EXPERIMENTAL STUDY AND MODELING OF COAL PYROLYSIS AT HIGH TEMPERATURES*

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INTRODUCTION

In a recent study, the vacuum pyrolysis behavior of a lignite and twelve bituminous coals was measured over the range 300 to 1000°C (1,2,3). The results were successfully simulated using a model which predicts the time and temperature dependent product evolution from a knowledge of the function group composition of the coal and a general set of kinetic rates which vary with evolved product but not with coal type.

This paper reports the extension of this investigation to temperatures up to 1450°C and to a wider number of measured and modeled pyrolysis products. Experiments have been performed in an apparatus which employs a Fourier Transform Infrared Spectrometer (FTIR) for on-line analysis of gas species. The FTIR allows the direct accumulation of release rate data for major species by monitoring the gas concentration during a pyrolysis run. Results have been obtained with a Pittsburgh seam bituminous and a Montana lignite. The temperature dependent evolution of corresponding products are similar for the two coals indicating that the use of coal independent kinetic rates is applicable for the additional products and higher temperatures. The dominant effect observed at higher temperatures is the trend toward increased yields of hydrogen gas and unsaturated compounds (olefins, acetylene and probably soot) at the expense of paraffins. These effects are being modeled by including additional parallel reaction paths for the decomposition of the aliphatic content of the coal.

EXPERIMENTAL

The apparatus is illustrated in Fig. 1. It consists of a small chamber in which the coal is pyrolized connected through a glass wool filter to a large gas cell for infrared analysis. The coal is evenly distributed between the folds of a stainless steel, molybdenum or tungsten screen and a current is passed through the screen to heat the coal. Coal temperatures of 1450°C and heating rates of 2000°C/sec were achieved using the tungsten screen. Gas analysis is performed with a Nicolet (FTIR) which permits low resolution analysis at 0.5 second intervals. The low resolution analysis can determine CO, CO_2, H_2O, CH_4, COS, SO_2, CS_2, HCN, C_2H_2, C_2H_4, C_3H_6, benzene and heavy paraffins and olefins. A high resolution analysis made at the completion of a run can determine all of the above plus C_2H_6, C_3H_8, C_4H_8, NH_3 and potentially many other species which have not yet been observed. H_2 is determined by difference. Other features of the apparatus are similar to those described previously (1,2,3).

Calibration of the FTIR has been made using pure gases or prepared gas mixtures. Unfortunately, most of the gases of interest show a marked increase in absorbance with dilution. The explanation for this effect is that the absorption lines for these gases are extremely sharp and for moderate concentrations all the infrared energy is

*Work supported by the Department of Energy under Contract ET-78-C-01-3167

absorbed at the line center in a path shorter than the absorption cell. The instrument resolution is substantially broader than the line width so the lines do not appear to be truncated. Dilution of the gas broadens the line, reducing the absorbance at line center so that a longer path contributes to the absorptivity, thus increasing the average absorbance. This effect makes calibration of these gases in the pyrolysis gas mixture difficult. The solution has been to dilute the mixture with nitrogen to a fixed pressure at which calibrations have been made.

Figure 2 shows the spectra obtained at several time intervals during an 80 second devolatilization run at about 500°C. Kinetic rate data for major species can be determined from such scans as indicated in Fig. 3 which shows the methane yield and the pressure rise in the system as a function of time.

Pyrolysis data were obtained up to temperatures of 1450°C for a Pittsburgh seam coal (PSOC 170) and a Montana lignite. For the Pittsburgh seam coal 80 second pyrolysis runs were made with 200 mg samples at temperatures from 400 to 1000°C. For these conditions, the temperature rise takes on the order of two seconds. More rapid heating (less than one second) was achieved using smaller (50 mg) samples. Ten second pyrolysis runs were made with 50 mg samples for both coals.

RESULTS

Using the procedure shown in Fig. 3 the methane kinetic constants were determined for the 10 and 80 runs. These data are plotted in Fig. 4 along with a line for the temperature dependent kinetic rate for methane previously determined (2). As can be seen the lignite and bituminous data are quite close and all data are in reasonable agreement with the previously determined line. The high temperature points for the 80 second runs are low because of the slow heating described above and presumably the same sort of limitations are affecting the 10 second runs at the very high temperatures.

Pyrolysis data for the 10 second runs are plotted in Fig. 5. Figs 5a and b show the product distribution. Included in the light gases are all the species listed except for those heavier than C_3, which are included with the heavier hydrocarbons (HC). An interesting feature of these data are the high volatile yields obtained at high temperatures. Volatile yields of up to 70% were observed as compared with ASTM volatile yields of 46% and 59% for the bituminous coal and lignite respectively.

Several of the gaseous species are shown in Figs. 5c-h. The similarity between lignite and bituminous coal is apparent in the temperature dependence of the evolution of each species. Figs. c to f show results for H_2, CH_4 and C_2H_2 and heavy olefins and paraffins. These figures illustrate the tendency for high temperature pyrolysis to favor molecular hydrogen and unsaturated compounds. Figures g and h show the distribution of oxygen containing species.

PYROLYSIS MODEL

A successful model was developed to simulate the pyrolysis behavior of the thirteen coals previously studied at low temperature (1,2,3). The model assumes that large molecular fragments ("monomers") are released from the coal "polymer" with only minor alteration to form tar while simultaneous cracking of the chemical structure forms the light molecules of the gas. Any chemical component of the coal can, therefore, evolve as part of the tar or as a species in the gas. The mathematical

description presented in detail in Refs. 2 and 3 represents the coal as a rectangular area with X and Y dimensions. The Y dimension is divided into fractions according to the chemical composition of the coal. Y_i^o represents the initial fraction of a particular component (carboxyl, aromatic hydrogen, etc) and $\Sigma Y_i^o=1$. The evolution of each component into the gas (carboxyl into CO_2, aromatic hydrogen into H_2, etc) is represented by the first order diminishing of the Y_i dimension, $Y_i=Y_i^o \exp(-k_i t)$. The X dimension is divided into a potential tar forming fraction X^o and a non-tar forming fraction $1-X^o$ with the evolution of the tar being represented by the first order diminishing of the X dimension $X=X^o \exp(-k_{tar}t)$. The amount of a particular component in the char is $(1-X^o+X)Y_i$ and the amounts in the gas and tar may be obtained by integration. It was found that a general set of kinetic constants (k_i's and k_{tar}) could be used for all the coals. The differences among coal results solely from the different mix of chemical groups (the Y_i^o's). As described in Ref. 3 many of the Y_i^o's may be determined from ultimate and infrared analysis.

Modifications of the model were made to include the high temperature production of unsaturated compounds. An an example, the production of acetylene and H_2 is assumed to be a third independent path for the evolution of an aliphatic component. The component is represented as a volume and the evolution of acetylene and H_2 is represented by the diminishing of the X dimension, $Z=Z^o \exp(-k_{ac}t)$ where $Z^o=1$. The amount of the component in the char is then $(1-X^o+X)Y_iZ$. The evolved amounts may be obtained by integration. Further competitive processes such as the production of olefins plus H_2 from paraffins and the production of soot and H_2 from aliphatics were incorporated in a like manner.

The results are the lines shown in Fig. 5. The kinetic constants are the same as those used in Ref. 2 with the exception of: $k_{H_2O} = 45 \exp(-4950/T)$, $k_{al} = 750 \exp(-8000/T)$ and the addition of: $k_{ac} = 1.9 \times 10^{10} \exp(-35000/T)$, $k_{ol} = 2.0 \times 10^7 \exp(-20000/T)$, $k_{soot} = 9.5 \times 10^{10} \exp(-35000/T)$. The model is in reasonable agreement with experiment for most species. Exceptions are H_2O and H_2. The decrease in H_2O at high temperatures has not been modeled. The effect could be a steam char reaction to form CO and H_2. Inclusion of this reaction would improve the agreement for CO and H_2 as well.

CONCLUSIONS

1. Using a heated grid apparatus with on-line gas analysis by FTIR, data has been obtained for a large number of pyrolysis products from a lignite and a bituminous coal at temperatures up to 1450°C.
2. The temperature dependent evolution of corresponding products from the lignite and bituminous coal vary in magnitude but are otherwise quite similar.
3. The pyrolysis behavior has been simulated by modifying a previously developed model which uses the same kinetic rates for all coals. Modifications of the model were made to include the high temperature evolution of H_2 and unsaturated compounds (olefins, acetylene, and soot) from the aliphatic material in the coal.
4. The coal parameters of the model are related to the functional group composition of the coal.

REFERENCES

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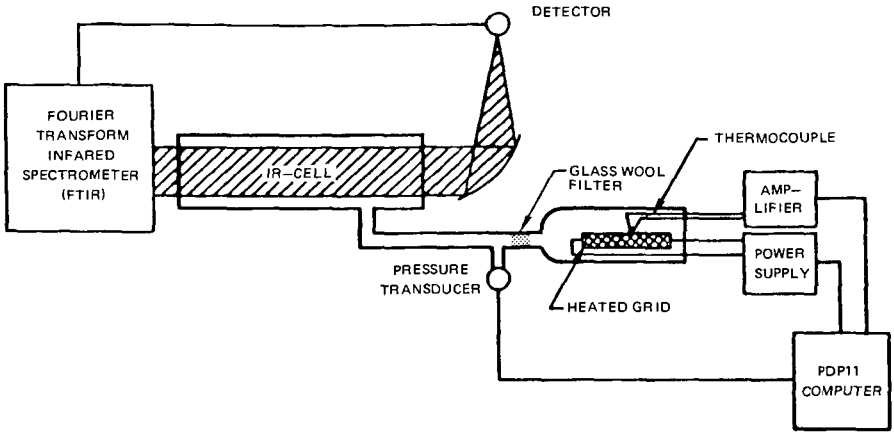

FIG. 1 PYROLYSIS APPARATUS

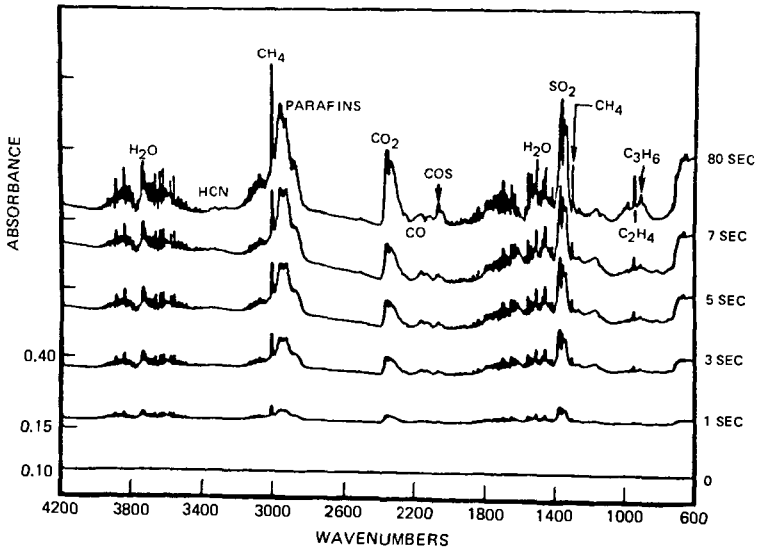

FIG. 2 INFRARED SPECTRA OF EVOLVING PYROLYSIS GAS

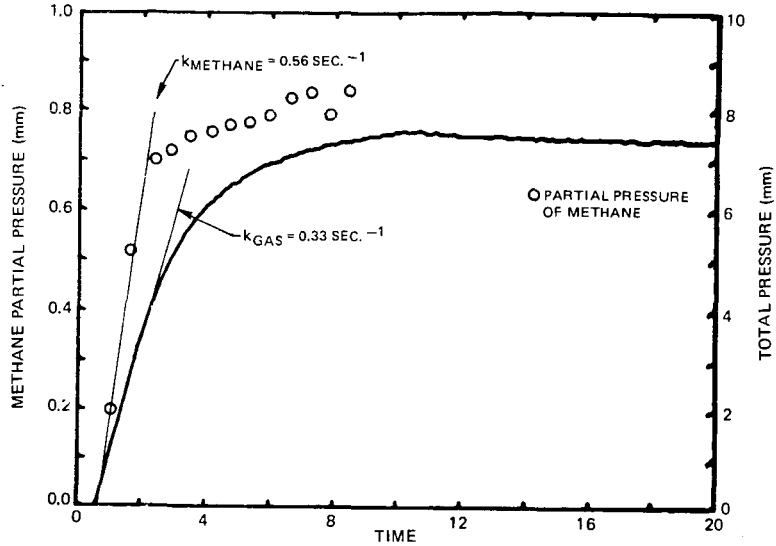

FIG. 3 TIME DEPENDENCE OF METHANE PARTIAL PRESSURE AND TOTAL PRESSURE DURING PYROLYSIS

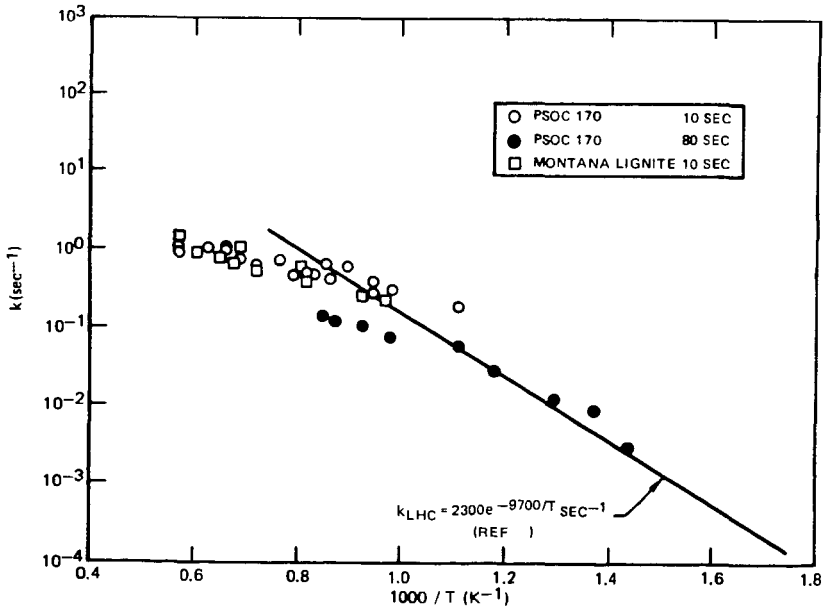

FIG. 4 RATE CONSTANT FOR METHANE EVOLUTION

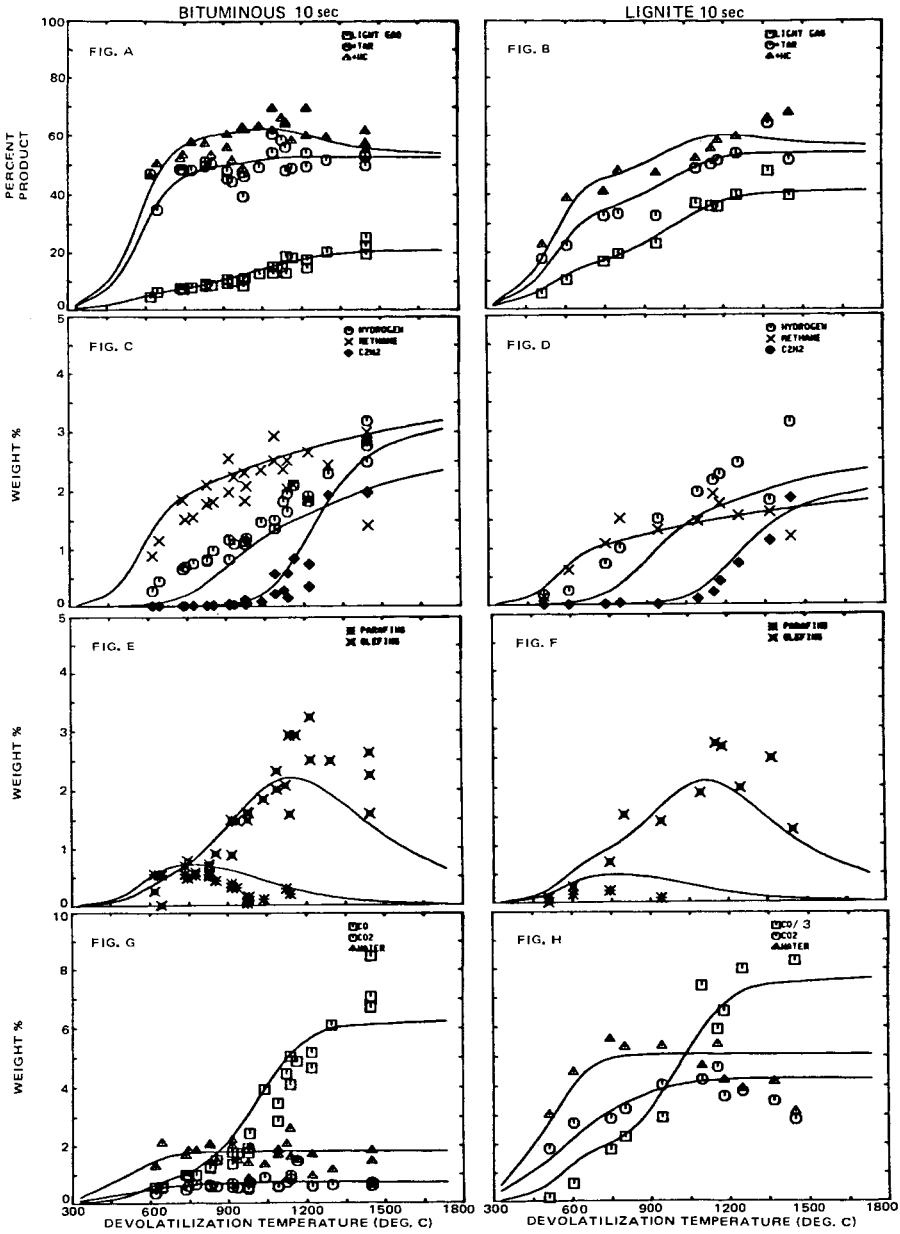

FIG. 5 PYROLYSIS PRODUCT YIELDS