Spectral Methods Applied to Fluidized-Bed Combustors

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CONTRACT INFORMATION

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Schedule and Milestones

FY95 Program Schedule

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OBJECTIVES

The goal of this research is to characterize coals and sorbents during the normal operation of an industrial-scale circulating fluidized bed (CFB) boiler. The method determines coal or sorbent properties based on the analysis of transient CO₂ or SO₂ emissions from the boiler. Fourier Transform Infrared (FTIR) spectroscopy is used to qualitatively and quantitatively analyze the gaseous products of combustion. Spectral analysis applied to the transient response of CO₂ and SO₂ resulting from introduction of a batch of coal or limestone into the boiler yields characteristic time constants from which combustion or sorbent models are developed. The method is non-intrusive and is performed under realistic combustion conditions.

BACKGROUND INFORMATION

References [1] and [2] describe the theoretical aspects of this coal combustion research and the development of combustion models. From the relations given for devolatilization and char burning rates in these references, it can be shown that the CO₂ profile resulting from introduction of a batch of coal into a fluidized bed combustor has a fast exponential decay in the devolatilization region and, for time less than the char time constant τ_c, a slower exponential decay in the char burnout region.

The calcination and sulfation processes resulting from introduction of a batch of limestone into a fluidized bed boiler are quite complex. Calcination results in the release of CO₂ from the limestone, while sulfation results in the decrease of SO₂ due to reaction with the calcined limestone. Calcination and sulfation models have been developed [3], but are not as mature as the coal combustion models. Refinement of calcination and sulfation models is ongoing.

Spectral Analysis

Taking the Fourier transform of time series data was developed as a means of finding the hidden periodicities of that data [4]. The modulus-squared of a Fourier transform of a finite data set, called the periodogram, is a statistic which is representative of a zero-mean data series. Plotting the periodogram (with the steady state background level removed and beginning at the time of the devolatilization peak) versus frequency on a log-log plot, called a Bode plot, gives a plot where the two cornering frequencies correspond to the reciprocal of the devolatilization and char time constants. This methodology resolves weak signals in a noisy steady-state background.

The combustion process is characteristic of two first-order processes acting in parallel (devolatilization and char burning). Figure 1 is an example of frequency domain analysis (Bode plot) of the signal from a CO₂ non-dispersive infrared analyzer (NDIR) when a 5 gram sample of 10x14 mesh Indiana bituminous coal is batched into a laboratory combustor. The low-frequency cut-off gives τ_c equal to 27.0 s, which is within 13% of the time-domain value. The high-frequency cut-off gives devolatilization time constant τ_v equal to 2.94 s, in excellent agreement with the value from the time-domain analysis. This spectral analysis method, while providing good results, is sensitive to the duration of the data set. If a long enough data set is not acquired, the analysis will provide a plot which gives clear, but erroneously low, cornering frequencies.

FTIR Theory

Fourier Transform Infrared (FTIR) spectroscopy is a tool which has long been used by analytical chemists, but its use is expanding as capabilities increase and ease of use is improved. Infrared spectroscopy can directly monitor the vibrations of the functional groups which
characterize molecular structure and govern the course of chemical reactions [5]. The "mid-IR" region of the electro-magnetic spectrum between 2.5 μm and 25 μm (normally expressed as wavenumber, 4000 - 400 cm⁻¹) is attractive because it includes the frequencies corresponding to the fundamental vibrations of virtually all of the functional groups of organic molecules. This region has meaningful, well understood absorption bands often adjacent to weakly absorbing regions. This is particularly true for the gases being considered: CO₂, CO, SO₂, NO, NO₂, and N₂O. Quantitative calibrations in the mid-IR are usually straightforward and robust. However, simple diatomic molecules, such as N₂ and O₂, are invisible to infrared radiation and cannot be detected with an FTIR.

The heart of the FTIR is a Michelson interferometer which consists of a beam splitter, compensating plate, and a pair of mirrors [5, 6]. By mechanically varying the linear position of one of the mirrors, the path length between the two arms is altered, giving rise to a time dependent variation in optical intensity, called the interferogram. If the optical source is a broad band infrared spectrum, the interferogram will correspond to the superposition of an infinite number of sine waves having different periods (but a common zero point which occurs when the lengths of the two arms are equal).

A digital computer is used to perform a Fourier transformation of the interferogram, yielding a composite spectrum of the source, the instrument, and any sample in the optical path. This is the basis of all modern rapid-scan FTIR spectrometers.

Water vapor is strongly absorbing in the mid-IR region and its bands overlap the bands of a number of other gases (particularly NO, NO₂, and SO₂) and can obscure their features. However, it can easily be dealt with by removing it from the sample gas stream or subtracting out a pure water vapor spectrum from the spectrum of interest.

Water vapor has been subtracted out of the spectra presented in this paper.

Chemical species are identified through spectral structure and the wavenumber regions in which those features exist. For example, the CO spectrum consists of a series of fine lines between 2250 and 2050 cm⁻¹, while SO₂ has a predominant smooth double hump between 1400 and 1300 cm⁻¹ with a sharp spike at 1355 cm⁻¹ in addition to smaller, less distinct regions about 1150 and 2400 cm⁻¹ (Fig. 2).

Quantification involves identifying a region of interest for each gas and taking spectra of the gases at a number of concentrations spanning the range of concentrations to be measured. A partial least squares approach based on Beer's Law and using Nicolet's Quantir software were used to develop quantification methods for CO₂, SO₂, CO, NO, NO₂, and N₂O.

PROJECT DESCRIPTION

An FTIR was chosen for this project because of its ability to detect and quantify multiple gas species with a single instrument. By developing new quantification methods, quantification of additional gases can be simply, quickly, and inexpensively accomplished. Conventional gas analysis equipment requires a separate instrument for each gas. Since the presence of unburned hydrocarbons, or other interfering gases, was unknown at the beginning of the project, the FTIR provided the ability to identify and deal with any such gases.

The rationale for choosing an FTIR spectrometer was to provide simultaneous, rapid quantification and analysis of a minimum of 6 gaseous combustion products with a single piece of equipment, encompassing the ability to interface with a personal computer for data processing and analysis. The system can detect and quantify the previously mentioned gases in the concentration ranges expected in the boiler flue gas with a small
volume (275 ml) gas cell at one second intervals. The small volume cell permits rapid gas exchange providing the ability to accurately detect fast transients of gas concentration. Inability to detect trace amounts of slightly absorbing gases (specifically H₂S and HCl), lower resolution, and increased lower detection limits are compromises resulting from use of the small-volume, short path length gas cell. Post-processing converts the transient sample spectra to concentrations of the gas species. Spectral analysis is performed on this quantified concentration data.

Experimental apparatus and methods used in the laboratory are described in [1]. A number of experiments similar to those described in [1] were run using the FTIR instead of the NDIR instruments for training, establishing operating parameters for the FTIR, and verifying comparability of the FTIR and reference [1] results.

Figure 3 is a schematic of the Ahlstrom Pyropower circulating fluidized bed boiler (CFB) installed at the Iowa State University power plant. At full load each of the two CFB boilers is rated at 170,000 lb/hr steam flow, 420 psig, 750°F, 250,000 lb/hr coal flow rate, and 8,070 lb/hr limestone flow rate. The bed material is limestone and ash. Normal operating condition is about 60% full load.

The gas sample is drawn from the hot cyclone outlet (at approximately 1600°F and 1/2" H₂O vacuum) by a vacuum pump through about 20 ft of 3/8" stainless steel tubing, three Balston 0.1 micron in-line filters in series to remove fly ash, a Permapure membrane dryer to remove water vapor, and then through the cell. The cell is maintained at 600 mm Hg pressure and 180°F.

A batch of about 25 pounds of double screened coal is injected into the boiler through a hopper installed on the end of the coal drag conveyor that dumps into the lower part of the bed opposite the loop seal. With a quick opening slide gate valve, the batch can be dumped into the boiler in less than two seconds, simulating an impulse input.

The FTIR system is set to record at 2 wavenumber resolution and 2 scans per spectrum giving approximately 1 second sampling intervals. Two to three minutes of steady state background are recorded before dumping the coal batch to verify the background steady state condition.

RESULTS

Laboratory Results

Figure 4 shows a typical FTIR CO₂ profile of a 5g batch of 14x16 Kentucky coal batch test. The devolatilization and char time constants calculated using FTIR data were within experimental error of those presented in [1], calculated from NDIR instrumentation. This confirmed the FTIR would provide experimentally consistent results.

Figure 2 is an FTIR spectrum of a gas sample of the above test at the devolatilization peak. The presence of the light hydrocarbons (methane and acetylene) could not have been identified using the NDIR and chemiluminescence instruments. This indicates that local oxygen starvation and incomplete combustion occurred. The methane spectrum overlapping SO₂ can alter the SO₂ quantification, but can be subtracted out.

Power Plant Results

Figure 5 is the CO₂ profile resulting from dumping a 25 lb batch of 16x18 sieve size Illinois wash coal into the CFB boiler. The +/- .3% fluctuations about the mean in the steady state background are true fluctuations in the CO₂ emissions, and not a result of instrument or flow noise in the sampling system. These fluctuations, due to variations in coal feed rate and coal particle fragmentation hamper calculation of char time.

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constants. The overall profile is similar to that seen in the laboratory testing, and is anticipated from combustion theory.

However, there are significant, and as of yet unexplained, differences from the laboratory test CO₂ profiles in the bubbling fluidized bed combustor. The CO₂ profile peaks sharply, before decaying to essentially background levels, rises slightly, flattens and begins a slow decay to background level. The sharp peak is clearly associated with devolatilization whereas the second peak is thought to be due to slow char combustion. This indicates char burnout does not begin until after devolatilization is complete, in contradiction to [1] which showed that devolatilization and char burnout occurred simultaneously. The maximum CO₂ level of the char burnout is much less than that seen in the lab results for similar sized particles. Particle fragmentation and slow heating of the char are potential explanations. Further investigation into this phenomenon is planned.

Devolatilization time constants calculated for the samples run in the CFB are within experimental range of error of those from lab tests. The char time constants are more difficult to calculate, and correlation with laboratory data has not yet been achieved due to the different profile. These observations are based on a very limited number of samples and cannot be considered conclusive.

The spectrum at the devolatilization peak, Fig. 6, shows CO₂, CO, SO₂, NO, acetylene, and methane with potentially trace amounts of N₂O. The presence of CO, acetylene, and methane during the devolatilization phase indicates that incomplete combustion occurs in this phase, at least near the batched particles. Methane and acetylene would not have been detected with conventional boiler instruments. The interpretation of these results are the subject of continuing research.

Due to the very recent completion of these CFB boiler tests, the results of spectral analysis applied to this data has not been completed.

FUTURE WORK

- Determine impact of the industrial-scale CFB boiler on combustion dynamics in comparison to the laboratory scale bubbling bed combustor, particularly as relates to the devolatilization and char CO₂ profile differences.
- Determine variation of τᵥ and τₖ with initial particle diameter and compare to laboratory results.
- Test two different coal types provided by Pyropower.
- Determine calcination and sulfation rate constants in the CFB.
- Refine calcination and sulfation models.
- Refine spectral analysis methods for the FTIR data.

REFERENCES

Figure 1. Example of Frequency-Domain Analysis for a Batch Sample

\[ \tau_c = \frac{1}{\omega_c} = 27.0 \text{ s} \]
\[ \tau_v = \frac{1}{\omega_v} = 2.94 \text{ s} \]

Figure 2. Example Spectrum of Devolatilization Peak From Laboratory Test
Figure 3. Instrumentation of the Pyropower Boiler at ISU Physical Plant

5 grams of 7x8 mesh Kentucky coal

Figure 4. Example of CO₂ Profile from Laboratory Bubbling Bed Combustor
25.0 pounds of 16x18 mesh Illinois Wash Coal

Figure 5. Example of CO₂ Profile from ISU Circulating Fluidized Bed Boiler

Figure 6. Example Spectrum of Devolatilization Peak from Power Plant Test