THE EFFECT OF RANK ON COAL PYROLYSIS KINETICS

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INTRODUCTION

The rank dependence of coal pyrolysis kinetics has been a subject of controversy for several years (1,2). Some have claimed that the rank variations are responsible for much of the several orders of magnitude variation in reported rates. Others have found that in experiments where the rank was the only experimental parameter, these differences were not very profound when compared to the large variations in reported rates. We subscribe to the latter view, but acknowledge that there are circumstances where relatively small rank variations may be important. One such case is the prediction of coal fluidity (3). The maximum fluidity observed experimentally depends strongly on rank and the time temperature history (heating rate, final temperature). When modeling fluidity, it was found that relatively small differences in the methane evolution rate (which is related in our model to moderate temperature crosslinking) and in the tar evolution rate (which is related to the bridge breaking rates) adversely affected the fluidity predictions (3).

This paper examines the variation in kinetic rate sat both low and high heating rate. The rate for methane and for tar evolution from the Argonne premium coals were determined from a series of experiments which were done with these coals over a range of low heating rates. These will be compared with kinetic parameters determined by Burnham et al. (4) for the same coals. In addition, we report weight loss data obtained at high heating rates in a transparent wall reactor (TWR) on samples of Pittsburgh Seam and Zap Lignite coals, which provide further information on the rank variations of kinetic rates.

EXPERIMENTAL

Coal Properties - Elemental data are given for the Argonne coals in Ref. 5. The analyses of the Zap Lignite and Pittsburgh Seam bituminous coals used in the TWR experiments are given in Ref. 6.

Reactors - Pyrolysis experiments were done with the Argonne premium coals at heating rates 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 is the TG/Plus from Bomem, Inc. The TG/Plus couples a Dupont 951 TGA with a Bomem Michelson 100 FT-IR spectrometer (7,8).

High heating rate measurements were made in a transparent wall reactor (TWR) which has been previously described (9). Nitrogen is passed through a heat exchanger and enters a reaction section at approximately 850°C. Coal entrained in cold nitrogen carrier gas is injected through a co-axial 7 mm diameter tube into the preheated stream. An octagonal glass enclosure shields the pyrolyzing stream from room air currents. This reactor allows particle temperature measurements to be made. One difficulty in making pyrolysis kinetic measurements at high temperatures is that the measurement of particle temperatures from the particle's emitted radiation is difficult if the pyrolysis reactor has hot walls. In this case, wall radiation scattered by the particles interferes with the emitted radiation. To overcome this problem, the reactor section has relatively cold walls. The glass enclosure has movable KBr windows to allow access to the flame for radiation measurements. Particle velocities were measured using a video camera under slightly oxidizing conditions which allowed a small percentage of the particle to ignite.

Temperature Measurements - To measure the temperature of pyrolyzing coal particles, several other problems had to be overcome. Because pyrolysis in this reactor occurs at relatively low temperatures (600-800°C), the measurements are made in the mid-infrared where sufficient energy is emitted. In addition, coal is not a gray-body and its emissivity changes during pyrolysis. To overcome this problem, the temperature has been measured using the amplitude of the radiated energy in a frequency range where the emissivity is close to one and independent of the extent of pyrolysis. The transmission is used to determine the emitting surface area of the particles. Finally, soot radiation can make the particle temperature appear much higher than it really is. Measurements have been made with a gas temperature of 850°C so soot formation did not occur.

RESULTS AND DISCUSSION

Low Heating Rate Studies - A recent paper reported the development of a network model for coal fluidity based on the FG-DVC model and its application to predict fluidity data for a wide range of coals (3). In order to fit both the fluidity data and species evolution data, the bridge breaking and methane kinetic rates were adjusted from those used in the original model which were rank independent (5,6,10). An independent investigation was made of the rank dependence of the pyrolysis kinetics by doing experiments in a TG-FTIR reactor over a series of heating rates (3, 30, 50, 100°C/min) with three coals (Pocahontas, Pittsburgh, No. 8, and Zap lignite) which are at the extremes and midpoint of the rank range for the Argonne set. A comparison of the rank dependence of the rate constants for bridge breaking, tar evolution and CH_4 evolution at 450°C determined from analyzing the TG-FTIR data at several heating rates and from fitting the FG-DVC model to fluidity, weight loss and methane evolution data at a single heating rate (3°C/min) is shown in Fig. 1.

The rates for tar evolution are lower than those used in the FG-DVC model for bridge breaking. This makes sense since the latter does not include transport. The rates for tar evolution or bridge breaking vary by about a factor of 10 if the Pocahontas coal is excluded, which is consistent with previous results for coals from the same range of ranks. If the Pocahontas is included, the rank variation for the tar evolution or bridge breaking rates is about a factor of 50. The rates for tar evolution are consistent with those obtained by Burnham et al. for total hydrocarbon evolution from Rock Eval analysis of the same coals (6). This data is also shown in Fig. 1.

The kinetic parameters determined by either method for methane (loose) evolution are similar and show a much lower rank dependence. Finally, the rank independent parameters used in the original FG model are shown as horizontal dashed lines. These are in better agreement with results from the lower rank coals, which was expected since the set of coals used to obtain those parameters did not include the higher rank coals (5,6,10).

Experiments in the TWR - Particle temperatures were determined by matching the theoretical curves to the radiance at 1600 cm^{-1}, where the emissivity is approximately 1.0 (11,12). Measurements were obtained for both coals at positions between 5 and 40 cm. In addition, char samples were captured at a number of locations. The results for the Zap lignite are summarized in Fig. 2. Figure 2a shows the temperature measurements in the reactor made using a thermocouple and the FT-IR E/T technique to determine both particle and CO_2 temperatures (9,11-13). The CO_2 and particle temperatures agree to within 100°C. The thermocouple temperature measurements averaged across the estimated width of the particle stream are also in reasonable agreement except early in the reaction when the particle are heating and late when the gas is cooling. The particle's heating rate is about

5000°C/sec.

Figure 2b shows the weight loss determined by ash tracer analysis. These are compared to predictions of the FG-DVC model (10). The kinetic rates for bridge breaking used in the FG-DVC model is k_B = 8.6 x 10^{14} exp(-228,500/RT) sec^{-1}. The predictions using 10 and 0.1 times this rate are also shown. The agreement for the Zap lignite is best with the highest of the three rates.

The results for the Pittsburgh Seam coal are presented in Fig. 3. These results also agree best for k_Bx10. Consequently, the high heating rate data do not show much of a rank variation. However, these measurements are not as sensitive to factors of 10 difference in rate.

CONCLUSIONS

- The rank dependence of the chemical kinetic rates is important in the prediction of fluidity data. It can also be important in predicting tar evolution rates for very high rank coals (>90% carbon). It is less important in the case of methane.
- Both the low and high heating rate experiments support the previous conclusion that the rank variations for kinetic rates are usually less than a factor of 10, except for the case of tar evolution from very high rank coals.

ACKNOWLEDGMENTS

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REFERENCES

1. Solomon, P.R. and Hamblen, D.G., Finding Order in Coal Pyrolysis Kinetics, Topical Report Submitted to the U.S. Department of Energy, under Contract No. DE-AC21-FE05122, (1983), also Progress in Energy and Combustion Science, **9**, 323, (1983).
2. Solomon, P.R. and Serio, M.A., "Evaluation of Coal Pyrolysis Kinetics", in Fundamentals of the Physical-Chemistry of Pulverized Coal Combustion, (J. Lahaye and G. prado, Eds.), 126, Marinus Nijhoff Publishers, (1987).
3. Solomon, P.R., Best, P.E., Yu, Z.Z. and Deshpande, G.V., A Macromolecular Network Model for Coal Fluidity, to be presented at ACS Fuel Chem. Div. Meeting, Miami, FL, (9/89).
4. Burnham, A.K., Oh, M.S., Crawford, R.W. and Samoun, A.M., Energy and Fuel, **3**, 42, (1989).
5. Serio, M.A., Solomon, P.R., Yu, Z.Z., Deshpande, G.V. and Hamblen, D.G., ACS Fuel Chem. Preprints, **33**, (3), 91 (1988).
6. Serio, M.A., Hamblen, D.G., Markham, J.R., Solomon, P.R., Energy and Fuel, **1**, 138, (1987).
7. Carangelo, R.M., Solomon, P.R. and Gerson, D.J., Fuel, **66**, 960, (1987).
8. Whelan, J.K., Solomon, P.R., Deshpande, G.V., and Carangelo, R.M., Energy and Fuel, **2**, 65, (1988).
9. Solomon, P.R., Chien, P.L., Carangelo, R.M., Best, P.E., and Markham, J.R., "Application of FT-IR Emission/Transmission (E/T) Spectroscopy to Study Coal Combustion Phenomena", 22nd Symp. (Int) on Combustion, The Combustion Institute, Pittsburgh, PA (in press).

10. Solomon, P.R., Hamblen, D.G., Carangelo, R.M., Serio, M.A. and Deshpande, G.V., Energy and Fuel, **2**, 405, (1988).
11. Best, P.E., Carangelo, R.M., Markham, J.R., and Solomon, P.R., Combustion & Flame, **66**, 47, (1986).
12. Solomon, P.R., Carangelo, R.M., Best, P.E., Markham, J.R., and Hamblen, D.G., 21st Symp. (Int) on Combustion, The Combustion Institute, Pittsburgh, PA p. 437, (1986).
13. Solomon, P.R., Carangelo, R.M., Best, P.E., Markham, J.R., and Hamblen, D.G., Fuel, **66**, 897, (1987).

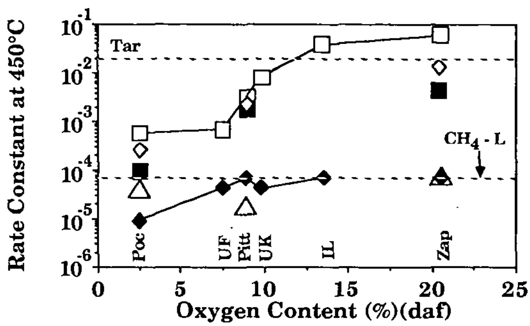

Figure 1. Comparison of Kinetic Rates at 450°C for Bridge Breaking (BB), Tar Formation, and Methane-Loose (CH_4-L) Formation. (■) BB, (△) CH_4-L from FG-DVC Model Fits; (□) Tar, (●) CH_4-L from TG-FTIR Data; (◇) Tar from Burnham et al. (4). Dashed Lines are Rank Independent Parameters.

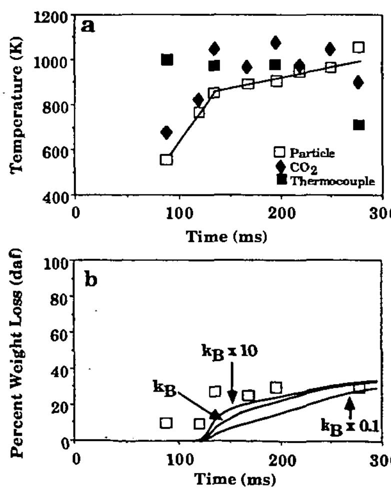

Figure 2. Pyrolysis Results for Zap North Dakota Lignite.
a) Temperatures and b) Weight Loss.

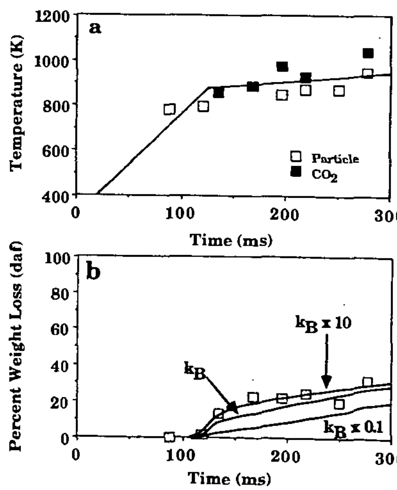

Figure 3. Pyrolysis Results for Pittsburgh Seam Bituminous.
a) Temperatures and b) Weight Loss.