

PRODUCT ANALYSIS FROM THE OPERATION OF A 10 TON/DAY, DIRECT, FLUIDIZED BED, BIOMASS GASIFIER AND HGCU SYSTEM

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Keywords: Gasifier Products, Hot Gas Cleanup, Molecular Beam Mass Spectrometry

Introduction

A principal goal of the DOE Biomass Power Program is the development of advanced high efficiency electric power generating cycles, such as integrated gasifier-gas turbine-generator systems. A key technical development required to economically produce electric power with an integrated gasifier-turbine system is the ability to remove chars and alkali metals from the gasifier product gas stream, to protect the turbines, and do so at high temperature and pressure. Westinghouse hot gas cleanup (HGCU) technology, based on ceramic membrane candle filters, has been selected for validation in this application [1]. The HGCU system was tested at the 10 ton/day scale, using a direct, pressurized, fluidized bed gasifier [2]. Two tests were conducted at the Institute of Gas Technology (IGT) RENUGAS process development unit (PDU) in Chicago, IL, during the weeks of October 31-November 5, 1994 and February 5-11, 1995.

The overall objective of the Westinghouse/IGT HGCU performance test program was to evaluate the performance of the hot gas filters with a dust-laden product gas generated from the gasification of bagasse in the RENUGAS PDU. This filter performance information will be used to determine the HGCU operating conditions for subsequent extended testing of the hot gas filters installed in a slipstream from the 100 ton/day bagasse demonstration gasifier in Hawaii [3]. Initially there was concern that tars produced in the gasifier would undergo coking reactions within the ceramic candles, leading to irreversible plugging of the filters. Consequently, a tar-cracking reactor was designed and installed ahead of the HGCU to remove the tars.

In order to characterize the tars and the performance of the process, the National Renewable Energy Laboratory's (NREL) Transportable Molecular Beam Mass Spectrometer (TMBMS) was interfaced with the PDU to monitor the performance of the RENUGAS gasifier, tar-cracker and candle filter unit operations. The development of a comprehensive, on-line, process monitoring capability has been a long term goal of NREL's Industrial Technologies Division. We have realized that goal with the successful demonstration of the TMBMS during the Westinghouse/IGT tests.

Experimental

The design and construction details of the TMBMS have been covered elsewhere [4]. In this application the instrument was interfaced with the PDU by a heat traced sampling system that permitted manual selection of three sampling ports with high temperature ball valves, as shown schematically in Figure 1. The sample ports A, B and C were installed at the tar-cracker inlet, tar-cracker outlet, and HGCU outlet, respectively. The sampling system incorporated the following functions. Particulate was removed from the gas samples with stainless steel filters at process pressure (nominally 300 psig) and at a temperature $\geq 300^\circ\text{C}$. The designed sample flow rate was 18.4 lb/h or 1% of the nominal process stream mass flow rate. The sample pressure was let-down in two stages with critical flow orifices (CFO1 and CFO2). The first stage caused the largest pressure drop from process conditions. A regulating valve between the CFO's was manually adjusted to maintain the pressure upstream of CFO2 at 20 psig by diverting most of the sample flow to vent. CFO2 dropped the pressure to 2-3 psig. The two stage CFO/diverted flow design of the sampling system enabled rapid detection of process fluctuations due to the dynamic nature of the sample flow.

The sample gas was then diluted 1:4 with preheated N_2 from a mass flow controller and a small amount of argon was blended (via mass flow controller) with the diluted sample as an internal standard. The sample then flowed through heat traced 0.5 inch stainless steel transfer lines to the TMBMS, while a constant temperature of 300°C was maintained. The diluted gas volumetric flow rate was measured by an orifice plate flow meter, just ahead of the TMBMS. This flow rate signal was recorded with the mass spectral data. The total diluted flow was directed past the TMBMS sampling orifice before being exhausted outside the building.

A port was provided in the sampling system for standards injection into the low pressure N_2 stream ahead of a static in-line mixer (see Figure 1). Multi-level calibration solutions of benzene, naphthalene, anthracene and pyrene were prepared. The standards were injected into the sampling system with a syringe pump several times each day, alone and as standard additions to sampled process gas.

IGT's sampling procedures for the PDU included product gas sampling at two points: downstream of the

gasifier and downstream of the tar-cracker. Gases, condensable liquids and entrained solids were collected from these points with iso-kinetic sampling systems, then separated for off-line analysis. The gases were analyzed with a Carle GC equipped with TCD and FID detectors. Immediately after the HGCU a Westinghouse alkali probe was installed. The product gas stream from this port was condensed and depressurized. The aqueous phase of the condensable liquids was analyzed for sodium and potassium. A breakthrough dust detector probe was installed at this same location. Solids collected on this probe were weighed but not analyzed because the quantity was too small. No gas or organic liquid analyses were performed from this third sample stream.

Results

The product gas composition measured by IGT, exiting the PDU gasifier is shown in Table 1. This raw gas composition reflects the non-optimized input of steam to the PDU and also nitrogen purges that are greater than would be used commercially. The condensed tar components collected after the gasifier measured 1.7 wt% of the bagasse feed on a moisture and ash free basis.

In the case of the TMBMS on-line measurements, tars are defined here as hydrocarbons with molecular weights starting with benzene on up. The TMBMS was programmed to scan to 350 amu (skipping masses 18 and 28 for H₂O, N₂ and CO to avoid saturating the detector) every 10 or 20 seconds. Figure 2 shows the total ion current vs. time trace for a 1 hour sampling period where we cycled through all of the sampling ports. Each point in the trace represents the acquisition of a complete mass spectrum. Thus the TMBMS is essentially a multi-channel on-line chemical analyzer. Figure 3 is the mass spectrum of the tars exiting the gasifier (sample port A), averaged over a six minute period starting at 2:00am (refer to Figure 2). The mass spectrum is representative of the tars produced in the gasification of bagasse in the IGT gasifier. They are of a tertiary nature, dominated by benzene ($m/z = 78$) and naphthalene ($m/z = 128$), along with smaller amounts of polycyclic aromatic hydrocarbons (PAH's) such as anthracene ($m/z = 178$) and pyrene ($m/z = 202$). Multi-level calibration of the TMBMS with standards allowed quantitative measurement of these species as shown in Figure 4. These data are from the first HGCU performance test and demonstrate that the tar-cracker was destroying about 75% of the tars and the HGCU was not removing much tar from the gas stream (< 10% of the raw tar). During the second test the tar-cracker was operated at a lower temperature and with different fluidizing media. In that test the TMBMS measured no significant change in tar concentration across either the tar-cracker or the HGCU.

The feeder system for the RENUGAS process was originally designed for wood chips. The change to bagasse in these tests forced numerous modifications to be made to the feeder system, many of which were anticipated and implemented before the first test. Further modifications to the feed injection screw, including water cooling and serrated threads, were made before the second test. In the field, analysis of the TMBMS data revealed some unexpected chemical behavior occurring in the process, which eventually lead to a new understanding of the importance of accurate feed level control in maintaining stable gasification.

The TMBMS monitored the concentrations of the various gases and vapors, which varied in a regular periodic fashion, during stabilized PDU operation. Figure 5 shows this behavior for just three of the numerous species monitored simultaneously: carbon dioxide ($m/z = 44$), benzene ($m/z = 78$) and methane ($m/z = 16$), sampled at port A. We observed that this cyclical behavior was correlated with the operation of the bottom feed lock-hopper valve and had a period of approximately 5 minutes. The feed lock-hopper was slightly over-pressurized with nitrogen, relative to the gasifier, to prevent back-flow of gasification product gas containing combustibles and steam. For this reason part of the concentration variation was probably due to nitrogen dilution of the products when the bottom gate valve opened. However, because the relative magnitude of the concentration drops were not the same for all products, we deduced that there were more complex effects of the lock-hopper operation on the gasification process than product dilution.

The concentration variation was not due to process pressure fluctuations because our sample gas flow meter, an orifice plate/differential pressure meter, was stable through this monitoring period. Sampling system artifacts such as distillation or chromatography in the sample transfer lines are largely ruled out by the fact that the variation magnitude was approximately the same for hydrocarbons from benzene through pyrene and only slightly less for methane. The swing effect was attenuated for tar compounds above mass 202, and this may be due to sampling artifacts because of the 300° C temperature of the transfer lines and the relatively low vapor pressures of the higher molecular weight species.

Our explanation for the product concentration swing is a momentary upset of the residence time of the bagasse in the gasifier when the bottom lock-hopper valve opens. At that moment, we believe that bagasse distributed along the feed injection screw was blown into the gasifier at an uncontrolled rate by the over-pressurized nitrogen from the lock-hopper. This was followed by a brief period during which no fresh bagasse was injected into the gasifier, as the feed injection screw grooves refilled. Thus, the bagasse residence time in the gasifier was disrupted causing the product concentrations to drop then return to normal.

Tars and methane are formed early in the gasification process, by pyrolytic mechanisms from the volatile components in the fresh bagasse [5,6]. Their residence time in the gasifier is short, being controlled by the steam and gas flow rate. In contrast, char has a longer residence time in the gasifier and distributes throughout the fluidized bed. Char continues to react with steam producing CO₂, CO and H₂ long after the volatile tars have left the reactor, explaining the less pronounced concentration drop for CO₂ than for tars and methane.

During the second test the TMBMS detected the effects of a feed interruption and change in feeder system operation, while monitoring port C. An overheating tar-cracker forced an interruption in bagasse feeding to permit the tar-cracker to cool down. Mechanical problems with the feed lock-hopper began as feeding was restarted. These problems took about 30 minutes to resolve, and when feeding recommenced the TMBMS made it apparent that the gasifier product concentrations were no longer varying during lock-hopper operation. Figure 6 shows the HGCU outlet concentrations of CO₂, benzene and methane before, during and after the feeder problems, starting at 9:14pm. These observations with the TMBMS were carefully correlated with events in the PDU control room. During the sample time frame of 10-24 minutes we see the concentration swing behavior characteristic of the PDU operation with bagasse to that point. At 24 minutes the PDU operator interrupted feeding to cool down the tar-cracker. The TMBMS detected this interruption as, for example, the drop in benzene concentration to baseline. It remained there until 33 minutes, and the methane behaved similarly, yet the CO₂ concentration remained high. A partial batch of fresh feed was delivered into the gasifier at 33 minutes, when the concentrations of all three products rise. Then the upper lock-hopper valve jammed at about 34 minutes. The TMBMS again detected this as the precipitous drop in methane and benzene concentrations and the more gradual drop in CO₂.

We presently do not have an explanation for the sudden unilateral rise in CO₂ at 46 minutes, but by 54 minutes the feeding problems were resolved and all the product concentrations were near normal by 10:09pm. The TMBMS monitoring of port C was interrupted between 10:09pm and 10:10pm and then sample dilution nitrogen was measured for background for 3 minutes. By 10:14pm the TMBMS was back on-line with port C, and we observed that the average product concentrations were roughly equivalent to those prior to the feed interruption, however, the periodic concentration swings were gone. The TMBMS detected the back-pulse of the HGCU at 104 minutes. The cause of the concentration spike for benzene and methane at 88 minutes has not been determined.

The reason for the improved chemical stability was that the PDU operator had made an operational change that increased the inventory of bagasse in the feeder section between the bottom lock-hopper valve and the injection screw. This change was made possible because the feed level sensor had spontaneously begun to operate in a satisfactory manner, during the correction of the feeder system mechanical problems in the previous half hour. (The capacitance-type feed level sensor had been reliable with wood chips but not with the bagasse up to this point). The higher feed level effectively sealed the gasifier from the pressure bursts associated with the lock-hopper operation. Thus, the actual bagasse feed rate into the gasifier was stabilized, the residence time of the feed in the gasifier was no longer disturbed and the product concentrations stabilized.

Conclusions

A Molecular Beam Mass Spectrometer was successfully interfaced with a high temperature/pressure, PDU scale biomass gasifier, hot gas conditioning and cleanup unit operations. We demonstrated the instrument's ability to continuously sample from the process and measure multiple products simultaneously. Statistical analysis of the calibration standards data demonstrated that the TMBMS response to the analytes was linear and very precise over the range of 10-1000 ppm. Excellent instrument calibration stability was achieved over a period of five days and the standard addition tests revealed no sample matrix effects on the calibration of the TMBMS for these analytes.

The identification and explanation of the process fluctuations and the feeder system operational change described above, as well as other transient phenomena, was facilitated by the on-line multi-species detection capabilities of the TMBMS. The TMBMS process gas measurements showed that the HGCU was not affecting the tar species concentrations, implying that coking would not be a problem. Analysis of the candle filters at Westinghouse showed no evidence of carbon deposition within the filters, confirming our conclusion.

The sampling experience with the TMBMS during transient feeding upsets demonstrated that chemical channels leading to the formation of benzene (and the other PAH's) and methane shut down rapidly in the absence of fresh feed. Thus, these compounds appear to be very sensitive indicators of feeding and gasification stability. Continuous measurement of one or more of these species would be very beneficial to process control.

References

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Acknowledgments

The authors are grateful to the numerous people who participated in these tests. Special thanks go to David Dayton, Steve Deutch, Robert Meglen, Steve Phillips, Ralph Oyerend and Tom Milne from NREL, and Rick Knight, Bob Schlusser, Ken Kozlar, Dave Parham and Jim Wangerow from IGT. This project was funded by the DOE's Solar Thermal and Biomass Power Program directed by Gary Burch. The NREL program manager was Rich Bain.

Table 1. Gasifier Product Gas Composition* (vol. %, wet)

H ₂	4.23	CH ₄	3.81
H ₂ O	56.14	C ₂ H ₄	0.14
N ₂	17.58	C ₂ H ₆	0.06
CO	6.83	C ₃ H ₆	0.00
O ₂	0.07	C ₃ H ₈	0.00
CO ₂	10.91	C ₆ H ₆	0.23 ^b

* Reflects non-optimized steam input and nitrogen purges.

^b Includes benzene from condensate.

Figure 1

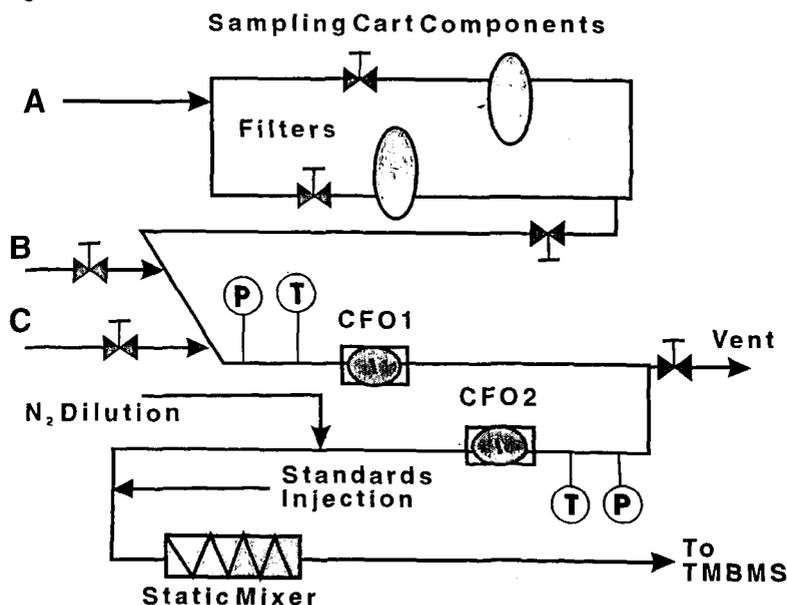


Figure 2

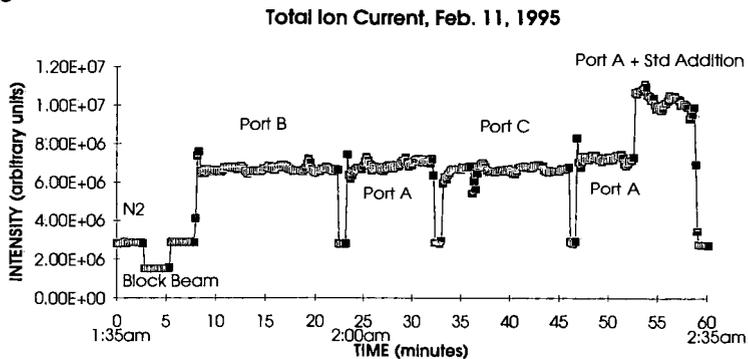


Figure 3

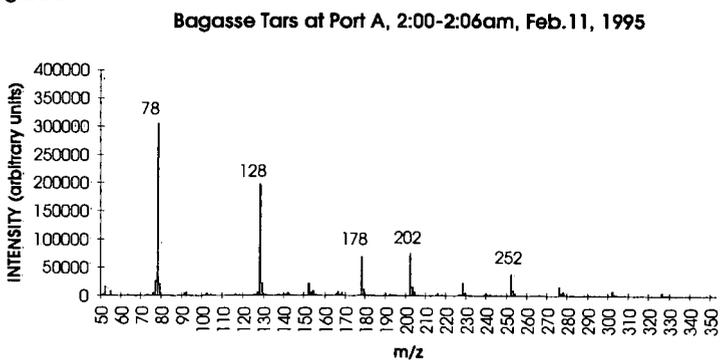


Figure 4

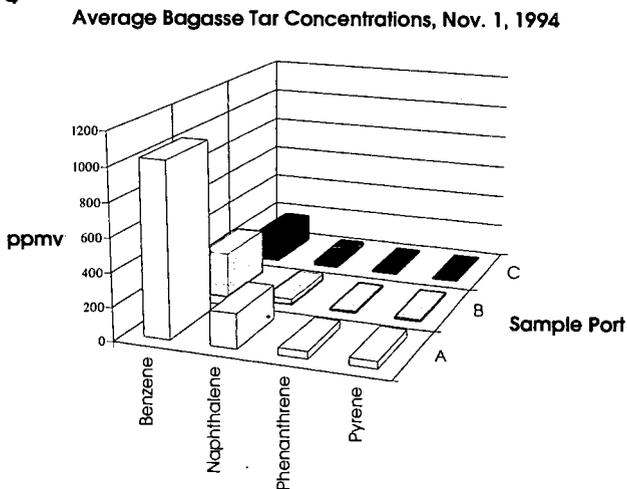
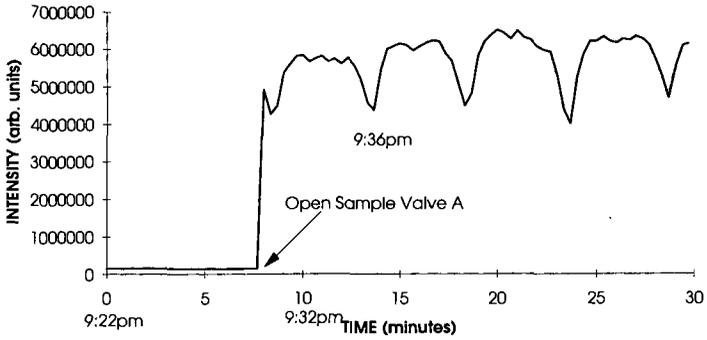
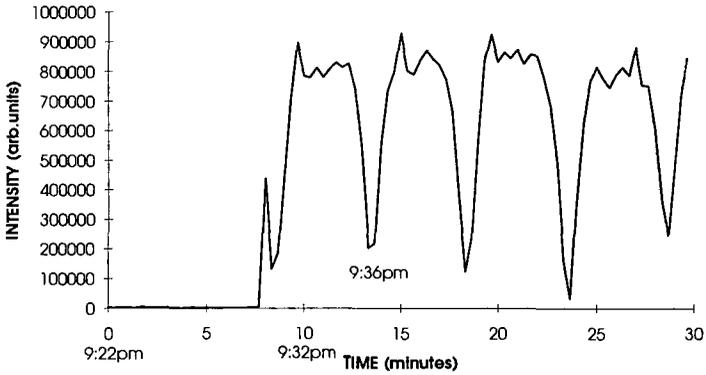


Figure 5

CARBON DIOXIDE at Port A: Tar-Cracker Inlet, Nov. 1, 1994



BENZENE at Port A: Tar-Cracker Inlet, Nov. 1, 1994



METHANE at Port A: Tar-Cracker Inlet, Nov. 1, 1994

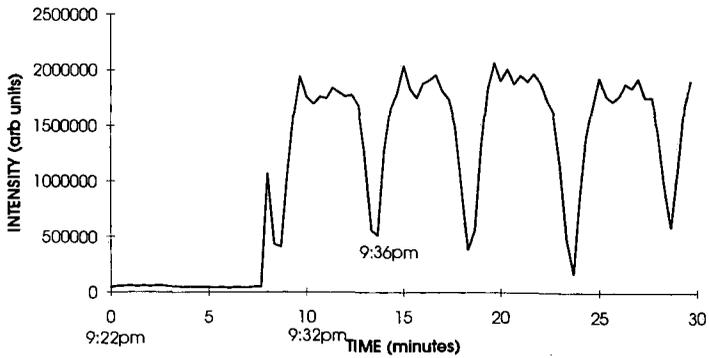
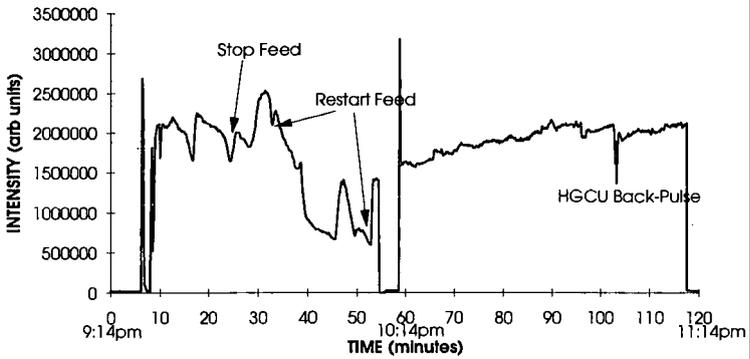
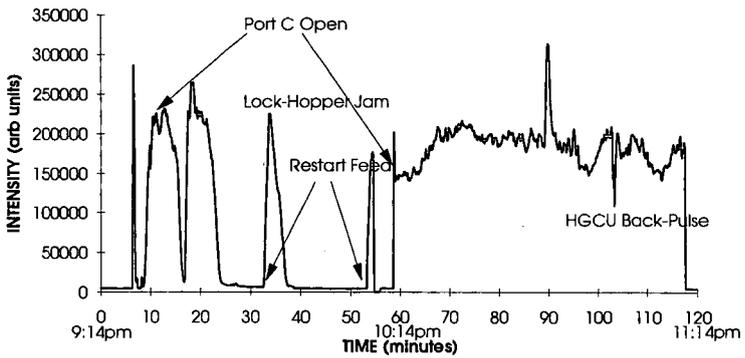


Figure 6

Carbon Dioxide at HGCU Outlet, Feb. 10, 1995



Benzene at HGCU Outlet, Feb. 10, 1995



Methane at HGCU Outlet, Feb. 10, 1995

