A CHEMICAL MODEL OF COAL DEVOLATILIZATION USING PERCOLATION LATTICE STATISTICS

D.M. Grant and R.J. Pugmire, University of Utah
Salt Lake City, UT 84112.
T.H. Fletcher and A.R. Kerstein, Sandia National Laboratories
Livermove, CA

ABSTRACT

We have developed a model for coal devolatilization that incorporates the diversity of coal structure in such a way that the analytical data obtained from solid state NMR provides the initial input data. Using an experimentally determined kinetic rate parameters, it is possible to fit the gas, tar and char production of a lignite and high volatile bituminous coal. We have employed percolation theory to provide analytical expressions for the lattice statistics required in devolatilization modeling. The percolation theory allows one to avoid the more time consuming Monte Carlo technique with no loss of generality or important statistical features. Percolation theory analytically describes the size distribution of finite clusters of sites joined by intact bridges but isolated from all remaining sites by broken bridges. The theory specifies a critical bridge population, depending only on the site coordination number, above which infinite arrays will coexist with clusters of finite size. It is a simple matter to adapt the structural features of percolation theory to both the tar and gas obtained in coal pyrolysis. The infinite arrays of percolation theory are interpreted as the macroscopic lattice of unreacted coal and/or char while the relatively small tar molecules may be identified with the fine clusters of percolation theory. The details of the model will be discussed together with the results obtained in modeling devolatilization behavior of coals of various ranks.

INTRODUCTION

A model for coal devolatilization, the chemical percolation devolatilization (CPD) model, has been developed[1] that incorporates the diversity of coal structure in such a way that the analytical data obtained from solid state NMR provides some of the initial input data. Using kinetic rate parameters reported by others[2], it is possible to fit the gas, tar, and char production of a lignite (Zap), and a high volatile bituminous coal (Illinois No. 6). Percolation theory is employed to provide analytical expressions for the lattice statistics required in the devolatilization modeling. Percolation theory allows one to avoid the time consuming Monte Carlo techniques with apparently no loss of generality or important statistical features. The straight forward computational technique is very efficient even on a small VAX computer as opposed to the more time consuming Monte Carlo methods which have shown that appropriate lattice statistics are important in coal devolatilization[3].

The CPD theory analytically describes the size distribution of finite clusters of sites joined by intact bridges but isolated from all remaining sites by broken bridges. In percolation statistics a critical bridge population exists which depends only on the site coordination number, σ, above which infinite arrays will coexist with clusters of finite size. It is a simple matter to adapt the structural features of percolation theory to both the tar and gas obtained in coal pyrolysis. The infinite arrays of

percolation theory are interpreted as the macroscopic lattice of unreacted coal and/or char while the relatively small tar molecules may be identified with the finite clusters of percolation theory.

EXPERIMENTAL

The devolatilization data is that reported by Serio, et. al.[2], for a heated tube reactor of advanced Fuel Research. The raw kinetic data was kindly supplied by Serio and Solomon. The kinetic parameters used in the model are those obtained by Serio, et. al.[2], and are given in Table I. The NMR data for the coals are from Solum, et. al.[4]. The initial and final coal specific parameters are given in Table II.

RESULTS AND DISCUSSIONS

The details of the Chemical Percolation Model have been described by Grant, et. al.[1], and the details of the model will not be repeated. The comparison of the theoretical simulations of the experimental data are given in Figures 1 and 2 for the Illinois No. 6 and ZAP coals. The yields of gas, tar and char/unreacted-coal are given as a function of reaction time along with the corresponding predicted dynamical variables required for the simulations. The success of the simulations is thought to be good considering the number of parameters which were constrained from other work. We are engaged in an assessment of the sensitivity of the simula-

tions upon the several parameters and eventually hope with more experimental data to employ multiregressional analysis of devolatilization data as a way to determine an optimal set of parameters. The correlation matrix between the several parameters is expected to enhance our understanding of the manner in which these parameters interact to influence the model.

Several of the features observed for these diverse coals are noteworthy and warrant comment in terms of the dynamical variables required in the simulations shown in Figures 1 and 2. The contrast in the material yields in both coals is quite apparent with the light gas exhibiting the typical exponential character, while the tar release exhibits a precipitous release or "flooding" because of the non-linear percolation statistics superimposed upon the multiexponential kinetic parameters which characterize the bridge-breaking processes. Even though the activation energy used for tar formation is lower than that for light gas release, considerable light gas is produced before any appreciable amount of tar is released. The "flood" of tar observed as the lattice begins to break down dramatizes the importance of lattice statistics in the tar release process. While the qualitative features are somewhat similar in both coals, significant quantitative differences may be observed in both material yields and the dynamical variables plotted for the two coals. The relative release with time of gas and tar have similar characteristics in both coals.

The model accurately predicts the modest but measurable loss of tar weight observed in the experimental data[2] after the initial "flooding" of tar. The maximum tar weight corresponds closely in time with the complete loss of labile bridges (see Figures 1 and 2). From this point on the decrease in tar weight arises from the release of light gases through continued cracking of the side chains as the material proceeds along the heated tube reactor. The rate of gas release slows with time as the more reactive bridge material is consumed in accordance with the distributed activation energy submodel. It is worth noting that this model predicts for both coals that a reasonably large side chain population will persist in both the tar and char throughout the whole process, and as a result light gases are released until the devolatilization is terminated at the end of the reactor tube. The gas release during the latter part of the process is not due to breaking of labile bonds with the accompanying release of bridge material, as the labile bridge population is zero during most of this latter period for the cases used in these simulations. Thus, the tar cluster size is not changing during this period of the reaction, but instead, the side chains are cracking to reduce the weight fraction of both the tar and the char.

For reaction conditions under 800°C, which obtain in the heated tube reactor experiments (Serio, et. al.[2]), the model predicts that a significant fraction of side chains persist throughout the whole reaction and

still exist even at the termination of the devolatilization process. Inspection of the plots of dynamical variables indicate that it is the δ variable (side chains) which exhibits the most interesting excursions with time rising and falling in concentration in the dynamical competition for bridge material. It is interesting to note that even when all of the labile bridges have been consumed and the number of char bridges have reached their final population, the reactive side chain population is still both appreciable and changing due to cracking of the side chain material. The amount of side chain material produced in the disappearance of the labile bonds is governed in part by the amount of transferable hydrogen. Thus, the rate constant of the side chain bond breaking would include explicitly the concentration of transferable hydrogen and a good test of the model would be its ability to simulated hydroliquifaction data obtained for various partial pressures of hydrogen.

The well known gas release occurring at early times is provided by low activation energies due to the distributed activation features incorporated in the model. The model also indicates a "tar" mass fraction of a few percent present at time zero in the unheated coals suggesting the presence of extractables in coals at ambient temperatures.

Future work will focus on model refinements to include a transport model. The molecular weight distribution of the tar is provided by the model and we will compare experimental molecular weight distribution data of Suuberg[5] with the theoretical predictions of the CPD model.

ACKNOWLEDGEMENTS

This work was supported by the Advanced Combustion Engineering Research Center (ACERC) under grant no. CDR-8522618 from the National Science Foundation and by the U. S. Department of Energy. Two authors (DMG and RJP) express appreciation for support from the Associated Western Universities (AWU) to allow them to work for a period of time as guests at the Combustion Research Facility, Sandia National Laboratories. Helpful suggestions and assistance in computing by ACERC personnel (P.J. Smith, L.D. Smoot, L.L. Baxter, and J.D. Smith) are also acknowledged.

REFERENCES

1. D.M. Grant, R.J. Pugmire, T.H. Fletcher, and A.R. Kerstein, submitted for publication, 1988.
2. M.A. Serio, D.G. Hamblen, J.R. Markham, and P.R. Solomon, Energy & Fuels, 1987, 1, 178.
3. P.R. Solomon, D.G. Hamblen, G.V. Desphande, and M.A. Serio, 1987. International Conference on Coal Science, J.A. Monlijn, K.A. Nater, H.A.G. Chermin (Eds., Elsevier, Amsterday, 1987, p. 601.
4. M.S. Solum, R.J. Pugmire, W.R. Woolfenden, and D.M. Grant, submitted for publication, 1988.
5. E.M. Suuberg, P.E. Unger, and J.W. Larsen, Energy & Fuels, 1987, 1, 305.

Table I

Kinetic Parameters for Coal Devolatilization

Parameter	Value	
	Fitting Parameters	Literature Derived Values
E_b		55.4 Kcal/mole
A_b	4×10^{15} sec^{-1}	
V_b	2 Kcal/mole	
E_g		69 Kcal/mole (69, 66, 71 Kcal/mole)[a]
A_g		3×10^{15} sec^{-1} ($3.5, 2.9, 2.6 \times 10^{15}$ sec^{-1})[a]
V_g	7 Kcal/mole	
ρ	0.89 sec^{-1} [b]	

a. Weighted average values for the Illinois #6 bituminous, Rosebud subbituminous, and Zap lignite coals, respectively.

b. As E_ρ and A_ρ can not be determined for the relatively small devolatilization temperature range affecting these data only a single effective rate parameter for ρ may be used in this fitting.

Table II

Coal Specific Parameters

Parameter	Zap Lignite	Rosebud Sub-Bit	Ill #6 High Vol. Bit.
Adjustable Fitting Parameter			
$\sigma + 1$	8.8 (>4.4)[a]	8.8 (>4.1)[a]	
Parameters Set from NMR and Ultimate Gas Yield Data			
$\sigma + 1$			4.3 (4.3)[a]
p_o (=$\pounds_o$)[b]	0.44	0.45	0.73
$f_{gas}(\infty)$ [c]	0.55	0.46	0.41
Calculated Parameters from Fitted and Set Parameters			
$1/\sigma$	0.13	0.13	0.30
$(\sigma + 1) \cdot p_o$ [d]	3.9	4.0	3.1
$r = m_b/m_a$ [e]	0.28	0.19	0.32

a. NMR estimates for σ given in parentheses.

b. The simulation value for $\pounds_o$, which becomes p_o under the assumption of c_o = zero, are estimated reasonably reliably from NMR data on the number of methyls and of side chains attached to an aromatic cluster.

c. Solomon's ultimate light gas yields may be obtained by summing the y_i from i = 1 to 17.

d. This quantity measures the number of intact bridges per cluster and is calculated from the above values of p_o and σ.

e. Calculated from σ and $f_{gas}(\infty)$.

f. The NMR estimates for r given in parentheses.

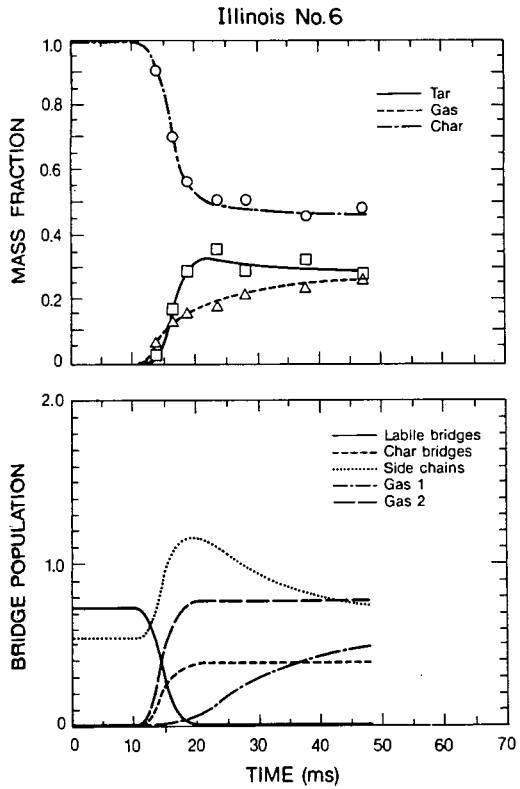

FIGURE 1. Simulation of devolatilization yields of char, tar, and light gases vs time for Illinois No. 6 high volatile bituminous coal are given in the upper plot. Experimental data are from Serio, et. al.[2]. Bridge dynamical variables are given as a function of time in the lower plot.

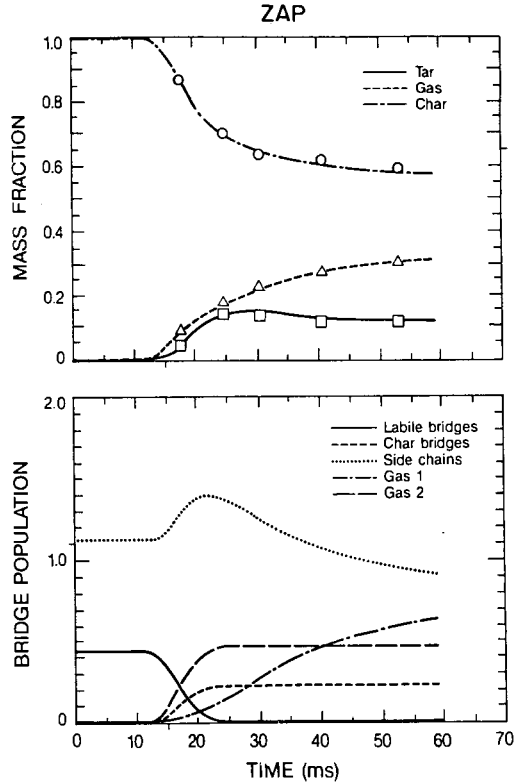

FIGURE 2. Simulations of devolatilization yields of char, tar, and light gases, vs. time for North Dakota lignite (ZAP) coal are given in the upper plot. Experimental data are from Serio, et. al.[2] Bridge dynamical variables are given as a function of time in the lower plot.