Milestone Report

Catalytic Steam Reforming of Gasifier Tars: On-line Monitoring of Tars with a Transportable Molecular Beam Mass Spectrometer

Milestone Completion Report

Daniel Carpenter, Matthew Ratcliff, and David Dayton

NREL

National Renewable Energy Laboratory

Catalytic Steam Reforming of Gasifier Tars: On-line Monitoring of Tars with a Transportable Molecular Beam Mass Spectrometer

Milestone Completion Report

Daniel Carpenter, Matthew Ratcliff, and David Dayton

NREL

National Renewable Energy Laboratory

NOTICE

MILESTONE COMPLETION REPORT

PROGRAM:	**Biomass Power**
TECHNOLOGY MANAGER:	**Kevin Craig**
MILESTONE TITLE:	**Catalytic Steam Reforming of Gasifier Tars: On-Line Monitoring of Tars with a Transportable Molecular-Beam Mass Spectrometer**
MILESTONE TYPE:	**C, FY01**
COMPLETION DATE:	**9/01**
REPORTED BY:	**D. Carpenter, M. Ratcliff, D. Dayton**
PARTICIPATING MILESTONE RESEARCHERS:	**C. Baca-Overly, S. Czernik, S. Deutch, C. Feik, R. French, J. Graham, J. Patrick, S. Phillips**
PROJECT:	**Integrated Systems Testing, BP012130**

CONTENTS

FIGURES

TABLES

Executive Summary

Catalytic tar decomposition remains a key technical hurdle to commercializing biomass gasification. Decomposition of the tars, i.e. catalytic steam reforming of the organic "tar" compounds to hydrogen and carbon monoxide, increases the overall yield of fuel gas from the biomass. More importantly, it minimizes (and potentially eliminates) the need for water scrubbing of the product gases, which is expensive in terms of equipment and operation/maintenance costs and process efficiency. The work presented here is a follow-up effort to catalyst tests performed at Battelle Columbus Laboratories' (BCL) biomass gasification facility during the winter of 1999-2000. That work was performed under Department of Energy (DOE) field work proposal (FWP) No. WU94, which in turn was related to DOE Contract No. DE-FB02-98CH10942. The focus of that contract was to operate a gas turbine on biomass-derived synthesis gas (more properly, and henceforth called pyrolysis gas), and to demonstrate that a BCL-patented catalyst (DN34) could effectively decompose gasifier tars. A 10-ton per day, integrated gasifier-gas turbine system at BCL's West Jefferson, OH facility was used for the contracted project. Under the FWP, NREL's Transportable Molecular Beam Mass Spectrometer (TMBMS) was installed on that system to monitor the performance of the catalyst in real-time. Difficulties with achieving suitably high temperatures in the catalytic reactor resulted in premature coking of the DN34 catalyst. Consequently, the catalyst was deactivated and virtually no tar decomposition was measured by the TMBMS. The fact that some tar was removed from the pyrolysis gas by the catalytic reactor (as measured by the collection of tar by Modified Method 5 impinger sampling) was attributed to the accumulation of high molecular weight (low vapor pressure) tar compounds on the DN34 catalyst as coke deposits.

The results reported here are from a smaller, but more selectively targeted effort to determine the efficacy of DN34 as a tar destruction catalyst. The catalyst testing was performed using NREL's Thermochemical Process Development Unit (TCPDU), in parallel with operations for integrated gasifier-engine-generator system tests. Mixed hardwood and softwood biomass was gasified at rates of 10-14 kg/h, which produced pyrolysis gas identical to that made by BCL's gasifier. A hot slip-stream of the raw pyrolysis gas was conducted to a 2-in. fluidized bed reactor (2FBR) system, specifically designed for testing steam reforming catalysts. The coupling of the TCPDU and 2FBR allowed independent operation and control of the catalyst bed, ensuring that the catalyst was at the desired conditions before exposure to the raw pyrolysis gas. The TMBMS, as well as rapid analysis gas chromatographs, were installed "across" the 2FBR to monitor the performance of the catalyst in real-time.

In addition to DN34, a commercial, nickel-based naphtha steam reforming catalyst and silica sand were tested for comparison. These materials were tested over the range of 700°-900°C, with and without supplemental steam. The results showed no conclusive evidence that DN34 possesses catalytic activity for gasifier tar decomposition, even at 850°C. A few compounds such as phenol and cresol were decomposed by DN34. However, this was probably the result of thermal decomposition (more time at temperature, plus surface area effects) due to the relatively labile nature of these compounds, since similar results were obtained with silica sand. In contrast, the nickel catalyst showed very high activity for tar decomposition, essentially 100% tar conversion at 750°C. Moreover, the nickel catalyst retained most of its activity for over 11 hours of operation.

While the results with the commercial nickel-based catalyst were encouraging, there are concerns with the environmental and health aspects of nickel. Subsequent work planned for fiscal year 2002 under the Biomass Power Program will identify and test other catalysts for tar decomposition that do not have the liabilities of nickel based formulations.

Catalytic Steam Reforming of Gasifier Tars: On-Line Monitoring of Tars with a Transportable Molecular-Beam Mass Spectrometer

Introduction

A key technical and economic barrier to commercialization of biomass gasification technologies is the removal of tars that are unavoidably formed in this thermochemical process. Tars contain fuel value; however, they are problematic in gas engines (both reciprocating and turbine) because they condense in the fuel delivery system, forming deposits that negatively affect operation and efficiency. These tars also combust with high luminosity, potentially forming soot particles. The conventional technology for tar removal is wet scrubbing. Although this approach has shown some success, there are significant equipment and operating costs associated with it. In order to prevent the generation of toxic wastewater, the tars must be separated and either disposed as hazardous waste or, preferably, combusted in the gasification plant.

A conceptually better approach is catalytic steam reforming of the tars to hydrogen and carbon monoxide (CO), effectively increasing the gasification efficiency and eliminating the problems mentioned above. In FY2000, Battelle Columbus Laboratories attempted to demonstrate integrated gasification-gas turbine operation using catalytic steam reforming of tars. NREL participated in those tests using the transportable molecular-beam mass spectrometer (TMBMS) to monitor the catalytic reactor's performance on-line [10]. Unfortunately, the pilot plant tests encountered operational problems that prevented conclusive determination of the efficacy of the selected catalyst (Battelle's DN34).

In FY2001, NREL performed on-site tar steam reforming tests using a slip-stream of hot pyrolysis gas from the Thermochemical Process Development Unit (TCPDU), which was directed to a bench-scale fluidized bed reactor system designed expressly for this purpose. Supporting this effort, the TMBMS was employed to provide on-line analysis of the tar conversion. The gas composition changes were monitored by two identical gas chromatographs (GCs), and modified method 5 sampling was performed to obtain gravimetric conversion data. The combination of these analytical techniques provided definitive catalyst performance data, as well as linkage to previous and on-going work elsewhere. Two catalysts were tested: nickel (Ni) on potassium promoted alumina (Süd-Chemie C11-NK), used commercially for naphtha steam reforming, and alumina (Battelle's DN34) claimed to be effective for gasifier tar decomposition. In addition, sand was tested as an inert reference material.

The process variables studied were the operating temperature of the bench-scale reactor and the steam-to-carbon ratio. The performance of the Ni-based catalyst was measured at 700º, 750º, 800º and 850ºC with supplemental steam, and without added steam at 850º and 900ºC. The DN34 catalyst and the sand were both tested at 850ºC with added steam. The Ni catalyst demonstrated complete tar destruction at temperatures above 750ºC, using supplemental steam. The DN34 catalyst and sand exhibited water-gas shift activity, but neither showed any significant tar destruction capability, despite operation at 850ºC with added steam.

Experimental Methods

The TMBMS Instrument

A TMBMS was employed to provide continuous, on-line chemical analysis of hot gases produced by NREL's TCPDU during biomass gasification. A complete description of the TCPDU, including a thorough analysis of the pyrolysis gas, can be found elsewhere [12]. The TMBMS instrument has been successfully used on several occasions for similar projects and has proven to be a useful tool for monitoring different chemical processes. The design and operation of the TMBMS have been described in detail previously [1,2] but a brief description follows. The hot gases exiting the process arrive at the entrance of the instrument by means of a heated sampling system, which will be described below. A molecular beam forms as the gases are extracted through a 300-µm orifice into a three-stage, differentially pumped vacuum system. The gases then undergo a free-jet expansion, essentially halting further chemical reactions and preventing condensation. Components of the molecular beam are then ionized by 22.5 eV electrons before passing through an Extrel [3] quadrupole mass analyzer and detected with an off-axis electron multiplier.

The TMBMS is equipped with several integrated system controls that allow it to interface with and monitor a variety of chemical process streams. Eight temperature controllers are used to maintain sample line temperatures and two mass flow controllers are used to introduce inert gases for sample dilution and internal standards. Additional mass flow meters provide nitrogen (N_2) purges to prevent line plugging and buildup of process gases. Pressure transducers are used to monitor the pressure across a heated critical-flow orifice and provide feedback to a pressure control valve. Information from each of these auxiliary channels is recorded during data collection for use in quantitative analysis.

Gas Sampling

In order to achieve representative sampling, the integrity of the hot product gas must be maintained to a high degree. The transfer of gas from the thermochemical process to the TMBMS thus becomes a crucial aspect of the experiment. Unfortunately, due to the condensable and reactive nature of these gases, this is not usually accomplished easily. Maintaining a gas temperature comparable to that of the reactor (700°-900°C in this case) would prevent condensation but would likely induce further thermal decomposition en route to the TMBMS. In addition, the various materials, valves, etc., used to transport the gas are not generally suited for these temperatures. Previous experience has shown that heated sample transfer lines, kept as short as possible and maintained at 300°-400°C, tend to be a good compromise between losses from condensation and losses from thermal decomposition.

The physical size of the TMBMS (45″D x 34″W x 56″H) allowed it to be positioned near the 2-in. fluid bed reactor (2FBR), located on the mezzanine level of the Thermochemical Users Facility. A heated sample transfer and conditioning system was constructed to filter particulate matter and control the temperature, flow and pressure of the hot synthesis gases (see Figure 1).
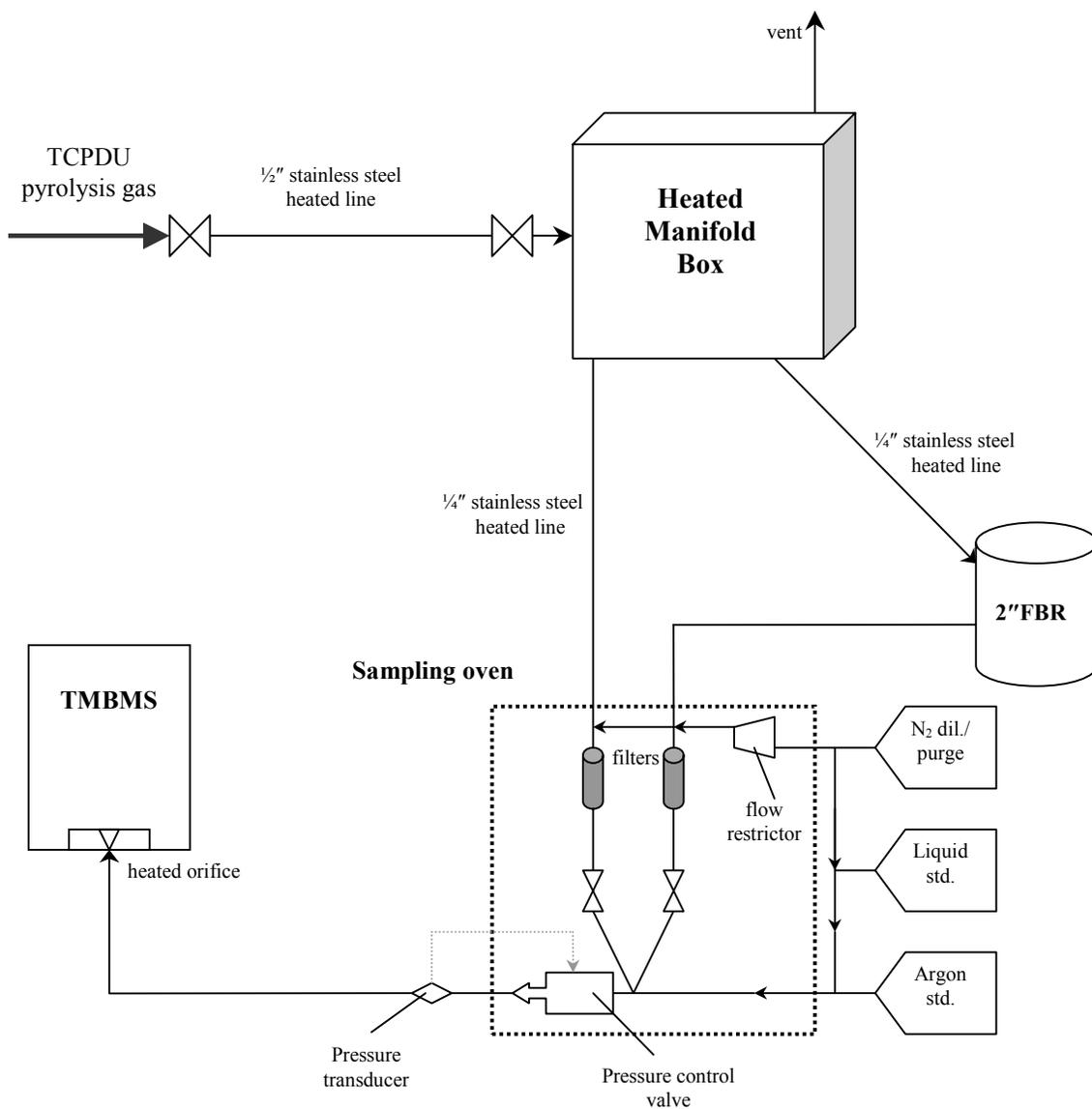
Figure 1. Schematic of system layout during catalyst testing.

The pyrolysis gas was sampled from the TCPDU process stream at a point after solids removal by cyclones and immediately before the wet scrubbing system. A ½-in. heated transfer line carried the raw product gas from the TCPDU to a heated manifold box, which housed an in-line filter, a high-temperature pneumatic shut-off valve and a high-temperature regulating valve (see Figs. 2 and 3). A pressure transducer, monitoring the pressure drop across an orifice-plate flowmeter, provided the regulating valve with feedback necessary for flow-control to the TMBMS and 2FBR. Three high-temperature hand valves were used for flow shut-off valves, one at the inlet from the TCPDU and one each to the 2FBR and an external vent.

Figure 2. Heated manifold box used during catalyst testing.

The process gas was then conducted from the manifold box to the TMBMS by means of a ¼-in. diameter stainless steel line, running co-linearly with another ¼-in. line from the outlet of the 2FBR. Both sample transfer lines, as well as the manifold box, were maintained at temperatures of 350°-400°C by electrical heaters and wrapped with ceramic blanket insulation and aluminum foil. Each line encountered another high-temperature shut-off valve in the sampling oven, used for selecting either the raw or the treated gas, before entering the TMBMS for analysis. The entire system, including the interior of the manifold box, was purged with N_2 when not in use to prevent condensation and the buildup of explosive gases. The sample transfer system was operated at a pressure of 5 psig at the 2FBR inlet and just above ambient pressure at the 2FBR outlet.
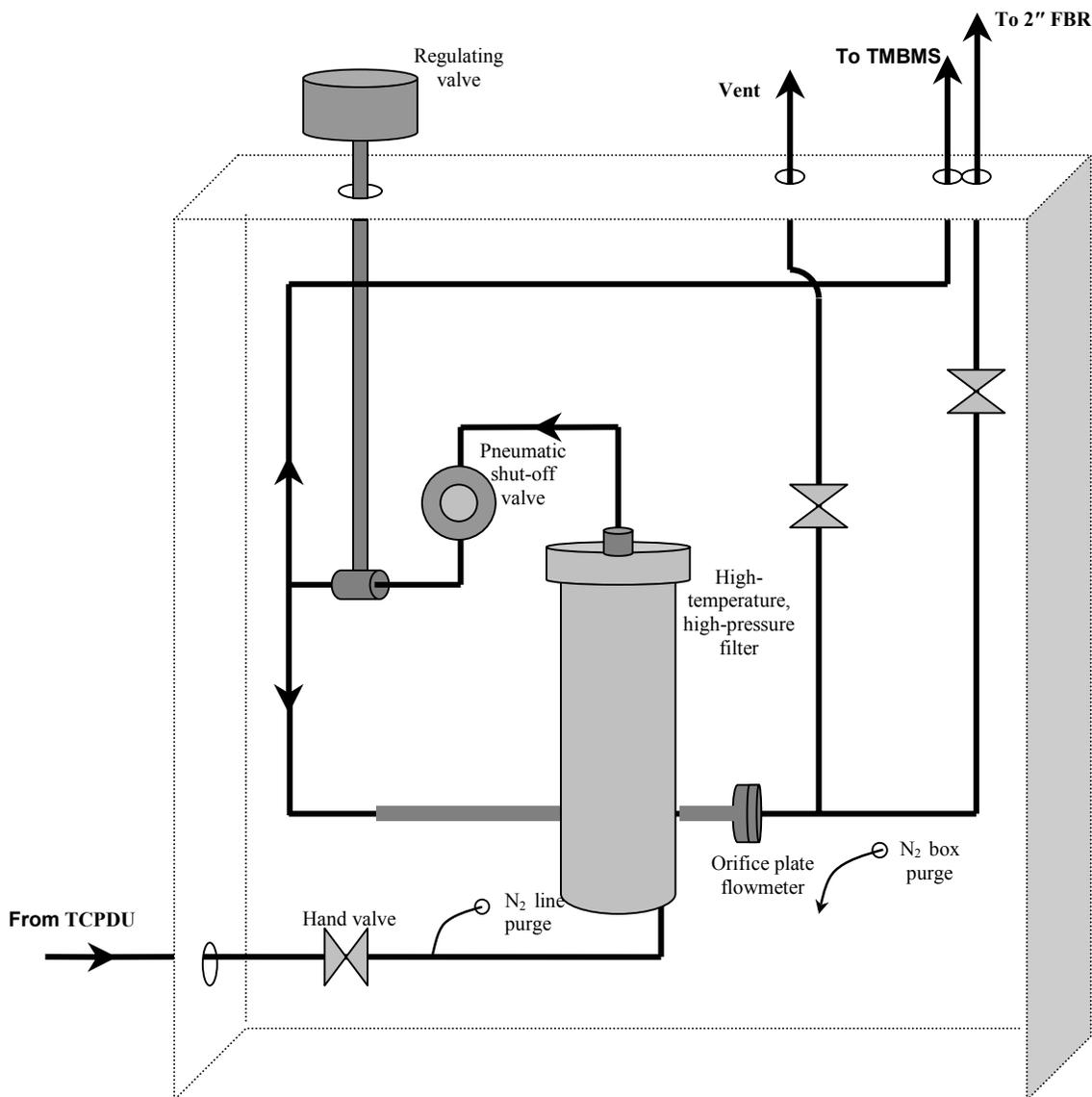
Figure 3. Schematic of heated manifold box used in catalyst tests.

The length of the slipstream from the TCPDU process line to the heated manifold box was approximately 4.5 m. From there, the raw gas traveled another 6 m before reaching the entrance of the TMBMS. During operation, the TCPDU typically delivered raw pyrolysis gas at a volume of 4.5-5.0 standard L/min (slm), resulting in a residence time of approximately 10 s from the TCPDU process line to the TMBMS. Raw gas diverted to the 2FBR for catalytic treatment traveled an additional 1.0 m before the entrance to the reactor, adding less than 0.20 s to the residence time.

Two-Inch Fluidized Bed Reactor

Steam reforming of tars in the raw synthesis gas was carried out using a bench-scale, 2″-diameter, fluidized bed reactor system (2FBR). This system has been used successfully in several other steam-reforming experiments and is described in detail elsewhere [4,5], but an explanation of the basic operation follows. The 2FBR system is comprised of a 2-in. inconel reactor inside a three-zone electric furnace. The bed material inside the reactor (sand or ground catalyst) was fluidized by 2.5 g/min of steam, produced in a boiler and superheated to 750°C before being introduced into the reactor, and N_2, which was added at a rate of approximately 1.0 slm. The Ni-based, C11-NK catalyst was tested at 700º, 750º, 800º and 850ºC with the added steam and also at 850º and 900ºC without adding steam to the 2FBR. The DN34 alumina catalyst and the sand were both tested at 850ºC with added steam. Both catalysts were ground and sieved to a size distribution of 300-500 μm. The surface area, as measured by nitrogen desorption BET, of the ground C11-NK has previously been reported to be 17.7 m^2/g [13], while that of the DN34 was 107 m^2/g [10]. The gas hourly space velocity ($G_{C_1}HSV$ – defined as C_1 equivalent volume of feed per hour per unit volume of catalyst) was estimated to be 1110 h^{-1} during all experiments

The product collection line included a cyclone and a hot-gas filter to capture fine catalyst particles and, possibly, char generated in the reactor. It also contained two heat exchangers to condense excess steam. The condensate was collected in a vessel whose weight was continuously monitored. The outlet gas flow rate was measured by a mass flow meter and by a dry test meter. The concentrations of carbon dioxide (CO_2), carbon monoxide (CO), and methane (CH_4) in the reforming gas were continuously monitored by a California Analytical Instruments non-dispersive, infrared analyzer (NDIR) [6]. Hydrogen concentrations were monitored by a thermal conductivity analyzer [7]. In addition, the gas was analyzed every 5 minutes by an on-line GC, providing concentrations of hydrogen, CO, CO_2, CH_4, ethylene, and N_2 as a function of time. The temperatures and flows in the 2FBR system were controlled and recorded by a PC-based data acquisition and control system.

Data Acquisition and Calibration

As mentioned, the TMBMS is composed of a molecular beam gas inlet system operating in conjunction with an Extrel quadrupole mass spectrometer. Data collection was automated using a ProLab Teknivent [8] data acquisition and control system interfaced with a personal computer. Mass spectra were recorded for m/z=13 to m/z=350 along with data from the auxiliary channels at the rate of 4.5 scans/min.

Several steps were taken to enable accurate calibration of the data. The temperatures of the sample lines and the orifice were all maintained between 350° and 400°C. Also controlled was the pressure in the sample line, which provided a constant flow to the orifice. In addition, as an internal measure of instrument stability, argon was introduced into the sampling system at a rate of 40 standard cc/min (sccm).

Periods of stable, concurrent TCPDU process, 2FBR and TMBMS operation were identified for each condition so that average values of the species of interest, before and after the 2FBR, could be determined. In addition, a liquid calibration standard containing benzene, toluene, phenol, cresol, naphthalene and phenanthrene was periodically injected into the sample line so that concentrations of those tar species could be quantified. Injection of these standards was made possible through a heated port downstream of the shut-off valves. The standard was injected off-line and diluted with the proper flow of N_2 to simulate on-line conditions. Table 1 displays the concentrations of the species contained in the standard used in this experiment.

Table 1. Composition of Liquid Calibration Standard

Species	Molecular Weight	Standard "A" Liquid Concentrations (ppm w/w)	Nominal Concentrations in Nitrogen (ppm v/v)
Benzene	78	637,100	10,000
Toluene	92	150,400	2000
Phenol	94	50,000	650
Cresol	108	29,200	325
Naphthalene	128	112,000	1050
Phenanthrene	178	21,200	150

The liquid standard was loaded into a 250-μL syringe and injected with a syringe pump into the sampling manifold through a stainless steel capillary at a nominal rate of 29 μL/min. The liquid was vaporized on entry into the sampling oven and diluted with approximately 500 slm of N_2, giving rise to the gas-phase concentrations shown in Table 1. Calibrations were generated for each standard injection according to the observed signal. For reference, a summary of these signals, reported in number of counts per volume percent, is shown in Figure 4. The variation seen in instrument response is mostly due to day-to-day changes in instrument settings, which were prompted by a need for greater sensitivity and did not affect the reliability of the calibrations. The observed argon signal from the tracer, which typically varied less than 2% during the course of a day, is more indicative of instrument stability. Figure 5 shows this and other sampling parameters plotted during a typical experimental run. For additional reference, Figure 6 depicts several critical TCPDU process parameters during a typical experimental run. As can be seen, these parameters generally remained very stable throughout the catalyst tests.
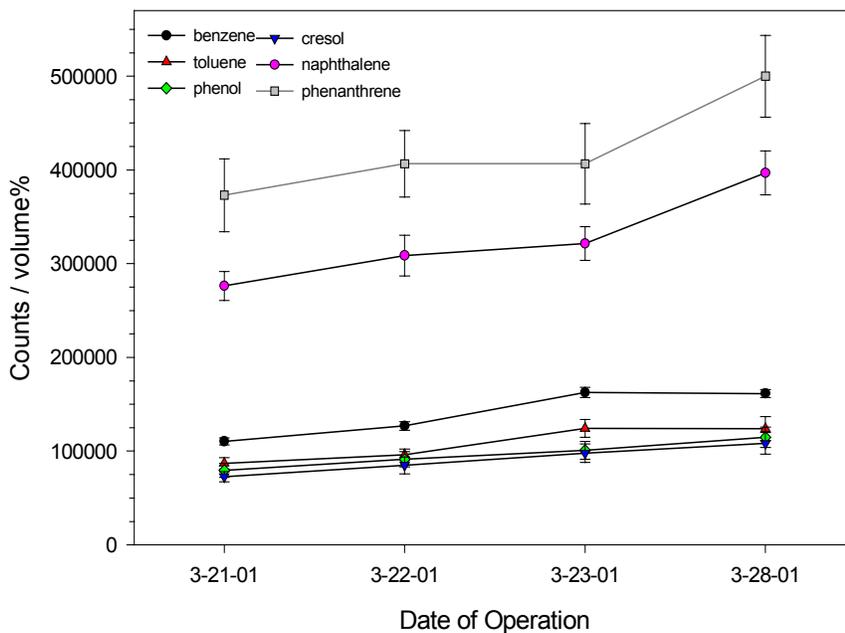
Figure 4. Summary of calibration results from standard injections made during catalyst testing.
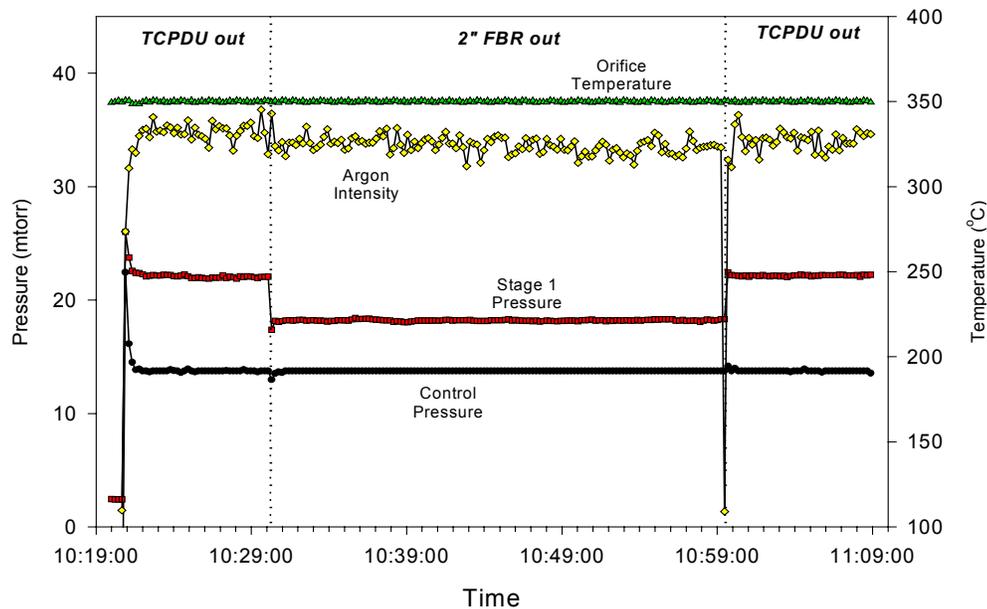
Figure 5. **TMBS sampling parameters from March 22, 2001—orifice temperature (green, °C, right axis), control pressure (black, mTorr, left axis), intensity of argon signal (yellow, arbitrary units), stage 1 pressure (red, mTorr, left axis).**
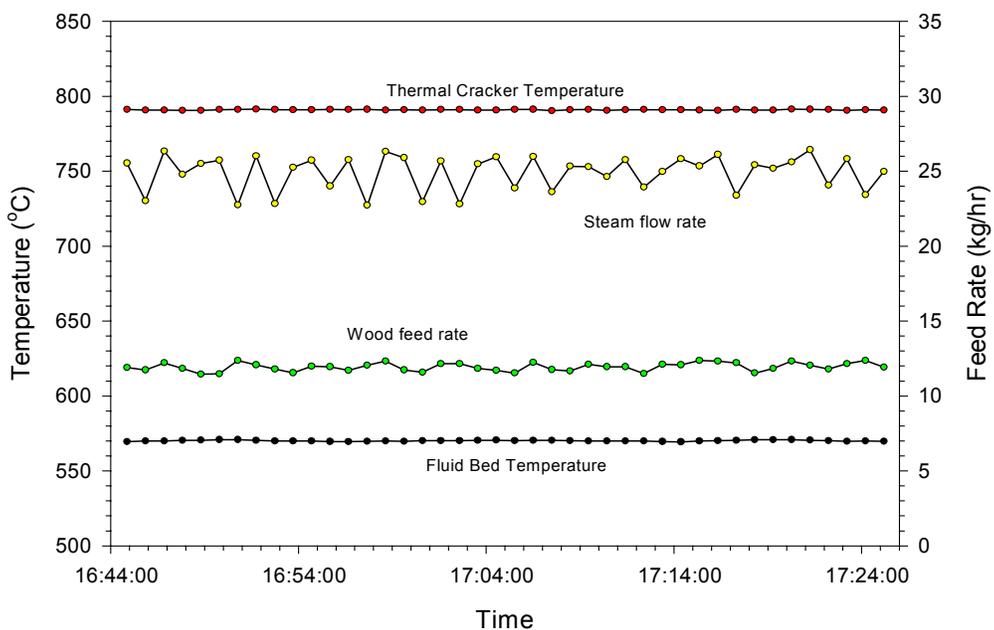
Figure 6. **Some critical TCPDU operating parameters from March 1, 2001-- thermal cracker temperature (red, °C, left axis), steam flow rate (yellow, kg/h, right axis), wood feed rate (green, kg/h, right axis), fluid bed temperature (black, °C, left axis).**

Results

Reference Case Using Sand

Initial systems testing was carried out using sand in the 2FBR as the fluidizing medium. The TCPDU fluid bed was operated at 570°C and the thermal cracker was held at 790°C. Biomass and steam were fed at rates of 12 kg/h and 25 kg/h, respectively, resulting in a pyrolysis gas flow rate of 9 kg/h. Approximately 4.5 slm of the wet gas was delivered from the TCPDU to the reactor, to which 1.1 slm of N_2 and 0.15 kg/h (~3.1 slm) of steam were added inside the 2FBR. To compare the data before and after the 2FBR, it was necessary to correct the tar concentration values at the outlet to account for this added volume of gas. During the experiments using sand, the 2FBR operated at 850°C.
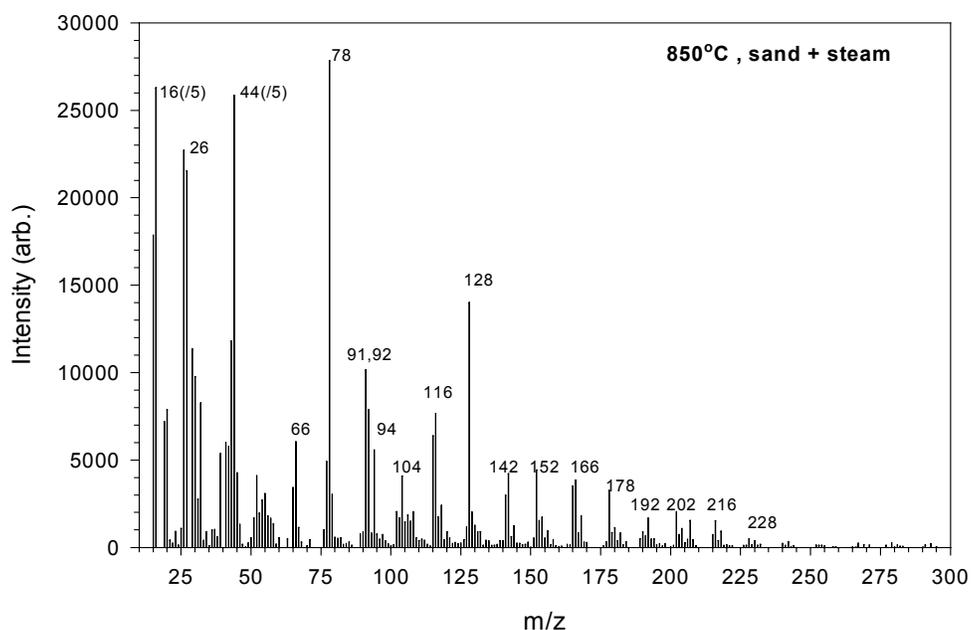
Figure 7. March 1, 2001 - Average mass spectrum of TCPDU gasifier products detected by TMBMS.

As expected, several tar compounds typical of biomass gasification were present in the pyrolysis gas. In the context of this report, the term *tars* is meant to include all aromatic hydrocarbons with a molecular weight of 78 (benzene) or higher. Figure 7 shows an average mass spectrum taken with the TMBMS of the raw pyrolysis gas, from which the background signal has been subtracted. Several prominent peaks are visible in the spectrum. The largest peaks, reduced by a factor of five in the figure, were attributed to CH_4 (m/z=15,16) and CO_2 (m/z=44). Carbon monoxide (m/z=28) was not monitored since it could not be distinguished from N_2 (also m/z=28) and the combined signals would have saturated the detector. Water (m/z=17,18) was also omitted from the scan because of saturation concerns. The remaining peaks in the spectrum are either hydrocarbon species or ion fragments produced during detection in the mass spectrometer.

The most prominent tar species seen are benzene (m/z=78), toluene (m/z=91,92) and naphthalene (m/z=128). However, several more species can be seen through m/z=300. Acetylene (m/z=26), a known soot precursor, was also present in relatively large amounts in the raw gas. Table 2 summarizes the mass spectral assignments for some of the major compounds discussed in this report.

Table 2. Summary of Mass Spectral Assignments for Peaks Observed During Catalyst Testing

m/z	Chemical Formula	Chemical Name
15,16	CH_4	methane
26	C_2H_2	acetylene
44	CO_2	carbon dioxide
66	C_5H_6	cyclopentadiene
78	C_6H_6	benzene
91,92	C_7H_8	toluene
94	C_6H_6O	phenol
104	C_8H_8	styrene
108	C_7H_8O	cresol
116	C_9H_8	indene
118	C_9H_{10}	indan
128	$C_{10}H_8$	naphthalene
142	$C_{11}H_{10}$	methylnaphthalenes
152	$C_{12}H_8$	acenaphthalene
166	$C_{13}H_{10}$	fluorene
178	$C_{14}H_{10}$	anthracene/phenanthrene
192	$C_{15}H_{12}$	methyl-anth./phenanthrene
202	$C_{16}H_{10}$	fluoranthene/pyrene
216	$C_{17}H_{12}$	benzo(a)fluorene
228	$C_{19}H_{14}$	benzo(a)anthracene

The period of stable operation for March 1, 2001 was determined to be 16:47 to 17:23. During this time, data was collected for several minutes from both the inlet and the outlet of the 2FBR. Using the calibration generated by the standard injection, concentration-versus-time plots were produced, allowing general trends to be seen. Figure 8 shows several such plots for this period. The first set shows the concentrations of benzene, toluene, naphthalene and acetylene as a function of time. It should be noted that the acetylene signal is reported in intensity, not in absolute concentration, as indicated on the right axis. According to the GC analysis of the raw pyrolysis gas (after wet scrubbing), the acetylene concentration averaged approximately 0.7% by volume (see Table 6, at the end of the report, for a summary of the GC analyses during these experiments). The second set of plots in Figure 8 shows the same information for phenol, cresol and phenanthrene. All concentrations are reported on the basis of the entire gas stream, i.e. including steam and nitrogen. As stated above, however, the tar levels reported for the outlet of the fluid bed reactor have been corrected for the steam and N_2 added at that point. The large increase in signal seen from 16:42-16:46 was due to a brief upset in the sampling line pressure.
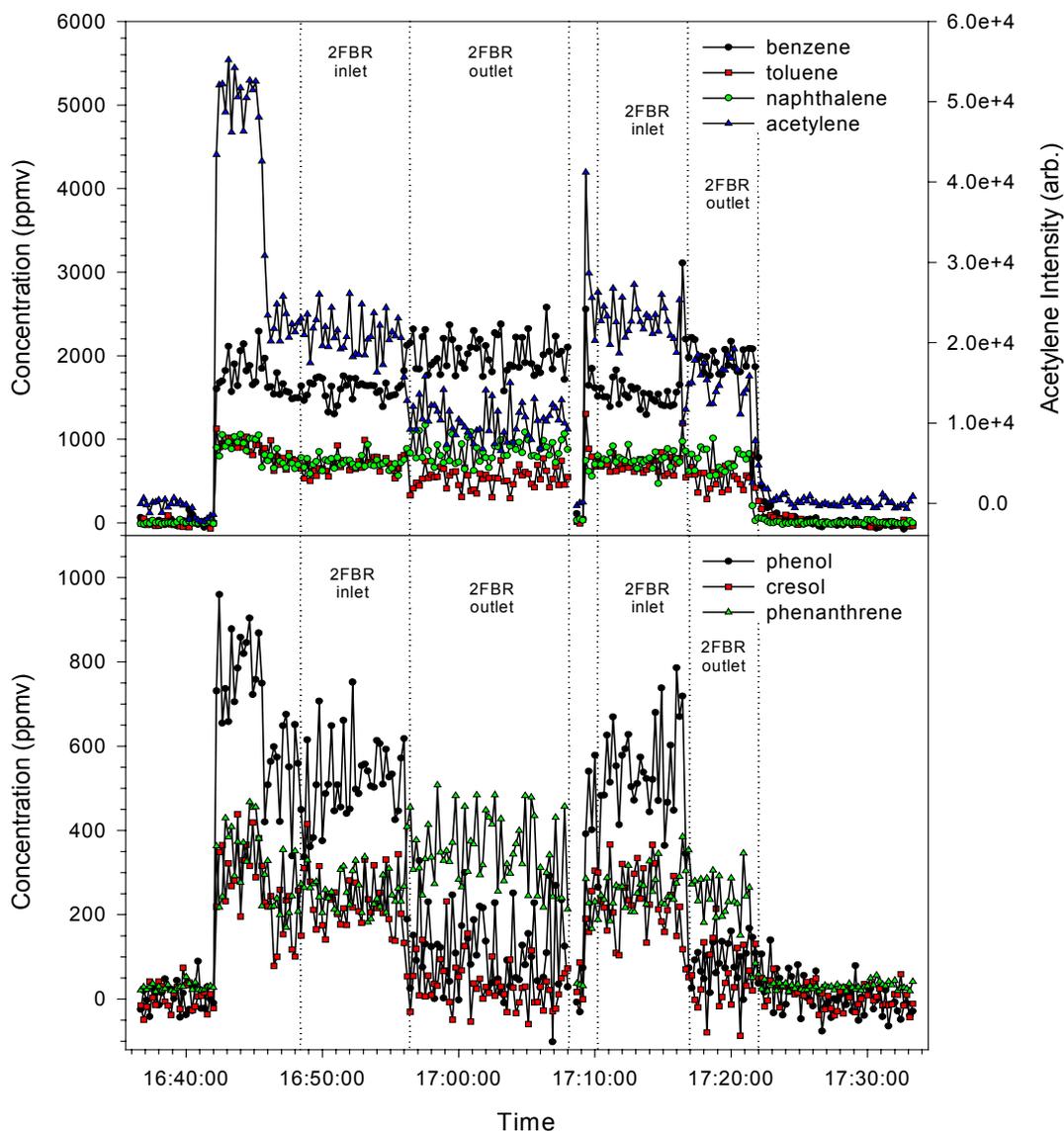
Figure 8. March 1, 2001 – Concentration vs. time plots of quantified products measured by the TMBMS, 2FBR operating at 850°C with sand and steam.

The vertical dotted lines in Figure 8 delineate periods when the TMBMS was monitoring either the inlet or the outlet of the 2FBR. As can be seen in this figure, the concentrations of acetylene, phenol and cresol showed a relatively sharp decline across the reactor, while there was only a slight decrease in toluene. The concentrations of benzene, naphthalene and phenanthrene all showed increases at the outlet of the 2FBR. Table 3 summarizes the average tar concentrations at the inlet and outlet of the 2FBR on March 1, 2001.

As seen in Table 3, the total tar concentration in the wet pyrolysis gas decreased by only about 3%. There was, however, a noticeable change in the gas composition. Namely, it was largely the oxygenated species, phenol and cresol, that appear to have decomposed by approximately 80% in the reactor. These species likely underwent thermal deoxygenation, where the relatively labile C-O bond between the benzene ring and the hydroxyl group was thermally cleaved, effectively creating benzene (78) and toluene (92) from phenol (94) and cresol (108).

Table 3. Average Tar Concentrations Before and After 2FBR with Sand (ppm v/v)
March 1, 2001

	Benzene (78)	Toluene (92)	Phenol (94)	Cresol (108)	Naphthalene (128)	Anthracene/ Phenanthrene (178)	Total
Inlet	1540	680	500	230	710	225	3885
Outlet	2000	520	90	50	820	285	3765

Although the observed increases in benzene can probably be explained by this mechanism, the increases in naphthalene and phenanthrene were likely attributed to similar thermal decomposition of higher molecular weight tars and/or to formation from reactive light hydrocarbon gases, such as acetylene and ethylene. According to the GC analysis of the raw gas, these light hydrocarbons typically comprised 5%-6% of the gas volume. The reactions of these gases leading to the formation of benzene, and on to polycyclic aromatic hydrocarbons (PAHs) and soot, have been studied in detail [9]. In addition, reactions of this nature have been observed during previous efforts to condition pyrolysis gas derived from wood gasification [10]. This would explain the behavior of the acetylene trace in Figure 8, which indicates that it is being consumed in the reactor, probably due to the formation of benzene, naphthalene and possibly anthracene/phenanthrene.

C11-NK Nickel Steam-Reforming Catalyst

In this set of tests, the Süd-Chemie C11-NK, Ni-based catalyst was loaded into the 2FBR to assess its tar decomposition capabilities. Tests on March 21, 2001 were conducted with added steam and reactor temperatures of 850°, 750° and 700°C. (The data taken at 800°C was corrupted, due to an apparent grounding issue with the data acquisition system.) Nitrogen was added to the reactor at a rate of 1.1 slm and steam was introduced at 0.10 kg/hr (~2.1 slm). The TCPDU was operated under the same conditions except that the steam temperature averaged 615°C instead of 650°C and the thermal cracker was maintained at 770°C instead of 790°C. The GC analysis showed notable increases in the ethane and propylene concentrations; the other components remained at the same levels.

With a reactor temperature of 850°C, data taken during the period of 11:37 to 12:22 was deemed acceptable even though the TCPDU experienced feed rate fluctuations for much of this time. The fluctuations seemed to be somewhat periodic, with no major upsets. Therefore, the data was averaged for approximately 25 min at the inlet and 13 min at the outlet in an attempt to minimize periodic changes in gas composition associated with changes in the feed rate. The mass spectra obtained by the TMBMS showed that the composition of the pyrolysis gas was nearly identical to

that produced on March 1, 2001 (Figure 7), although the overall tar concentrations were 15%-20% lower.
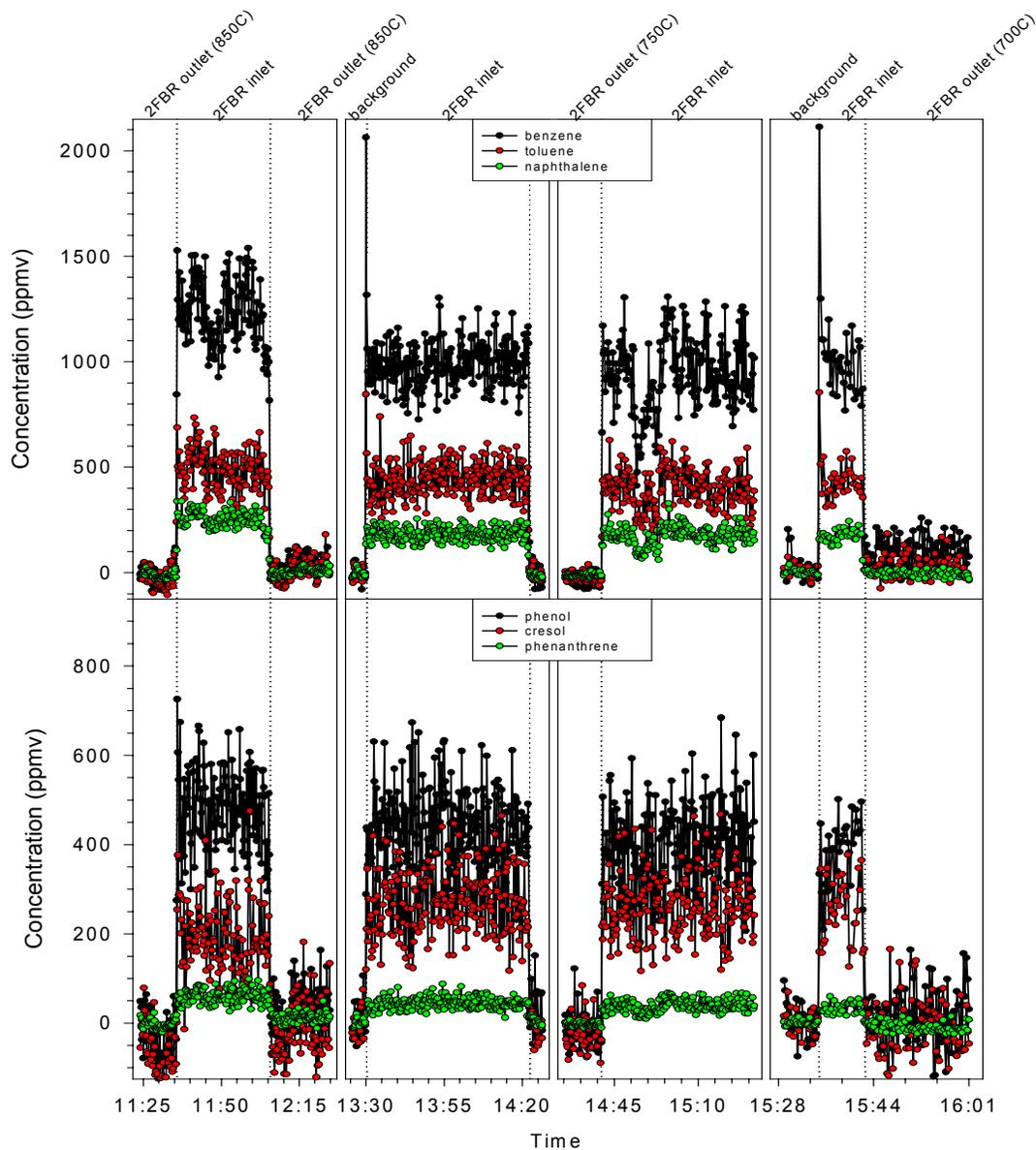
Figure 9. March 21, 2001 – Concentration vs. time plots of quantified products measured by the TMBMS, 2FBR operating at 700°, 750°, 850°C/C11-NK/steam.

Figure 9 shows concentration versus time traces of several tar species observed on March 21, 2001. As seen in these plots, the C11-NK catalyst exhibits exceptional tar-destruction capabilities. In fact, the only noticeable gas-phase components detected by the TMBMS at the outlet were CO_2, which increased by 120%, and CH_4, which decreased by 80%. All tar species underwent 100% conversion. No discernable signals from any tar species were detected until the 2FBR temperature was lowered to 700°C. Even then, breakthrough was observed only for

benzene, toluene and phenol at levels of 11%, 6% and 3%, respectively. Cresol, naphthalene and phenanthrene still underwent complete conversion under these conditions.

Another noticeable feature in these plots is the apparent increase in pyrolysis gas tar levels during the period centered around 11:50 when compared to the remainder of the day. This was likely related to the feed rate fluctuations mentioned earlier, which may have contributed to problems controlling the steam flow rate and temperature. During this period, the steam flow rate averaged 20 kg/h at 600°C, compared with 25 kg/h and 620°C for the remainder of the day. Despite these differences, the GC analysis did not indicate a noticeable change in the permanent gas composition throughout the day.

The difference between the 2FBR inlet and outlet gas compositions can perhaps be more clearly seen in a difference spectrum, where the inlet mass spectrum is subtracted from the outlet mass spectrum. Such a difference spectrum can be seen in Figure 10, where components that were removed by the catalytic reactor lie below the x-axis. The small peaks at m/z=19 and 45 have been identified as isotopes of water ($^1H^2HO$, $H_2^{17}O$) and carbon dioxide ($^{13}CO_2$), respectively. These time-averaged spectra were taken at a reactor temperature of 850°C operating with the Ni catalyst and added steam. Figure 10 provides direct evidence for complete tar destruction.
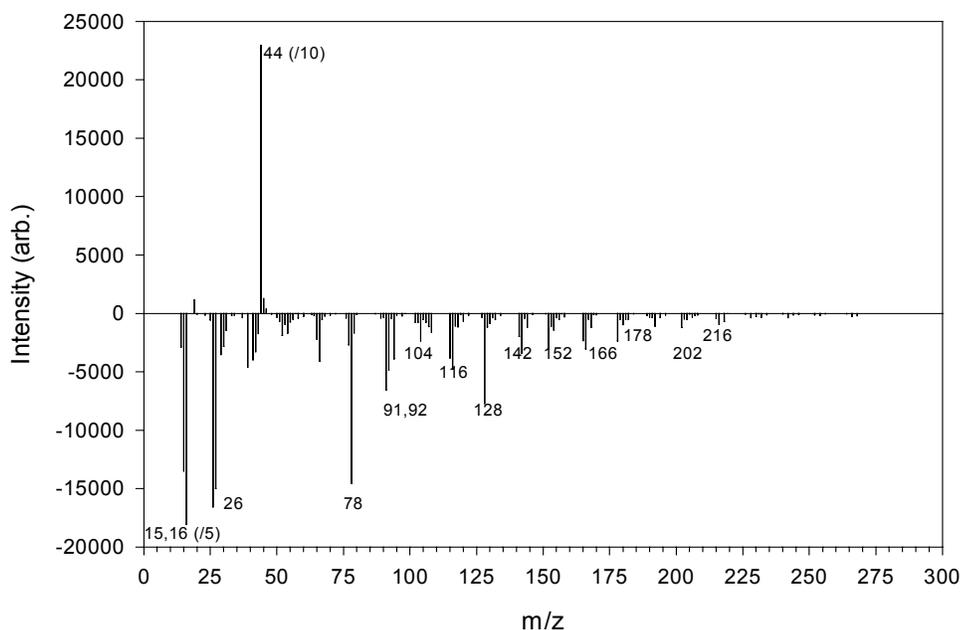

Figure 10. March 21, 2001 – Difference spectrum. Catalyst outlet (11:30-11:35) minus catalyst inlet (11:39-11:45), 850°C/C11-NK/steam.

17

The following day, March 22, 2001, the Ni catalyst performance was again tested, this time without the use of added steam, at temperatures of 850° and 900°C. To assure fluidization of the catalyst, additional N_2 flow was added to the 2FBR for a total of 3.5 slm. Pilot plant operations were relatively smooth on this day. Steam and biomass feed rates in the TCPDU were again 25 kg/h and 12 kg/h, respectively. The fluid bed was maintained at 580°C and the thermal cracker at approximately 790°C. Data from the GC analysis showed that, compared to March 21, 2001, the average concentration of ethane in the pyrolysis gas was slightly lower, and that of acetylene was slightly higher.
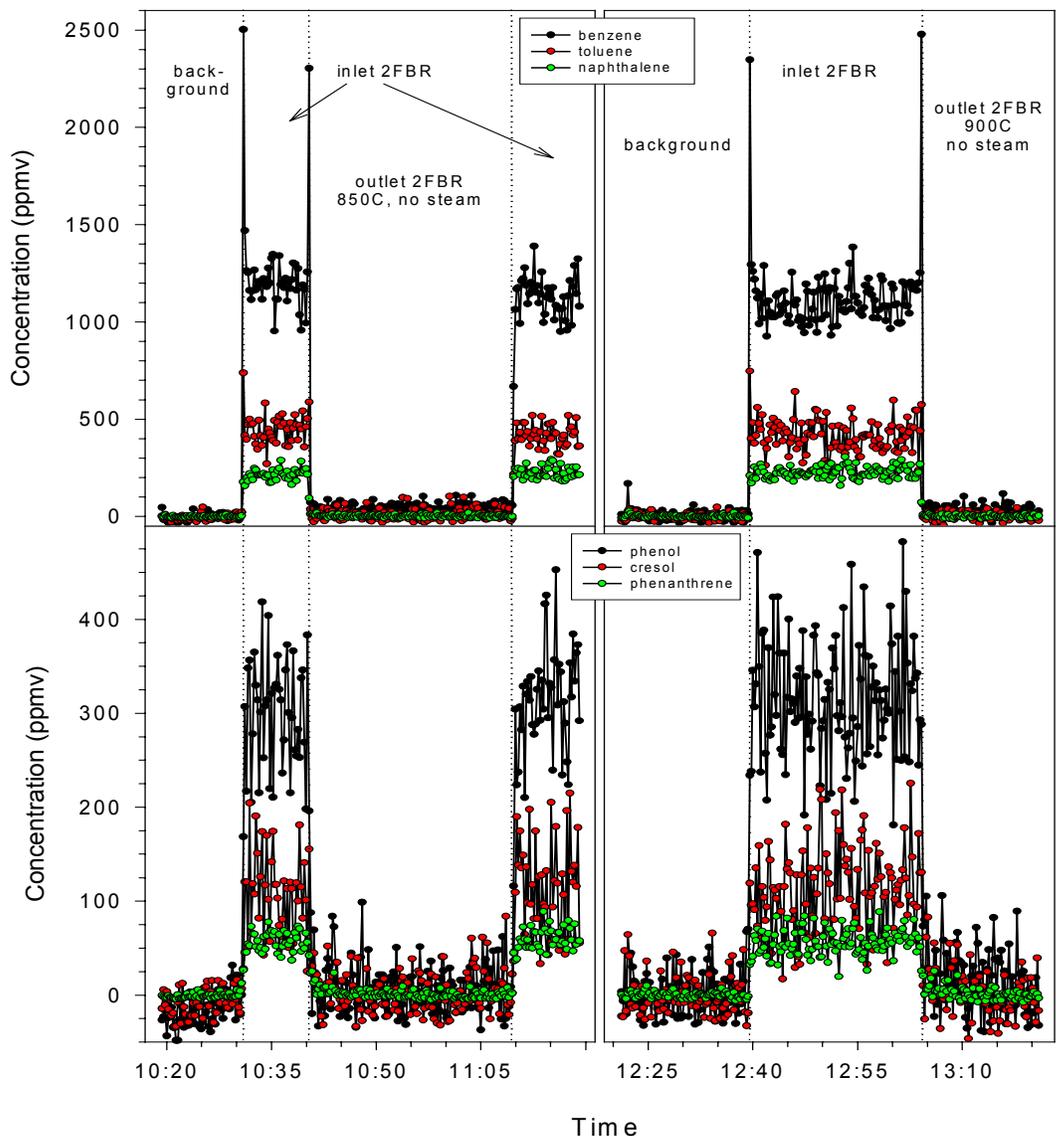

Figure 11. March 22, 2001—Concentration vs. time plots of quantified products measured by the TMBMS, 2FBR operating at 850° and 900°C/C11-NK/no steam.

The concentration versus time plots for the tars observed during these tests can be seen in Figure 11. As is evident in the graph, tar destruction was again nearly complete, at least to within the detection limits of the TBMBS. A small amount of benzene, 50-60 ppm, was seen at the catalyst outlet at both temperatures. This represented about 5% of that detected at the inlet. Toluene showed up in trace amounts (~20 ppm) at 850°C and phenol was present at approximately the same level at both temperatures. For both of these compounds, this amounted to a 2%-3% breakthrough. Whether this breakthrough was due to the lack of steam, or catalyst deactivation, is not clear. However, as discussed later, some catalyst deactivation was evident on the following day.

Operations on March 23, 2001 were, for the most part, intended for impinger sampling of gasifier tars before and after the catalyst bed. An attempt was made to collect TMBMS data during this time. However, due to the configuration of the sampling system, pressure stability issues arose during impinger sampling, and useful data was not obtained. Some data though, was collected prior to this while the 2FBR operated at 850°C, under conditions similar to March 21, 2001. The pilot plant was also operated under the same conditions and the GC analysis showed the raw gas composition to be nearly identical to previous days.

Figure 12 shows the concentration versus time plots for tars observed by the TMBMS on March 23, 2001. A dramatic loss of catalytic activity can be seen on this day. Cresol and phenanthrene were the only two quantified species that still appeared to have been completely converted in the 2FBR.

Table 4 displays the average tar concentrations before (11:38-12:00) and after (12:00-12:15) the catalyst bed on March 23, 2001. The values here indicate that the conversion for benzene was only about 50%, while that for toluene was approximately 70% and just over 80% for phenol and naphthalene. Cresol and phenanthrene were still fully converted. This rather significant decrease in catalytic activity over this period suggests that the experiments carried out without added steam may have contributed to coking of the catalyst and its subsequent deactivation. The Ni catalyst had accumulated 11.5 hours of on-line use, five of which were without added steam, prior to the start of experiments on March 23, 2001.

Table 4. Average Tar Concentrations Before and After Ni Catalyst Bed (ppmv)
March 23, 2001

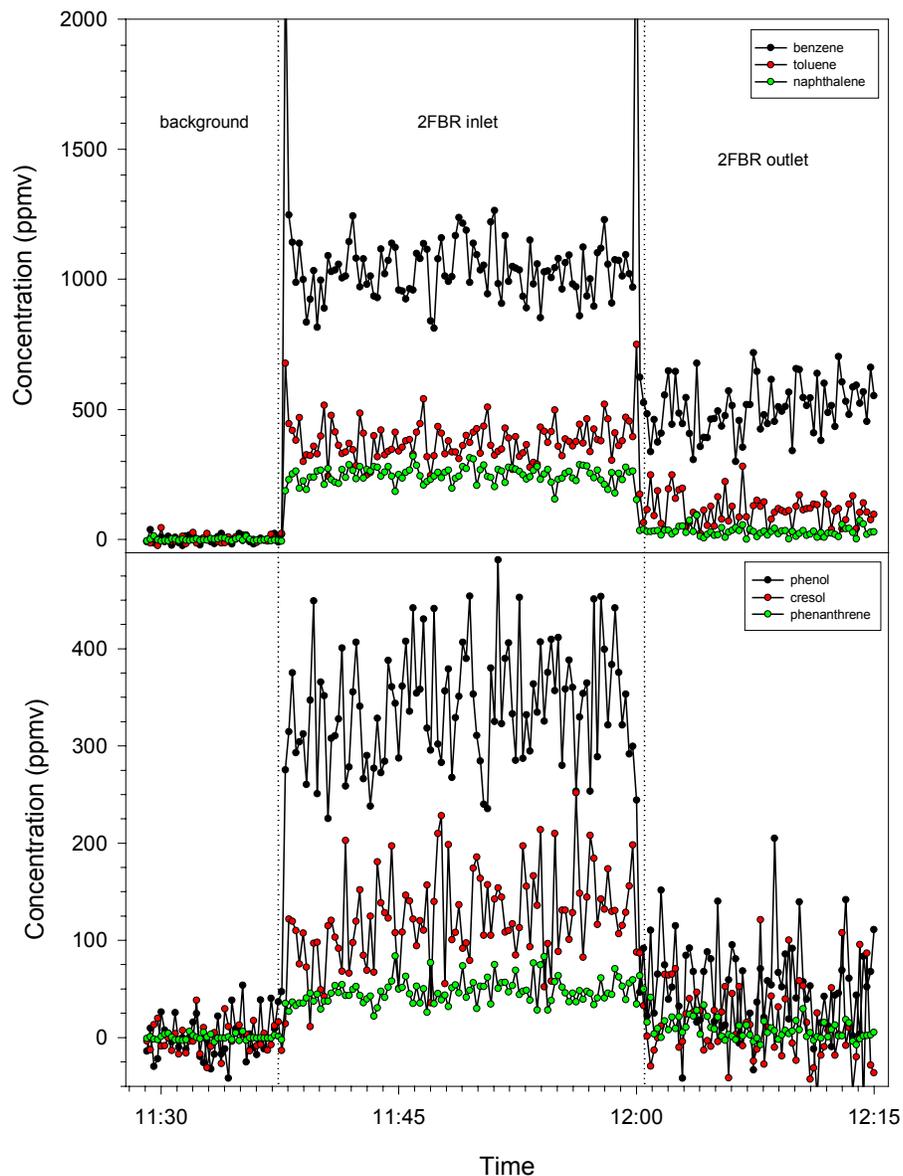|	Benzene (78)	Toluene (92)	Phenol (94)	Cresol (108)	Naphthalene (128)	Anthracene/ Phenanthrene (178)	Total
Inlet	1035	375	340	125	250	50	2175
Outlet	505	110	55	0	30	0	700

Figure 12. March 23, 2001 - Concentration vs. time plots of quantified products measured by the TMBMS, 2FBR operating at 850°C/used C11-NK/steam.

DN34 Alumina Catalyst

The last day of testing was used to investigate the performance of the alumina-based DN34 catalyst and obtain impinger samples of the catalyst bed inlet and outlet gas. As mentioned before, the impinger sampling interfered with the ability to obtain useful TMBMS data. Although some TMBMS data was collected before the sampling began, difficulties with multiple systems limited data collection to just a few minutes at each port. The TCPDU was operating under conditions similar to the previous days, except that the thermal cracker averaged 760°C.
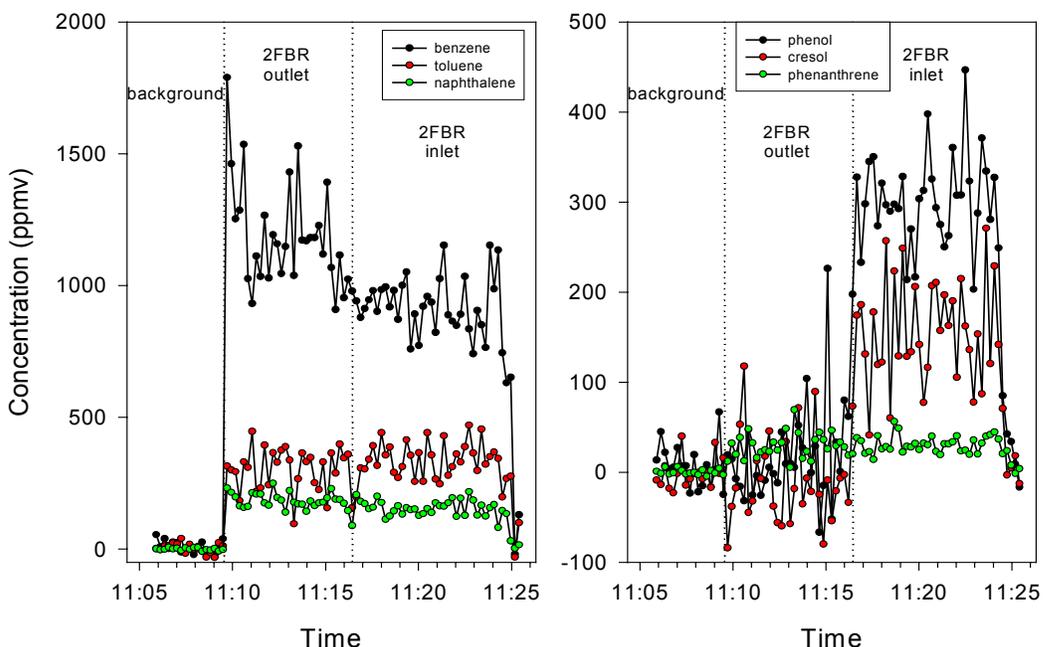
Figure 13. March 28, 2001 - Concentration vs. time plots of quantified products measured by the TMBMS, 2FBR operating at 850°C/DN34 catalyst/steam.

Figure 13 shows the concentration versus time plots for the period 11:05-11:30, where approximately five minutes of data was collected at each port. The average tar concentrations during this time are summarized in Table 5. On the whole, the tar destruction behavior of the DN34 catalyst was similar to that of the sand. The overall decrease in tars was roughly 10%. The benzene and naphthalene concentrations both increased by approximately 20% over the catalyst bed, and the phenol and cresol both appeared to be completely destroyed. The toluene signal decreased by 10% and no change in the phenanthrene signal was observed.

**Table 5. Average Tar Concentrations Before and After DN34 Catalyst Bed (ppmv)
March 28, 2001**

	Benzene (78)	Toluene (92)	Phenol (94)	Cresol (108)	Naphthalene (128)	Anthracene/ Phenanthrene (178)	Total
Inlet	915	340	290	150	155	30	1880
Outlet	1165	305	0	0	185	30	1685

21

The only notable indication of possible catalytic activity was the full conversion of the two oxygenated species, phenol and cresol. This has been observed during previous tests, which indicated the DN34 catalyst had a relatively high activity for dealkylation and deoxygenation of these secondary tar species [10,11]. Using this catalyst, phenol and cresol underwent complete conversion, whereas with the sand, this conversion was closer to 80%. This suggests that some catalytic activity was taking place in addition to thermal deoxygenation, which again appeared to be the dominating process in the destruction of these species while using sand in the reactor. If this were indeed the case, some of the increase in benzene (78) and naphthalene (128) could be explained by the catalytic dealkylation of toluene (92) and methylnaphthalenes (142). Benzene and toluene may have also been formed by the catalytic deoxygenation of phenol (94) and cresol (108).

Summary and Discussion

Several experiments were carried out to test the tar destruction capabilities of two catalysts, using sand as a reference case. The catalysts were ground and loaded into a 2″ fluid bed reactor (2FBR) which operated between 700° and 900°C. A hot slipstream of pyrolysis gas, produced by steam-gasification of wood in NREL's Thermochemical Process Development Unit (TCPDU), was fed into the 2FBR. Table 6 summarizes, for each day, the operating conditions of the TCPDU and the 2FBR, as well as the gas composition before and after the 2FBR, as measured by gas chromatographs at these points. The raw pyrolysis gas, as well as the catalytically treated gas, was monitored on-line with a transportable molecular-beam mass spectrometer (TMBMS). The raw gas was found to contain several tar compounds that are typical of biomass gasification, six of which were quantified by means of an off-line standard injection.   The combined concentrations of benzene, toluene, phenol, cresol, naphthalene, and phenanthrene ranged from 1880 to 3885 ppm (v/v) in the wet syngas.

A comparison of the tars detected at the inlet with those detected at the outlet can be seen for several experimental conditions in Figure 14. The first graph, Figure 14-A, shows the change in tar concentrations while using sand in the 2FBR bed. As can be seen, about 80% of the phenol and cresol was converted in the 2FBR, and the toluene level decreased by about 25%. The benzene, naphthalene and phenanthrene concentrations all increased. A summary of the tar conversion under each experimental condition can be seen in Table 7, reported on a percentage basis.   Figure 14-B shows the Ni steam-reforming catalyst to have excellent tar reforming capabilities, with the virgin catalyst destroying 100% of the tars in the raw pyrolysis gas. It was only when the 2FBR temperature was lowered to 700°C that any tars were detected at the outlet. The results from the experiments without the added steam on March 22, 2001, seen on the same graph, also showed little tar breakthrough. By March 22, 2001 the Ni catalyst had accumulated 6.5 hours of on-line time with steam and 5 hours without. Some deactivation of the catalyst was noticed over time (see Figure 14-C) and was probably accelerated by the experiments carried out not using steam. The performance of the DN34 catalyst, seen in Figure 14-D, was slightly better than the sand.   Here, phenol and cresol were the only species that appeared to have been completely converted and the benzene and naphthalene concentrations showed an increase over the catalyst bed.

Though these results demonstrate very satisfactory performance of the C11-NK catalyst, experiments of longer duration are needed to determine its activity as a function of time-on-stream for different process conditions such as temperature, steam-to-carbon ratio and space velocity. Another important issue that should be addressed is the ability to regenerate the catalyst for reuse.

Table 6. Critical Operating Parameters and Gas compositions for Catalytic Steam Reforming Experiments

| DATE OF OPERATION	03/01/01		03/21/01					03/22/01			03/23/01		03/28/01	
2FBR PARAMETERS														
Bed Material	**Sand**		**C11-NK Ni Catalyst**					**Ni Catalyst**			**Ni Catalyst (after11.5 hrs)**		**DN34 catalyst**	
Fluid bed temperature (°C)	850		700, 750, 800, 850					850, 900			850		850	
Steam flow rate (kg/h)	0.15		0.10					0			0.10		0.14	
N_2 flow rate (slm)	1.1		1.1					3.5			0.93		0.96	
TCPDU PARAMETERS														
Fluid bed temperature (°C)	570		570					570			570		575	
Wood feed rate (kg/h)	12		12					12			12		12	
Steam flow rate (kg/h)	25		25					25			25		26	
Steam temperature (°C)	650		615					580			600		600	
Thermal cracker temperature (°C)	790		790					790			790		765	
GAS COMPOSITION BEFORE (IN) AND AFTER (OUT) 2FBR - BY GC ANALYSIS (VOL %, N_2-FREE)														
Compound	In	Out	In	Out 700C	Out 750C	Out 800C	Out 850C	In	Out 850C	Out 900C	In	Out	In	Out
Hydrogen	20.5	44.9	21.2	59.3	62.0	62.8	62.8	21.3	58.3	57.5	22.3	59.1	22.0	50.1
Methane	16.5	10.3	16.5	4.8	3.3	1.6	0.68	16.6	3.5	3.3	16.3	5.3	16.1	10.1
Carbon monoxide	33.6	13.7	32.1	3.7	4.7	5.9	7.9	32.6	8.8	9.5	32.7	7.2	32.5	10.5
Carbon dioxide	19.0	26.3	21.1	28.8	27.9	26.5	25.4	20.4	26.5	25.4	20.3	27.4	21.8	26.6
Ethylene	4.3	2.0	4.2	0.11	0.07	0.06	0.05	4.5	0.15	0.16	4.4	0.29	4.5	1.5
Ethane	0.54	0.07	0.72	0.17	0.10	0.03	0	0.55	0.03	0	0.57	0.07	0.67	0.17
Acetylene	0.71	0.06	0.69	0	0	0	0	0.86	0	0	0.78	0	0.68	0
Propylene	0.15	0	0.55	0	0	0	0	-	0	0	0.42	0	0.56	0
Total	**95.3**	**97.3**	**97.1**	**96.9**	**98.1**	**96.9**	**96.8**	**96.8**	**97.3**	**95.9**	**97.8**	**99.4**	**98.8**	**99.0**
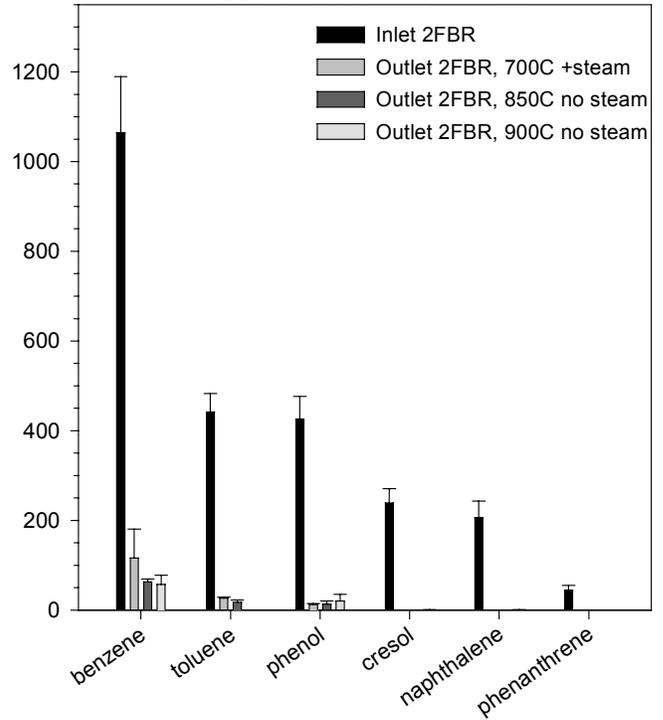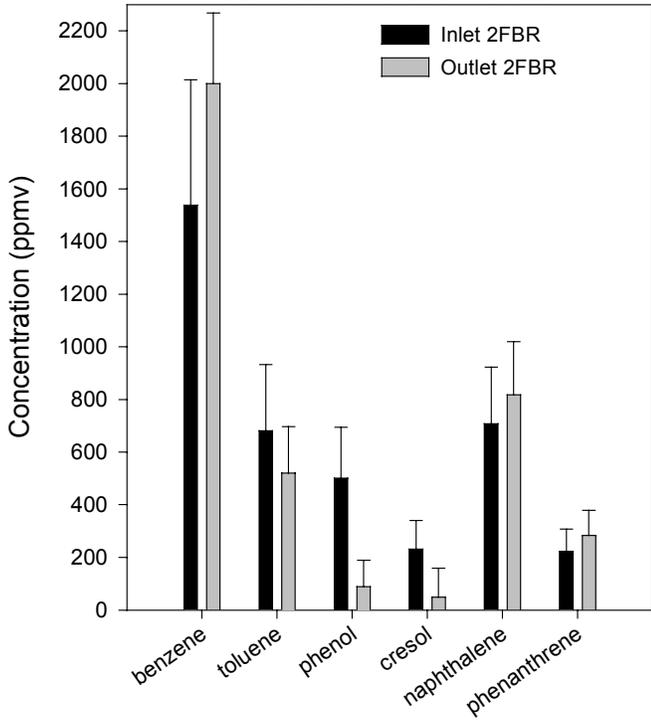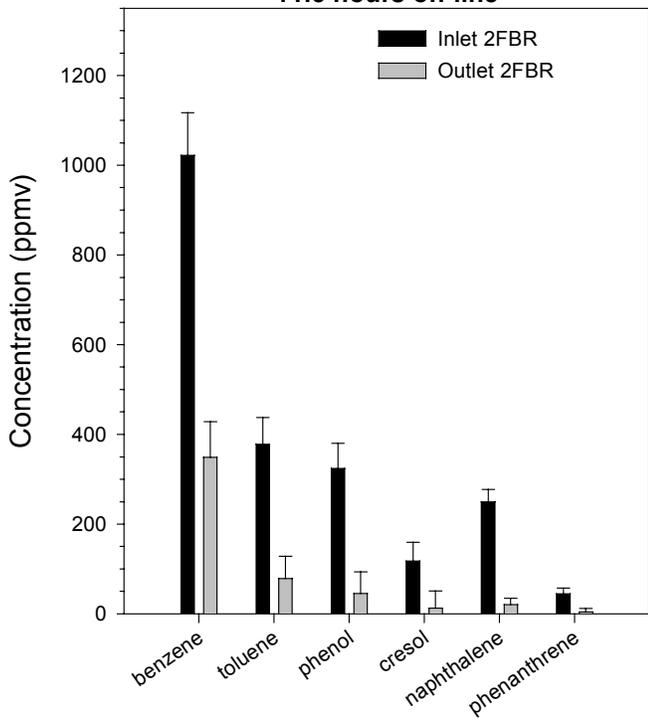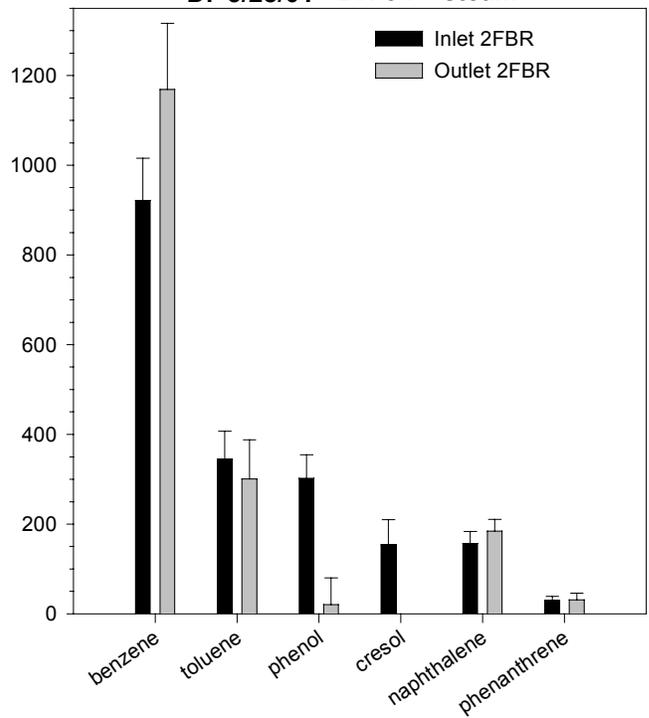
Figure 14. Summary of average tar concentrations at the inlet and outlet of the 2FBR during catalytic steam reforming experiments.

Table 7. Summary of Tar Conversion in 2FBR During Catalytic Steam Reforming Experiments (%)

	850°C sand/ steam	700°C C11-NK steam	750°C C11-NK steam	800°C C11-NK steam	850°C C11-NK steam	850°C C11-NK no steam	900°C C11-NK no steam	850°C C11-NK (used) steam	850°C DN34 steam
Benzene	(30)*	89	100	100	100	95	96	51	(27)
Toluene	24	94				97	100	71	10
Phenol	82	97				98	97	84	93-100
Cresol	78	90-100				100	100	100	100
Naphthalene	(15)	100						88	(19)
Phenanthrene	(27)	100	↓	↓	↓	↓	↓	100	0

*() indicates tar production

Acknowledgements

References

1. Ratcliff, M.A. "Design and Construction of a Transportable Molecular Beam Mass Spectrometer and Its Application to the Analysis of Diesel Exhaust," Masters Thesis T4606, Colorado School of Mines (1994).

2. Ratcliff, M.A., French, R.J., Patrick, J.A., Anselmo, M. and Netter, J. "Development of a Third Generation Transportable MBMS for More Versatile and Cost-Effective Field Applications," Final Report, NREL FIRST Program (1998).

3. ABB Extrel, Pittsburgh, PA 15238.

4. Chornet, E., Czernik, S., Feik, C. and French, R. "Fluidized Bed Catalytic Steam Reforming of Trap Grease," NREL Milestone Report (2000).

5. Czernik, S., Wang, D., Montané, D., and Chornet, E. "Catalytic Steam Reforming of Biomass-Derived Fractions from Pyrolysis Processes," *Developments in Thermochemical Biomass Conversion,* Bridgwater, A.V. and Boocock, D.G.B., Blackie Academic & Professional, eds., pp. 672-686 (1997).

6. California Analytical Instruments, Orange, CA 92865.

7. Model TCM4 manufactured by Gerhard Wagner, Germany.

8. Teknivent Corp., Maryland Heights, MO 63043.

9. Kennedy, I.M. "Models of Soot Formation and Oxidation," *Prog. Energy Combust. Sci.* 23, pp. 95-132 (1997).

10. Ratcliff, M.A., French, R.J., Carpenter, D., Patrick, J.A.. and Looker, M. "MBMS Monitoring of Battelle Turbine Tests", NREL/TP-510-31223 (2000).

11. Gebhard, S.C., Gratson, D.A., French, R.J., Ratcliff, M.A., Patrick, J.A., Paisley, M.A., Zhao, X. and Cowley, S.W. "Characterization and Catalytic Conditioning of Synthesis Gas Produced by Biomass Gasification," *ACS Fuel Division*, 39, (4), pp. 1048-1052 (1994).

12. Ratcliff, M., Deutch, S., Feik, C., French, R., Graham, J., Meglen, R., Overly, C., Patrick, J., Phillips, S. and Prentice, B. "Biosyngas Characterization Test Results," NREL/TP-510-31224.

13. Garcia, L., French, R., Czernik, S., Chornet, E. "Catalytic Steam Reforming of Bio-oils for the Production of Hydrogen: Effects of Catalyst Composition," *Applied Catalysis A*, 201, pp.225-239 (2000).

REPORT DOCUMENTATION PAGE

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE May 2002	3. REPORT TYPE AND DATES COVERED Milestone Completion Report	
4. TITLE AND SUBTITLE Catalytic Steam Reforming of Gasifier Tars: On-line Monitoring of Tars with a Transportable Molecular Beam Mass Spectrometer			5. FUNDING NUMBERS BP01.2130
6. AUTHOR(S) Daniel Carpenter, Matthew Ratcliff, and David Dayton			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)			8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) National Renewable Energy Laboratory 1617 Cole Blvd. Golden, CO 80401-3393			10. SPONSORING/MONITORING AGENCY REPORT NUMBER NREL/TP-510-31384
11. SUPPLEMENTARY NOTES NREL Technical Monitor:			
12a. DISTRIBUTION/AVAILABILITY STATEMENT National Technical Information Service U.S. Department of Commerce 5285 Port Royal Road Springfield, VA 22161			12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

A method for evaluating catalytic tar decomposition in real time is presented. The effectiveness of two catalysts are compared.

14. SUBJECT TERMS biomass gasification, tar decomposition, catalytic steam reforming, transportable molecular beam mass spectrometer (TMBMS)			15. NUMBER OF PAGES
			16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL