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IN SITU GAS CONCENTRATION AND TEMPERATURE
MEASUREMENTS IN LABORATORY AND PILOT-SCALE
COMBUSTION ENVIRONMENTS**

D.M. MARTIN, P.J. MEDVE CZ, AND K.M. NICHOLS

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D.M. Martin, P.J. Medvecz, and K.M. Nichols

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APPLICATION OF FT-IR ABSORPTION SPECTROSCOPY FOR *IN SITU* GAS
CONCENTRATION AND TEMPERATURE MEASUREMENTS IN LABORATORY AND
PILOT-SCALE COMBUSTION ENVIRONMENTS

Denise M. Martin, Patrick J. Medvecz*, Kenneth M. Nichols

The Institute of Paper Science and Technology, 500 10th St. N.W., Atlanta, GA 30318

*(D.M.M.), Appleton Papers Inc., P.O. Box 359, Appleton, WI 54912 (P.J.M.), Weyerhaeuser
Technology Center, Tacoma, WA 98477 (K.M.N.)*

ABSTRACT

In situ FT-IR absorption spectroscopy was used as a diagnostic tool to evaluate the gas phase above a heterogeneous combustion reaction. Absorption spectra were collected in the gas phase of laboratory and pilot-scale black liquor char combustion environments. Previously developed calculation methodologies were used to determine the CO and CO₂ concentrations and the CO rotational temperatures from the absorption spectra. Spectroscopically obtained gas temperatures and concentrations from laboratory scale experiments were compared to thermocouple and NDIR measurements. Quantitative evaluations of the gas phase during these experiments indicated that gas temperatures can be measured with an accuracy of 2-3 % at 450-750 K and gas concentrations can be measured with accuracies of less than 10 % at gas concentrations between 0.3-1.3 %.

Gas temperatures obtained during pilot-scale combustion were between 1118-1183 K while concentrations were between 0.35-0.76 %. Differences among gas concentrations and temperatures calculated from the absorption spectra, compared to NDIR measurements and thermocouples, were greater than those from laboratory combustion due to the dynamics of the gas phase. The need is exemplified for a well characterized combustion environment for

* Author to whom correspondence should be sent.

effective use of FT-IR as a diagnostic tool for pilot-scale combustion and for advancing the fundamental understanding of combustion processes.

Index Headings: Infrared; FT-IR; Absorption spectra; Temperature analysis; Concentration analysis; Combustion gases.

INTRODUCTION

In the pulp and paper industry, black liquor is the spent chemical solution which is produced during the pulping of wood by the Kraft process. The recovery of energy and inorganic chemicals from the liquor is critically important to the economic and environmental feasibility of the pulping process. Both the energy and pulping chemicals are recovered by firing the concentrated liquor in a furnace appropriately called a recovery boiler. The heat energy is recovered by steam generation while inorganic chemicals are recovered from molten smelt at the bottom of the furnace.

Optimizing the combustion is essential for maximizing economic benefits and minimizing environmental impacts. This requires a fundamental understanding of the chemical events occurring within the furnace. However, in both commercial scale boilers as well as laboratory simulations of the process, the high temperature and sooting nature of the black liquor combustion process makes it difficult to perform *in situ* gas concentration and temperature measurements with intrusive sampling probes. Furthermore, depending upon the size of the probe, the measurement can affect the combustion process. Therefore, there is incentive to use spectroscopic techniques such as Fourier transform infrared absorption spectroscopy. Identification of gaseous combustion products, along with their concentrations and temperatures, can be derived from FT-IR absorption spectra. This

information can play a key role in furthering the fundamental knowledge of the combustion process.

FT-IR has been previously used for various *in situ* analyses of laboratory and commercial scale combustion systems. Solomon *et al.*¹ used FT-IR to model coal combustion behavior. Ottesen and Stephenson² applied the technique to gas phase measurements in sooting hydrocarbon flames and Thorne and Ottesen studied the combustion of pulverized coal.^{3,4} FT-IR has also been used in a commercial scale recovery boiler.⁵

More recently, calculation methodologies have been reported for the determination of gas concentrations and temperatures from high temperature (up to 1250 K) FT-IR absorption spectra.⁶⁻⁸ These methodologies included corrections for photometric errors resulting from the limited resolution of the spectrometer (which cause distortions of the absorbance peak height and width) and corrections for the temperature dependence of the absorption coefficients for many CO and CO₂ vibrational-rotational absorption lines. Results of high temperature (295-1250 K) gas analyses by Medvecz *et al.*^{6,7} showed that concentrations were determined with an accuracy of 3-7 % at concentrations of CO and CO₂ in the range of 0.5-5.0 %. Simultaneously, temperatures were measured with an accuracy of 3-4 %. These results demonstrated the usefulness of FT-IR as a diagnostic tool for the evaluation of combustion processes.

In previous work by Medvecz,^{6,7} CO and CO₂ were the two gas species most thoroughly evaluated. This was done in anticipation of the application of FT-IR absorption spectroscopy to the combustion processes. In fuel combustion, the ratio of CO to CO₂ is critically important. First, the amount of stoichiometric air required is directly proportional to the amount of CO or CO₂ that is generated as combustion products; twice as much

oxygen is required for oxidation of carbon to CO_2 .⁹ Second, when the rate of combustion is kinetically controlled, the heat generated at the combustion surface is much greater (as much as 3.5 times greater) for the oxidation to CO_2 than it is for oxidation to CO .¹⁰ This large difference in heat evolution can result in large differences in burning temperatures and therefore, in the products that are released into the gas phase. Accurate mathematical modeling of combustion depends on accurate knowledge of the CO/CO_2 ratio, because of the large effect the CO/CO_2 ratio will have on surface (and other local) temperatures.

In coal combustion, Mitchell¹¹ has reported the CO/CO_2 ratio leaving the surface to be between 5.67 and 10 at 6-12 mole percent oxygen and temperatures of 1600-1800 K. Tognotti¹⁰ also reported a CO/CO_2 ratio of 10 for the coal combustion of single char particles. However, at 870 K and $P_{\text{O}_2} = 0.2$ bar, the CO/CO_2 ratio was 1.96. The ratio was found to vary depending on the carbon source and was also found to decrease with increasing oxygen partial pressures.¹⁰

The CO/CO_2 ratio is also of interest in black liquor combustion where the combustion rate is oxygen diffusion controlled. Limited measurements in the gas phase above black liquor char combustion indicate that the CO/CO_2 ratio is approximately 0.5.⁹ Accurate measurement of this ratio, however, has been hindered by rapid gas phase oxidation of CO to CO_2 . It is also known that water vapor catalyzes homogeneous CO oxidation making the determination of the primary combustion products still more difficult.¹² Therefore, there is a need to develop techniques which permit the determination of gas concentrations and temperatures close to the point of combustion. Data from these techniques would be less biased by the possibility of gas phase reactions secondary to the combustion process.

This study focuses on the use of FT-IR absorption spectroscopy to make *in situ* gas phase concentration and temperature measurements in both laboratory-scale and pilot-scale combustion environments; specifically, to measure the concentrations of CO and CO₂ and gas phase temperatures above a burning black liquor char bed. Measurements from the FT-IR analyses are compared with measurements made with thermocouples and remote NDIR gas analyzers. The usefulness of FT-IR as an *in situ* diagnostic tool is discussed. Furthermore, the ratio of CO and CO₂ formed during black liquor combustion is reported. A detailed explanation of the theory associated with the calculation of gas temperatures and concentrations from infrared absorption spectra has already been presented by Medvecz *et al.*,⁶⁻⁸ and will not be discussed here.

EXPERIMENTAL

Optics. A KVB Analect (formerly Laser Precision Analytical), model RFX-75, FT-IR spectrometer with a maximum resolution of 0.125 cm⁻¹ was used for this work. A high intensity water cooled Globar coil was used as the infrared source. Within the spectrometer, a Michelson interferometer was used to modulate the infrared beam that was passed through the combustion reactors and to a Mercury-Cadmium-Telluride (MCT) detector. To transfer the IR beam from the interferometer, through the combustion chambers, and to the detector, Optibus[®] optical components from KVB Analect were used. The path of the IR beam was different for the laboratory and pilot-scale studies as shown in Fig. 1. For the laboratory reactor, the collimated beam exited the interferometer and was focused by an 8-in.-focal-length parabolic mirror through an 800-μm aperture. The beam struck a second 8-in. parabolic mirror which sent a collimated beam to a third 8-in. parabolic mirror. The focused beam passed through the reactor to a fourth 8-in. mirror, to the MCT detector where the collimated beam was finally focused onto the detector chip.

For the pilot reactor, the beam traveled from the interferometer into a 48-in. internally reflecting optical conduit. The collected collimated beam was reflected off a flat mirror onto a 6-in.-focal-length parabolic mirror. The beam was then focused through an aperture to a 4-in.-focal-length parabolic mirror. The focused beam traveled 40 in. through the pilot-scale reactor to a similar 4-in. parabolic mirror and through a second aperture to a 6-in. parabolic mirror. Finally, the collimated beam entered the MCT detector. Focusing the beam through apertures was necessary in both systems to prevent stray radiation from the reactors from becoming modulated and interfering with the normal infrared absorption spectrum.

The infrared beam entered the laboratory-scale reactor through sapphire windows, 1 in. diameter and wedged 0.7° (General Ruby and Sapphire Corp.). Zinc selenide windows 2 in. diameter, and 3.0 mm thick (Infrared Optics, Inc.) were chosen for the pilot scale reactor and were wedged to a 0.25° angle. The higher transmitting zinc selenide windows were chosen for the pilot scale equipment because the windows were sufficiently far from the furnace to keep them relatively cool (below 570 K).

The FT-IR instrument resolution for each optical configuration was made by measuring the full width at half height (FWHH) of triangularly apodized, low pressure CO absorption lines. Absorption spectra of low pressure (approximately 1 Torr) gaseous CO samples were collected at room temperature in a 10 cm gas cell (Janos Technology, Inc.).

Laboratory Reactor. The laboratory-scale combustion occurred in the reactor shown schematically in Fig. 2. Either pre-purified air or air diluted with nitrogen was heated to 750-850 K and then introduced through 4 nozzles at 3 slpm to support combustion. Windows were positioned between the air jets, in the same horizontal plane, to provide an

opening for the infrared beam. The gases which flowed in and out of the lab scale reactor were monitored by rotameters, mass flow meters, and gas analyzers.

Dried and partially pyrolyzed char particles were preheated in the reactor to 998-1073 K for 1 hour. A 5 % mixture of CO in nitrogen was used to purge the char during the heat-up period to reduce char consumption by sodium carbonate decomposition. FT-IR absorption spectra were collected above the "steady state" combustion of the char bed. At least 7 spectra were collected during a 1.5 hour combustion period with each spectrum being the average of 50-150 scans. Measurements were repeated, varying the distance between the initial char surface and the infrared beam in the range of 0.75-3 in. to allow various gas phase reaction times.

Pilot-Scale Reactor. A schematic of the pilot-scale reactor is provided in Fig. 3. Combustion occurred in a metal reactor surrounded by electrical heating panels which confined the black liquor char to a 4 × 8 in. retaining insert. The char bed was comprised of black liquor droplets which were in a dried and partially devolatilized state. The combustion air was provided by a cross flow slot jet allowing a preheated air-nitrogen mixture to flow perpendicular to the infrared beam. Contact between the gas jet and the char bed surface was maintained during burning by the use of a variable speed drive which continuously moved the char bed upward. The drive speed was adjusted by visual observation of the burning bed surface as seen through a viewport.

The pilot-scale combustion chamber had an internal temperature of approximately 1020 K. The reactor was preheated for 30 minutes prior to the start of combustion to complete drying and pyrolysis of the black liquor droplets. The air-nitrogen stream, preheated to approximately 420 K, entered the system at 200 slpm to support combustion. FT-IR absorption spectra of the combustion product gases were collected 4 inches above the

char bed at varying oxygen concentrations (7, 14, and 21 % O₂). Two spectra were collected during a 10 minute burn at each O₂ concentration, with each spectrum being the average of 100-150 scans.

RESULTS AND DISCUSSION

The use of FT-IR as a diagnostic tool for the elucidation of the chemical events occurring in a combustion environment, requires first, that well resolved absorption spectra can be recorded, and second, that gas temperatures and concentrations can be accurately determined from the absorption spectra. In the first of the following sections, spectra recorded in a black liquor char laboratory combustion environment will be presented. It will be shown that these spectra contain high quality CO and CO₂ absorption lines, from which gas temperatures and concentrations can be made. It will also be shown that a large part of the mid infrared region, 800-4400 cm⁻¹, is available for the identification and quantification of additional gaseous species which absorb in this region. In the second section, the gas temperatures measured from spectra recorded during black liquor char laboratory combustion experiments will be presented. The accuracy of these measurements will be established by comparisons with temperatures recorded simultaneously with a suction pyrometer. In the third section, gas concentrations will be calculated from a number of spectra recorded under various combustion conditions. The spectroscopically measured concentrations will be compared to those determined by an NDIR instrument. From these comparisons, the accuracy of CO and CO₂ gas concentration measurements, in a black liquor char combustion environment, will be established. The application of gas phase FT-IR measurements during pilot-scale combustion are then discussed briefly. In the final sections, the significance of the spectroscopic gas phase measurements and of its application during black liquor combustion is presented.

ABSORPTION SPECTRA RECORDED DURING LABORATORY BLACK LIQUOR

CHAR COMBUSTION. The laboratory reactor was used to record absorption spectra during char combustion. This reactor has provided the means to first, heat black liquor solids to temperatures up to 1250 K and second, to record the infrared absorption spectra of the gases directly above the sample surface. The black liquor solids were burned in the reactor in a bed configuration, and the experiments were run in a batch mode.

In Fig. 4, a spectrum is presented which was recorded during char combustion; the quality of which was representative of all those recorded in the reactor. The signal to noise is very good and there are no obvious distortions resulting from the presence of fume (solid particle formed during combustion). This spectrum provides an easy means of qualitatively identifying the infrared active components present in the gas phase. For example, CO absorbs in the region of $1900\text{--}2250\text{ cm}^{-1}$ and CO_2 absorbs in the region from $2250\text{--}2400\text{ cm}^{-1}$. The two additional bands centered at $3600\text{--}3700\text{ cm}^{-1}$ are also CO_2 absorption lines. On a qualitative basis, this spectrum demonstrates the potential of FT-IR absorption spectroscopy to yield information regarding the gas composition above a combusting sample.

The use of these types of spectra, for gas temperatures and concentration determinations, requires that the individual absorption lines are well resolved and free from interfering peaks. The spectra provided in Figs. 5 and 6 are the CO and CO_2 lines from Fig. 4. The quality of these spectra are as good as those obtained in a high temperature gas cell, reported in previous work.^{6,7}

GAS PHASE TEMPERATURE DETERMINATIONS. CO infrared absorption spectra, recorded during black liquor combustion, have been used to determine the gas temperature above a burning black liquor char bed. The accuracy of these measurements has been established by comparisons with temperatures simultaneously recorded with a

thermocouple. The char samples consisted of 15-20 grams of fully dried and pyrolyzed softwood black liquor droplets.

Before combustion was started, the crucible containing the sample was raised several inches upward, into the middle of the reactor. The bed was moved to increase the proximity of the spectroscopic analysis relative to the char surface; 0.5-1.0 inches at the start of combustion. The time required for complete combustion of the char was approximately two hours. The rate of char combustion was controlled by the oxygen flow rate and concentration. The combustion gas, comprised of 5 % O_2 in nitrogen, was preheated to 773-873 K, and was fed into the reactor at a rate of 3 l/min. This rate was selected to provide a product gas stream which contained CO and CO_2 concentrations in the range between 0.5-5 %.

The gas temperature above the char was measured during combustion by a suction pyrometer. The thermocouple was placed at the same height in the reactor as the infrared beam. The pyrometer consisted of a K type thermocouple and was shielded by both stainless steel and ceramic shields. The gas from the reactor was drawn through the stainless steel tube. The thermocouple tip was heated by convection of the gas past the thermocouple junction.

Absorption spectra were recorded above three different char beds. Ten spectra were recorded during combustion of the first burn, nine during the second, and six during the third. The results of the temperatures calculated from the absorption spectra are presented in Table I. Also included in the table are the gas temperatures recorded by the thermocouple, as well as the relative and absolute difference between the thermocouple and spectroscopic measurements.

The agreement between spectroscopic and thermocouple measurements is very good. The average percent differences for each of the three burns was 2.2, 2.0, and 1.0 %, respectively. The largest percent difference, for any one spectrum was 4.9 %. These results are as good as those previously reported from a pure gas environment,⁶ at similar temperatures. There is no evidence that the combustion environment has affected the accuracy of the calculation methodology. These results also support the conclusion that the absorption spectra recorded in the reactor are photometrically accurate.

The excellent agreement between spectroscopic and thermocouple measurements indicates that gas temperatures can be accurately measured in a combustion environment using FT-IR absorption spectroscopy. There is no indication that the accuracy should be less for similar measurements recorded at higher gas temperatures.

GAS CONCENTRATION DETERMINATIONS. In addition to gas temperatures, spectroscopic CO and CO₂ concentration measurements have also been made during black liquor combustion in the laboratory-scale reactor. The accuracy of these measurements was evaluated by comparing the calculated concentrations with measurements recorded on the outside of the reactor with a CO/CO₂ gas analyzer.

Room Temperature Concentration Calculations in the Laboratory Reactor. Before experiments were run during char combustion, room temperature absorption spectra of CO/CO₂/N₂ gas mixtures were recorded in the reactor. These spectra were collected to verify that concentration measurements could be accurately made under controlled conditions. Twenty six room temperature spectra were recorded in the reactor in three separate trials. Nine spectra were recorded in each of the first two trials and eight were recorded in the third. The concentration accuracy, evaluated by comparison with the metered quantities, is presented in Tables II and III for CO and CO₂, respectively.

The agreement between the calculated and metered CO gas concentrations is very good. The average absolute percent difference is between 3-4 % which agrees well with the calculation accuracy reported for the gas cell.⁷ In addition, the low and high values are both negative and positive, respectively, indicating no bias among the results towards over or under predicting the gas concentration. The room temperature CO₂ results, however, are not as good. The average absolute percent difference between calculated and metered gas concentrations was between 7-10 %, and all but one of the 26 spectra had a calculated gas concentration which was lower than the metered concentration. In the gas cell,⁷ the average absolute percent difference for CO₂ at room temperature was between 3-5 %.

The accuracy of the results from the room temperature CO calculations, suggest that the increased error with the CO₂ is not due to differences between the gas cell and the reactor. Instead, an explanation for the differences is derived from a comparison of the CO₂ individual results, obtained in the gas cell,⁷ at room temperature. The overall accuracy of the CO₂ results, in the gas cell, was between 3-5 %. However, this average value included calculations from spectra with a broad range of concentrations (0.72-3.24 %). Among the spectra recorded at lower concentration, 0.5-1.5 % (similar to 90% of those in Table III), all but one of the calculated CO₂ concentrations were less than the measured values (3.60, -6.02, -4.17, -4.00, -10.45, -9.30, and -9.65). Among these values, the average absolute percent difference was 6.7 %. These results suggest that the calculation accuracy is concentration dependent.

Part of the reason for the lower accuracies obtained from the CO₂ data may be linked to the concentration dependence of the CO₂ line strengths. The line strengths used for this work were obtained from spectra recorded previously.⁷ A concentration dependence for line strengths has already been shown for higher temperature spectra.^{7,8} Table IV is a

listing of the calculated line strengths of lines 53-61, along with the concentration for each of the spectra, from which each of the line strengths were calculated.

The line strengths presented in this table show a slight concentration dependence. The average of the line strengths, calculated at concentrations between 1.82-2.24 %, was 2.1-5.9 % higher than the line strengths calculated at concentrations between 0.72-1.34 %. The reason for this dependence is the overlap of the neighboring R branch band and/or incomplete correction for the overlap of neighboring lines. The net effect of these errors is an increase in the average line strengths for each line. These conclusions are supported by the observation that the room temperature theoretical line strengths, presented previously were lower than those calculated in this work.⁸ While this overlap leads to inaccuracies in the calculated concentrations, the errors which have been described here are relatively small. In general, the results suggest that accurate room temperature CO and CO₂ concentrations can be measured from absorption spectra recorded in the laboratory-scale reactor.

Concentration Calculations During Laboratory Char Combustion. Absorption spectra were recorded in the reactor during the combustion of six char samples. The char samples and combustion conditions were the same as those described for the temperature results, except for the following; the char bed was not lifted after the preheating trials 4, 5, and 6, and the char was only heated to temperatures of 1173 and 1073 K, respectively, in trials 5 and 6. These changes provided some variability in the CO and CO₂ gas concentration, among the trials. For each trial, 6-9 spectra were recorded during the combustion of each char sample. The concentration accuracy, evaluated by comparison with the metered quantities is presented in Tables V and VI for CO and CO₂, respectively.

Among the trials, the difference between the average calculated CO concentration and NDIR measured concentrations varied from 4.3-10.4 %, while the CO₂ results varied from 8.6-17.0 %. Both the CO and CO₂ data are biased towards under predicting the gas concentration. In the case of the CO data, with the exception of trial #3, the range of error predicted from the gas cell work was only slightly higher than those measured in the gas cell (2-5 %).⁷

The CO₂ data recorded during char combustion are similar to the room temperature reactor results. An explanation for the relatively high percent errors from these spectra can again be derived from a consideration of the concentration dependence of the line strengths. The line strengths determined in the gas cell⁸ were calculated over a wide range of CO₂ concentrations (0.81-3.91). The line strengths were recorded at the higher concentrations are affected to a greater extent by peak overlaps from the neighboring CO₂ band. This band raises the average line strengths, for lines with lower values of m . Table VII lists the calculated line strengths as a function of concentration for lines 53-67.

Only the first of the six spectra in Table VII were recorded at a concentration within the range of the concentrations calculated in the reactor. The percent difference between the line strength calculated at a CO₂ concentration of 0.81 %, compared to the average line strength calculated from the other five spectra, was 14.6, 11.7, 9.8, 6.7, 3.7, 1.5, 2.2, and 1.0 % respectively, for lines 53-67. These calculations clearly illustrate the effect of concentration on the line strength. The error diminishes as the lines move out towards the wing, because the lines are further from the overlap of the neighboring R branch band and because the peak intensity of the lines is decreasing, reducing the effect of overlap from neighboring CO₂ lines.

To test the importance of the concentration dependence of line strength on the results in Table VII, the calculations were repeated. This time, however, lines 53-67 were excluded from the calculations. In addition, line 77 was excluded, since it yielded calculated concentrations which were 10-20 % lower than the other lines. The results of these calculations are presented in Table VIII. These results presented in this table show a significant reduction in the average absolute difference between the calculated and measured CO₂ concentrations. The overall average percent difference, calculated prior to the exclusion of lines 53-65 and 77, was 12.0 % and after exclusion of these lines it has been reduced to 8.6 %. Clearly, the temperature dependence of the line strengths has affected the concentration calculation accuracy. The level of accuracy reported for CO₂, after these corrections, approaches that obtained in the gas cell.⁷

The results presented in this table still show a bias towards under predicting the actual concentrations. It is unlikely that the observed concentration differences, between the spectroscopic measurements and the analyzer values, are a result of a secondary CO oxidation reaction,



First, the gas temperature is very low which prohibits this reaction, and second, an increase in CO₂ concentration at the NDIR meter should be coupled with a corresponding decrease in the CO concentration at the meter. However, this has not been observed.

The overall accuracy of the char combustion concentration calculations is 6.6 and 8.6 % for the CO and CO₂, respectively. The calculated concentrations of CO and CO₂, were between 0.3-1.2 %. This is the most difficult range of concentrations to make accurate measurements, since relatively small deviations in the concentration, ± 0.05 %, result in

relative large percent errors, 16.7-4.0 %. As the concentration of the gas increases, with faster rates of char combustion, it is likely that the accuracy will improve.

PILOT-SCALE COMBUSTION. Representative spectra for the CO and CO₂ recorded in the pilot-scale reactor are provided in Fig. 7 and 8, respectively. For these spectra, the absorption lines were well resolved and indicated minimum interference from overlapping peaks. Calculated temperatures were compared to thermocouple measurements for char bed surface temperatures reported by Brown *et al.*¹³ and are provided in Table IX. It was expected that the gas phase temperature at the point of measurement, 4 in. above the burning surface, would be lower than the bed surface temperature based on the temperature of the combustion air jet (423 K) and flow patterns within the reactor. Simultaneous temperature measurements using a suction pyrometer were not made in the pilot-scale reactor, because of limited accessibility through the reactor.

Concentrations of CO and CO₂ calculated from the absorbance spectra were compared to NDIR exhaust gas analysis. These values are reported in Table X and indicate large absolute percent differences with the FT-IR calculated concentrations. The lower calculated concentrations of CO and CO₂ are partly a result of inaccuracies with the line strengths, but also may result from the nature of the combustion environment. Above the char bed, the gas phase may not be well mixed and/or concentration and temperature gradients may exist. Furthermore, the path of the infrared beam may have been located in an oxygen rich/carbon lean location in the pilot-scale reactor due to air jet position, temperature, velocity, and mixing.

Jet profile and diffusion calculations support the possibility for the IR measurements to have been made in an oxygen rich/carbon lean zone above the bed. Based on the gas phase temperatures and flow patterns within the combustion chamber, it appears likely that

this is the case. This is further supported by the total amount of carbon oxides (CO and $\text{CO}_2 \equiv \text{CO}_x$) identified by both methods. A significantly larger amount (28.6 % on average) of CO_x was determined in the exhaust gas analysis than in the combustion chamber. Plug flow was assumed during steady state combustion when absorption spectra were collected. The flow patterns within the pilot-scale reactor did not allow true plug flow to exist at the location of the infrared beam. Sufficient residence time and good mixing of gases had been achieved when the gases left the combustion chamber making plug flow a valid assumption for exhaust gas analysis.

The potential exists for the CO_x to react with inorganics released during char combustion and become aerosol fume species.¹⁴ The CO and CO_2 may react with Na species lowering the observed CO_x concentrations. Large amounts of fuming were noted upon initiation of pilot-scale combustion at both 14 and 21 % oxygen levels. Again, the conversion of CO to CO_2 was considered as a possibility of lowering the CO concentration. The temperature of the gas phase during pilot-scale combustion was sufficient for oxidation of CO. However, because H_2O was not observed in the absorption spectra, it would not be present in the gas phase to catalyze the conversion.

SIGNIFICANCE OF FT-IR MEASUREMENTS. The FT-IR spectra collected within the laboratory and pilot-scale combustion environments had good resolution and intensity which allowed for easy calculation of gas temperatures and concentrations. The capability of *in situ* FT-IR measurements to closely track remote concentration measurements has been established. Furthermore, these spectra have demonstrated that a large window of the mid infrared region is available for both qualitative and quantitative analysis of multi-component gaseous systems in a combustion environment. The results illustrate that a meaningful analysis of black liquor char combustion can be obtained using FT-IR absorption spectroscopy. However, it is of critical importance to be able to fully characterize and

understand the flow patterns and mixing which occurs within the combustion chamber.

The importance of a well characterized combustion environment is exemplified in the pilot-scale combustion results. Explanation for variations of determined concentrations and temperatures between *in situ* and remote measurements becomes a difficult task when the nature of the combustion environment is not fully understood.

SIGNIFICANCE OF MEASUREMENTS TO BLACK LIQUOR COMBUSTION. The concentrations reported here can be used to determine the CO/CO₂ ratio for char combustion in the two reactors. The values determined at the various oxygen levels are reported in Table XI. The 5 % oxygen CO/CO₂ ratio was determined from the laboratory reactor concentrations while the remaining values were determined from pilot-scale concentrations. The absolute percent difference between FT-IR and NDIR reported values are very good with the exception of that given by the NDIR measurement at 14 % oxygen. Statistically, this result can be rejected. The resulting average CO/CO₂ ratio was 1.04 with a standard deviation of 0.07. This value is twice as large as that reported by Grace *et al.*⁹ where the ratio was 0.5 for the gas composition above the bed in a commercial recovery furnace where 10-20 % excess air is typical. The difference in the CO/CO₂ ratio values are explained as the ratio is known to vary with the carbon source and to decrease with increasing oxygen partial pressure.¹⁰

SUMMARY

The results have demonstrated that the gas phase of a combustion environment can be qualitatively and quantitatively evaluated using Fourier transform infrared absorption spectroscopy. Qualitative evaluations lead to the identification of the gaseous components present above a burning black liquor char bed in both a laboratory and pilot-scale combustion environment. Quantitative results provided gas temperature and concentration

information in a high temperature combustion environment. The black liquor char combustion chambers have been used to record high quality infrared absorption spectra above a burning char bed. From these spectra, qualitative evaluations have been made of the gas phase above the char bed during laboratory and pilot-scale combustion where the gas phase species CO and CO₂ were identified.

Quantitative evaluations of the gas phase during laboratory combustion indicated that gas temperatures can be measured with an accuracy of 2-3 % in the range of 450-750 K. Gas concentrations have been measured with accuracies better than 10 % at concentrations between 0.3-1.3 %. During the pilot-scale char combustion, temperature measurements made *in situ* for the gas phase were found to be in the range of 1118-1183 K and indicated good agreement with reported char surface temperatures. The concentrations were calculated to be in the range of 0.35-0.71 % and 0.35-0.76 % for CO and CO₂, respectively. These values were considerably lower (30.5 and 19.6 % on average for CO and CO₂, respectively) than those measured by NDIR.

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Table I. Comparison of spectroscopic (calculated) and thermocouple (measured) determinations of the gas temperatures above three different char combustion experiments.

Spectrum	Spectroscopic Temp. (K)	Thermocouple Temp. (K)	Temp. Dif. (K) (Calc.- Meas.)	Abs. Percent Dif. (%)
CHAR BURN #1				
C75A	433	441	-8	1.8
C75B	575	589	-14	2.4
C75C	590	573	17	3.0
C75D	588	5667	21	3.7
C75E	594	566	28	4.9
C75F	584	578	6	1.0
C75G	589	589	0	0.0
C75H	653	645	8	1.2
C75I	656	667	-11	1.6
				Average = 2.2 %
CHAR BURN #2				
C75A	564	560	4	0.7
C75B	576	555	21	3.8
C75C	573	559	14	2.5
C75D	573	576	-3	0.5
C75E	598	581	17	2.9
C75F	608	602	6	1.0
C75G	636	628	8	1.3
C75H	648	656	-8	1.2
C75I	703	673	30	4.4
				Average = 2.0 %

CHAR BURN #3

		567	2	0.3
C75A	569			
		581	7	1.2
C75B	588			
		585	-2	0.3
C75C	583			
		603	-5	0.8
C75D	598			
		628	11	1.7
C75E	639			
		665	-13	1.9
C75F	652			

Average = 1.0 %

Table II. Results of CO gas concentration calculations from room temperature spectra recorded under controlled conditions in the laboratory reactor.

Measured Conc. Calculated Avg. Avg. Abs. % Dif.						
Trial #	# of Spectra	Range (%)	Gas Temp. (K)	of Calc. CO	Low (%)	High (%)
1	9	0.41-2.34	290	3.32	-4.42	8.46
2	9	0.33-1.42	296	3.60	-5.38	10.32
3	8	0.34-1.65	294	3.54	-2.32	14.88

Table III. Results of CO₂ gas concentration calculations from room temperature spectra recorded under controlled conditions in the laboratory reactor.

Measured Conc. Calculated Avg. Avg. Abs. % Dif.						
Trial #	# of Spectra	Range (%)	Gas Temp. (K)	of Calc. CO ₂	Low (%)	High (%)
1	9	0.40-1.89	290	9.45	-15.65	-3.65
2	9	0.34-1.56	296	7.65	-16.45	-2.70
3	8	0.37-1.59	294	9.60	-15.95	8.05

Table IV. Illustration of the concentration dependence of CO₂ lines 53-61 at 296 K. Line strengths (L.S.) are in units of 1/(atm-cm²).

	L.S.	L.S.	L.S.	L.S.	L.S.
Conc.(%)	m = 53	m = 55	m = 57	m = 59	m = 61
0.72	2.695	1.887	1.275	0.832	0.535
0.77	2.785	1.955	1.299	0.890	0.587
1.33	2.640	1.809	1.210	0.798	0.530
1.34	2.720	1.881	1.295	0.849	0.529
1.82	2.805	1.958	1.301	0.861	0.572
1.89	2.868	1.988	1.314	0.888	0.581
2.24	2.815	1.899	1.279	0.845	0.563
2.46	2.853	1.963	1.290	0.865	0.564
2.87	2.802	1.926	1.302	0.857	0.564

Table V. Results of CO gas concentration calculations from the spectra recorded during char combustion.

Trial #	# of Spectra	Measured	Calculated	Avg. Abs. %		
		Conc. Range (%)	Avg. Gas Temp. (K)	Dif. of Calc. CO	Low (%)	High (%)
1	8	0.41-1.99	586	4.50	-6.68	12.36
2	9	0.21-0.93	609	6.56	-15.66	-0.01
3	7	0.65-0.86	611	10.42	-11.78	-9.05
4	7	0.42-1.21	676	8.89	-11.19	-5.72
5	6	0.37-0.99	644	4.91	-9.31	0.70
6	6	0.26-0.60	594	4.32	-7.06	2.86

Table VI. Results of CO₂ gas concentration calculations from the spectra recorded during char combustion.

Trial #	# of Spectra	Measured	Calculated	Avg. Abs. % Dif. of Calc. CO ₂	Low (%)	High (%)
		Conc. Range (%)	Avg. Gas Temp. (K)			
1	8	0.51-0.81	586	8.60	-14.88	-2.96
2	9	0.55-1.10	609	13.06	-16.36	-9.00
3	7	0.53-1.01	611	17.00	-19.37	-16.34
4	7	0.52-0.90	676	13.36	-15.99	-6.38
5	6	0.55-0.91	644	11.11	-13.65	-9.48
6	6	0.59-1.04	594	9.20	-11.94	-3.78

Table VII. Illustration of the concentration dependence of CO₂ lines 53-67, at 573 K. Line strengths (L.S.) are in units of 1/(atm-cm²).

Conc.	L.S.	L.S.	L.S.	L.S.	L.S.	L.S.	L.S.	L.S.
(%)	m = 53	m = 55	m = 57	m = 59	m = 61	m = 63	m = 65	m = 67
0.81	5.860	5.125	4.124	3.353	2.747	2.222	1.702	1.352
1.32	6.130	5.266	4.256	3.372	2.700	2.194	1.743	1.366
2.00	6.506	5.255	4.426	3.365	2.722	2.207	1.710	1.358
2.29	6.772	5.457	4.327	3.570	2.747	2.197	1.698	1.329
3.10	7.391	6.169	4.614	3.708	2.975	2.348	1.774	1.402
3.91	7.513	6.882	5.232	3.960	3.118	2.339	1.776	1.372

Table VIII. Results of CO₂ gas concentration calculations from the spectra recorded during char combustion. Lines 53-67 have been excluded from the calculations because of the concentration dependence of line strengths for these lines.

Trial #	# of Spectra	Measured	Calculated	Avg. Abs. % Dif. of Calc. CO ₂	Low (%)	High (%)
		Conc. Range (%)	Avg. Gas Temp. (K)			
1	8	0.51-0.81	586	6.62	-13.71	1.56
2	9	0.55-1.10	609	9.25	-14.58	-3.75
3	7	0.53-1.01	611	12.25	-15.62	-7.02
4	7	0.52-0.90	676	10.09	-14.08	-2.13
5	6	0.55-0.91	644	7.57	-10.37	-5.80
6	6	0.59-1.04	594	5.97	-8.32	-0.86

Table IX. Pilot combustion temperature measurements.

	FT-IR Calc. Gas Phase	Brown <i>et al.</i> ¹³ Char	Avg. Abs. %
% O ₂	Avg. Temp. (K)	Bed Temp (K)	Dif.
7	1156	1173	1.47
14	1118	1273	13.86
21	1183	1373	16.06

Table X. Pilot-scale combustion CO and CO₂ concentrations determined by FT-IR and by NDIR analysis.

	Avg. % CO	Avg. % CO	Avg. % Abs.	Avg. % CO ₂	Avg. % CO ₂	Avg. % Abs.
% O ₂	(FT-IR)	(NDIR)	Dif. CO	(FT-IR)	(NDIR)	Dif. CO ₂
7	0.35	0.49	22.7	0.35	0.48	24.0
14	0.51	1.08	51.7	0.47	0.62	25.0
21	0.71	0.88	17.2	0.76	0.86	9.8

Table XI. Calculated CO/CO₂ ratio for FT-IR and NDIR concentration measurements at varying oxygen levels.

	Avg. CO/CO ₂	Avg. CO/CO ₂	Avg. Abs. %
% O ₂	(FT-IR)	(NDIR)	Dif.
5	1.15	1.07	6.92
7	1.00	1.02	2.00
14	1.09	1.74	37.36
21	0.93	1.02	8.82

Fig. 1. Schematic diagram of optical equipment illustrating the path (not simultaneous) of the infrared beam through the combustion reactors.

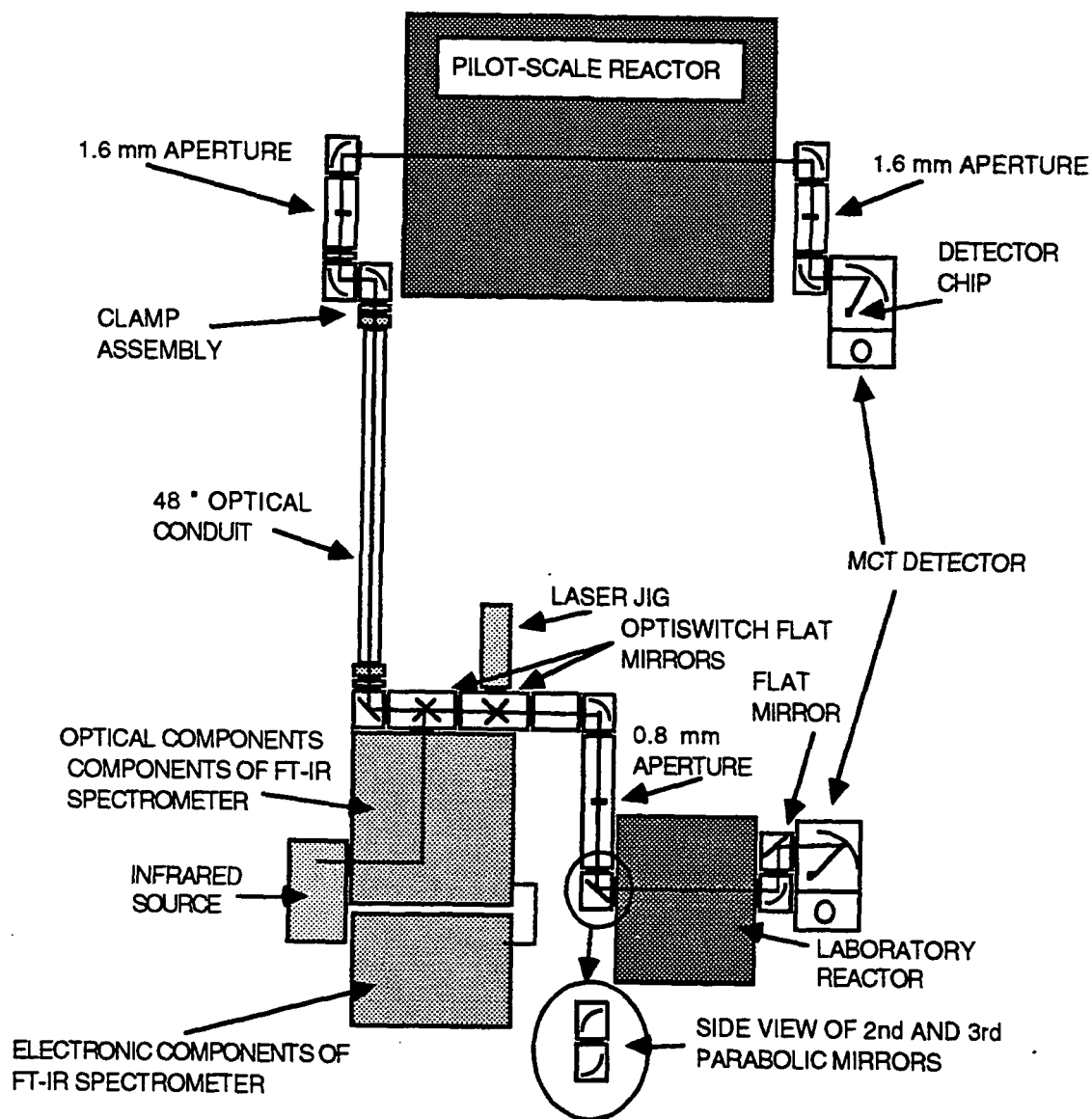


Fig. 2. Schematic diagram of the laboratory-scale black liquor combustion chamber.

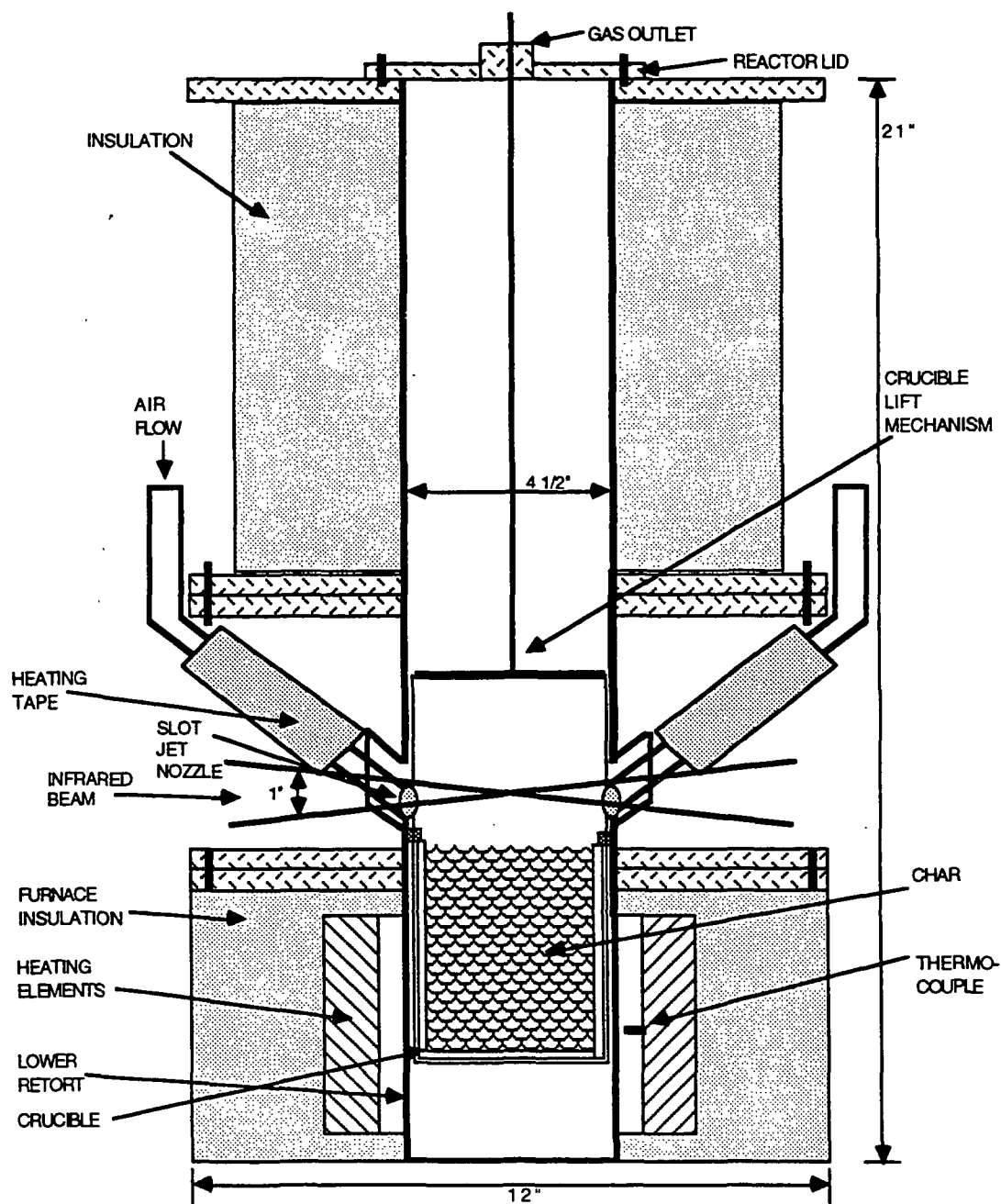


Fig. 3. Schematic diagram of the pilot-scale black liquor char reactor.

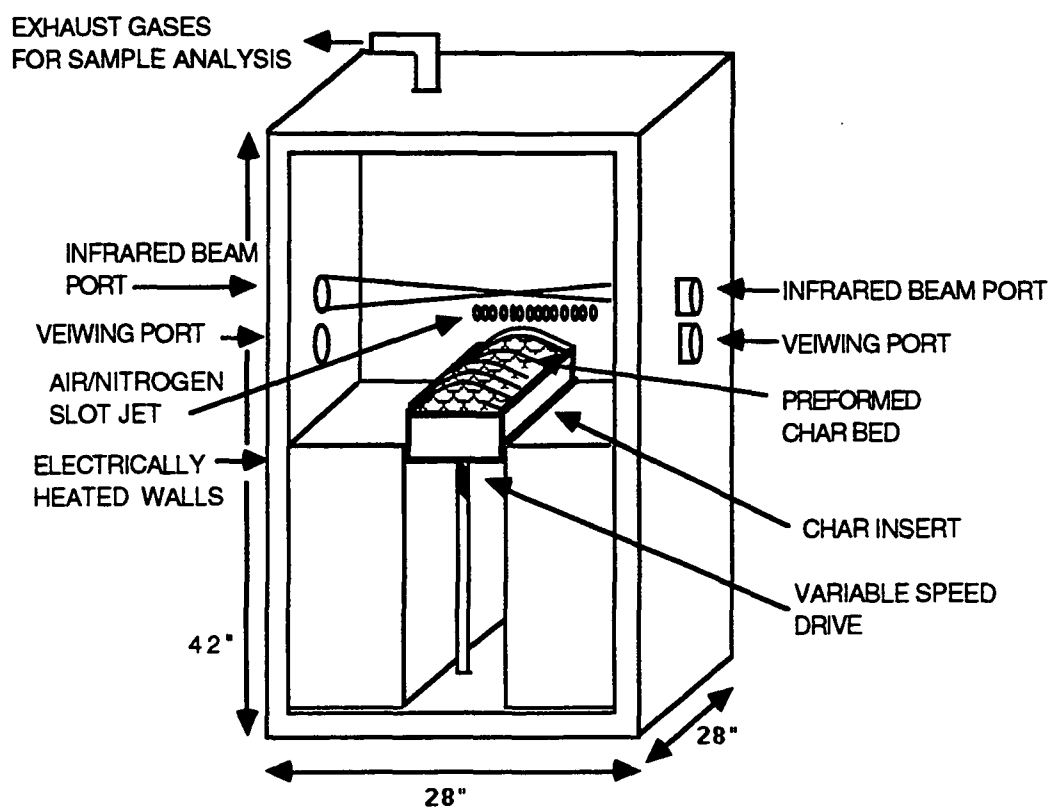


Fig. 4. Absorption spectrum recorded during laboratory char combustion: CO (1900-2250 cm^{-1}) and CO₂ (2250-2400 cm^{-1}) absorbing species.

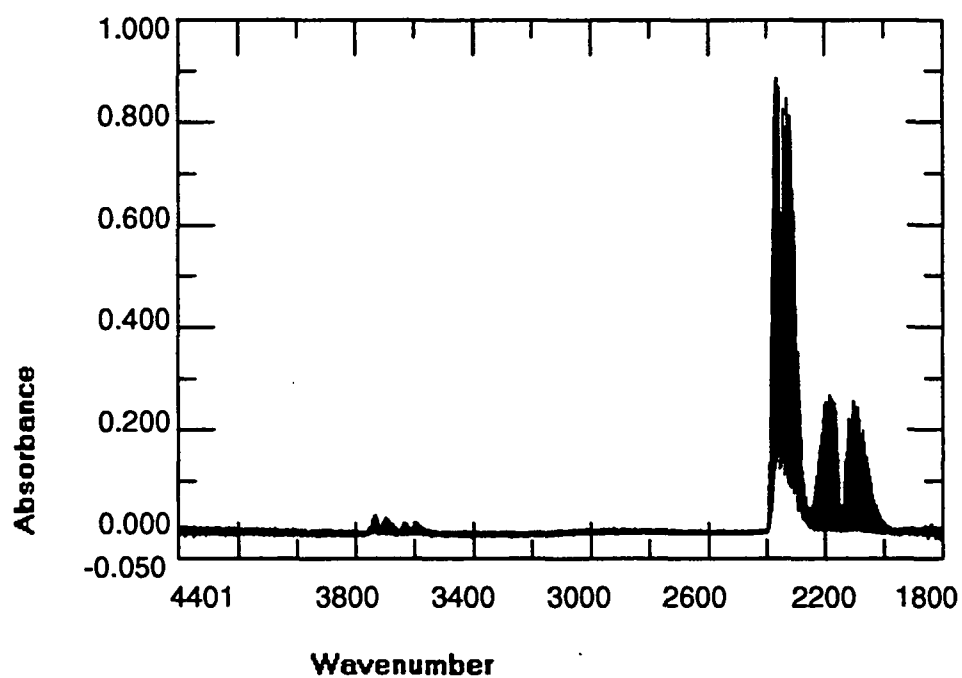


Fig. 5. CO absorption spectrum recorded during laboratory char combustion above a burning black liquor char bed.

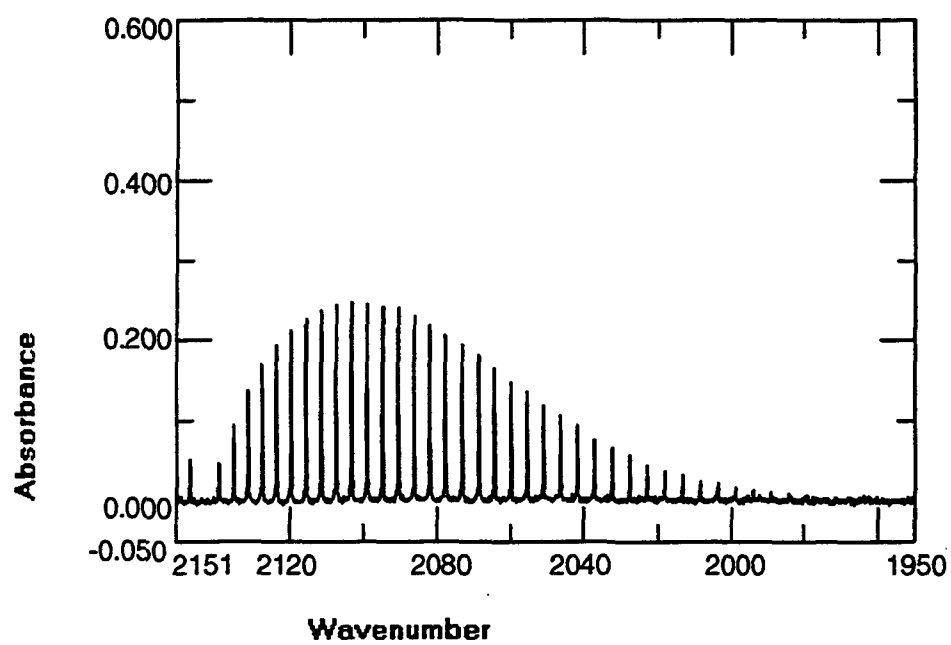


Fig. 6. CO₂ absorption spectrum recorded during laboratory char combustion above a burning black liquor char bed.

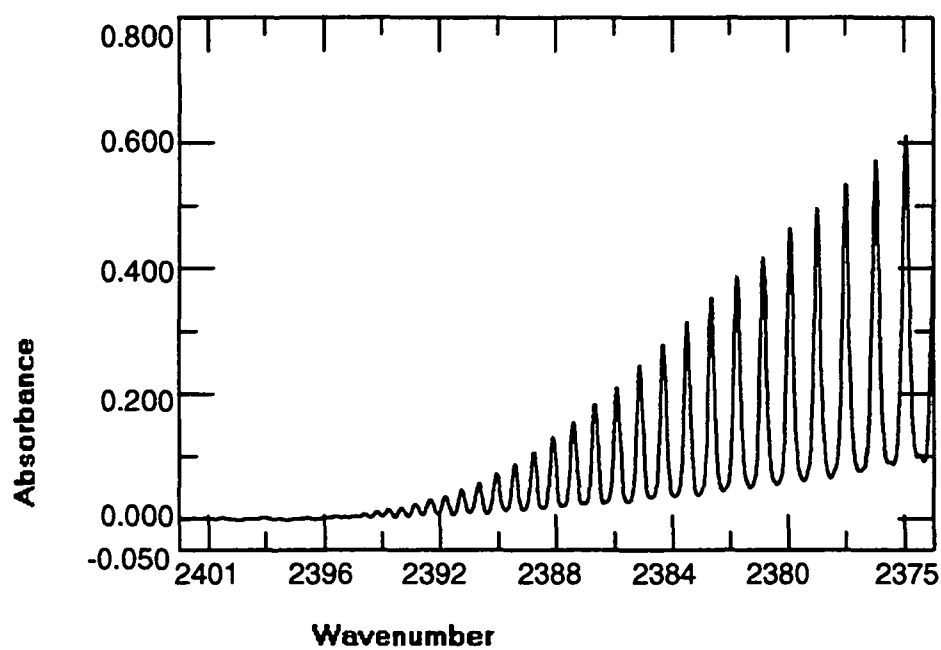


Fig. 7. CO absorption spectrum recorded during pilot-scale char combustion above a burning black liquor char bed.

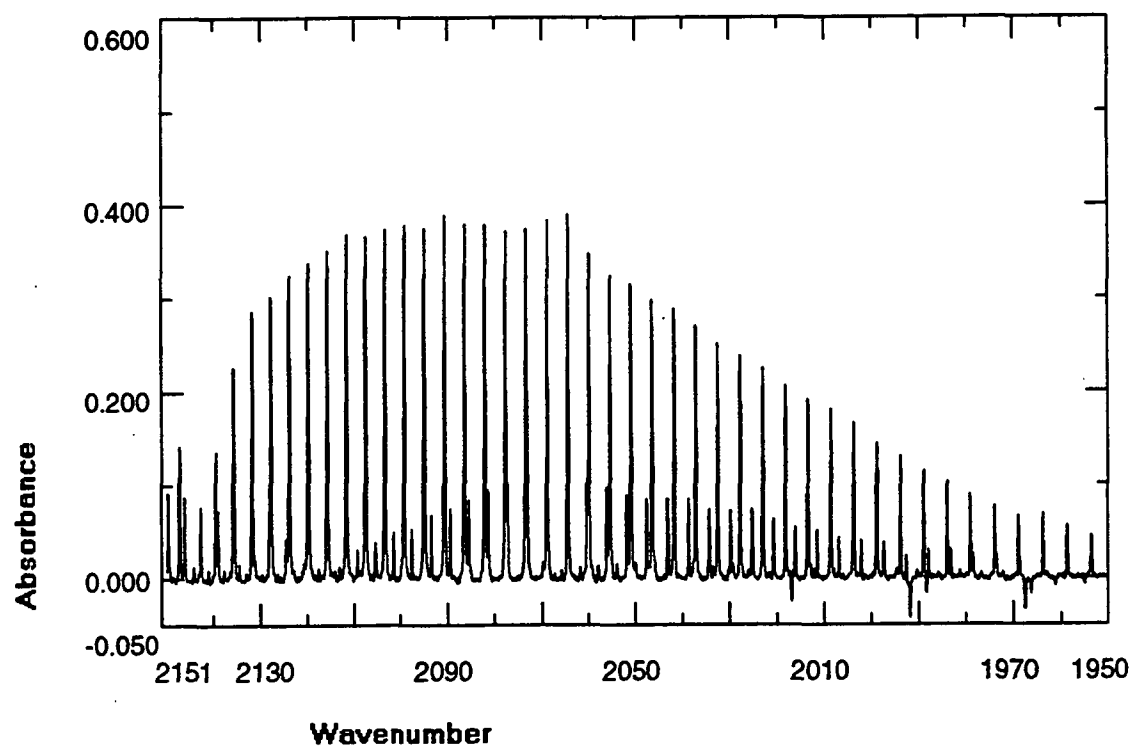


Fig. 8. CO₂ absorption spectrum recorded during pilot-scale char combustion above a burning black liquor char bed.

