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AFR

FINAL TECHNICAL REPORT

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Golden, CO**

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In-Situ FT-IR Monitoring of a Black Liquor Recovery Boiler

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In-Situ FT-IR Monitoring of a Black Liquor Recovery Boiler

Abstract

This project developed and tested advanced Fourier transform infrared (FT-IR) instruments for process monitoring of black liquor recovery boilers. The state-of-the-art FT-IR instruments successfully operated in the harsh environment of a black liquor recovery boiler and provided a wealth of real-time process information. Concentrations of **multiple gas species** were simultaneously monitored in-situ across the combustion flow of the boiler and extractively at the stack. Sensitivity to changes of **particulate fume and carryover levels** in the process flow were also demonstrated. Boiler set-up and operation is a complex balance of conditions that influence the chemical and physical processes in the combustion flow. Operating parameters include black liquor flow rate, liquor temperature, nozzle pressure, primary air, secondary air, tertiary air, boiler excess oxygen and others. The in-process information provided by the FT-IR monitors can be used as a boiler control tool since species indicative of combustion efficiency (carbon monoxide, methane) and pollutant emissions (sulfur dioxide, hydrochloric acid and fume) were monitored in real-time and observed to fluctuate as operating conditions were varied. A high priority need of the U.S. industrial boiler market is improved measurement and control technology. The sensor technology demonstrated in this project is applicable to the need of industry.

Appendix E of this Final Report presents a report of our 1998 field test at a black liquor recovery boiler located at a mill in the Southeast U.S. It is suggested that Appendix E be reviewed before proceeding past this abstract. The Executive Summary of Appendix E includes a section on "General Advantages of FT-IR Technology."

Prior to this project Advanced Fuel Research, Inc. (AFR) had developed a Fourier Transform Infrared (FT-IR) emission and transmission method for in-situ diagnostics of furnaces and boilers. The method provided information on gases (concentration and temperature), particles (size, concentration, and temperature), and furnace walls (temperature). Feasibility tests have been performed on coal burning utility boilers and black liquor recovery boilers with good success. Spatial variations in temperature and concentration of species in flames had also been successfully determined in the laboratory through tomographical conversion of measurements taken with multiple lines-of-sight. In addition to the development of the measurement techniques, AFR had invented a vibration immune spectrometer that can operate in harsh industrial environments. A spin-off company, On-Line Technologies (On-Line), was formed to develop and manufacture the spectrometer. This project, in collaboration with On-Line, was to further develop and test a rugged, commercial FT-IR based sensor that would be specifically designed to operate in black liquor recovery boilers. In addition, the project would develop control strategies for improving boiler performance and emission levels.

The result of this project is a new sensor for in-situ and extractive diagnostics for black liquor recovery boilers and other combustion devices. The FT-IR developed specifically for process and environmental monitoring applications is very rugged and thermally stable. A first generation prototype for this project was field tested at a black liquor recovery boiler in Sweden in late 1994. In-situ monitoring through the 30' line-of-sight of combustion at the bullnose level resulted in concentration trends as a function of time for carbon monoxide (CO), carbon dioxide (CO₂), water vapor (H₂O), and fume. The project culminated in late 1998 when three second generation prototypes for this project were simultaneously installed at a black liquor recovery boiler in the southeast U.S. Two in-situ monitors (6th floor at the bullnose and 8th floor in front of the superheater) quantitatively determined concentrations through the combustion flow for CO, CO₂, H₂O, and hydrochloric acid (HCl). All gases were measured simultaneously with data continuously collected and averaged over one minute time intervals. In addition, relative measurements of fume and carryover were obtained in the boiler. The third process monitor was located at the effluent

stack of the boiler where stack gas was continuously extracted and sampled in the flow cell of this monitor. For these stack gas measurements, data were continuously collected and averaged over two minute intervals. Simultaneous and quantitative process measurements of CO₂, CO, HCl, H₂O, sulfur dioxide (SO₂), nitric oxide (NO), nitrous oxide (NO₂), and methane (CH₄) were obtained.

During both the 1994 and 1998 field tests, boiler operating conditions were varied and sensitivity of the FT-IR monitors was demonstrated. The FT-IR instrumentation provides on-line monitoring of numerous boiler species concentrations that are directly influenced by boiler operating conditions. The instrumentation is a valuable tool for studying species indicative of combustion efficiency (CO, CH₄) as well as the relationships between reacting boiler species such as SO₂, HCl and fume. The FT-IR data provide the information necessary for recovery boiler operators to balance operating conditions for boiler control with high combustion efficiency and minimal pollutant emissions.

Acknowledgements

Acknowledgements go to the following companies for their substantial participation in this project. Their participation and resultant financial expenditures point to the critical need for advanced sensors in industrial process monitoring.

- A Paper Mill in the Southeast United States
- Measurement Technologies AB (Sweden)
- Södra Cell AB (Sweden)

Gratitude especially to the Engineers and Boiler Operators of the mill in the Southeast U.S. for arranging, participating, and supplying valuable guidance during the final field test of this project.

Gratitude also to

- Rutger Johansson (MTech AB)
- Torbjörn Johansson (MTech AB)

for arranging, participating and supplying valuable guidance during the first field test of this project at the Mörrum pulp mill of Södra Cell AB in Sweden.

Thanks also to Bob Bareiss of Bareiss Associates (Florida) for recommending several contacts in the forest products industry to call to explore the possibility of field testing. This led to the collaboration for the final field test of the project.

Our subcontractor, On-Line Technologies, Inc. (East Hartford, CT), is acknowledged for their work to provide state-of-the-art FT-IR spectrometer systems to the project. Much appreciation goes to

- Martin Spartz
- Carl Brouillette
- Tony Bonanno
- Martin Carangelo
- Robert Carangelo
- David Wilson

Finally, thanks goes to the DOE and Project Officers Ken Johnson and Doug Hooker at the DOE's Golden Field Office for support of this project.

In-Situ FT-IR Monitoring of a Black Liquor Recovery Boiler

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In-Situ FT-IR Monitoring of a Black Liquor Recovery Boiler

Project Description (verbatim from the Management Plan of Nov. 29, 1993)

The Problem

The safe efficient and environmentally acceptable operation of black-liquor recovery boilers requires careful control of the operating parameters. The black-liquor must be introduced to the furnace in such a way that the liquor burns with a minimum of carryover without allowing water to reach the smelt bed. Fume formation must be minimized and levels of SO₂, NO_x, HCl and CO in the flue gas maintained below required limits. Such control could be more efficiently achieved with better understanding of the chemical and physical processes taking place in the boiler and with better in-situ sensors to monitor the boiler.

Better understanding, monitoring and control of the boiler could lead to improvements in many areas: 1) improved energy efficiency by reducing soot blowing, by higher solids loading in the black-liquor and other improvements; 2) improved strategies to reduce harmful emissions (sulfur species, NO_x, particles, unburned combustibles in flue gases, and unburned combustibles in the smelt); 3) fewer accidents and unwanted plant shutdowns; 4) increased tolerance to feedstock variations; 5) increased throughput. Thus, better control can improve performance safety and compliance with regulations. These improvements could affect existing as well as advanced technology, leading to more competitive American technology in both the paper and boiler industries.

The Opportunity

Advanced Fuel Research, Inc. (AFR) has successfully performed the first in-situ diagnostics within an operating black-liquor recovery boiler using Fourier Transform Infrared (FT-IR) emission and transmission (E/T) spectroscopy. The FT-IR E/T method was developed and patented by AFR. The FT-IR spectra yield information on the gases (concentration and temperature), particles (size, concentration, and temperature), and walls (temperature). In a more recent field test, AFR demonstrated the FT-IR for in-situ measurements of gas species at the 1-10 ppm level in the stack of a coal burning utility boiler. AFR has also successfully demonstrated for the first time, the use of FT-IR tomography to convert multiple lines-of-sight into spatially resolved data and the measurement of emissivity, temperature, and physical properties of surfaces. The application of this technology for on-line monitoring of recovery boilers could lead to: a) better understanding of the processes occurring in the boiler; b) technology for on-line monitoring and control; and c) data for the development and validation of recovery boiler models. *These benefits can be obtained using an advanced vibration immune instrument currently under development at AFR.*

The Project

This program would be performed in two phases. The primary objective of Phase I would be to demonstrate a sensor for fume monitoring at the furnace outlet. Additional objectives would be to determine other furnace characteristics which could be measured and to devise control strategies based on the measured characteristics. In addition, the requirements for a commercial instrument would be assessed. For Phase I a single FT-IR monitor will be prepared and installed for automated analysis with remote data acquisition and instrument control. Assessments would be made of additional data needs and steps taken to acquire these data. A six month field trial will test the instrument's use for both control and compliance with environmental laws.

The second phase of the program would have as its objective, the determination of additional furnace characteristics and their use in control strategies. Emphasis would be placed on using multiple lines-of-sight to measure spatial variations of parameters within the furnace. In addition, data would be obtained for model validation.

This will be a cost shared program in which the costs of developing the instrumentation hardware, and software will be supported with funds from private investments, and other government contracts. In addition, some of the field test costs will be underwritten by the host organization where the field testing will take place.

Overall Project Objectives

To develop an FT-IR sensor and control strategy to improve the performance of black liquor recovery boilers and to obtain multiple line-of-sight data to assess spatial variations within the boiler for model development and validation. The program would be carried out over 3 years, 8 months in two phases.

Project Results

Appendices A through G are included in this final report. These contain the following documents:

Appendix A: A document generated for a DOE review of the project (circa Sept./Oct. of 1994) which presents early results of the project to develop a new in-situ sensor for Black Liquor Recovery Boilers. This paper was presented at the 1994 DOE/Industry Advanced Sensors Technology Conference in Gaithersburg, MD. The document presents a survey of sensor needs, information on the new FT-IR spectrometer and gas analysis software, and presents the schedule and boiler geometry for the field test planned in Sweden (Appendix C).

Appendix B: Proceedings reprint of the SPIE meeting held in McLean, Virginia (7-10 November 1994). This reprint presents improvements in the FT-IR hardware that will allow improvements in detection sensitivity, scan speed, and the ability to operate in harsh environments. This DOE project was credited in the acknowledgement section for contributing to these improvements.

Appendix C: Report which presents the field test results at the Black Liquor Recovery Boiler at the Mörrum Pulp Mill (Mörrum, Sweden): Nov. 28, 1994 – Dec. 8, 1994.

Appendix D: A paper presented at the 1995 International Incineration Conference (May 8-12, 1995), Seattle, Washington. This paper describes the advanced FT-IR instrument and presents results of the 1994 field test (Appendix C) at the recovery boiler in Sweden.

Appendix E: Report which presents the field test results at the Black Liquor Recovery Boiler of a mill in the Southeast U.S.: Sep. 20 – Oct. 2, 1998.

Appendix F: AFR transparency presentation of field test results to the mill in the Southeast U.S., including photographs of the FT-IR installations: April 20, 1999.

Appendix G: FT-IR Product Brochures

Appendices A-F present the documents in chronological order through the duration of the project. These documents will be referred to in below sections as each task of this project is described. The project was

carried out in two phases over the 5 years, 5 months under thirteen tasks. The described objective for each task is verbatim from the Management Plan of Nov. 29, 1993.

Task 1.1 - Management Plan

Objective

To provide a research plan detailing the work to be accomplished in Phase I. Phase II will also be generally laid out, and the correlation between Phase I and Phase II will be defined.

Work Performed

A management plan was prepared laying out the detailed steps for Phase I (Tasks 1.2 to 1.9) and a general layout for Phase II (Tasks 2.1, 2.2, 2.3, and 2.5; note – there was no task 2.4). This was submitted to DOE on November 29, 1993. This document had attached to it six publications of AFR's previous work in combustion diagnostics.

Task 1.2 - Determination of Sensor Applications and Requirements

Objective

To determine sensor requirements by discussions with industry experts and to write a set of specifications for the FT-IR sensor based on these requirements.

Work Performed

Two areas have been identified where the FT-IR can be beneficial in the monitoring and control of recovery boilers. These are: 1) continuous emissions monitoring (CEM) for environmental regulations – extractive or in-situ in the stack; and 2) in-situ monitoring within the furnace. The measurement requirements in each area are summarized on page 2 of Appendix A.

Task 1.3 - Instrument Design

Objective

To design a commercial quality FT-IR spectrometer which can achieve continuous unattended operation in the paper mill environment. The design will include all required ancillary equipment such as mounting systems, electronic interfaces between the instrument and typical paper mill monitoring and recording devices, etc.

Work Performed

The spectrometer design and its advanced components are described in detail in Appendices A, B, and C, and also in the product brochures of Appendix G. Continuous unattended operation and software is well demonstrated in the field test documents of Appendices C and E, where data were continuously collected.

This task was successful for spectrometer design and software goals. However, ancillary equipment such as permanent mounting systems and electronic interfaces with recording devices at boiler control rooms were not addressed to conclusion. During the field tests of the project, temporary mounting of FT-IR systems and data collection by AFR's computer systems were used. This approach put less burden and less interruptions on routine operations of the host companies of our field tests, which greatly facilitated

scheduling and AFR's access to boiler operations. An important incremental advance was made in the final field test of the project where data transmission cables were installed to extend from the 6th and 8th floor locations on the boiler to the boiler control room. We installed our desktop computer in the control room so operators could observe our on-line data stream.

Task 1.4 - Instrument Fabrication and Assembly

Objective

When progress in Task 1.3 has achieved the following goals: i) the instrument design is satisfactory, ii) the instrument can be manufactured at an acceptable cost and meet quality standards and operational needs, and iii) paper companies are likely to use the instrument, then three FT-IR spectrometers for field testing will be fabricated and assembled. The units will be made to commercial standards as defined in Task 1.3.

Work Performed

The products assembled for the field test in Sweden (Appendices A and C) were considered first generation prototypes. Three 2nd generation FT-IR spectrometers were ultimately assembled with the most recent improvements in hardware and software for the final field test in the U.S. (Appendix E). The 2nd generation spectrometers meet the specifications shown in the commercial product brochures of Appendix G. Photographs of the FT-IR systems at recovery boiler and stack locations are shown within the presentation of Appendix F.

Task 1.5 - Other Sensor Identification, Acquisition, and Modification

Objective

To identify and arrange for other sensors which are needed to validate or compliment the FT-IR sensor.

Work Performed

During the 1994 field test (Sweden), AFR was provided with native determinations of tertiary air volume and concentrations of CO, CO₂, and oxygen O₂. During the 1998 field test (U.S.), AFR was provided with native data traces for the following boiler operating parameters:

- Black liquor flow
- Boiler excess O₂
- Primary air flow
- Secondary air flow
- Primary duct pressure
- Secondary duct pressure
- Tertiary duct pressure
- Nozzle pressure
- Liquor temperature
- Liquor percent solids
- Steam flow
- Final steam temperature
- Differential pressure levels of the boiler and economizers

Task 1.6 – Field Tests

Objective

To field test the FT-IR instrument fabricated in Task 1.4 and compare the results to data from instruments selected in Task 1.5.

Work Performed

The 1994 field test (Sweden) is discussed in detail in Appendix C, and summarized in the paper of Appendix D that was presented at the 1995 International Incineration Conference.

Task 1.7 - Development of Control Strategies

Objective

To develop control strategies to improve the boiler performance based on the FT-IR data.

Work Performed

As commented on in the report of the 1994 Sweden field test (Appendix C), a control system designed to monitor the fundamental CO bands in the mid-IR spectrum ($\sim 5\mu\text{m}$ or 2000 cm^{-1}) would be significantly useful to the industry. However, with the project advances in both FT-IR hardware and software that were utilized in the 1998 U.S. field test (Appendix E), significantly more on-line information was obtained that would be important to a control strategy. The 1998 U.S. field test results demonstrated that the FT-IR instrumentation provides on-line monitoring of numerous boiler species concentrations that are directly influenced by boiler operating conditions. The instrumentation is a valuable tool for studying species indicative of combustion efficiency (CO, CH₄) as well as the relationships between reacting boiler species such as SO₂, HCl and fume. The FT-IR data provide the information necessary for recovery boiler operators to balance operating conditions to control boilers to perform at high combustion efficiency with minimum pollutant emissions. The expanse of data from the final field test (task 2.2) provides significant information that indicates that the FT-IR data can serve as part of control strategies for large boiler systems.

Task 1.8 - Black Liquor Reaction Chemistry Model Development

Objective

To provide data models and suggestions on black liquor reaction chemistry to other DOE sponsored projects.

Work Performed

Black liquor or Kraft recovery boilers are large and complex components of the forest products industry. There are a handful of Kraft recovery boiler manufacturers, and AFR has performed field tests on Babcock & Wilcox (B&W), and Götaverken boilers. The complexity of boilers leads to many controlling parameters. B&W (a McDermott company) continues to work on global models which can predict turbulent flow, combustion and heat transfer in Kraft recovery boilers. B&W has expressed interest in the results of our field test as a means of validation data for model predictions. As we install more FT-IR analyzers on boilers, significant information will be obtained to improve the models. This will lead to new operating strategies for improved efficiency with reduced emissions and greater safety.

In May of 1997, AFR visited McDermott Technology, Inc. in Alliance, Ohio. Dr. Christopher Verrill of McDermott has been working on predictive models for combustion and fume formation in black liquor recovery boilers, and the visit concluded with agreement that data from AFR's field tests could be used for model development and validation. AFR and McDermott have since been in contact. Unfortunately, a McDermott proposal submitted to the FY1999 AFPA/DOE was not selected for funding, but has been resubmitted for FY2000 consideration. AFR plans to re-visit McDermott now that the culminating 1998 field test of the project is complete (Appendix E).

Task 1.9 - Phase I Reporting

Objective

To report the results of Phase I.

Work Performed

The original 1993 plan called for AFR to submit a draft report describing results of Phase I to DOE for comment within 30 days of conclusion of Phase I. Three events actually occurred before proceeding to Phase II: 1) a DOE representative (Jerry Ledingham) visited AFR on Aug. 24, 1994; 2) Dr. Peter Solomon presented a paper (Appendix A, circa Sept./Oct. 1994) at the DOE/Industry Advanced Sensors Technology Conference in Gaithersburg, MD; and 3) Dr. Peter Solomon traveled to Washington D.C. to present Phase I results and Phase II plans to DOE. Present at this Feb. 1995 meeting were Jerry Ledingham, Doug Hooker, and Valri Wright.

Task 2.1 - Management Plan

Objective

To provide a research plan detailing the work to be accomplished in Phase II.

Work Performed

The Feb. 1995 presentation to DOE in Washington, DC included the Phase II research plan. In addition, Dr. Peter Solomon provided a presentation at the contract review "2020 Sensors and Controls Operating Task Group," (Feb. 27, 1997) in Washington, DC. Also, on March 31, 1997, a no-cost project extension request was submitted to the DOE's Golden Field Office. In this document, it was indicated most charges to the contract were temporarily ceased after June 1996 and that \$281,250 of funds from On-Line Technologies, Inc. were spent to complete the design and construction of prototypes, and design the production unit. Program funds were being conserved mainly to allow completion of the culminating field test of the project (Appendix E).

Task 2.2 - Field Tests for Continuous Monitoring along Multiple Paths

Objective

To field test several instruments simultaneously to determine parameter variations within the boiler and to obtain data for model validation.

Work Performed

Appendix E contains our report of the field test at the black liquor recovery boiler of a mill in the Southeast U.S. As described in the report, three advanced FT-IR monitors were installed. To accomplish and complete this field test, the following sequence of events occurred between AFR and the mill:

Sequence of Events

Dec. 17, 1997:	Initial AFR telephone conversation to the mill to explore the possibility of a field test at the recovery boiler.
April 23, 1998:	Initial meeting at the mill for AFR to present the technology.
July 1, 1998:	Planning meeting at the mill.
July 29, 1998:	Collaborative non-disclosure agreement in place.
August 4, 1998:	Second planning meeting at the mill.
Sept. 20-Oct 3, 1998:	Field test on the recovery boiler.
Jan. 8, 1999:	1 st draft of field test report submitted to the mill.
Feb. 25 1999:	AFR/mill teleconference pertaining to field test report.
March 25, 1999:	2 nd draft of field test report submitted to the mill.
April 5, 1999:	AFR/mill teleconference pertaining to field test report.
April 13, 1999:	Final field test report submitted to the mill.
April 20, 1999:	AFR presentation of field test results at the mill.

Over 70 e-mails were exchanged between AFR and the mill, as well as numerous telephone discussions and packets of information mailed in the sequence of events that led to this field test and resulting document shown in Appendix E which details the results. Photographs of the FT-IR systems at the recovery boiler and stack locations are shown within the presentation of Appendix F. The process monitors successfully monitored multiple gas concentrations at three locations in the mill's black liquor recovery boiler. Two monitors were installed for line-of-sight measurements through the boiler's 30 foot wide combustion flow at 6th and 8th floor locations. The third process monitor was located at the effluent stack of the boiler where stack gas was continuously extracted and sampled in the flow cell of this monitor.

Task 2.3 - Analysis of Multiple Path Data

Objective

To analyze the data from Task 2.2 to develop control strategies and to provide 3-D data for boiler model validation.

Work Performed

Analysis of the final field test data is presented in Appendix E. The results show that FT-IR instruments can function in the harsh environment of the recovery boiler and provide useful information. The data presented demonstrates that the advanced FT-IR process monitors provide substantial information that can be used to optimize boiler operation.

The original research plan called for in-situ boiler temperatures to be measured by FT-IR emission/transmission (E/T) spectroscopy in addition to species concentrations by absorption

spectroscopy. The technique for E/T spectroscopy is described in detail in Appendix E (specifically, see Attachment A within Appendix E). Literature citations are provided for previous field tests where AFR has applied the technique. It should be noted that previous field tests were performed with a then state-of-the-art commercially available FT-IR spectrometer that AFR purchased from a Canadian manufacturer (Bomen) and modified to provide E/T capabilities. AFR holds the patent on the FT-IR E/T method and system. At the most recent 1998 recovery boiler field test, AFR's proprietary advanced FT-IR spectrometers were used. These present state-of-the-art FT-IR systems provide the advances in hardware and software necessary for routine industrial process monitoring. These are manufactured by AFR's spin-off company, On-Line Technologies, Inc., but the capability for simultaneous E/T spectroscopy with these new spectrometers is still under development, so in-situ boiler temperature measurements were not obtained from the boiler during the 1998 field test.

Task 2.5 - Phase II Reporting

Objective

To report the results from Phase II.

Work Performed

This document with attached Appendices A-G completes this task.

Conclusions and Recommendations

Conclusions

The result of this project is a new prototype sensor for in-situ and extractive diagnostics for black liquor recovery boilers and other combustion systems. The FT-IR developed specifically for process and environmental monitoring applications is rugged and thermally stable. The FT-IR is now manufactured and marketed by AFR's spin-off company, On-Line Technologies, Inc., as shown in the product brochures of Appendix G.

This project has been successful in the development of advanced sensors for better understanding, monitoring, and control of recovery boilers and other industrial combustion systems. A high priority need of energy-intensive and waste-intensive U.S. industries is improved measurement and control technology. The harsh environments of these industries has made it difficult to utilize advanced optical sensors in-process. The new sensor offered has been proven in the industrial environment. Two important goals in this project that were not brought to completion, however, are: 1) 6 month on-boiler installations with electronic interfaces to mill monitoring and recording devices; and 2) detailed development and testing of control strategies with experts from the host organization. After the project's final field test the mill expressed the interest to continue the collaboration to complete these goals, and has indicated that they would be willing to provide support to a continuation of this work. AFR has made the business decision to continue to improve and apply new sensors to the boiler industry and looks forward to a continued collaboration.

U.S. industry relies heavily on the combustion process, and the need for improved in-process sensors is a high priority driver in the industry's 20 year vision. The combustion market is large, with the industrial boiler market (recovery boilers and others) in the U.S. exceeding 50,000 installed units and process heating market near 25,000 installed units. The products that this project has initiated will benefit industry and the nation for present and future combustion processes.

Recommendations

Planning roadmaps of many large U.S. industries (i.e., forest products, metal casting, aluminum, chemical, glass, and steel) have identified the need for advanced sensors for process monitoring and control. AFR's next step in this research focus area is to move advanced sensors into these industries to provide monitoring and control for increased process efficiency and reduced environmental emissions. Continued support by government and industry will facilitate the benefits to these industries.

AFR's presentation to the mill of the project's final field test results included a summary of tasks that will build on the results of this project and will lead to the permanent installation of FT-IR based sensors on boilers. The tentative work plan is shown below and addresses identified improvements in process measurement capabilities, physical coupling of sensors to boilers, and control software.

Summary of Tasks for the Next Step in FT-IR Spectroscopy for Black Liquor Boiler Performance Monitoring

Task 1 – 2nd Generation Temporary Installation of AFR's Systems on a Recovery Boiler

- With E/T capability for in-situ boiler temperatures
- With liquid cooled or 3-stage thermo-electric cooled MCT detectors for enhanced information on particles
- Systematic changes of individual boiler parameters
- With improved gas analysis for trace species such as reduced sulfur compounds and hydrocarbons
 - Lower instrument resolution (possible x4 gain in sensitivity)
 - Dry extracted stack gas stream and also increase from 5 m gas cell effective pathlength to 20m (another x4 gain in sensitivity)

Task 2 – Design, Construct and Evaluate Methods for Permanent Coupling of Instrumentation to Boiler

- Direct coupling with purge protected intermediate window
- Flexible waveguide coupling
- Rigid, enclosed optical coupling
- Purge protected window on boiler, non-contact coupling

Task 3 – Advancement of Fume/Carryover Analysis

- Receive carryover sample
- Receive fume sample
- Characterize for size, shape, and composition
- Measure optical constants n & k
- Model extinction (absorption & scattering) with Mie theory
- Apply to measurements in boiler

Task 4 – Improve Software and Tailor Data Stream Output for Industry Requirements and Requests

Task 5 – Build Boiler Process Monitoring Package with Next Generation State-of-the-Art FT-IR Spectrometers that Result from Other Current AFR/On-Line Projects

Task 6 – Permanent Installation on the Recovery Boiler

Task 7 – Follow-up Service by AFR to the Mill on Installed Process Monitoring Package

Task 8 – Collaborate with Boiler Design/Supply Industry (possibly McDermott)

- Boiler data for validation of model predictions

Appendix A

A document generated for a DOE review of the project (circa Sept./Oct. of 1994) which presents early results of the project to develop a new in-situ sensor for Black Liquor Recovery Boilers. This paper was presented at the 1994 DOE/Industry Advanced Sensors Technology Conference in Gaithersburg, MD. The document presents a survey of sensor needs, information on the new FT-IR spectrometer and gas analysis software, and presents the schedule and boiler geometry for the field test planned in Sweden (Appendix C).

IN-SITU FT-IR MONITORING OF A BLACK LIQUOR RECOVERY BOILER

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ABSTRACT

This paper presents the results of a project to develop a new in-situ sensor for black liquor recovery boilers. The sensor is based on Fourier Transform Infrared (FT-IR) spectroscopy. The FT-IR spectrometers, measuring both emitted light and transmitted light in the furnace can provide data for concentrations and temperatures of gases and fume as well as fume particle size. The FT-IR can also be employed for quantitative measurements of gases extracted from the stack. The paper presents information on the new FT-IR spectrometer and gas analysis software being developed in preparation for a field test of both the in-situ and extractive FT-IR measurements. The field test is scheduled for the week of Nov. 28, 1994 at a mill in Karishamn, Sweden. The instrument will be commercially available through On-Line Technologies, Inc., a spin-off company of Advanced Fuel Research, Inc.

INTRODUCTION

The safe efficient and environmentally acceptable operation of black-liquor recovery boilers requires careful control of the operating parameters. Better understanding, monitoring and control of the boiler could lead to improvements in many areas: 1) improved energy efficiency by reducing soot blowing, or by higher solids loading in the black-liquor; 2) improved strategies to reduce harmful emissions (sulfur species, NO_x , particles, unburned combustibles in flue gases, and unburned combustibles in the smelt); 3) fewer accidents and unwanted plant shutdowns; 4) increased tolerance to feedstock variations; and 5) increased throughput. Thus, better control can improve performance safety and compliance with regulations.

Advanced Fuel Research, Inc. (AFR) has successfully performed the first in-situ diagnostics within an operating black-liquor recovery boiler using Fourier Transform Infrared (FT-IR) emission and transmission (E/T) spectroscopy (1). The FT-IR spectra yield information on the gases (concentration and temperature), particles (size, concentration, and temperature), and walls (temperature). In a more recent field test, AFR demonstrated the FT-IR for in-situ measurements of gas species with accuracies at the 1-10 ppm level in the stack of a black liquor boiler and coal burning utility boiler.

The objectives of this project are the development of an FT-IR sensor for the monitoring and control of black liquor recovery boilers. The project tasks include the design of advanced, rugged, FT-IR hardware, the implementation of robust analysis software and the development of

boiler control strategies. The first phase of the work includes testing of the sensor for in-situ monitoring at the furnace exit and extractive monitoring in the stack.

SURVEY OF SENSOR NEEDS

Telephone conversations and meetings were held with a number of paper industry experts. Two areas have been identified where the FT-IR can be beneficial in the monitoring and control of recovery boilers. These are: 1) Continuous Emission Monitoring (CEM) for environmental regulations - extractive or in-situ in the stack; 2) In-Situ monitoring within the furnace. The measurement requirements in each of the areas is as follows:

1. CEM Requirements

- SO₂
- Total Reduced Sulfur (TRS)
- CO
- NO_x
- HCl
- Methanol
- Opacity
- VOC's
- Formaldehyde
- Furans
- Portable CEM

2. In-Furnace Monitoring Requirements

- Measure at furnace exit near bullnose
- Fume concentration
- Fume size
- CO
- SO₂
- Temperature determination

ADVANCED FT-IR COMPONENTS

To perform measurements in a process environment, the FT-IR must be resistant to ambient vibrations and temperature swings, must be fast and must be highly reliable. This section describes the advanced FT-IR instrument designed to meet these requirements. This system includes the following innovative components:

- a) An advanced interferometer which is immune to vibrations, is permanently aligned, has no bearing surfaces to wear out, is thermally stable, and can operate in any orientation.
- b) An advanced data system which achieves high SNR through a high speed digitizer.
- c) A microprocessor based diagnostic system for low-cost maintenance and high reliability.

These advanced components can provide significantly improved accuracy, information content, speed and reliability, compared to current generation instruments for on-line and in-situ applications on process monitoring.

a) Advanced Interferometer

The interferometer, using a single moving corner cube in a folded beam design, has been developed under a DOE SBIR Phase II program (2). The "Inertial Isolation Interferometer" design is based on a flexing parallelogram as shown in Fig. 1. This proprietary interferometer is the subject of one patent (3) and one patent pending (4).

Figure 1. *The Flexing Parallelogram is the Basis for the "Inertial Isolation Interferometer". The Inertial Balance Design Efficiently Decouples the Mirror Motion from all External Vibrations.*

The parallelogram is allowed to change shape by the flexure pivots in each corner. A corner cube attached to the top (B) will move parallel to its original position. The dynamic balance is achieved by mounting the parallelogram by flexures (E & F) at the mid-points of the parallelogram ends, and by properly locating the centers of gravity (CG) of the top and bottom of the parallelogram (including the attached corner cube). In an ideal case, where the ends (A & C) have no rotational inertia, the proper positions of the centers of gravity are coincident. With this geometry, there is no first order influence of external vibrations (either linear or rotational) on the "Isolation Interferometer" mirror motion. We are aware of no other commercial interferometer or interferometer design in the publication or patent literature which has this property. For the real case of non-

zero rotational inertia in the parallelogram ends, the centers of gravity are slightly displaced as shown in Fig. 1.

The optical design is shown in Fig. 2. This design uses one moving corner cube with folded optics. It is an extremely rugged and stable design. The folding mirrors provide both shear and tilt compensation for optical alignment. In addition, the two folding mirrors and beamsplitter are mounted rigidly together. Any vibration of the folding mirrors is accompanied by a compensating motion of the beamsplitter, making the system insensitive to such motions. The moving corner cube is mounted on the balanced parallelogram. The parallelogram

Figure 2. *Auto-Aligned, Self Compensating Optics. The Optical Design of the Interferometer Compensates for Beamsplitter Vibration as Well as Corner Cube Shear by Using Folding Mirrors that are Rigidly Mounted to the Beamsplitter Assembly.*

is immune to low frequency vibrations and the system is isolated from high frequency vibration.

An interferometer based on this design reduces the effect of external ambient vibrations on the motion of the interferometer mirrors by more than a factor of 60 compared to an unbalanced interferometer. Results of this feature are illustrated in Fig. 3, which presents the movement of the mirrors measured using a laser interferometer. In response to the ambient laboratory vibrations, the balanced interferometer moves less than one half of a laser fringe ($\sim 0.3 \text{ m}$ - see Fig. 3a), while the unbalanced interferometer (which is comparable to current commercial designs) moves over 30 laser wavelengths (18 m - see Fig. 3b).

The system is also very thermally stable. Thermal stability over a 20 to 120 F temperature range is achieved since intrinsic dimensional stability derives automatically from the self-compensating, monolithic optical element which combines the beamsplitters and folding mirrors. Its construction as a single aluminum part with integral mirrors and a thermally stable beamsplitter mount ensures continuous optical alignment under the most severe conditions. All parts are pinned so that they are automatically assembled in their correct respective positions.

b) Advanced Data Acquisition and Processing System

The advanced data system employs circuitry to accomplish high speed digitization, detector linearization, oversampling, and decimation. These modifications developed

Figure 3. Response of: a) Balanced, and b) Unbalanced Isolation Interferometer to Vibration as Measured with HeNe Laser. Each Cycle Corresponds to Motion Over a Distance of One Laser Wavelength ($0.63 \mu\text{m}$).

under a DoD sponsored Research and Development program (5) improve SNR by about a factor of ten.

For high speed and high sensitivity, a cooled Mercury Cadmium Telluride (MCT) detector is employed. Accurate quantitative analysis requires detector linearity. MCT detectors are highly sensitive and fast, but are notoriously non-linear. On-Line has developed and patented a detector correction circuit based on the fundamental mechanisms governing carrier concentrations in

photoconducting detectors (6). Figure 4 compares an uncorrected MCT signal with a corrected signal and a signal from a deuterated triglycine sulfate (DTGS) detector which is linear but much slower and less sensitive. The corrected signal clearly matches the DTGS signal extremely well, while the uncorrected signal does not. This correction scheme is incorporated into On-Line's data processing electronics.

Figure 4. Absorbance Spectrum of Polystyrene Measured with: a) a Saturated MCT Detector, b) an MCT Detector using a Linearization Circuit, and c) a Non-Saturating Pyroelectric Detector (DTGS).

In conventional FT-IR spectrometry, there is a heavy dynamic range demand on digitizing the detector signal (7). At the point of equal paths in the interferometer (centerburst), the signal is the sum of the intensities at all of the wavelengths in the spectrum, and therefore is very large. When a 16-bit digitizer is used with the gain matched to the centerburst signal, digitizer resolution in the wings of the interferogram (low signal) can often become the limiting factor contributing to noise. To alleviate this problem, a method has been developed which involves oversampling and decimation. This is accomplished by

extending the IR filter bandwidth by a factor of 8 and digitizing 8 times more rapidly (oversampling) with a high speed A/D converter. Then the total number of data points are reduced back to the original number by co-adding neighboring points about the desired data points in a weighted fashion (finite impulse response filtering) and eliminating the extra points in between (decimation). By increasing the sampling speed, the required SNR in the interferogram and therefore the dynamic range requirements of an A/D converter are reduced. Accuracy is then recovered by decimation after digitization. Oversampling has the added advantage of making the measurement 64 times less sensitive to velocity jitter. At the same time the high speed digitizer permits scanning the mirrors 8 times faster. This further reduces the dynamic range requirements and effects of velocity jitters. The combination of these three design features provides an additional 3 bits of dynamic range (effective 19 bit digitizer) and improves the SNR obtainable in a single scan by a factor of 8.

The high speed data system provides an oversampled 0.5 cm^{-1} resolution single-sided spectrum every 0.25 sec, and an on-board digital signal processor (DSP) can perform a 0.5 cm^{-1} Fourier transform (64 K FFT) in less than 200 msec. A low resolution single sided spectrum can be delivered every 20 milliseconds.

c) Self Diagnostic Maintenance System

On-Line's FT-IR electronics include sensors and probe points for diagnostics during operation and maintenance. These are reported to an on-board microprocessor which provides alarm warnings of parameter

drifts. This effectively allows the instrument to forecast problems. This system supports maintenance by minimally trained personnel with remote assistance from the factory's service center. By connecting the system to the service center via modem, the system's health can be monitored, and questionable parts can automatically be ordered for replacement prior to failure.

The advanced designed components provide improvements in all the important FT-IR performance categories:

- vibration isolation
- stability
- speed
- signal-to-noise
- resolution
- compactness
- reliability

QUANTITATIVE GAS ANALYSIS SOFTWARE

Both in-situ and extractive monitoring requires the development of robust software algorithm for quantitative analysis of gases. This is done by comparing the measured spectrum to a spectrum for a known reference gas. This is performed using a classical least squares (CLS) algorithm. Figure 5 presents the spectrum for a reference gas containing about 5 ppm of SO_2 , NO , and CO in nitrogen. The spectrum is taken at 1 wavenumber resolution in a 5.26 m cell as an average over 50 seconds. The temperature of the gas cell is 150°C . Clearly, the spectra for these three species are easily identified, well above the noise and free of cross interference.

The main problem with quantitative measurement is interference from water and CO_2 . Figure 6 presents the same calibration gas diluted with an equal volume flow of air containing CO_2 and H_2O . Water is a little over 1% and CO_2 is at 500 ppm. Figure 6 is on an absorbance scale 100 times larger than Fig. 5 and the spectra for SO_2 , CO , and NO are no longer visible.

An attempt to perform a quantitative analysis for SO_2 , CO and NO using a CLS algorithm is presented in Fig. 7. The x-axis gives the time of the measurement, the y-axis is concentration in ppm. Each data point represents an average concentration measured over 5 seconds. The CO which has little interference from water and CO_2 exhibits an accurate quantitative analysis. It shows the introduction of the calibration gas near 100 seconds and the increase in concentration to almost the value in the calibration gas as the gas filled the cell. At 300 sec, an equal volume of air containing H_2O and CO_2 is introduced, and the CO_2 level doped to roughly half the full value. At about 750 sec, the flow of calibration gas is shut off. The increase of CO_2 at 600 sec was obtained by breathing into the air intake and the increase in H_2O was obtained by heating a water bath in the air line. At 900 sec, the air is replaced by dry nitrogen. It is clear from Fig. 7 that water interferes with the measurement of SO_2 and NO , since their concentrations are distinctly different from their expected values.

Work on the quantitative analysis algorithm included two methods to improve the accuracy. In the first method, certain spectral regions where there are strong absorption lines from interfering species are eliminated from the CLS fit. The results are

Figure 5. Spectrum of Calibration Gas (CO: 5.3 ppm; NO: 5.0 ppm; and SO₂: 4.6 ppm) in 5.26 m Gas Cell at 150 °C. 50 sec average at 1 Wavenumber Resolution.

Figure 6. Spectrum of Calibration Gas (CO: 5.3 ppm; NO: 5.0 ppm; and SO₂: 4.6 ppm) with Equal Flow of Air in 5.26 m Gas Cell at 150 °C. 50 sec average at 1 Wavenumber Resolution.

Figure 7. CLS Analysis for CO_2 , H_2O , SO_2 , CO , and NO .

presented in Fig. 8. Clearly, this procedure improves the accuracy of the analysis. However, the NO value appears to be too low when water is present.

The second method considers the problem that the water spectrum is not linear with concentration. To describe this, both multiple references as well as a perturbation spectrum, which describes the first order change about each reference with concentration, is employed as an additional species in the CLS. The results are presented in Fig. 9. Application of the two procedures improves the results so that the errors in SO_2 , CO , and NO are 1 ppm or less, although the NO still appears to be low in the presence of H_2O . For the water concentration presented, which was between 0 and 3%, only a single reference was required. Good results have been obtained at water concentration up to 30%, but an additional water reference is required for the higher concentrations.

MILL TRIALS

Field tests in an operating pulp mill in Karishamn, Sweden are scheduled for the week of Nov. 28, 1994. Both in-situ and extractive measurements will be made. The extractive measurements are to be made in the stack with an integrated package of FT-IR, heated gas cell, electronics, and computer. The components are packaged in a 10 1/2" high x 19 1/2" wide box which can fit a relay rack. It is an improved version of On-Line Technologies' Multi-Gas 2000 pictured in Fig. 10.

The in-situ measurements will be made in the upper part of the furnace. Figure 11 shows the locations of ports with cover a line-of-

Figure 8. CLS Analysis for CO_2 , H_2O , SO_2 , CO , and NO with Regions Containing Strong Absorption Lines Eliminated.

Figure 9. CLS Analysis for CO_2 , SO_2 , CO , and NO with Regions Containing Strong Absorption Lines Eliminated and Perturbation Spectrum for H_2O Added.

Figure 10. On-Line Technologies' Multi-Gas 2000 Analyzer.

Figure 11. Schematic of Boiler and Location of Optical Ports.

sight in front of the bullnose as well as ports of secondary interest in the economizer. The in-situ tests seek to follow variations in the concentrations of CO and fume which can indicate inefficient operation of the boiler. These measurements will be used to develop a control strategy to improve boiler operation.

CONCLUSION

An advanced FT-IR sensor has been developed for monitoring the performance of a black liquor recovery boiler. The sensor will be tested in a commercial recovery boiler to determine its effectiveness as a sensor for improved boiler control. Additional tests are being planned and suggested sites are solicited.

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Appendix B

Proceedings reprint of the SPIE meeting held in McLean, Virginia (7-10 November 1994). This reprint presents improvements in the FT-IR hardware that will allow improvements in detection sensitivity, scan speed, and the ability to operate in harsh environments. This DOE project was credited in the acknowledgement section for contributing to these improvements.

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Recent Advances in FT-IR Technology

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ABSTRACT

For the monitoring of hydrocarbons and toxic air contaminants, Fourier Transform Infrared (FT-IR) spectroscopy has advantages in the ability to rapidly measure multiple species accurately at low concentrations. During the last few years, FT-IR spectrometers have improved substantially in ruggedness, speed, sensitivity, and flexibility for performing air emission measurements. This paper will discuss advances made at On-Line Technologies, Inc. (On-Line) in:

- a rugged interferometer
- an advanced data system
- linearized photoconductive detectors
- analysis software
- operating software

These improvements in the FT-IR hardware will allow improvements in detection sensitivity, scan speed, and the ability to operate in harsh environments.

1. INTRODUCTION

Process monitoring by Fourier Transform Infrared (FT-IR) spectroscopy can provide real-time data on:

- a) gas concentrations and temperature
- b) small particle size, number density, compositions, and temperature
- c) thin film thickness, composition, and temperature
- d) liquid composition and temperature

To perform these functions in a process environment, the FT-IR must be resistant to ambient vibration and temperature swings, must be fast and must be highly reliable. This paper describes an advanced FT-IR instrument designed by On-Line Technologies, Inc. (On-Line) to meet these requirements. The paper describes the advanced components and presents performance data for the instrument. The new FT-IR has been incorporated into a relay rack mountable package (10 1/2" high) which includes a multi-pass cell, computer, and user interface touch screen for gas analysis. The software and performance for quantitative gas analysis is also discussed.

2. ADVANCED FT-IR COMPONENTS

To perform measurements in a process environment, the FT-IR must be resistant to ambient vibrations and temperature swings, must be fast and must be highly reliable. This section describes the FT-IR instrument designed to meet these requirements. This system includes the following components:

- a) An interferometer which is immune to vibrations, is permanently aligned, has no bearing surfaces to wear out, is thermally stable, and can operate in any orientation.
- b) A data system which achieves a high signal-to-noise ratio (SNR) and high speed through a high speed digitizer which permits oversampling.
- c) Software which includes an object oriented flexible user interface for linking the FT-IR with other sensors or controllers and a microprocessor based diagnostic system for maintenance.

These components can provide improved accuracy, information content, speed and reliability, compared to current generation instruments for on-line and in-situ applications in process monitoring.

2.a) Interferometer

The interferometer, using a single moving corner cube in a folded beam design, has been developed under a DOE SBIR Phase II program.¹ The "Inertial Isolation Interferometer" design is based on a flexing parallelogram as shown in Fig. 1. This interferometer is the subject of one patent² and one patent pending.³

The parallelogram is allowed to change shape by the flexure pivots in each corner. A corner cube attached to the top (B) will move parallel to its original position. The dynamic balance is achieved by mounting the parallelogram by flexures (E & F) at the mid-points of the parallelogram ends, and by properly locating the centers of gravity (CG) of the top and bottom of the parallelogram (including the attached corner cube). In an ideal case, where the ends (A & C) have no rotational inertia, the proper positions of the centers of gravity are coincident. With this geometry, there is no first order influence of external vibrations (either linear or rotational) on the "Isolation Interferometer" mirror motion. For the real case of non-zero rotational inertia in the parallelogram ends, the centers of gravity are slightly displaced as shown in Fig. 1.

The optical design is shown in Fig. 2. This design uses one moving corner cube with folded optics. It is an extremely rugged and stable design. The folding mirrors provide both shear and tilt compensation for optical alignment.⁴ In addition, the two folding mirrors and beamsplitter are mounted rigidly together. Any vibration of the folding mirrors is accompanied by a compensating motion of the beamsplitter, making the system insensitive to such motions. The moving corner cube is mounted on the balanced parallelogram. The parallelogram is immune to low frequency vibrations and the system is isolated from high frequency vibration.

Figure 1. The Flexing Parallelogram is the Basis for the "Inertial Isolation Interferometer". The Inertial Balance Design Efficiently Decouples the Mirror Motion from all External Vibrations.

Figure 2 Auto-Aligned, Self Compensating Optics. The Optical Design of the Interferometer Compensates for Beamsplitter Vibration as Well as Corner Cube Shear by Using Folding Mirrors that are Rigidly Mounted to the Beamsplitter Assembly.

An interferometer based on this design reduces the effect of external ambient vibrations on the motion of the interferometer mirrors by more than a factor of 60 compared to an unbalanced interferometer. Results of this feature are illustrated in Fig. 3, which presents the movement of the mirrors measured using a laser interferometer. In response to the ambient laboratory vibrations, the balanced interferometer moves less than one half of a laser fringe ($\sim 0.3 \mu\text{m}$ - see Fig. 3a), while the unbalanced interferometer (which is comparable to current commercial designs) moves over 30 laser wavelengths ($18 \mu\text{m}$ - see Fig. 3b).

The system is also very thermally stable. Thermal stability over a 20 to 120 F temperature range is achieved from the self-compensating, monolithic optical element which combines the beamsplitters and folding mirrors. Its construction as a single aluminum part with integral mirrors and a thermally stable beamsplitter mount ensures dimensional stability.

2.b) Data Acquisition and Processing System

The advanced data system employs circuitry to accomplish high speed digitization, detector linearization, oversampling, and decimation. These features developed under a DoD sponsored Research and Development program⁵ provide for detector limited SNR when a high speed, and high sensitivity, cooled Mercury Cadmium Telluride (MCT) detector is employed. However, accurate quantitative analysis requires detector linearity. MCT detectors are highly sensitive and fast, but are notoriously non-linear. On-Line has developed and patented a detector correction circuit based on the fundamental mechanisms governing carrier concentrations in photoconducting detectors.⁶ Figure 4 compares an uncorrected MCT signal with a corrected signal and a signal from a deuterated triglycine sulfate (DTGS) detector which is linear but much slower and less sensitive. The corrected signal clearly matches the DTGS signal extremely well, while the uncorrected signal does not. This correction scheme is incorporated into On-Line's data processing electronics.

Figure 3. Response of: a) Balanced, and b) Unbalanced Isolation Interferometer to Vibration as Measured with HeNe Laser. Each Cycle Corresponds to Motion Over a Distance of One Laser Wavelength ($0.63 \mu\text{m}$).

Figure 4. Absorbance Spectrum of Polystyrene Measured with: a) a Saturated MCT Detector, b) an MCT Detector using a Linearization Circuit, and c) a Non-Saturating Pyroelectric Detector (DTGS).

In conventional FT-IR spectrometry, there is a heavy dynamic range demand on digitizing the detector signal.⁷ At the point of equal paths in the interferometer (centerburst), the signal is the sum of the intensities at all of the wavelengths in the spectrum, and therefore is very large. When a 16-bit digitizer is used with the gain matched to the centerburst signal, digitizer resolution in the wings of the interferogram (low signal) can often become the limiting factor contributing to noise. To alleviate this

problem, a method has been developed which involves oversampling and decimation. This is accomplished by extending the IR filter bandwidth by a factor of 8 and digitizing 8 times more rapidly (oversampling) with a high speed A/D converter. Then the total number of data points are reduced back to the original number by co-adding neighboring points about the desired data points in a weighted fashion (finite impulse response filtering) and eliminating the extra points in between (decimation). By increasing the sampling speed, the required SNR in the interferogram and therefore the dynamic range requirements of an A/D converter are reduced. Accuracy is then recovered by decimation after digitization. Oversampling has the added advantage of making the measurement 64 times less sensitive to velocity jitter. At the same time the high speed digitizer permits scanning the mirrors 8 times faster. This further reduces the dynamic range requirements and effects of velocity jitters. The combination of these three design features provides an additional 3 bits of dynamic range (effective 19 bit digitizer). The high speed data system provides an oversampled 0.5 cm^{-1} resolution single-sided spectrum every 0.25 sec. A low resolution single sided spectrum can be delivered every 20 milliseconds.

2.c) Software

The user interface software employs's National Instrument's LabVIEW for the basic programming language. LabVIEW is an object orientated software development package in which programming is performed graphically with icons which represent different instruments, components of a sensor or control system, computing operations, or display functions. On-Line has created a library of icons for all the functions necessary to operate the FT-IR, perform Fourier Transform, apply quantitative analysis algorithms, display results, and interact with other components.

On-Line's FT-IR electronics include sensors and probe points for diagnostics during operation and maintenance. These are reported to an on-board microprocessor which provides alarm warnings of parameter drifts. This allows the instrument to forecast problems. This system supports maintenance by minimally trained personnel with remote assistance from the factory's service center. By connecting the system to the service center via modem, the system's health can be monitored, and questionable parts can automatically be ordered for replacement prior to failure.

3. PERFORMANCE

Performance in several categories is illustrated in Figs. 5 - 8. The instrument's signal-to-noise performance is illustrated in Fig. 5. In Fig. 5a, forty-five second's average of data at 4 wavenumbers is ratioed to a similar reference. The data were taken by a Thermoelectric (TE) cooled MCT detector with a cut-off at 1250 cm^{-1} . Peak to peak noise at 2500 cm^{-1} is about 0.001. In Fig. 5b, a one second average of data at 4 wavenumbers, are ratioed to similar reference. These data were taken with a higher sensitivity TE cooled MCT detector whose cut-off is at 1700 cm^{-1} . The peak to peak noise at 2500 cm^{-1} is about 0.0005. The instrument's speed performance is illustrated in Fig. 6. The figure presents a single 32 wavenumber scan ratioed to a 16 scan reference taken with the higher sensitivity TE cooled detector. The scan takes 20 milliseconds. The instrument's resolution performance is illustrated in Fig. 7. This spectrum was obtained through a multi-pass 5 meter gas cell. The On-Line FT-IR provides 0.5 wavenumber spectra which is important in removing interferences from species with overlapping bands. Spectra at 0.5 wavenumber resolution can be taken at 4 scans/sec.

The instrument stability is illustrated in Fig. 8. A collection of 10 scans at 1 cm^{-1} resolution taken at 10 minutes, 1 hour, and 6 hours is shown ratioed to a reference of 10 scans taken at time zero. The noise at 1 cm^{-1} taken through a 5 m cell is on the order of 0.005% peak to peak. The average position of the spectrum shows less than 0.001 variations from 1.000 at 10 minutes and less than 0.0025 variations at 6 hours. The major change at 6 hours is the water and CO_2 concentration.

4. QUANTITATIVE GAS ANALYSIS SOFTWARE

Both in-situ and extractive monitoring requires the development of robust software algorithm for quantitative analysis of gases. Such algorithms compared the measured spectrum to a spectrum for a known reference gas. On-Line's software uses a classical least squares (CLS) algorithm. Figure 9 presents the spectrum for a reference gas containing about 5 ppm of SO_2 , NO , and CO in nitrogen. The spectrum is taken at 1 wavenumber resolution in a 5.26 m cell as an average over 50 seconds. The temperature of the gas cell is 150°C . Clearly, the spectra for these three species are easily identified, well above the noise and free of cross interference.

Figure 5. Transmittance Spectra. a) A 45 Second Average at 4 wavenumbers Ratioed to a 45 Second Average at 4 Wavenumbers using a TE Cooled Detector with a 1250 Wavenumber Cut-off. b) A One Second Average at 4 Wavenumbers Ratioed to One Second Averaged at 4 Wavenumbers using a TE Cooled Detector with a 1700 Wavenumber Cut-off.

Figure 6. Transmittance Spectrum. A Single Scan at 32 Wavenumbers Resolution Ratioed to a 16 Scan Reference at 32 Wavenumbers Taken with a TE Cooled MCT Detector with a 1700 Wavenumber Cut-off.

Figure 7. Single Transmission Spectrum at 0.5 cm^{-1} Resolution Showing Water Lines.

Figure 8. Comparison of 100% Lines (10 Scans at 1 Wavenumber Resolution Taken at a Time Delay after a 10 Scan Reference at 1 Wavenumber). Spectra are taken with an On-Line Spectrometer through a 5 Meter Cell. a) Time Delay of 10 Minutes, b) Time Delay of 1 Hour, and c) Time Delay of 6 Hours.

Figure 9. Spectrum of Calibration Gas (CO: 5.3 ppm; NO: 5.0 ppm; and SO₂: 4.6 ppm) in 5.26 m Gas Cell at 150°C. 50 sec Average at 1 Wavenumber Resolution.

The main problem with quantitative measurement is interference from water and CO₂. Figure 10 presents the same calibration gas diluted with an equal volume flow of air containing CO₂ and H₂O. Water is a little over 1% and CO₂ is at 700 ppm. Figure 10 is on an absorbance scale 100 times larger than Fig. 9 and the spectra for SO₂, CO, and NO are no longer visible.

Figure 10. Spectrum of Calibration Gas (CO: 5.3 ppm; NO: 5.0 ppm; and SO₂: 4.6 ppm) with Equal Flow of Air in 5.26 Gas Cell at 150°C. 50 sec Average at 1 Wavenumber Resolution.

An attempt to perform a quantitative analysis for SO₂, CO and NO using a CLS algorithm is presented in Fig. 11. The x-axis gives the time of the measurement, the y-axis is concentration in ppm. Each data point represents an average concentration measured over 5 seconds. The CO which has little interference from water and CO₂ exhibits an accurate quantitative analysis. It shows the introduction of the calibration gas near 100 seconds and the increase in concentration to almost the value in the calibration gas as the gas filled the cell. At 300 sec, an equal volume of air containing H₂O and CO₂ is introduced, and the CO₂ level doped to roughly half the full value. At about 750 sec, the flow of calibration gas is shut off. The increase of CO₂ at 600

sec was obtained by breathing into the air intake and the increase in H_2O was obtained by heating a water bath in the air line. At 900 sec, the air is replaced by dry nitrogen. It is clear from Fig. 11 that water interferes with the measurement of SO_2 and NO, since their concentrations are distinctly different from their expected values.

Work on the quantitative analysis algorithm included two methods to improve the accuracy. In the first method, certain spectral regions where there are strong absorption lines from interfering species are eliminated from the CLS fit. The results are presented in Fig. 12. Clearly, this procedure improves the accuracy of the analysis. However, the NO value appears to be too low when water is present.

The second method considers the problem that the water spectrum is not linear with concentration. To describe this, both multiple references for water at different concentrations as well as a perturbation spectrum, which describes the first order change about each reference with concentration, are employed as an additional species in the CLS. The results are presented in Fig. 13. Application of the two procedures improves the results so that the errors in SO_2 , CO, and NO are 1 ppm or less, although the NO still appears to be systematically low in the presence of H_2O . For the water concentration presented, which was between 0 and 3%, only a single reference was required. Good results have been obtained at water concentration up to 30%, but an additional water reference is required for the higher concentrations.

5. CONCLUSIONS

The advanced interferometer and data system developed, provides improvements in performance in: vibration isolation, stability, speed, SNR, resolution and compactness. These performance improvements translate into better accuracy, speed, detection limits, repeatability, ruggedness, and maintainability.

ACKNOWLEDGMENT

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Figure 11. CLS Analysis for CO_2 , H_2O , SO_2 , CO , and NO .

Figure 12. CLS Analysis for CO_2 , H_2O , SO_2 , CO , and NO with Regions Containing Absorption Lines Eliminated.

Figure 13. CLS Analysis for CO₂, SO₂, CO, and NO with Regions Containing Strong Absorption Lines Eliminated and Perturbation Spectrum for H₂O Added.

Appendix C

Report which presents the field test results at the Black Liquor Recovery Boiler at the Mörrum Pulp Mill (Mörrum, Sweden): Nov. 28, 1994 – Dec. 8, 1994.

Note: This field test was facilitated by the Sweden company, Measurement Technologies AB. Beginning in mid – 1994, telephone discussions and fax transmissions were routine between AFR and MTech AB in preparation for the field test.

The document in this Appendix was abstracted from the submitted monthly status report dated Dec. 1994/Jan. 1995 and begins with the heading "Task 1.6 – Field Tests."

Task 1.6 - Field Tests

The field test at the Mörrums Bruk mill were initiated the week of Nov. 28, 1994. The measurements were successful in following CO concentration in the upper part of the boiler.

Mörrums Bruk Black Liquor Recovery Boiler - The Mörrum Pulp Mill (Mörrum, Sweden) is part of Södra Cell AB, which also has pulp mills at Mönsterås and Värö. The total annual capacity is over 1 million tonnes of kraft pulp.

At Mörrum, pulp production started in 1962. Presently, continuous production results in 375,000 tonnes of pulp per year of which ~ 240,000 tonnes is hardwood, and ~ 135,000 tonnes is softwood. The recovery boiler, which was modernized between 1987-1991, produces 260,000 MWh/year, making the plant self-supporting on electricity. The amount is enough for a medium sized town.

Figure 4 presents a picture of Mörrums Bruk (Mörrums Mill), with the recovery boiler located in the green painted structure in the center of the picture (just to the left of the tallest stack; with the Mörrums Bruk name and logo near the top). The mill is located on the south-eastern tip of Sweden, with the Baltic Sea providing the background in the picture.

Configuration of Instrumentation for In-Situ Recovery Boiler Measurements - Discussions and fax transmissions with our Swedish liaison to the mill, Measurement Technologies AB, allowed us to understand the location, geometry, and conditions of the measurement site, and design our instrumentation appropriately.

The Götaverken recovery boiler has a lot in common with B&W boilers of the United States. The physical size of the main combustion zone is about 30 feet by 30 feet. Normal running conditions are 115% load with 65 - 68% dry content.

Our task was to perform in-situ measurements across the 30 foot combustion span just prior to the Bull Nose of the boiler. The measurement location is shown in the schematics of Fig. 5. This line-of-sight location was advantageous for our purpose of demonstrating real-time process monitoring since plant adjustable process variables, such as liquor injection nozzles and wind boxes, were located immediately prior to our measurement location. The line-of-sight was located about 2/3 of the way up the ~ 100 feet high recovery boiler building shown in Fig. 4.

Figure 6 presents photographs of the side-wall of the recovery boiler at the measurement location. Shown are "manhole" covers (~ 30" diameter) with native instruments attached. The manhole covers were well-insulated by several inches of fume built up on the inside surfaces. Through our liaison, the Mill agreed to replace two opposing manhole covers with flat boiler plates containing centered 4" diameter apertures for passage of our FT-IR beam through the combustion zone. Replacement of the manhole covers had never been

Figure 4.

MÖRRUMS BRUK

a View of Boiler from Above

b Side-View of Boiler

Figure 5. Schematics of Mörrums Bruk Black Liquor Recovery Boiler. The Ports for Line-of-Sight were Utilized for FT-IR Transmission Measurements for On-Line In-Situ Monitoring. a) Top View; b) Side View.

a

b

Figure 6. Photographs of Side-Wall of Mörrums Bruk Recovery Boiler at Measurement Location. Shown are Standard "Manhole" Covers with Attached Native Instruments. Photographs are Courtesy of Measurement Technologies AB.

done previous to the request of our liaison. The 4" apertures would be located 32" above the catwalk surrounding the boiler at this level.

The On-Line Technologies FT-IR bench was housed in a NEMA 4 rated enclosure (13" x high x 17" wide x 14" deep) with connections for a dry air purge. The portable unit was outfitted with a 2" diameter potassium bromide (KBr) window for passage of the near-collimated 1 1/4" diameter infrared beam. To minimize beam divergence and hence, infrared energy loss, across the 30' span of the boiler, a simple beam expander was constructed to increase the beam diameter by a factor of 3, to 3.75", for unrestricted passage through the 4" diameter aperture into the recovery boiler. Figure 7 presents a schematic of the optical arrangement. The modulated infrared beam exiting the portable NEMA 4 box goes through a focus in the two mirror telescope and is expanded, as designed. After traversing the 30', a receiver telescope condenses the beam and provides focus on the detector (a mercury-cadmium-telluride detector, liq. N₂ cooled). The beam expander housing was also designed to accommodate the attachment of a Bomem MB FT-IR.

Installation at the Mörrums Bruk Recovery Boiler - The FT-IR system was transported from East Hartford, CT to Stockholm, Sweden via a standard air freight shipment. The shipment was 1) trucked to Bradley International Airport; 2) flown to Newark, NJ International Airport, and 3) flown to and unloaded in Stockholm. The instrumentation was then carried by trailer the 400 miles south to Mörrums Bruk.

Nov
On Monday, Dec. 28, 1994, the system was moved from an outdoor enclosure (ambient temperature ~ 40°F) to the line-of-sight location (ambient temperature ~ 75°F). The components were unpacked and set up to traverse a 30' span directly next to the wall of the boiler. Alignment of the system was facilitated by a visible diode laser beam (5 mW, red) which was incorporated to precisely follow the expanded infrared beam. The IR signal response obtained was essentially the same as that obtained in the AFR laboratory before shipment.

Figure 8 presents photographs of the FT-IR based instrument when located to pass the beam through the combustion zone of the boiler. The red glow of the combustion environment is obvious from each hole in the boiler plates. We initially planned to physically connect the bellows flange of each telescope to each boiler wall. Air purges in the telescope enclosures were to maintain a positive pressure in the direction of the boiler to guard against mirror and/or window fouling. However, high pressure "puffs" from the boiler (up to six feet in the horizontal direction) and the surface temperature of the non-insulated boiler plates (> 600°C near center, dull glow) prevented direct physical coupling for this test installation. Instead, the transmitter and receiver were located 2 - 3 feet back from the boiler plates, and high pressure plant air was blown across each aperture to both cool the plates and redirect "puffs" away from the instrument as they came out of the boiler.

Figure 7. Schematic of On-Line Technologies' FT-IR With Optics to Transmit and Receive Modulated Infrared Beam Over the 30 Foot Span of the Recovery Boiler.

Figure 8. On-Line Spectrometer Measuring Across a Black Liquor Recovery Boiler. a) FT-IR and Transmitting Telescope; b) Receiving Telescope and Detector.

The visible alignment laser was of no use for aiming the transmitted IR beam through each aperture (30' apart). The particle/flume level was sufficiently dense to completely scatter visible light (e.g., by eye you could not see through, and the red laser beam would not traverse). A weak IR signal from the modulated source was initially obtained, however, and fine tuning of the position and tilt of the transmitter and receiver resulted in a maximized and acceptable signal for measurement.

Results - Results were obtained for both the On-Line spectrometer at 1 cm^{-1} resolution and a Bomem spectrometer at 4 cm^{-1} resolution. Measurements were made across the boiler during a period where the boiler controls were adjusted.

On-Line - The boiler operation is shown by the trend lines in Figs. 9 (tertiary air) and Fig. 10 (CEM analyzer for CO_2 , CO, NO_x , and O_2). Our measurements were made continuously between 16:24 hours and 17:20 hours.

Figure 11, which presents an FT-IR measurement across the boiler, indicates that near-IR radiation below $2.9\text{ }\mu\text{m}$ (above 3400 cm^{-1}) is completely blocked by this combustion environment. At longer wavelengths, above $2.9\text{ }\mu\text{m}$ (below 3400 cm^{-1}) however, mid-IR radiation does partially transmit.

A control system designed to monitor the fundamental CO bands in the mid-IR ($\sim 5\text{ }\mu\text{m}$, 2000 cm^{-1}) would be significantly useful to industry. Figure 12 presents a difference spectrum calculated from two FT-IR measurement through the boiler. Each measured spectrum is scaled so that the H_2O will be subtracted in the CO region. One measurement was during a high volume of air injection into the combustor (low CO), the other for a low volume of air injection (high CO). The figure also shows a CO reference and a water reference. The figure shows that there are CO bands which are clear of H_2O interference. Clearly, mid-IR measurements can be used to monitor and control the process by CO concentration at the combustion zone.

To analyze the CO concentration, we employed the peaks designated with stars. The relative magnitude of the CO is plotted in Fig. 13. We also monitored the fume concentration, Fig. 14 and the H_2O concentration, Fig. 15. It can be seen that the increase in CO concentration corresponds to the reduction in the tertiary air in Fig. 9.

Bomem - Bomem data were taken at 4 cm^{-1} . The boiler trends are presented in Figs. 16 and 17 our data were taken between 14:17 and 15:43. Figure 18 presents a comparison of the difference spectra and the CO reference at 4 cm^{-1} . Figure 18a shows a high CO value while Fig. 18b shows a low value. The trends for CO, H_2O , and fume are presented in Figs. 19 - 21, respectively. Again, the trend for CO is in agreement with the air adjustment and the CEM CO monitor.

Task 1.7 - Development of Control Strategies

No work scheduled for this period.

Figure 9. Tertiary Air Concentration Trend.

Figure 10. CEM Analyzer Trend for CO₂, CO and O₂.

Figure 11. FT-IR Measurement Through a Recovery Boiler of a Paper Mill. Partially Transparent Windows in the Spectrum, where Light Scattering by the Fume is Decreased are Labeled. The 2000 cm⁻¹ Region Provides a Measurement Window for Direct Combustion Zone CO Monitoring.

Figure 12. Analysis of CO in Boiler. a) High CO; b) High CO on Expanded Scale; and c) Low CO on Expanded Scale.

Figure 13. Trend For CO Concentration Determined by FT-IR.

Figure 14. Trend for Fume Concentration Determined by FT-IR.

Figure 15. Trend For H₂O Concentration.

Figure 16. Boiler Trends for Air Flows. The Curve with the Increase Between 15.24 and 15.36 is the Tertiary Air.

Figure 17. CEM Analyzer Trend for CO₂, CO and O₂.

Figure 18. Difference Spectrum from Two Measurements Through the Recovery Boiler, Overlaid with a CO Reference Spectrum. Conditions for Secondary Air Injected into the Boiler were Varied to Influence CO Concentration. Changes in CO Concentration can be Monitored Directly in the Combustion Zone in the Spectral Window from 2000 cm^{-1} to 2100 cm^{-1} . a) High CO Value; b) Low CO Value.

Figure 19. Trend for CO Concentration Determined by FT-IR.

Figure 20. Trend for H₂O Concentration Determined by FT-IR.

Figure 21. Trend for Fume Concentration Determined by FT-IR.

Appendix D

A paper presented at the 1995 International Incineration Conference (May 8-12, 1995), Seattle, Washington. This paper describes the advanced FT-IR instrument and presents results of the 1994 field test (Appendix C) at the recovery boiler in Sweden.

FT-IR MONITORING OF INCINERATORS

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ABSTRACT

This paper presents the results of a project to develop a new sensor for extractive and in-situ diagnostics for incinerators and other combustion devices. The sensor is based on Fourier Transform Infrared (FT-IR) spectroscopy. The FT-IR, measuring both emitted radiation and transmitted radiation in the stack or furnace can provide data for concentrations and temperatures of gases. The FT-IR can also be employed for quantitative measurements of gases extracted from the stack. The FT-IR being developed specifically for environmental and process monitoring applications is very rugged and thermally stable. The paper presents information on the new FT-IR spectrometer and software being developed for quantitative gas analysis. The paper also presents some results of field tests in a recovery boiler and in an apparatus for NO control technology development.

INTRODUCTION

The use of FT-IR spectrometry as a continuous emission monitor (CEM) in incinerators offers several advantages. A single instrument can be used to simultaneously monitor several pollutant species, thereby greatly reducing the cost and complexity of the CEM system. The flexibility of FT-IR offers different sampling strategies depending on the type of analysis required. Extractive measurements provide a low maintenance approach for simultaneously determining concentrations of several species, including CO, CO₂, NO, SO₂, and unburned hydrocarbons. Alternatively, in-situ measurements can be used for rapid response in control applications or to determine concentrations of species that are otherwise difficult to monitor, for example, NH₃ and HCl. Although FT-IR is an established laboratory tool, the use of FT-IR for industrial applications is still in the developmental stage [1-8]. A number of issues need to be addressed to convert a successful laboratory tool into a reliable industrial sensor. Improvements are required in:

- tolerance to vibration and temperature variations
- sensitivity
- data reduction methods
- user friendliness
- reliability.

This paper describes an advanced FT-IR instrument designed by On-Line Technologies, Inc. (On-Line) to meet these requirements. The paper describes the advanced components, presents performance data for the instrument, and describes tests in industrial applications.

ADVANCED FT-IR COMPONENTS

To perform measurements in a process environment, the FT-IR must be resistant to ambient vibrations and temperature swings, must be fast and must be highly reliable. This section describes the FT-IR instrument designed to meet these requirements [8]. This system includes the following components: a) An interferometer which is immune to vibrations, is permanently aligned, has no bearing surfaces to wear out, is thermally stable, and can operate in any orientation. b) A data system which achieves a high signal-to-noise ratio (SNR) and high speed through a high speed digitizer which permits oversampling. c) Software which includes an object oriented, flexible user interface for linking the FT-IR with other sensors or controllers and a microprocessor based diagnostic system for maintenance. These components can provide improved accuracy, information content, speed and reliability, compared to current generation instruments for on-line and in-situ applications in process monitoring.

Interferometer

The interferometer, using a single moving corner cube in a folded beam design, has been developed under a DOE SBIR Phase II program [9]. The "Inertial Isolation Interferometer" design is based on a flexing parallelogram as shown in Fig. 1. This interferometer is the subject of two patents [10,11].

The parallelogram is allowed to change shape by the flexure pivots in each corner. A corner cube attached to the top (B) will move parallel to its original position. The dynamic balance is achieved by mounting the parallelogram by flexures (E & F) at the mid-points of the parallelogram ends, and by properly locating the centers of gravity (CG) of the equally weighted top and bottom of the parallelogram (including the attached corner cube). In an ideal case, where the ends (A & C) have no rotational inertia, the proper positions of the centers of gravity are coincident. With this geometry, there is no first order influence of external vibrations (either linear or rotational) on the "Isolation Interferometer" mirror motion. For the real case of non-zero rotational inertia in the parallelogram ends, the centers of gravity are slightly displaced as shown in Fig. 1.

The optical design is shown in Fig. 2. This design uses one moving corner cube with folded optics. It is an extremely rugged and stable design. The folding mirrors provide both shear and tilt compensation for optical alignment [12]. In addition, the two folding mirrors and beamsplitter are mounted rigidly together. Any vibration of the folding mirrors is accompanied by a compensating motion of the beamsplitter, making the system insensitive to such motions. The moving corner cube is mounted on the balanced parallelogram. The parallelogram is immune to low frequency vibrations and the system is isolated from high frequency vibration.

An interferometer based on this design reduces the effect of external ambient vibrations on the motion of the interferometer mirrors by more than a factor of 60 compared to an unbalanced interferometer. Results of this feature are illustrated in Fig. 3, which presents the movement of the mirrors measured using a laser interferometer. In response to the ambient laboratory vibrations, the balanced interferometer moves less than one half of a laser fringe ($\sim 0.3 \mu\text{m}$ - see Fig. 3a), while the unbalanced interferometer (which is comparable to current commercial designs) moves over 30 laser wavelengths ($18 \mu\text{m}$ - see Fig. 3b). The system is also very thermally stable. Thermal stability over a 20 to 120°F temperature range is achieved from the self-compensating, monolithic optical element which combines the beamsplitters and folding mirrors. Its construction as a single aluminum part with integral mirrors and a thermally stable beamsplitter mount ensures dimensional stability.

Figure 1. The Flexing Parallelogram is the Basis for the "Inertial Isolation Interferometer". The Inertial Balance Design Efficiently Decouples the Mirror Motion from all External Vibrations.

Figure 2. Auto-Aligned, Self Compensating Optics. The Optical Design of the Interferometer Compensates for Beamsplitter Vibration as Well as Corner Cube Shear by Using Folding Mirrors that are Rigidly Mounted to the Beamsplitter Assembly.

Figure 3. Response of: a) Balance and b) Unbalanced Isolation Interferometer to Vibration as Measured with HeNe Laser. Each Cycle Corresponds to Motion Over a Distance of One Laser Wavelength ($0.63 \mu\text{m}$).

Figure 4. Absorbance Spectrum of Polystyrene Measured with: a) Saturated MCT Detector. b) an MCT Detector using a Linearization Circuit, and c) a Non-Saturating Pyroelectric Detectors (DTGS).

Data Acquisition and Processing System

The advanced data system employs circuitry to accomplish high speed digitization, detector linearization, oversampling, and decimation. These features developed under a DoD sponsored research and development program [13] provide for detector limited signal-to-noise ratio (SNR) when a high speed, and high sensitivity, cooled Mercury Cadmium Telluride (MCT) detector is employed. However, accurate quantitative analysis requires detector linearity. MCT detectors are highly sensitive and fast, but are notoriously non-linear. On-Line has developed and patented a detector correction circuit based on the fundamental mechanisms governing carrier concentrations in photoconducting detectors [14]. Figure 4 compares an uncorrected MCT signal with a corrected signal and a signal from a deuterated triglycine sulfate (DTGS) detector which is linear but much slower and less sensitive. The corrected signal clearly matches the DTGS signal extremely well, while the uncorrected signal does not. This correction scheme is incorporated into On-Line's data processing electronics.

In conventional FT-IR spectrometry, there is a heavy dynamic range demand on digitizing the detector signal [15]. At the point of equal paths in the interferometer (centerburst), the signal is the sum of the intensities at all of the wavelengths in the spectrum, and therefore is very large. When a 16-bit digitizer is used with the gain matched to the centerburst signal, digitizer resolution in the wings of the interferogram (low signal) can often become the limiting factor contributing to noise. To alleviate this problem, a method has been developed which involves oversampling and decimation. This is accomplished by extending the IR filter bandwidth by a factor of 8 and digitizing 8 times more rapidly (oversampling) with a high speed A/D converter. Then the total number of data points are reduced back to the original number by co-adding neighboring points about the desired data points in a weighted fashion (finite impulse response filtering) and eliminating the extra points in between (decimation). By increasing the sampling speed, the required SNR in the interferogram and therefore the dynamic range requirements of an A/D converter are reduced. Accuracy is then recovered by decimation after digitization. Oversampling has the added advantage of making the measurement 64 times less sensitive to velocity jitter. At the same time the high speed digitizer permits scanning the mirrors 8 times faster. This further reduces the dynamic range requirements and effects of velocity jitters. The combination of these three design features provides an additional 3 bits of dynamic range (effective 19 bit digitizer). The high speed data system provides an oversampled 0.5 cm^{-1} resolution single-sided spectrum every 0.25 sec. A low resolution single sided spectrum can be delivered every 20 milliseconds.

Software

The user interface software employs's National Instrument's LabVIEW for the basic programming language. LabVIEW is an object orientated software development package in which programming is performed graphically with icons which represent different instruments, components of a sensor or control system, computing operations, or display functions. On-Line has created a library of icons for all the functions necessary to operate the FT-IR, perform Fourier transforms, apply quantitative analysis algorithms, display results, and interact with other components.

On-Line's FT-IR electronics include sensors and probe points for diagnostics during operation and maintenance. These are reported to an on-board microprocessor which provides alarm warnings of parameter drifts. This allows the instrument to forecast problems. This system supports maintenance by minimally trained personnel with remote assistance from the factory's service center. By connecting the system to the service center via modem, the system's health can be monitored, and questionable parts can automatically be ordered for replacement prior to failure.

PERFORMANCE

Performance in several categories is illustrated in Figs. 5 - 7. The instrument's signal-to-noise performance is illustrated in Fig. 5. In Fig. 5a, forty-five second's average of data at 4 wavenumbers is ratioed to a similar reference. The data were taken by a Thermoelectric (TE) cooled MCT detector with a cut-off at 1250 cm^{-1} . Peak to peak noise at 2500 cm^{-1} is about 0.001. In Fig. 5b, a one second average of data at 4 wavenumbers, are ratioed to similar reference. These data were taken with a higher sensitivity TE cooled MCT detector whose cut-off is at 1700 cm^{-1} . The peak to peak noise at 2500 cm^{-1} is about 0.0005.

Figure 5. Transmittance Spectra. a) A 45 Second Average at 4 Wavenumbers Ratioed to a 45 Second Average at 4 Wavenumbers using a TE Cooled Detector with a 1250 Wavenumber Cut-off. b) A One Second Average at 4 Wavenumbers Ratioed to One Second Averaged at 4 Wavenumbers using a TE Cooled Detector with a 1700 Wavenumber Cut-off.

Figure 6. Comparison of 100% Lines (10 Scans at 1 Wavenumber Resolution Taken at a Time Delay after a 10 Scan Reference at 1 Wavenumber). Spectra are taken with an On-Line Spectrometer through a 5 Meter Cell. a) Time Delay of 10 Minutes, b) Time Delay of 1 Hour, and c) Time Delay of 6 Hours.

The instrument stability is illustrated in Fig. 6. A collection of 10 scans at 1 cm^{-1} resolution taken at 10 minutes, 1 hour, and 6 hours is shown ratioed to a reference of 10 scans taken at time zero. The noise at 1 cm^{-1} taken through a 5 m cell is on the order of 0.005% peak to peak. The average position of the spectrum shows less than 0.001 variations from 1.000 at 10 minutes and less than 0.0025 variations at 6 hours. The major change at 6 hours is the water and CO_2 concentration.

The instruments vibration immunity is illustrated in Fig. 7. To test vibration immunity, a comparison was made between the Model 2001 Multi-Gas Analyzer and a commercial instrument. Both instruments were placed on a vibration table and subjected to vibration from 28 to 60 Hz. Figure 7 presents some typical results taken at 35 Hz. The figure compares 10 100% lines taken by ratioing 1/2 sec of data at 4 cm^{-1} to 1/2 sec of data at 4 cm^{-1} taken at 10 subsequent times. If there were no effects of vibration, the 100% lines would be at exactly 1.000. The On-Line spectrometer exhibits much less change in the 100% line compared to the commercial spectrometer.

Figure 7. Comparison of 100% Lines for On-Line and Commercial Spectrometer. 1/2 Sec Collection at 4 cm^{-1} . a) On-Line 2001, TE Cooled MCT, through Gas Cell; b) Commercial Spectrometer, Liquid N_2 Cooled MCT, No Gas Cell.

The maximum resolution of On-Line's instrument is 0.5 cm^{-1} which is important for resolving interferences such as NO to H_2O . The instrument is also very fast. Spectra at 0.5 wavenumber resolution can be taken at 4 scans/sec. Spectra at 32 cm^{-1} can be collected in 20 msec.

APPLICATIONS

Quantitative Gas Analysis

Both in-situ and extractive monitoring requires the development of robust software algorithm for quantitative analysis of gases. Such algorithms compared the measured spectrum to a spectrum for a known reference gas. On-Line's software uses a classical least squares (CLS) algorithm. Figure 8 presents the spectrum for a reference gas containing about 5 ppm of SO_2 , NO , and CO in nitrogen. The spectrum is taken at 1 wavenumber resolution in a 5.26 m cell as an average over 50 seconds. The temperature of the gas cell is 150°C . Clearly, the spectra for these three species are easily identified, well above the noise and free of cross interference.

The main problem with quantitative measurement is interference from water and CO_2 . Figure 9 presents the same calibration gas diluted with an equal volume flow of air containing CO_2 and H_2O . Water is a little over 1% and CO_2 is at 700 ppm. Figure 9 is on an absorbance scale 100 times larger than Fig. 8 and the spectra for SO_2 , CO , and NO are no longer visible.

The application of a quantitative classical least squares (CLS) analysis for SO_2 , CO and NO is presented in Fig. 10. The x-axis gives the time of the measurement, the y-axis is concentration in ppm. Each data point represents an average concentration measured over 5 seconds. The CO which has little interference from water and CO_2 exhibits an accurate quantitative analysis. It shows the introduction of the calibration gas near 100 seconds and the increase in concentration to almost the value in the calibration gas as the gas filled the cell. At 300 sec, an equal volume of air containing H_2O and CO_2 is introduced, and the CO level dropped to roughly half the full value. At about 750 sec, the flow of calibration gas is shut off. The

Figure 8. Spectrum of Calibration Gas (CO: 5.3 ppm; NO: 5.0 ppm; and SO₂: 4.6 ppm) in 5.26 m Gas Cell at 150 °C. 50 Sec Average at 1 Wavenumber Resolution.

Figure 9. Spectrum of Calibration Gas (CO: 5.3 ppm; NO: 5.0 ppm; and SO₂: 4.6 ppm) with Equal Flow of Air in 5.26 Gas Cell at 150 °C. 50 Sec Average at 1 Wavenumber Resolution.

Figure 10. CLS Analysis for CO₂, SO₂, CO, and NO with Regions Containing Strong Absorption Lines Eliminated and Perturbation Spectra for H₂O Added.

increase of CO₂ at 600 sec was obtained by breathing into the air intake and the increase in H₂O was obtained by heating a water bath in the air line. At 900 sec, the air is replaced by dry nitrogen.

As described in Ref. 8, water interferes with the measurement of SO₂ and NO. Two methods are used to address this problem. In the first method, certain spectral regions where there are strong absorption lines from interfering species, are eliminated from the CLS fit. The second method considers the problem that the water spectrum is not linear with concentration. To describe this, both multiple references for water at different concentrations, as well as perturbation spectra, which describe the first order change about each reference with concentration, are employed as an additional species in the CLS. Application of the two procedures removes most of the interference, so that the errors in SO₂, CO, and NO are 1 ppm or less, although the NO still appears to be systematically low in the presence of H₂O.

Application in a Black Liquor Recovery Boiler

One application being explored is in-situ monitoring in a pulp mill recovery boiler to improve the combustion performance. A field test at the Mörrums Bruk mill was performed to determine what species could be measured within the boiler. The measurement location was a line-of-sight located about 2/3 of the way up the ~ 100 feet high recovery boiler building. CO and fume concentrations were successfully measured in this part of the boiler.

Figure 11, which presents an FT-IR measurement across the boiler, indicates that near-IR radiation below 2.9 μm (above 3400 cm^{-1}) is completely blocked by the combustion environment (mostly fume). At longer wavelengths, above 2.9 μm (below 3400 cm^{-1}) however, mid-IR radiation does partially transmit.

Figure 11. FT-IR Measurement through a Recovery Boiler of a Paper Mill. Partially Transparent Windows in the Spectrum, where Light Scattering by the Fume is Decreased, are Labeled. The 2000 cm^{-1} Region provides a Measurement Window for Direct Combustion Zone CO Monitoring.

Figure 12. Analysis of CO in Boiler.

Figure 12 presents a difference spectrum calculated from two FT-IR measurements through the boiler. Each measured spectrum is scaled so that the H₂O will be subtracted in the CO region. One measurement was made during a high volume of air injection into the combustor (low CO), the other for a low volume of air injection (high CO). The figure also shows a CO reference and a water reference. The figure shows

that there are CO bands which are clear of H₂O interference. Thus, mid-IR measurements can be used to monitor CO concentration at the combustion zone. To analyze the CO concentration, we employed the peaks designated with stars. The measured CO within the boiler was well correlated with the volume of tertiary air and with the measurement of CO in the stack.

In-situ FT-IR Process Monitoring for Selective Noncatalytic Reduction of NO_x (SNCR)

The SNCR process can drastically reduce NO_x emissions from combustion facilities. However, improper control of the process can lead to the production of undesirable process byproducts. In-situ FT-IR provides the capability to simultaneously monitor the concentrations of NO_x and the process byproducts (NH₃, CO, N₂O) without the difficulties associated with extractive sampling. This will provide the feedback required to implement effective control of the SNCR process.

In order to demonstrate the feasibility of in-situ FT-IR for SNCR process monitoring, a series of measurements were made during a test at a lab-scale oil combustor used for SNCR process development [16]. A nitro-containing compound was added to the fuel to provide a controllable source of NO_x, and the SNCR reagent (aqueous urea solution) was injected into a temperature-controlled reaction zone (~1000°C). In-situ FT-IR measurements were made downstream (gas temperature of 450-550°C) with an On-Line Technologies Model 2100 FT-IR spectrometer. The spectrometer was installed with the IR beam traversing a 2-meter length of the flue duct longitudinally. Spectra measured during the test demonstrated that in-situ FT-IR could rapidly provide useful data for optimization of the process conditions.

The absorbance spectrum shown in Fig. 13 was computed by ratioing a spectrum collected during urea injection to a spectrum collected with no urea injection. Figure 13a shows the absorption of NH₃ resulting from the injection of excess reagent. Quantitative analysis was performed using a HITRAN reference spectrum to determine the NH₃ concentration (440 ppm). Figure 13b shows a negative absorbance for nitric oxide, indicating that the NO concentration in the flue gas was reduced with the introduction of the SNCR reagent. The quantitative analysis determined a 460 ppm reduction of NO, consistent with the data provided by the facility's CEM system.

Figure 13. Absorbance Ratio Spectrum (After/Before Reagent Injection) Showing the Presence of Excess NH₃ (a) and Reduction of NO (b). The Upper Spectra in a and b are the HITRAN Reference Spectra.

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Appendix E

Report which presents the field test results at the Black Liquor Recovery Boiler of a mill in the Southeast U.S.: Sep. 20 – Oct. 2, 1998.

Sequence of Events

Dec. 17, 1997:	Initial AFR telephone conversation to the mill to explore the possibility of a field test at the recovery boiler.
April 23, 1998:	Initial meeting at the mill for AFR to present the technology.
July 1, 1998:	Planning meeting at the mill.
July 29, 1998:	Collaborative non-disclosure agreement in place.
August 4, 1998:	Second planning meeting at the mill.
Sept. 20-Oct 3, 1998:	Field test on the recovery boiler.
Jan. 8, 1999:	1 st draft of field test report submitted to the mill.
Feb. 25 1999:	AFR/mill teleconference pertaining to field test report.
March 25, 1999:	2 nd draft of field test report submitted to the mill.
April 5, 1999:	AFR/mill teleconference pertaining to field test report.
April 13, 1999:	Final field test report submitted to the mill.
April 20, 1999:	AFR presentation of field test results at the mill.

Note: Over 70 e-mails were exchanged between AFR and the mill, as well as numerous telephone discussions and packets of information mailed in the sequence of events that led to this field test and resulting document.

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AFR

**FT-IR Spectroscopy
for Black Liquor Recovery Boiler Performance Monitoring**

May 3, 1999

(An Executive Summary is presented on pages ii – v)

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Executive Summary

Advanced Fuel Research, Inc. (AFR) is a 19 year old R&D firm located in East Hartford, CT. One research focus area of AFR is Fourier transform infrared (FT-IR) spectroscopy for industrial process monitoring. With sponsorship from the U.S. Department of Energy (DOE), AFR has developed advanced FT-IR hardware and FT-IR software for improved process monitoring of black liquor recovery boilers (1). The project recently concluded with the installation of three advanced FT-IR process monitors for a two week field test. The FT-IR instruments functioned in the harsh environment of the recovery boiler and provided real-time, important information regarding boiler conditions. This information can be utilized to enable better understanding and improved control of the boiler environment for increased combustion efficiency with minimal pollutant emissions.

The process monitors successfully monitored multiple gas concentrations at three locations in the black liquor recovery boiler. Two monitors were installed for line-of-sight measurements through the boiler's 30 foot wide combustion flow at 6th and 8th floor locations. At the bullnose (6th floor) and in front of the superheater (8th floor), the infrared light beams originating from the FT-IR spectrometers on one side of the boiler were aimed through open inspection ports so that they would traverse the combustion flow. The beams exited at opposing inspection ports where they were received by the infrared detector of each monitor. Both of these in-situ monitors quantitatively determined concentrations through the combustion flow for carbon dioxide (CO₂), carbon monoxide (CO), hydrochloric acid (HCl), and water (H₂O). All gases were measured simultaneously with data continuously collected and averaged over one minute time intervals. In addition, relative measurements of fume and carryover were obtained in the boiler.

The third process monitor was located at the effluent stack of the boiler where stack gas was continuously extracted and sampled in the flow cell of this monitor. For these stack gas measurements, data were continuously collected and averaged over two minute intervals. Simultaneous and quantitative process measurements of CO₂, CO, HCl, H₂O, sulfur dioxide (SO₂), nitric oxide (NO), nitrous oxide (NO₂), methane (CH₄) and reduced sulfur compounds were obtained.

The data presented in this report demonstrates that the FT-IR process monitors provide substantial information that can be used to optimize boiler operation. For example, CO is one indicator of combustion efficiency. High CO levels indicate poor combustion. Fig. E1 presents CO concentration measured through the combustion flow in front of the superheater (8th floor). Parts per million (ppm) of CO measured every minute for nearly 4 days is presented. CO ranges from near-zero ppm to over 1000 ppm during the 4 days. Also in Fig. E1 is the liquid flow rate of black liquor into the boiler in gallons per minute (GPM) over the same 4 days. Three times in the liquor flow rate trace (indicted by *), the liquor flow is increased and stabilized. CO is observed to increase many hundreds of ppms when the liquor is increased, but note that CO stays elevated for many hours at the new stable liquor flows. Combustion efficiency is down and pollutant emission is up for hours. Other parameters of boiler control could be adjusted in response to the high CO levels to optimize boiler operation, and the FT-IR process monitor provides on-line, real-time information to target optimized conditions.

In this executive summary, only one gas in the combustion flow and only one boiler operational parameter are presented. Black liquor boilers operate by complex chemical and physical processes, and a wealth of process information is necessary for improved control. The following report shows that the FT-IR instrumentation allows for on-line monitoring of numerous boiler species concentrations that are directly influenced by boiler operating conditions. The instrumentation is a valuable tool for studying species indicative of combustion efficiency (CO, CH₄) as well as the relationships between reacting boiler species such as SO₂, HCl and fume. Also, with appropriate modifications, the in situ monitors can obtain line-of-sight temperature measurements in the boiler which will further improve the understanding of

CO concentration measured by the in-situ instrument at the 8th floor location

Black Liquor Flow Rate

Figure E1. CO concentration (8th floor, in situ) and black liquor flow rate over 4 days.

boiler processes. The FT-IR data provide the information necessary for recovery boiler operators to control boilers to perform at high combustion efficiency with minimum pollutant emissions.

General Advantages of FT-IR Technology

Fourier transform infrared (FT-IR) gas analysis is based on the fact that every molecule, except homonuclear diatomics, has a unique set of rotational and vibrational frequencies that absorb and emit infrared energy in a characteristic manner. In general, it is possible to identify and quantify gases based on the location and magnitude of these absorptions, which occur throughout much of the infrared spectrum. Fig. E2 presents a spectrum which shows characteristic absorbance features for several selected gases in the long list of infrared active compounds. Since an FT-IR spectrometer is capable of recording infrared absorptions from about 500 cm^{-1} ($20\text{ }\mu\text{m}$) to 5000 cm^{-1} ($2\text{ }\mu\text{m}$), it can be used to identify and quantify an almost unlimited variety of compounds. This makes FT-IR unique in its ability to monitor many species simultaneously over a very wide concentration range, from sub-ppm to percent.

For in-situ analysis, such as through the recovery boiler, the FT-IR monitor is unique in its ability to provide simultaneous information on multiple gases and particles in the harsh process flow. For extractive gas analysis, such as at the recovery boiler stack where stack gas is continuously extracted into the flow cell of the FT-IR monitor, FT-IR offers substantial savings over traditional multi-species emissions stations. A single FT-IR based gas analyzer is capable of consolidating several racks of single gas analyzers into a single compact instrument, as well as reporting concentrations on species previously difficult to measure. Cheaper/Faster/Better features of FT-IR extractive multigas analyzers include:**

- ~ 70% less expensive than the cost of the traditional suite of single gas analyzers.
- ~ 6x less time required for routine calibration checks.
- one analyzer to measure CO_2 , H_2O , CO , NO , NO_x , SO_2 , CH_4 , C_2H_4 , CH_3OH , C_3H_6 , $\text{C}_2\text{H}_2\text{O}$, HCO_2H , HNO_2 , others
- only 1 or 2 routine calibration gases needed instead of every gas
- desktop size, takes up little space
- two people can lift it, easy to transport
- can fit in van, no trailer required
- measures "wet" gas stream, no gas dryers needed, no additional calculations back to wet basis concentrations
- speciation of hydrocarbons
- analysis library expands as needed for additional gases; no need to purchase additional single gas analyzers
- not limited in dynamic range as traditional analyzers

** The features listed are compared to the traditional multi-species emission station used to monitor the exhaust of gas turbine engines in engine test cells and on aircraft runways (2). A traditional emissions station is typically made up of 6-8 individual gas analyzers, and fully packaged costs up to \$200,000. Sponsored by the U.S. Air Force (3), AFR has performed head-to-head comparisons of the FT-IR analyzer to traditional emission stations at engine facilities of the U.S. Air Force and Pratt & Whitney.

Figure E2. FT-IR spectrum showing characteristic absorbance features of several selected gases in the long list of infrared active components.

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Introduction

A key operation in the Kraft pulping process is the firing of the black liquor recovery boiler where the two main objectives are the recovery of sodium and sulfur utilized in the pulping process and the generation of energy for mill use. Safe, efficient and environmentally acceptable operation of the boiler requires careful control of the operating conditions. Fume formation and carryover must be minimized and SO_2 , NO_x , HCl and CO levels in the flue gas maintained within required limits. Operation of the recovery boiler could be more efficiently achieved with better understanding of the chemical and physical processes in the boiler and with better sensors to monitor the boiler.

In the following report, the methodology, apparatus, and data are presented for a field test where Fourier transform infrared (FT-IR) spectroscopy was used to perform in situ and extractive measurements during the operation of a black liquor recovery boiler. Advanced Fuel Research, Inc. (AFR) transported three FT-IR based instruments to a paper mill for measurements during the period September 21 - October 2, 1998. Two in situ monitors were installed for line of sight measurements in the boiler and were used to determine H_2O , CO_2 , CO and HCl concentration as well as fume and carryover relative concentrations. In addition, a FT-IR based gas analyzer was located at the stack for extractive measurements of H_2O , CO_2 , SO_2 , NO_x , HCl , CO , CH_4 , and reduced sulfur compounds.

The FT-IR data for species concentrations demonstrated trends that correlated well with boiler operating conditions. The FT-IR data provides the additional information necessary for recovery boiler operators to better optimize operating conditions to control boilers to perform at high combustion efficiency with minimum pollutant emissions.

The data analysis portion of this report is organized in three sections. Section 1 presents FT-IR measurements at the three locations on the boiler for nominally constant boiler operating conditions (a "baseline" week). Section 2 presents FT-IR measurements at the three locations on the boiler when the boiler operating conditions were intentionally varied. Section 3 compares the FT-IR data to recorded operating conditions (e.g., black liquor flow rate, boiler excess O_2 , primary and secondary air flows) that were provided to AFR by the mill. Section 3 begins on page 21.

Methodology

Gas Analysis using Fourier Transform Infrared (FT-IR) Spectroscopy - FT-IR spectroscopy is a versatile method for quantifying a wide range of gases and is based on the fact that almost every molecule has a unique set of rotational and vibrational frequencies that absorb and emit infrared (IR) energy in a characteristic manner. For a stream containing only gases, a portion of incident IR energy can be transmitted through the stream if the product of gas concentration and pathlength is sufficiently low to avoid complete absorbance (i.e., opacity). The transmission is related to gas concentrations through Beer's Law, which can be expressed as:

$$\tau(\nu) = I(\nu)/I_0(\nu) = \exp [-k_g(\nu)C_gL] \quad (1)$$

where $\tau(\nu)$ = transmittance

$I(\nu)$ = intensity of IR radiation transmitted through the sample

$I_0(\nu)$ = intensity of transmitted IR with no sample

$k_g(\nu)$ = absorptivity for the gas, cm^2/mole

C_g = concentration of the gas, mol/cm^3

L = pathlength of IR beam through the sample

ν = spectral quantity in wavenumbers (cm^{-1})

Note that $k_g(\nu)$ is zero outside the gas absorption bands and is proportional to the gas concentration inside the absorption bands. Certain gases such as N_2 , O_2 and H_2 are IR inactive while most others have distinctive absorption bands. For very low concentrations of gas, a multipass cell can be employed to increase L and thus increase the absorption and sensitivity.

In general, it is possible to identify and quantify gases based on the location and magnitude of these absorptions, which occur throughout much of the infrared spectrum. Since a FT-IR spectrometer is capable of measuring infrared absorptions from about 500 cm^{-1} ($20\text{ }\mu\text{m}$) to 5000 cm^{-1} ($2\text{ }\mu\text{m}$), it can potentially identify and quantify an almost unlimited variety of compounds. FT-IR is unique in its ability to monitor many species simultaneously over a very wide concentration range. A single unit is capable of replacing several racks of single gas analyzers as well as reporting concentrations on species otherwise difficult to measure.

Calibration of the instrument for gas analysis requires the generation of a spectral library of references containing all the compounds of interest over the range of concentrations expected to be encountered. Since changes in temperature alter a molecule's rotational and vibrational energy distribution, these references should be recorded at the measurement temperature. This is a simple matter for extractive measurements, where the gas cell can be maintained at a constant temperature (150°C in the present case). However, for in situ measurements (e.g. in the boiler) temperature fluctuations and inhomogeneous temperature distributions make the choice of reference temperature more difficult. For the in situ work performed in this study, a temperature of 900°C was used to generate the references and assumed as a reasonable average temperature across the two lines-of-sight in the boiler.

(Note: in this present work, the in-situ monitors were configured for line-of-sight infrared transmission measurements. If line-of-sight emission spectroscopy is used simultaneously with transmission spectroscopy, the two measurements can be combined to provide the line-of-sight average temperature. This temperature information can then be used to improve the accuracy of the gas concentration measurements, as well as provide additional process information for process control. The emission/transmission (E/T) method is described in Attachment A.)

Particle Analysis using Fourier Transform Infrared (FT-IR) Spectroscopy - Equation 1 above defines the transmittance through a sample stream when only gases are present. For a sample stream containing both gases and particles, where one defines the extinction (F_{ext}), absorption (F_{abs}) and scattering (F_{sca}) efficiencies, the transmittance is given as:

$$\tau(\nu) = \exp \{ - [k_g(\nu)C_g + NAF_{\text{ext}}(\nu)] L \} \quad (2)$$

where:

N = number density of particles, no./cm^3

A = projected area of a particle, cm^2

$F_{\text{ext}}(\nu) = F_{\text{abs}}(\nu) + F_{\text{sca}}(\nu)$, (dimensionless)

The first term is due to gas absorption and the second term is due to particle absorption and scattering. The combination of gases and particles produces a spectrum with gas absorption peaks superimposed upon a baseline shift caused by particle extinction. It is important to note that gas absorptions occur as relatively narrow peaks on order of a few wavenumbers wide (or as bands up to a few hundred wavenumbers wide) whereas $F_{\text{ext}}(\nu)$ varies smoothly across the entire spectrum. Simple baseline subtraction can be applied to isolate the gas and particle spectral features.

As seen in Eq. 2, $-\ln \tau(\nu)$ is proportional to the particle number density. In addition, Mie theory, which requires knowledge of the particle composition, can be used to predict $F_{\text{ext}}(\nu)$ (4) and thus enable a determination of particle size provided that the measurement contains both scattering and absorption information. In addition, the analysis can be extended to include multiple particles and sizes by replacing $NAF_{\text{ext}}(\nu)$ in Eq. 2 with the sum: $\sum N_i A_i F_{\text{ext}i}(\nu)$.

In general, there are three size ranges to be considered for analysis of particles in the wavelength range of 20-2 μm (500-5000 cm^{-1}). When the particle diameters are large ($> 75 \mu\text{m}$), the particles scatter (by reflection and refraction) or absorb all the light incident upon them and consequently, $F_{\text{ext}}(\nu)$ is roughly independent of ν and the resulting extinction spectrum is essentially flat. When the particles are in the range of 2 - 75 μm , diffraction scattering also occurs and the data will exhibit a broad absorption-like feature at a wavelength that is related to the particle diameter. As the diameter decreases, this broad feature moves to shorter wavelengths (higher wavenumbers). In the third case, where the particles are smaller than the incident light wavelength (e.g., submicron particles), Rayleigh extinction occurs and the scattering is proportional to ν^4 .

Figures 1a and 1b illustrate the dependence of particle size on the predicted extinction spectra for two particle size ranges of titanium dioxide (TiO_2). TiO_2 is presented here since AFR has previous experience with this material. In Figure 1a, where the mean particle diameter is 0.6 μm , scattering below about 1500 cm^{-1} is observed to be nearly zero. The peak centered around 750 cm^{-1} is an absorption band characteristic of TiO_2 and is directly proportional to the particle mass. Above 1500 cm^{-1} , the scattering, which is a function of the particle size distribution, is observed to increase exponentially with increasing wavenumber (decreasing wavelength). In contrast, the extinction spectrum for particles with a mean diameter of 100 μm , shown in Figure 1b, is relatively flat and featureless throughout most of the spectrum. Below 1000 cm^{-1} the extinction begins to tail up due to diffraction scattering. One should note that the absorption feature for TiO_2 in the large particle case is minimal because the extinction is dominated by scattering.

As described above, the analysis can be extended to particle streams consisting of different particle size ranges. If the two TiO_2 size ranges in Figure 1 are mixed, the resulting extinction spectrum is simply the summation of the two individual extinction spectra and the two effects are easily separated. This particular situation is very similar to the environment in the recovery boiler.

In general, two classes of particles are of interest in the recovery boiler: fume and carryover. The fume is composed of submicron aerosols generated during the combustion of the black liquor on the bed, whereas the carryover is primarily composed of larger particles ($> 75 \mu\text{m}$) formed from the smelt residue left over from in-flight combustion of the liquor (5,6). Thus the fume particles are considered to be smaller in diameter and the carryover particles are considered to be larger in diameter than the wavelengths monitored by the FT-IR, much like the examples of TiO_2 in Figure 1. As a result, the fume and carryover will exhibit very different extinction effects which are readily distinguishable by FT-IR.

As described above, if the particles are not large and have unique absorption bands (e.g., fume), Mie theory can be employed to predict F_{ext} and then fit F_{ext} to the measured spectrum (assuming a flat baseline offset due to carryover) to determine the particle size and number density. Unfortunately, the main absorption band for fume ($\sim 1200 \text{ cm}^{-1}$) is just below the detector cutoff for the measurements obtained during this test. Thus, fume size and number density cannot be conclusively determined for these measurements. In this case, the measurement represents the total projected area of the fume particles across the boiler line of sight (7). However, if we assume that the size and chemical composition of the fume does not change significantly as operating conditions vary, we can measure relative changes in

Figure 1. Predicted extinction spectra for TiO_2 particles with mean diameters of a) $0.6 \mu\text{m}$ and b) $100 \mu\text{m}$.

concentration of the fume over time. The data reported for these measurements makes this assumption and is plotted as relative concentration.

Absolute determination of carryover size and number density is probably not possible by infrared analysis even if the measurement range is extended. The carryover particles are relatively large and thus will not exhibit strong absorption bands. Consequently, transmission measurements of carryover yield only the projected area of the carryover across the line of sight. Again, if we assume that composition and size do not change much, then relative changes in carryover concentration can be measured.

Apparatus

Figure 2 depicts a schematic of the black liquor recovery boiler and shows the locations for the in situ measurements and the extractive gas measurements. As shown, the in situ measurements were performed at the sixth and eighth floors which correspond to the bullnose and superheater sections of the boiler, respectively. Extractive measurements were primarily performed on the stack, where the gas analyzer was located in a small shed for protection against the elements.

For both the extractive and in situ measurements, analysis of the gas species concentrations was performed using the On-Line Technologies (On-Line) MG-2000 real-time analysis software. This software uses a classical least squares (CLS) routine that compares the measured spectra to the calibrated reference spectra measured for each of the expected compounds. To account for any non-linearity of the absorbance with concentration, each reference gas is recorded at several different concentrations, and the analysis software automatically selects the reference spectrum closest in concentration for the species being analyzed.

In situ Measurements – Both monitors employed for in situ measurements in the recovery boiler consisted of a FT-IR spectrometer, a set of beam expanding optics, a detector to acquire infrared transmission spectra and a computer to operate the instrument and analyze the data. Data were continuously collected over one minute time intervals at 1 cm^{-1} resolution in the range 1200 cm^{-1} to 5000 cm^{-1} ($8\mu\text{m}$ to $2\mu\text{m}$). The spectrometer, an On-Line Technologies Series 2100 Process FT-IR, was housed in a custom-designed, climate-controlled enclosure. Climate control was necessary due to the high temperatures ($100 - 115\text{ }^{\circ}\text{F}$) and humidity (up to 100 %) typical of the ambient environment during the course of these measurements. For temperature control, the enclosure was equipped with a Supercool™ air-to-liquid thermoelectric cooler (model AL-111-24-20) and maintained at $\sim 75\text{ }^{\circ}\text{F}$. In addition, the enclosure was purged with mill instrument air to avoid moisture condensation.

A spectrometer and its enclosure, together with the external beam expanding optics are depicted in Figure 3. Beam expanding optics were utilized to minimize beam divergence (and hence, infrared energy loss), across the boiler. As shown, the 1.25 " diameter IR beam exiting the spectrometer is expanded to 2.8 " upon passing through a dual off-axis paraboloidal mirror beam expander. An aperture limits the width of the IR beam to 1.5 inches so that the beam passing through the boiler is smaller than the optical access ports (discussed below). Two flat mirrors are then employed to steer the IR beam through the boiler. The flat mirrors provide fine control of horizontal and vertical positioning of the beam as well as two-axis, tilt control. This arrangement greatly simplifies alignment of the beam through the boiler and eliminates the need for large, heavy-duty positioning equipment.

The beam is projected across the boiler to a receiver where it is condensed to its original size and focused onto a thermoelectrically-cooled, mercury-cadmium-telluride (MCT) detector. The receiver, shown in Figure 4, also incorporates two flat mirrors to aid in alignment. Because the detector must be operated in an environment less than $100\text{ }^{\circ}\text{F}$ in temperature, it was housed in a cooled enclosure, where cooling was provided using Vortex™ coolers fed by mill instrument air.

Figure 2. Schematic of recovery boiler showing measurement locations for in-situ monitors and extractive gas monitor.

Figure 3. Photograph and schematic of the FT-IR spectrometer and coupling optics.

Figure 4. Photograph and schematic of the MCT detector and coupling optics .

Line of sight access through the 30 foot wide boiler was provided by two opposing 2" x 8" open ports. Both the spectrometer and receiver components of each system were located about four feet from each opposing port. Although the boiler operating pressure was slightly negative, occasional puffs of particles and gases were emitted from these openings due to turbulence in the boiler. To avoid potential contamination of the external optics of the spectrometer and receiver, high velocity fans were positioned at each port to direct escaping dust away from the instruments. During seven days of data collection, no significant buildup of dust on the optics was observed.

Extractive Gas Measurements – As mentioned previously, the majority of extractive measurements were obtained at the stack using the system depicted in Figure 5. The heart of the system is an On-Line FT-IR

Figure 5. Schematic of extractive gas analyzer installed at the stack.

based Multigas analysis system (MG-2010). The instrument combines a proprietary, aberration corrected, long-path gas cell (series 20/20TM, 5.26 meter optical pathlength, 1.6 liter internal volume) with a high-speed FT-IR spectrometer. As seen in the figure, sample gas is extracted from the stack using a 5' long, 1/4" stainless steel probe, and is diluted with dry instrument air. Due to the high concentration of water in the stream, the sample gas was diluted (2 to 1) to improve the analysis for some of the trace gases. The stream is then fed into a sample conditioning system (i.e., pump and flowmeter) through a 10' heat traced teflon line held at 150 °C. Particle filters are utilized to avoid contamination of the optics in the gas cell. A pressure transducer, located at the outlet of the Multigas analyzer, monitors the gas cell pressure. For these measurements, data were continuously collected and averaged over two-minute intervals while operating at 0.5 cm⁻¹ resolution.

Results and Discussion

Figure 6 displays a representative absorbance spectrum obtained with the extractive gas analyzer. The dominant absorption bands present in the spectrum are due to H₂O and CO₂ (H₂O absorbs in the two broad regions centered around 1600 cm⁻¹ and 3600 cm⁻¹, the CO₂ absorption occurs at ~ 2300 cm⁻¹). The inset in Figure 6 is an expanded region where CO absorption occurs, and is shown superimposed with a 340 ppm CO reference (red); a nearly perfect match.

Figure 6. Typical absorbance spectrum recorded with the extractive gas analyzer. Shown in the inset is a 340 ppm CO reference (red) superimposed over the sample spectrum.

Figure 7 depicts a representative absorbance spectrum recorded with an in situ monitor. Again, the dominant absorption bands are due to H_2O and CO_2 . In addition, the spectrum shows a wavelength dependent baseline shift, denoted by the solid line, which is caused by a combination of fume and carryover particle scattering. A blue dashed line demarcates the scattering contributions of the fume and carryover. Also shown is an expanded region where HCl absorption occurs, and is superimposed with a 21 ppm HCl reference (red).

Figure 7. Typical absorbance spectrum recorded with the in situ instrument. Contributions to the baseline shift by fume (wavelength dependent scattering) and carryover (wavelength independent scattering) are indicated. The inset contains an expanded spectral region superimposed with a 21 ppm HCl reference (red).

Detection limits for species in the extractive gas analyzer are indicated below in Table 1. The detection limits for the gas analyzer are estimated using a two minute scan at 0.5 cm^{-1} , twice the noise equivalent absorbance in the analysis region indicated, and assume a dry sample. The analysis regions were selected to reduce the impact of water interference. This is most critical for NO_2 , NO , and SO_2 , which had less than 1 ppm error related to water interferences encountered during the test. Also given in Table 1 is the range of concentrations for which the instrument was calibrated. H_2S is not listed in Table 1 since it is a weak absorber of IR radiation and has a minimum detection limit on the order of 1000 ppm, which is much too high to be useful for boiler monitoring.

Species	FT-IR Multigas Analyzer		
	Detection Limit (ppm)	Analysis Region (cm^{-1})	Calibrations Recorded
H_2O	900 (.09%)	1100-1173	0 to 44%
CO_2	2700 (.27%)	1000-1100	0 to 20%
CO	2	2207.8-2229.1	0 to 10%
NO	4.5	1849.4-1857.8	0 to 2000 ppm
NO_2	1	1583.8-1589.3	0 to 400 ppm
SO_2	10	1100-1173	0 to 400 ppm
HCl	1	2695-2872	0 to 50 ppm
CH_4	3.5	2671-3000	0 to 5%
Methyl Mercaptan	15	2814-3000	0 to 200 ppm
Methyl Sulfide	7	2814-3000	0 to 400 ppm
Methyl Disulfide	4	2814-3000	0 to 300 ppm

Table 1. Detection limits for species measured with the extractive FT-IR gas monitor.

Table 2 lists the species measured with the in situ monitors, as well as estimates of their respective detection limits. The species listed as "Particle Loading" corresponds to the regions used to calculate the relative amounts of fume and carryover present during the measurements.

Species	FT-IR In-Situ Analyzer	
	Detection Limit (ppm)	Analysis Region (cm^{-1})
H_2O	1000	2782-3002
CO_2	1500	2060-2125
CO	15	2098-2113
HCl	10	2695-2872
CH_4	15	2671-3000
Particle loading	-	2520-2560
	-	4580-4620

Table 2. Detection limits for species measured with the in situ FT-IR monitors.

Measurement results and analyses for the two weeks of on-site testing are presented in the following three sections:

Section 1: Week 1, baseline data, nominally constant boiler conditions (September 24-26, 1998), comparing FT-IR data at the three locations on the boiler.

Section 2: Week 2, variable boiler conditions (September 28 – October 2, 1998), comparing FT-IR data at the three locations on the boiler.

Section 3: Week 2, variable boiler conditions, comparing FT-IR data to boiler operating conditions.

Section 1: Week 1, baseline data, nominally constant boiler conditions (September 24-26, 1998), comparing FT-IR data at the three locations on the boiler.

(Note: During this first week, the three instruments were running simultaneously for only a relatively short period, as will be apparent in the presented data traces.)

Figure 1.1. presents the concentrations of CO₂ measured at the three locations on the boiler during "baseline" conditions. Similar concentration levels (~10% CO₂) and trends are observed in the period where instruments are running simultaneously.

The H₂O data in Figure 1.2 contain short term oscillations which are a result of the automated sootblowing sequence employed for cleaning the heat transfer tubes in the boiler; the steam injected by the sootblowers raises the local H₂O concentration. The effect is most pronounced at the in situ locations. The H₂O traces at the three locations show good agreement in concentrations and trends, as did the CO₂.

Figure 1.3 presents the data traces for CO concentration measured at the three locations. Again, the three measurement locations agree in pattern, but show that CO concentration is not as stable as CO₂ and H₂O. The CO data indicates periods of incomplete combustion in the boiler (this will be discussed further in Section 3).

Other trace gases (CH₄, HCl, SO₂, NO, NO₂) were looked for in both the in situ and extractive measurements. During this week of baseline conditions the stack gas data presented no indication of SO₂. Minimal CH₄ was detected (up to 6 ppm), and NO and NO₂ concentrations were measured at the stack with ranges of 45-75 ppm and 0-12 ppm, respectively. HCl data at the 6th and 8th floors are presented in Figure 1.4, showing agreement where the two data traces overlap. Extractive measurements of HCl are not considered reliable due to adsorption problems onto the gas transfer lines, and are not presented.

Section 2: Week 2, variable boiler conditions (September 28 – October 2, 1998), comparing FT-IR data at the three locations on the boiler.

(Note: For the data traces presented in this section, the extractive system was not in place to collect data until ~ 28 hours after the start of the data collection with two in situ systems)

Figures 2.1, 2.2 and 2.3 present the measured concentrations of CO₂, H₂O, and CO, respectively.

Figure 2.1 for CO₂ indicates similar trends and concentration levels at all three measurement locations. The short term oscillations caused by the steam injection of the soot blowers is apparent as in the previous baseline data, but the larger, abrupt shifts in the concentration traces are caused by changes in boiler operating conditions that will be presented and discussed in Section 3.

Similar correspondence at the three measurement locations for H₂O is shown in Figure 2.2, and for CO in Figure 2.3.

Figure 2.4 presents HCl concentration data for week 2 from the in situ locations. The in situ measurements of HCl obtained on the sixth and eighth floors track each other quite well.

(Note: Text continues on p.21)

Figure 1.1 CO₂ concentrations measured at the three locations on the recovery boiler (baseline week)

Figure 1.2 H₂O concentrations measured at the three locations on the recovery boiler (baseline week)

Figure 1.3 CO concentrations measured at the three locations on the recovery boiler (baseline week)

Figure 1.4 HCl concentrations measured at the in-situ locations on the recovery boiler (baseline week). Note: the extractive HCl measurement is not deemed reliable and is not plotted.

CO₂ concentration measured by the extractive gas analyzer at the stack

CO₂ concentration measured by the in-situ instruments on the 6th and 8th floor

Figure 2.1 CO₂ concentrations measured at the three locations on the recovery boiler (second week)

Figure 2.2 H₂O concentrations measured at the three locations on the recovery boiler (second week)

Figure 2.3 CO concentrations measured at the three locations on the recovery boiler (second week)

Figure 2.4 HCl concentrations measured at the in-situ locations on the recovery boiler (second week). Note: the extractive HCl measurement is not deemed reliable and is not plotted.

The gases CH_4 , SO_2 , NO and NO_2 were only monitored at the stack by the extractive system. The data traces for these gases are shown in Figure 2.5. As will be discussed in more detail in Section 3, CH_4 concentration changes correlated well with CO , and SO_2 correlated with HCl .

The in situ monitors also provide information regarding the particulate species present in the boiler. Trend lines for submicron particles (fume) and much larger particles (carryover) are displayed in Figure 2.6. The measurements reported for the carryover are for the eighth floor, in situ monitor only. The sixth floor ports tended to foul with dendritic growths that caused errors in the carryover measurements at that location. Please note that gaseous and fume measurements are not affected by the spectrally flat baseline shift caused by partial port fouling. Again, these measurements are relative values only and the units are arbitrary. The data shown represent some fraction of IR light (which, in the case of fume, is wavelength dependent) which is attenuated by the particles. If we assume that the composition and particle size distribution of the fume and carryover do not change significantly, then the data can be directly related to concentration. The concentrations (attenuation) of both the fume and carryover are observed to fluctuate significantly during the test.

Section 3: Week 2, variable boiler conditions, comparing FT-IR data to boiler operating conditions

Since in situ FT-IR data from the 6th and 8th floors agreed in trends and magnitude, the following comparisons to boiler operating conditions will concentrate on 8th floor in situ data and extractive stack data.

Figure 3.1 compares the in situ concentration traces of CO_2 and H_2O to the black liquor flow rate. Clearly demonstrated is the sensitivity of the in situ measurement to changes in liquor flow rate. When liquor is decreased, measured gas concentrations decrease. Likewise, liquor increases result in increased gas concentrations.

Figure 3.2 compares the in situ concentration trace of CO to the liquor flow rate and to boiler excess O_2 . We believe this comparison to be an important presentation of the process monitoring feature of the FT-IR system. At each location where the liquor rate is increased, CO rises significantly and maintains elevated concentration even well after the liquor rate is stabilized. However, elevations of CO concentration correlate extremely well with when the boiler excess O_2 level drops below 3%, and corresponding decreases in CO occur when excess air is brought back above 3%. Many operating parameters influence the state of the combustion conditions in the expanse of the boiler. During this particular boiler set-up the data indicates that when the liquor flow rate is at the 200 GPM level, one is not able to operate the boiler below 3% excess O_2 without elevating levels of CO . When the liquor flow rate is up at the 240 GPM level, it appears that one is not able to operate below about 4% without elevating CO . Boiler set-up is a complex balance of conditions that influence the chemical and physical processes in the combustion flow. The FT-IR system provides the gas concentration data that can be used to balance the many boiler operating parameters for high combustion efficiency.

(Note: Text continues on p. 26)

Figure 2.5 CH₄, SO₂, NO, and NO₂ concentrations measured at the stack location on the recovery boiler (second week).

Figure 2.6 Relative fume and carryover concentrations measured at the in-situ locations on the recovery boiler (second week). Note: occasional slagging of the 6th floor ports resulted in unreliable carryover measurements, which are not plotted.

Figure 3.1 CO₂ and H₂O concentrations (8th floor, in situ) and the black liquor flow rate.

CO concentration measured by the in-situ instrument at the 8th floor location

Black Liquor Flow Rate

Boiler Excess Oxygen

Figure 3.2 CO concentration (8th floor, in situ), black liquor flow rate, and boiler excess O₂.

In Figure 3.3, the in situ CO trace is again presented with boiler excess O₂, and the CH₄ trace at the stack is also included. Elevated levels of CH₄ would be expected to accompany elevated levels of CO since both gases indicate incomplete combustion. Elevated levels of both gases correspond to a condition where the boiler excess O₂ drops below 3% (Note: The extractive CH₄ data does not begin until ~28 hours after the start of the in situ measurements, so there is no CH₄ data for comparison early in the run).

Figure 3.4 compares boiler excess O₂ to the measured concentrations of HCl (in situ) and SO₂ (extractive at stack). SO₂ measured at the stack is proportional to the HCl measured in the boiler, and both are related to the boiler excess O₂. HCl and SO₂ are observed to generally be at highest levels when boiler excess O₂ is above 5%.

The FT-IR measurements indicate that to maximize combustion efficiency for this particular boiler set-up, as indicated by low levels of CO₂ and CH₄, boiler excess O₂ at about 4% is necessary. Dropping below 4% with liquor rate approaching 240 GPM results in increases of hundreds of ppm for CO and tens of ppm for CH₄. But the boiler excess air must be maintained below 5% for reduced levels of HCl and SO₂. NO and NO₂ concentrations were also continuously monitored (refer back to Figure 2.5), but no clear correlation was identified with boiler operating conditions at this time.

This analysis of the data (CO vs excess O₂ vs liquor rate) during the second week of varying boiler conditions is confirmed by revisiting week 1 baseline data during nominally constant boiler conditions. In Figure 3.5, the baseline traces for liquor flow and excess O₂ are compared to measured CO. For nominally constant liquor flow in the 240 GPM range, excess O₂ is, for the most part, constrained between 3 and 4%. Approaching 4% excess O₂ results in the low concentration periods of CO, while dropping towards 3% excess O₂ results in considerable CO increase (hundreds of ppms). The FT-IR data suggest that operating slightly above 4% excess O₂ at this liquor flow would have optimized combustion efficiency without greatly influencing (i.e., elevating) HCl and SO₂ levels during the baseline week.

Figure 3.6 compares the relative fume and carryover measured in situ at the eighth floor with the flow rates of both primary and secondary air. Changes in concentrations for both the fume and carryover are evident throughout the week. In particular, the fume is observed to track changes in the primary and secondary air flow which also corresponds with a change in liquor firing rate. In addition, the relative concentration of carryover is observed to increase 60% (from 25 to 40) and 48% (27 to 40) during two periods where air flows were abruptly increased.

Figure 3.7 compares a plot of relative fume with the excess O₂ and the HCl concentration (measured in situ). We note an inverse relationship between the fume and HCl. The regions of highest fume concentration correspond to regions where the boiler excess O₂ drops and to where the HCl concentration is relatively low.

Conclusions

The results show that FT-IR instruments can function in the harsh environment of the recovery boiler and provide useful information. The data presented in this report has demonstrated that the advanced FT-IR process monitors provide substantial information that can be used to optimize boiler operation.

(Note: Text continues on p.32)

CO concentration measured by the in-situ instrument at the 8th floor location

CH₄ concentration measured by the extractive gas analyzer at the stack

Boiler Excess Oxygen

Figure 3.3 CO concentration (8th floor, in situ), CH₄ concentration (stack, extractive) and the boiler excess O₂.

HCl concentration measured by the in-situ instrument at the 8th floor location

SO₂ concentration measured by the extractive gas analyzer at the stack

Boiler Excess Oxygen

Figure 3.4 HCl concentration (8th floor, in situ), SO₂ concentration (stack, extractive) and the boiler excess O₂.

CO concentration measured by the in-situ instrument at the 8th floor location

Black Liquor Flow Rate

Boiler Excess Oxygen

Figure 3.5 Week 1 CO concentration (6th and 8th floor in situ), black liquor flow rate, and boiler excess O₂.

Relative fume concentration measured by the in-situ instrument at the 8th floor location

Relative carryover concentration measured by the in-situ instrument at the 8th floor location

Primary and secondary air flow rates

Figure 3.6 Relative fume and carryover concentrations (8th floor, in situ) and the boiler air flow rates (primary and secondary).

Relative fume concentration measured by the in-situ instrument at the 8th floor location

Boiler Excess Oxygen

HCl concentration measured by the in-situ instrument at the 8th floor location

Figure 3.7 Relative fume concentration (8th floor, in situ), the boiler excess O₂, and HCl concentration (8th floor, in situ).

The FT-IR instrumentation provides on-line monitoring of numerous boiler species concentrations that are directly influenced by boiler operating conditions. The instrumentation is a valuable tool for studying species indicative of combustion efficiency (CO , CH_4) as well as the relationships between reacting boiler species such as SO_2 , HCl and fume. With appropriate modifications, the in situ monitors can also obtain line-of-sight temperature measurements in the boiler which will further improve the understanding of boiler processes. In addition, the measurement range of the instrument can be extended for more conclusive measurements of fume size and number density. The FT-IR data provide the information necessary for recovery boiler operators to balance operating conditions to control boilers to perform at high combustion efficiency with minimum pollutant emissions.

References

- 1 DOE Cooperative Agreement No. DE-FC02-93CH10565, "In-Situ FT-IR Monitoring of a Black Liquor Recovery Boiler," PI: Dr. Peter Solomon; DOE Project Monitor: Ken Johnson (tel. 303-275-4726), Golden Field Office, Golden, CO.
- 2 Marran, D., Nelson, C., Markham, J., Jalbert, P., and Gardner, D., "The Application of FT-IR Spectroscopy to Turbine Engine Exhaust Monitoring-A Compact, Less Expensive Alternative to Single Gas analyzers," (to be published). A joint publication between AFR and Arnold Engineering Development Center (AEDC) of Arnold Air Force Base.
- 3 DoD/AF SBIR Phase II Contract #F41624-97-C-0003, "Advanced FT-IR Gas Analysis Instrument for Improved Process Monitoring and On-Site Characterization," (March 1997 - March 1999), PI: James R. Markham; Gina Graziano of Air Force Research Laboratories (Tyndall AFB) is the AF Project Officer (Phone #850-283-6259).
- 4 Bohren, G.F. and Huffman, D.R., Absorption and Scattering of Light by Small Particles, Wiley, New York, 1983.
- 5 Adams, T.N., Frederick, W.J., Kraft Recovery Boiler Physical and Chemical Processes, The American Paper Institute, Inc., 1998.
- 6 Sinquefield, S.A., Baxter, L.L., and Frederick, W.J., "An Experimental Study of the Mechanisms of Fine Particle Deposition in Kraft Recovery Boilers", TAPPI Proceedings, 1998 Int. Chemical Recovery conference, p. 443-467.
- 7 Morrison, P.W. Jr., Cosgrove, J.E., Carangelo, M.D., Solomon, P.R., Leroueil, P., and Thorn, P.A., "Fourier Transform Infrared (FTIR) Instrumentation for Monitoring Recovery Boilers," Tappi Journal, Vol 74, #12, p. 68-78, (1991).

Attachment A

Emission/Transmission (E/T) Spectroscopy for In-Situ Temperature Measurement

AFR has been one of the leaders in developing in-situ diagnostics based on FT-IR spectroscopy. FT-IR emission/transmission line-of-sight spectroscopy has been developed, patented, and applied to industrial combustors for energy production, incineration, and chemical recovery. AFR publications which include the methodology and measurements include:

Markham, J.R., Cosgrove, J.E., Nelson, C.M., Bonanno, A.S., Schlieff, R.E., Stoy, M.A., Glatzmaier, G.C., Bingham, C.E. and Lewandowski, A.A., "In-Situ FT-IR Monitoring of a Solar Flux Induced Chemical Process," *ASME Journal of Solar Energy Engineering*, **119**, 219-224 (1997, August). A joint publication with the DoE National Renewable Energy Laboratory (Golden, CO) and Solar Reactor Technologies, Inc (Miami, FL).

Morrison, P.W.Jr., Cosgrove, J.E., Carangelo, M.D., Solomon, P.R., Leroueil, P., and Thorn, P.A., "Fourier Transform Infrared (FTIR) Instrumentation for Monitoring Recovery Boilers", *Tappi Journal*, Vol 74, #12, p. 68-78, (1991).

Solomon, P.R., and Best, P.E., "Fourier Transform Infrared Emission/Transmission Spectroscopy in Flames," Chapter 11 in Combustion Measurements, N. Chigier (Editor), Hemisphere Publishing, NY 1991.

Morrison, P.W., Jr., Solomon, P.R., Serio, M.A., Carangelo, R.M., and Markham, J.R., "FT-IR Spectroscopy in Process Monitoring, Parts I & II," *Sensors Magazine*, 8, (12) pp. 32-38, & (13) pp. 26-30 (1991).

The second publication in the above list pertains to AFR's first field test at a black liquor recovery boiler. This earlier work (1991) was the precedent that led to the present DOE sponsored project concerned with FT-IR hardware and software improvements, and further field testing to prove the instrumentation and analysis for routine process monitoring of recovery boilers.

Basically, the E/T method utilizes two pieces of information from the same optical path: 1) the transmission information where a modulated infrared beam originating at the FT-IR spectrometer is sent through the hot process flow to the transmission detector; and 2) the emission information where the infrared energy emitted by the hot process flow is collected by the spectrometer and directed to an emission detector.

Figures A1 and A2 present laboratory data to demonstrate the analysis for two cases: hot gases (Fig. A1) and hot gases with soot particles (Fig. A2). Infrared transmittance through the hot streams, infrared radiance from the hot streams, and the infrared temperature spectrum (radiance divided by 1-transmittance) compared to blackbody radiance for each hot stream are presented. For each hot stream, gas and particle concentrations can be quantified by absorption and radiance intensities since the temperature is accurately determined. The broad-band continuum in the presence of particles is obvious in Fig. A2. For this example, the gases and soot are at the same temperature (Fig. A2c).

If the gases were at higher or lower temperature than the soot, gas bands would protrude above or below the soot continuum, respectively, and could be analyzed independently for temperature.

Figure A1. Spectra for acetylene, CO₂, and butane at 555 K in the heated tube reactor: a) 100 (1-transmittance), b) radiance, and c) normalized radiance (b + a). The black-body spectrum at 565 K is fit ignoring the shaded regions away from the absorption bands.

Figure A2. Butane and CO₂ in the entrained flow reactor at 1300 K: a) 100 (1-transmittance), b) radiance, and c) normalized radiance (b + a).

As expected, industrial process flows offer additional analysis challenges. In the case of a black liquor recovery boiler, the hot fume particles not only emit radiance, but also scatter (reflect) a significant amount of hot boiler wall radiance into the emission beam path. Fig. A3 presents two representative normalized radiance spectra (i.e., the temperature spectra obtained from emission/(1-transmission)) measured in the heat transfer section of a recovery boiler during AFR's first field test in 1991. One was measured for a liquor flow of 200 GPM, the other for 325 GPM. Two blackbody (Planck function) curves are overlaid on each spectra. The higher temperature blackbody for each overlays in spectral bands for H₂O, CO and fume (indicated by circles). Intuitive expectation is that the fume and gas temperature should be the same. The lower temperature blackbody for each overlays in spectral bands where fume scattering of wall radiation is dominant at large wavenumbers (indicated by rectangles). The comparison of the two spectra indicate that both gas and wall temperatures increased 100 degrees Kelvin for the higher liquor flow.

It should be noted that the 1991 field test was performed with a then state-of-the-art commercially available FT-IR spectrometer that AFR purchased from the Canadian manufacturer and modified to provide E/T capabilities. AFR holds the patent on the FT-IR E/T method and system. At the most recent 1998 field test, AFR's proprietary advanced FT-IR spectrometers were used. These present state-of-the-art FT-IR systems provide the advances in hardware and software necessary for routine industrial process monitoring. These are manufactured by AFR's spin-off company, On-Line Technologies, Inc., but the capability for simultaneous E/T spectroscopy with these new spectrometers is still under development.

Figure 3A. Normalized radiance spectra at two different flows of black liquor. The spectra are overlaid with best-fit Planck functions for the gas and fume temperatures (upper curves) and the boiler wall temperature (lower curves).

Appendix B

Supplemental Boiler Data

Figure B1. Black liquor flow, secondary gas flow, and boiler excess oxygen.

Primary Air

Secondary Air

Primary+Secondary Air

Figure B2. Primary and secondary air flows.

Figure B3. Primary, secondary, and tertiary air duct pressure.

Figure B4. Black liquor nozzle pressure, temperature, and percent solids.

Figure B5 Steam flow, final steam temperature, and total liquor firing rate.

Figure B5. Steam flow, final steam temperature, and total liquor firing rate.

Figure B6. Boiler and economizer DP.

Appendix F

AFR transparency presentation (April 20, 1999) of the project's final field test results to the mill in the Southeast U.S. Included in the presentation is a comparison of extractive FT-IR gas concentration measurements to traditional single gas analyzers at a gas turbine engine or jet engine test cell (we acknowledge DOD/Air Force contract #F41624-97-C-0003 for support of this work). This comparison was made to show validation of our FT-IR measurements since native gas measurement data were not available at the boiler. Included in this presentation are photographs of the FT-IR systems at the recovery boiler and the stack location.

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Schematic of Recovery Boiler Showing Measurement Locations for In-Situ Monitors and Extractive Gas Monitor

Fourier Transform Infrared (FT-IR) Spectroscopy

- Over 110 publications on FT-IR technology
- Eighteen FT-IR patents and six FT-IR patents pending
- Fifty-six FT-IR field tests
- Spin-off company manufacturing / marketing FT-IR systems
- R&D 100 Award in 1994
- R&D 100 Award in 1995
- R&D 100 Award in 1996

FT-IR Gas Analysis

Almost every compound has a unique set of rotational and vibrational frequencies

Full Spectral Measurement

- Permits post-test data validation

Field Tests

- Utility Boilers
- Paper Mill Recovery Boilers
- Incinerators
- Semiconductor Fabrication
- Glass Plant
- High Flux Solar Furnace
- Jet Engine Test Cells

F100-PW-220/F100-PW-220E TURBOFAN ENGINE

Vital Statistics

Maximum Thrust (Full Augmentation)	23,770 pounds (105.7 kN)
Intermediate Thrust (Nonaugmented)	14,590 pounds (64.9 kN)
Weight	3,234 pounds (1467 kg)
Length	191 inches (4.85 m)
Inlet Diameter	34.8 inches (0.88 m)
Maximum Diameter	46.5 inches (1.18 m)
Bypass Ratio	0.6
Overall Pressure Ratio	25 to 1

Schedule

Qualification Complete	March 1985
Production Introduction	November 1985
Operational Introduction	June 1986

The F100-PW-220E engine is an upgraded F100-PW-100 or F100-PW-200 with the operability, durability and maintainability features of the F100-PW-220.

Pratt & Whitney

A United Technologies Company

P.O. Box 109600
West Palm Beach, FL 33410-9600
561 796-2000

Single Gas Analyzers vs. FT-IR

Many single gas analyzers are traditionally used for turbine exhaust monitoring

- ♦NO
- ♦NO₂
- ♦CO
- ♦CO₂
- ♦H₂O
- ♦Methane
- ♦Formaldehyde
- ♦Ethylene
- ♦Propylene
- ♦Methanol
- ♦Formic Acid
- ♦Nitrous Acid
- ♦SO₂

+ Almost any other IR active compound

A single rugged, portable FT-IR multigas analyzer can replace the bulk of traditional analyzers + measure many other gases

Typical Spectra Recorded During Test (test point 60, 5:33 PM)

Head to Head Comparisons: Nitrogen Compounds

Head to Head Comparisons: Incomplete Combustion Products

AFR Events in Turbine Engine Exhaust Monitoring

Near Future

- *AEDC to have a 2 month trial (June-July)*
- *2nd Pratt & Whitney test vs. EPA certified trailer*
- *Joining SAE Committee at their request*
- *Continued updates to PIWG*

In-Situ and Extractive FT-IR Monitoring of Black Liquor Recovery Boilers

Mr. James Markham

Mr. Joseph Cosgrove

Dr. David Marran

Dr. Chad Nelson

Mr. Jorge Neira

Dr. Peter Solomon

Department of Energy Cooperative
Agreement No. DE-FC02-93CH10565

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Recovery Boiler Project Goals

- To demonstrate the feasibility of *In-Situ* FT-IR monitoring of recovery boilers
- To obtain data that provides insight to process chemistry
- To implement extractive FT-IR for monitoring gas emissions in real-time
- Ability to determine process variations
- Develop complete system that can help improve efficiency of the recovery boiler

Schematic of Recovery Boiler Showing Measurement Locations for In-Situ Monitors and Extractive Gas Monitor

6th and 8th Floor In-Situ Measurement Geometry. The FT-IR Beam Passes Through the 30' Wide Combustion Flow

Photographs of the FT-IR Process Monitor Installed at the 8th Floor of the Black Liquor Recovery Boiler

The infrared beam is entering the open slot on the wall of the boiler and passes through the 30 feet of black liquor combustion (note high temperature orange color in slot) to a matching open slot and detector on the other side of the boiler.

Schematic of Extractive Gas Analyzer Installed at the Stack

Photograph of the Effluent Stack of the Recovery Boiler

*An FT-IR Stack Gas Monitor is Installed in the
Enclosure on the Side of the Stack*

Typical Absorbance Spectra Recorded with the Extractive Gas Analyzer

Typical Absorbance Spectrum Recorded with the In-Situ Instrument

Detection Limits for Species Measured with the Extractive FT-IR Gas Monitor

Species	FT-IR Multigas Analyzer		
	Detection Limit (ppm)	Analysis Region (cm ⁻¹)	Calibrations Recorded
H ₂ O	900 (.09%)	1100-1173	0 to 44%
CO ₂	2700 (.27%)	1000-1100	0 to 20%
CO	2	2207.8-2229.1	0 to 10%
NO	4.5	1849.4-1857.8	0 to 2000 ppm
NO ₂	1	1583.8-1589.3	0 to 400 ppm
SO ₂	10	1100-1173	0 to 400 ppm
HCl	1	2695-2872	0 to 50 ppm
CH ₄	3.5	2671-3000	0 to 5%
Methyl Mercaptan	15	2814-3000	0 to 200 ppm
Methyl Sulfide	7	2814-3000	0 to 400 ppm
Methyl Disulfide	4	2814-3000	0 to 300 ppm

Detection Limits for Species Measured with the In Situ FT-IR Monitors

Species	FT-IR In-Situ Analyzer	
	Detection Limit (ppm)	Analysis Region (cm ⁻¹)
H ₂ O	1000	2782-3002
CO ₂	1500	2060-2125
CO	15	2098-2113
HCl	10	2695-2872
CH ₄	15	2671-3000
Particle loading	-	2520-2560
	-	4580-4620

Many Operating Parameters Influence Combustion Conditions in the Expanse of the Recovery Boiler

Recovery Boiler

- *Black Liquor Flow Rate*
- *Liquor Temperature*
- *Nozzle Pressure*
- *Percent Solids*
- *Primary Air*
- *Secondary Air*
- *Tertiary Air*
- *Mixing/Flow Patterns*

Variable Condition Week

CO₂ concentration measured by the in-situ instrument at the 8th floor location

H₂O concentration measured by the in-situ instrument at the 8th floor location

Black Liquor flow rate

CO₂ and H₂O Concentrations
(8th floor, in situ) and the
Black Liquor Flow Rate

Variable Condition Week

CO Concentrations Measured at
the Three Locations on the
Recovery Boiler (second week).

Variable Condition Week

CO concentration measured by the in-situ instrument at the 8th floor location

Black Liquor Flow Rate

Baseline Condition Week

CO concentration measured by the in-situ instrument at the 8th floor location

Black Liquor Flow Rate

Week 1 CO Concentration
(6th and 8th floor in situ) and
Black Liquor Flow Rate

Baseline Condition Week

CO concentration measured by the in-situ instrument at the 8th floor location

Black Liquor Flow Rate

Boiler Excess Oxygen

Week 1 CO Concentration
(6th and 8th floor in situ) and
Black Liquor Flow Rate,
and Boiler Excess O₂

How HCl is Formed

Reaction

- $2\text{NaCl} + \text{SO}_2 + \text{H}_2\text{O}(\text{v}) + 1/2 \text{O}_2 \Rightarrow \text{Na}_2\text{SO}_4 + 2 \text{HCl}$
- *Occurs between the tertiary air level and boiler bank inlet*
- *Can be limited by low SO_2 levels*

Variable Condition Week

HCl concentration measured by the in-situ instrument at the 8th floor location

SO₂ concentration measured by the extractive gas analyzer at the stack

HCl Concentrations (8th floor, in situ) and
SO₂ Concentration (stack, extractive)

Variable Condition Week

Relative fume and carryover concentrations measured at the in-situ locations on the recovery boiler (second week).
Note: occasional slagging of the 6th floor ports resulted in unreliable carryover measurements, which are not plotted.

Variable Condition Week

Relative fume concentration measured by the in-situ instrument at the 8th floor location

Relative carryover concentration measured by the in-situ instrument at the 8th floor location

Primary+Secondary Air

Relative fume and carryover concentrations (8th floor, in situ) and the boiler air flow rates (primary and secondary).

Summary

- In-Situ FT-IR Transmission Spectroscopy Across Boiler

- H_2O
- CO_2
- CO
- HCl
- CH_4
- *Particle Loading*

- Extractive FT-IR Spectroscopy of Stack Gas

- H_2O
- CO_2
- CO
- NO
- NO_2
- SO_2
- HCl
- CH_4

Conclusions

- FT-IR provides simultaneous on-line monitoring of numerous key boiler species: an advancement in boiler process monitoring
- FT-IR provides information for better understanding of the boiler and improved process control

Advances to the Industry

- Improved combustion efficiency
- Improved strategies to reduce harmful emissions
- Improved compliance with regulations
- Increased tolerance to feedstock variations
- Fewer accidents and unwanted plant shutdowns
- May lead to less frequent soot blowing
- Improved energy efficiency

Summary of Tasks for the Next Step in FT-IR Spectroscopy for Black Liquor Boiler Performance Monitoring

Task 1 – 2nd Generation Temporary Installation of AFR's Systems on a Recovery Boiler

- With E/T capability for in-situ boiler temperatures
- With liquid cooled or 3-stage thermo-electric cooled MCT detectors for enhanced information on particles
- Systematic changes of individual boiler parameters
- With improved gas analysis for trace species such as reduced sulfur compounds and hydrocarbons
 - Lower instrument resolution (possible x4 gain in sensitivity)
 - Dry extracted stack gas stream and also increase from 5 m gas cell effective pathlength to 20m (another x4 gain in sensitivity)

Task 2 – Design, Construct and Evaluate Methods for Permanent Coupling of Instrumentation to Boiler

- Direct coupling with purge protected intermediate window
- Flexible waveguide coupling
- Rigid, enclosed optical coupling
- Purge protected window on boiler, non-contact coupling

Task 3 – Advancement of Fume/Carryover Analysis

- Receive carryover sample
- Receive fume sample
- Characterize for size, shape, and composition
- Measure optical constants n & k
- Model extinction (absorption & scattering) with Mie theory
- Apply to measurements in boiler

Task 4 – Improve Software and Tailor Data Stream Output for Industry Requirements and Requests

Task 5 – Build Boiler Process Monitoring Package with Next Generation State-of-the-Art FT-IR Spectrometers that Result from Other Current AFR/On-Line Projects

Task 6 – Permanent Installation on the Recovery Boiler

Task 7 – Follow-up Service by AFR to the Mill on Installed Process Monitoring Package

Task 8 – Collaborate with Boiler Design/Supply Industry (possibly McDermott)

- Boiler data for validation of model predictions

Appendix G

FT-IR Product Brochures

SERIES 2100 PROCESS FT-IR

New Standards of Performance

■ High Sensitivity	■ High Speed
■ High Accuracy	■ Simple to Operate
■ Vibration Tolerance	■ Reliability and Long Life
■ Good Thermal Stability	■ Easy Serviceability
■ Permanent Alignment	■ Portability

Measurement and Control for Productivity, Quality and Compliance

SENSITIVITY

The Series 2100 Process FT-IR achieves the HgCdTe detector noise limit, not the digitizer noise limit. This is obtained using a proprietary 1 MHz, 16 bit digitizer to obtain an effective 19 bit accuracy at 125 KHz by over sampling, digital filtering and decimating. In combination with the high scan speed, an order of magnitude better tolerance to mirror velocity variations is achieved. The dynamically balanced (U.S. Patent #5,349,438) mirror translation system eliminates bearing chatter and vibration induced noise.

ACCURACY

Even with a precise laser standard, frequency accuracy can be affected by detector, cell, or laser misalignment and by differences between library and sample digitizing frequencies. An embedded quality control monitoring system insures frequency accuracy to 0.01 cm^{-1} by employing an internal water vapor frequency standard compared to atmospheric water vapor.

VIBRATION TOLERANCE AND THERMAL STABILITY

The interferometer design, for which a patent is pending, consists of three optical elements: 1) a moving retroreflector (corner cube); 2) a double-sided folding mirror; and 3) an optical combiner consisting of a beam-splitter/compensator pair and a parallel mirror. When these three components are arranged to produce an interferometer, as shown in Figure 1, the properties of the three elements

are such that the interferometer is immune to shear and tilt of any of the components. Because these components provide both shear and tilt immunity, their precise position on an interferometric scale is not important. The elements may thus be flexibly mounted to a frame to isolate them from thermal, mechanical and gravitational stresses which may be introduced by the frame. The self-compensation in the moving element (the corner reflector) makes the system immune to shear and tilt inaccuracies in the mirror translation system. The system's balanced mirror translation system, together with vibration isolation mounts, ensures less than 1% velocity errors with up to 10 g vibration loads.

PERMANENT ALIGNMENT AT ANY ANGLE

There are no bearings to wear. The mirror translation system employs a precision cross-spring flexure system which, together with corner-cube optics, provides a permanently aligned system which can be operated in any orientation.

SPEED

The high-speed digitizer provides an oversampled 0.5 cm^{-1} resolution, single-sided spectrum every 0.25 sec. A 32 cm^{-1} single-sided spectrum can be delivered every 40 milliseconds.

SIMPLICITY

On-Line's easy-to-use VISTA™ user interface employs National Instruments' LabVIEW™ software, with On-Line's FT-IR functions. The VISTA™ software provides an easy-to-use application for collecting and analyzing spectral data.

Figure 1. Optical Design of the FT-IR Made Up of Three Elements, Each of Which Provides Shear and Tilt Immunity to the Interferometer.

RELIABILITY AND LONG LIFE

All mechanical and electrical parts were designed for the factory floor. Mechanical parts were designed or selected to insure vibration tolerance, thermal stability, and durability. A diode laser provides longer life than traditional HeNe lasers. High reliability electrical components and connectors are employed through-out. Important instrument parameters are continuously monitored by an on-board microprocessor-based system and made available to the application software for display and analysis.

PORTABILITY

A separate electronic module and 6" x 12" x 13" optical module makes the system portable and easy to install for process monitoring.

SPECTRA

The user may select a real time display of spectra or interferograms.

APPLICATIONS

Software and sample interfaces have been developed for a variety of applications including: in-situ gas composition and temperature monitoring, thin film monitoring, and particle size analysis. An example is presented showing the determination of the thickness of an epitaxial silicon layer. The layer is determined to be 4.306 microns thick by matching a reflectance spectrum (blue) with a theoretical spectrum (dashed red line).

The figure below shows the analysis of a powder consisting of silica spheres. The average diameter is determined to be 10.8 microns based on matching the measured transmittance to a theoretical prediction.

MAINTENANCE

The maintenance display allows viewing of all important parameter levels to ensure that they are within proper operating ranges. Selection of any parameter provides information on proper maintenance procedures.

CUSTOMIZED MEASUREMENT AND DISPLAY

The 2100 FT-IR may be used to control a process or record and employ auxiliary sensors. The user may customize the instrument configuration using On-Line's VISTA™ software based on National Instruments' LabVIEW™. As shown in the example on the right, object oriented programming is performed by linking function icons graphically on the screen. LabVIEW's library of icons for instrument interfacing and display have

been augmented by On-Line's library of FT-IR control and quantitative analysis functions. The example shown is for performing quantitative analysis and display of criteria pollutants.

SPECIFICATIONS

Spectral Range:	Mid-Infrared region from 7000 to 400 cm^{-1}
Spectral Resolution:	User selectable from 0.5 cm^{-1} to 32 cm^{-1}
Detectors:	MCT-TE cooled, MCT-LN ₂ cooled, MCT-refrigerator cooled
Scan Speed:	4 scans/sec at 0.5 cm^{-1} resolution 25 scans/sec at 32 cm^{-1} resolution
Quality Control Microprocessor:	68HC11
High Speed FFT:	Analog Devices 21020 DSP processor 200 msec FFT time for 0.5 cm^{-1} resolution
Dimensions of Electronic Module:	17-1/2" w x 7" h x 17" d
Dimensions of Optical Module:	6" x 12" x 13"
Power:	120 or 240 VAC, 2 Amps
Installation of Electronics Module:	19" rack mount or table top
Weight of Electronics Module:	35 lbs.
Weight of Optical Module:	25 lbs.
PC Interface:	IEEE 488
User Interface Software:	On-Line VISTA™

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SERIES 2010 MULTI-GAS ANALYZER

- On-Line Gas Analysis for:**
- Process Monitoring and Control
 - Continuous Emission Monitoring (CEM) for Stacks
 - Ambient Air Monitoring

Key Benefits

- Transportable to Site Specific Locations, Operational within Minutes
- Simple to Calibrate and Operate
- Permanent, Transferable Calibration
- Simultaneous Analysis and Display of more than 20 Gases
- Interchangeable Corrosion Resistant Gas Cells up to 20 meters
- Standard Configuration, 20/20™ Long Path Gas Cell, Ambient to 170°C
- Incorporates Rugged 2102 Series Process FTIR
- Operates with Desktop or Laptop Pentium PC under Windows®95/98/NT
- Analysis Software Included with Spectrometer
- Automatic Temperature and Pressure Compensation
- Continuous Self-Diagnostics on All Important Instrument Parameters
- 10 ppb Sensitivity for Many Species
- Analysis of Criteria Pollutants with up to 30% H₂O
- Optional Factory Pre-calibration

Measurement and Control for Productivity, Quality and Compliance

Operating Principles

The 2010 Multi-Gas™ Analyzer employs a 2102 Process FTIR Spectrometer, On-Line's patented, high throughput sampling cell, applications specific analysis software, and a precalibrated, transferable reference library. On-Line's spectrometer is the world's fastest, most sensitive and most stable process FTIR available. The spectrometer is permanently aligned and requires no adjustments. The spectrometer obtains high resolution infrared spectra which are compared to the quantitative library reference spectra for high sensitivity and accurate analysis of most gases and vapors. Our FTIR Multi-Gas analyzers have significant advantages when compared with competing gas analysis methods in speed, sensitivity, ease and permanence of calibration, quantitative accuracy (especially in complex mixtures), and low maintenance requirements.

The 2102 Process FTIR Spectrometer is a compact and rugged instrument designed specifically for process and environmental monitoring. The spectral resolution is user defined from 0.5 – 128 cm⁻¹. It can operate in hostile environments with high vibrational and temperature immunity. An advanced high speed data processor provides low noise infrared spectra.

2102 Process FTIR Spectrometer

The FTIR can be coupled to a variety of gas cells. The Model 20/20™ 5.26 m or 21.04 m path gas cell with non-spherical, aberration-correcting mirrors provides more than twice the throughput of a standard White Cell. Single pass gas cells between 1 cm and 30 cm can be used for corrosive gases. Robust quantitative analysis software, performed on a Pentium PC, can simultaneously analyze more than 20 gases.

The software includes automatic corrections for gas temperature and pressure variations. Self-diagnostics are provided by an internal microprocessor. A complete spectrum can be obtained within 1 sec, Fourier transformed within 200 msec, and analyzed within 1 sec.

The system is fully automated and can be operated by minimally trained personnel.

20/20™ Long Path Aberration-Correcting Gas Cell

Detection Limits

A list of attainable lower detection limits utilizing a 21 m gas cell for typical gases in the absence of interference species is as follows:

Name	Formula	Lowest Detectable Limit with 20/20™ Cell and 5 min Measurement	Lowest Detectable Limit with 20/20™ Cell and 1 sec Measurement
Carbon Monoxide	CO	18 ppb	300 ppb
Carbon Dioxide	CO ₂	2.4 ppb	45 ppb
Water	H ₂ O	30 ppb	510 ppb
Sulfur Dioxide	SO ₂	9 ppb	153 ppb
Nitric Oxide	NO	51 ppb	900 ppb
Nitrous Oxide	N ₂ O	21 ppb	360 ppb
Nitrogen Dioxide	NO ₂	6 ppb	102 ppb
Hydrogen Chloride	HCl	21 ppb	360 ppb
Methane	CH ₄	9 ppb	150 ppb
Ammonia	NH ₃	6 ppb	108 ppb
Hydrofluoric Acid	HF	3 ppb	51 ppb
Benzene	C ₆ H ₆	2.1 ppb	36 ppb
Toluene	C ₇ H ₈	15 ppb	255 ppb
Xylenes	C ₈ H ₁₀	15 ppb	255 ppb
Formaldehyde	H ₂ CO	9 ppb	150 ppb

Exhaust Flue Gas Spectrum with CO and CO₂ Calibration Spectra Overlaid

Setup and Calibration

The user interface contains a menu to select quantitative data displays, diagnostic routines, or spectral information. The Multi-Gas Setup Utility is used to select the analysis gases and files for computed results, spectra and interferograms. The user can manually add temperature and pressure data or have it read from the sensors.

Graphical User Interface for Setup

On-Line's Multi-Gas software allows for multiple point calibration curves that provide 7-9 orders of dynamic range. The 5.26 m cell can be used even with % level concentrations to produce accurate results. Calibration spectra for many species are provided with the instrument. User calibrations can be generated by flowing known concentrations of the species into the cell while spectra are being recorded. Spectrometer calibration is achieved by entering each concentration level into the user interface window. Once the quantitative region is selected the calibration is automatically calculated and saved.

Graphical User Interface for Calibration

Display and Control

During data collection the Multi-Gas software continuously acquires, processes and computes the concentrations for gases that are selected. The data may be displayed as the current spectrum, a table of concentrations, concentration histories or spectral residuals. Once data have been collected they may be reprocessed at anytime using the same or different calibration.

Graphical User Interface for Concentration Histories

Health Diagnostics

Spectrometer diagnostics are continuously updated and provide the user with quick access to the instrument's operating condition.

Graphical User Interface for Health Diagnostics

Specifications

Measurement Technique:	Infrared Spectrometry with Model 2102 Process FTIR
Gases and Vapors Measurable:	Most heteroatomics
Ranges:	Full scale concentration setting between 10 ppb and 100% full scale
Lower Detectable Limit:	10 ppb for many species
Measurement Time:	1-300 sec
Sample Cell:	20/20™ aberration-correcting long path gas cell with 5.26 or 21.04 m path, heated to 170°C. Single pass gas cells for corrosive gases
Computer Requirements:	Desktop or Notebook Pentium with 32 MB Ram and XGA display running Windows® 9x or NT 4.0
High Speed FFT:	200 msec FFT for 0.5 cm ⁻¹ resolution
Dimensions:	20¼"w x 12½"h x 27½"d
Power:	120 or 240 VAC, 2 Amps
Installation:	19" rack mount or table top

Process and Environmental FT-IR Monitors

Applications Note - PARTICLE ANALYSIS BY FT-IR SPECTROSCOPY

CAPABILITIES

On-Line Technologies, Inc. (ON-LINE) is developing the methodology, hardware, and software to perform on-line, at-line or off-line measurements of particulate samples. Infrared spectroscopic techniques are capable of probing gas suspended samples that are optically opaque at visible wavelengths due to particle scattering. The measurements can determine:

- Particle size distributions
- Particle stream temperature
- Chemical composition of particle streams
- Reactant gas properties (temperature and composition)

DEMONSTRATED APPLICATIONS

The methods have been demonstrated for the measurements of combustion products, ceramics, water vapor, chemical fumes and hot sprayed metal alloy particles. Measurements have been performed of:

- Paper mill black liquor recovery boilers (fumes)
- Titanium dioxide particle production
- Metal particle production by supersonic spray atomization
- Water aerosols
- Coal dust
- Lignite dust
- Silica spheres
- Fly ash

METHODOLOGY

PARTICLE SIZE DISTRIBUTIONS

The diffraction of radiation from small particles leads to a wavelength dependent extinction which contains particle size information. Measurements of the wavelength dependent extinction are employed to extract size distributions. The analysis is based on the

Mie theory of electromagnetic radiation scattering from spherical and ellipsoidal particles. Distributions are calculated by fitting simulated size distributions to measured extinction spectra.

PARTICLE TEMPERATURE

The particle stream temperature is determined by an innovative patented emission/transmission (E/T) measurement technique. For opaque particles, the analysis yields precise values for the spectral emittance as well as the temperature, independent of the particle size distribution and interfering gaseous species.

INSTRUMENTATION

Instruments can be configured for on-line, at-line, or off-line measurements. A system includes an FT-IR spectrometer, a particle sampling optical interface, and analysis software. Data collection times range between 1 and 30 seconds, depending on the sampling noise due to particle motion. Typical optics provide a spot size between 1 mm and 5 cm. Sized distribution calculation times can be as short as 1 sec. The technique is applicable to particle sizes ranging from 0.2 μm to $\sim 20 \mu\text{m}$. Tomographic reconstruction of streams to obtain spatial distribution can also be applied.

RESULTS

METAL PARTICLE PRODUCTION

On-line measurements of the production of fine alloy particles by atomization of molten metal were performed at the National Institute of Standards and Technology in Gaithersburg, MD. Figure 1 shows the result of E/T measurements of an atomized hot spray of nickel alloy 625, with superimposed black body spectra calculated for different temperatures. The results show that the radiating metal particles were at approximately 1550°C. Discrepancies between the measured and calculated spectra indicate that a distribution of particle temperatures provides a better description of the particle stream radiance than does a single temperature. Figure 2 shows a series of particle extinction measurements sampled from a

downstream position in the reactor. The measurements clearly show time variations in the particle extinction that can be related to particle size and number density. Refinements to the numerical analysis are being developed to perform deconvolutions of arbitrary size distributions from extinction spectra in the presence of particle noise.

Figure 1. E/T Measurements of Hot Metal Spray to Determine Temperature. Theoretical Spectra Calculated for Different Particle Temperatures are Shown for Comparison.

SILICA, COAL AND FLY ASH

Extinction measurements of air suspended streams of silica spheres, coal and fly ash were performed. The results are shown in Figure 3, comparing measured and theoretical extinction based on Mie theory. Extracted particle size distributions are shown on the right. Theoretical curves for silica, labeled a and b, were calculated assuming solid and 65% sphere porosity, respectively. Theoretical curves for fly ash, labeled a and b, were calculated assuming solid and 57% porosity, respectively. Coal data were taken from two size cuts (sieved) 200 x 325 and 325 x 400 mesh.

Figure 3. FT-IR Particle Size Analysis for Silica, Fly Ash and Coal.

Figure 2. On-line Measurements of Particle Extinction. Measurements were Performed at the N.I.S.T. Supersonic Inert Gas Molten Atomization (SIGMA) Facility. The Measurements were taken Before, During and After an Atomization Run of a Nickel Based Alloy.

Process and Environmental FT-IR Monitors

Applications Note - COMBUSTION MONITORING

CAPABILITIES

On-Line Technologies, Inc. (ON-LINE) has developed the methodology, hardware, and software to perform on-line and in-situ monitoring of combustion systems including:

- Gas composition
- Gas temperature (500 to 2000°C)
- Soot concentration and temperature
- Particle size, composition and temperature
- Emission and transmission tomography

DEMONSTRATED APPLICATIONS

The methods have been demonstrated for the measurements in utility boilers, pulp and paper recovery boilers, incinerators, and combustion research including:

- Extractive stack monitoring (NO_x , SO_x , CO , CO_2 , H_2O , Hydrocarbons).
- In-situ gas monitoring (NH_3 , HCl , SO_2 , SO_3 , NO_x)
- Black liquor recovery boiler diagnostics (fume particle size and concentration)
- Flame diagnostics (temperature and concentration of gases and soot)
- In-situ particle characterization (ash, char, etc.)

METHODOLOGY

FT-IR spectroscopy can be used for combustion monitoring in several ways. A sample can be extracted from any point in the furnace or stack using a probe. This sample can then be preconditioned (removal of water or particles, dilution with air) and analyzed in a gas cell at a user specified path length using absorption spectroscopy. Alternatively, in-situ measurements can be made along a line-of-sight through the furnace or stack using either absorption, emission or combined absorption/emission spectroscopy.

Measurements of gas concentration are based on the absorption of radiation from an infra-red source. Temperature can be obtained from gas band shapes (which reflect the population of vibrational and rotational energy levels) in absorption or in emission. Temperatures can also be obtained from a combination of emission and absorption. Particle size is obtained from radiation scattering by diffraction. Tomographic reconstruction of spectra for multiple lines-of-sight can be used to obtain spatially resolved spectra, from which analysis of temperature and concentration may be performed. Several of these measurement methods have been successfully employed in commercial industrial plants under harsh conditions.

RESULTS

FT-IR Line-of-Sight Transmission Analysis in a Smoke Stack of a Pulp and Paper Mill Recovery Boiler

Transmission measurements were made across a 5 meter diameter smoke stack of an operating recovery boiler. Results for the quantitative analysis are presented in Table 1. Most species can be observed at the ppm level, even with the high concentrations of water. The uncertainties for these measurements are

Spectrum Quantitative Technique	Concentration (PPM)
Gas:	
CO	15.7 ± 0.1
NO	54.8 ± 4.5
NO ₂	6.0 ± 0.09
NH ₃	-1.1 ± 0.4
HCl	1.7 ± 0.3
CH ₄	-5.8 ± 0.5
SO ₂	9.8 ± 8.0

Table 1: Gas concentrations from a Black Liquor Recovery Boiler.

mainly due to the high water concentrations. Similar quantitation performed on spectra with no water have extremely low uncertainties for the gases in the table (< 0.05 ppm). The concentration of NO and NO₂ were in good agreement with the total NO_x concentration, determined by an extractive measurement. The negative value for CH₄ indicates that there was more CH₄ in the air outside the stack (where the reference was taken) than in the stack itself.

To improve quantitation in the presence of interfering species, ON-LINE has developed a method which employs a library spectrum and a library perturbation spectrum which includes features which vary with pressure, concentration or temperature. Figure 1 shows applications of this software for the quantitation of NO in the presence of H₂O. These computer screens show the calculated amount of NO, using simulated spectra, of 10 ppm of NO, as shown in the lower window of each screen, while the upper windows show the amount of H₂O (varied from 1000 ppm to 10000 ppm). In the top screen, only the H₂O reference is used. Clearly, there is a spectral interference which causes the calculated NO to decrease when the H₂O increases. In the lower screen, both the reference H₂O spectrum and a perturbation H₂O spectrum are used. In this case, there is little effect (interference) of the water concentration on the NO determinations.

Figure 1. Computer screen showing effect of quantitative algorithm applied to 10 ppm of NO in the presence of 1000 - 10000 ppm H₂O in 1 atmosphere of air at 30°C. a) Single H₂O reference, b) H₂O reference and perturbation reference.

FT-IR Emission/Transmission Measurements in a Pulp and Paper Mill Recovery Boiler

Absorption and emission measurements were made directly across a black liquor recovery boiler itself. Typical results are presented in Fig. 2. Although the eye cannot see through the fume because of scattering in the visible region of the spectrum, Fig. 2a shows that the stream is not opaque to the IR beam. The spectrum contains opaque regions because of the absorptions by CO₂ (2350 cm⁻¹), H₂O (3500 cm⁻¹ and 1600 cm⁻¹), and the fume (1200 cm⁻¹). The absence of a strong absorption near 2143 cm⁻¹ (the CO region) indicates that the boiler is operating fairly efficiently.

Figure 2. Tests of an FT-IR monitor on the recovery boiler of a paper mill revealed that for sub micro fume particles, scattering decreased rapidly with decreasing wavenumber (a), creating partially transparent windows in the spectrum. The experiment also demonstrated that a set of temperature measurements could be derived from the radiance spectrum (b) and from the normalized radiance (c) with a gas temperature of 1140 K, wall temperature of 980 K, and cold gas temperature of 700 K.

A set of temperature measurements can be derived from the radiance spectrum (Fig. 2b) and the normalized radiance (Fig. 2c). The sharp notch in the radiance near 2400 cm^{-1} is due to cold CO_2 outside the boiler absorbing the hot CO_2 radiation. However, at both edges of the band, the radiation from hot CO_2 is not absorbed by the cold CO_2 , and these regions can be used to determine the hot CO_2 temperature. Figure 2c shows that several temperatures are present. The 1140 K black body curve fits the gas absorptions for CO_2 and H_2O , and the fume absorption. This is the gas temperature inside the furnace. The 700 K curve fits the cold CO_2 band and identifies the temperature near the boiler optical access port. The radiance at high wavenumbers is due to fume scattering of the wall radiation. We find that a temperature of 980 K (Fig. 2c) is in agreement with the estimated wall temperature.

The fume particle size can be derived from the absorption spectra. By fitting the fume absorption and scattering derived using Mie theory, one finds that the $0.2\text{ }\mu\text{m}$ particle size is incorrect because the fume absorption features are too large to be consistent with the observed scattering spectrum. Similarly, a $0.6\text{ }\mu\text{m}$ particle size is also incorrect since it predicts absorption peaks that are too small to fit the measured scattering spectrum. The best fit is clearly a $0.4\text{ }\mu\text{m}$ particle size in agreement with measurements on captured fume particles.

FT-IR Measurements in Power Plants

Both in-situ and extractive FT-IR measurements were performed during field tests at a Cogentrix coal-fired cogeneration plant (Richmond, VA). Urea injection is used at two locations in the furnace to control NO_x formation.

For extractive FT-IR measurements, the flue gas was sampled prior to the lime spray dryer, using an STI Dilution Probe (Graseby/STI, Waldron, AR). In general, the FT-IR measurements were in reasonable agreement with those of the resident CEM systems.

In-situ FT-IR spectra were collected across a 2.34-meter duct directly after the economizer section. The operating conditions at this site were very harsh; the ambient temperature was in excess of 73°C (110°F) and vibrations were significant. In spite of this, the system performed well for three full days of testing. Both NH_3 and HCl were measured, and were consistent with changes in the boiler operating conditions. Clearly, the ability to determine NH_3 concentrations on a short time scale (< 30 seconds) will be very useful in the control of urea injection used for NO_x reduction.

Tomography

For non-homogeneous samples, measurements of emission and transmission will yield an average across the line-of-sight. Alternatively, it is possible to employ tomography to obtain spatially resolved data. Tomography refers to the construction of a three dimensional image by stacking up two-dimensional slices of the image. The two-dimensional images can be mathematically "reconstructed" from line-of-sight measurements across the object. We have employed tomography for both transmission and emission spectra for an ethylene diffusion flame.

For the absorbance spectra, a Fourier reconstruction of the two-dimensional images from the projections has been performed. For radiance, the spectra were corrected for self-absorption. The Fourier reconstruction technique was then applied to these corrected radiation spectra to give local radiance.

The analysis of these local spectra has been performed in the same manner as for thin homogeneous samples as described above. Plots showing the concentrations and temperatures in the center plane of the flame are presented in Figs. 3 and 4. A photograph of the flame is shown alongside reconstructed images (color scale) of organics, soot, CO_2 , and H_2O . FT-IR tomography has thus demonstrated the unique capability of measuring local species concentrations and temperatures in mixed phase systems.

Figure 3. *The Ethylene Diffusion Flame with Central Plane Images of Relative Concentration Reconstructed from FT-IR Transmission.*

Figure 4. *Central Plane Images of Temperature Reconstructed from FT-IR Transmission and Radiance Spectra.*