686
Initial- R**	2674	2700	2595	2700	2600	2627
Softening- R**	2700	2700	2616	2700	2618	2689
Hemispherical- R**	2700	2700	2636	2700	2656	2700
Fluid- R**	2700	2700	2680	2700	2700	2700

*in an oxidizing atmosphere

**in a reducing atmosphere

Table 13: Char analysis for oak samples cont.

Sample ID	OK_87085b	OK_87095	OK_97075	OK_97085	OK_97085b	OK_97095
Sample Date Taken	12/18/07	12/12/07	11/28/07	11/28/07	12/17/07	11/20/07
Sample Date Received	12/20/07	12/20/07	12/3/07	12/3/07	12/20/07	12/3/07
Sample Date Report	1/11/08	1/11/08	12/21/07	12/21/07	1/11/08	12/21/07
Loss on drying, %	0.47	0.65	0.67	0.31	0.97	0.48
Carbon, %	86.66	86.35	70.82	71.36	88.64	54.48
Hydrogen, %	1.26	1.04	1.12	1.11	1.17	0.68
Nitrogen, %	0.08	0.19	0.3	0.3	0.21	0.25
Oxygen, % (by diff)	4.38	2.32	0	0	0.87	0
Sulfur, %	0.02	0.01	0.05	0.03	0.02	0.03
Chlorine, %	0	0	0.005	0.005	0	0.005
Ash, %	7.13	9.44	28.41	30.28	8.12	45.04
Volatile matter, %	8.46	7.26	4.24	4.32	7.95	3.1
Fixed carbon, %	83.94	82.65	66.68	65.09	82.96	51.38
HHV, Btu/lb	13534	13089	10634	10353	13212	8205
Ash Al, %	0.22	0.57	0.92	0.97	0.49	1.26
Ash Ca, %	30.2	26.6	6.05	6.65	24.2	3.44
Ash Fe, %	3.65	4.47	7.66	7.59	4.34	7.89
Ash Mg, %	18.3	22.2	43.5	42.7	23	45
Ash P, %	1.88	1.58	0.42	0.41	1.5	0.26
Ash K, %	13.4	11.3	2.45	2.61	10.7	1.47
Ash Si, %	19.17	23.04	38.3	38.1	23.42	40.01
Ash Na, %	0.42	2.26	0.15	0.11	0.26	0.09
Ash S, %	0.53	0.38	0.25	0.13	0.31	0.15
Ash Ti, %	0.04	0.04	0.00	0.00	0.04	0.00
Ash Cl, %	0.05	0.01	0.00	0.02	0.02	0.02
Ash CO2, %	13.87	10.29	1.13	1.76	15.04	1.84
Ash fusion temps, °F (those reported as 2700 are actually >2700)						
Initial- O*	2700	2500	2700	2700	2500	2700
Softening- O*	2700	2511	2700	2700	2517	2700
Hemispherical- O*	2700	2519	2700	2700	2536	2700
Fluid- O*	2700	2525	2700	2700	2547	2700
Initial- R**	2700	2608	2700	2700	2629	2700
Softening- R**	2700	2618	2700	2700	2634	2700
Hemispherical- R**	2700	2621	2700	2700	2640	2700
Fluid- R**	2700	2624	2700	2700	2644	2700

*in an oxidizing atmosphere

**in a reducing atmosphere

Table 14: Char analysis for pine samples

Sample ID	PI_77075	PI_77085	PI_77095	PI_87075	PI_87085
Sample Date Taken	9/2/08	9/3/08	9/4/08	9/9/08	9/8/08
Sample Date					
Received	9/10/08	9/10/08	9/10/08	9/19/08	9/19/08
Sample Date Report	9/17/08	9/17/08	9/17/08	10/1/08	10/1/08
Loss on drying, %	0.99	1.08	1.16	0.6	0.51
Carbon, %	81.63	67.54	74.08	82.53	81.53
Hydrogen, %	1.07	0.53	0.62	1.15	1.1
Nitrogen, %	0.14	0.1	0.14	0.1	0.1
Oxygen, % (by diff)	0.35	0.88	0.15	0.06	0.01
Sulfur, %	0.01	0.01	0.01	0.01	0.01
Chlorine, %	0.01	0.01	0.01	0.02	0.03
Ash, %	15.82	29.87	23.85	15.56	16.88
Volatile matter, %	5	3.7	3.01	3.27	4.35
Fixed carbon, %	78.19	65.35	71.98	80.57	78.26
HHV, Btu/lb	12484	10244	11055	12767	12305
Ash Al, %	2.05	1.09	0.96	0.85	0.94
Ash Ca, %	6.63	3.4	5.14	7.03	4.69
Ash Fe, %	7.17	7.96	7.49	6.81	7.31
Ash Mg, %	40.4	47.7	45.5	38.8	41.6
Ash P, %	1.01	0.43	0.8	1.27	0.85
Ash K, %	3.83	1.6	3	4.39	3.08
Ash Si, %	37	41.31	38.12	33.52	36.62
Ash Na, %	0.15	0.07	0.15	0.14	0.04
Ash S, %	0.12	0.08	0.14	0.3	0.14
Ash Ti, %	0.18	0.04	0.05	0.01	0.04
Ash Cl, %	0.04	0.01	0.05	0.01	0.01
Ash CO2, %	1.97	0.72	1.88	5.33	3.99
Ash fusion temps, °F (those reported as 2700 are actually >2700)					
Initial- O*	2700	2700	2700	2505	2700
Softening- O*	2700	2700	2700	2519	2700
Hemispherical- O*	2700	2700	2700	2531	2700
Fluid- O*	2700	2700	2700	2549	2700
Initial- R**	2700	2700	2700	2700	2700
Softening- R**	2700	2700	2700	2700	2700
Hemispherical- R**	2700	2700	2700	2700	2700
Fluid- R**	2700	2700	2700	2700	2700

*in an oxidizing atmosphere

**in a reducing atmosphere

Table 14: Char analysis for pine samples cont.

Sample ID	PI_87095	PI_97075	PI_97085	PI_97085b	PI_97095
Sample Date Taken	9/5/08	8/28/08	8/27/08	9/11/08	8/25/08
Sample Date Received	9/19/08	9/10/08	9/10/08	9/19/08	9/10/08
Sample Date Report	10/1/08	9/17/08	9/17/08	10/1/08	9/17/08
Loss on drying, %	0.42	0.99	0.92	1	0.94
Carbon, %	76.44	75.17	71.16	88.67	71.37
Hydrogen, %	1.01	0.92	0.78	1.29	0.68
Nitrogen, %	0.06	0.13	0.17	0.01	0.18
Oxygen, % (by diff)	0.01	0.01	0.01	0.38	0.74
Sulfur, %	0.01	0.01	0.01	0.01	0.01
Chlorine, %	0.03	0.01	0.02	0.03	0.01
Ash, %	22.06	22.84	27.26	8.65	26.09
Volatile matter, %	3.67	4.4	5.32	4.09	4.56
Fixed carbon, %	73.85	71.77	66.5	86.26	68.41
HHV, Btu/lb	11443	11364	10789	13470	10798
Ash Al, %	1.02	2.82	9.92	1.08	15.52
Ash Ca, %	4.09	3.08	5.21	12.7	4.18
Ash Fe, %	7.47	7.4	5.38	5.6	4.39
Ash Mg, %	42.8	43.4	30.4	31.6	24.5
Ash P, %	0.74	0.4	0.56	2.28	0.67
Ash K, %	2.7	1.48	1.83	8.49	1.01
Ash Si, %	37.19	38.95	29.4	26.67	27.32
Ash Na, %	0.03	0.07	0.14	0.18	0.06
Ash S, %	0.13	0.07	0.11	0.64	0.11
Ash Ti, %	0.04	0.18	0.68	0.01	0.45
Ash Cl, %	0.01	0.06	0.07	0.01	0.08
Ash CO ₂ , %	3.56	1.36	3.15	8.43	0.49
Ash fusion temps, °F (those reported as 2700 are actually >2700)					
Initial- O*	2700	2700	2700	2611	2700
Softening- O*	2700	2700	2700	2689	2700
Hemispherical- O*	2700	2700	2700	2700	2700
Fluid- O*	2700	2700	2700	2700	2700
Initial- R**	2700	2700	2673	2645	2660
Softening- R**	2700	2700	2678	2649	2694
Hemispherical- R**	2700	2700	2680	2651	2700
Fluid- R**	2700	2700	2682	2657	2700

*in an oxidizing atmosphere

**in a reducing atmosphere

Appendix B—Mass Balances

Table 15: Mass balances for oak gasification conditions

	OK_HY_77075			OK_HY_77085			OK_HY_77085b		
	Mass In, kg/hr	Mass Out, kg/hr	Mass Out/Mass In, %	Mass In, kg/hr	Mass Out, kg/hr	Mass Out/Mass In, %	Mass In, kg/hr	Mass Out, kg/hr	Mass Out/Mass In, %
Closure	32.5	29.1	89.7%	32.5	30.8	94.8%	32.5	28.5	87.7%
Ash	0.10	0.09	90.5%	0.10	0.57	577.1%	0.10	0.05	53.4%
C	9.05	6.85	75.7%	9.05	7.87	87.0%	9.04	7.05	78.0%
H	2.50	2.58	103.5%	2.50	2.65	106.1%	2.50	2.54	101.7%
O	19.69	20.5	104.1%	19.69	20.6	104.7%	19.69	19.8	100.7%
N	0.009	0.002	21.3%	0.009	0.006	59.1%	0.009	0.001	5.6%
S	0.006	0.000	1.2%	0.006	0.003	45.8%	0.006	0.002	40.9%
Hx	0.001	0.000	5.8%	0.001	0.000	10.2%	0.001	0.000	0.0%
Ash_Al	0.001	0.001	95.5%	0.001	0.005	551.7%	0.001	0.000	28.7%
Ash_Ca	0.042	0.015	35.0%	0.042	0.031	74.7%	0.042	0.014	34.6%
Ash_Fe	0.001	0.006	810.6%	0.001	0.045	6437.3%	0.001	0.002	327.6%
Ash_Mg	0.002	0.029	1455.9%	0.002	0.256	12827.2%	0.002	0.011	575.8%
Ash_P	0.003	0.001	35.9%	0.003	0.002	85.9%	0.003	0.001	33.4%
Ash_K	0.019	0.006	30.5%	0.019	0.014	73.0%	0.019	0.006	31.9%
Ash_Si	0.004	0.027	719.6%	0.004	0.219	5799.5%	0.004	0.012	310.9%
Ash_Na	0.000	0.000	58.9%	0.000	0.001	147.6%	0.000	0.000	59.6%
Ash_S	0.003	0.000	13.1%	0.003	0.001	39.5%	0.003	0.000	10.5%
Ash_Hx	0.000	0.000	90.5%	0.000	0.000	192.4%	0.000	0.000	0.0%
Ash_CO2	0.024	0.004	15.4%	0.024	0.007	27.1%	0.024	0.003	14.1%

Table 15: Mass balances for oak gasification conditions cont.

	OK_HY_77095			OK_HY_87075			OK_HY_87085		
	Mass In, kg/hr	Mass Out, kg/hr	Mass Out/ Mass In, %	Mass In, kg/hr	Mass Out, kg/hr	Mass Out/ Mass In, %	Mass In, kg/hr	Mass Out, kg/hr	Mass Out/ Mass In, %
Closure	32.4	29.2	90.0%	31.2	28.2	90.3%	31.3	29.7	94.9%
Ash	0.10	0.52	529.1%	0.07	0.10	141.2%	0.07	0.11	147.3%
C	9.02	8.56	94.9%	6.74	5.60	83.0%	6.76	5.81	86.0%
H	2.49	2.49	99.7%	2.65	2.61	98.5%	2.65	2.77	104.8%
O	19.67	18.8	95.7%	20.91	20.6	98.4%	20.92	21.6	103.4%
N	0.009	0.008	87.5%	0.007	0.001	11.9%	0.007	0.001	10.0%
S	0.006	0.004	67.5%	0.004	0.000	7.4%	0.004	0.005	109.6%
Hx	0.001	0.000	12.5%	0.001	0.000	0.0%	0.001	0.000	0.0%
Ash_Al	0.001	0.005	587.2%	0.001	0.000	69.8%	0.001	0.001	82.5%
Ash_Ca	0.042	0.042	99.6%	0.031	0.023	74.3%	0.031	0.023	72.9%
Ash_Fe	0.001	0.038	5469.8%	0.001	0.006	1065.8%	0.001	0.006	1109.8%
Ash_Mg	0.002	0.212	10686.6%	0.001	0.032	2138.6%	0.001	0.032	2129.1%
Ash_P	0.003	0.003	115.1%	0.002	0.001	70.0%	0.002	0.001	72.5%
Ash_K	0.019	0.020	105.3%	0.014	0.010	68.4%	0.014	0.010	68.4%
Ash_Si	0.004	0.186	4958.5%	0.003	0.029	1017.1%	0.003	0.030	1055.7%
Ash_Na	0.000	0.001	147.7%	0.000	0.000	137.9%	0.000	0.000	82.2%
Ash_S	0.003	0.000	14.1%	0.002	0.001	30.6%	0.002	0.000	24.1%
Ash_Hx	0.000	0.000	705.5%	0.000	0.000	0.0%	0.000	0.000	0.0%
Ash_CO2	0.024	0.016	65.5%	0.018	0.006	30.6%	0.018	0.006	34.1%

Table 15: Mass balances for oak gasification conditions cont.

	OK_HY_87085b			OK_HY_87095			OK_HY_97075		
	Mass In, kg/hr	Mass Out, kg/hr	Mass Out/ Mass In, %	Mass In, kg/hr	Mass Out, kg/hr	Mass Out/ Mass In, %	Mass In, kg/hr	Mass Out, kg/hr	Mass Out/ Mass In, %
Closure	31.2	30.5	97.8%	31.1	30.0	96.3%	30.4	29.4	96.8%
Ash	0.07	0.07	94.1%	0.07	0.08	109.2%	0.05	0.29	538.5%
C	6.73	6.26	93.0%	6.70	5.85	87.4%	4.93	4.29	87.1%
H	2.64	2.85	107.9%	2.64	2.84	107.5%	2.78	2.86	102.9%
O	20.90	22.3	106.6%	20.87	21.9	104.7%	22.00	22.5	102.3%
N	0.007	0.001	11.2%	0.007	0.002	23.3%	0.005	0.003	60.3%
S	0.004	0.005	116.1%	0.004	0.005	118.0%	0.003	0.001	17.4%
Hx	0.001	0.000	0.0%	0.001	0.000	0.0%	0.001	0.000	10.0%
Ash_Al	0.001	0.000	22.8%	0.001	0.000	68.4%	0.000	0.003	544.4%
Ash_Ca	0.031	0.021	67.0%	0.031	0.021	68.5%	0.023	0.018	76.8%
Ash_Fe	0.001	0.003	483.9%	0.001	0.004	687.3%	0.000	0.022	5809.9%
Ash_Mg	0.001	0.013	852.7%	0.001	0.018	1199.8%	0.001	0.126	11596.8%
Ash_P	0.002	0.001	67.5%	0.002	0.001	65.8%	0.001	0.001	86.3%
Ash_K	0.014	0.009	66.7%	0.014	0.009	65.3%	0.010	0.007	69.8%
Ash_Si	0.003	0.013	472.3%	0.003	0.018	658.4%	0.002	0.111	5399.3%
Ash_Na	0.000	0.000	91.9%	0.000	0.002	573.8%	0.000	0.000	187.9%
Ash_S	0.002	0.000	19.0%	0.002	0.000	15.8%	0.001	0.001	51.2%
Ash_Hx	0.000	0.000	156.9%	0.000	0.000	36.4%	0.000	0.000	0.0%
Ash_CO2	0.018	0.010	53.3%	0.018	0.008	45.9%	0.013	0.003	24.9%

Table 15: Mass balances for oak gasification conditions cont.

	OK_HY_97085			OK_HY_97085b			OK_HY_97095		
	Mass In, kg/hr	Mass Out, kg/hr	Mass Out/ Mass In, %	Mass In, kg/hr	Mass Out, kg/hr	Mass Out/ Mass In, %	Mass In, kg/hr	Mass Out, kg/hr	Mass Out/ Mass In, %
Closure	30.3	29.1	95.9%	30.3	30.1	99.6%	30.3	30.3	100.0%
Ash	0.05	0.27	505.1%	0.05	0.12	234.1%	0.05	0.62	1167.5%
C	4.90	4.23	86.3%	4.86	5.00	102.8%	4.87	4.66	95.7%
H	2.78	2.83	102.0%	2.77	2.89	104.1%	2.77	2.95	106.2%
O	21.97	22.2	101.0%	21.94	22.6	102.9%	21.95	22.7	103.5%
N	0.005	0.003	53.0%	0.005	0.003	64.2%	0.005	0.003	68.7%
S	0.003	0.003	112.2%	0.003	0.004	125.7%	0.003	0.001	40.3%
Hx	0.001	0.000	8.8%	0.001	0.000	0.0%	0.001	0.000	13.7%
Ash_Al	0.000	0.003	538.4%	0.000	0.001	126.0%	0.000	0.008	1616.5%
Ash_Ca	0.023	0.018	79.2%	0.023	0.030	133.6%	0.023	0.021	94.7%
Ash_Fe	0.000	0.020	5399.7%	0.000	0.005	1430.9%	0.000	0.049	12973.7%
Ash_Mg	0.001	0.115	10677.2%	0.001	0.029	2665.3%	0.001	0.279	26007.9%
Ash_P	0.001	0.001	79.0%	0.001	0.002	134.0%	0.001	0.002	115.9%
Ash_K	0.010	0.007	69.8%	0.010	0.013	132.5%	0.010	0.009	90.8%
Ash_Si	0.002	0.103	5037.8%	0.002	0.029	1435.1%	0.002	0.248	12227.8%
Ash_Na	0.000	0.000	129.2%	0.000	0.000	141.5%	0.000	0.001	244.4%
Ash_S	0.001	0.000	25.0%	0.001	0.000	27.6%	0.001	0.001	66.6%
Ash_Hx	0.000	0.000	336.7%	0.000	0.000	156.1%	0.000	0.000	778.3%
Ash_CO2	0.013	0.005	36.3%	0.013	0.019	143.9%	0.013	0.011	87.8%

Table 15: Mass balances for oak gasification conditions cont.

	OK_HY_97095b		
	Mass In, kg/hr	Mass Out, kg/hr	Mass Out/ Mass In, %
Closure	30.3	28.5	94.0%
Ash	0.05	0.22	406.3%
C	4.89	5.05	103.4%
H	2.77	2.73	98.5%
O	21.96	21.1	96.2%
N	0.005	0.001	24.3%
S	0.003	0.005	180.3%
Hx	0.001	0.000	0.0%
Ash_Al	0.000	0.002	361.6%
Ash_Ca	0.023	0.041	179.2%
Ash_Fe	0.000	0.013	3364.5%
Ash_Mg	0.001	0.069	6415.7%
Ash_P	0.001	0.002	165.9%
Ash_K	0.010	0.018	177.1%
Ash_Si	0.002	0.065	3180.9%
Ash_Na	0.000	0.001	359.0%
Ash_S	0.001	0.001	54.1%
Ash_Hx	0.000	0.000	270.8%
Ash_CO2	0.013	0.010	74.7%

Table 16: Mass balances for pine gasification conditions

	PI_HY_77075			PI_HY_77085			PI_HY_77095		
	Mass In, kg/hr	Mass Out, kg/hr	Mass Out/ Mass In, %	Mass In, kg/hr	Mass Out, kg/hr	Mass Out/ Mass In, %	Mass In, kg/hr	Mass Out, kg/hr	Mass Out/ Mass In, %
Closure	32.1	30.3	94.6%	32.0	29.3	91.5%	32.0	27.4	85.6%
Ash	0.05	0.33	633.8%	0.05	0.66	1250.7%	0.05	0.18	345.4%
C	8.72	8.06	92.5%	8.70	7.95	91.4%	8.69	6.92	79.7%
H	2.66	2.77	103.9%	2.66	2.74	102.9%	2.66	2.57	96.7%
O	18.98	20.8	109.7%	18.97	20.4	107.3%	18.96	19.1	100.6%
N	0.011	0.003	28.0%	0.011	0.002	20.9%	0.010	0.001	10.1%
S	0.004	0.000	6.0%	0.004	0.001	25.5%	0.003	0.001	20.9%
Hx	0.000	0.000	120.2%	0.000	0.000	125.6%	0.000	0.000	43.4%
Ash_Al	0.001	0.007	843.7%	0.001	0.007	885.3%	0.001	0.002	215.3%
Ash_Ca	0.015	0.022	144.9%	0.015	0.022	146.6%	0.015	0.009	61.2%
Ash_Fe	0.001	0.024	2249.8%	0.001	0.052	4928.7%	0.001	0.014	1280.6%
Ash_Mg	0.006	0.135	2438.7%	0.006	0.313	5682.0%	0.006	0.082	1496.6%
Ash_P	0.003	0.003	122.2%	0.003	0.003	102.6%	0.003	0.001	52.7%
Ash_K	0.010	0.013	128.4%	0.010	0.011	105.9%	0.010	0.005	54.8%
Ash_Si	0.003	0.124	4350.9%	0.003	0.271	9586.0%	0.003	0.069	2442.5%
Ash_Na	0.000	0.001	243.8%	0.000	0.000	224.5%	0.000	0.000	132.8%
Ash_S	0.002	0.000	23.3%	0.002	0.001	30.7%	0.002	0.000	14.8%
Ash_Hx	0.000	0.000	149.1%	0.000	0.000	73.6%	0.000	0.000	101.6%
Ash_CO2	0.011	0.007	58.7%	0.011	0.005	42.3%	0.011	0.003	30.5%

Table 16: Mass balances for pine gasification conditions cont.

	PI_HY_87075			PI_HY_87085			PI_HY_87095		
	Mass In, kg/hr	Mass Out, kg/hr	Mass Out/ Mass In, %	Mass In, kg/hr	Mass Out, kg/hr	Mass Out/ Mass In, %	Mass In, kg/hr	Mass Out, kg/hr	Mass Out/ Mass In, %
Closure	31.5	28.1	89.2%	31.5	30.5	96.9%	31.5	29.9	95.0%
Ash	0.04	0.21	507.1%	0.04	0.18	434.2%	0.04	0.26	620.6%
C	6.91	6.88	99.5%	6.89	6.80	98.7%	6.89	5.92	86.0%
H	2.79	2.72	97.7%	2.78	2.84	101.9%	2.78	2.81	101.1%
O	20.41	20.8	101.8%	20.40	21.6	105.8%	20.39	21.7	106.3%
N	0.008	0.001	16.3%	0.008	0.001	12.9%	0.008	0.001	8.4%
S	0.003	0.000	4.9%	0.003	0.001	22.5%	0.003	0.001	21.9%
Hx	0.000	0.000	195.5%	0.000	0.000	231.5%	0.000	0.000	253.2%
Ash_Al	0.001	0.002	279.9%	0.001	0.002	265.0%	0.001	0.003	411.1%
Ash_Ca	0.012	0.015	122.9%	0.012	0.008	70.2%	0.012	0.011	87.5%
Ash_Fe	0.001	0.014	1709.6%	0.001	0.013	1571.1%	0.001	0.019	2295.2%
Ash_Mg	0.004	0.082	1873.9%	0.004	0.075	1720.1%	0.004	0.110	2529.9%
Ash_P	0.002	0.003	122.9%	0.002	0.002	70.4%	0.002	0.002	87.6%
Ash_K	0.008	0.009	117.8%	0.008	0.006	70.8%	0.008	0.007	88.7%
Ash_Si	0.002	0.071	3153.7%	0.002	0.066	2949.7%	0.002	0.096	4282.4%
Ash_Na	0.000	0.000	182.0%	0.000	0.000	44.5%	0.000	0.000	47.7%
Ash_S	0.001	0.001	46.7%	0.001	0.000	18.6%	0.001	0.000	24.7%
Ash_Hx	0.000	0.000	29.8%	0.000	0.000	25.5%	0.000	0.000	36.5%
Ash_CO2	0.009	0.011	127.1%	0.009	0.007	81.4%	0.009	0.009	103.9%

Table 16: Mass balances for pine gasification conditions cont.

	PI_HY_97075			PI_HY_97085			PI_HY_97085b		
	Mass In, kg/hr	Mass Out, kg/hr	Mass Out/ Mass In, %	Mass In, kg/hr	Mass Out, kg/hr	Mass Out/ Mass In, %	Mass In, kg/hr	Mass Out, kg/hr	Mass Out/ Mass In, %
Closure	30.6	30.5	99.8%	30.6	29.4	96.3%	30.6	29.0	94.6%
Ash	0.03	0.21	695.8%	0.03	0.63	2083.2%	0.03	0.06	188.0%
C	5.00	5.31	106.1%	4.98	5.56	111.6%	5.03	5.08	101.0%
H	2.88	3.00	104.2%	2.87	3.12	108.7%	2.88	2.84	98.8%
O	21.60	22.9	105.8%	21.59	24.3	112.7%	21.61	21.8	101.0%
N	0.006	0.001	19.8%	0.006	0.004	65.0%	0.006	0.000	1.1%
S	0.002	0.000	4.6%	0.002	0.001	31.0%	0.002	0.000	21.4%
Hx	0.000	0.000	91.4%	0.000	0.000	458.5%	0.000	0.000	195.6%
Ash_Al	0.000	0.006	1274.2%	0.000	0.062	13419.2%	0.000	0.001	131.8%
Ash_Ca	0.009	0.006	73.9%	0.009	0.033	374.3%	0.009	0.007	82.3%
Ash_Fe	0.001	0.016	2549.1%	0.001	0.034	5548.4%	0.001	0.003	521.1%
Ash_Mg	0.003	0.091	2876.1%	0.003	0.191	6031.4%	0.003	0.018	565.7%
Ash_P	0.002	0.001	53.1%	0.002	0.004	222.6%	0.002	0.001	81.8%
Ash_K	0.006	0.003	54.5%	0.006	0.011	201.7%	0.006	0.005	84.4%
Ash_Si	0.002	0.082	5028.4%	0.002	0.184	11363.0%	0.002	0.015	930.1%
Ash_Na	0.000	0.000	124.9%	0.000	0.001	747.8%	0.000	0.000	86.8%
Ash_S	0.001	0.000	14.9%	0.001	0.001	70.3%	0.001	0.000	36.9%
Ash_Hx	0.000	0.000	245.6%	0.000	0.000	857.8%	0.000	0.000	11.1%
Ash_CO2	0.006	0.003	44.5%	0.006	0.020	308.5%	0.006	0.005	74.5%

Table 16: Mass balances for pine gasification conditions cont.

	PI_HY_97095		
	Mass In, kg/hr	Mass Out, kg/hr	Mass Out/ Mass In, %
Closure	30.5	26.9	88.2%
Ash	0.03	0.07	228.7%
C	4.98	4.79	96.2%
H	2.87	2.98	103.5%
O	21.58	22.3	103.5%
N	0.006	0.001	9.2%
S	0.002	0.000	1.4%
Hx	0.000	0.000	86.8%
Ash_Al	0.000	0.011	2359.5%
Ash_Ca	0.009	0.004	43.2%
Ash_Fe	0.001	0.003	474.3%
Ash_Mg	0.003	0.017	533.6%
Ash_P	0.002	0.000	27.5%
Ash_K	0.006	0.001	20.4%
Ash_Si	0.002	0.017	1056.0%
Ash_Na	0.000	0.000	129.0%
Ash_S	0.001	0.000	8.4%
Ash_Hx	0.000	0.000	80.7%
Ash_CO2	0.006	0.001	16.7%

Appendix C—Tar Concentrations

Table 17: Absolute wet gas concentrations (mg/Nm³) of selected tars measured during steady-state oak gasification.

Run ID	77075	77085	77085b	77095	87075	87085	87085b	87095	97075	97085	97085b	97095	97095b
S:B ratio	0.74	0.74	0.74	0.74	1.25	1.25	1.25	1.25	2.00	2.00	2.00	2.00	2.00
TC Temp (°C)	750	850	850	950	750	850	850	950	750	850	850	950	950
<i>Tars (mg/Nm³)</i>													
Benzene	4870	7638	9790	12400	4290	7310	6728	10520	2980	4990	4724	7790	6874
Toluene	2520	2290	2950	440	2200	2240	2060	400	1460	1550	1470	390	330
Phenol	1770	810	880	30	1610	820	730	20	1580	730	650	50	40
Cresol	1320	120	110	20	1100	110	100	10	910	110	80	30	20
naphthalene	1000	2090	3040	4010	940	2050	1940	3570	610	1300	1200	2380	1830
phenanthrene	260	650	1040	1290	250	640	580	1190	170	420	360	790	540
“other tars” ^(a)	6060	4360	5910	3200	5350	4110	4060	2810	3960	3170	2640	2160	1690
“heavy tars” ^(b)	7210	6030	3790	8720	5440	4720	2340	6040	3930	3070	2790	5670	4280
Total (>m/z 78)	20130	16350	17710	17710	16900	14700	11800	14040	12630	10350	9190	11470	8720

^(a)Summation of mass spectral peak intensities (m/z 80–176)—response for naphthalene used, ^(b)Summation of mass spectral peak intensities (m/z 180–400)—response for phenanthrene used

Table 18: Absolute wet gas concentrations (mg/Nm³) of selected tars measured during steady-state pine gasification.

Run ID	77075	77085	77095	87075	87085	87095	97075	97085	97085b	97095
S:B ratio	0.81	0.81	0.81	1.25	1.25	1.25	2.00	2.00	2.00	2.00
TC Temp (°C)	750	850	950	750	850	950	750	850	850	950
<i>Tars (mg/Nm³)</i>										
benzene	4310	8130	12530	3830	8650	9260	2580	4970	4405	7490
toluene	2470	2720	490	2040	2850	420	1380	1640	1430	280
phenol	3270	1570	80	2530	1700	60	1710	1180	1000	20
cresol	1580	150	20	1100	150	20	790	110	90	—
naphthalene	1000	2450	4210	890	2460	3020	620	1470	1150	2520
phenanthrene	400	1090	1860	350	1040	1290	260	670	480	1150
“other tars” ^(a)	6870	5770	3860	5440	5720	2830	3710	3560	2820	2840
“heavy tars” ^(b)	7690	7560	9990	5480	6210	5810	4000	4300	2880	5830
Total (>m/z 78)	23280	21310	20507	17830	20110	13450	12470	12910	9850	12630

^(a)Summation of mass spectral peak intensities (m/z 80–176)—response for naphthalene used, ^(b)Summation of mass spectral peak intensities (m/z 180–400)—response for phenanthrene used

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