# APENDIX C

## Application of FT-IR E/T Spectroscopy to Study Coal Combustion Phenomena

# APPLICATION OF FT-IR E/T SPECTROSCOPY TO STUDY COAL COMBUSTION PHENOMENA

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## INTRODUCTION

Better understanding of coal combustion process would promote more reliable utilization of coals having a diversity of characteristics and would enable improved combustion systems to be designed and developed. Many aspects of coal combustion are understood and can be adequately modeled. However, several unresolved fundamental issues remain: among these are ignition, soot formation, swelling, char reactivity, ash formation and the influence of turbulence on chemical reactions and particle dispersion.

Techniques to measure these phenomena must be capable of following the behavior of the solid particles as well as the gas species. Many of the techniques for gas analysis were recently reviewed (1-3). For particle temperature, 2 or more color pyrometry has been used extensively (4-9). Advances in optical emission techniques to simultaneously measure size, velocity, and temperature of single particles have also been reported (10,11).

Recently, Fourier Transform Infrared (FT-IR) Spectroscopy has shown promise as a versatile technique. FT-IR transmission spectroscopy has been used as an in-situ diagnostic technique to determine both gas concentrations (12,13) and temperatures (14-17). An FT-IR emission and transmission (E/T) spectroscopy technique has been applied to particles, gases and soot in flames (18-22). The E/T technique has been used previously for gases and soot (7,8,23-26). The disadvantage of FT-IR E/T spectroscopy are that the measurements are for an ensemble of particles over a line of sight. Tomographic techniques must be used to obtain spatially resolved data. Advantages of the technique include: 1) the capability to determine separate temperatures and concentrations for individual gas species as well as for solid particles by employing different regions of the infrared spectrum; ii) the capability to determine temperatures as low as 100°C and so follow particle temperatures

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prior to ignition; and iii) the capability to measure the radiative contribution from soot by comparing low frequencies (where contributions from soot are minimized) to high frequencies (large soot contributions). This paper describes the application of the FT-IR E/T technique to study coal flames produced in a transparent wall reactor.

## EXPERIMENTAL

The Transparent Wall Reactor (TWR) facility shown in Fig. 1 consists of an electrically heated furnace and a heat exchanger. Gas is passed through the heat exchanger and exits the top of the furnace after passing a screen to smooth the flow. The hot gas stream, which is 10 cm in diameter, remains relatively hot and undisturbed for approximately 20 cm above the screen. Coal entrained in a cold carrier gas is injected through a co-axial 4 mm diameter tube.

The coal is fed using a previously described system (14) in which gas enters the top end of an enclosed cylinder filled with coal and exists through a tube which is slowly lowered through the bed of coal at a constant rate. Three cylinders were used to achieve a steady flow. Nitrogen was used for pyrolysis studies and air for combustion. The feed rate for the carrier gas was 0.3 l/min and for the hot gas, 400 l/min. The hot gas exits the screen at a temperature of 910°C and a velocity of 3.4 m/sec. Short exposure photographs show particle tracks which indicate that the coal particles are moving at about 3.7 m/sec near the injector and 6.2 m/sec in the flame.

An octagonal glass enclosure shields the reacting stream from room air currents. The enclosure has a movable KBr window to allow access to the flame by the FT-IR spectrometer which is shown in Fig. 2. A flow of air along the inside of the enclosure keeps the glass from overheating. The cooling air and reacting stream are vented into a duct connected to an exhaust fan through a gate valve. The gate valve, coal feed, and gas flows were adjusted to achieve a steady flame under combustion conditions. Figure 3 shows photographs of a lignite which ignites close to the nozzle and a low volatile bituminous coal which ignites higher up.

The Nicolet 20SX FT-IR and transfer optics to focus the beam within the sample stream are illustrated in Fig. 2. Emission measurements are made with the movable mirror in place. Transmission measurements are made with the movable mirror removed.

The samples used in these experiments were -200, +325 mesh sieved fractions of a lignite, a subbituminous coal, and several bituminous coals. The samples were also characterized in a TGA to determine their weight loss at constant heating rate in nitrogen and in air.

## ANALYSIS

For multi-phase reacting systems, measurements are made of the transmittance and the radiance, and from these a quantity called the normalized radiance is calculated. The analysis, which follows Siegel and Howell (27) has been presented previously (18). The relevant equations for a homogeneous medium are presented below.

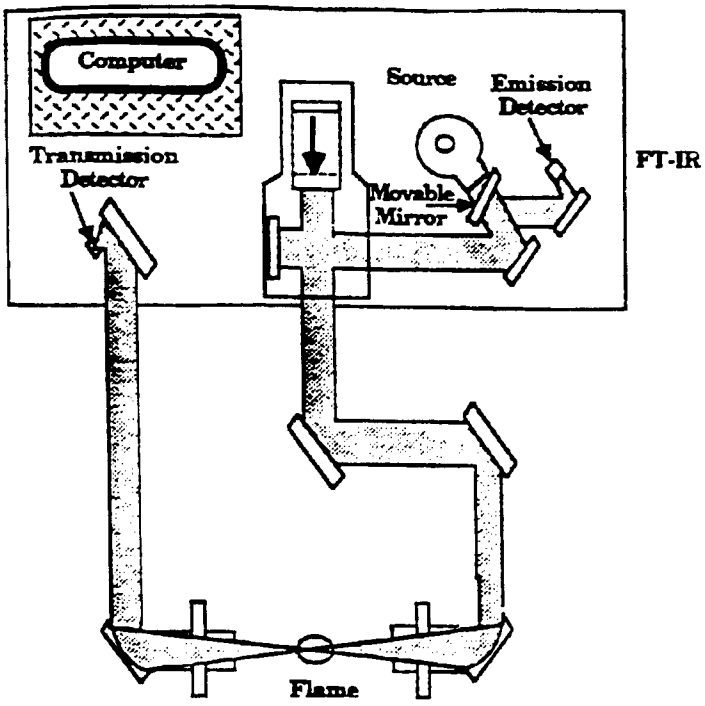


Figure 2. Spectrometer and Transfer Optics.

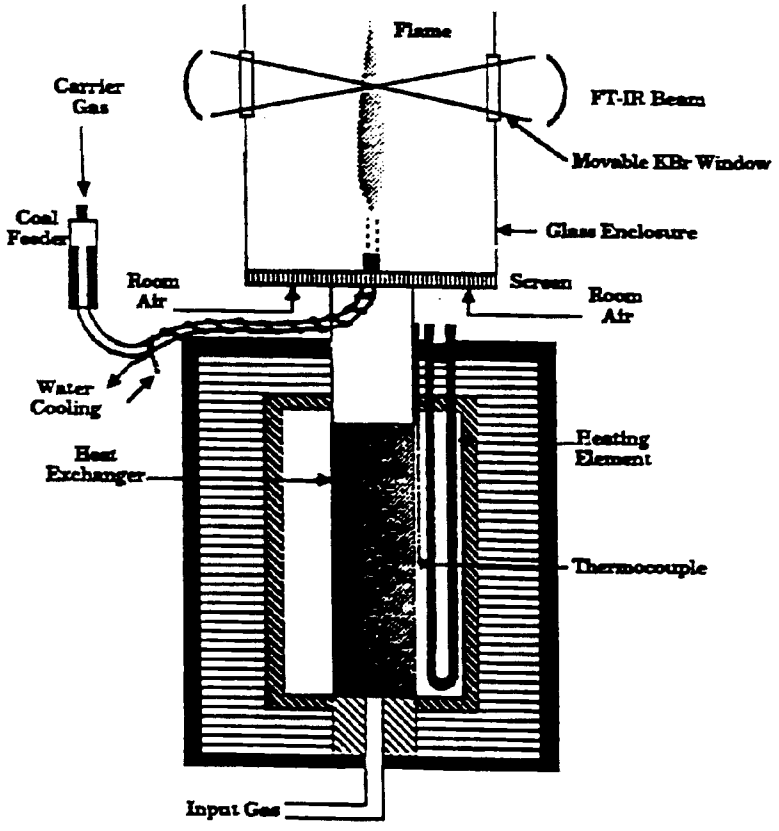


Figure 1. Transparent Wall Reactor.

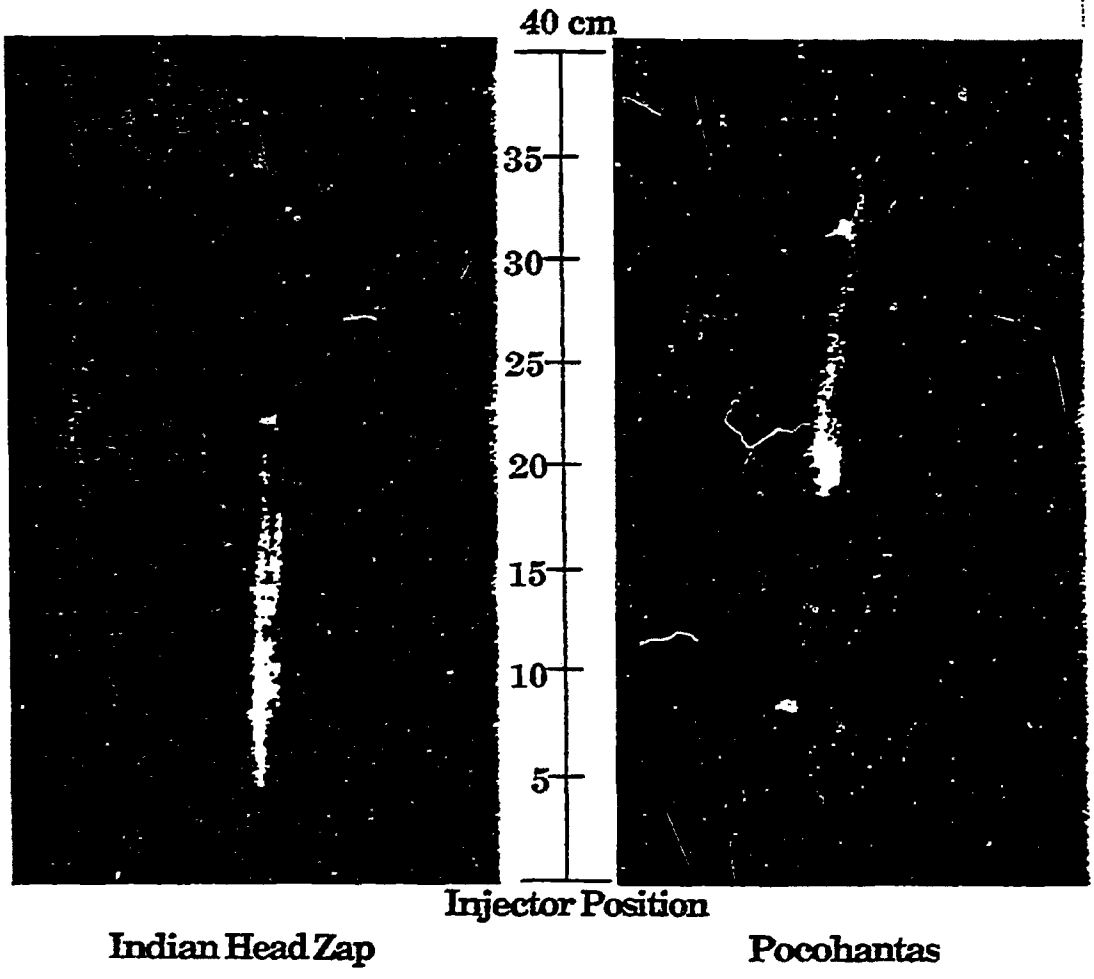


**Figure 3. Photographs of a Zap North dakota Lignite Flame (left) and a Pocahontas Bituminous Coal Flame (right). The scale in the center is the distance above the injector nozzle.**

**Transmittance, $\tau_\upsilon$**

The transmittance, $\tau_\upsilon$, is defined as

$$\tau_\upsilon = I_\upsilon / I_{o\upsilon} \qquad (1)$$

where $I_{o\upsilon}$ is the intensity transmitted in the absence of sample, while $I_\upsilon$ is that transmitted with the sample stream in place. For a medium containing gases and soot with absorption coefficients $\alpha^g_\upsilon$ and $\alpha^s_\upsilon$ and particles of geometrical cross sections area A at a density of N particles $cm^{-3}$,

$$\tau_\upsilon = \exp(-(\alpha^s_\upsilon + \alpha^g_\upsilon + NAF^t_\upsilon)\, L) \qquad (2)$$

where $F^t_\upsilon$ is the ratio of the total cross section (extinction) to geometric cross section, and L is the path length. $\tau_\upsilon$ is sometimes plotted as a percent.

**Radiance, $R_\upsilon$**

To measure the sample radiance, $R_\upsilon$, the radiative power emitted and scattered by the sample with background subtracted, $S_\upsilon$, is measured, and converted to the sample radiance,

$$R_\upsilon = S_\upsilon / W_\upsilon \tag{3}$$

where $W_\upsilon$ is the instrument response function measured using a black-body cavity.

**Normalized Radiance, $R^n_\upsilon$**

The normalized radiance, $R^n_\upsilon$, is defined as,

$$R^n_\upsilon = R_\upsilon / (1 - \tau_\upsilon) \tag{4}$$

which can be expressed in terms of the properties of the medium as

$$R^n_\upsilon = \frac{\alpha^s_\upsilon R^b_\upsilon(T_s) + \alpha^g_\upsilon R^b_\upsilon(T_g) + NA\ \epsilon_\upsilon R^b_\upsilon(T_p) + NAF^{s'}_\upsilon R^b_\upsilon(T_w)}{\alpha^s_\upsilon + \alpha^g_\upsilon + NAF^t_\upsilon} \tag{5}$$

where $R^b_\upsilon(T_g)$, $R^b_\upsilon(T_s)$ and $R^b_\upsilon(T_p)$ are the black-body emission spectra at the temperatures of the gas, soot, and particle, respectively. $\epsilon_\upsilon$ is the particle's emittance and $F^{s'}_\upsilon$ is the cross section for scattering radiation into the spectrometer. No scattering is assumed for soot particles in the IR region. For the geometry of the TWR where measurements are made perpendicular to the length of an optically thin flame, the scattering term may be neglected.

**RESULTS**

**FT-IR Measurements**

FT-IR measurements were made along the center of the flame at several positions above the coal injector for flames from several coals under identical conditions. Figures 4 and 5 are spectra obtained with a Zap North Dakota lignite. Figure 4 presents four transmittance spectra at: 3 cm above the nozzle, in the region prior to ignition (Fig. 4a); 6 cm, at the beginning of the ignition region (Fig. 4b); 8 cm, in the brightest part of the flame (Fig. 4c); and 44 cm, above the flame (Fig. 4d).

The attenuation in Fig. 4a is almost entirely from particles i.e., $\alpha^g_\upsilon$ and $\alpha^s_\upsilon \approx 0$. The shape of the spectrum slopes due to diffraction effects. In the optically thin limit, the amplitude of $(1-\tau_\upsilon)$ is proportional to the intersected surface area of the particles, NAL, times the extinction efficiency, $F^t_\upsilon$. $F^t_\upsilon$ has the shape predicted by Mie theory for 200 x 325 mesh particles and a 2° collection angle in the spectrometer. In Fig 4b, the attenuation is lower due to spreading and heating of the particle stream. A few particles have ignited and attenuation from $CO_2$ and $H_2O$ is larger. The attenuation in the ignition zone (Fig. 4c) contains larger contribution for $CO_2$ and $H_2O$, a contribution from soot, as shown in the figure, as well as a contribution from the particles. $F^t_\upsilon$ for the particles is assumed to have the same shape as prior to ignition and the soot contribution is the difference between the particle attenuation and the total. Much larger soot contributions are observed for bituminous coals. Figure 4d illustrates the spectrum above the flame. $(1-\tau_\upsilon)$ is

substantially reduced as the particles have burned out.

Radiance measurements are shown in Fig. 5. In the absence of soot and in regions of the spectrum away from gas lines Eqs. 2, 4 and 5 reduces to $R_\upsilon = NAL\ \epsilon_\upsilon R^b_\upsilon(T_p)$ in the optically thin limit. NAL can be determined from the transmittance spectrum using the theoretical value of $F^t_\upsilon$ at one wavelength ($F^t_\upsilon \approx 1.2$ at 6500 $cm,^{-1}$). The temperature can then be determined by comparing $R_\upsilon$ /NAL with $R^b_\upsilon(T_p)$ if $\epsilon_\upsilon$ is known. Figure 5a shows $R_\upsilon$ /NAL prior to ignition. A particle temperature (740 K) is determined from the region between 1200 and 1600 $cm^{-1}$ where for coal (which is non-gray (18-20)) $\epsilon_\upsilon$ 1. Figure 5b shows $R_\upsilon$ /NAL in the region where a few particles have ignited. The temperature of the ignited

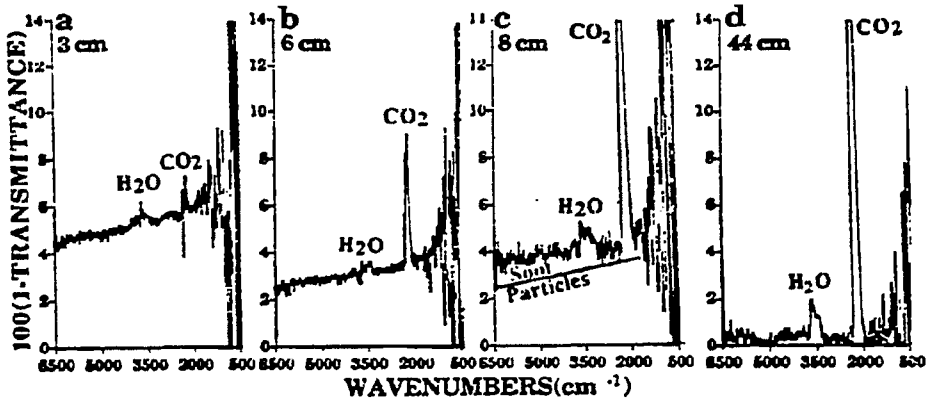


**Figure 4. 100(1-transmittance) Spectrum for Combustion of Zap North Dakota Lignite.**

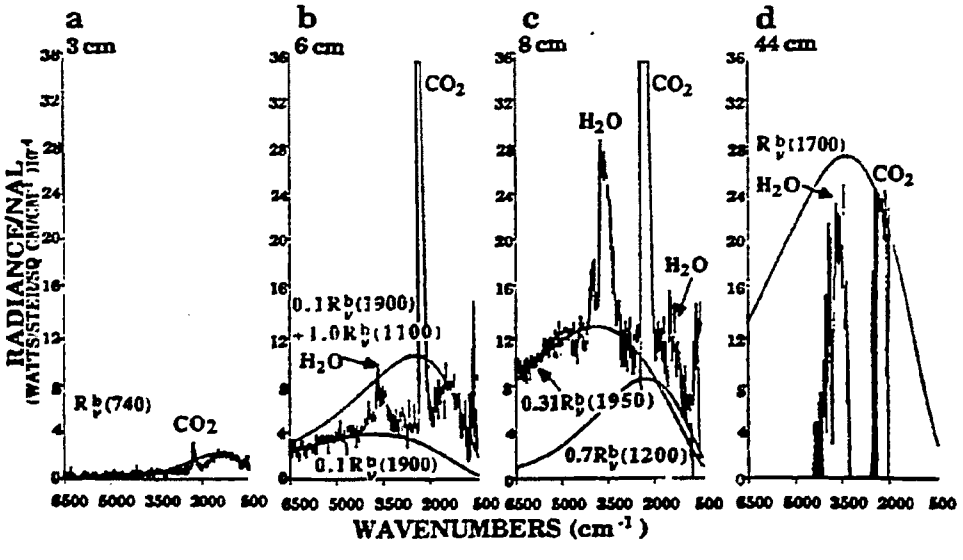


**Figure 5. Radiance Spectrum for Combustion of Zap North Dakota Lignite. Figure d is for Normalized Radiance in the $H_2O$ and $CO_2$ Regions only.**

particles (1900 K) is determined from the shape of the region above 4000 $cm^{-1}$ assuming a gray-body for char (18). It is substantially higher than the unignited particles (1100 K). Figure 5c shows the $R_\upsilon$ /NAL in the

region where most of the particles are ignited. The shape of the spectrum is consistent with a temperature of 1950 K but the amplitude is only 0.31 of the black-body. This is lower than expected, assuming $\epsilon_\upsilon = 0.7$ for char (18) and will be discussed below. In Fig. 5d, the particle contributions to the radiance is very low and a particle temperature can not be accurately determined.

After the particle temperatures and attenuation contributions from particles have been determined, the $CO_2$ temperatures can be obtained from the normalized radiance by application of Eq. 5. In the absence of particles such as in Fig. 5d, Eq. 5 reduces to $R^n_\upsilon = R^b_\upsilon(T_g)$. The $CO_2$ temperatures, particle temperatures and uncorrected thermocouple temperatures are summarized in Table I for the Zap North Dakota lignite.

**TABLE I. Temperature Measurements for the Zap North Dakota Lignite Flame.**

| Position | Temperatures | | |
|---|---|---|---|
| | TC | $CO_2$ | Particles |
| | (K) | (K) | (K) |
| 3 cm | 693 | 1100 | 740 |
| 6 cm | 818 | 1610 | 1100-1900 |
| 8 cm | 1610 | 2080 | 1950 |
| 20 cm | 1500 | 2080 | 1950 |
| 44 cm | 931 | 1700 | -- |

Interference from soot appears to be the most likely explanation for the low value of radiance in the ignition region (8 cm). The abnormally low particle area due to a surrounding soot cloud discussed by Timothy et al. (4) is similar. Support for this explanation can be found in the $1-\tau_\upsilon$ spectra which suggest the presence of soot. Soot clouds around particles have also been observed by other investigators (9,28,29). Timothy, et al. (29) observed the particles to be colder than the cloud. Assuming soot is an important contribution to the radiance, the particle temperature can still be obtained by matching the amplitude of $0.7\ R^b(T_p)$ at low frequencies where the soot contribution is small. This gives a particle temperature of 1200 K. This is reasonable considering that the evolving products from a pyrolyzing particles will tend to thermally isolate it from its surroundings. The soot temperature can be determined using Eqs. 2 and 5 in the high frequency end of the spectrum where radiation contributions from the particles and gases can be neglected. $T_s = 1900$ in agreement with the $CO_2$ temperature of 2080.

**Ignition Behavior**

A number of coals were run in the TWR. The ignition delay, or distance above the injection nozzle, was observed to vary from a few cm to over 30 cm. For example, the lignite in Fig. 3 ignites at 8 cm while the Pocahontas bituminous ignites at 23 cm. The ignition delay increased with increasing rank and decreasing volatile matter content. The average temperature of the coal particles prior to ignition varied from 800 to 900 K. To provide understanding of what controls the ignition delay, weight loss profiles were measured in a TGA under nitrogen and under air. There was a good correlation between the relative reactivity under pyrolysis conditions and the relative ignition distance in the TWR (i.e., the lower the temperature at which pyrolysis occurs, the smaller the ignition distance). The correlation with reactivity in air was not good.

The results suggest that for the coals and conditions studied here, ignition is controlled primarily by combustion of the volatiles.

## CONCLUSIONS

1. The FT-IR E/T technique appears to be a versatile technique for coal combustion diagnostics.
2. Results in the ignition region suggest a hot burning soot cloud surrounding colder particles.
3. Ignition delays appear to be controlled by the kinetics of volatile release rather than heterogeneous oxidation.

## ACKNOWLEDGEMENT

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