

Final Report

Project Title: Biomass Gasification Research Facility

Award Number: DE-FC36-02GO12024

Recipient: Gas Technology Institute

Project Location: Birmingham, Alabama

Project Period: June 1, 2002 to June 30, 2007

Date of Report: September 30, 2007

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Subcontractors: University of Alabama at Birmingham

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Executive Summary

To enable the potential uses for syngas derived from biomass gasification to be fully exploited, GTI has carried out two companion projects (under Cooperative Agreements DE-FC36-02GO12024 and DE-FC36-03GO13175) to characterize, assess, and enable the improvement of syngas conditioning processes. These two cooperative agreements between DOE and GTI evolved from the initial configuration of Cooperative Agreement DE-FC36-02GO12024, which was executed by DOE with Southern Research Institute in September 2002. The original objective of Cooperative Agreement DE-FC36-02GO12024 was to design, and subsequently construct and operate, a flexible and versatile research facility, the Research and Development Platform for Biomass Power Systems Integration. This facility was to be a “plug-and-play” platform for the arrangement and integration of process components and was intended as a means to solve technical issues involving process integration in order to make biomass gasification an acceptable commercial option. Reduced funding available from DOE, and a coincident desire of Southern Research Institute to end its participation in this area of research, led to a redefinition of the project’s scope and objectives, and to the eventual transfer of the project’s remaining funds to GTI in October of 2003. Two separate, companion projects resulted from this transfer – Cooperative Agreement DE-FC36-03GO13175, initiated between DOE and GTI in October 2003, and Cooperative Agreement DE-FC36-02GO12024, novated to GTI by DOE in April 2004.

As mentioned above, the reduction in available funding and this Cooperative Agreement’s novation to GTI resulted in the redefinition of this project’s primary objective. After being transferred to GTI, the objective of Cooperative Agreement DE-FC36-02GO12024 became the selection, acquisition, and application of a suite of gas analyzers capable of providing near real-time gas analyses to suitably conditioned syngas streams. Although a brief review of the early activities on this project (conducted by Southern Research Institute) are included here, this Final Report will focus on the activities under this Cooperative Agreement after its novation to GTI. Concurrent with the transfer of Cooperative Agreement DE-FC36-02GO12024 to GTI, DOE also set up Cooperative Agreement DE-FC36-03GO13175 with GTI, which had as its specific objective the development of comprehensive in situ and extractive gas sampling equipment and protocols to enable the evaluation, optimization and integration of syngas treatment technologies at various gasification facilities. (Additional information is available in the Final Report issued under Cooperative Agreement DE-FC36-03GO13175.) The sampling equipment and protocols developed in these projects were proven in the field through evaluations of syngas quality at two sites where biomass-derived syngas was generated.

In a stepwise series of field demonstrations conducted under these two projects, GTI developed the sample delivery and distribution methods and hardware, and sample conditioning interfaces, necessary to make use of state-of-the-art on-line analyzers to evaluate and optimize syngas cleanup and conditioning in thermochemical process streams. Initial tests at GTI’s Flex-Fuel Test Facility (FFTF) in late 2004 and early 2005 successfully demonstrated the transport and subsequent analysis of a single depressurized, heat-traced

syngas stream to a single analyzer (an Industrial Machine and Control Corporation (IMACC) Fourier-transform infrared spectrometer (FT-IR)) provided by GTI. In March 2005, our sampling approach was significantly expanded when this project participated in the U.S. Department of Energy's National Energy Technology Laboratory's Novel Gas Cleaning (NGC) project. Syngas sample streams from three locations in the FFTF were transported to a distribution manifold for selectable analysis by three analyzers (the IMACC FT-IR, a Stanford Research Systems QMS300 Mass Spectrometer (SRS MS) obtained under Cooperative Agreement DE-FC36-02GO12024, and a Varian micro gas chromatograph with thermal conductivity detector (μ GC)) provided by GTI. In addition, a syngas stream from a fourth location in the FFTF process stream was transported to a separately located Agilent Model 5890 Series II gas chromatograph for highly sensitive gas analyses. The on-line analyses made possible by our sampling system and the analyzers provided by Cooperative Agreement DE-FC36-02GO12024 and GTI verified the syngas cleaning achieved by the NGC process.

In June 2005, GTI completed a field test campaign in collaboration with Weyerhaeuser to characterize the ChemrecTM black liquor gasifier at Weyerhaeuser's New Bern, North Carolina pulp mill. Over a ten-day period, a broad range of process operating conditions were characterized with GTI's online sampling capabilities, which comprised the IMACC FT-IR, the SRS MS, the Varian μ GC, and an integrated Gas Chromatograph, Mass Selective Detector, Flame Ionization Detector and Sulfur Chemiluminescence Detector (GC/MSD/FID/SCD) system acquired under Cooperative Agreement DE-FC36-02GO12024 from Wasson-ECE. In this field application, a single sample stream was extracted from this low-pressure, low-temperature process and successfully analyzed by the four devices listed above. In October and November 2005, GTI conducted intensive field characterizations of biomass-derived syngas at GTI's FFTF during a concurrent test of pelletized wood-fueled gasification and catalyst performance investigated under DOE Cooperative Agreement DE-FG36-04GO14314. In March 2006 we continued our sampling development and verification activities at GTI's FFTF with a follow-on set of calibration measurements.

Because of the increased importance of gasification of underutilized biomass materials, and the specific opportunities that corn stover material could have as a feedstock for gasification, this project adapted the sampling train developed and tested in this project to the 2-inch gasification unit. Although this specific interface has not been built, its components are all either commercially available, or have been thoroughly evaluated under Cooperative Agreement DE-FC36-02GO12024 and Cooperative Agreement DE-FC36-03GO13175.

The combination of the sample conditioning and sample stream transport methods developed under Cooperative Agreement DE-FC36-03GO13175, and the assembly and coordination of gas analyzers and data collection and analyses under Cooperative Agreement DE-FC36-02GO12024, have provided a new, powerful, enabling capability for on-line data characterizations of biomass- and coal-derived syngas from thermochemical conversion process streams.

Background

Thermochemical conversion processes offer the promise of effectively utilizing all biomass and fossil fuels. Gasification processes create recoverable heat plus a useful product (syngas) that can be converted through multiple pathways into additional heat, power, liquid and/or gaseous fuels, and chemical feedstocks. Gasification can be carried out at a variety of temperatures and pressures, with pressurized gasification offering advantages for syngas conversions to higher-value products, particularly for larger (~ 100 MW) facilities that integrate gasification with the generation of power, and with downstream refining operations for fuels and chemicals that previously were accessible only at a dedicated petrochemical refinery. For such processes, the rapid assessment of syngas quality is of paramount importance for process optimization and control. For example, catalytic chemical conversions such as methanation or Fischer-Tropsch processes, and high-efficiency power conversion with solid oxide fuel cells impose requirements for syngas quality that severely limit contaminants (sulfur species, halides, alkalis) to levels that can be lower than 10 ppbv. Thus, the availability of robust methodologies to provide rapid and precise assessment of syngas quality will be of great value for the development and wide-spread deployment of these syngas conversion technologies.

Potential applications for thermochemically-produced syngas include electric power generation, liquid fuels production, substitute natural gas, and other chemical production. In order to optimize process operation and reliability, and to ensure that the product gas meets acceptable quality standards, these thermochemical process operations should continuously include up-to-date, accurate information describing syngas composition and characteristics throughout the process stream. With this information, operators can monitor syngas cleanup processes, protect sensitive downstream conversion equipment (e.g. turbines, fuel cells, chemical reformers), document and optimize product gas quality, and identify and diagnose potentially damaging discrete process events.

While thermochemical syngas production facilities are already employed worldwide, exploitation of their potential has been inhibited by limitations encountered when attempting to obtain the type of real-time compositional data identified above.

Project Overview

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objective of Cooperative Agreement DE-FC36-02GO12024 was to design, and subsequently construct and operate, a flexible and versatile research facility, the Research and Development Platform for Biomass Power Systems Integration. This facility was to be a “plug-and-play” platform for the arrangement and integration of process components and was intended as a means to solve technical issues involving process integration in order to make biomass gasification an acceptable commercial option. Reduced funding available from DOE, and a coincident desire of Southern Research Institute to end its participation in this area of research, led to a redefinition of the project’s scope and objectives, and to the eventual transfer of the project’s remaining funds to GTI in October of 2003. Two separate, companion projects resulted from this transfer – Cooperative Agreement DE-FC36-03GO13175, initiated between DOE and GTI in October 2003, and Cooperative Agreement DE-FC36-02GO12024, novated to GTI by DOE in April 2004.

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Early in this project, a review was conducted of sampling options, available analysis technologies, and commercially available analyzers, that could be successfully applied to the challenging task of on-line syngas characterization. The majority of thermochemical process streams comprise multicomponent gas mixtures that, prior to crucial, sequential cleanup procedures, include high concentrations of condensable species, multiple contaminants, and are often produced at high temperatures and pressures. Consequently, it is usually not feasible to introduce flowing sample streams from these thermochemical processes to most analyzers without some type of sample stream preparation, or conditioning. Safety concerns associated with thermochemical process operation constrain the location and configuration of potential gas analysis equipment. In addition to these factors, initial analyzer costs, reliability, accuracy, and operating and maintenance costs were also considered prior to the assembly of suitable analyzers for this task.

As this project developed, it became apparent that appropriate preparation of the syngas stream was critical for successful, continuous, on-line syngas analyses. The approach to performing this gas stream preparation was to identify the most useful analyzers, and to condition the syngas sample stream to the specific extent necessary for it to be introduced to the analyzer on a continuous basis. The conditioning steps used to prepare the syngas

streams were filtration, depressurization, dilution with inert, metered nitrogen, and thermally-managed transport to locations suitable for installation and operation of the analyzers. The overall sample management system that GTI developed under Cooperative Agreement DE-FC36-03GO13175 enabled the delivery of multiple syngas sample streams, through customized sample distribution manifolds, to the selected analyzers, at temperatures and pressures acceptable to the analyzers. Further details of the development and verification of the sample stream conditioning steps, and the equipment and procedures used to carry them out, are detailed in the Final Report, and in a Special Topical Report (Design and Protocol for Monitoring Gaseous Species in Thermochemical Processes), issued under Cooperative Agreement DE-FC36-03GO13175.

In a stepwise series of field demonstrations conducted under these two projects, GTI developed the sample delivery and distribution methods and hardware, and sample conditioning interfaces, necessary to make use of state-of-the-art on-line analyzers to evaluate and optimize syngas cleanup and conditioning in thermochemical process streams. Initial tests at GTI's Flex-Fuel Test Facility (FFTF) in late 2004 and early 2005 successfully demonstrated the transport and subsequent analysis of a single depressurized, heat-traced syngas stream to a single analyzer (an Industrial Machine and Control Corporation (IMACC) Fourier-transform infrared spectrometer (FT-IR)) provided by GTI. In March 2005, our sampling approach was significantly expanded when this project participated in the U.S. Department of Energy's National Energy Technology Laboratory's Novel Gas Cleaning (NGC) project. Syngas sample streams from three locations in the FFTF process stream were transported to a distribution manifold for selectable analysis by three analyzers (the IMACC FT-IR, a Stanford Research Systems QMS300 Mass Spectrometer (SRS MS) obtained under Cooperative Agreement DE-FC36-02GO12024, and a Varian micro gas chromatograph with thermal conductivity detector (μ GC)) provided by GTI. In addition, a syngas stream from a fourth location in the FFTF process stream was transported to a separately located Agilent Model 5890 Series II gas chromatograph for highly sensitive gas analyses. The on-line analyses made possible by our sampling system in conjunction with the analyzers provided by Cooperative Agreement DE-FC36-02GO12024 and GTI verified the syngas cleaning achieved by the NGC process.

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Initial Project Activities

The overall objective of this project was to accelerate the deployment of biomass gasification technology for power generation by addressing and resolving systems integration issues, such as issues with fuels handling, gasifier design, and hot gas cleanup. Initially this objective was to be addressed through a research and development platform. As such, the initial emphasis of this project was the design of a flexible and versatile research facility, which was to be a "plug-and-play" platform for the arrangement of process components that need to be integrated in order to make biomass gasification an acceptable commercial option. The scale of this research and development platform was to be approximately 10 tons/day of fuel input. Systems integration issues were to be studied experimentally, and the results would be planned to be generalized through computational modeling of the processes tested.

The major activities planned for the overall project are listed in Table 1. A number of specific accomplishments, summarized below, were made under the original statement of work for this project while under the control of Southern Research Institute.

Table 1. Major Activities Originally Planned in the Overall Project

Phase I	Design, test plan, and equipment relocation
Phase II	Facility construction
Phase III	Component startup and initial testing
Phase IV	Systems testing and analysis

Within the activity structure shown in Table 1, the project initially included four specific tasks, as detailed in Table 2.

Table 2. Initial Project Tasks

Task 1	Facility Design
Subtask 1.1	Site - zoning, permitting
Subtask 1.2	GTI RENUGAS® documentation
Subtask 1.3	Conceptual design
Subtask 1.4	Detailed design
Subtask 1.5	CFD model
Task 2	Test Plan Development
Task 3	Move GTI Equipment to Birmingham
Task 4	Documentation and Reporting

Work was conducted on all of these initial project tasks. There were two decision points in the project schedule corresponding to two phases of Subtask 1.3 Conceptual Design. The first decision point was at the conclusion of the Facility Planning level of design, which yielded a $\pm 30\%$ estimated cost for the Biomass Gasification R&D Platform. This milestone was completed in February 2003 and the decision of the project Technical Advisory Panel, with concurrence of DOE, was to proceed with the next level of design. The project reached the second decision point in August 2003 with the completion of the Basic Engineering phase of the design, which produced a $\pm 10\%$ cost estimate for the Biomass Gasification R&D Platform. This concluding effort under Subtask 1.3 produced process and instrumentation drawings, equipment specifications and bid packages, building and services systems specifications and layouts, and bids to supply process, control, and analytical equipment. The results of the $\pm 10\%$ engineering design were documented in a Final Scope and Estimate report that was previously provided to DOE by Southern Research Institute prior to the novation of this Cooperative Agreement to GTI. The $\pm 10\%$ engineering design produced in Subtask 1.3 was the final facility design task in this project. This decision was based on discussions with the Technical Advisory Panel and with DOE.

The initial assignment and first two milestones under Subtask 1.5 were also achieved. A graphical user interface and a computational framework for fluid dynamic modeling of the RENUGAS® Process Development Unit (PDU) gasifier were completed. This work provided the tools and the foundation for planned subsequent CFD modeling of integrated system components, and the gasifier module was envisioned as the cornerstone piece of the Biomass Gasification R&D Platform. Concurrent with Task 1 efforts was the assembly of information needed to develop a test plan for the Biomass Gasification R&D Platform. An extensive review of the prior research and development work in biomass gasification, and a review of computational tools for modeling biomass gasification processes, were carried out.

The RENUGAS® PDU equipment was relocated from Chicago to Birmingham in anticipation of use in the Biomass Gasification R&D Platform. This move completed work under Subtask 1.2 and Task 3. The documentation of the project under Task 4 consisted primarily of engineering design information including drawings and specifications, and the test plan. Two special reports were prepared and submitted to DOE from Subtask 1.3, Conceptual Design, which documented the Facility Planning and Basic Engineering phases. The overall project technical and financial status was reported quarterly. Three of the four project Tasks remained incomplete as of the time Southern Research Institute became disengaged from this project. Only Task 3 was 100 % completed. Two of the five subtasks under Task 1 were completed, and some work was initiated in two of the other subtasks under Task 1.

Technical Advisory Panel

A Technical Advisory Panel (TAP) of experts in gasification and process technologies, the pulp & paper industry, and the electric utility industry was also assembled to help the project team prioritize research objectives for the express purpose of accelerating the development and deployment of biomass gasification systems. Periodic meetings were sponsored to solicit the advice and expertise of a broad range of persons involved in biomass gasification research and development. In these meetings, technical and market issues, and potential project plans were discussed in an open forum. This Technical Advisory Panel met in February and June, 2003 at Southern Research Institute, and again in March and November, 2004 at GTI's offices in Birmingham, Alabama. Over the duration of Cooperative Agreement DE-FC36-02GO12024 and Cooperative Agreement DE-FC36-03GO13175, the advisory panel included representatives from the U.S. DOE, Golden Field Office, Southern Company Services, Inc., American Electric Power, Institute of Paper Science & Technology, Tennessee Valley Authority (TVA), TVA / Public Power Institute, BE&K Engineering, University of Alabama at Birmingham, North Carolina State University, EPRI, VTT Energy, and Gas Technology Institute. The panel conducted discussions of various aspects of biomass gasification research and development, including costs and market forces, setting research priorities, options for future work, system integration, system design, measurement techniques, fuels and fuel handling, and gas cleanup. The exchange of information and opinions contained in these discussions were used to establish project objectives and guide the execution of project activities for both cooperative agreements.

The Technical Advisory Panel recommended that this project focus on analytical capabilities, gas cleanup, and/or biomass feeding. One option discussed was a proposal from the American Forest and Paper Association (AF&PA) to perform a technical and economic analysis of BLG syngas use. Another focus for future work that was generally endorsed by the TAP was the stepwise approach for sample extraction, and sample conditioning and analysis with a suite of continuous, on-line analyzers. The attendees suggested that a transportable

analytical platform be developed. Such a platform would allow the expertise of the research project team in process sampling and analysis to be applied to various pilot-scale and demonstration-scale gasification facilities.

As a result of these discussions and the reduction in funding from DOE and the transfer of the project to GTI, the specific objectives of this project were refined as detailed above. The focus of remaining effort on the project became centered specifically on the integration and evaluation of syngas cleanup and treatment technologies. The broader objective, which included operating a complete gasification system, was set aside. The revised near-term goals of this project were still directed to provide needed and valuable support for the original project objectives. For a variety of reasons, including project management and availability of funding, slipstreams of syngas produced by existing or previously planned demonstration-scale gasifiers were identified as the source of future project field efforts.

Process Sampling

The general approach of using on-line analyzers to provide timely, accurate, and dependable analyses of the syngas through the various steps of its production and cleanup depends on two primary components: 1) the selection of appropriate analyzer(s) with which to perform the analyses; and 2) the ability to provide these analyzer(s) with continuous, representative streams of syngas from the process locations of interest. Support activities to these two major objectives include safety of operation, management of initial and operating costs, QA/QC, and adaptability of the overall approach to the various sampling locations and the expected gas constituents throughout the syngas production process.

Technical issues arising from the syngas sample stream extraction and transport that is required to provide the analyzer(s) with suitable syngas for analysis are dependent on the conditions of the transport (primarily temperature, pressure, and particulate loading). Therefore, the development of the sampling approach was primarily driven by the operating constraints of the candidate analyzers. In our initial review of gas analyzers, it was apparent that almost all of the analyzers could not accept a sample syngas stream at the conditions present at the point of extraction from the process. When paired up with the environmental conditions within typical thermochemical process streams, the limitations of these instruments made it apparent that significant reductions in pressure and temperature, as well as the removal of any entrained particulates, would have to be accomplished prior to performing the syngas analysis.

One of the key requirements in evaluating the options for the delivery of suitable sample streams to the analyzers being considered for use was the maintenance of gas species in their vapor state all the way to the introduction of the sample stream to the analyzers. This

requirement was adhered to because of documented changes in key syngas components (especially tars and oils) when they were allowed to condense prior to analysis. In response, the project team developed an approach to sample extraction, conditioning and transport that enabled the successful application of a variety of state-of-the-art gas analyzers. This approach is documented in the Final Report issued under Cooperative Agreement DE-FC36-03GO13175, and also documented in more detail in a Special Topical Report (Design and Protocol for Monitoring Gaseous Species in Thermochemical Processes), issued under Cooperative Agreement DE-FC36-03GO13175.

The project team also set as a priority the ability to use any sampling system developed under this project at multiple sites. This objective required that the primary components of the sampling and analysis system be rugged, and small enough to move, as well as being adaptable to syngas streams with widely different environmental conditions and component constituents.

Evaluation of Candidate Gas Analyzers – An initial survey performed of candidate gas analyzers is summarized in Table 3. The table compares the key factors influencing the ultimate selection of analyzers for use in this work. The schematic diagram in Figure 1 shows how stepwise conditioning of the extracted syngas stream could be configured to meet the requirements of the some of the more promising candidate instruments. This extractive approach was seen as a way to enable the desired syngas analyses, while at the same time avoiding more expensive, complicated sampling arrangements that were previously evaluated as part of the originally conceived Research and Development Platform for Biomass Power Systems Integration. (The sampling arrangements evaluated earlier in this project are detailed in reports issued to DOE by Southern Research Institute.) The approach shown in Figure 1 was significantly refined before its final application. The Special Topical Report issued under Cooperative Agreement DE-FC36-03GO13175 details these refinements and the final design of the sample extraction and transport system.

Based on the information in Table 3, and the availability of instruments, this project assembled and tested a suite of versatile, state-of-the-art process monitoring instrumentation that were used in field demonstrations in combination with GTI's novel sample management techniques. The suite of analyzers utilized in this project grew and evolved as our sample extraction and transport capabilities improved, and as instruments became available or were acquired under this Cooperative Agreement.

Table 3. Major and Minor Species in Coal and Biomass-Derived Fuel Gas and Instrumentation for their Measurement.

Component	Range, vol %, or as noted ^a	Instrument or Method	Supplier	Model Number	Data Output	Sample Temp., °F	Sample Press, psig	Sample Flow, lpm	Sample Cond. ^b	Sample Time ^c	Cost ea, k\$
O ₂	~ 0	paramagnetism	Rosemount	755A	4-20 mA	50 - 150	< 10	0.25	4	cont.	11.9
CO	4 - 8	NDIR ^d	Rosemount	880AS	4-20 mA	59 - 95	< 10	0.5 - 1	4	cont.	9.9
CO ₂	12 - 17	NDIR ^d	Rosemount	880AS	4-20 mA	59 - 95	< 10	0.5 - 1	4	cont.	8.2
NH ₃	0.01 to 1	NDIR ^d	Rosemount	880AS	4-20 mA	59 - 95	< 10	0.5 - 1	4 ^e	cont.	8.5
H ₂ O	30 - 45	dipole polarization	Dewcon	108 SVT	RS232C	< 842	< 725	-	0	cont.	29
H ₂ , N ₂ , Ar, CO, CO ₂ , NH ₃ , H ₂ S, COS, C ₁ to C ₃	0.001 to 30	Micro GC ^f with TC ^g detector	Agilent	3000	TCP/IP	ambient	< 30	~ 0.1	4	2 min	48.2
H ₂ O, CO, CO ₂ , NH ₃ , HCN, H ₂ S, COS, HCl, C ₁ to C ₆₊	0.001 to 45	FT-IR ^h	IMACC	custom	TCP/IP	< 365	< 10	10-15	3	1 min	128.1
H ₂ , Ar, H ₂ O, CO ₂ , NH ₃ , HCN, H ₂ S, COS, HCl, CH ₄	0.001 to 45	MS ⁱ	SRS or Agilent	QMS 300 5000A	RS232C	< 800 ^j	~0	0.001-0.01	1, 2, or 3	1 min	25.4 90.3 ^p
Tar, oil, total HC	5.6 to 15 as C ₁	FID ^k	Ratfish	TA120-3	RS232	< 572	0.07-0.44	1.7 - 5	2	2 min	47
Tar and oil species	0.03 to 1.2 total	GC/MS ^l	Shimadzu	QP5050A	10BASE-TX/ 10BASE-T	< 662	2 - 60	~ 0.5	2	30-60 min	116.6
Particle conc., size, compos., etc.	100 g/m ³ 10 g/m ³ 0.0001 g/m ³	filter, cyclones, impactor ^m	q	custom	q	800	< 450	isokinetic ⁿ	0	60 min	q
Particle concentration	0.0001-10 g/m ³	charge induction ^m	PCME	DT 990	RS232	< 932	< 350	> 6 m/s	0	cont.	11.7 ^r
Na, K, Mg, Ca, Si, Al	~ 1 g/m ³	LIBS ^o	probe/interface Sp-Phys (laser) Roper (ICCD, spectrograph) Dolch (PC) accessories ^s	custom PRO-290-10 PI-MAX SP-500i FXPAC6	TCP/IP	800	< 450	-	0	cont.	20 ^t 149.5 ^t 62.3 ^t 7.9 ^t 50 ^t

Notes for Table 3.

- a. Including H₂O and inert gases.
- b. Sample conditioning:
 - 0 - cooled to ~800 °F
 - 1 - particles removed, sample at ~800 °F
 - 2 - heavy tar removed, sample at ~550 °F
 - 3 - light tar removed, sample at ~300 °F
 - 4 - oil and water removed (~32 °F dewpoint), sample at room temperature
- c. Estimate of time required to collect sample, analyze, and prepare instrument for next sample.
cont.: continuous.
- d. Non-dispersive infrared absorption.
- e. Need to determine whether ammonia loss on drying the sample is acceptable.
- f. Gas chromatography.
- g. Thermal conductivity.
- h. Fourier transform-infrared spectrometry.
- i. Mass spectrometry.
- j. There is a capillary, external to the instrument, in which the pressure is let down to 0.3 torr. Downstream from the capillary, the sample returns to room temperature before introduction to the mass spectrometer. If the capillary is heated, by wrapping with resistance wire or in an oven or furnace, we can deliver to it any species that will not condense at room temperature and 0.3 torr. Another requirement is that we not form coke inside the capillary, at least not too rapidly.
- k. Flame ionization detector.
- l. Gas chromatography/mass spectrometry.
- m. Upstream from cyclone, take value of 9.2 grain/dscf leaving gasifier, from summary of GTI data (Evans et al., 1988⁶) by BE&K (Drawing No. 100-F0-104, Dec. 13, 2002). Assume 40 vol% water vapor, pressure of 21.77 atm, temperature of 1530 °F. Downstream from cyclone, assume collection efficiency of 90%. Downstream from barrier filter, assume collection efficiency of 99.9999%. Particle concentrations entered in the table are at 1530 °F and 450 psig.
- n. Flow rate depends upon local gas velocity and diameter of probe.
- o. Laser-induced breakdown spectrometry.
- p. Either of these mass spectrometers, SRS or Agilent, may be suitable for this application. Cost for the Agilent instrument does not include sales tax. The total on the Agilent quote is \$97,496, including tax of \$7,198.
- q. Use existing equipment.
- r. Placed on hold, due to experience at the Power Systems Development Facility using this instrument.
- s. Housing, breadboard, mounts, lenses, fiber optics, power meter, delay generator, chiller, calibration rig.
- t. New project was being sought for support of LIBS work, in collaboration with the University of Alabama at Birmingham and Sandia National Laboratories.

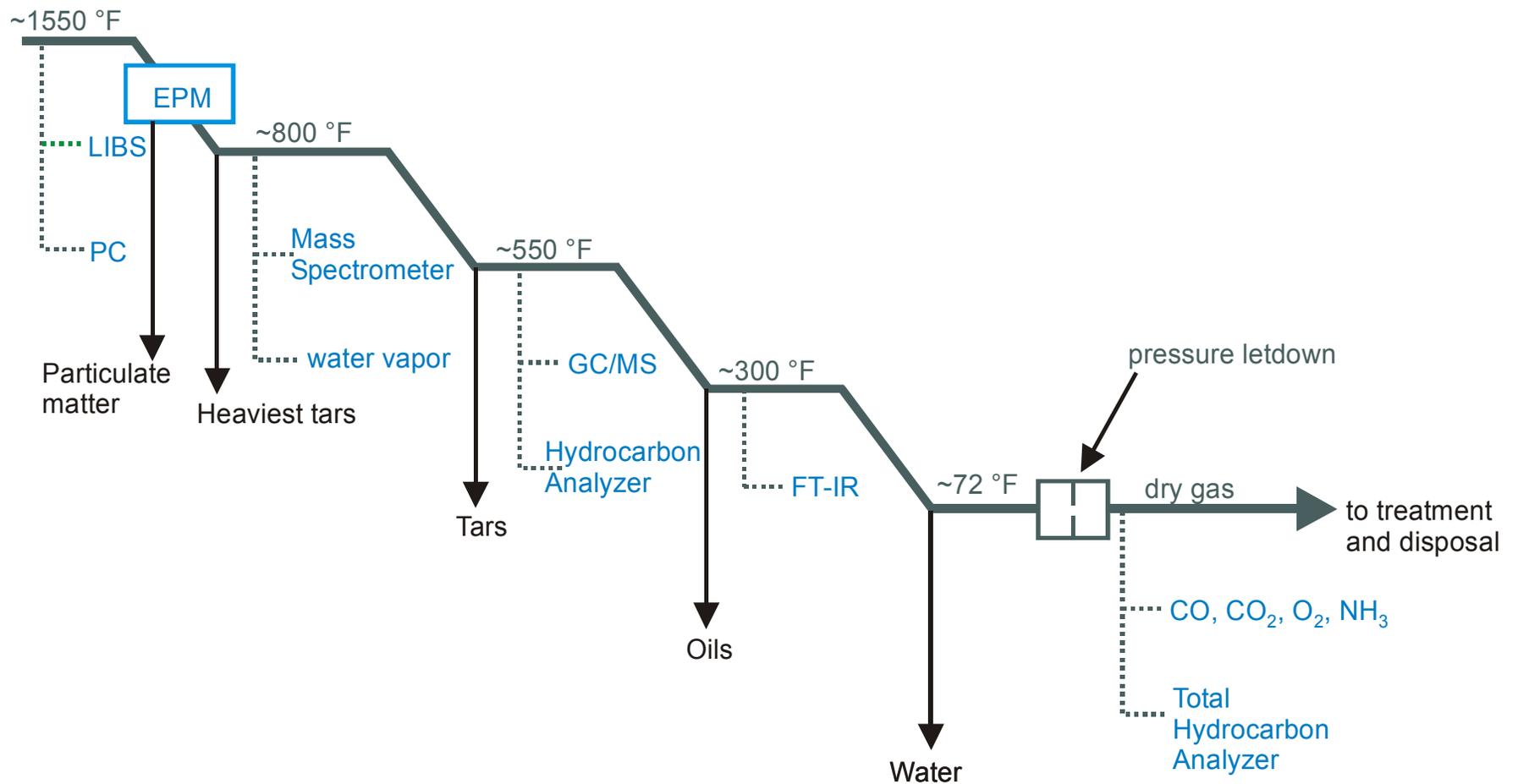


Figure 3. An early version of the general approach for stepwise sample conditioning for selected analysis instrumentation.

Initial Testing at the GTI Flex-Fuel Test Facility – Fourier transform-infrared spectrometry (FT-IR) is among the most powerful methods for determination of the composition of gas mixtures. This is because the intensities of multiple infrared absorption lines, or even entire absorption bands, can be used to determine the concentration of each infrared active species in a mixture, in contrast, for example, to the laser diode-based technique, that measures absorption at one, or perhaps two wavelengths. For this reason, FT-IR was chosen as the first technique to be evaluated for its ability to quantify major and minor species in coal and biomass-derived gas. FT-IR only detects molecules having permanent dipole moments, so is not able to quantify the photonuclear diatomic species, N_2 , O_2 , and H_2 .

The FT-IR instrument we used in these demonstrations is owned by GTI and was built by the Industrial Monitor and Control Corp. (IMACC), of Round Rock, TX, based on a Nicollet optical bench. The instrument has a heated absorption cell and an optical path length of 10 meters. The sample cell can operate at temperatures from ambient to 185 °C, so it can tolerate relatively high concentrations of water vapor and other condensable species, another advantage of FT-IR. Reference spectra for detectable gases are typically available at 25 and 185 °C.

For initial testing at the FFTF, a high temperature gas sample extraction and transport system was designed and assembled at the GTI FFTF in Des Plaines, IL. Independently, provision for a low temperature sampling system (Figure 4) was in progress as part of basic monitoring of gasifier operation utilizing a Rosemount analyzer (CH_4 , CO , H_2 , and O_2). Figure 4 shows the actual hardware of the low temperature system before heat tracing and insulation was attached. The interface subsequently installed between the low- and high-temperature systems is shown in Figure 5. This interface was configured to extract high temperature sample gas at the exit of sintered metal filters of the low temperature system, drop pressure to analyzer specifications, and transport heat-traced sample gas to the FT-IR analyzer while maintaining the temperature at the lower of that received from the low temperature system or that tolerated by the analyzer. The maximum design temperature for this hardware was 1000 °F.

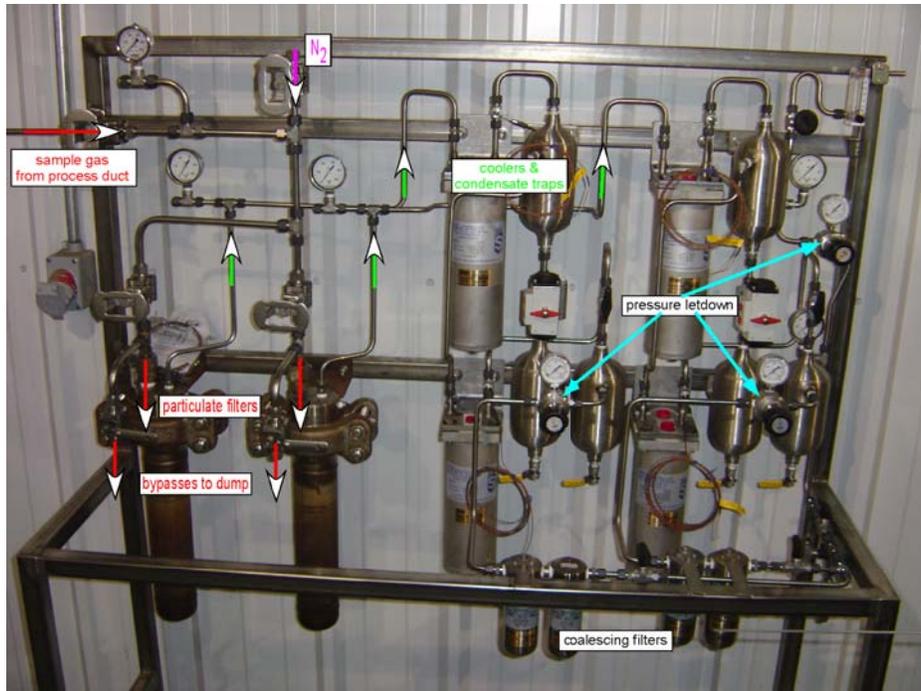


Figure 4. Low temperature sample gas conditioning system for providing batch samples and dry ambient temperature gas to the Rosemount analyzer.

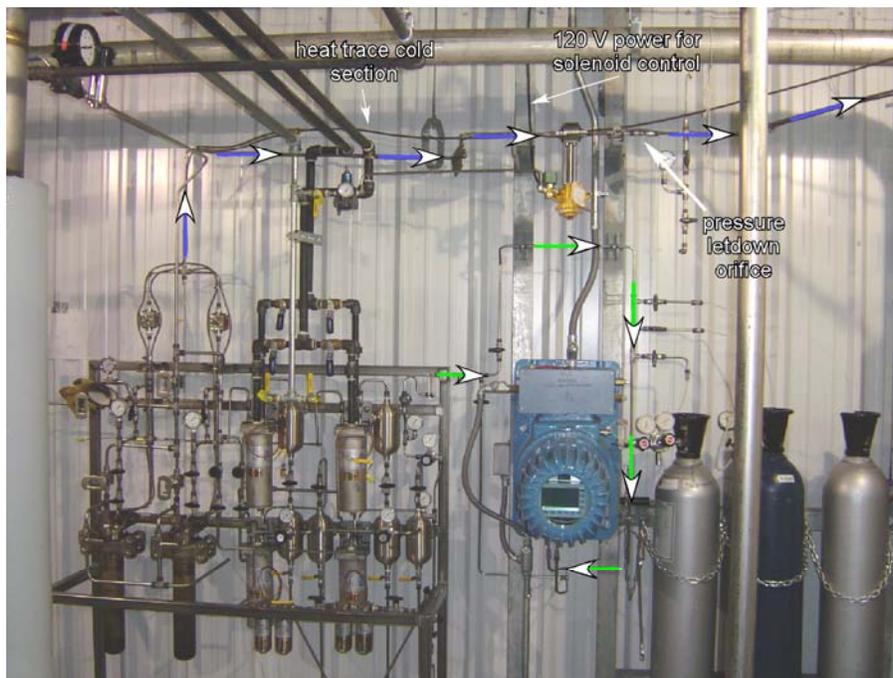


Figure 5. Sample gas conditioning system for low and high temperature analysis with the Rosemount (low temperature) analyzer on the right. Low temperature gas sample lines are indicated by green arrows and high temperature gas sample lines are indicated by blue arrows.

Preparations were also made to develop gas analysis procedures based upon mass spectrometry in parallel with FT-IR. A Stanford Research Systems QMS300 analyzer was installed on the sample extraction and transport system. A PEEK™ capillary was inserted into the heated sample extraction and transport line providing filtered process gases maintained at 185°C to the QMS300. The location for the MS was selected to permit its sampling capillary to be positioned inside of the hot sample transport line. Figure 6 shows this installation. The transport line used for these tests was convenient for temperatures up to about 200°C which has been appropriate for the FT-IR temperature limit. On-line FT-IR measurements that were performed from November 19 to November 20, 2004 are summarized in Figure 7. Calibration checks and comparisons to the Rosemount gas Analyzer data and to batch sample analyses indicated accurate results for six gases as well as reliable operation.

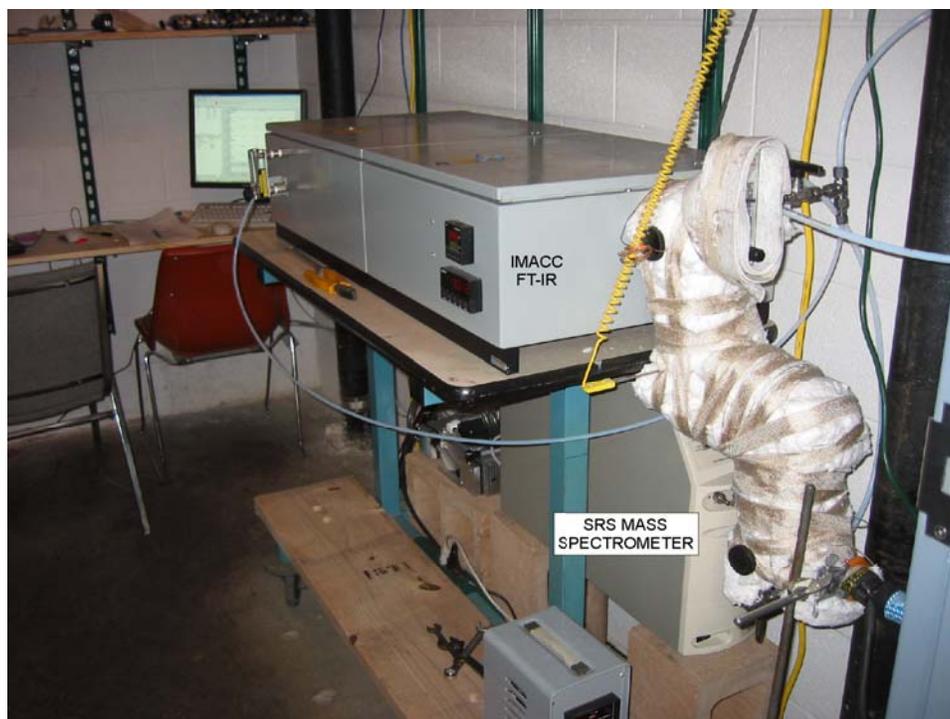


Figure 6. Instrument room used at GTI's FFTF in initial testing of the IMACC FT-IR and the Stanford Research Systems QMS300 analyzer.

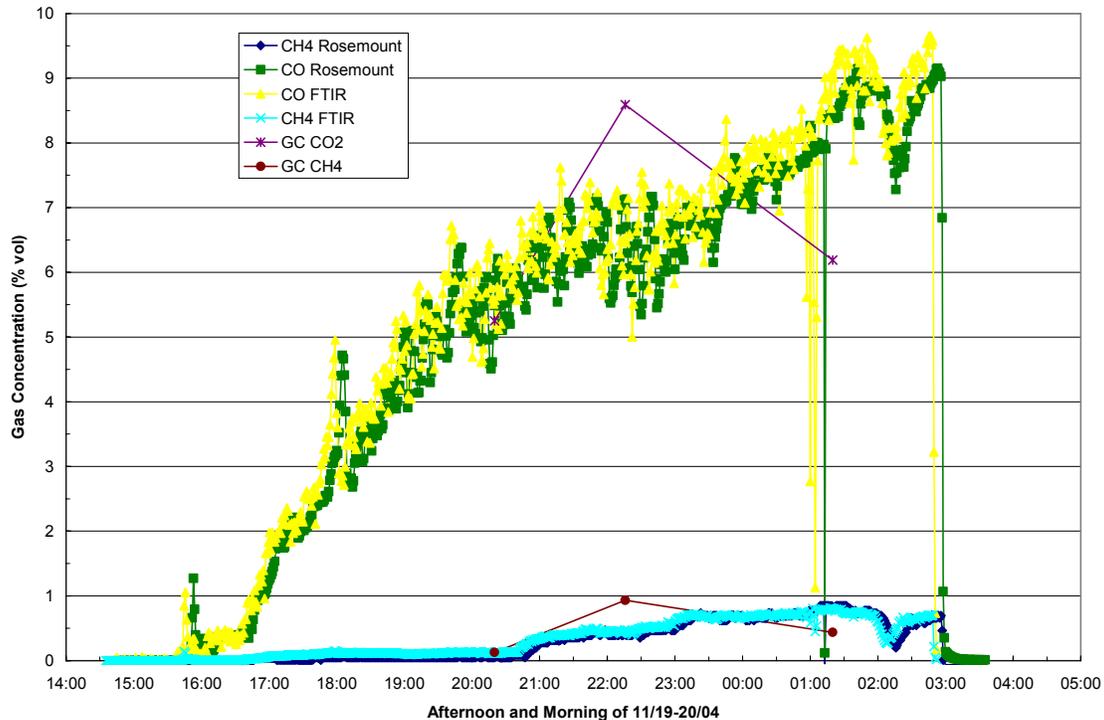


Figure 7. Concentrations of CO₂, CO, and CH₄ as measured by the IMACC FT-IR spectrometer, Rosemount Process Analyzer, and GC analysis of batch gas samples during early testing at the GTI Flex-Fuel Test Facility.

Novel Gas Cleaning Project Testing at the GTI Flex-Fuel Test Facility – During March 2005, this project participated in a series of tests of Novel Gas Cleaning (NGC) technology at GTI's Flex-Fuel Test Facility. The schedule for FFTF operation and the overall objectives of the FFTF testing were set by the NGC project (DOE/NETL and Siemens Westinghouse Power Corporation (SWPC)). The configuration of the GTI FFTF during these tests of the SWPC NGC process is shown schematically in Figure 8. The general objectives of the NGC project for these tests were to confirm the feasibility of reducing, through barrier filtration, the particulate content of the syngas to < 0.1 ppmw, and also to remove total reduced sulfur compounds (H₂S and COS) and halide (mainly HCl) to < 60 ppbv and < 10 ppbv, respectively, via selected dry, fine sorbent injection. The NGC project plans included batch measurements of syngas quality (primarily halide and sulfur contents) at various points in the NGC process.

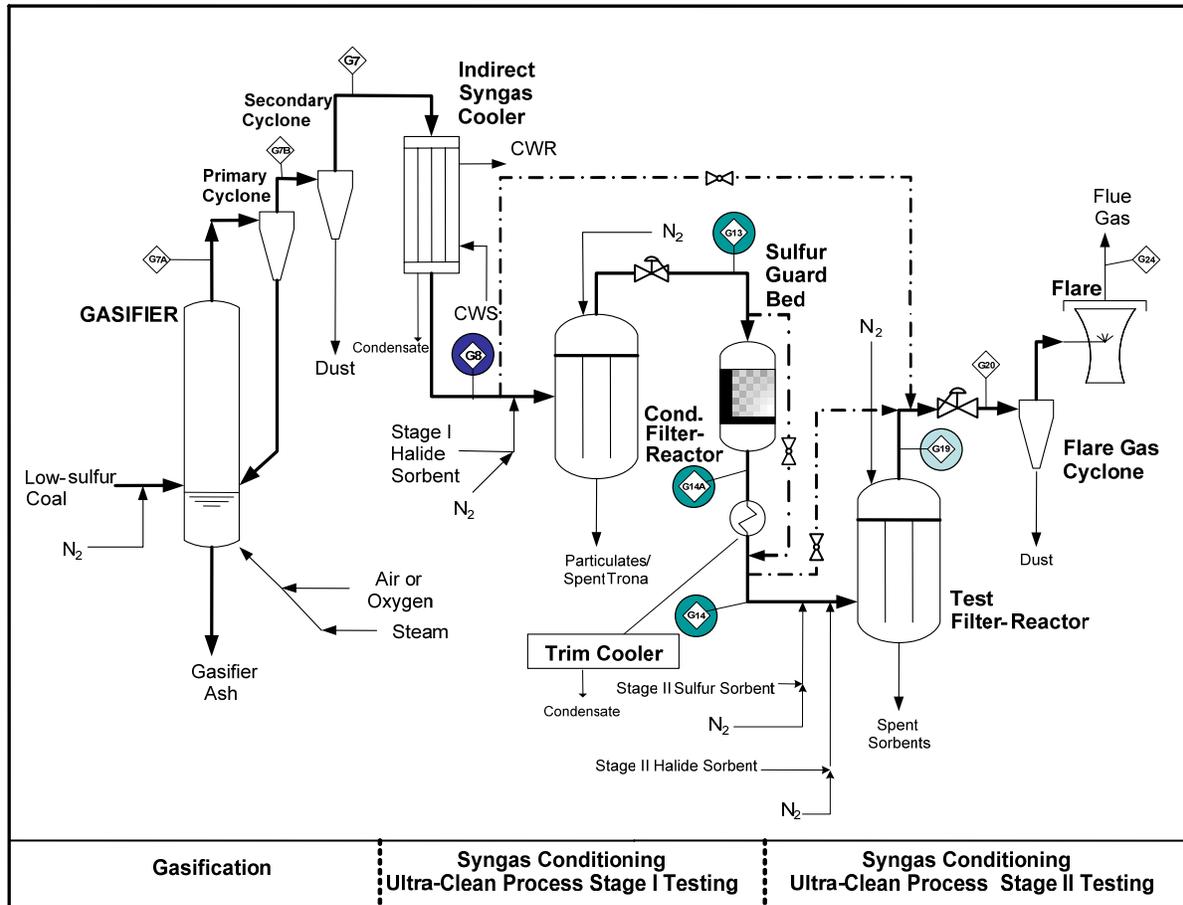


Figure 8. GTI Flex-Fuel Test Facility configuration with the SWPC Novel Gas Cleaning Process.

With the NGC process stream and objectives in place, this project was able to identify several locations (G8, G13, G14, G14A, and G19) within the FFTF configuration shown in Figure 16 where syngas could be extracted for on-line characterizations. In addition to location G8 (which was initially configured for syngas sample extraction, conditioning, and transport prior to the tests performed at the FFTF November 19 – 20, 2004), three additional sampling locations were prepared and characterized during March 2005. Prior to the commencement of NGC testing on March 7, preparations were made for sampling syngas sample streams from downstream of the Conditioning Filter-Reactor (location G13 in Figure 16), and downstream of the Sulfur Guard Bed (and a bypass around the Sulfur Guard Bed) (locations G14 and G14A in Figure 8). Preparation of the extraction and transport line located downstream of the Test Filter-Reactor (location G19 in Figure 8) was completed prior to the resumption of testing on March 21. The arrangement of the sample transport lines and the analyzers listed in Table 4 were determined by the level of syngas cleaning and treatment that existed at each of these sample points in the process stream, in combination with the capabilities of the various

analyzers available for use, the suitable space available within the FFTF to locate the analyzers, and also coordination with the objectives of the NGC project.

Based on the NGC test conditions to be evaluated and the expected performance of the NGC process, these locations were expected to provide syngas streams that had been cleaned to various degrees prior to our on-line analyses. Therefore participating in the NGC test program allowed evaluation of the syngas extraction and conditioning systems, and the analysis suite, over a range of process temperature and composition conditions. In addition, this project's participation in the NGC test also provided some of the FFTF site preparation and proof-of-concept verification required for subsequent biomass feedstock gasification testing at the FFTF.

Table 3 lists the expected and potential effects on syngas composition at the different stages in the NGC process.

Table 3. Gas Conditioning Effects in Novel Gas Cleaning Process Stages

Inlet ^a	Outlet ^a	Major Processes Spanned	Components Affected
G8	G13	Primary particle filter, primary halide sorbent	HCl, sulfur?, hydrocarbons?
G13	G14A	Sulfur Guard Bed	sulfur, hydrocarbons?
G14A	G14	Temperature reduction from 800°F to 550°F	hydrocarbons?
G14	G19	Sulfur sorbent, candle filter	sulfur, HCl?, hydrocarbons?

^a referring to process points identified in Figure 8

Our participation in the NGC testing had three specific objectives:

- 1) Approach - demonstrate that the syngas sample extraction/conditioning approach developed in this Biomass project could transport process syngas constituents to near real-time, on-line analyzers without significant line losses or condensation of vapor-phase vapor species.
- 2) Accuracy - evaluate our on-line analyses by determining the agreement between measurement data obtained by the suite of on-line analyzers assembled for the March 2005 NGC test campaign and data obtained with the NGC project batch syngas analyses.
- 3) Sensitivity and Response - demonstrate the ability of the on-line analyzers to rapidly identify and quantify low levels of constituent vapors in the extracted syngas sample streams to measure the performance of gas cleanup systems down to ultra-clean levels of contaminants.

For a pressurized gasification process syngas stream that has been filtered (particle-free), the key components of our syngas sample extraction/conditioning approach are:

- 1) Heating - use external heaters on sample extraction and transport lines to maintain the syngas components in their vapor state by maintaining syngas temperature at, or slightly above, the temperature of the process at the point of extraction.
- 2) Depressurization - passing the extracted syngas stream through an in-line orifice in each extraction line reduces the partial pressure of all vapor species in the syngas downstream of the orifice, thus reducing the chances for unwanted condensation.
- 3) Dilution - when necessary, dilute and/or cool the extracted syngas stream. (Dilution was not required for the March 2005 sampling at the FFTF.)
- 4) Transport - the depressurized syngas streams exited the orifices with sufficient pressure to drive them through heated tubing leading to the vicinity of the on-line gas analyzer(s).
- 5) Analyzer Selection - direct the syngas stream to any of the on-line analyzers through a syngas flow distribution manifold. (This step applies when an individual analyzer is used to characterize syngas streams from multiple sample locations.)

The first three components listed above condition the gas to reduce the chances for condensation by decreasing the ratios of the partial pressures of the various vapor species in the syngas to the partial pressures required for condensation of these species at the pressure of the conditioned gas. The last two components above involve the delivery of the prepared syngas stream to the suite of available on-line analyzers.

During testing at GTI's FFTF in November 2004, syngas obtained from upstream of the Conditioning Filter-Reactor was extracted, conditioned, and analyzed with the IMACC FT-IR spectrometer and the SRS Mass Spectrometer. For the March 2005 testing, we continued our use of these two instruments, while also significantly expanding our analysis capabilities by adding a Varian μ GC, an Agilent Model 5890 Series II GC with a Flame Photometric Detector (FPD), and a Varian model 3800 GC with a pulsed flame photometric detector (PFPD). The three GC's were available from GTI's laboratories in Des Plaines, Illinois. Pertinent operating characteristics and capabilities of the complete suite of analyzers assembled for the March 2005 testing are presented in Table 4.

Table 4. Overview of On-Line Gas Analysis Suite (March 2005 FFTF Tests)

Analyzer	FT-IR Spectrometer	Mass Spectrometer	Gas Chromatograph (μ GC)	Gas Chromatograph (FPD)	Gas Chromatograph (PFPD)
manufacturer	IMACC	SRS	Varian	Agilent	Varian
model		QMS300	Micro GC	5890 Series II	3800
detector(s)	deuterated triglycine sulfate (DTGS)	Residual gas analyzer (RGA)	thermal conductivity (TCD)	flame photometric (FPD)	pulsed flame photometric (PFPD)
capabilities	0.5 wave number resolution	0-300 amu	H ₂ , N ₂ , Ar, CO, CO ₂ , NH ₃ , H ₂ S, COS, C ₁ -C ₃	sulfur sensitivity (to ~0.1 ppm)	sulfur sensitivity (to ~10 ppb)
limitations	<185°C	400°C	30°C, dry	30°C, dry	30°C, dry
cycle time	3 min	~1.5 min	~ 5 min	~10 min.	~45 min
required flow rate	5-20 slpm	0.01 lpm	0.1 l	~0.05 l	~0.05 l
inlet gas temperature	185°C	260°C	20°C	20°C	20°C
receiving syngas from	G8, G13, G14	G8, G13, G14	G8, G13, G14	G8, G13, G14	G19
location within the FFTF	2 nd floor analysis station	2 nd floor analysis station	2 nd floor analysis station	2 nd floor analysis station	4 th floor analysis station

In order to install and operate the various on-line analyzers described above, we had to set up suitable space to locate and operate the analyzers in the FFTF. Available space was identified on the second and fourth floors of the FFTF where our instruments could be temporarily housed. These spaces were then outfitted with power and access to GTI's network. As indicated in Table 4, the IMACC FT-IR, SRS MS, Varian μ GC, and the Agilent Model 5890 Series II GC were installed at the second floor analysis station. Because the second floor space was not sufficiently large to house the Varian Model 3800 GC (PFPD), a separate analysis station was set up on the fourth floor of the FFTF to house that instrument. Although the working space at the second floor station was limited, the close proximity of the analyzers to each other allowed simpler, more reliable selection and pairing of sample flows from G8, G13, and/or G14 with each of the analyzers at the station. (Syngas from location G14A was not directed to the analysis suite during the March 2005 testing.) A photograph of the second floor station is shown in Figure 9. In addition to distributing sample syngas flow to each of the on-line analyzers located at the station, each sample line was also configured to allow syngas

entering the analysis station to be sampled by an impinger train. Impinger trains were performed during the March 2005 tests on a regular basis as part of the NGC project.

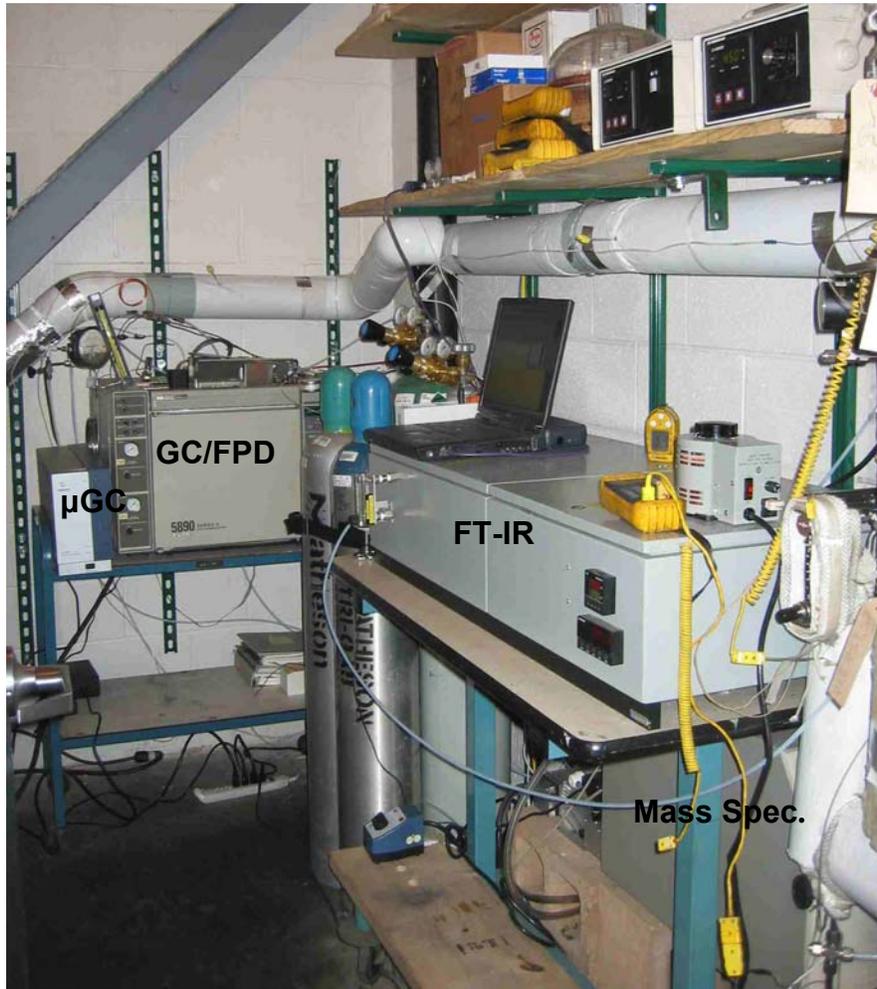


Figure 9. FFTF second floor analysis station.

Table 5 identifies the interfaces of the syngas sample extraction lines with the FFTF process stream and the NGC test equipment, the key characteristics of each sample transport line, and the physical location of each analyzer.

Table 5. Overview of Sample Extraction and Transport Lines

sample extraction location	G8	G13	G14	G19
temperature of line (set point)	450-900°F	450-600°F	450-650°F	350-650°F
length of transport line	~ 65 ft.	~ 75 ft.	~ 80 ft.	~ 85 ft.
sample line termination point (analysis station location)	FFTF 2nd floor, flow distribution manifold			FFTF 4th floor

The long runs of 3/8" diameter transport lines leading to the analyses stations were heated with long, continuous cable heaters that were tightly attached to the sample transport lines with twisted wire. The transfer of heat from the cable heaters to these lines was augmented by the application of Thermon 63, a high temperature heat transfer compound, to the bundle of transport line(s) and cable heater(s). Each of these bundles, after being coated with heat transfer material to evenly distribute heat along the transport line, was then insulated to minimize heat loss. Thermocouples were placed in contact with the sample transport lines and the cable heaters for temperature monitoring, control, and protection of the cable heaters. Figure 10 shows the general arrangement of the cable heater used for the bundled sample transport lines from G13, G14/G14A and G8. After being withdrawn from the sample point, all extracted syngas streams passed through a manual ball valve, an actuated ball valve (discussed below), an in-line filter, and then through an orifice for expansion/pressure reduction. In order to drop the process system pressure from its nominal value of 200 to 300 psig down to about 30 in. H₂O, in-line orifices were installed in each of the sample lines (from G8, G13, G14/G14A, and G19). Figure 10 also shows the arrangement of these orifices and filters for the G8, G13, and G14/G14A sample lines, as well as selected details of the calibration gas spike lines, transducers, and cable heater.

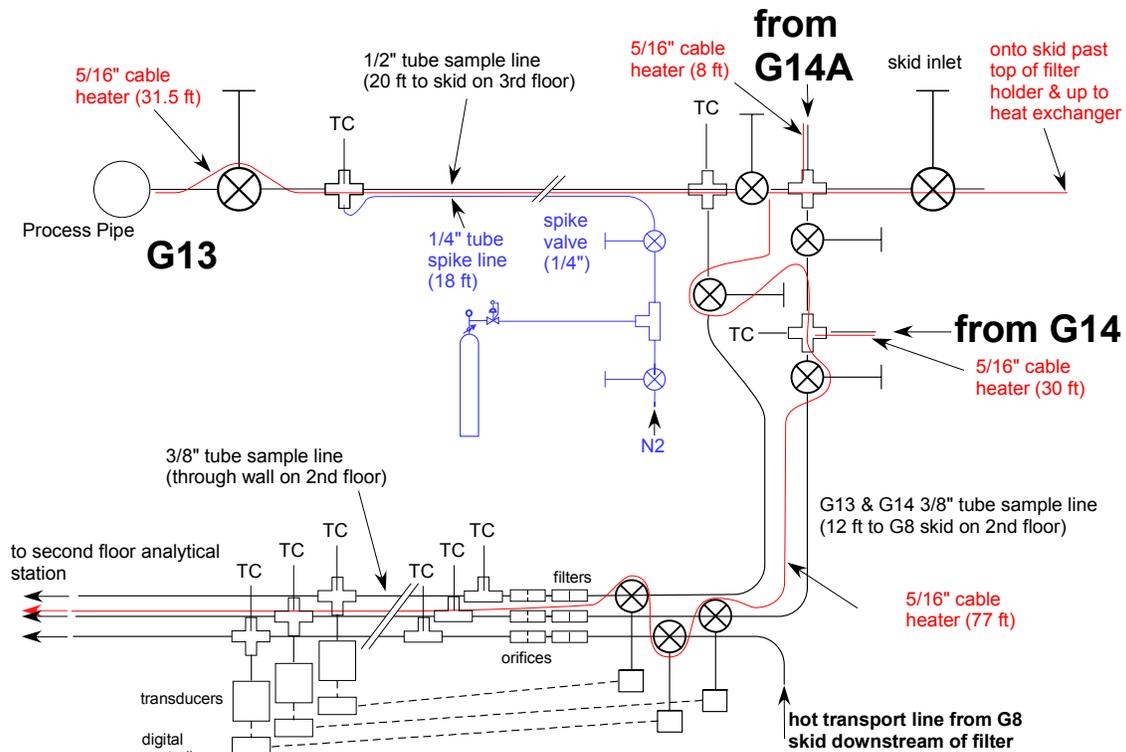


Figure 10. Schematic of gas sample transport lines from G13, G14/G14A and G8.

Small, sintered metal in-line filters placed just upstream of each orifice ensured that unexpected particulate material would not be allowed to block the orifices. Because the in-line orifices would only be able to reduce the pressure of the gas in the transport line from the process pressure of 200 to 300 psig down to the low level required by the analyzers (generally < 20 in. H₂O) when gas was flowing through the line, it was necessary to provide an open exhaust path for all the sample lines at any time they were connected to either the process syngas stream, or to the FFTF's high-pressure nitrogen source (used in the analytical suite primarily for purge purposes). These open exhaust paths prevented any over pressurizing of the plumbing and instruments in the analysis station(s). Because each analysis station was usually receiving a continuous flow of gas (either purge nitrogen or process syngas) through the transport lines and on through the on-line analyzers, it was necessary to take the exhaust flow from each of the analyzers and the impinger trains to exhaust dump lines that extended outside of the FFTF building.

A transducer was attached to each sample transport line to continuously monitor the pressure in the line downstream of the pressure-reduction orifice. The actuated ball valve located upstream of the orifice was automatically closed if the line pressure downstream of the orifice exceeded a predetermined set point (normally 100 in. H₂O). When it was not possible to maintain a flow of process syngas through the heated

sample lines, nitrogen was passed through these lines. When necessary for maintenance or modification of the analytical setup in the analysis station or related plumbing, the manual and actuated ball valves in the sample line were closed to shut off all flow in the sample line(s).

Before assembly, a surface-passivation process coating (Silcosteel[®]) was applied to the heated 3/8" diameter transport tubing leading to the analysis stations. Silcosteel[®] was also applied to the small in-line particulate filters, and as many of the valves, plumbing components, and fittings in the sample extraction and transport lines as possible prior to assembly. This pretreatment step was carried out to minimize the potential reaction between gas-phase sulfur and chlorine species and the type 316 stainless steel surfaces in the transport lines. Although self-passivation of sample lines by the syngas sample streams might render this precaution unnecessary for vapor species compounds in concentrations greater than 50 - 100 ppmv, the NGC project was specifically designed to address the cleaning of sulfur and halide species to very low levels, as mentioned above. In order for our on-line analyzers to identify these species in the process stream and quantify such low contaminant concentrations, it was imperative to transport these species through the transport lines without significant loss or modification. This Silcosteel[®] coating was most important for the sample stream extracted from location G19. The sample streams obtained at G13 and G14 also benefited from the Silcosteel[®] coating. Although much of the plumbing leading from the G8 sampling location was Silcosteel[®] coated, the need at that location was not critical, because the main syngas stream had not yet been treated for removal of halides, sulfur species, or particulate matter.

Depending on the proximity of the sample location to the analysis station, the syngas had to travel through various lengths of transport tubing to reach the analysis stations. At the FFTF second floor analysis station, each of the three sample lines entering the station entered the Flow Distribution Manifold, which is shown schematically in Figure 11, and a photograph of the manifold is presented in Figure 12. One of the hot sample transport lines exiting the manifold led to the FT-IR, while another hot sample transport line exiting the manifold led to the two GC's. The capillary sample line leading to the Stanford Research Systems QMS300 Mass Spectrometer was inserted into the third of the hot sample transport lines exiting the manifold.

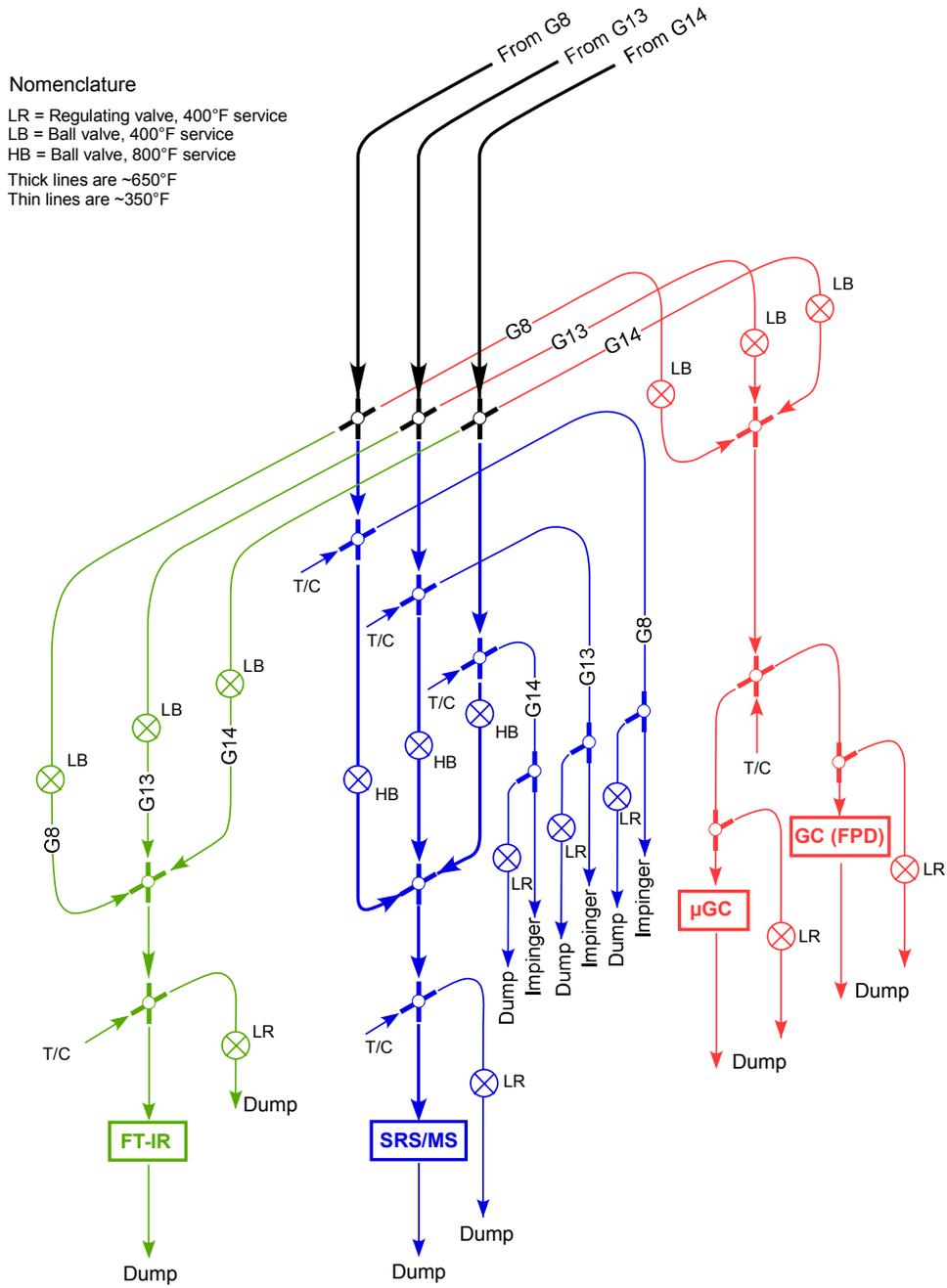


Figure 11. Schematic diagram of the flow distribution multiplexer at the FFTF second floor analysis station.



Figure 12. General plumbing arrangement in the flow distribution multiplexer at the second floor analysis station prior to the application of the Thermon heat transfer compound.

At the analysis station on the fourth floor of the FFTF, a much simpler flow distribution arrangement was required. Because the only source of syngas being delivered to this station was from sampling location G19, no provisions for syngas source switching had to be made. Therefore at this analysis station, tees were installed in the sample line for sample to be withdrawn for impinger measurements, mass spectrometer

measurements, and GC PFPD measurements. Each of these analyzer streams included its own tee and regulating valve for an adjustable dump line to an outside vent. In addition, the excess flow through the line not entering any of the analyzer streams was also dumped to an outside vent. Although provision was made to install the SRS MS at the fourth floor station, the MS was used exclusively at the second floor station during the March tests. A photograph of the GC/PFPD installed at the fourth floor analytical station is shown in Figure 13.



Figure 13. GC/PFPD Installed at the Fourth Floor Analytical Station.

Except for vent lines, all of the sample lines at each analysis station were heat traced and insulated. Like the lines from G8, G13, and G14/G14A, the sample transport line from G19 to the fourth floor analysis station included a manual and actuated ball valve, an in-line filter and orifice, and a pressure transducer to actuate the ball valve in the event excess pressure was detected within the sample line. A cable heater was used to heat trace this line, and the line was insulated.

During the entire NGC test each of the sample extraction and transport lines maintained the capability to reliably deliver syngas streams to the analysis stations without any

indications of condensation. The high-temperature process interface approach for syngas sampling and conditioning was validated at G8 and G13 process locations. For the process conditions encountered, the sample gas was maintained at temperatures above 400° F, the pressure of the gas was reduced from 200 psig to 1-2 psig, and dilution was not required to prevent condensation leading to or within the FT-IR or mass spectrometer. A Nafion® dryer was used on the sample gas stream ahead of the gas chromatographs at the second floor analysis station to protect the GC columns from moisture in the sample gas.

Comparisons between various batch sampling methods and the data produced by the on-line analyzers during the NGC tests showed good agreement. Using a certified 7.7 ppmv HCl-N₂ gas mixture and spike-and-recovery techniques, EPA Method 26 impingers were used to collect samples from the high-temperature process interface sample lines from a tee at the inlet to the on-line instruments. Concentrations of HCl measured (using ion chromatography) 8.1, 7.7, and 6.8 ppmv HCl from these spike samples, yielding an average 100% recovery.

The EPA Method 26 impinger HCl measurements and on-line FT-IR analyses showed very good agreement. Both approaches for sampling were able to identify and quantify the effect of char on HCl concentrations in the syngas. Data from the inlet and outlet of the Conditioning Filter-Reactor (see Figure 8) showed a marked drop in HCl levels. Char was determined to be a significant factor in this reduction by monitoring the HCl levels with the FT-IR and mass spectrometer through the system, and by measuring HCl captured in the Method 26 impinger solutions. The effect was quantified by sampling downstream of one of the switchable particulate filters shown in Figure 4 for an extended period while char was accumulated on the filter and then switching to the other filter (which was clean) and monitoring HCl levels as char was built up on that filter surface. These data revealed a very rapid and significant response to the accumulation of char. This behavior is shown in Figure 14. The peak value of HCl measured immediately after switching to the clean filter was consistent with the maximum expected HCl in the process gas based on an analysis of chloride in the fuel.

The measurement approach for sulfur species required adaptation of the initial skid batch sampling system. Silcosteel®-coated sample bombs were used to collect process gas for analysis of H₂S concentrations at the skid. Initially the heaters on the sample lines were set to maintain process gas temperatures above 300 °F to the sample bombs. Results from measurements with this approach are shown in Figure 15. The shaded region in Figure 15 covers sample results that were compromised by the condensation of water in the sample bombs. Laboratory analyses of H₂S were erratic when liquid water from the samples was trapped in the GC sample column. (The

process gas had moisture content above 40% for most of the test conditions.) Excluding the compromised data, the results show a level of H₂S in the process gas that provides a good material balance for sulfur from the fuel and the unspent carbon in the gasification process.

The operation of the skid system was modified in subsequent tests to deliberately condense the water from the process gas by using cold water to chill the process gas to below laboratory temperatures. The gases were cooled to below 40°F.

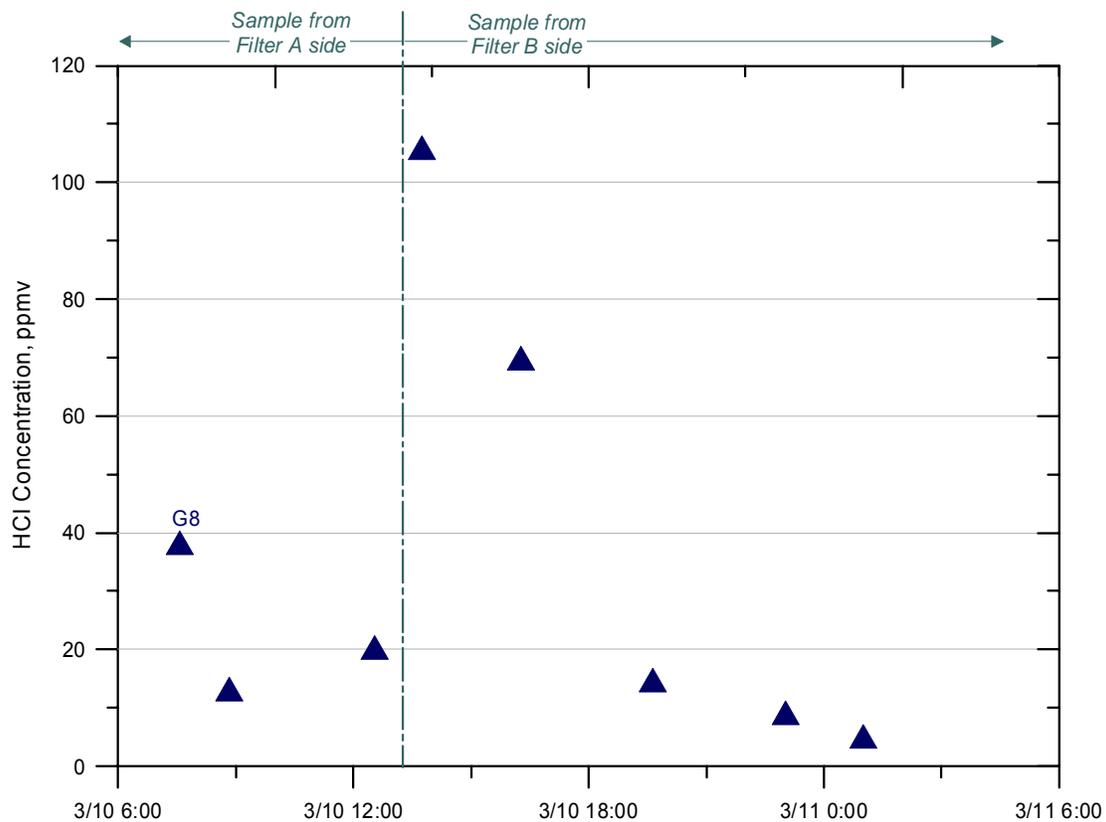


Figure 14. Effect of Char on EPA Method 26 HCl Measurements when Switching from a Filter with Char (A side) to a Cleaned Filter (B side).

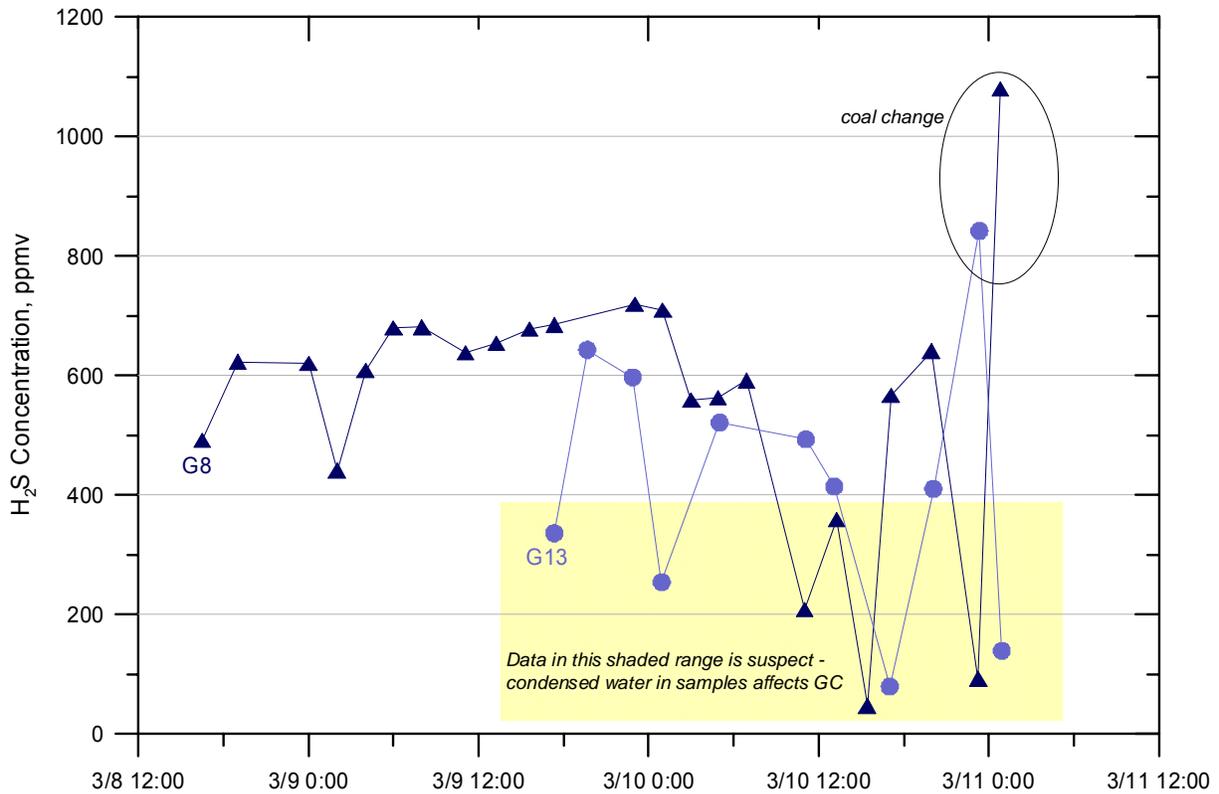


Figure 15. Laboratory H₂S Measurements from Sample Bombs Collected at the Skids.

The sensitivity and response time of the on-line analyzers was assessed through on-line analyses of sulfur species conveyed through the hot-gas sample line performed primarily with the GC/PFPD instrument shown in Figure 13. The mass spectrometer and the μ GC also measured sulfur species. Figure 16 shows the results of COS measurements made with the GC/FPD, during the injection of a sodium sesquicarbonate sorbent material (Trona) into the process. The on-line analyzer, providing spectra at about 15-minute cycle time, nevertheless, revealed a detailed, strong response of COS to the feed rate of the sorbent material. The greatest sensitivity of the on-line instruments we used was obtained with the GC/PFPD.

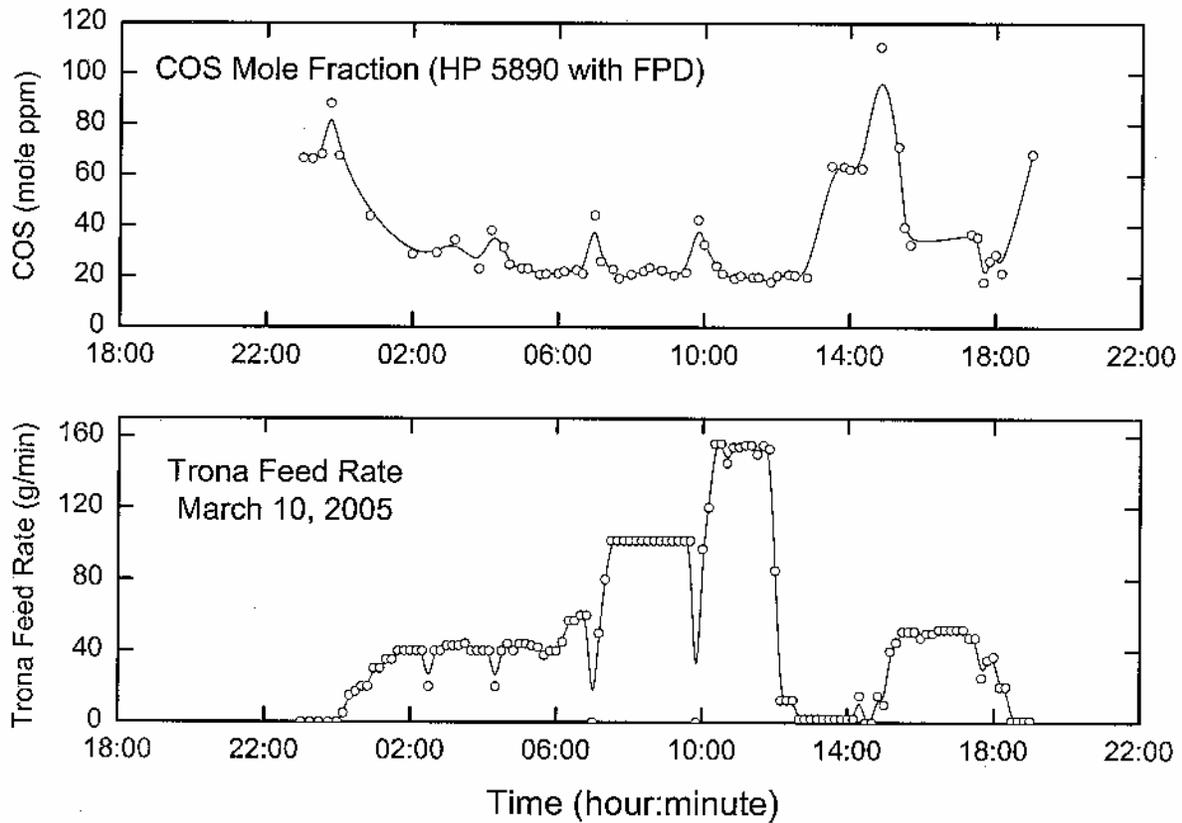


Figure 16. Relationship between sorbent feed rate and COS concentration in the process gas.

Characterization of the Chemrec™ black liquor gasifier – During June 2005, this project participated in a series of tests at the Chemrec™ Gasifier at the Weyerhaeuser Pulp Mill in New Bern, North Carolina. The specific objectives for participation in this test were to:

- Extract representative syngas samples
- Condition syngas samples without losses or altered composition
- Deliver continuous process gas samples to analyzers and batch samplers
- Accommodate QA/QC spike and recovery protocols
- Obtain and report time-averaged and near real-time measurements of major gas constituents, sulfur species, and hydrocarbon species.

A general schematic diagram of the Chemrec™ gasifier identifying the location where syngas was extracted for analysis is presented in Figure 17. A sample port was available downstream of the venturi scrubber to extract process gas for on-line analysis. The process gas contained about 40% to 60% water vapor by volume, and was at a pressure of only about 7 psig and a temperature of about 225 °F at the point of extraction. Therefore, heating and dilution of this sample stream was incorporated into the sample conditioning system. GTI designed a sample extraction, conditioning, and transport system to serve as an interface between the sampling location and the suite of on-line analyzers assembled for the field characterization.

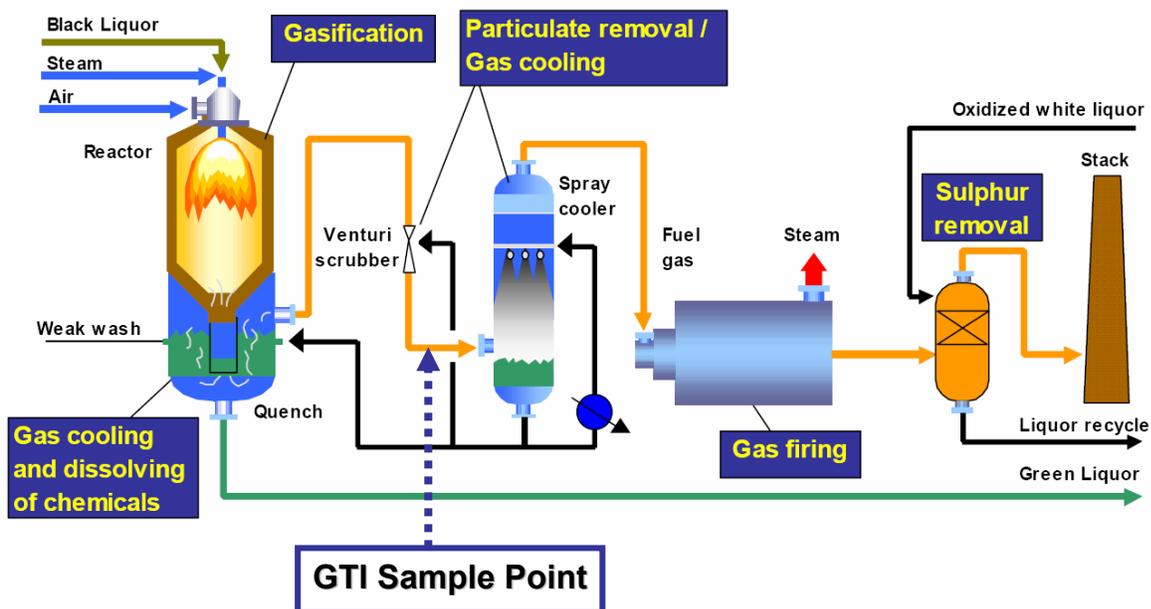


Figure 17. New Bern black liquor gasifier.

The suite of analyzers assembled for these tests, included:

- a Stanford Research Systems (SRS) QMS300 Mass Spectrometer (MS)
- an integrated Gas Chromatograph, Mass Selective Detector, Flame Ionization Detector and Sulfur Chemiluminescence Detector (GC/MSD/FID/SCD) system acquired from Wasson-ECE
- an Industrial Machine and Control Corporation (IMACC) Fourier-transform infrared spectrometer (FT-IR)
- a Varian micro gas chromatograph with thermal conductivity detector (μ GC).

Figure 18 presents a schematic diagram of the extraction, conditioning, and transport system that was set up at the gasifier site prior to the start of testing. The general approach was to keep the extracted gas hotter than the process line from which it was extracted, and to make use of the pressure of the syngas in the Chemrec™ process to drive the gas sample through the plumbing in the interface system. In-line orifices placed at various points in the system reduced gas pressure and metered gas flow. Transducers reported the pressure drop across these orifices to digital display meters. Manually operated valves were used to direct and regulate sample flows to the various analyzers. The sample lines were externally heated and insulated, and thermocouples were placed both inside the gas stream and on the outside surfaces of the sample lines. All of the lines through which syngas passed, with the exception of dump lines used to vent excess syngas flow, were pretreated with the Silcosteel® passivation process, and then heat-traced and insulated on site to prevent condensation. The Dilution Cooling Unit (DCU) was used in this field application to add preheated nitrogen to the already hot syngas sample stream to lower the dew point of the sample stream delivered to the analyzers without altering its temperature. The specific need for this reduction in dew point was the potential for condensation of water in the GC/MSD/FID/SCD and the μ GC. The dilution factors used during the two week test period were 10:1 and 20:1. The syngas sample stream directed to the MS and the FT-IR was often undiluted, since the operation of these two instruments precluded any water condensation during analysis.

The GTI sample probe was inserted into the process stream through a shut-off ball valve that was already installed on the Chemrec™ process pipe. The extracted syngas was heated to about 185 °C (365 °F) for transport to the on-line analyzers. A sheath around the main sample line was used in conjunction with two seal glands and a vented dump line to allow the GTI probe to be inserted or removed from the process while the process was operating.

The syngas sample stream passed vertically up through the probe and through the shut-off valve and made a 90° turn at the top of the probe. After passing through a 47

mm filter, a pressure transducer was used to measure the absolute pressure of the syngas in the sample transport line. An in-line orifice used to reduce the pressure of the sample stream to a level acceptable to the rest of the sample conditioning equipment was located just downstream of the tee connection to the pressure transducer.

The sample probe was connected to the rest of the sample conditioning and analysis equipment through two 25-foot heated sample hoses – the syngas transport line and the purge nitrogen line (visible in Figure 19). The heated purge nitrogen line was connected to the sample line in the probe just upstream of the 47 mm filter. A flow of heated nitrogen was used to purge the sample probe during times when syngas was not being conveyed to the analyzers through the sample conditioning system. The syngas transport line maintained the temperature of the syngas at about 185 °C on its way to the sample distribution and dilution plumbing (Figures 19 and 20).

The sample distribution and dilution plumbing used to distribute the sample stream to the four analyzers either with or without dilution is visible, before it was insulated, in Figure 19, but can be more clearly understood by examining the schematic diagram presented in Figure 18. The flowrate of the nitrogen used to dilute the syngas entering the DCU was metered and controlled by two mass flow controllers. One controller set the main dilution flow rate, and the second controller set the flow of nitrogen through the annular sheath around the syngas sample entry tube into the DCU body. These two nitrogen streams were preheated before entering the DCU. The flow rates of the syngas sample streams directed to the analyzers was regulated by manual adjustment of excess sample flow through unheated vent lines.

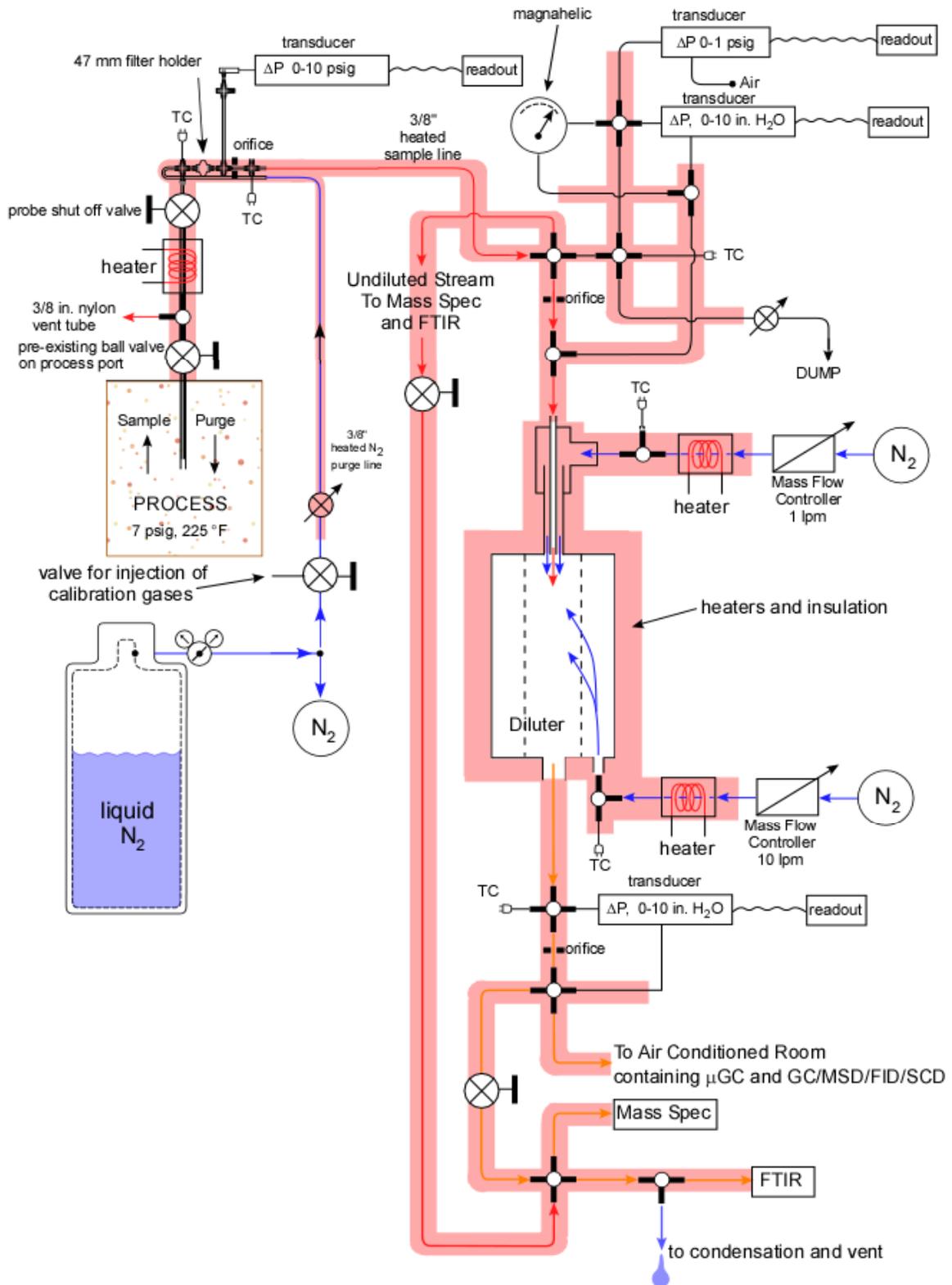


Figure 18. Sample extraction, conditioning, and transport system that provided an interface between the Chemrec™ gasification process and the GTI suite of on-line analyzers.



Figure 19. Sample distribution plumbing and diluter prior to insulation.

As shown in Figure 18, a portion of the heated syngas sample stream was conveyed into a portable, climate-controlled building that was purchased, and erected on site especially to house the GC/MSD/FID/SCD system and the Varian μ GC. The portable building is pictured in Figure 20. The GC/MSD/FID/SCD system is shown installed in the building in Figure 21. A heated sample transport line carried the syngas sample stream into the building through the rear wall (opposite the door) for distribution to the GC/MSD/FID/SCD and the μ GC. Lines carrying the additional compressed gases needed for calibration and system operation also entered this building through its walls. The SRS MS and the IMACC FT-IR, which were located outside of the building, are shown in Figure 22.

A selection of the data obtained with the SRS QMS300 Mass Spectrometer that quantify the major components of the syngas are presented in Figures 23 and 24. These data show the quick response of the on-line sampling approach to changes in gasifier operation.



Figure 20. Climate-controlled building housing the GC/MSD/FID/SCD and the μ GC.



Figure 21. The Wasson-ECE GC/MSD/FID/SCD system.

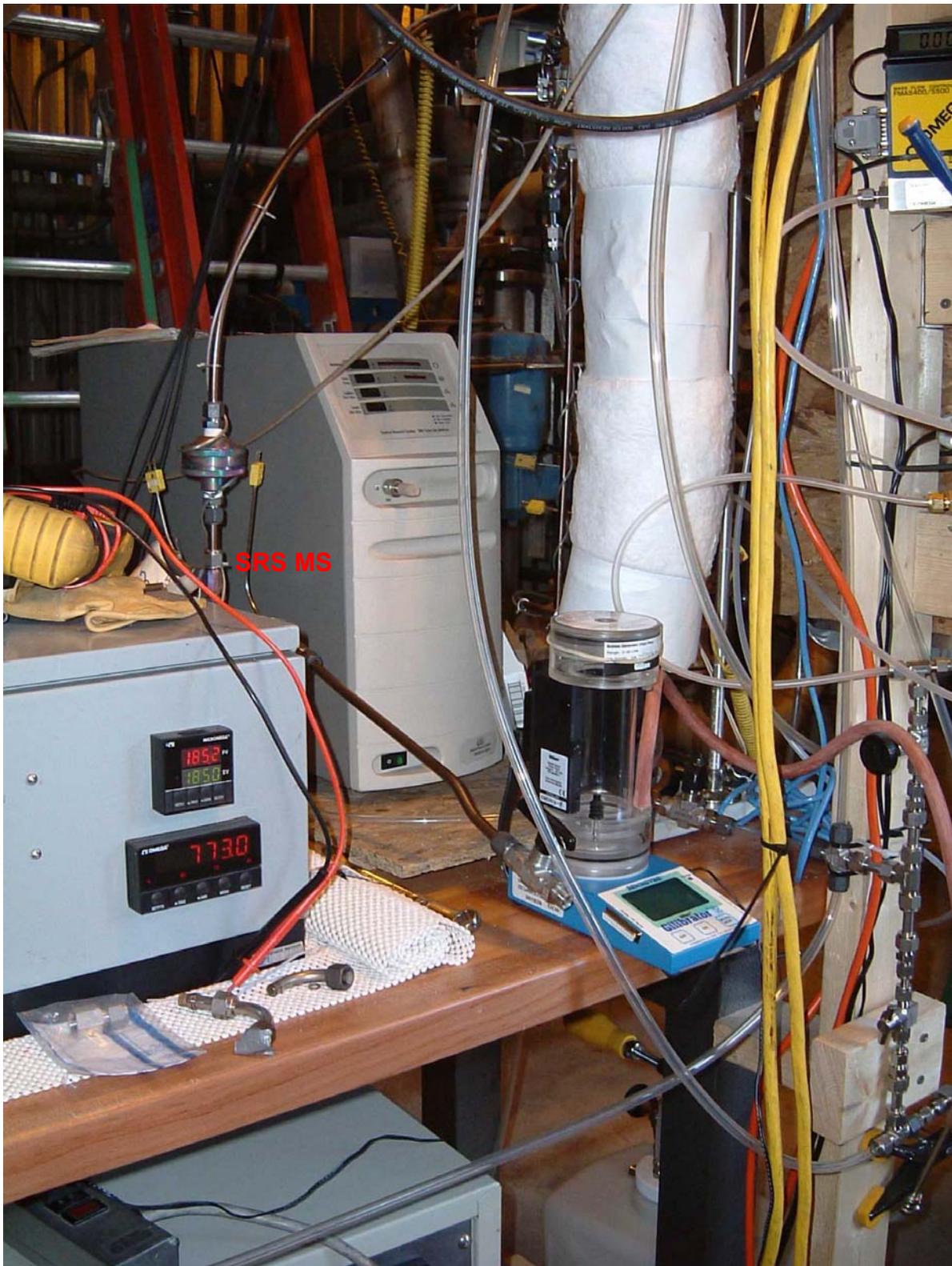


Figure 22. Preliminary installation of the SRS Mass Spectrometer at New Bern.

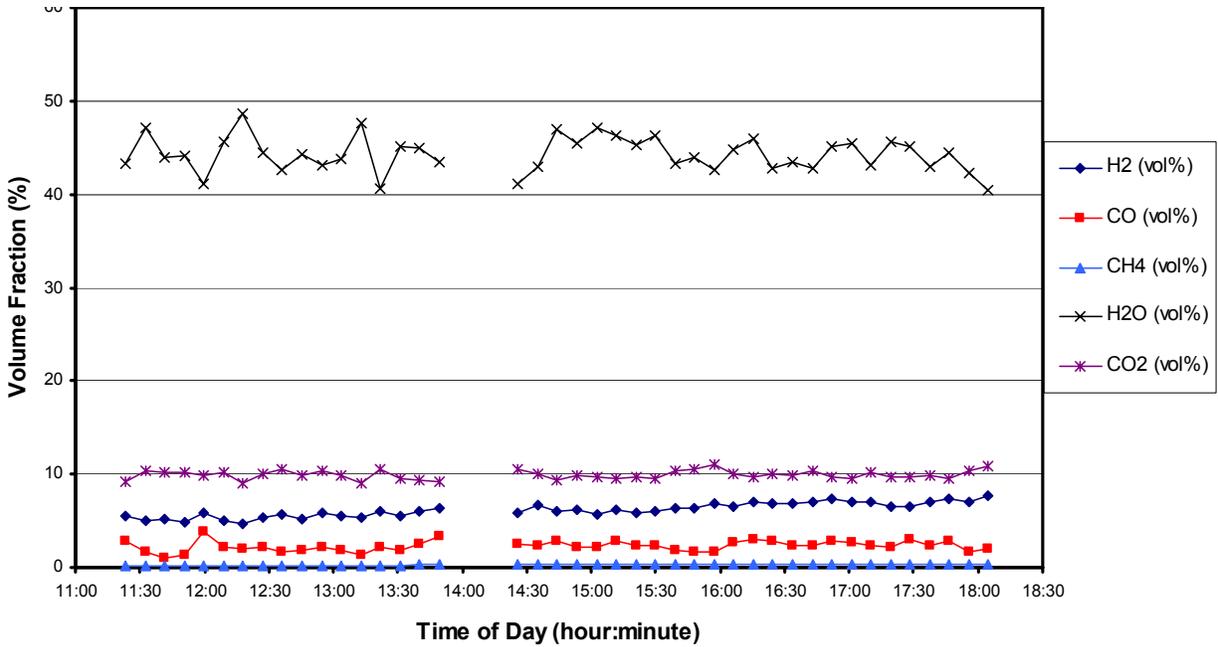


Figure 23. Composition of syngas produced on June 23, 2005 by the Chemrec™ black liquor gasifier as measured from compositional data obtained from the SRS QMS300 Mass Spectrometer.

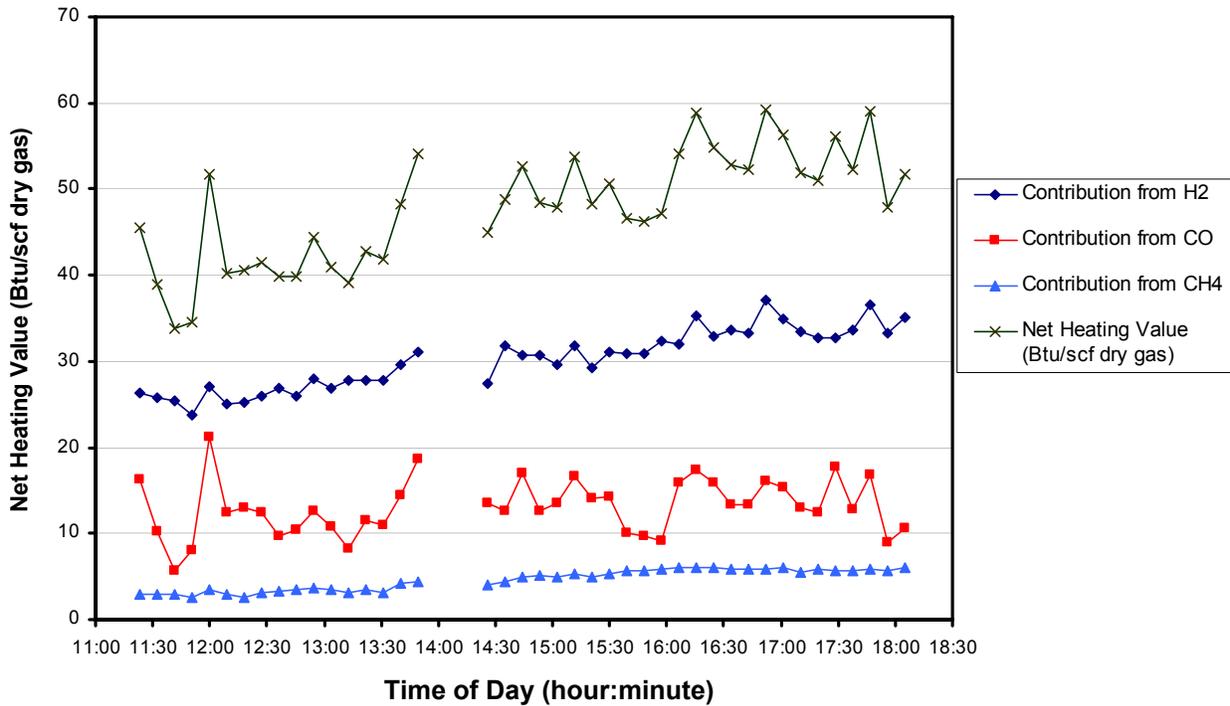


Figure 24. Heating value of syngas produced on June 23, 2005 by the Chemrec™ black liquor gasifier as computed from measured compositional data obtained from the SRS QMS300 Mass Spectrometer.

Fall 2005 Biomass Gasification Testing at GTI's FFTF – The most extensive testing in this project occurred at GTI's Flex Fuel Test Facility from October 27 to November 2, 2005. This testing focused specifically on the on-line analyses of syngas produced during pelletized wood-fueled gasification tests performed in collaboration with initial evaluations of the tar-cracking abilities of alumina and sintered olivine bed materials under DOE Cooperative Agreement DE-FG36-04GO14314. During these tests, we used second-generation Sample Expansion and Dilution Interfaces (SEDIs) that performed the key steps in preparing syngas streams extracted from two locations in the FFTF process for transport to the suite of instruments we assembled for on-line syngas analyses. (The extraction and transport of these two streams is described in reports issued under Cooperative Agreement DE-FC36-03GO13175.) One extractive sample train was installed at the G8 location in the Flex-Fuel Test Facility process (upstream of the high-temperature, high-pressure (HTHP) barrier filter), and the second train was installed at the G13 location (downstream of the HTHP barrier filter).

Because significant concentrations of entrained particulate matter were expected in the syngas extracted at G8 upstream of the barrier filter, the sampling train at G8 included a prefilter upstream of the SEDI that could be cleaned online. Although the design of the Flex-Fuel Test Facility process should ensure that the G13 sampling location should remain free of entrained particulate matter, the SEDI installed at G13 included two small in-line filters just upstream of the two depressurization orifices as a backup to protect the transport lines and analytical instruments from particulate contamination in case of a breach of the Flex-Fuel Test Facility barrier filter. No provision was made in the design of the G13 sampling train for online cleaning of these two small filters.

During the fall 2005 testing we withdrew syngas from G8 and G13 in the gasification process stream and delivered appropriately conditioned, continuous streams of syngas to our suite of analytical instruments for near real-time, on-line analyses. The suite included a Stanford Research Systems QMS300 Mass Spectrometer (SRS MS), an Industrial Machine and Control Corporation (IMACC) Fourier-transform infrared spectrometer (FT-IR), an integrated Gas Chromatograph, Mass Selective Detector, Flame Ionization Detector and Sulfur Chemiluminescence Detector (GC/MSD/FID/SCD) system acquired from Wasson-ECE, and an Agilent 5890 gas chromatograph with flame photometric detector (GC/FPD).

The diluted streams from these two sample trains were transported to a sample distribution manifold located in a second-floor utility room, allowing either one of them to be analyzed by any of the instruments in the analytical suite located in the utility room. In Figure 25, the sample distribution manifold and the analytical instruments in this utility

room (Wasson GC/MSD/FID/SCD system, IMACC FT-IR, and Agilent GC/FID/FPD) are shown.

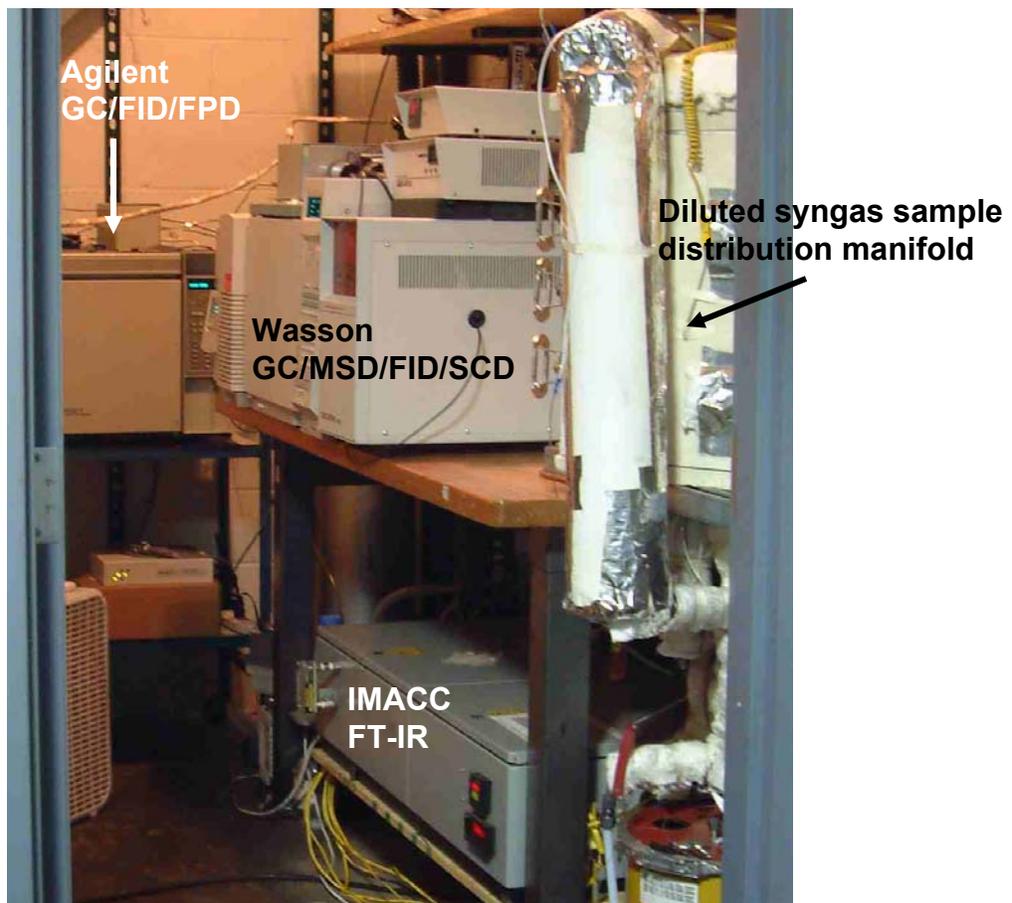


Figure 25. The Analytical Suite installed in the second-floor utility room.

The undiluted syngas streams exiting the two SEDIs were transported through separate heated, insulated transport lines to another sample distribution manifold, located in the Flex-Fuel Test Facility process area adjacent to a NEMA enclosure that was used to house the SRS Mass Spectrometer (Figure 26).



Figure 26. NEMA housing for the SRS Mass Spectrometer in the process area underneath the insulated, heat traced Mass Spectrometer manifold that received and directed the undiluted sample streams to the Mass Spectrometer.

The Flex-Fuel Test Facility processed biomass into syngas for three distinct operating periods between October 28 and November 2, 2005. There were several objectives for these experiments: (1) to determine what gasification conditions were necessary to gasify biomass effectively; (2) to provide syngas from biomass for detailed characterization for the tar-cracking evaluations conducted under DOE Cooperative Agreement DE-FG36-04GO14314; and (3) to provide a biomass-derived syngas product stream for sampling technique verification and biomass syngas compositional analysis under DOE Cooperative Agreements DE-FC36-03GO13175 and DE-FG36-02GO12024.

The first test segment was successfully conducted on October 28. The procedures and equipment instituted for gasification of the wood fuel worked well, with olivine as the bed material. Over an operating period of more than eleven hours of gasification, several processing parameters were varied in order to determine preferred operating conditions for the subsequent test segments. Gasifier pressure was varied from less than 200 psig to over 300 psig, and biomass was fed at up to 1300 lbs/hr, resulting in a syngas production rate of up to 4000 lbs/hr. Some equipment problems were noted, and adjustments were accomplished before the subsequent test segments.

The second test segment was conducted mostly on October 31, but extended just slightly into November 1. This experiment, also with olivine as the bed material, was quite successful, with very steady gasifier operations for about fourteen hours, with very consistent equipment operation. Gasifier pressure was maintained between 215 and 240 psig, gasifier bed outlet temperatures were between 1800 and 1850 °F, and the syngas production rate was 3800 to 3900 lbs/hr, with a filter outlet temperature from 800 to 850 °F. With the stable operation of the gasifier, the composition of the syngas appeared to remain relatively constant.

The third test segment was conducted on November 2. This test segment, with alumina as the bed material, was also successful, as biomass was gasified almost continuously for over nine hours. However, this operating period included several episodes affecting the consistency of the gasifier operation. Gasifier pressure was essentially constant at 220 psig, with gasifier bed outlet temperature in the range of 1725 to 1825 °F; resulting in production of up to 4000 lbs/hr of syngas, declining to 3500 lbs/hr by the end of the test segment. There was one episode of feeding difficulties with the screw feeder for biomass. More significantly, from a few hours into this run the filter experienced high differential pressure (probably from the breakage of some filter elements). The alumina bed material also required higher classifier velocities than did the olivine bed to maintain gasifier bed levels; and consequently the frequent make-up additions of alumina caused

some minor upsets in the gasifier process conditions and possibly also in syngas quantity and quality.

Before the Flex-Fuel Test Facility began producing syngas, we observed flow rates through one portion of the G13 SEDI that may have been indicative of a leak around one of the pressure-reducing orifices in the SEDI. Therefore the only diluted syngas sample stream delivered to the analysis suite after the Flex-Fuel Test Facility began producing syngas was from the G8 location. At some point during the operation of the Flex-Fuel Test Facility during this testing, approximately half of the ceramic filter elements in the facility's barrier filter fractured, allowing periodic passage of entrained particulate matter through the filter element failsafe devices located at the exit of each of the fractured filter elements. The G13 SEDI produced an undiluted syngas stream sent to the Mass Spectrometer manifold for analysis until these filter element failures in the Flex-Fuel Test Facility process blinded the small filter in the SEDI at the inlet of the undiluted sample line in the SEDI. From that point forward, all undiluted and diluted syngas streams that were analyzed were drawn from the G8 location.

Figures 27, 28 and 29 present syngas compositional data obtained with the SRS Mass Spectrometer on October 31 with the gasifier operating with the olivine bed material. Figures 30, 31 and 32 present syngas compositional data obtained with the SRS Mass Spectrometer on November 2 with the gasifier operating with the alumina bed material. In Figure 33, data obtained on October 31 with the IMACC FT-IR are presented. These data demonstrate the ability of the FT-IR to track the concentrations of various gaseous species in the syngas over time. Periodic nitrogen purge and cleaning procedures carried out on the G8 prefilter are identified in the space between the two graphs shown in Figure 33.

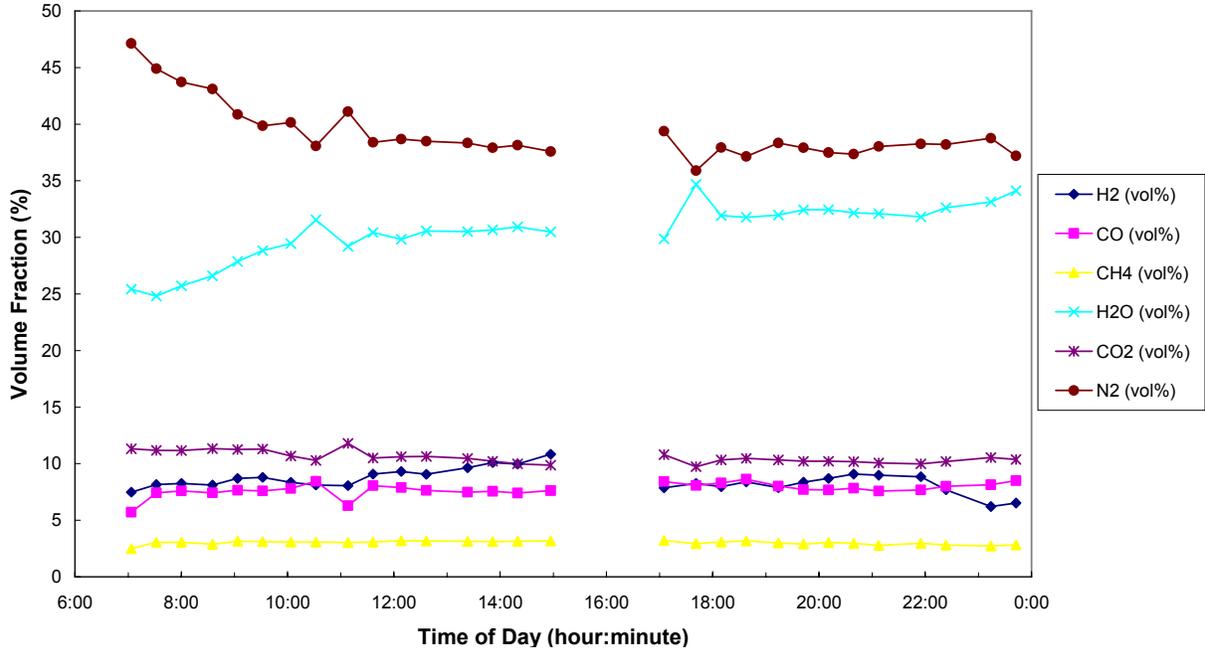


Figure 27. Major components in the syngas produced at G8 in the Flex-Fuel Test Facility process stream on October 31, 2005 as measured by the SRS Mass Spectrometer.

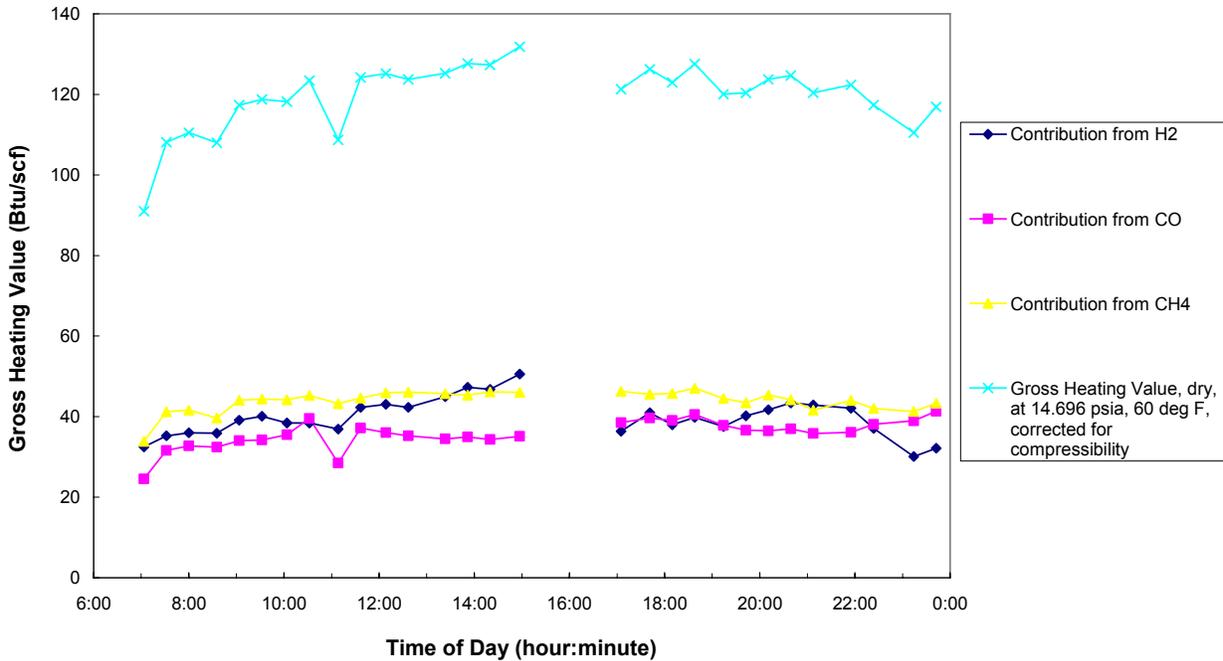


Figure 28. Gross heating value of the dry syngas produced at G8 in the Flex-Fuel Test Facility process stream on October 31, 2005 as measured by the SRS Mass Spectrometer.

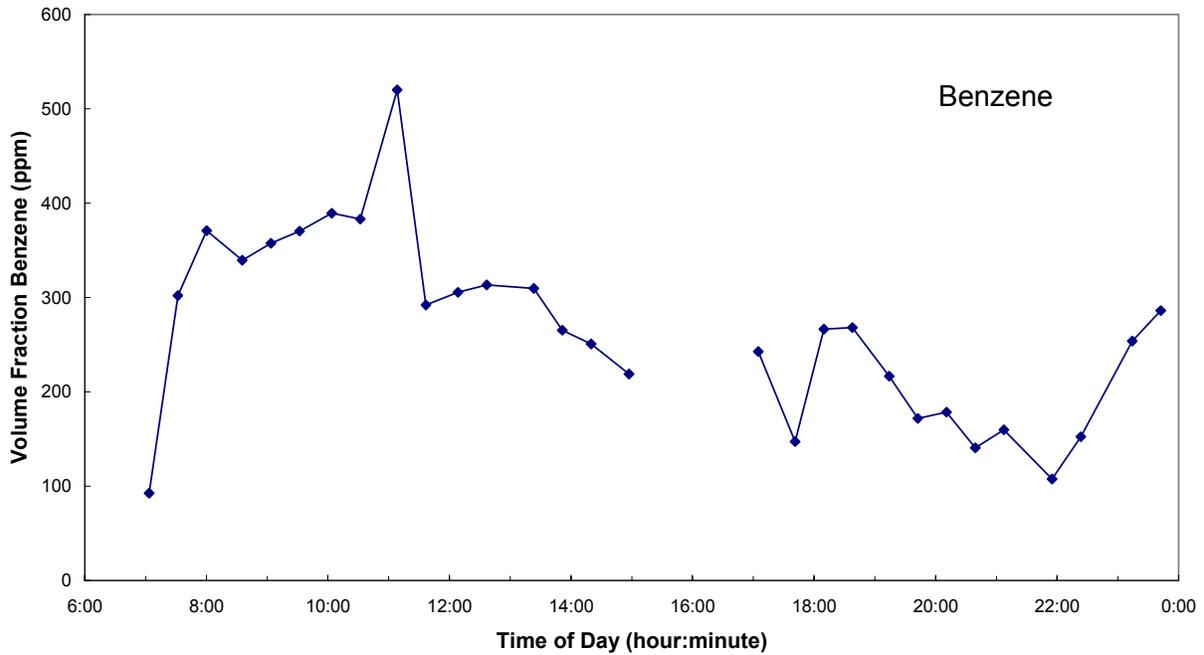


Figure 29. Volume fraction of benzene in the syngas produced at G8 in the Flex-Fuel Test Facility process stream on October 31, 2005 as measured by the SRS Mass Spectrometer.

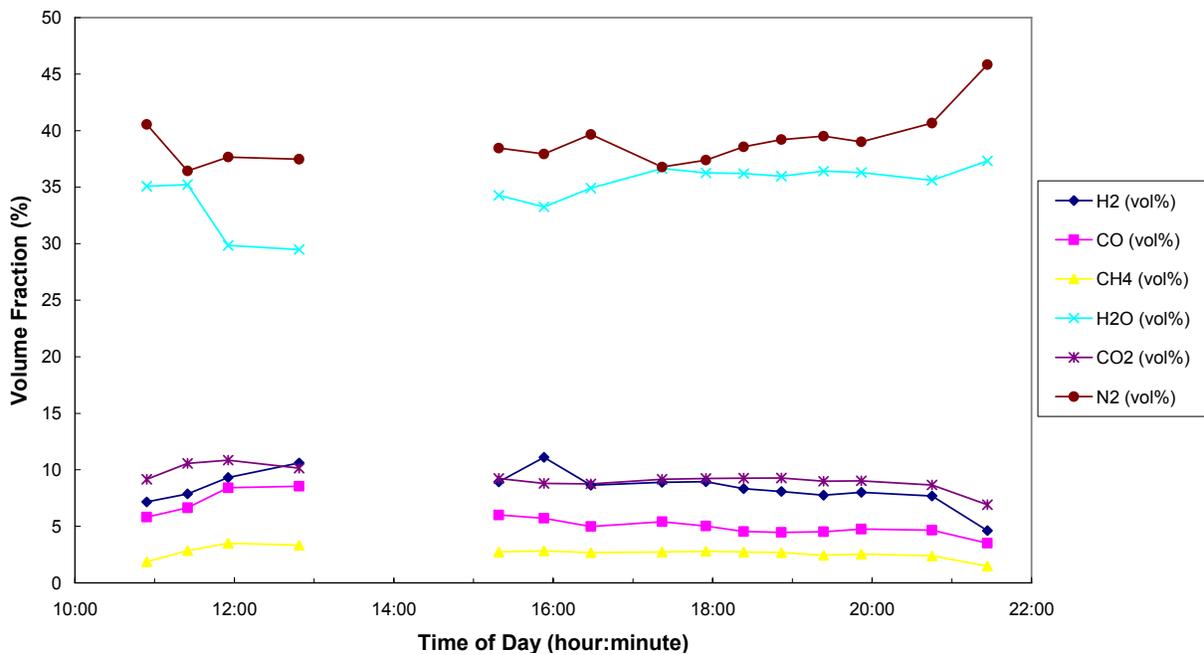


Figure 30. Major components in the syngas produced at G8 in the Flex-Fuel Test Facility process stream on November 2, 2005 as measured by the SRS Mass Spectrometer.

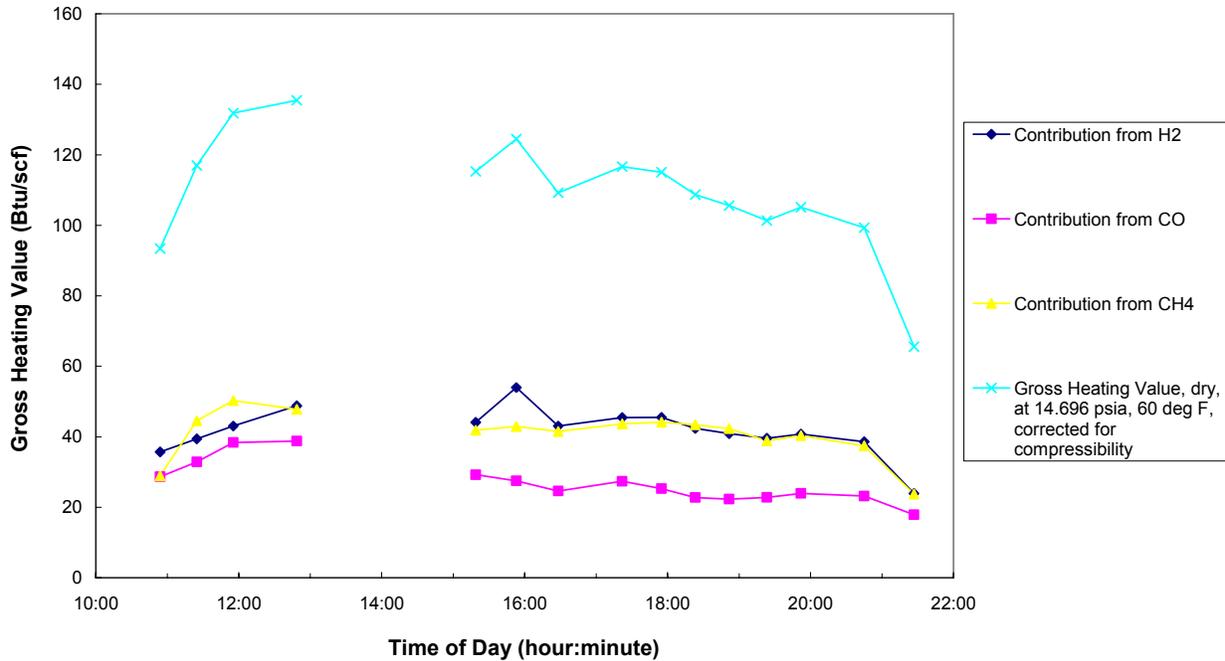


Figure 31. Gross heating value of the dry syngas produced at G8 in the Flex-Fuel Test Facility process stream on November 2, 2005 as measured by the SRS Mass Spectrometer.

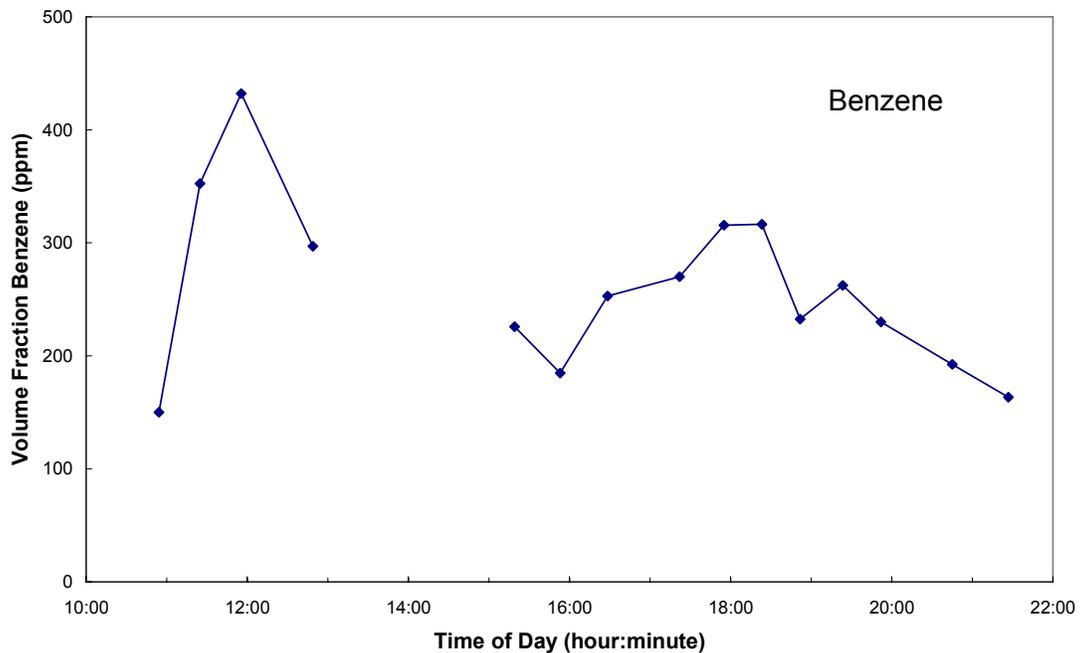


Figure 32. Volume fraction of benzene in the syngas produced at G8 in the Flex-Fuel Test Facility process stream on November 2, 2005 as measured by the SRS Mass Spectrometer.

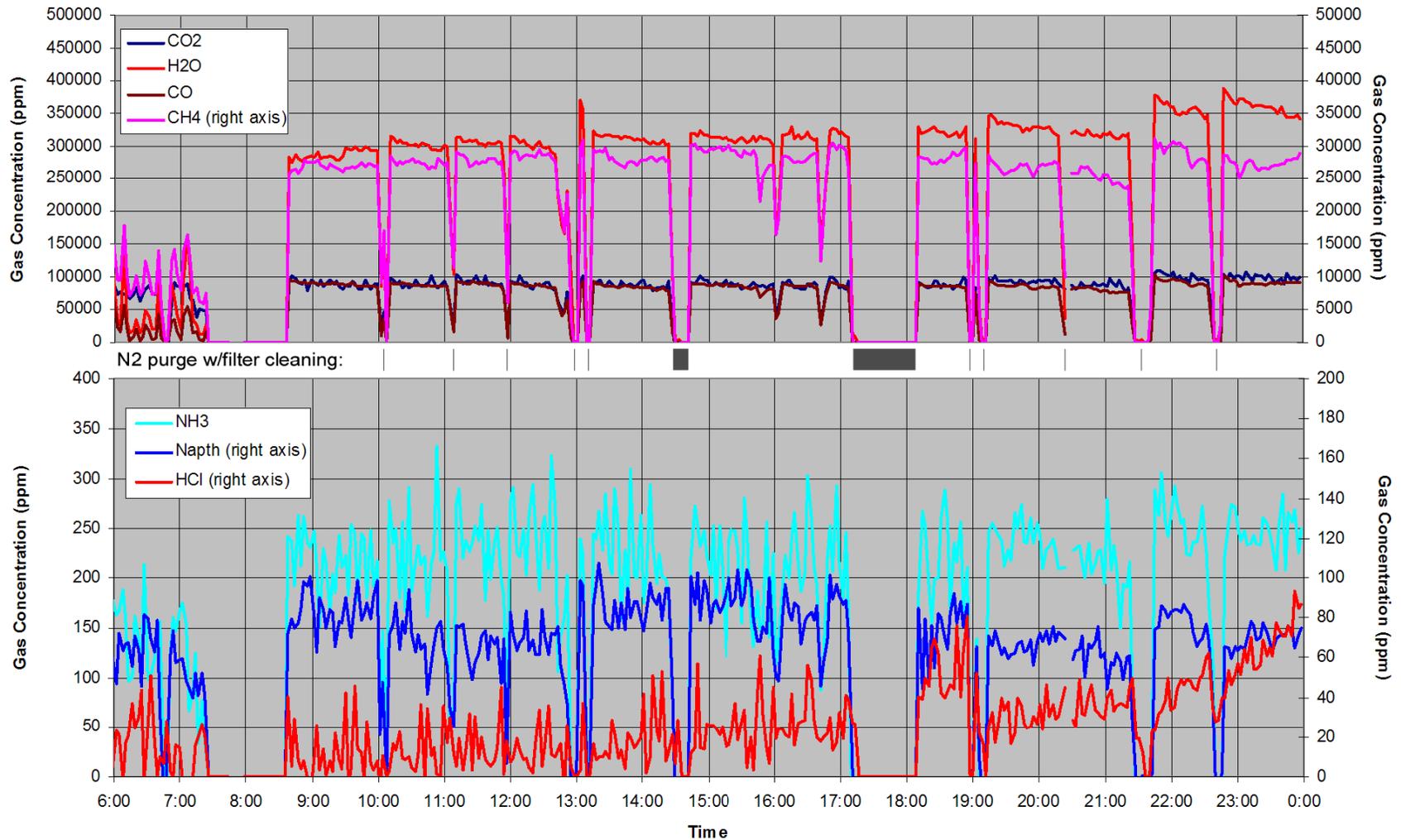


Figure 33. Major components in the syngas produced at G8 in the Flex-Fuel Test Facility process stream on October 31, 2005 as measured by the IMACC FT-IR. Periodic nitrogen purge and cleaning procedures carried out on the G8 prefilter are identified in the space between the two graphs.

IMACC FT-IR – Interest in water content in syngas has typically been limited to qualitative information in monitoring gasification processes. When gas measurement systems necessarily must function by removing water, and other condensable species, from the syngas, the direct results of other gas concentration measurements are on a dry basis. In several respects the dry basis for gas species levels is more fundamental in process control so usually actual precise values of water concentration in syngas are not necessary. However, the measurement approaches developed in this project have as the first priority on-line, continuous concentrations of both major (non condensable) species and condensable species. The methods developed provide results at essentially actual process gas concentrations; that is, on a wet basis. Regardless of benefits that may exist for species levels on a wet basis, availability of water concentration measurements allow easy conversion to a dry basis for process control and evaluation purposes. Of course this means that the accuracy of results for all gas species are dependent on the accuracy of the water data.

Recently we have focused on accuracy of water concentration data with our developed methods, mass spectrometry at 800 °F and process pressure and FT-IR at 365 °F and ambient pressure. Frequent on-line calibrations of several gas species is considered as inherent in the developed method but these do not include water, because a source of adequate calibration gas requiring minimal labor is not known.

In principle FT-IR measurements provide absolute results; that is, no calibration constants associated with the specific instrument are involved. Analysis includes selection of specific wavenumber intervals that have distinct absorption signatures for each species. At practical spectral resolutions, overlap of absorption spectra may not be avoidable so interferences between species exist that depend on the overall mix of gas species. Another source of uncertainty in practice is the result of nonlinearities that exist in absorption spectra increasing with gas concentration. Such nonlinearities are specific to each species. Analysis handles these by using series of reference spectra that cover the entire range of concentrations of interest combined with an iterative analysis procedure that locates the reference spectrum for concentration nearest each actual current gas concentration and interpolates across intervals between concentrations at which available reference spectra were obtained.

At the beginning of this development effort an analysis method was constructed in collaboration with the IMACC instrument developer based upon initial spectra resulting from gasification of coal from India at GTI's Flex Fuel Test Facility. Over the course of four major test campaigns involving six different processes, gas compositions varied substantially. Water composition in particular ranged from about 10 to 60 % by volume. The initial FT-IR method was modified to evaluate potential error associated with the

sources of uncertainty discussed above for varying levels of water and CO₂. While these considerations are not complete, it appears conclusive thus far that including an additional wavenumber range (1870-1980 cm⁻¹ along with the original 3206-3389 cm⁻¹) for water determination significantly improves the resulting concentrations. This conclusion is based on reduced residual error (from about 8 to 3%) in fitting the reference spectra to syngas spectra and agreement with mass spectrometry data. For our most recent test campaign in which water concentrations varied from about 20 to 40% this additional wavelength interval resulted in water concentrations values about 20% lower. It appears that the developed monitoring methods of this project should include initial batch water reference measurements to assist in customization and establishment the FT-IR analysis method for a given process.

SRS QMS 300 Mass Spectrometer – The attractive feature of mass spectrometry as a tool for analysis of syngas is that it is capable of determining all of the major species, H₂, CO, CH₄, CO₂, H₂O, N₂, and Ar, present at levels on the order of 1 percent and higher in the product from air blown gasification. Our instrument is the QMS 300 residual gas analyzer from Stanford Research Systems (SRS), having a mass/charge ratio range from 1 to 300. Syngas samples are extracted from the GTI sampling and sample transfer system, undiluted, through the standard 3-foot-long, 0.005-inch-i.d. stainless steel capillary tube supplied by SRS. The first 14 inches of the capillary tube are enclosed in the sampling system, where the temperature is typically 600 °F. A length of large bore 1/16-inch o.d. stainless steel tubing connects the outlet from the capillary to the instrument.

Calibrations for H₂, CO, CH₄, CO₂, and N₂ are performed using a standard gas mixture containing 5 vol % each of H₂, CO, and CH₄, 10 vol % CO₂, and 75 vol % N₂. The gas mixture is introduced through the sampling system under conditions of temperature and pressure similar to those present during fuel gas sampling. Calibration for H₂O has been performed using ambient air of known relative humidity sampled through the unheated capillary and by sampling air or calibration gas bubbled through distilled water in a flask immersed in a constant temperature bath. The calibration for argon is done using ambient air.

The method for extracting the partial pressure and volume fraction of each species from the mass spectra is described below and summarized in Table 5.

Carbon dioxide: There is no significant interference with the signal from the carbon dioxide parent ion at a mass/charge ratio (m/q , mass of ion in atomic mass units/charge in electronic charge units) of 44, so the partial pressure of CO₂ is determined by direct comparison with the signal at this mass/charge ratio from the standard gas mixture.

Water Vapor: There is no significant interference with the signal from water vapor at $m/q = 18$, so the partial pressure of H_2O is determined by direct comparison with the signal from water vapor in moist air or in air or syngas saturated with water vapor at known temperature. Care is taken to ensure that the capillary outlet pressure during calibration is the same as during measurement of unknown syngas compositions (1.5 mbar). Neither of these approaches has proven to be entirely satisfactory. The volume fraction of water vapor in air (~2 vol %) is far less than that usually present in fuel gas (~40 vol %), requiring long extrapolation of the calibration factor. The signal from saturated air or syngas after bubbling through water is somewhat noisy, perhaps due to withdrawal into the capillary of liquid water condensed on the tip or nonuniformity of the degree of saturation. Also, the dissolution of CO_2 from air or syngas in the water may influence its vapor pressure. During an upcoming test (funded through an industrial sponsor), we plan to use nitrogen as the gas to be saturated, rather than air or syngas.

Methane: There is no significant interference with the signal from methane at $m/q = 15$, which has an intensity almost as great as that of the parent peak at $m/q = 16$ (40 versus 46 % of total methane signal), so the partial pressure of CH_4 is determined by direct comparison with the signal at $m/q = 15$ from the standard gas mixture.

Hydrogen: There are no significant contributions other than H_2 to the signal at $m/q = 2$. However, there is a background signal from hydrogen, due to the low efficiency of the turbo-molecular pump for removing hydrogen from the vacuum system. The contribution from the background is evaluated using the signal at $m/q = 2$ when sampling ambient air. This contribution is subtracted from the intensity at $m/q = 2$ before calculating the calibration factor from the H_2 signal from the standard gas mixture, and subtracted from the H_2 signal from syngas, before applying the calibration factor to obtain the partial pressure of H_2 .

Carbon Monoxide: The signal from CO at $m/q = 28$ is far less than the signal from N_2 in the fuel gas from an air-blown gasifier. Attempts to extract the CO signal from the total at $m/q = 28$, making use of the nitrogen signal at $m/q = 14$, were unsuccessful. Fortunately, although the signal from CO at $m/q = 12$ is much weaker than the parent ion peak (5 versus 92% of the total CO signal), the interferences from CO_2 and CH_4 , at this mass/charge ratio can be well quantified. There are two reasons for this: (1) the signals used to determine CO_2 and CH_4 , at $m/q = 44$ and 15, respectively, are free from interferences, so the measurements of these species have good precision and accuracy and (2) the contributions from the three species at $m/q = 12$ are all from the carbon atom, so the same calibration factor applies to all.

Nitrogen: Nitrogen is determined using the intensity of its parent ion peak at $m/q = 28$, including corrections for the contributions from CO and CO₂.

Argon: Argon is determined using the intensity of its singly-charged ion peak at $m/q = 40$. There are no significant interferences from other components of syngas at this mass/charge ratio.

To determine the composition of syngas, typically 25 spectra are recorded covering the mass/charge ratio range from 1 to 161. Because rapid turn-around of results has not been needed, the upper end of the range has been extended to 161, to be able to see any high molecular weight species such as naphthalene (128 amu), should they appear. Collection of 25 mass spectra takes 30 minutes. The 25 spectra, or any number of spectra one chooses, are averaged to improve the signal/noise ratio. The averaged spectrum is then analyzed incorporating the scheme outlined above and in Table 1. If the analysis were required on a shorter time scale, the mass/charge ratio range could be reduced to 1 to 50, which would still capture all of the data needed for analysis of the major gaseous species.

The precision of the results has been greatly improved during the course of the research program by the averaging procedure described above, and by incorporating corrections for drift of the mass/charge scale. The latter is done by inspection of a representative set of calibration spectra on each day of testing, to determine the average offset of all of the peaks used in the analysis scheme. Correcting for offset when selecting intensities from both the calibration gas spectra and the fuel gas spectra reduces the scatter in the results markedly, because intensity is increasingly sensitive to mass/charge ratio as one moves away from the center of a peak.

The partial pressures determined as described above are divided by their total to determine the volume fractions of the constituents. The lower heating value of the dry gas is then calculated from heating values for the three major combustible components, H₂, CO, and CH₄.

Table 5. Mass/Charge Ratios Used to Quantify Major Gaseous Species in Syngas Using Mass Spectrometry.

Component	Parent Ion Mass/ Charge Ratio ^a	Mass/Charge Ratio Used for Analysis	Interferences	Notes
H ₂	2	2	background	b
CO	28	12	CO ₂ , CH ₄	c
CH ₄	16	15	none significant	d
CO ₂	44	44	none significant	
H ₂ O	18	18	none significant	
N ₂	28	28	CO, CO ₂	
Ar	40	40	none significant	

a. This would be the most desirable peak for analysis, if it were not for interferences. The mass/charge ratio, m/q , is the mass of the ion in atomic mass units divided by its charge in electronic charge units.

b. There is a background signal from hydrogen, always present due to the low efficiency of the turbo-molecular pump in removing hydrogen from the vacuum system. The signal at $m/q = 2$ is corrected using the background observed in moist air, which is small compared with the signal from hydrogen in most syngas.

c. The interference from N₂, at least in air blown gasification, at $m/q = 28$ is too strong for this peak to be usable for CO quantification. The peak at $m/q = 12$, though much weaker, gives a robust analysis because the interferences from CO₂ and CH₄ can be well quantified.

d. The intensity of the signal from methane at $m/q = 15$ is almost as great as that at $m/q = 16$ (40 versus 46% of total methane signal). Water vapor, CO, CO₂, and O₂ (when it is present, for example during start-up, shut-down, or upset condition) all interfere at $m/q = 16$.

Overview of Technologies for Syngas Cleanup and Reforming

Catalytic candle filters suited for operation at temperatures of up to 900 °C, have been developed at Vrije Universiteit Brussel¹, Ni-olivine catalysts for tar reforming have been developed through research funded by the European Commission^{2,3}, monolithic NiO tar-reforming catalysts have been developed at the Fraunhofer UMSICHT⁴, and a moving-bed granular filter has been developed at the University of Iowa⁵. In addition to tar destruction, such commercially available catalysts have also shown an affinity to decompose a significant portion of ammonia (NH₃) which is expected to become an increasingly important focus of syngas cleaning efforts.

Gas cleaning technology for removal of reduced sulfur and halide (e.g., HCl) compounds from fuel gases is also commercially available, using regenerable and non-regenerable sorbents. For sulfur removal, candidate regenerable sorbents include zinc titanate, which has undergone significant development work within the context of the Integrated Gasification Combined Cycle (IGCC) for coal-based gasification systems, and other sorbents such as those based on the oxides of copper (CuO), iron (Fe₂O₃), and manganese (Mn₂O₃). Non-regenerable or disposable sulfur sorbents include the standard zinc oxide (ZnO) guard-bed and the Sulfatreat iron oxide sorbent. Both of these materials are commercially available and are widely used for low- to medium-temperature desulfurization applications (up to 750°F for the ZnO sorbent and up to 500 °F for the iron oxide sorbent). Chlorine removal, which is also commercially available, can be accomplished using non-regenerable materials, such as sodium-promoted alumina or other sodium-containing sorbents.

One approach for improvement of syngas cleaning alternatives is to use developing desulfurization technologies that rely on the use of a regenerable metal-oxide-based sorbent material, such as zinc titanate, as a polishing sorbent, in a common desulfurization reactor configuration, such as a packed-bed, a moving-bed, a fluidized-bed, or a transport reactor operating in the range of 900 to 1100 °F. Given the relatively low contaminant concentrations in biomass gasification product gases, a better approach may end up relying on sorbent injection in the gasifier product gas, following tar destruction and partial gas cooling, immediately upstream of a hot gas filter. Such an approach would be attractive economically since inexpensive single-use or once-through sorbents can be employed as “bulk” sorbents to accomplish significant gas cleaning. Further deep cleaning can be accomplished via injection of highly reactive materials, such as BASF’s R5-12 for sulfur control or Süd Chemie’s G-72E and G-92C for sulfur and halide control, respectively. In a DOE/NETL-funded project, GTI and Siemens Westinghouse demonstrated that the G-72E sorbent was capable of removing H₂S from simulated fuel gas mixtures to less than 85 ppbv at 572 °F, which was the

detection limit of the analytical method. The G-92C material was shown to control HCl to concentrations as low as 10 ppbv. Cooling of syngas for bulk and/or polishing contaminant control steps will also accomplish the removal of alkali metals (characteristically found at relatively high concentrations in biomass gasification systems) through interaction with cool surfaces, and possibly by adsorption on particulate matter. Decomposition of up to 75% of residual NH_3 is possible due to gas interactions with catalytically active nickel alloys commonly used in various locations in hot gas filter vessels.

Design of Sampling Interface for GTI's 2" Bench-Scale Gasifier during Gasification Tests of Corn Stover

Because of the increased importance of gasification of underutilized biomass materials, and the specific opportunities that corn stover material could have as a feedstock for gasification, this project adapted the sampling train developed and tested in this project to the 2-inch gasification unit that GTI has successfully operated in its Des Plaines, Illinois laboratories. Successful demonstration and characterization of syngas production from corn stover material would directly serve several DOE objectives. We designed the adaptations necessary to interface our sampling approach to the output of GTI's bench-scale gasifier in Des Plaines, IL. Drawings of the basic design of the interface are provided in Figures 24, 25, and 26. Although this specific interface has not been built, its components are all either commercially available, or have been thoroughly evaluated under Cooperative Agreement DE-FC36-02GO12024 and Cooperative Agreement DE-FC36-03GO13175.

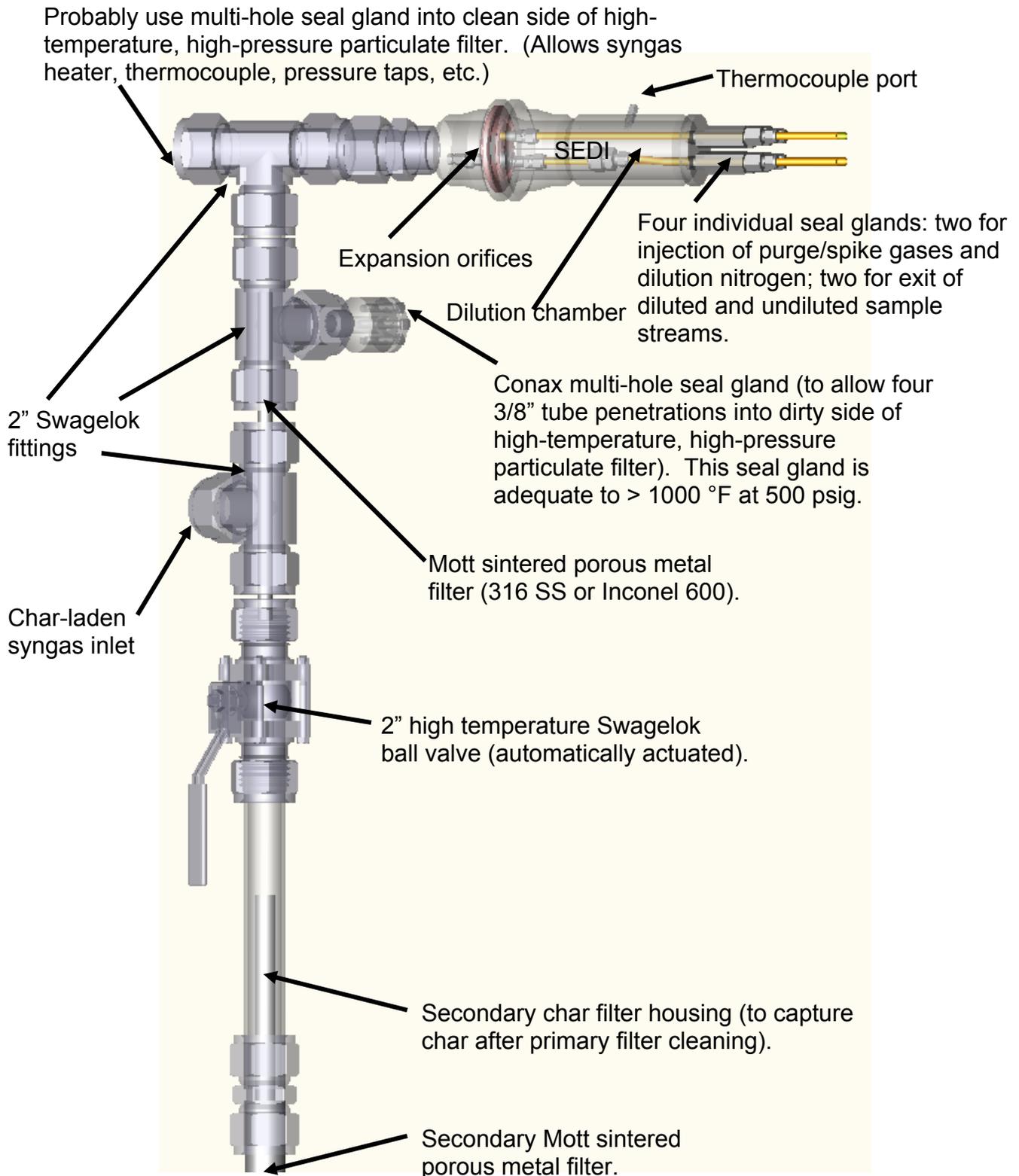


Figure 24. Isometric design view of the interface required between GTI's 2" bench-scale gasifier and on-line sampling system for characterizations of corn stover gasification product gas.

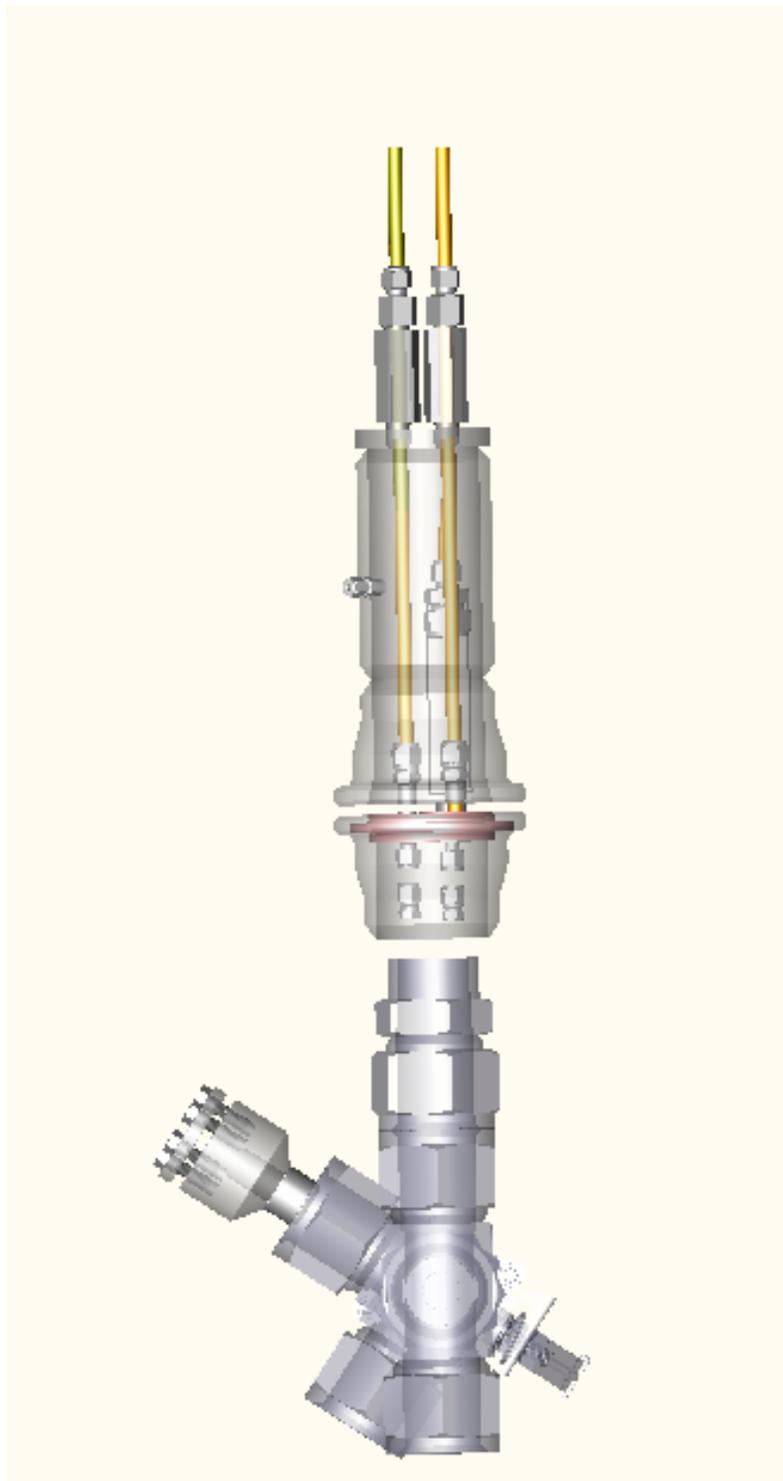


Figure 25. Top design view of the interface required between GTI's 2" bench-scale gasifier and on-line sampling system for characterizations of corn stover gasification product gas.



Figure 26. Rear design view of the interface required between GTI's 2" bench-scale gasifier and on-line sampling system for characterizations of corn stover gasification product gas.

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