

KINETICS OF VOLATILE PRODUCT EVOLUTION FROM THE ARGONNE PREMIUM COALS

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Keywords: Coal Pyrolysis, Kinetics, Argonne Premium Coals

ABSTRACT

This paper describes the development of a set of rank dependent kinetic parameters for the evolution of the major volatile species from pyrolysis of the eight Argonne Premium coals. Programmed pyrolysis experiments are done over a range of heating rates (3, 30, 50, 100 °C/min) in an instrument which combines Thermogravimetric Analysis (TG) with evolved product analysis using Fourier Transform Infrared Spectroscopy (FT-IR) (the Bomem TG/Plus). An analysis of the data on the temperature for the peak evolution rate (T_{max}) for tar, CH_4 , and CO_2 as a function of heating rate is used for obtaining a preliminary estimate of the mean kinetic parameters. The parameters are further refined by using the FG-DVC model for coal pyrolysis to best fit the complete evolution profiles at each of the four heating rates. A final test is done by use of the parameters to predict pyrolysis data obtained under high heating rate conditions. The kinetics are found to vary systematically with rank and are faster for lower rank coals. The variations with rank are most significant for high rank coals with greater than ~ 86% daf carbon (< 8% daf oxygen). These differences can be important in accurately predicting coal fluidity and ignition phenomena.

INTRODUCTION

This paper is a continuation of work reported previously, related to the measurement and modeling of the pyrolysis kinetics for the Argonne Premium coals (1-3). In the first paper (1), the results for pyrolysis of the Argonne Premium coals at 30 °C/min in the TG-FTIR and 3 °C/min in a Field Ionization Mass Spectrometer (FIMS) apparatus were reported. Comparisons were made of the T_{max} values for the evolution of major volatile products and the molecular weight distributions (MWD) of the tars from pyrolysis-FIMS experiments. In the next paper (2), the FG-DVC coal pyrolysis model was used to simultaneously fit the pyrolysis data from the 30 °C/min TG-FTIR experiments, the 3 °C/min (vacuum) FIMS experiments and the ~ 5000 K/s entrained flow reactor (EFR) experiments.

The third paper (3) was a preliminary evaluation of the rank dependence of the pyrolysis kinetic rates for tar, CH_4 , and weight loss for the Argonne coals based on TG-FTIR experiments at four different heating rates with all eight coals and from entrained flow reactor experiments in a Transparent Wall Reactor (TWR) with two of the coals (Zap lignite, Pittsburgh Seam bituminous) at ~ 5000 K/s. In the current paper, the rank dependent kinetic parameters have been further refined and developed for additional species (CO_2). For the Illinois coal, an extrapolation has been made to high heating rate conditions for the case of tar evolution.

EXPERIMENTAL

Coal Properties

The elemental and ultimate analysis data for the Argonne Premium coals are given in Refs. 4 and 5.

Reactor System

Pyrolysis experiments were done with the Argonne premium coals at heating rates of 3, 30, 50, and 100 °C/min up to 900 °C in a TGA with FT-IR analysis of evolved products (TG-FTIR). The TG-FTIR apparatus consists of a sample suspended from a balance in a gas stream within a furnace. As the sample is heated, the evolving tars and gases are carried out of the furnace directly into a 5 cm diameter gas cell (heated to 150 °C) for analysis by FT-IR. With this geometry under low heating rate conditions, the temperature of the sample is assumed to be the same as that of a thermocouple which is next to the sample. The TG-FTIR system used in the current work is the TG/Plus from Bomem, Inc.

The TG/Plus couples a Dupont 951 TGA with a Bomem Michelson 100 FT-IR spectrometer (6,7).

High heating (~ 20,000 K/s) pyrolysis rate measurements were previously made in a heated tube reactor (HTR) with an Illinois No. 6 coal, as described in Ref. 8. These experiments included in-situ FT-IR diagnostics for measurement of the coal particle temperature. A heat transfer model was developed which provided a good fit to the measured temperature profile (8,9). The predictions of the heat transfer model were subsequently input into the FG-DVC pyrolysis model.

RESULTS

The TG-FTIR results for the Pittsburgh Seam coal at three heating rates are given in Fig. 1. The dashed lines are the prediction of the FG-DVC model (9-11) while the experimental data are plotted as asterisks connected by solid lines. The left hand set of curves is for the cumulative weight loss from the balance. Superimposed on each of these plots is the time-temperature profile. Except for very low heating rates, the coal is heated first to 150°C for drying before heating at the designated rate to 900°C.

The agreement between the experimental and predicted weight predictions is quite good at each of the three heating rates. The predicted weight loss is the sum of the tar evolution and the major gases (CO, CO₂, H₂, H₂O, CH₄, paraffins, olefins) which are included in the FG-DVC model.

The middle set of curves in Fig. 1 is for the tar evolution while the right hand set is for CH₄ evolution. The prediction of tar evolution is based on the breaking of weak linkages between an assumed polymeric structure for coal followed by transport of the molecule out of the coal if it meets the volatility criteria (10). The position and shape of the main tar peak is predicted very well for the Pittsburgh Seam coal and for several other coals that have been tested. The early part of the tar evolution is not as well predicted. This part of the tar evolution arises primarily from "guest" molecules which are physically bound in the coal. We are working on a new version of the FG-DVC model which includes the guest molecules (11).

The evolution of CH₄, shown on the far right hand side of Fig. 1 is also well predicted. The CH₄ evolution is modeled using two sources which evolve in a manner such that the peaks are usually merged into a single peak (9,10).

Both the tar and CH₄ evolution profiles show a systematic shift with increasing heating rate. The change in the temperature for the maximum evolution rate (T_{max}) with temperature can be used in preliminary analysis to derive kinetic parameters (12,13). We have used this approach to obtain a preliminary estimate of the mean values of the distributed activation energy parameters. The parameters are further refined by using the FG-DVC model to best fit the complete evolution profiles at each of four heating rates.

Similar comparisons are made in Figs. 2-5 for other coals in the Argonne series. In this case, the data are shown for a single heating rate (30°C/min) but one additional species (CO₂). Again, good agreement is obtained for the actual weight loss and the predicted values from all four coals. In the case of the Utah Blind Canyon coal and the Zap lignite, the predicted curves have been horizontally displaced to match the weight loss after moisture evolution since the model predictions are all done on a dry basis.

The prediction of the tar evolution profile is also good except for the very early tar as discussed above for the Pittsburgh Seam coal. The methane evolution profile is very well predicted in each case. The CO₂ evolution profiles are not as well predicted as the evolution of hydrocarbon species. The CO₂ evolution is predicted based on three assumed sources (extra loose, loose, and tight) (9,10). At 30°C/min, the peaks are centered at approximately 16, 22, and 28 minutes, respectively. However, because the mineral sources are not included in the model, the quality of the fits is not the same as for hydrocarbon species where there are no mineral contributions.

DISCUSSION

The use of the TG-FTIR method over a range of heating rates has allowed the development of a set of rank dependent kinetic parameters for tar, CH₄, and CO₂ (and indirectly the weight loss). The

parameters for the tar evolution were obtained by adjusting the value of the pre-exponential and activation energy for the bridge breaking rate in the FG-DVC model in order to match the evolution profiles at the four heating rates. In general, these rates increase monotonically with decreasing rank (increasing oxygen content). For very low rank coals, the contribution of polymethylenes is sufficiently large that it partly obscures the tar evolution from bridge breaking. In this case, the TG-FTIR results from demineralized coals are used to obtain a more reliable estimate of the bridge breaking rate. The lower amount of crosslinking in the demineralized coals reduces the relative contribution of the polymethylene tar.

In the case of the CH_4 and the CO_2 , good results were obtained by adjusting only the pre-exponential factors. The values of the activation energies used were the same as those reported previously (10).

The importance of the rank dependence of the pyrolysis kinetics for tar and CH_4 evolution was evident in the modeling of coal fluidity behavior (14). When modeling fluidity, it was found that relatively small differences in the methane evolution rate (which is related in our model to the moderate temperature crosslinking which shuts down the fluidity) and the tar evolution rate (which is based on the bridge breaking rate as discussed above) have a large effect on the fluidity predictions. In Fig. 6 are shown comparisons of the measured fluidity with the predicted fluidity (based on the rank dependent rates) for five of the eight coals. With the possible exception of the Pocahontas coal, the agreement between the measured and predicted fluidity is quite good.

A good test of the validity of using the TG-FTIR method over a range of low heating rates to obtain kinetic parameters is the ability to use the kinetic parameters to extrapolate to high heating rate conditions. An example of this is shown in Fig. 7, where the parameters obtained for the Illinois No. 6 coal using the TG-FTIR method were used to simulate previously obtained high heating rate (~ 20,000 K/s) data for tar evolution (9). Again, the agreement between the theory and data is quite good.

Finally, a comparison can be made for results obtained for T_{max} for tar evolution at 3°C/min for the eight Argonne premium coals using the TG-FTIR method with results obtained by Burnham et al. (15) using a Rock-Eval experiment at 4°C/min. This comparison is shown in Fig. 8. The agreement between the two experiments is generally very good.

CONCLUSIONS

The conclusions of this work are as follows:

- The TG-FTIR method has been used to provide a set of rank dependent kinetic parameters for tar, CH_4 , CO_2 , and weight loss for the eight Argonne coals.
- These rank dependent kinetic parameters will be important in predicting fluidity and ignition behavior.
- The parameters obtained by this method extrapolate well to high heating rate conditions.
- Good agreement was found with low heating rate kinetic data obtained elsewhere with a different technique.

ACKNOWLEDGEMENTS

This work was supported under DOE Contract DE-AC21086MC23075. Richard Johnson is the Project Manager.

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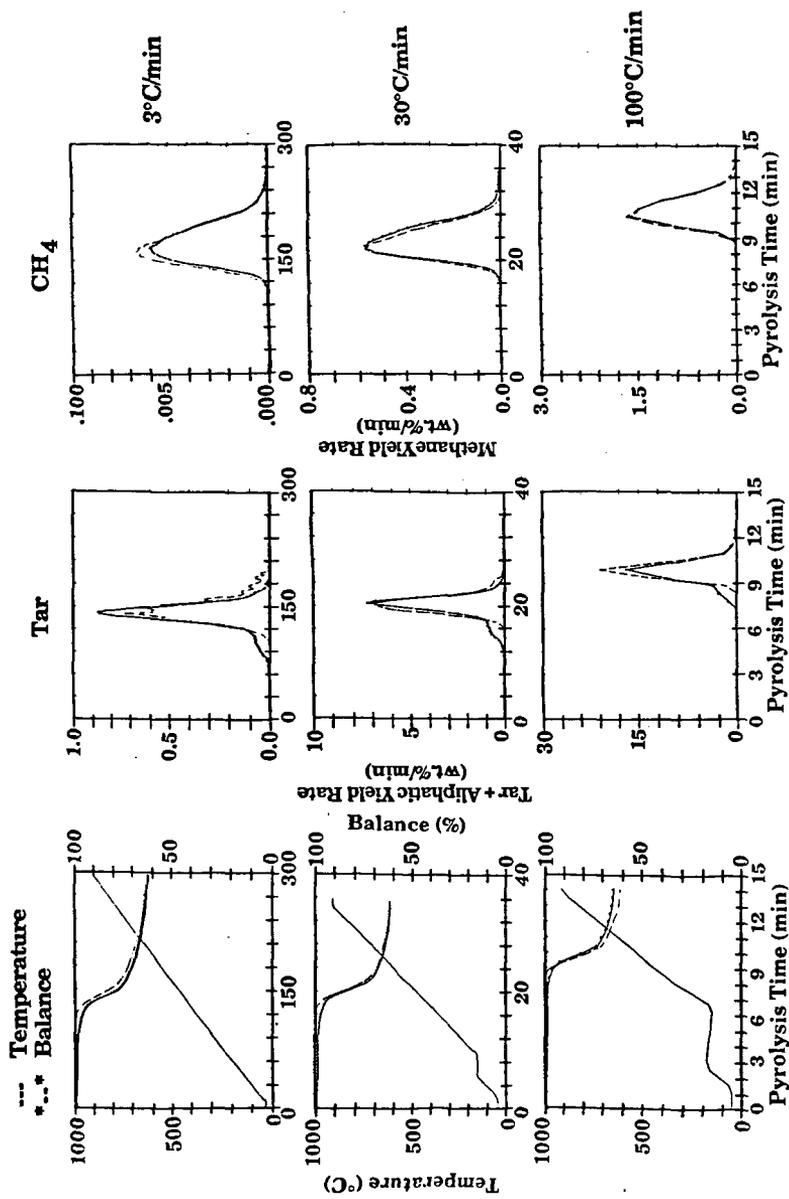


Figure 1. Kinetic Analysis at Three Heating Rates for Pittsburgh Seam Coal. Comparison of Theory (---) and Data (—).

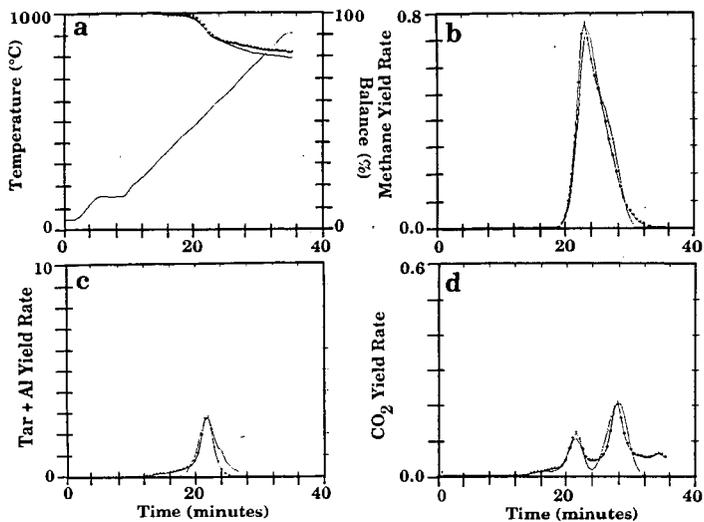


Figure 2. Kinetic Analysis at 30°C/min for Major Volatile Products. Comparison of Theory (—) and Data (***) for Pocahontas Coal.

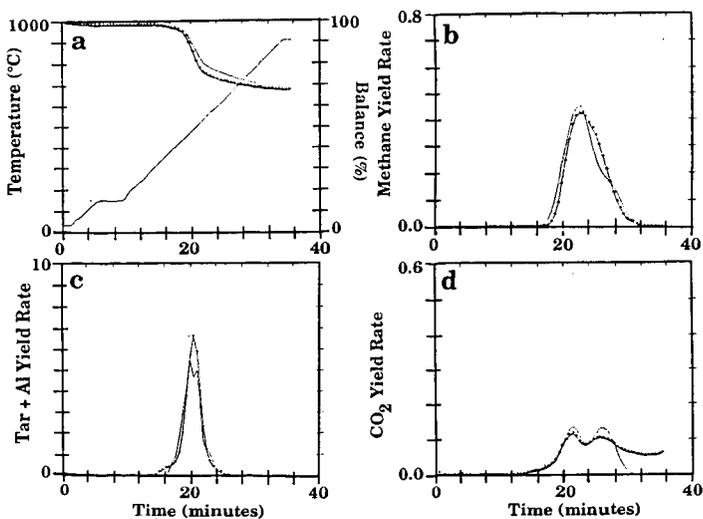


Figure 3. Kinetic Analysis at 30°C/min for Major Volatile Products. Comparison of Theory (—) and Data (***) for Lewis-Stockton Coal.

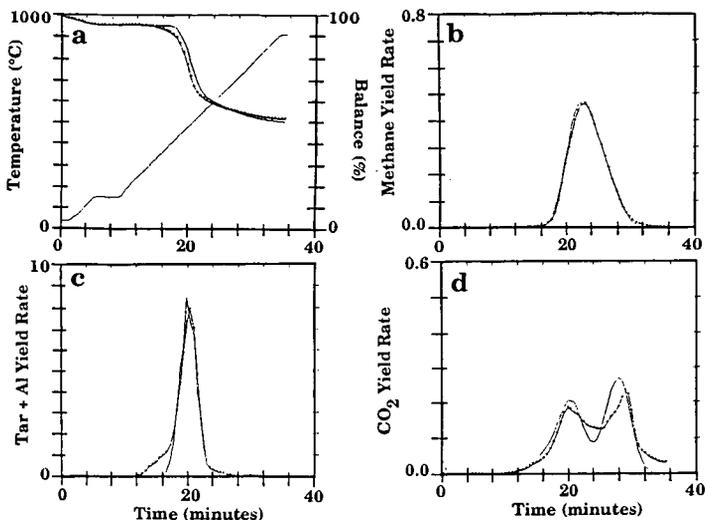


Figure 4. Kinetic Analysis at 30°C/min for Major Volatile Products. Comparison of Theory (—) and Data (*-*) for Utah Blind Canyon Coal.

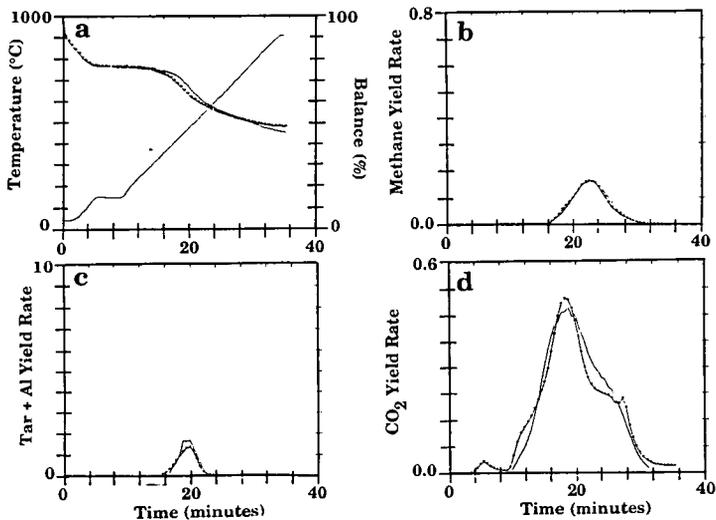


Figure 5. Kinetic Analysis at 30°C/min for Major Volatile Products. Comparison of Theory (—) and Data (*-*) for Zap Lignite

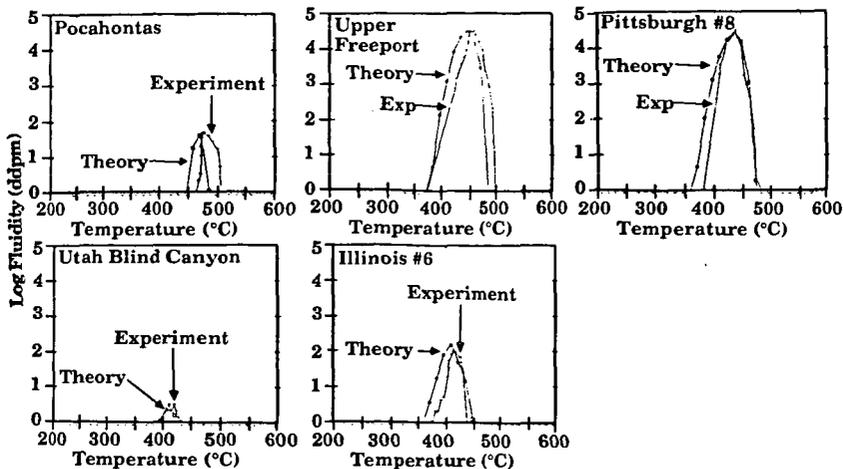


Figure 6. Comparison of Measured (**) and Predicted (o-o) Fluidity for Five Argonne Coals.

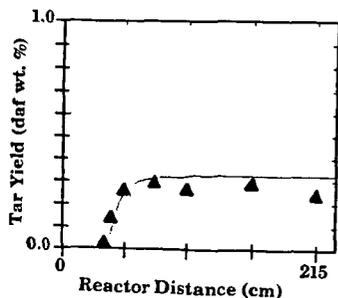


Figure 7. Pyrolysis Tar Yield Results for Illinois No. 6 Coal, 200 x 325 mesh, in the HTR at an Equilibrium Tube Temperature of 800°C. The Solid Lines are Predictions of the FG-DVC Model.

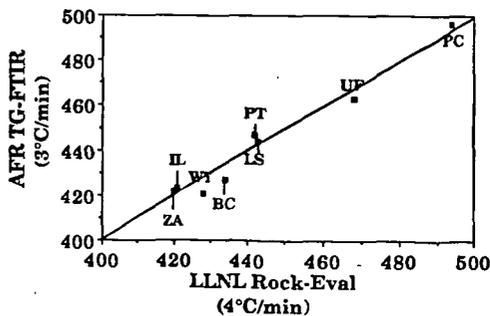


Figure 8. Comparison of AFR Data for T_{max} from TG-FTIR Analysis at 3°C/min with Rock-Eval Data from LLNL at 4°C/min.