Final Report

Project Title: Biomass Gasification Research Facility

Award Number: DE-FC36-03GO13175

Recipient: Gas Technology Institute

Project Location: Birmingham, Alabama

Project Period: October 1, 2003 to June 30, 2007

Date of Report: September 30, 2007

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Executive Summary

The specific objective of DE-FC36-03GO13175 was to develop comprehensive in situ and extractive gas sampling equipment and protocols that enable the evaluation, optimization and integration of syngas treatment technologies at various gasification facilities. After its novation to GTI, the companion project, Cooperative Agreement DE-FC36-02GO12024, primarily covered the selection, acquisition, and application of a suite of gas analyzers capable of providing near real-time analyses of suitably conditioned syngas streams. The sampling equipment and protocols developed under both 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 Cooperative Agreement DE-FC36-03GO13175, GTI developed the sample delivery and distribution methods and hardware, and sample conditioning interfaces, necessary to make use of 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)). 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), and a Varian micro gas chromatograph with thermal conductivity detector (μ GC)). 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.

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 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.

The sample management system that GTI developed uses thermally-controlled, inert gas to lower the dew points of condensable species in the process gas. This in turn permits direct sampling, and on-line, real-time analyses of the process gas without the loss of condensable species from the sampled gas stream. This sample conditioning approach enables the delivery of multiple sample streams to suitable analyzers, through customized sample distribution manifolds, at temperatures and pressures acceptable to the analyzers. The field demonstration in New Bern, NC included selective use of the first-generation dilution unit designed and fabricated under Cooperative Agreement DE-FC36-03GO13175. A second-generation version of this sample conditioning approach, the Sample Expansion and Distribution Interface (SEDI), was used in biomass gasification tests conducted in October and November 2005 under this Cooperative Agreement and Cooperative Agreement DE-FC36-02GO12024. This intensive field evaluation of our updated approach for thermochemical process sampling occurred at GTI's FFTF during a concurrent evaluation of pelletized wood-fueled gasification and catalyst performance investigated under DOE Cooperative Agreement DE-FG36-04GO14314. Our field evaluation was focused on the depressurization, spiking and calibration, dilution, and sample distribution capabilities of the SEDI. This field effort included evaluation of redesigned sample transport lines, heat tracing, and syngas sample distribution manifolds. This test verified the effectiveness of our sampling approach for the challenging task of continuous syngas sampling and analysis from biomass-fueled gasification process streams. In March 2006 we continued our sampling development and verification activities with an intensive set of calibration measurements at GTI's FFTF.

In FY2007 GTI completed the preparation of a special topical report documenting the standard designs and protocols for sampling from thermochemical processes developed under Cooperative Agreement DE-FC36-03GO13175. The report includes descriptions of the design, fabrication, and installation of the equipment used to provide the complete interface between the thermochemical process stream and the on-line analyzer(s) that were selected to characterize the syngas. (Although our experiences with the specific analyzers we used under Cooperative Agreement DE-FC36-02GO12024 were referenced to enhance these descriptions, the interface design presented in this topical report was generic enough to adapt to other analyzers that may be more appropriate to alternate process streams or facilities.)

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

To enable the potential uses for syngas derived from biomass gasification to be fully exploited, GTI has carried out two companion projects (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, which would be a “plug-and-play” platform for the arrangement and integration of process components. This facility 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 concurrent 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. (Additional information describing activities carried out under Cooperative Agreement DE-FC36-02GO12024 is included in its Final Report.)

The specific objective of DE-FC36-03GO13175 was to develop comprehensive in situ and extractive gas sampling equipment and protocols that enable the evaluation, optimization and integration of syngas treatment technologies at various gasification facilities. After its novation to GTI, the companion project, Cooperative Agreement DE-FC36-02GO12024, primarily covered the selection, acquisition, and application of a suite of gas analyzers capable of providing near real-time analyses of suitably conditioned syngas streams. The sampling equipment and protocols developed under both these projects were proven in the field through evaluations of syngas quality at two sites where biomass-derived syngas was generated.

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The sample management system that GTI developed includes a dilution, or dilution/cooling capability that uses thermally-controlled, inert gas to lower the dew points of condensable species in the process gas. This in turn permits direct sampling, and on-line, real-time analyses of the process gas without the loss of condensable species from the sampled gas stream. This sample conditioning approach enabled the delivery of multiple sample streams, through a customized sample distribution manifold, at temperatures and pressures acceptable to the suite of analyzers. The field demonstration in New Bern, NC included selective use of the first-generation dilution cooling unit (DCU) designed and fabricated under Cooperative Agreement DE-FC36-03GO13175. A second-generation version of this sample conditioning approach, the Sample Expansion and Distribution Interface (SEDI), was used in biomass gasification tests conducted in October and November 2005 under this Cooperative Agreement and Cooperative Agreement DE-FC36-02GO12024. This intensive field test of our updated approach for thermochemical process sampling occurred at GTI's FFTF during a concurrent evaluation of pelletized wood-fueled gasification and catalyst performance investigated under DOE Cooperative Agreement DE-FG36-04GO14314. Our field evaluation was focused on the depressurization, spiking and calibration, dilution, and sample distribution capabilities of the SEDI. This field effort included evaluation of redesigned sample transport lines, heat tracing, and syngas sample distribution manifolds. This test verified the effectiveness of our sampling approach for the challenging task of continuous syngas sampling and analysis from biomass-fueled gasification process streams. In March 2006 we continued our sampling development and verification activities with an intensive set of calibration measurements at GTI's FFTF.

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Initial Project Activities

The specific objectives of this project were refined during the initial stages of the project as various experts in the field were consulted, existing literature on the applicable gasification processes was examined, and as potential host sites for the ultimate demonstrations of on-line sampling techniques were evaluated.

Slipstream Syngas Cleanup and Conditioning System

Early in the project, the design, construction and operation of a Slipstream Syngas Cleanup and Conditioning System was investigated as a means for developing and evaluating on-line syngas sampling capabilities. Also, in the initial phases of this project, two host sites for potentially installing and implementing the Slipstream System were being evaluated: the DOE Wilsonville, AL Power Systems Development Facility (PSDF), and GTI's Flex-Fuel Test Facility.

The Slipstream System that was being considered was envisioned as a series of modular components that could be connected together in a variety of configurations to process and/or reform a stream of synthesis gas from a gasification process. Utilizing a slipstream for the evaluation of modular syngas cleanup systems is well-suited to provide performance data for optimization of overall syngas conditioning systems. Access to a representative syngas slipstream produced at pilot-scale process development units, combined with versatile, targeted, syngas cleanup modules, and on-line syngas sampling and analysis, is a cost-effective means to address current developmental gaps for large-scale deployment of biomass gasification. This results obtainable with this type of slipstream and syngas analysis system should be able to help ensure that syngas production facilities can meet specific end-use gas quality requirements by characterizing and mitigating interface issues between various gas treatment options. Figure 1 shows how such a system might be configured in three modules for use at the PSDF.

Figure 1. A potential Slipstream System configuration for use at the PSDF.

In the configuration shown in Figure 1, synthesis gas from the KBR Transport Reactor would enter from the left into a tar-cracking module that could decompose or reform tars thermally or by exposing the synthesis gas to a fluidized or stationary bed catalytic reactor. Two other modules would follow, one to treat and filter synthesis gas at process temperatures up to 1200 °F, and a second module to treat and filter synthesis gas at lower process temperatures. Other modules could be added to this design to test specialized fuel gas reforming and/or technologies for fuel cell or biorefinery applications for synthesis gas generated from arbitrary fuels. Determination of the optimum size for each module would need to incorporate the space availability at the various sites where this system might be utilized to assess the practicality and economics of reforming and/or cleaning synthesis gas to meet process specifications.

Technologies of the sort that could be evaluated with such a Slipstream System include catalytic candle filters suited for operation at temperatures of up to 900 °C, developed at Vrije Universiteit Brussel¹, Ni-olivine catalysts for tar reforming developed through research funded by the European Commission^{2,3}, monolithic NiO tar-reforming catalysts developed at the Fraunhofer UMSICHT⁴, and a moving-bed granular filter developed at the University of Iowa⁵. In addition to tar destruction, commercially available catalysts have also shown affinity to decompose a significant portion of ammonia (NH₃) which could also be a feature of interest.

Gas cleaning technology for removal of reduced sulfur and halide (e.g., HCl) compounds from fuel gases is 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 is to use developing desulfurization technologies relying 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 would be to rely 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 NH₃ is possible due to gas interactions with catalytically active nickel alloys commonly used in various locations in hot gas filter vessels.

Technical Advisory Panel

In a continuation of an approach developed under the initial activities under Cooperative Agreement DE-FC36-02GO12024 (prior to its novation from Southern Research Institute to GTI), meetings were sponsored to solicit the advice and expertise of a broad range of persons

involved in biomass gasification research and development. 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.

Evaluation of Sampling Opportunities at the DOE Power Systems Development Facility

Because of the significant developmental work that had been performed into coal gasification at the PSDF, and the expertise and equipment available through the PSDF staff and facilities, a careful evaluation was performed of the possibility of installing a Slipstream Syngas Cleanup and Conditioning System at that facility to support the objectives of Cooperative Agreement DE-FC36-03GO13175. GTI and PSDF staff met several times to review the opportunities for collaboration. These discussions eventually centered on the potential use of the Research Testing Island (RTI) that had already been constructed at the PSDF. The primary purpose of the RTI was to test gas conditioning technologies needed to provide high-efficiency removal of sulfur, alkali, and halides for use of syngas in solid oxide fuel cells. The RTI takes a slipstream of syngas from the KBR Transport Reactor process downstream of the gas cooler and barrier filter particulate control device. This is shown schematically in Figure 2.

Figure 2. Schematic diagram of the Research Testing Island at the PSDF. (Figure reproduced from: Longanbach, James R., "Transport Gasifier Operation at the Power Systems Development Facility," *Proceedings of the 29th International Technical Conference on Coal Utilization and Fuel Systems*, April 18 – 22, 2004, Clearwater, Florida.)

The RTI at the PSDF would provide an existing platform for the evaluation of gas conditioning downstream of a barrier filter. Southern Company offered access to the RTI to GTI under Cooperative Agreement DE-FC36-03GO13175 with the provision that if GTI designed modifications and installed new gas conditioning equipment in the existing RTI slipstream it would become a permanent fixture for the RTI, and not removable for installation as a component of a slipstream facility at another site. However, during GTI's negotiations over site access with Southern Company, the operating plans of the PSDF were changed. The biomass gasification tests planned by Southern Company were rescheduled, placing them outside of the scope of project activities under Cooperative Agreement DE-FC36-03GO13175. Consequently GTI began evaluation of additional testing sites and opportunities.

Methods Development and Field Testing

A central feature and requirement of this project was the use of existing, large pilot-scale gasification facilities to provide 'authentic' syngas for the project studies. The sites at which the project was planning testing (the DOE PSDF and GTI's Flex-Fuel Test Facility) were expected to typically run continuous tests of 100 to 300 hours duration during the testing time

frame available under Cooperative Agreement DE-FC36-03GO13175. The fact that these test campaigns were usually scheduled two or three months apart makes suitable testing time with syngas precious. Furthermore, tests of filtering, catalytic and sorbent processes for gas conditioning are subject to short-term variability. Filter pressure drop buildup and cake cleanability can change very rapidly. Catalyst blinding, poisoning, or deactivation by other means can be noted in relatively short trends. Sorbent activity and capacity can show rapid changes. These factors, and the desire to maximize the productivity of the evaluation program, require that accurate samples of untreated and treated syngas be provided from each of the conditioning streams on a basis as close to continuous and real time as possible. It was therefore crucial to incorporate the appropriate interfaces from the Slipstream System to requisite instrumental measurement methods given anticipated syngas components and concentrations in various stages of conditioning.

Reported evaluations of biomass gasification systems were studied to anticipate the composition of the syngas stream that would be entering the Slipstream System. This information provided design guidance on the temperature, pressure, and flow variations the system needed to be able to tolerate before compromising the integrity of the sample of gas being evaluated. As a crucial part of the testing required to characterize and optimize the Slipstream System, specific attention was paid to the development of an overall approach for extracting, conditioning, and analyzing small sample streams obtained from various locations within the main slipstream process flow stream.

It became a primary objective of the project team to extract and condition the sample syngas streams in such a way as to essentially prevent the condensation of vapor-phase hydrocarbon species present in syngas. An integral component of this objective was development of a novel approach to cool the syngas enough to be introduced to the on-line analyzers while preventing vapor condensation. Over the course of this project, three patent applications were filed covering various features of this approach. Effective, quantifiable syngas dilution, and novel means of heating an extracted syngas sample stream during its transport for remote, on-line analysis were the two primary advances made under this project. (These developments are specifically identified under the Patent Applications section of this report).

Dilution Cooling Unit Design and Fabrication

The initial embodiment of the approach that was developed as a means to cool and dilute the syngas sample streams is the Dilution Cooling Unit (DCU). An assembly drawing of the prototype DCU is shown in Figure 3. A prototype dilution cooler was fabricated out of type 316 stainless steel and Macor[®] machinable glass ceramic. The design of the device provides optimum thermal management of the syngas sample stream to avoid any condensation or other degradation in sample integrity. In addition to the provision for external supplementary

heating, the use of void space and non-porous and non-shrinking insulating materials help to control the syngas temperature to the mixing zone of the device. The prototype DCU has a six-inch long mixing zone, which was selected based on conventional engineering guidelines for the length required for gases to completely mix in a turbulent flow regime. The sintered metal diffuser has a pore size chosen to force a uniform flow of controlled-temperature nitrogen into the core of the device. A photograph of the DCU after fabrication is shown in Figure 4.

Figure 3. Design of the prototype Dilution Cooling Unit.

Figure 4. Dilution Cooling Unit with its inlet cap removed.

The DCU concept is designed for low-pressure (< 1 psig) syngas streams entering the DCU at temperatures up to $1000\text{ }^{\circ}\text{F}$ ($538\text{ }^{\circ}\text{C}$). The DCU can then cool the stream to room temperature if necessary before passing the diluted stream on to instruments for on-line analyses. In practice, the requirements for the delivery of suitably prepared syngas streams to on-line analyzers may not necessitate such immediate or extensive cooling. Depending on the thermal limits of the analyzer(s), and the proximity of the analyzers to the DCU, the diluted syngas exiting the DCU can be allowed to cool through thermal radiation during transport to the analyzer(s), if the sampling configuration allows.

The DCU shown in Figure 4 was used during field measurements in June 2005, when the GTI project team participated in a series of tests at the ChemrecTM Gasifier located at the Weyerhaeuser Pulp Mill in New Bern, North Carolina. These tests are discussed later in this report.

Simulation Software Tool for Evaluation of Dilution and Cooling Systems for Gas Samples Containing Condensable Species

During this project, the Department of Mechanical Engineering of the University of Alabama at Birmingham (UAB) delivered a simulation program that describes the flow and cooling of a gas sample in a device with the general configuration of the GTI dilution cooler concept. The simulation model provided insight into design features and operating modes for the GTI dilution cooler concept that may result in concentrations of gas components at temperatures that will

cause them to condense. Therefore, the computer model was developed by UAB with a great deal of flexibility in geometry and in the operating conditions that can be simulated. The deliverable was a software package whose input parameters could be specified and which could be run by GTI engineers to evaluate the ability of candidate devices to avoid formation of aerosol or wet surface during cooling and dilution of gas samples containing condensable species.

The core of the model is a Real Fluids Version of a Finite-Difference Navier-Stokes computational fluid dynamics (CFD) code for 2-D/3-D flow field simulations and analyses. The code was developed for engineering analyses of general fluid dynamics problems. The current version of the code can be used to solve the 2-D planar, axisymmetric or 3-D forms of the Navier-Stokes equations and other scalar transport equations using primitive variables and general multi-zone, multi-block curvilinear coordinates. Compressible or incompressible, laminar or turbulent flow problems are solved using a pressure based predictor/multi-corrector solution algorithm. The code is a fully transparent and user friendly CFD code which is used to analyze a wide variety of fluid dynamics related engineering problems (e.g. internal and/or external flows with complex geometries, cases with laminar or turbulent flow conditions, and flows with ideal, real or reacting gas effects for all speed ranges -- incompressible to hypersonic flow regimes).

For the dilution cooler model, the variables are: sample composition, flow rate, and temperature; length and diameter of the dilution chamber; diameters and lengths of the sample and sheath flow injectors; the temperature and flow rate of the sheath and dilution flows; and the thermodynamic properties of the condensable species. Table 1 lists the default composition of the gas. This set of gases was chosen to permit an accurate representation of syngas major components and allow the concentration of a key condensable hydrocarbon species to be varied.

Table 1. Default Composition of Fuel Gas (mole fractions)

H ₂ O	0.1
CO ₂	0.1
H ₂	0.15
CO	0.15
CH ₄	0.03
Ar	0.005
NH ₃	0.001
C ₁₀ H ₈ (naphthalene)	0.0005
N ₂	0.4635 (balance)

Several simulations were run to check the qualitative performance of the model; such as, the plausibility of calculated temperature gradients and flows, and convergence of the calculations toward consistent and realistic flows and partial pressures of gases. The following figures are images of the model results visualization screens.

Figures 5 - 8 show a simulation of the prototype (six-inch-long mixing zone) dilution cooler. This simulation was run for 300,000 iterations to assure computational convergence. The conditions for this simulation were as follows:

Table 2. Input Conditions for Dilution Cooler Simulation

Syngas flow rate, alpm	3
Sheath nitrogen flow rate, alpm	1
Dilution nitrogen flow rate, alpm	16
Syngas temperature, °F	1000
Sheath nitrogen temperature, °F	1000
Dilution nitrogen temperature, °F	200
Syngas composition	(Table 1)

Figure 5. Modeled steady-state axial velocity of the gases mixed within the prototype (six-inch-long mixing zone) dilution cooler.

Figure 6. Modeled steady-state radial velocity of the gases mixed within the prototype (six-inch-long mixing zone) dilution cooler.

Figure 7. Modeled steady-state static pressure of the gases mixed within the prototype (six-inch-long mixing zone) dilution cooler.

Figure 8. Modeled steady-state partial pressure of the inlet syngas as it is diluted within the prototype (six-inch-long mixing zone) dilution cooler.

The results shown in Figures 5 - 8 provide confidence that the flow solver equations have accurately accounted for the mixing of the sample and dilution gases. Figure 7 shows the combination of diluent and syngas achieves an outlet temperature of about 300 °F. This agrees with the computed final temperature of a completely mixed combination of gases at the flows and temperatures being modeled. The gross dilution factor for the inlet syngas in this combination of gases is calculated to be approximately 12. Figure 8 indicates a relatively rapid mixing of the dilution air and the syngas in the device, achieving the ultimate dilution quite uniformly. In summary, the results of the simulation are plausible and they suggest excellent mixing behavior for the dilution cooler concept as conceived and designed.

Based on these results, the model should be able to help economically evaluate different operating parameters and improved diluter designs. For example, based on the results produced by the simulation represented in Figures 5 - 8, it may be feasible to significantly shorten the mixing zone. To illustrate the possible effects of such a design change, a simulation with the same input parameters as the run represented above for the six-inch-long mixing zone (conditions listed in Tables 1 and 2) was performed with a two-inch-long mixing zone. Selected outputs from that simulation are shown in Figures 9 - 11, which indicate excellent mixing of syngas and diluent gas in the shortened geometry.

Figure 9. Modeled steady-state axial velocity of the gases mixed within a modified compact (two-inch-long mixing zone) dilution cooler design.

Figure 10. Modeled steady-state static pressure of the gases mixed within a modified compact (two-inch-long mixing zone) dilution cooler design.

Figure 11. Modeled steady-state mass fraction of the inlet syngas as it is diluted within a modified compact (two-inch-long mixing zone) dilution cooler design.

Verification and Improvement of GTI's On-Line Syngas Sampling Approach

Over the course of this project, several sampling and analysis configurations were evaluated during various FFTF test campaigns. GTI's overall approach to sample extraction, conditioning, transport, and analysis gradually evolved and improved as these configurations were designed, installed, and tested. This Final Report provides a review of the various iterations of GTI's sampling and analysis systems, with increased emphasis on the final configurations that were able to incorporate several significant advances in the state-of-the-art of on-line syngas sampling and analysis. The Final Report issued under the companion project (Cooperative Agreement DE-FC36-02GO12024) provides the majority of information related to the particular analyzers used in these evaluations, and to the analyses of the syngas streams after their extraction, conditioning, and transport to those analyzers.

Initial Testing at the GTI Flex-Fuel Test Facility – Fourier transform-infrared spectrometry (FT-IR) is among the most powerful instruments 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 GTI used 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 12) was in progress as part of basic monitoring of gasifier operation utilizing a Rosemount analyzer (CH_4 , CO , H_2 , and O_2). Figure 12 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 13. 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 12. Low temperature sample gas conditioning system for providing batch samples and dry ambient temperature gas to the Rosemount analyzer.

Figure 13. 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 PEEKTM 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 14 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 15. 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 14. Instrument room used at GTI's FFTF in initial testing of the IMACC FT-IR and the Stanford Research Systems QMS300 analyzer.

Figure 15. Concentrations of CO_2 , CO, and CH_4 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 16. 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 (H_2S 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 16. 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 16). Preparation of the extraction and transport line located downstream of the Test Filter-Reactor (location G19 in Figure 16) 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 16

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 17. 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 17. 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 18 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 18 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 18. 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 19, and a photograph of the manifold is presented in Figure 20. 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 19. Schematic diagram of the flow distribution multiplexer at the FFTF second floor analysis station.

Figure 20. 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 21.

Figure 21. 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 16) 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 12 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 22. 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 23. The shaded region in Figure 23 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 22. 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 23. 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/FPD instrument shown in Figure 17. The mass spectrometer and the μ GC also measured sulfur species. Figure 24 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 24. Relationship between sorbent feed rate and COS concentration in the process gas.

Characterization of the ChemrecTM black liquor gasifier – During June 2005, this project participated in a series of tests at the ChemrecTM 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 ChemrecTM gasifier identifying the location where syngas was extracted for analysis is presented in Figure 25. 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 25. New Bern black liquor gasifier.

The suite of analyzers assembled for these tests, which are discussed in more detail in the Fianl Report issued under Cooperative Agreement DE-FC36-02GO12024, 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 26 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 ChemrecTM 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 ChemrecTM 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 27). 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 27 and 28).

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 the photographs (Figures 27 and 28), but can be more clearly understood by examining the schematic diagram presented in Figure 26. 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 26. Sample extraction, conditioning, and transport system that provided an interface between the Chemrec™ gasification process and the GTI suite of on-line analyzers.

Figure 27. Sample distribution plumbing and diluter prior to insulation.

Figure 28. Close up of sample distribution plumbing and DCU prior to insulation.

As shown in Figure 26, 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 29. The GC/MSD/FID/SCD system is shown installed in the building in Figure 30. 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 31.

A selection of the data obtained with the SRS QMS300 Mass Spectrometer that quantify the major components of the syngas are presented in Figures 32 and 33. These data show the quick response of the on-line sampling approach to changes in gasifier operation.

Figure 29. Climate-controlled building housing the GC/MSD/FID/SCD and the μ GC.

Figure 30. The Wasson-ECE GC/MSD/FID/SCD system.

Figure 31. Preliminary installation of the SRS Mass Spectrometer at New Bern.

Figure 32. Composition of syngas produced on June 23, 2005 by the ChemrecTM black liquor gasifier as measured from compositional data obtained from the SRS QMS300 Mass Spectrometer.

Figure 33. 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.

Biomass Gasification Testing at GTI's Flex-Fuel Test Facility – In the fall of 2005, GTI augmented its efforts under Cooperative Agreements DE-FC36-03GO13175 and DE-FC36-02GO12024 with a concurrent evaluation of pelletized wood-fueled gasification and catalyst performance investigated at the GTI FFTF under DOE Cooperative Agreement DE-FG36-04GO14314. In this intensive field evaluation of our updated approach for thermochemical process sampling, we developed and used a second-generation version of our sample conditioning approach, the Sample Expansion and Distribution Interface (SEDI). Some of the main objectives of our field evaluation were the depressurization, spiking and calibration, dilution, and sample distribution capabilities of the SEDI. This field effort also evaluated our redesigned sample transport lines, heat tracing, and syngas sample distribution manifolds. The test verified the effectiveness of our sampling approach for the challenging task of continuous syngas sampling and analysis from biomass-fueled gasification process streams.

During this biomass testing, the gas sampling system shown schematically in Figure 34 allowed for extraction of samples from two sampling locations in the FFTF process stream, heated transport of syngas sample streams to distribution manifolds, and subsequent direction of a selected sample syngas stream to our suite of analytical instruments for near real-time, on-line analyses. The major components of the interface system are identified in the drawing key in Figure 34. In addition to the delivery of sampled syngas streams to the analysis suite, it was also necessary that the sample extraction/transport system address issues of safety, protection of sensitive equipment, thermal control of specific heated zones, syngas sample selection, calibration and spiking capabilities, on-line system documentation and control, and the ultimate disposal of a variety of sampled syngas streams. Much of the apparent complexity of the overall system relates to rigorous constraints introduced by these issues. Consequently, the successful performance of the system during these tests marked a significant milestone verifying the syngas sampling approach developed in this project.

The analytical suite we used in these tests included an Industrial Machine and Control Corporation (IMACC) Fourier-transform infrared spectrometer (FT-IR), a Stanford Research Systems QMS300 Mass Spectrometer (SRS 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 Agilent 5890 gas chromatograph with flame photometric detector (GC/FPD), and a Varian micro gas chromatograph with thermal conductivity detector (μ GC). These instruments, and the systems we developed to extract and transport continuous streams to them for analysis, reliably met the majority of the specific objectives of these tests. (Additional descriptions of these analyzers can be found in the Final Report issued under DOE Cooperative Agreement DE-FG36-02GO12024.)

The sampling system was designed and constructed to provide interfaces between the SEDIs and the analyzers used to characterize the syngas streams. For each of the two sampling

locations, G8 and G13, the overall system included sample trains that obtained a continuous syngas stream from the process and passed it into the heated and insulated SEDI at that location. For the G8 sample train that was located upstream of the FFTF high-temperature particulate filter, a small prefilter was installed upstream of the SEDI. This prefilter, an isolation valve (V4), and the SEDI at G8 are shown in Figure 35. The SEDI at G13 and its interface with the process is shown in Figure 36. Each SEDI split its single inlet pressurized (~280 psig) syngas sample stream into two depressurized (~1 psig) streams at its outlet, one of which was diluted inside the SEDI with metered nitrogen. The diluted streams from G8 and G13 were heat-traced for transport at over 500 °F to a heated analytical manifold (Figures 37 and 38), and the undiluted streams from G8 and G13 were delivered through heated transport lines (around 800 °F) to the SRS Mass Spectrometer manifold (Figure 39). Because the SRS MS depressurizes its inlet sample stream to a near vacuum in its capillary tubing, it was able to sample from an hot undiluted syngas stream. (The absolute pressure of the syngas stream at the inlet to the mass spectrometer capillary tubing needs to be approximately one atmosphere.) With the high temperatures required to prevent condensation in the undiluted sample streams, it was beneficial to limit the distance these undiluted sample streams needed to be transported. Therefore, the SRS MS was located in a purged NEMA box in the FFTF process area (Figure 40). At each of these manifolds, an arrangement of valves was installed to allow syngas to be sent to the analyzer(s) from either of the two sample locations. These two manifolds were built with the capability to add sample streams from two additional locations, probably G14 and G19 in the FFTF process stream, to the overall sampling and analysis system.

The system design also included a versatile purge/spike manifold for delivery of high pressure nitrogen, low pressure nitrogen, or calibration gases to each SEDI (and for G8, the prefilter upstream of the SEDI). The flows of these gases were metered through mass flow controllers. This syngas sample conditioning and delivery system also incorporated vents for waste syngas streams at various points.

An extensive data acquisition and control system based on Labview™ hardware and in-house software was developed by GTI for these tests. Pressures and temperatures were monitored throughout the system, with controls for the numerous heaters in the system governed by appropriately placed thermocouples. This software controlled most of the heaters in the system, as well as the two actuated valves and two solenoid valves (V4, V8, V51 and V52). The system also logged temperatures, pressures, heater settings, and solenoid and actuated valve positions. A purged NEMA box (Figure 41) was installed in the process area to house the thermocouple interfaces, power relays, and controls for the heaters and actuated valves installed throughout the extraction/transport system. Example display screens showing the interfaces the software provided to the GTI system operators are shown in Figures 42 - 44.

Figure 35. G8 sampling train, including the prefilter, actuated valve (V4), and SEDI.

Figure 36. G13 sampling train, including the process isolation valve (V7), actuated valve (V8), and SEDI.

Figure 37. Analytical suite manifold shown prior to installation. This manifold was used to select and distribute diluted syngas sample streams to the FT-IR and the GC/MS.

Figure 38. Analytical suite manifold shown following installation in the custom oven built in place around the manifold in the utility room housing the manifold, the FT-IR, and the GC/MS. This oven was used to keep the manifold at about 450 °F.

Figure 39. Mass Spectrometer manifold (shown prior to insulation) used to select and distribute hot, undiluted syngas sample streams to the SRS Mass Spectrometer and to a port for impinger measurements.

Figure 40. NEMA box housing the SRS Mass Spectrometer in the process area just underneath the insulated, heat traced mass spectrometer manifold.

Figure 41. NEMA box housing the heater controls and thermocouple interfaces to the data acquisition and control system.

Figure 42. Data Acquisition control screen used to monitor temperatures in the extraction/transport system.

Figure 43. Data Acquisition control screen used to monitor temperatures and control heaters in the extraction/transport system.

Figure 44. Data Acquisition control screen used to monitor pressures in the extraction / transport system. The display shown in this figure covers a procedure that was used to periodically clean the prefilter upstream of the G8 SEDI.

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.

Before the FFTF 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. The G13 SEDI produced an undiluted syngas stream sent to the Mass Spectrometer manifold for analysis until filter element failures in the FFTF 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 analyzed were drawn from the G8 location. The successful operation of the G8 SEDI, and the blinding of the small internal filter in the G13 SEDI, suggest the prudent system design should include a prefilter upstream of all SEDIs, like the one installed upstream of the G8 SEDI, to protect the sample train from process upsets and/or filter failures.

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. 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.

Figures 45 and 46 present some representative data from the biomass gasification testing conducted at GTI's Flex-Fuel Test Facility. The Final Report issued under Cooperative Agreement DE-FG36-02GO12024 includes a more extensive presentation and discussion of the analytical data measured in these tests.

Figure 45. 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 46. 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.

Calibration and Verification Measurements at the FFTF – In March 2006, we performed a series of system component inspections, and calibration and verification procedures relevant to validation of measurement approaches and hardware utilized in the October/November 2005 biomass gasification testing at the FFTF. These procedures were used to verify the analytical data from the October and November 2005 test periods.

Five cylinders of compressed gases were used as calibration sources in combination with an injection manifold that allowed compressed nitrogen, or any one of these five calibration gases, to be injected into the G8 prefilter and/or the G8 purge/spike line at high-pressure (~200 – 210 psig). This required the addition of a direct injection line leading into the G8 prefilter. We also added the capability to preheat the gas injected into the G8 prefilter with the same type preheating components already installed on the G8 purge/spike line. The five calibration gas sources used are detailed in Table 6. In addition to the components of these gases identified in Table 6, the balance of each of these gases was N₂.

Table 6. Compressed Gases used in Calibration/Verification Tests

source cylinder	component gas(es)	
	as labeled when received	GTI analysis results
simulated major syngas mixture	10.04 % CO ₂ , 4.886 % H ₂ , 4.970 % CH ₄ , 4.910 % CO	10.04 % CO ₂ , 4.886 % H ₂ , 4.97 % CH ₄ , 4.91 % CO
Btex hydrocarbon mixture	305 ppm benzene, 20 ppm toluene, 10 ppm m-xylene	268 ppm benzene, 18.5 ppm toluene, 4.8 ppm m-xylene
H ₂ S/COS mixture	46.6 ppm H ₂ S, 1.09 ppm COS	47.6 ppm H ₂ S, 1.17 ppm COS
HCl	208 ppm HCl	data not available
NH ₃	549 ppm NH ₃	606 ppm

One of the key objectives for the measurements performed at the Flex-Fuel Test Facility in March 2006 was the verification of the ability of the extraction/transport system to efficiently convey various components of the syngas from the point of extraction to the various analyzers. To address this objective direct measurements were made of source cylinder gas with our on-line analyzers (SRS Mass Spectrometer and the Agilent GC/MS) or with silica-coated bomb samples followed by analyses in GTI's analytical laboratory. These measurements were compared with corresponding measurements of gases injected into the G8 prefilter and/or SEDI and transported for analyses to the two sample distribution manifolds. In other words, these validation tests were conducted identically to normal on-line monitoring except surrogate calibration gases from cylinders replaced syngas sample streams. Undiluted surrogate sample gas was transported from the SEDI to the SRS Mass Spectrometer manifold located in the

process area, and diluted surrogate sample gas was transported from the SEDI to the analytical manifold located in the utility room that housed the GC/MS and the FT-IR during the October/November 2005 tests.

Sample Bombs – Batch gas samples were obtained with sample bombs during the calibration and verification testing for subsequent laboratory analysis. Sample bombs were filled directly at the source cylinders, as well as at the Mass Spectrometer manifold. The analyses of these gas samples are included in Table 7. Comparisons of gas analyses for samples taken directly from the cylinders with those taken from the undiluted transport line at the Mass Spectrometer manifold indicate high transport efficiency for H₂S, COS, benzene, toluene, and m-xylene.

Table 7. Analyses of Gas Samples Obtained with Sample Bombs*

injected gas	location	~ time after injection begun	analysis, ppm		
			benzene	toluene	m-xylene
Btex	CYL	NA	271	17.3	3.2
Btex	MSM	1 minute	262	15.6	2.5
Btex	MSM	7 minutes	255	14.9	2.3
Btex	MSM	12 minutes	258	15.8	2.9
Btex	MSM	22 minutes	265	17.1	3.5
Btex	MSM	32 minutes	265	16.8	3.4
Btex	MSM	52 minutes	261	16.8	3.4
Btex	MSM	72 minutes	262	17.1	3.6
Btex	MSM	92 minutes	266	16.6	3.1

injected gas	location	~ time after injection begun	analysis, ppm	
			H ₂ S	COS
H ₂ S, COS	CYL	NA	37.6	1.12
H ₂ S, COS	MSM	1 minute	BDL	0.96
H ₂ S, COS	MSM	7 minutes	BDL	0.07
H ₂ S, COS	MSM	14 minutes	12.7	1.06
H ₂ S, COS	MSM	24 minutes	1.46	1.02
H ₂ S, COS	MSM	34 minutes	0.3	1.01
H ₂ S, COS	MSM	44 minutes	43.5	1.13
H ₂ S, COS	MSM	65 minutes	44.8	1.15
H ₂ S, COS	MSM	85 minutes	41.8	1.11
H ₂ S, COS	MSM	105 minutes	42.9	1.11
H ₂ S, COS	MSM	165 minutes	43.1	1.11

injected gas	location	~ time after injection begun	analysis, ppm	
			H ₂ S	COS
N ₂ (after H ₂ S, COS)**	MSM	1 minute	BDL	0.15
N ₂ (after H ₂ S, COS)**	MSM	6 minutes	BDL	0.25
N ₂ (after H ₂ S, COS)**	MSM	15 minutes	BDL	0.16

injected gas	location	CO, %	H ₂ , %	CH ₄ , %	CO ₂ , %
simulated fuel gas	CYL	4.96	5.1	5.35	10.1

*samples were obtained after gases had been injected into the G8 SEDI through the purge/spike line

** injected immediately after the injection of the H₂S/COS mixture was discontinued

MSM = bomb sample obtained at Mass Spectrometer manifold

CYL = bomb sample obtained at the source gas cylinder

DBL = below detection limit

The data in Table 7 suggest the components of the Btex gas were transported efficiently (around 96 to 98 %) through the undiluted transport line leading to the Mass Spectrometer manifold. The bomb data indicate that the time required to passivate the lines with the Btex components is minimal.

Compared with the concentration values of sulfur compounds in the source cylinder provided by the gas supplier (47.6 ppm H₂S and 1.17 COS), the bomb data suggest 90 to 95 % transport efficiency through the lines transporting the undiluted syngas to, and through the mass spectrometer manifold. These system components were maintained at about 800 °F. Coupled with the initial indications regarding the possible losses of H₂S through the diluted syngas transport lines (maintained at about 450 °F), our data may indicate that efficient transport of H₂S through the sample extraction and transport system is significantly improved by increasing the temperature of the system. The bomb data indicate that a short time (from 0 to 15 minutes) may have been required to passivate the transport lines with COS, and that about 44 minutes may have been necessary to passivate the lines with H₂S. Once the injection of H₂S and COS was discontinued, recovery of the lines (depassivation) was nearly immediate for the H₂S, but probably was not complete for the COS after 15 minutes of nitrogen injection.

The final row of data presented in Table 7 indicate that the bomb sampling method and analysis agreed very well with the direct laboratory analysis of the simulated fuel gas presented in Table 6.

SRS Mass Spectrometer – The SRS mass spectrometer (SRS MS) was used in these calibration/verification tests to determine CO₂, H₂, CH₄, and CO. The SRS MS sampled directly from two source cylinders (the simulated syngas mixture and the Btex hydrocarbon mixture), and from the Mass Spectrometer Manifold. The SRS MS results, which agreed with the bomb sample analyses data discussed above, show high transport efficiency for the gases in Table 6 from the G8 sample train through the heated MS transport lines and on through the Mass Spectrometer manifold.

Agilent GC/MS – The Agilent GC/MS was used for assessments of the transport efficiency of H₂S, COS, CH₄, and the Btex calibration gas components (benzene, toluene, m-xylene) through the diluted sample transport lines. Like the measurements that were performed with the SRS MS, samples were taken directly at the source cylinders, and at the diluted gas distribution manifold (after injection into the G8 prefilter

and/or the SEDI, and then diluted and transported through the rest of the heated line leading from the G8 SEDI to the analytical manifold in the second floor utility room).

Final analysis of the results for transport efficiency of benzene, toluene, and m-xylene suggest no losses within measurement accuracy. All transports efficiencies were in the range 95-108%. Initial (tentative) results suggested loss of benzene but updated calibration just after these test in March 2006 demonstrated no (or very low loss). Results based on the original GC/MS calibration for H₂S and COS, combined with the sample gas dilution factor, are substantially higher than expected. Results for H₂S based on calibrations just after these test in March indicate 40 % loss in transport while results for COS are 15 % high. These results, when considered along with the excellent transport efficiencies measured with sample bombs for the undiluted sample transport lines, suggests that maintenance of high gas temperature (800 °F in these tests) reduces loss of H₂S that was observed at the lower temperature (450 °F) during transport. The observed transport efficiency at the lower temperature was continuing to rise after 2 hours, 45 minutes and had a 2 %/hr rate of increase.

Analysis of the data from the GC/MS involves concern with linearity because the transported “sample” gas is diluted by a factor of about 10; i.e., cylinder gas concentrations were a factor of 10 higher than the diluted/transported cylinder gas. Measurements were performed with multiple calibration gases with varying concentration in order to obtain a response function versus concentration of H₂S. Indications from the transport efficiency measurements obtained with the GC/MS are that there may be significant losses of H₂S and benzene through the prefilter, G8 SEDI, and the transport lines leading to the diluted gas distribution manifold. GC/MS results for CH₄ viewed during the testing indicated excellent transport efficiency.

IMAAC FT-IR – During the calibration and verification tests conducted in March 2006, the IMAAC FT-IR sampled diluted calibration gases from the diluted-gas manifold, as in normal syngas process monitoring, and it was also moved during the latter portion of the verification tests to sample HCl and NH₃ calibration gases from the Mass Spectrometer manifold located in the Flex-Fuel Test Facility process area.. Of the calibration gases available for these tests, the FT-IR was used in this program to monitor CO₂, CO, CH₄, HCl, and NH₃. Responses of the FT-IR to CO₂ and CH₄ were within 5 % of the expected levels for perfect transport while the response to CO was 20 % high. Improvement of these results would be expected with refinements of the FT-IR spectral analysis procedure. The analysis method was developed originally for undiluted syngas so linearity corrections should be modified for these lower levels reaching the instrument when utilizing dilution. Similarly the current method we used during the syngas testing uses a line shift correction procedure based on water spectra

which are not present when injecting calibration gases. For improved accuracy, a line shift correction based on one of these calibration gases should be implemented.

Recent analysis indicates that reduction of optical absorbance levels would significantly improve the accuracy for the major constituent gases, present at relatively high concentrations. This could be accomplished by decreasing the optical path length or increasing dilution factor. However, these changes would also reduce the accuracy of compounds present at levels that produce low absorbance levels. The first option cannot be accomplished during testing but the latter can, and thus offers some flexibility to optimize FT-IR data analysis while on-line to optimize tradeoffs to be appropriate to the priorities for a given set of measurements.

Responses of the FT-IR to HCl and NH₃ were within 5 % of the expected levels based on the cylinder gas concentrations from the supplier. As indicated in Table 6, analysis results for the NH₃ cylinder were 10% higher than supplier values. Analysis of the HCl cylinder gas was not available.

System Component Inspections – As discussed above, problems with the operation of the G13 SEDI, and filter element failures in the Flex-Fuel Test Facility's high-temperature, high-pressure process syngas filter vessel located upstream of the G13 sampling location, resulted in all analyzer and batch measurements made during the October/November 2005 tests being performed on syngas extracted from the G8 location. As part of the system inspections conducted in March 2006, the G13 SEDI was removed, disassembled, and inspected. This inspection revealed that two of the threaded connections sealed with Grafoil tape failed to completely seal. Based on these observations, we have concluded that future designs of high-temperature, high-pressure sample extraction system designs should avoid the use of high-temperature threaded connections. (Similar inspections of the G8 SEDI, conducted at the conclusion of the calibration tests discussed in this report, indicated that the threaded connections in that unit remained intact throughout the testing period.) The detailed inspections of the G13 SEDI indicated, that as expected, the failure and breaching of the FFTF candle filter elements during the October/November 2005 test resulted in entrained char entering the body of the SEDI and blinding the small internal filter included in the G13 SEDI.

As part of our system component inspections, we performed procedures to assess the effectiveness of the SEDI, and the conventional heat-traced and novel heated transport lines (discussed above) for preventing deposits, condensation, or plugging of these lines. Visual inspections indicated that no significant condensed hydrocarbon deposits were formed in the various transport lines. Following our verification measurements with the five gases identified in Table 6, we washed out the transport lines with

tetrachloroethylene (also called perchloroethylene) and collected the rinses for a quantitative assessment of any dissolved solids. Three separate sections of the extraction/transport system were washed with perchloroethylene: 1) the heated lines that transported the undiluted syngas to the mass spectrometer manifold, 2) the heated mass spectrometer manifold, and 3) the heated lines that transported the diluted syngas to the analytical manifold in the second floor utility room. These rinses, which visually appeared quite clean, were analyzed for total dissolved solids (Table 8).

Table 8. Total Dissolved Solids Washed from Portions of the Sample Transport Lines

system component	dissolved solids, g	total tar transported through system component, g (est) ¹	transport efficiency, %
1 line to MS manifold	0.11	100 to 315	99.89 to 99.97
2 MS manifold	0.03	100 to 315	99.97 to 99.99
3 line to analytical manifold	0.48	unknown ²	not determined

1 estimates based on the range of condensable materials determined by bomb and impinger samples

2 total syngas tars passing through this line have not been estimated because the service history of this line includes too broad an array of test periods, flow rates, and episodes of particulate contamination and partial line cleaning/replacement. (The total dissolved solids in the diluted transport line are presented to illustrate the general cleanliness of this line after extensive service and the effectiveness of its transport during the biomass testing.)

The high transport efficiencies of the system components (system components 1 and 2 above) agree with the visual observations of the components. Although small amounts of solids were washed from these system components, these solids were not analyzed for composition, and may not represent condensed material. It is clear that, for all intents and purposes, the transport lines remained clean and clear of any significant deposits of condensed compounds.

Inspection of accumulated deposits in the FT-IR sample cell – Another indication of the effectiveness of the overall approach we have used for sample transport (including depressurization, dilution, and heated transport lines leading to the analyzers) was observed in the condition of the FT-IR optical components following the calibration and verification tests. After the tests of this reporting period were completed, the cylindrical sample cell of the FT-IR was disassembled to evaluate the amount of deposition on optical surfaces and to be cleaned if needed. This maintenance was last performed almost two years earlier. In the intervening time syngas samples were passed through the cell in eight tests for periods averaging 3-4 days each. During fourteen of these days the sampled syngas was produced from coal in which the sample pressure was

reduced from 300 psig to ambient and the temperature was maintained above 165°C. During ten of these days of operation the sampled syngas was produced from black liquor at 7 psig followed by a venturi water scrubber at 100°C. During three of these days sampled syngas was produced from wood in which the sample pressure was reduced from 250 psig followed by dilution by a factor of about 10 to 20, and the temperature maintained above 165 °C.

Figure 47 presents a photograph of the FT-IR sample cell optics. Nonmetal surfaces were found to be absolutely clean while metal surfaces show deposits that appear to be condensed hydrocarbons. Evidently maintaining the cell's tubular wall at 165°C and sample gas entering it at higher temperatures prevented condensation on the optical surfaces but the relatively high thermal conductivity of the cells ends (that are not heated) allowed those surfaces to cool enough to cause condensation of hydrocarbons. There is no reason to believe these deposits affected measurement results since they are completely out of the beam path, and because their total mass is a very small fraction of that in the sample gas.

Figure 47. Sample cell optics of the FT-IR including the beam inlet and outlet ZnSe windows (to the right and left respectively) and the gold coated field mirror (at the center).

Design and Protocol for Monitoring Gaseous Species in Thermochemical Processes – A special, comprehensive topical report was prepared under Cooperative Agreement DE-FC36-03GO13175 and submitted to DOE under separate cover that summarized the various advances made in sampling technology under this project and its companion Cooperative Agreement DE-FG36-02GO12024. The topical report included a review of existing approaches for sampling thermochemical processes and described the impetus and approach we applied to improve those sampling technologies. The report reviewed the various analyzer technologies we used in the field to obtain meaningful measurements at these harsh processes conditions. We described in detail the various sampling interfaces we investigated and tested under this Cooperative Agreement. Our experiences and selected data from field demonstrations of our approach were presented, and the report concluded with recommendations concerning custom design issues for specific processes and platforms, including the integration of sampling into initial process designs, sampling interface locations, installation factors, and safety issues.

Patent Applications

Applications for three patents have been made with the USPTO under this Cooperative Agreement:

GTI 1580 (DOE S 107,848) “Method and Apparatus for Maintaining Multi-Component Sample Gas Constituents in Vapor Phase During Sample Extraction and Cooling,” patent applied for April 22, 2005.

GTI 1658 (DOE S 110,662) “Method and Apparatus for Maintaining Condensable Constituents of a Gas in a Vapor Phase During Sample Transport,” patent applied for October 6, 2006.

GTI 1666 (DOE S 112,237) “Apparatus and Method for Maintaining Multi-Component Sample Gas Constituents in Vapor Phase During Sample Extraction and Cooling,” patent applied for February 28, 2007.

Publications and Presentations

A presentation was made in September 2005 to DOE and Weyerhaeuser on the results of the characterization of the ChemrecTM black liquor gasifier at New Bern, North Carolina.

A paper was submitted, and a presentation was made entitled “Enabling the Real-Time Measurement of Gas Concentration and Composition for High-Temperature and High-Pressure Industrial Processes” was made at the 6th Annual International Symposium & Exhibition: Gas Cleaning at High Temperatures held in Osaka, Japan on October 20-22, 2005.

A paper was submitted, and a presentation was made entitled “The Real-Time Measurement of Gas Concentration and Composition for High-Temperature and High-Pressure Industrial Processes” was made at the 14th European Biomass Conference and Exhibition: Biomass for Energy, Industry, and Climate Protection held in Paris, France on October 17-21, 2005.

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