

## ADVANCES IN THE FG-DVC MODEL OF COAL DEVOLATILIZATION

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### INTRODUCTION

The FG-DVC general model for coal devolatilization, which combines a functional group (FG) model for gas evolution and a statistical depolymerization, vaporization, and crosslinking (DVC) model for tar formation, has previously been presented (1). The FG model describes the evolution of gases from sources in the coal, char and tar. The DVC model describes the decomposition and condensation of a macromolecular network representation of coal under the influence of bond breaking and crosslinking to predict (using Monte Carlo statistical method) the molecular weight distribution of the network fragments. The crosslinking reactions are related to the evolution of CO<sub>2</sub> at low temperature and CH<sub>4</sub> at moderate temperature (2). Tar is formed from the light fraction of the network fragments which vaporizes and is transported by the light gases.

As discussed in Ref. 1, the FG-DVC model was based on a number of simplifying assumptions which provided a good first approximation of the devolatilization process. Included in the approximations were the assumptions that: i) the coal molecular structure could be described as substituted aromatic ring clusters of various sizes linked into a macromolecular network or present as guest molecules, ii) tar consists of fragments of that network and so has a similar composition. (except for a higher hydrogen content due to a larger number of methyl groups), iii) kinetics are independent of coal rank, iv) transport is controlled by the vapor pressure of tar fragments in the escaping gases.

Since the presentation of the original FG-DVC model, a number of improvements have been made. First we have added a second class of material, polymethylenes, to the macromolecular network. These polymethylenes can form a large part of the tar in low rank coals and so make the tar dissimilar to the parent structure (which is primarily the aromatic ring clusters). Second, the molecular weight distribution of macromolecular network fragments has been used as the basis for a theory of viscosity (3). This theory is quite sensitive to the accuracy of the kinetic rates. Consequently, third, rank dependent kinetics have been added to the model (3,4). Fourth, we have tested the tar transport theory by comparing its predictions on molecular weight distributions to measurements made with a Field Ionization Mass Spectrometer (FIMS). The results suggest that the vapor pressure law (5) used in the original model (1) appears to fit the data in its dependence on molecular weight and temperature, but was about a factor of 10 too low in its vapor pressure. Finally, we are exploring the use of percolation statistics as an alternative to the Monte Carlo calculations. An approximation is presented which includes the evolution of tar molecules and is based on a previously presented two coordination number percolation theory (6).

### MODEL IMPROVEMENTS

#### Polymethylenes

Varying amounts (typically 0-9%, but in some cases as high as 18%) of long-chain aliphatics (polymethylenes) have been reported in pyrolysis products by Nelson (7) and by Calkins and coworkers (8-11) and references quoted therein. The chains appear alone and attached to aromatic nuclei. The presence of these polymethylenes makes the tar more aliphatic than the parent coal. Also, for most coals, there is a low temperature tar peak which results from the vaporization of unattached small polymethylenes plus small aromatic ring clusters. This vaporization peak is illustrated in Fig. 1. Polymethylene chains can also crack or be released into the second tar peak. Further cracking of this material under more severe devolatilization conditions produces ethylene, propylene, and butadiene from which the concentration of polymethylenes may be determined (11). Originally, the polymethylenes were included in the FG model as part of the aliphatic functional group pool, which is assumed to decompose to produce gas products, not tar. This leads to predicted H/C ratios in the tar for low rank coals which are lower than those measured by Freihaut et al. (12).

Polymethylenes have now been added to the DVC part of the model as a second class of material whose molecular weight distribution and functional group composition are different from the main macromolecular network. The starting coal molecule now includes a distribution of oligomer sizes for polymethylenes and other guest molecules (with the chemical composition of the network). The vaporization of these molecules produces a peak which matches the early vaporization peak as shown in Fig. 1. We also account for polymethylenes which are attached to the coal matrix and removed by bond breaking by including them as species in the FG model. Those polymethylenes are then added to the tar after vaporization.

The model requires a value for the total polymethylene content in the coal. Calkins determined that the yields of ethylene, butadiene, and propylene correlated well with the polymethylene content (11). It was decided that this is the most general and fruitful approach to take and we have used the coals which are in our set and Calkins' set to calibrate the method. As a first approximation, we arbitrarily chose to use polymethylene = 0.7 (C<sub>2</sub>H<sub>4</sub>). This gave -CH<sub>2</sub>- contents slightly above Calkin's values, but within 15% of Calkin's. The model also assumes that 50% of the polymethylenes are small enough to vaporize and are included in the oligomer pool while the other 50% are not and are included in the FG pool.

A prediction for the total tar yield including polymethylenes is compared in Fig. 1 with measurements from a TG-FTIR experiment (13-15). The agreement is good. Comparisons between the predicted and measured (12) tar hydrogen compositions are shown in Fig. 2. The prediction is good for high rank coals and shows the correct trend with rank. The tar hydrogen composition is, however, overpredicted for lower rank coals. This is due to the fact that the model underpredicts, for these coals, the tar yield at high heating rates. The relative contribution of polymethylene is then more important. By improving the tar prediction with adjustments of DVC parameters, we should be able to obtain more accurate values of the tar hydrogen composition.

#### Viscosity Model

We have developed a model for coal fluidity as an extension of the FG-DVC model (2). The FG-DVC model predicts the yield of liquids (all fragments released from the network) produced during heating of the coal. The fluidity is dependent on the relative amounts of the liquid, and solid (the remaining network) and on the fluidity of the liquid component. The fluidity of the liquid component depends on the average molecular weight of the liquid and on the temperature. The details of the fluidity model and comparisons to literature values of viscosity are presented in Ref. 3. Excellent agreement has been obtained between the model predictions for fluidity and low temperature fluidity measurements of Oxley and Pitt (16), Fitzgerald (17), and van Krevelen (18).

Recently, we have applied the model to predict the fluidity data for the Argonne premium samples obtained using a Geissler plastometer (19). To properly predict the fluidity we found that the rank independent kinetics were no longer accurate enough. Rank dependent rates for bond breaking, low temperature crosslinking, and moderate temperature crosslinking were determined using the evolution rates for tar, CO<sub>2</sub>, and CH<sub>4</sub> in a TG-FTIR experiment as discussed in the next section. Their rank dependent rates were used to make the predictions of viscosity.

Figure 3 compares the measured and predicted viscosity for Upper Freeport coal. Figure 4 shows the predicted and measured values for the temperature of the initial softening point (where the plastomer first reads 1 DDM), the temperature of maximum fluidity, the maximum fluidity is, and the solidification temperature (where the plastometer last reads 1 DDM). The agreement is good, generally within  $\pm 10^\circ\text{C}$  for the temperature predictions and within a factor of 5 for the fluidity maximum.

#### Rank Dependent Kinetics

As discussed above, in order to fit the fluidity data, the tar formation, carbon dioxide, and methane kinetic rates had to be adjusted from those used in the original model which were rank independent (1,20). These rates control the bridge breaking, low temperature crosslinking and moderate temperature crosslinking rates, respectively. The rank dependent rates were chosen by fitting the TG-FTIR data at 30°C/min and the Geissler fluidity data (19) at 3°C/sec.

In addition to this study, 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) for the Argonne coal set (4).

The rank dependences of the rate constants for bridge breaking, (or tar evolution) and CH<sub>4</sub> evolution at 450°C determined from analyzing the TG-FTIR data at several heating rates and from fitting the FG-DVC model to fluidity data at 3°C/min and the tar and methane evolution data at 30°C/min are shown in Fig. 5. The two methods agree fairly well and show a systematic variation in rates with the coal's oxygen concentrations. 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 (21). If the Pocahontas is included, the rank variation for the tar evolution or bridge breaking rates is about a factor of 25. The rates for tar evolution are consistent with those obtained by Burnham et al. (22) for total hydrocarbon evolution from Rock Eval analysis of the same coals.

### Tar Transport Model

The tar transport model assumes that the tars reach their equilibrium vapor pressure in the light gases and evolve with these gases as they are transported through the pores or by bubble transport. The details of the model are presented in Ref. 1. We have used the vapor pressure correlation of Suuberg et al. (5) for the equilibrium vapor pressure. Since this vapor pressure law is a function of molecular weight and temperature, we tested the accuracy of our model in predicting the evolution of tar fragments of specific molecular weight as a function of temperature.

The experimental data used was obtained from FIMS analysis, where the FIMS apparatus is in line with a probe used to heat the sample. The FIMS analysis was performed by Ripudaman Malhotra at SRI International on coals, which pyrolyze in the apparatus (coal FIMS), and on already formed coal tar, which vaporizes in the apparatus (tar FIMS). We divided the tar oligomers (from both data and theory) into five different bins: 50-200 amu, 201-400 amu, 401-600 amu, 601-800 amu, and > 800 amu. The evolution with temperature of each bin is then plotted.

Tar FIMS - We found good agreement between the tar FIMS data and our simulation (Fig. 6). A small mismatch is present for large molecular weight oligomers (> 800 amu), where the maximum of rate evolution occurs later in the simulation. The peak is also narrower, i.e. the temperature range of evolution is shorter than found experimentally. The vaporization of smaller oligomers is, however, well predicted. This validates the temperature and molecular weight dependence of the vaporization law (5) used in the model but not the absolute magnitude of the vapor pressure.

Coal FIMS - We compared the results of the simulation with coal FIMS data for two coals, Pittsburgh No. 8 and Wyodak. We found the best agreement when the Suuberg et al. correlation (5) is multiplied by ten. For the Pittsburgh No. 8, the theory gave an accurate prediction for the evolution temperature of low molecular weight oligomers, as well as the relative amounts of all oligomer classes (Fig. 7). It, however, predicted higher evolution temperatures for high molecular weight oligomers (> 600 amu), while the data showed a unique temperature of maximum evolution rates ( $T_{max}$ ) for all molecular weights. A shift to higher  $T_{max}$  with higher molecular weight is consistent with the fact that large oligomers need higher temperatures to vaporize, as confirmed by the tar FIMS data. Since coal FIMS data doesn't present this feature, we suspect some additional limitations occur as the fluid coal melt resolidifies.

The simulation for Wyodak coal gave a good prediction for the evolution of all molecular weight classes oligomers, including large ones (Fig. 8). The data (Fig. 8b) shows that the evolution of high molecular weight oligomers occurs slightly before the smaller oligomers. This also suggests the presence of additional limitations. In our simulation for low rank coals, the peak position is regulated by the low temperature cross-linking rate (which reduces the number of large oligomers which can vaporize) rather than by the vaporization law.

In order to obtain a better prediction for Pittsburgh No. 8, we considered additional transport limitations related to the reduction in the fluidity of the coal. However, none of the simple modifications tried gave a significant improvement in the model for both low and high rank coals. The current model gives good predictions for the relative amounts of the oligomers in each size classification. It also predicts accurately the evolution temperature of low molecular weight (< 600

amu) oligomers. The vapor pressure dependence on temperature and molecular weight is also validated by the good prediction of the tar FIMS data. The present model, therefore, uses the original FG-DVC transport assumption (1) with the Suuberg et al. vapor pressure correlation (5) multiplied by ten.

### Percolation Theory

The statistical Monte Carlo method used in our FG-DVC model has been quite successful in predicting the depolymerization and crosslinking processes of the coal macromolecular network. However, the method has a few drawbacks. First, it is computationally time-consuming compared with other statistical methods. Second, its statistical nature presents a certain degree of fluctuation in the final results. The latter becomes increasingly significant and poses some difficulties for the modeling of coal fluidity and swelling.

To address these problems, attempts have been made to use the mathematics of percolation theory as an alternative to Monte Carlo calculations (6,23,24). Percolation theory gives closed-form solutions for a Bethe lattice. Keeping in mind that an actual coal network contains some different features from the Bethe lattice (e.g. the Bethe lattice has no loops), we made use of some basic concepts of percolation theory while we further modified the mathematics of this theory to describe vaporization processes in coal devolatilization.

One of the key parameters of percolation theory is the coordination number,  $\sigma + 1$  which describes the possible number of bridge attachments per ring cluster (monomer). A linear chain has  $\sigma + 1 = 2$ , while a rectangular "fish net" has  $\sigma + 1 = 4$ . The higher the coordinator number, the more bridges must break to create network fragments. In attempting to apply percolation theory to the FG-DVC model (6), it became obvious that the single coordination number lattice used in most applications of percolation theory was not appropriate to describe coal network decomposition. It appears from solvent swelling data (25-29) and NMR data (30), that coal begins as a chain-like material with crosslinks every 2 to 8 ring clusters, i.e.,  $\sigma + 1$  between 2.2 and 2.5. So, its decomposition requires a low coordination number. However, crosslinking processes can occur at elevated temperature to increase the coordination number. Therefore, we extended the mathematics of percolation theory from a one-dimension probability computation into a two-dimensional probability computation to describe the coal network as a lattice with two bond types per cluster, i.e., two coordination numbers. This modified theory is referred to as the two- $\sigma$  model (6).

Two important new features in our two- $\sigma$  percolation theory are: (i) tar vaporization and (ii) molecular weight distribution of monomers. These features are basically treated the same way as in the original DVC model. The molecular weight of monomers is described by a probability distribution, which allows for the fact that monomers are made of various multi-ring structures. Tar molecules are removed out of the coal network using Suuberg's modified vaporization law. Molecular weight distributions of tar and char are kept track of during pyrolysis by a bookkeeping of the vaporization process in each mass bin. The percolation theory gives the mass fraction of all n-mers during pyrolysis. Combining this with a given molecular weight distribution of monomers, one can obtain the mass fraction of coal in each mass bin, which consists of two components: char and tar. Tar vaporization is computed for each mass bin. Tar in each mass bin monotonically increases and reduces the amount of char available for vaporization in the same bin until the char bin is emptied. Figure 9 shows the comparison of predicted tar yields between the Monte Carlo method and the modified percolation theory. Also, a two- $\sigma$  prediction of the fluidity for the same coal is included in Fig. 3. The Monte Carlo and two- $\sigma$  predictions agree reasonably well with each other and with the data.

### **CONCLUSIONS**

This paper describes a number of improvements and extensions of the FG-DVC model of coal devolatilization.

- 1) Polymethylenes have now been included in the model. They account for part of the low temperature vaporization peak observed for some coals, and for the increase in the H/C ratio of coal tar observed for low rank coals.

- 2) A fluidity model has been added to the FG-DC model. The fluidity is dependent on the relative amounts of the liquid and solid, and on the fluidity of the liquid component. The fluidity of the liquid component depends on the average molecular weight of the liquid and on the temperature. The model accurately predicts the measured fluidities for the Argonne coals using rank dependent kinetics.
- 3) Rank dependent kinetics for tar formation, CO<sub>2</sub> formation and CH<sub>4</sub> formation have been obtained for the Argonne coals by fitting the fluidity data. These agree with rates obtain by fitting data from a TG-FTIR experiment at several heating rates and with the rates obtained by Burnham et al. (22) for the same set of coals.
- 4) The tar transport model used in the original FG-DVC model (i.e., the tars reach their equilibrium vapor pressure in the light gases and evolve with these gases as they are transported through the pores or by bubble transport) was examined by comparing the temperature and molecular weight predictions for tar evolution measured in a FIMS analysis. The original assumptions give reasonably good fits to the data if the Suuberg et al. vapor pressure correlation (5) is multiplied by ten.
- 5) A new two- $\sigma$  percolation theory was developed with an approximation for tar evolution. The predictions of this model agree with the predictions using Monte Carlo statistics and with the data.

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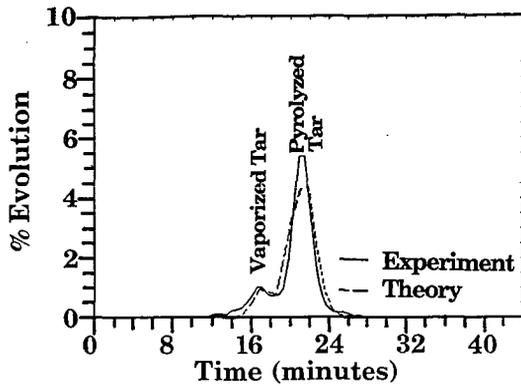


Figure 1. Comparison of FG-DVC Model Predictions for Tar Evolution Rate from Upper Freeport Coal with TG-FTIR Data.

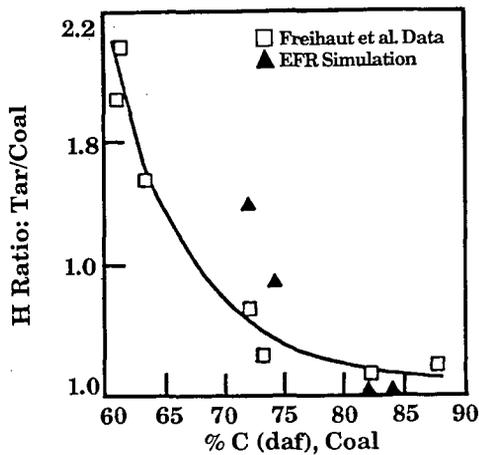


Figure 2. Ratio of % H in Tar to % H in Coal as a Function of Coal Rank. (from Freihaut et al. (12)).

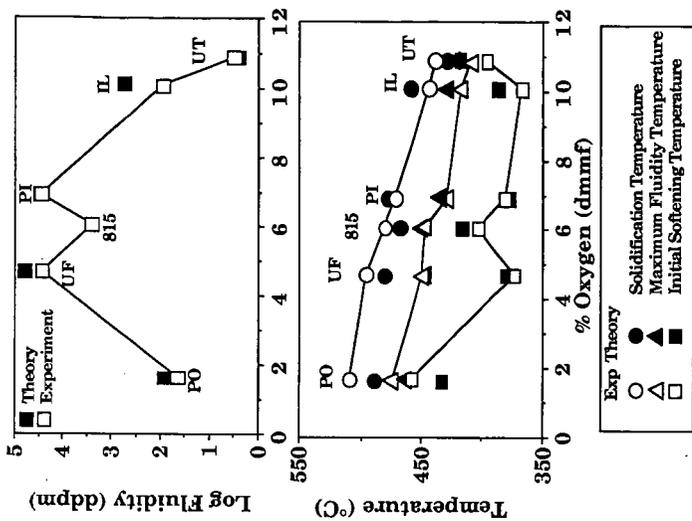


Figure 4. Fluidity Behavior as a Function of Coal Rank: Theory and Experiment. a) Maximum Fluidity Values and b) Fluidity Temperatures.

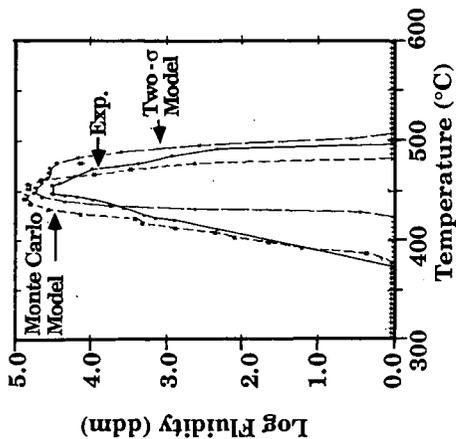


Figure 3. Fluidity of Upper Freeport Coal: Experiment (solid), Monte Carlo Theory (dashed) and Percolation Theory (long dashed).

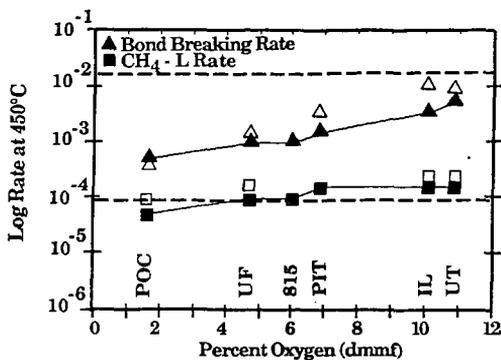


Figure 5. Rank Dependence of Kinetic Rates for Argonne Coals. Open Symbols: From Analysis of TG-FTIR Data at Four Heating Rates. Closed Symbols: From Fitting Fluidity Data at 3°C/min and TG-FTIR Data at 30°C/min. Dashed Lines: Rank Independent Rates used in Original FG-DVC Model.

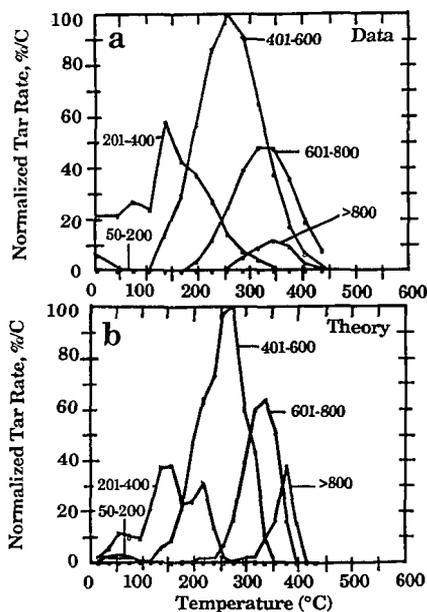


Figure 6. Comparison of a) FIMS Data and b) Theory for Pittsburgh No. 8 Coal Tar.

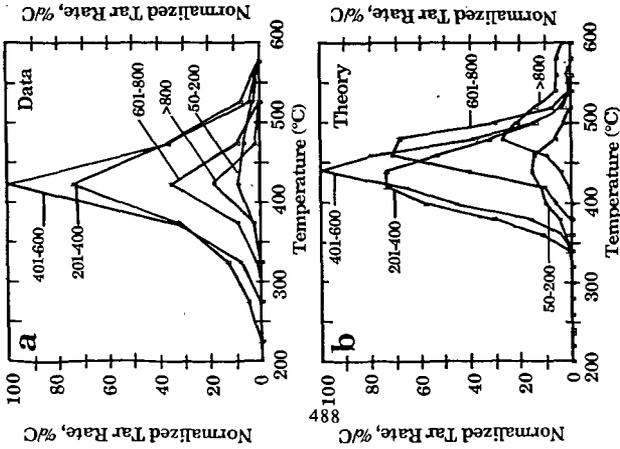


Figure 7. Comparison of a) FIMS Data and b) Theory for Normalized Tar Rate for Pittsburgh No. 8 Coal Pyrolyzed in the FIMS.

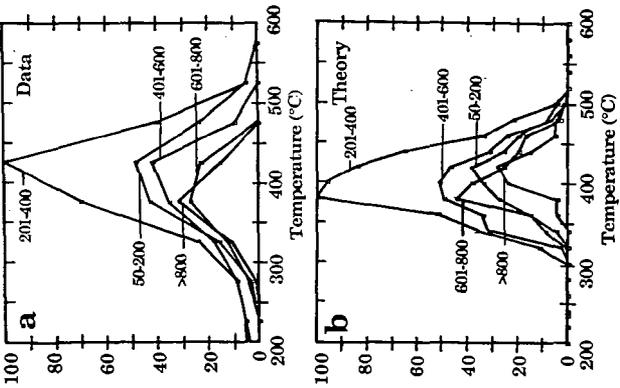


Figure 8. Comparison of a) Data and b) Theory for Normalized Tar Rate for Wyodak Coal Pyrolyzed in the FIMS.

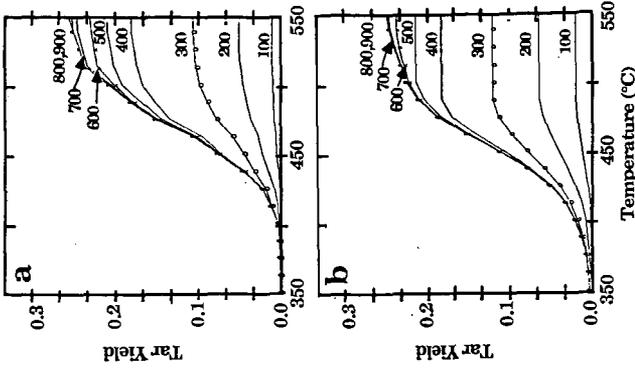


Figure 9. Comparison of Tar Molecular Weight Distribution Predicted with: a) Monte Carlo Method and b) Two- $\sigma$  Percolation Theory.