

USE OF TG-FTIR ANALYSIS FOR THE CHARACTERIZATION OF FUELS AND RESOURCES

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ABSTRACT

Thermogravimetric (TG) analysis combined with Fourier Transform Infrared (FT-IR) analysis of evolved products has proven to be a powerful technique for characterization of coal, source rock, heavy hydrocarbons, biomass, waste materials, and plastics. The TG-FTIR method can be used to determine the resource potential of a material, i.e., the types of products a material is likely to produce when subjected to processing by pyrolysis or combustion. It can also provide kinetic information for model validation or extrapolation and can provide the equivalent information to proximate and ultimate analysis. In addition, TG-FTIR analysis can be used to characterize the adsorbent potential and combustion reactivity of solids. The TG-FTIR method can provide this information in a more rapid, reproducible, and inexpensive way when compared to most other types of laboratory characterization methods such as drop tube reactors. This paper reviews the application of TG-FTIR analysis to hydrocarbon fuels and resources.

INTRODUCTION

Thermogravimetric analysis (TGA) has been employed in coal science to perform a number of characterizations including: proximate analysis,¹ kinetics of weight loss,² char reactivity,^{3,6} and gas adsorption measurements.⁷ A complementary technique, evolved product analysis, has been employed to study pyrolysis product distributions and kinetics,⁸⁻¹¹ functional group compositions,^{10,12,13} and temperature programmed desorption.¹⁴⁻¹⁵ A TG-FTIR instrument combines TGA with evolved product analysis by Fourier Transform Infrared (FT-IR) spectroscopy. FT-IR analysis of evolved products has advantages over mass spectroscopy in allowing analysis of very heavy products, and over gas chromatography in speed.

TG-FTIR instruments are available from several instrument manufacturers, including On-Line Technologies, Inc. (On-Line), an affiliate of Advanced Fuel Research, Inc. (AFR). In addition, Bio-Rad and Perkin-Elmer, among others, offer a TG-FTIR instrument. One of the differences among these instruments is the method used to analyze and quantitate the heavy liquid products from pyrolysis of the sample, which form an aerosol upon subsequent cooling prior to entry into the multi-pass FT-IR cell. These instruments have primarily been used for the analysis of polymers, pharmaceuticals, minerals, etc., including a limited amount of work done at AFR.^{17,36,37} Nearly all of the work on the application of TG-FTIR to hydrocarbon fuels and resources has been done at AFR or its collaborators. Consequently, the scope of this review will be limited to this body of work.

The application of TG-FTIR to coal analysis at AFR has been described in several publications.¹⁶⁻²⁵ To analyze coal, a sequence of drying, pyrolysis and combustion is employed to obtain: proximate analysis, volatiles composition, volatiles kinetics, and relative char reactivity. By using several different heating rates, kinetic rate constants for volatiles evolution have been obtained.^{17,21} TG-FTIR analysis has also been used at AFR to characterize other hydrocarbon materials such as modified coal samples,²⁶⁻²⁸ coal liquefaction resids,²⁹ petroleum source rocks,³⁰ lubricants,³¹ biomass,^{32,33} waste tires,^{34,35} and polymers.^{17,36,37} This paper will briefly review the use of the TG-FTIR technique at AFR for the characterization of hydrocarbon fuels and resources.

EXPERIMENTAL

Apparatus - A schematic of the AFR TG-FTIR instrument is presented in Fig. 1. Its components are as follows: a DuPont™ 951 TGA; a hardware interface (including a furnace power supply); an Infrared Analysis 16 pass gas cell with transfer optics; a Bomem 110 FT-IR; (Resolution: 4 cm⁻¹, Detector: MCT). A helium sweep gas (250 cc/sec) is employed to bring evolved products from the TGA directly into the gas cell. A window purge of 700 cc/sec is employed at each end of the cell. The system is operated at atmospheric pressure. This instrument package is available commercially as the *TG/plus* from On-Line Technologies, Inc. (East Hartford, CT).

The most difficult volatiles to analyze are the heavy decomposition products which condense at room temperature, such as tars from coal. In the *TG/plus*, the high conductivity helium sweep gas and the rapid cooling cause these products to form an aerosol which is fine enough to follow the gas through the analysis cell. The cell is connected without restrictions to the sample area. The aerosol is also fine enough that there is only a little scattering of the infrared beam and it is thus attenuated almost as though the tar was in the gas phase, as shown in Fig. 2. Based on the aerosol's Rayleigh scattering of infrared radiation, the diameter of the aerosol droplets in this case is less than 1.0 μm. As indicated above, the

technique for analysis of the heavy liquid aerosols is one of principal features that differentiate the various commercial TG-FTIR instruments.

Procedure - As an example of the analysis procedure, the pyrolysis and oxidation of a lignite is described. More detail can be found in Refs. 16 and 17. Figure 3a illustrates the weight loss from this sample and the temperature history. A 35 mg sample of Zap lignite, loaded in the sample basket of the DuPont™ 951, is taken on a 30 °C/min temperature excursion in the helium sweep gas, first to 150 °C to dry for 240 sec, then at 30 °C/min to 900°C for pyrolysis. Upon reaching 900 °C, the sample is immediately cooled to 250 °C over a twenty minute period. After cooling, a small flow of O₂ (0.3 cc/sec) is added to the helium sweep gas at the 57 minute mark and the temperature is ramped to 700 °C at 30 °C/min (or as high as 1000 °C) for oxidation.

During this excursion, infrared spectra are obtained once every thirty seconds. As shown in Fig. 2, the spectra show absorption bands for CO, CO₂, CH₄, H₂O, SO₂, COS, C₂H₆, and NH₃. The spectra above 250 °C also show aliphatic, aromatic, hydroxyl, carbonyl and ether bands from tar. The evolution of gases derived from the IR absorbance spectra are obtained by a quantitative analysis program which employs a database of integration regions and calibration spectra for different compounds^{16,17}. The routine employs regions of each calibration spectrum which permit the best quantitation with the least interferences. The routine is fast enough to allow the product analysis to be displayed on the computer screen during the actual experiment.

Figure 3b illustrates the integral of the evolution curves to obtain the cumulative evolved product amounts. Because the data are quantitative, the sum of these curves match the weight loss as determined by the TGA balance. Discrepancies occur in this match because of missing components such as H₂ which cannot be seen by IR. Also, when O₂ is introduced, the balance shows a net gain in weight due to O₂ chemisorption.

The TG-FTIR system provides all of the usual capabilities of a TGA for measurement of char reactivity or surface characterization by Temperature Programmed Desorption (TPD) with the additional advantage of measurement of the evolved products. A non-isothermal reactivity test developed at AFR using a conventional TGA system^{3,5} was later adapted to the TG-FTIR.³⁸ Studies of coal chars using TPD have also been made in this apparatus.²⁴

RESULTS AND DISCUSSION

Examples of analyses done with the TG-FTIR apparatus will be presented in detail for coal samples and selected examples will be given for lignin and polymers. The coal data included in this paper is primarily from samples from the Argonne Premium sample bank, which have been extensively characterized using this technique.^{18,19,21,24-26} Other characterizations of the Argonne samples have been summarized by Vorres.³⁹

Measurement of Char Properties - The results from the application of the TG-FTIR instrument to measurements of the critical temperature (T_c) (an index of reactivity that defines the temperature at which a small but measurable rate of weight loss occurs) and the oxygen chemisorption capacity (OCC) for the Argonne Premium coals are shown in Fig. 4. As expected, the values of T_c decrease with decreasing rank (increased oxygen content) which indicates that lower rank coals are more reactive. This variation in reactivity with rank is primarily due to mineral contributions to reactivity.^{2,5} The measurements of oxygen chemisorption capacity (OCC), which are related to the active site concentration, are inversely related to T_c, and are also shown in Fig. 4. In our work, we have found that the value of T_c is a more useful correlative parameter for reactivity than the OCC.³⁸

Measurement of Volatile Product Evolution - The TG-FTIR system has been used to conduct programmed pyrolysis experiments on the Argonne premium coals over a range of heating rates (3, 30, 50, 100 °C/min).^{18,19,21,24-26} The changes in the positions of the evolution curves with temperature for the various volatile components can be used to define the kinetic parameters. An example is shown in Fig. 5 where the temperature for the maximum tar evolution rate is plotted for the eight Argonne coals at two different heating rates. Similarly, the changes in the integrated amounts of each volatile product can be used to characterize the coal functional group composition, as shown in Fig. 6 for the evolution of NH₃.

An example of results from TG-FTIR analysis of eight lignin samples is shown in Fig. 7. This plot shows a summary of the gas, tar and char yields for a study where high tar yields were desired to allow subsequent processing of lignin into carbon materials.²² The tar yields from the eight lignin samples varied from ~10 wt% for the H₂SO₄ lignin to >50 wt.% for the Iotech lignin. Another feature of the use of TG-FTIR for the analysis of hydrocarbon materials is the ability to conduct an on-line spectroscopic analysis of the heavy liquid products. An example is shown in Fig. 8, which compares the spectrum obtained at the temperature of the maximum evolution rate for six polymers. The slope of the baseline indicates the degree of scattering and hence the size of the tar aerosols, as discussed above. This is a characteristic of the material which depends on the molecular weight distributions of the oligomers formed, the viscosity, and surface tension. Since the tar aerosol droplets are components of smoke and, ultimately of soot, the technique has the potential to provide information which correlates with these important combustion properties of polymers. Figure 8 indicates that the TG-FTIR method reveals

significant differences in the tar structure and in the size of the tar aerosols between these different polymers.

Relationships between Kinetic Rates of Different Volatile Species - It has been found that some pools in the different volatile species have peak evolution rates at the same temperature and those peaks have the same shifts when the heating rate changes. The Utah Blind Canyon coals provides a good example of this phenomenon^{19,24}. The TG-FTIR measurements indicate that the tar evolution, the CO₂-Loose, CO-Loose, and the H₂O-Loose pools all show very close peak evolution rate temperatures, at about 480 °C for 30 °C/min., at about 519 °C for 100 °C/min. and at about 430 °C for 3 °C/min. runs. This feature implies that these volatile pools can be fit with the same kinetic parameters. This may also imply that there is some common evolution chemistry.

Modeling of Devolatilization Processes - The kinetic parameters for the functional group pools from the eight Argonne premium coals and some additional coals have been determined using a set of rules that were developed to allow a systematic method of establishing the rank variations (e.g., the frequency factors were fixed at values of less than 10¹⁵/sec. and only the activation energies were allowed to vary with rank)²¹. The kinetic and compositional parameters obtained from TG-FTIR analysis are used along with other characterization information to calibrate our Functional Group - Depolymerization, Vaporization, Crosslinking (FG-DVC) model of coal devolatilization.²¹ A typical comparison of theory and TG-FTIR data is shown in Figs. 9 and 10. Figure 9 shows a comparison of theory and experiment for the weight loss and major volatile species for pyrolysis of a Consol #2 coal at 30 °C/min. Figure 10 shows a comparison of FG-DVC model predictions and experimental data for the tar evolution rate at 30 °C/min. from all eight Argonne Premium Coals. The agreement between the theory and experiment is generally quite good except for species where mineral contributions are important in Fig. 9 (CO₂, H₂O). The kinetic parameters obtained from the TG-FTIR method extrapolate well to very low heating rates, as in natural maturation processes,^{20,28} as well as to the high heating rates of importance in most coal gasification and combustion processes.^{18,21} Other versions of the FG-DVC model have been developed for lignin³³ and phenol-formaldehyde³⁶ using the same approach.

CONCLUSIONS

Thermogravimetric (TG) analysis combined with Fourier Transform Infrared (FT-IR) analysis of evolved products has proven to be a powerful technique for characterization of coal, source rock, heavy hydrocarbons, biomass, waste materials, and plastics. The TG-FTIR method can be used to determine the resource potential of a material, i.e., the types of products a material is likely to produce when subjected to processing by pyrolysis, or combustion. It can also provide kinetic information for model validation or extrapolation and can provide the equivalent information to proximate and ultimate analysis. In addition, TG-FTIR analysis can be used to characterize the adsorbent potential and combustion reactivity of solids.

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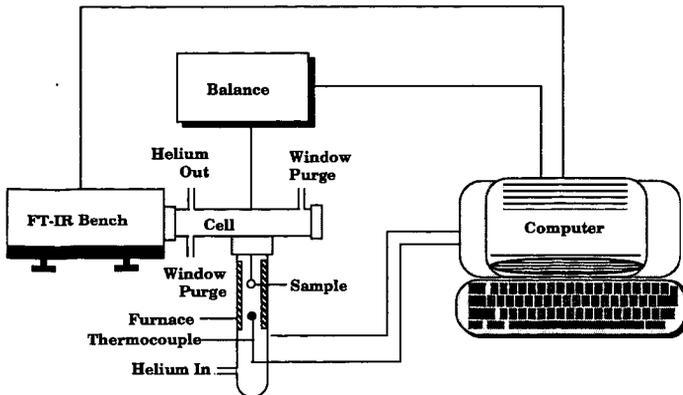


Figure 1. Schematic diagram of the standard TG/FT-IR instrument.

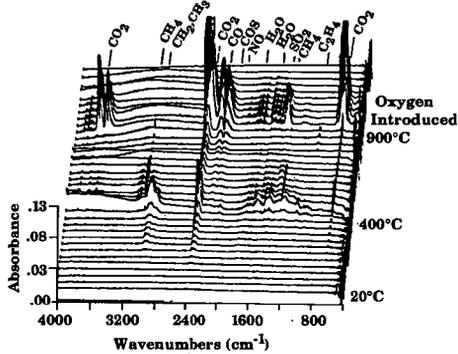


Figure 2. Spectra from TG/FT-IR of coal. Heating rate is 0.5°C/s^{-1} from 20 to 900°C . The remaining char is then burned at 700°C .

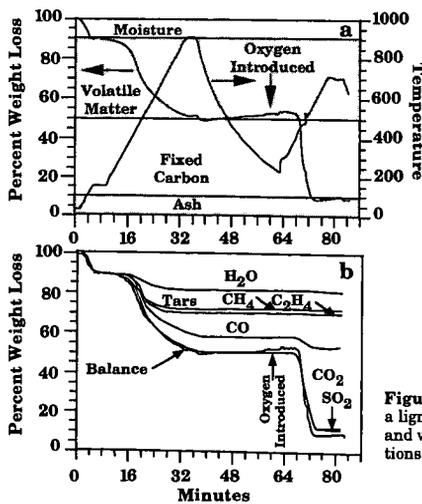


Figure 3. TG/FT-IR analysis of a lignite. a) Temperature history and weight loss; b) Species contributions to weight loss.

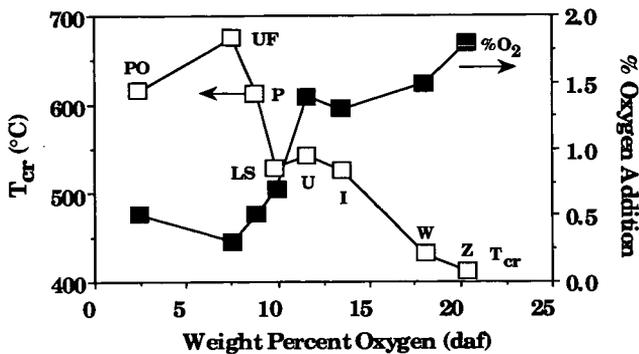


Figure 4. Rank variation of T_{cr} and oxygen chemisorption.

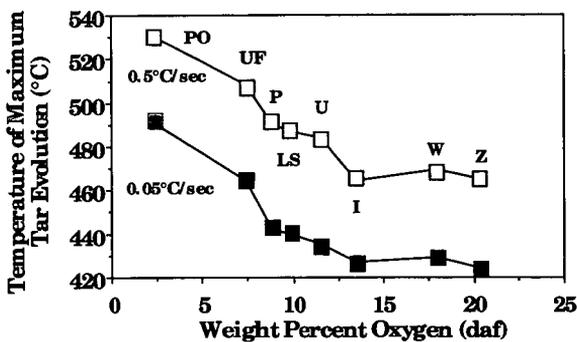


Figure 5. Rank variation of tar evolution temperature.

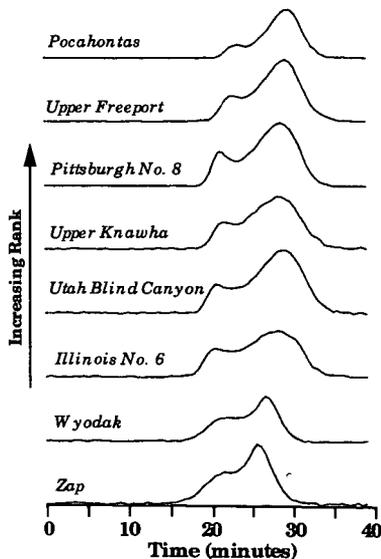


Figure 6. Evolution of NH_3 from programmed pyrolysis ($30^\circ C/min$) of the Argonne premium coals.

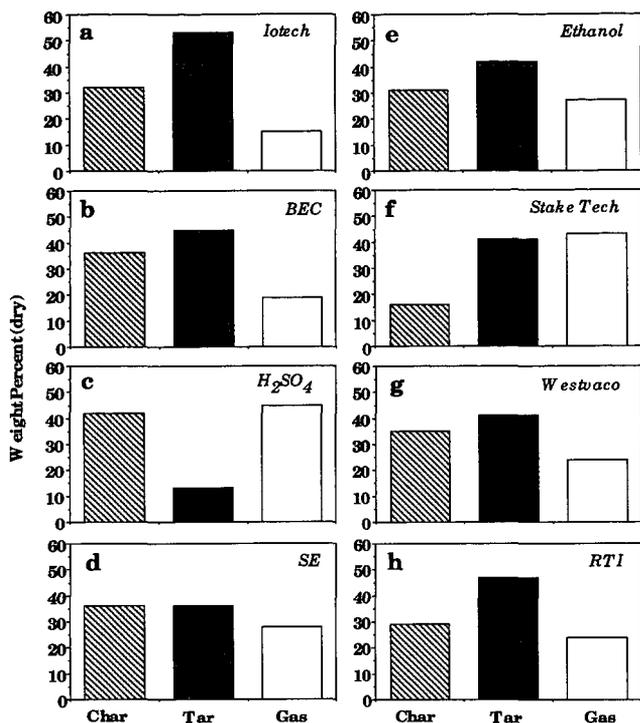


Figure 7. Comparison of char, tar and gas yields from programmed pyrolysis of eight lignins.

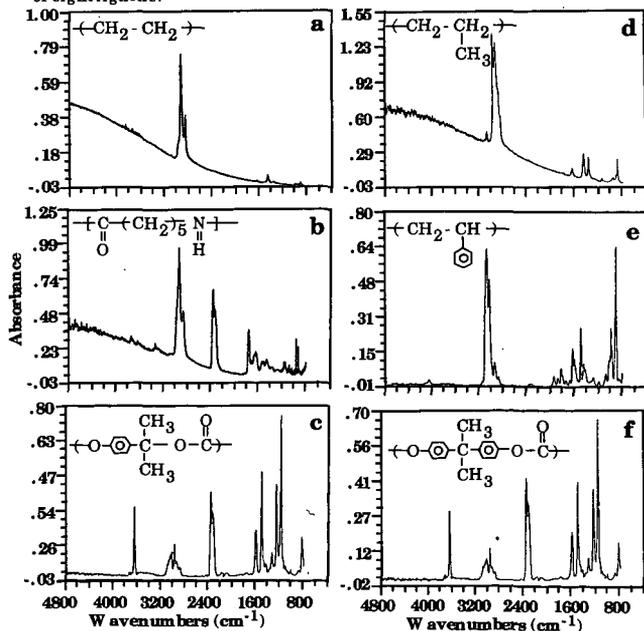


Figure 8. Comparison of IR spectra at peak temperature in tar evolution profile from TG/FT-IR analysis of several polymers. a) Polyethylene (PE); b) Nylon; c) Lexan (standard); d) Polypropylene (PP); e) Polystyrene (PS); f) Lexan (flame retardant).

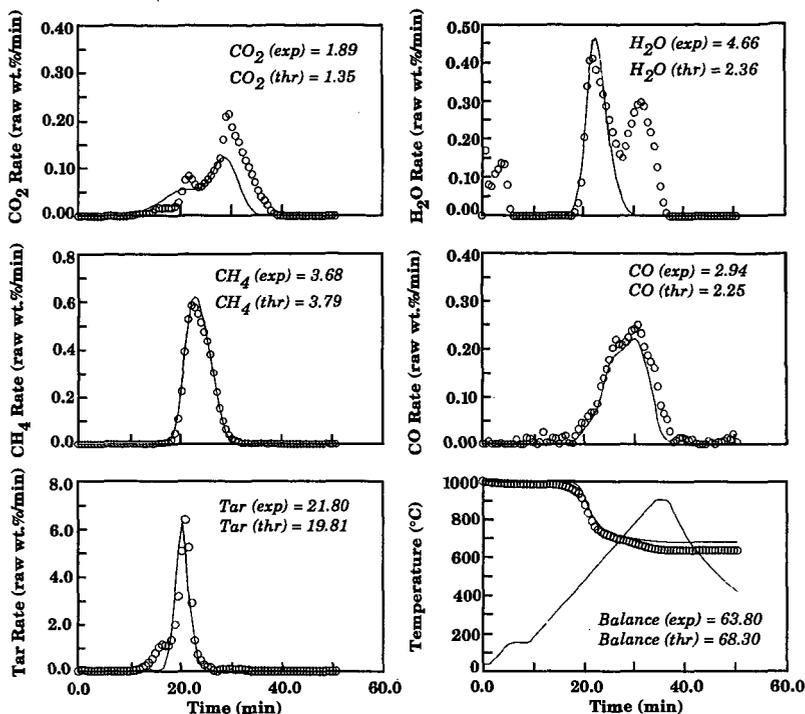


Figure 9. Comparison of TG/FT-IR data and FG-DVC model predictions for CONSOL #2 coal, pyrolyzed at 30°C/min.

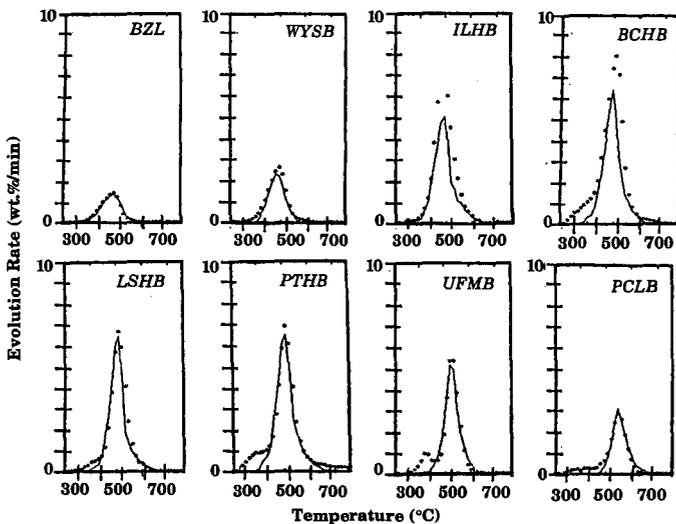


Figure 10. Comparison of measured and predicted tar evolution from pyrolysis of the eight Argonne premium coals.