

A MACROMOLECULAR NETWORK MODEL FOR COAL FLUIDITY

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ABSTRACT

We have developed a model for coal fluidity based on the decomposition and condensation of the macromolecular network under the influence of bond breaking and crosslinking reactions. The model is an extension of the FG-DVC model of coal pyrolysis. It employs a macromolecular network consisting of aromatic ring clusters linked by bridges. In the FG-DVC model, bond scissions are described by a single first order reaction with a distribution of activation energies, and crosslinking is related to CO₂ and CH₄ formation. The FG-DVC model predicts the yield of liquids produced during heating of the coal. The fluidity is dependent on the relative amounts of the liquid, (molecules detached from the network) 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. Excellent agreement has been obtained between the model predictions for fluidity and low temperature fluidity measurements of Oxley and Pitt, Fitzgerald and van Krevelen. Good agreement has been obtained at high temperatures between the model predictions and measurements of Fong for the onset of the fluidity and the peak fluidity value. The loss of fluidity, however, is predicted to occur sooner than is indicated by the data. The data covers over four orders of magnitude in fluidity and four coals with carbon concentration between 80 and 90%.

INTRODUCTION

When bituminous coals are heated, they can decompose sufficiently to become liquid. Those in the range of 82 to 89% carbon achieve the highest fluidity (1,2), but even lignites, if heated rapidly enough can exhibit some fluidity (3). The understanding and ability to predict a coal's fluid properties is important in many processes. In liquefaction, highly fluid coals dissolve quickly in the process solvent so that further chemistry occurs by liquid/liquid interactions while non-fluid coals must undergo slower solid/liquid interactions. In combustion or gasification, fluidity controls particle swelling (4), agglomeration of particles, char reactivity (5), and subsequent fragmentation (6) of char. In coke making, fluidity controls the coke properties (7,8). Fluidity also affects the growth of carbon fibers from coal tars.

There are a number of factors which contribute to the fluidity of coal liquid. They include: i) the fluidity of the liquid part itself, with and without molecular entanglements; ii) the dependence of this fluidity on temperature; iii) the contributions of suspended solids in the liquid, both "chunks" of char, and mineral particles; and iv) the formation of a foam due to trapped gases.

Several models for coal liquid viscosity have been proposed which consider all of the influences except the trapped gases. The models were based on the two step process described by van Krevelen and coworkers (1,9), which assume the following reactions to occur on heating.



where k_1 and k_2 are reaction rate constants. In the viscosity models the change of fluidity is assumed to result only from the change in solids mass fraction, ϕ_s (coal and coke) in the melt. Thus Bronowski et al. (10) used an expression in which fluidity was directly proportional to the mass fraction $(1-\phi_s)$ of fluid (metaplast) present. Expanding on this, Fitzgerald (11,12) used an equation which described the relative fluidity as depending on fluid fraction raised to a power n (where n was chosen to be 2.5). This power law expression was based on earlier work by Roscoe (13) and Brinkman (14). In a similar manner, Fong et al. (15) used an expression put forward by Frankel and Acrivos (16), in which the fluidity also depends on a power of the fluid fraction. Their model has the

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extra feature of a critical solids-volume-fraction at which fluidity disappears. This critical value occurs at the maximum volume fraction that the solids can occupy as limited by particle-particle interaction. At this critical value, the liquid fraction is insufficient to separate the solid particles. Its value is 0.64 for randomly close-packed spheres, while it ranges from 0.5 to 0.9 for other systems, depending on particle shape and state of agglomeration (17). Viscosity models predict that the fluidity vanishes for volume fractions equal to or greater than the critical value, and we refer to this as the inhomogeneous gel point. The chosen critical value in Fong's model was at a volume fraction of unity, somewhat higher than usual (17). A similar model was used by Oh (18). The above models gave good fits to data, although in each case the model parameters (k_1 , k_2 , n and the critical solids volume fraction) were chosen to fit data from a particular coal studied in a limited number of experiments covering a narrow range of heating rates, or holding temperatures.

Based on the observation that coal can be considered as a macromolecular network to which theories of crosslinked polymers may be applied (1,2,19,25,26), we have examined the polymer literature of viscosity in polymer melts (17,27-32). For non-reacting melts of branched polymers at molecular sizes below those sufficiently large for entanglements, there is experimental and theoretical support for viscosities which depend exponentially on side-arm molecular mass (27). These same authors determined temperature-dependent activation energies for viscosity, for temperatures below 200°C. It is noted that at higher temperatures (~ 600 K) Nazem found temperature independent activation energies for the viscosity of carbonaceous mesophase pitch (28).

In reacting melts, the manner in which average molecular weight varies with extent of reaction in a homogeneous melt has been considered in the branching theory described by Macosko and coworkers (29). Insofar as it describes molecular weight distributions, this theory duplicates and extends the results of older combinatorial methods developed by Flory (30) and by Stockmayer (31). A particular result of Macosko's work is that measured viscosity correlates well with the weight average molecular weight of the largest linear path through the molecules. This theory predicts that the homogeneous gel-point (the point at which the viscosity goes to infinity) appears at the first occurrence of a solid phase.

It is not clear whether Macosko's approach is appropriate for coal and it has not been tested. Coal is typically an inhomogeneous reacting melt where the reaction coal \rightarrow metaplast is the inverse of the polymerization, and metaplast \rightarrow coke is an example of repolymerization and crosslinking. The inhomogeneities result from several factors including: starting with a powdered solid (which would be sufficient to insure inhomogeneity), having a material consisting of diverse maceral types, and containing mineral grains. Theories which describe the viscosity of a suspension of a solid in a liquid, such as those mentioned above for coal, are general in their application (17,32), and also apply to suspensions of a solid in a polymer melt.

We have employed polymer concepts to describe tar and extract formation in coal pyrolysis, initially employing linear chain statistics (33,34) and subsequently employing network statistics (35-38). Our "DVC" model includes the processes of **Depolymerization** (bond breaking), **Vaporization** (mass transport), and **Crosslinking**. This model was combined with our functional group (FG) model for gas evolution (4,39-41) to provide the general FG-DVC coal pyrolysis model in which the crosslinking process is related to the evolution of certain gas species (42,43). The FG-DVC model employs Monte Carlo methods to compute the network properties. More recently, network models of thermal decomposition have been proposed employing percolation theory (44,45). We have also employed percolation methods for the statistical calculations in the FG-DVC model (46).

The fluidity model presented here employs the FG-DVC model to predict the molecular weight distribution of the decomposing macromolecular network. From this distribution, a solid fraction ϕ_s and a liquid fraction with a weight-average molecular weight are defined. These parameters are employed using the concepts of inhomogeneous mixtures to predict the fluidity from the solid fraction, the liquid viscosity and the temperature (17,28,32). The model predictions are compared with measurements made with a Gieseler plastometer (1,47,48) and with the high temperature fluidity measurements of Fong et al. (15).

EXPERIMENTAL

The low temperature fluidity data employed in this paper is literature data obtained with a Gieseler plastometer. Descriptions of the apparatus and operation may be found in the literature (49,50). The viscosity is determined by measuring the rotation rate of a stirrer in the sample when constant torque is applied. There are many problems of translating stirrer rotation speed to viscosity in poise and most researchers simply report data in degrees/min or dial divisions/min (DDPM) where one DDPM = 3.6°/min. Some data of van Krevelen was reported in poise (1). We have used these data in conjunction with data for the same coal reported in degrees/min to obtain the calibration $1^\circ/\text{min} = 0.7 \times 10^{-8}$ rhe's where 1 rhe = 1/poise.

In making fluidity measurements on coal, it has been found that there is an initial softening of coal on heating which is reversible, and has been associated with melting and hydrogen bond breaking. This is followed by a sharp rise in fluidity due to the decomposition of the macromolecular network due to covalent bond breaking, and it is from this point that our model seeks to describe the processes. This sharp rise is illustrated in Fig. 1 which presents the measured fluidity of a bituminous coal as a function of time as the coal was heated from 300°C at 3°C/min to 407°C and held at constant temperature (48). The slower fall in fluidity with time is due to crosslinking which resolidifies the network. This crosslinking rate is linearly correlated with the initial rate for the evolution of CH_4 (38,42,43,51).

The high temperature data was obtained by Fong et al. (15) in a device designed for rapid heating. Coal is contained in a pancake shaped cavity in which a disk driven at constant torque is allowed to rotate. The rotation speed was related to viscosity in poise using standards of known viscosity.

The model we present employs both the coal composition and the kinetic rates for bond breaking and gas evolution. The crosslinking rate is related to the gas evolution. Since it was not possible to obtain samples of the original coals used for the viscosity measurements we have selected from the Argonne coal sample collection, those which best match the reported coals in carbon concentration and volatile matter. Table I presents the available data on the coals whose viscosities have been measured and the Argonne coal used in the model. More complete composition data for the Argonne coals were presented by Voores (52). The previously determined kinetic rates and model parameters were presented by Serio et al. (41,53). A comparison of the weight loss at constant heating rate of the Argonne coals and the coals employed in the study of van Krevelen (1) is presented in Fig. 2.

THEORY

The theory of coal fluidity consists of two parts: i) a macromolecular network model (FG-DVC) to predict the liquid fraction and average molecular weight of the liquid as a function of time and temperature; and ii) empirical expressions to predict fluidity from the liquid fraction, the average molecular weight of the liquid and the temperature.

To predict the liquid fraction and its average molecular weight, we employ a model which describes the decomposition or condensation of the macromolecular network under the influence of bond breaking and crosslinking reactions (42,43). Our model employs a sample macromolecular network in the computer consisting of aromatic ring clusters (monomers) linked by bridges. The bridges are either broken by bond scission reactions or are formed by crosslinking. As discussed previously (38,42,51), crosslinking occurs at low temperatures for low rank coals by a process apparently associated with CO_2 evolution. Crosslinking at moderate temperatures occurs by a process associated with CH_4 evolution. It is this process which leads to the reduction of fluidity shown in Fig. 1. The chemical justification for the association of crosslinking with CH_4 evolution is that the CH_4 is released by an ipso-substitution reaction involving a free radical connected to a ring cluster. Other peripheral groups may also be released in a similar manner.

A simple example of the model is shown in Fig. 3. Figure 3a shows the starting molecule. As explained previously (42,43), the number of branch points (initial crosslinks) is chosen to match the expected molecular weight between crosslinks. The length of the linear chains ℓ which are crosslinked is selected so that the fraction of unattached small monomer clusters matches the

measured fraction of pyridine solubles. The position of the bonds is randomly chosen. The molecular weight distribution is shown in Fig. 3b. When bonds are broken, more small molecules are formed as shown in Fig. 3c and 3d.

As discussed below, the viscosity is related to the liquid fraction produced during the break up of the network. The liquid fraction consists of all molecules detached from the starting macromolecular network (the solid fraction). Operationally we count the largest 3 molecules as belonging to the solid fraction and all others as belonging to the liquid fraction. This is a convenient approximation which gives results that agree reasonably well with experiment and do not depend on the molecular weight of the starting computer molecule. We have also used just the largest molecule as the solid fraction and found that computed results are similar but noisier.

An important feature of a homogeneous network model is that the break-up or solidification of the network occurs near a homogeneous "gel point" where the number of unbroken bonds per ring cluster (monomer), α , reaches a sufficiently low value. This gel point for a polymerizing melt occurs at the first appearance of the solid (or in the case of a decomposing network when the liquid fraction goes to 1.0) since the solid in a homogeneous melt extends throughout the entire melt. For most network geometries the break-up of the network occurs between $\alpha = 1.0$ and $\alpha = 0.8$.

For an inhomogeneous melt (such as expected for a liquefying powdered coal sample), the solids can appear as isolated particles so the gel point occurs at a higher solid fraction (lower liquid fraction). Based on the inhomogeneous model of fluidity discussed below, the liquid fraction must only exceed 0.3 before appreciable fluidity can occur. With the network geometry assumed for this model, this minimum liquid fraction is achieved at a critical value α_c of 0.95. For bituminous coals, this critical value can be achieved in pyrolysis and the coal melts and becomes fluid. For low rank coals, the effects of low temperature crosslinking is to increase α so that in some cases the network cannot come apart by normal pyrolytic reactions. Figure 4 compares the variation in α with time at constant temperature for a lignite and a bituminous coal. Also shown are the individual contributions to the total bond count and resulting fraction of the network which becomes liquid. The value of α for the lignite has a sharp increase at low temperatures due to CO₂ related crosslinking. This can be seen by the appearance of CO₂ related bonds in Fig. 4d. These bonds are a significant fraction of the total bonds connecting the network. With this large number of additional bonds, the value of α never achieves the critical value ($\alpha_c = 0.95$) and the solid fraction of the coal remains too high to liquefy. On the other hand, α for the bituminous coal is not increased by CO₂ related crosslinking. The value of α falls below the critical value and sufficient liquid fraction is produced for the network to disintegrate and become fluid.

The viscosity model used here has terms that depend on the coal liquid temperature, the weight average molecular weight of the liquid fraction, and the volume fraction of solids, with an inhomogeneous gel-point. It is the last two factors which are most important.

In common with previous studies of coal viscosity a two-phase model is used. The particular equation chosen is that put forward by Mooney (17,32)

$$\ln (\eta / \eta_{liq}) = \frac{k_E \phi_s}{1 - \phi_s / \phi_c} \quad (1)$$

where η is the viscosity of the suspension, η_{liq} the viscosity of the liquid, k_E is the Einstein coefficient, and ϕ_s is the volume fraction of solids, having a critical value ϕ_c at which η goes to ∞ . Values of the constants are listed below.

Based on the model by Bartels et al. (27), the viscosity of the liquid phase is given by

$$\eta_{liq} = C \exp (E_\eta / RT^*) \exp (M_w / M_a) \quad (2)$$

which on combining with Eq. 1 leads to

$$\eta = C \exp(E_{\eta}/RT^*) \exp(M_w/M_0) \exp \frac{k_E \phi_s}{1 - \phi_s/\phi_c} \quad (3)$$

The constants used in the viscosity theory are as follows:

- C: proportionality constant, $C = 1.0 \times 10^{-24}$ Poise
- k_E : Einstein coefficient, $k_E = 5.0$
- E_{η} : Activation energy for viscosity, $E_{\eta} = 8 \times 10^4$ kcal/mole
- M_0 : Molecular weight parameter, $M_0 = 1000$
- ϕ_c : Volume fraction of the solid phase at the gel-point, $\phi_c = 0.7$
- M_w : Weight average molecular weight of the liquid
- T^* : Absolute temperature, cut-off at 708 K

i.e., $T^* = T$ for $T \leq 708$ K: $T^* = 708$ for $T > 708$ K

The value of $k_E = 5$ was arrived at empirically, i.e., to fit the data. This value, however, matches the situation in which liquid is entrapped within large agglomerates of solid (54). The value of the activation energies for coal was chosen based on measured liquid viscosities (from 5×10^7 to 10×10^8 kcal/mole) determined by Waters (55). Waters also showed that coal liquid behaves as a Newtonian fluid at strain rates encountered in standard viscosity measurements. The use of a cut-off temperature was introduced by Nazem (28).

RESULTS

There are two aspects to validating the model by comparison with data. The first is that the FG-DVC model should provide good predictions for pyrolysis products; the second is the comparison of predictions to fluidity data. Extensive comparisons of the FG and FG-DVC models have been made by Solomon et al. (39,40,42,43) and Serio et al. (41,53). These comparisons show good agreement between theory and experiment using rank independent kinetics for the Argonne coals and several other coals. An example of the fit of methane evolution for pyrolysis at 30°C/min for several coals used in this study is presented in Fig. 5. There are some differences between the predicted and observed evolution curves (the observed evolution in high rank coals is slightly slower than predicted), but in general the agreement is good.

All the viscosity data were fitted using the same viscosity equations and same constants. The only variable was the kinetic rate for bond breaking and crosslinking. When fitting the viscosity data, it was found that the slight differences in methane evolution (which is related to moderate temperature crosslinking) and in tar evolution (which is related to the bond breaking rates) adversely affected the viscosity prediction. For the viscosity results, the bond breaking and methane rates were adjusted to match the slow heating rate evolution curves. An example of the new predictions for the Upper Freeport coal is presented in Fig. 6. The new rates are presented in Table I. One additional change was made in the FG-DVC model to better match the fluidity data. This was to increase the crosslinking efficiency for methane from 1 to 1.5 crosslinks formed per methane evolved. This improved the fits to the fluidity data and can be justified on the basis that the evolution of gases formed from other peripheral groups (ethane, propane, etc.) may also lead to crosslinking.

The first example of the application of the model to predict fluidity is shown in Fig. 7. The data is from Oxley and Pitt (47) obtained by heating during an 11 minute period to constant temperatures of 400, 420, and 440°C. The coal is believed to be similar to the Upper Freeport. The agreement is excellent in following the increase and decrease in fluidity due to bond breaking and crosslinking, and in fitting the two orders of magnitude change in fluidity over a 40°C change in temperature.

Results for a higher rank coal studied by van Krevelen at constant heating rates are presented in Fig. 8a. The coal composition picked to represent the coal was that of the Pocahontas. However, the fluidity maximum for the coal is lower than expected based on the weight loss curve for Pocahontas. The bond breaking rate for this coal was, therefore, picked to be higher than we would expect for the Pocahontas coal. The theoretical predictions in Fig. 8b are in excellent agreement with the data.

Results for a Pittsburgh Seam coal obtained at high heating rates by Fong et al. (15) are presented in Fig. 9 as the symbols. The theory is shown as the lines. There is good agreement between theory and experiment for the onset of fluidity and for the maximum fluidity. The loss of fluidity is, however, predicted to occur much sooner than expected. The extract yield obtained by Fong et al. (15) in a heated grid experiment is also shown as a dashed line. The disappearance of fluidity predicted by our model does, however, appear to coincide with the disappearance of the extract yield. This is as expected since the model is dependent on the liquid fraction. The fact that the fluidity and extract data do not agree, may suggest that there are differences in temperature between the two apparatuses.

A number of additional comparisons were made between theory and experiments. A summary of the predicted and measured maximum fluidities for all the cases is presented in Fig. 10. There is good agreement over a fluidity range of five orders of magnitude and a temperature range of several hundred degrees.

CONCLUSION

- 1) A model for fluidity of coal has been developed based on a macromolecular network concept.
- 2) The network model is used to predict the fraction of liquids and the average molecular weight of the liquids under the combined effects of bond breaking and crosslinking.
- 3) The empirical model for an inhomogeneous melt assumes the fluidity to depend on the liquid fraction in the melt, on the viscosity of the fluid and on the temperature.
- 4) Good agreement is obtained with data for four coals which covers five orders of magnitude in fluidity and several hundred degrees in temperature. This agreement is obtained with fixed parameters in the empirical fluidity equations but with adjustments of the bond breaking and crosslinking rates to better fit the pyrolysis product yields.
- 5) At this stage of the development, we have a model which works for a variety of data, but is not necessarily unique. Emphasis is currently being placed on extending the range of applicability and on optimizing the model assumptions and constants.

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TABLE 1 - SUMMARY OF COAL PROPERTIES

EXPERIMENTS:	FITZGERALD	FONG	OXLEY & PITT	VAN KREVELEN
Volatile Matter	34.4%	41.7%	30.3%	24.0%
C %	N/A	83.2	N/A	N/A
COAL USED FOR MODELING	UPPER KNAWHA	PITTS NO. 8	UPPER FREEPORT	POCAHONTAS [†] Composition
Volatile Matter (MAF)	37.6%	41.7%	31.6%	19.5%
C% (MAF)	82.6	83.2	85.6	91.1
E _{bonds} (cal/mole)	59200	60000	62000	63000
A _{bonds}	5.08 x 10 ¹⁵	8.57 x 10 ¹⁴	3.08 x 10 ¹⁵	7.0 x 10 ¹⁶ *
σ _{bonds}	1500	1500	1500	1500
Bond Breaking Rate @ 450°C	8.43 x 10 ⁻³	8.17 x 10 ⁻⁴	7.37 x 10 ⁻⁴	8.39 x 10 ⁻³
E _{CH₄-L} (cal/mole)	60000	60000	56000	60000
A _{CH₄-L}	4.5 x 10 ¹³	7.5 x 10 ¹³	3.0 x 10 ¹²	1.0 x 10 ¹³
σ _{CH₄-L}	1500	1500	1000	1800
CH ₄ - L Rate @ 450°C	4.29 x 10 ⁻⁵	7.15 x 10 ⁻⁵	4.55 x 10 ⁻⁵	9.54 x 10 ⁻⁵

N/A: Not Available

*Based on fluidity data, the van Krevelen coal (24% volatile) appears to have kinetic rates comparable to the 90% carbon coals in Fig. 2 rather than the Pocahontas coal. For this reason the kinetic rates in the Table are higher than expected for Pocahontas.

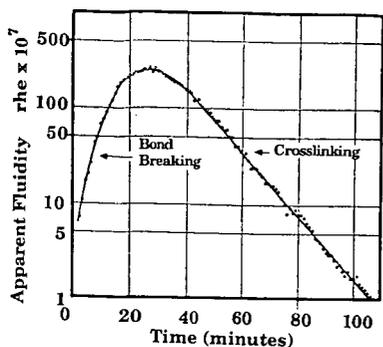


Figure 1. Apparent Fluidity as a Function of Time at 407°C for a Typical Coking Coal (34.4 percent dry ash free volatile matter, coal rank code number 401b). From Ref. 48.

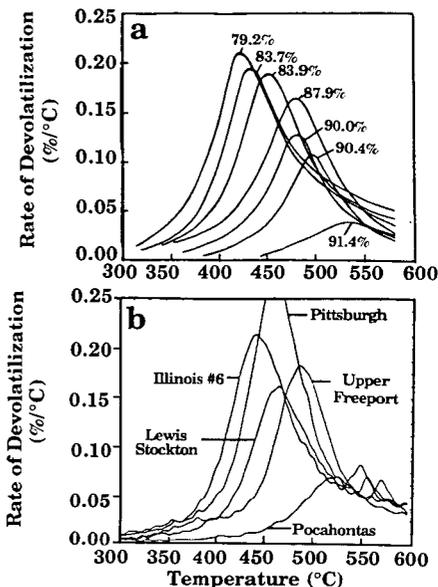


Figure 2. Rate of Devolatilization at a Constant Heating Rate of 3.0°C/min. a) Data of van Krevelen (1), b) Data for Argonne Premium Samples.

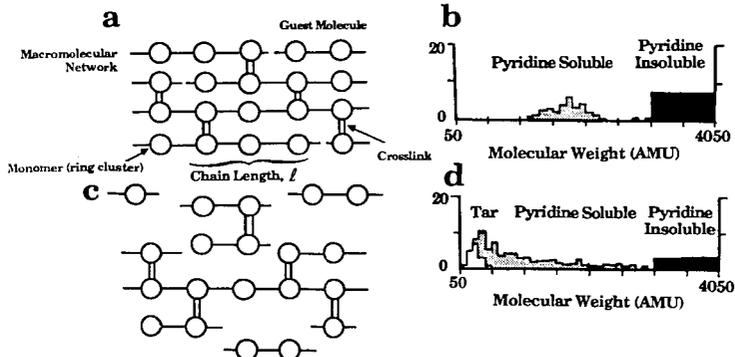


Figure 3. Representation of a Coal Molecular Network in a Monte Carlo Simulation (a and c) and Corresponding Molecular Weight Distribution (b and d). In the Molecule, the Circles Represent Monomers (ring clusters with their peripheral groups). The Molecular Weight Distributions of the Network are Shown as Histograms in b and d. The Histogram is Divided into Tar, Pyridine-Soluble and Pyridine-Insoluble Fractions. The Area Under the Histogram Corresponds to the Weight Percent of the Oligomers.

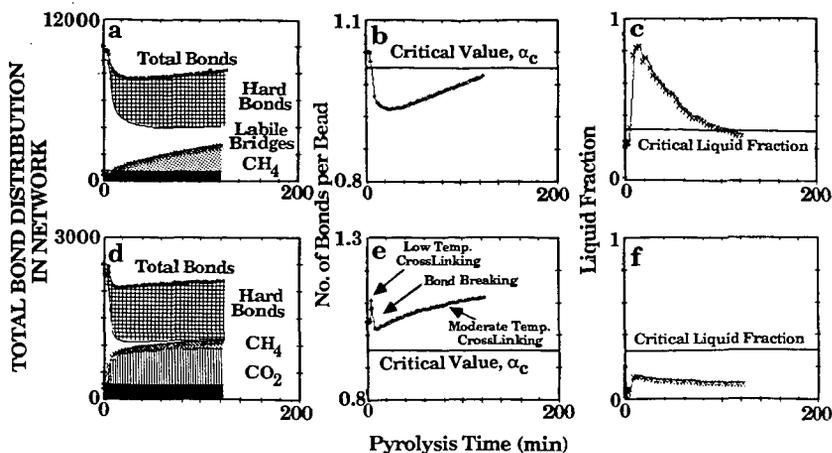


Figure 4. Comparison of the Variation in the Unbroken Bond Concentration, Bonds/Cluster, α and Liquid Fraction with Time at Constant Temperature of 440°C for a-c) Upper Freeport Bituminous Coal and d-f) Zap Lignite. \square Unbreakable Bridges; \square Labile Bridges; \square CH₄ Related Crosslinks; \square CO₂ Related Crosslinks; \blacksquare Initial Crosslinks.

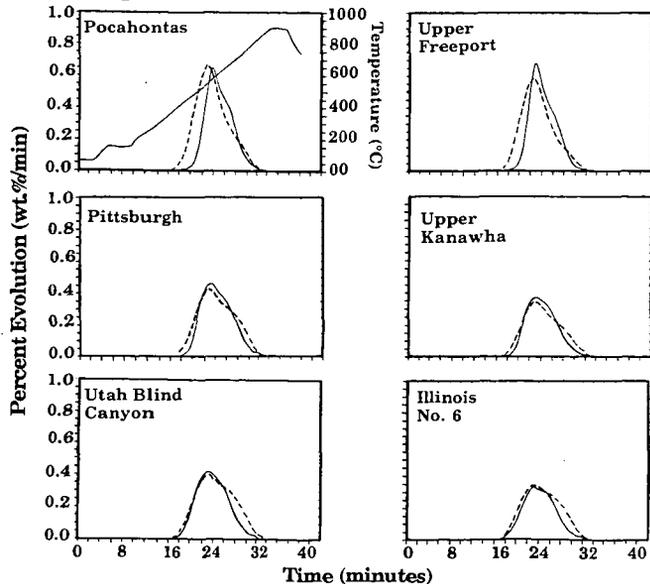


Figure 5. The Evolution of Methane from Argonne Premium Samples in a TG-FTIR at a Constant Heating Rate of 30°C/min (53). Solid Line is Data, Dashed Line is Theory. The Temperature History is shown on the Pocahontas Plot.

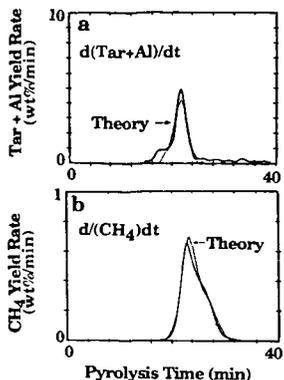


Figure 6. Comparison of Theory with TG-FTIR Experiment on Upper Freeport Coal for the Evolution of a) Tar plus Aliphatic and b) Methane Using the Improved Rates shown in Table 1.

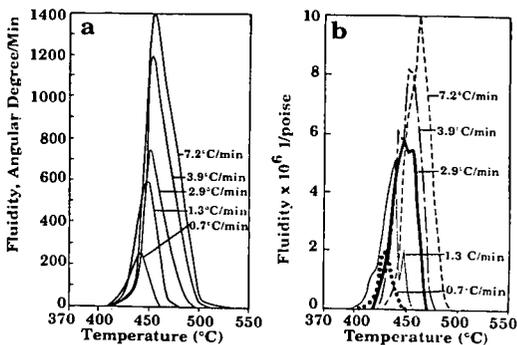


Figure 8. Fluidity at Constant Heating Rate. a) Experiment Data of Van Krevelen (1) for 24% Volatile Coal and b) Theory for Pocahontas Coal Composition (see note in Table 1).

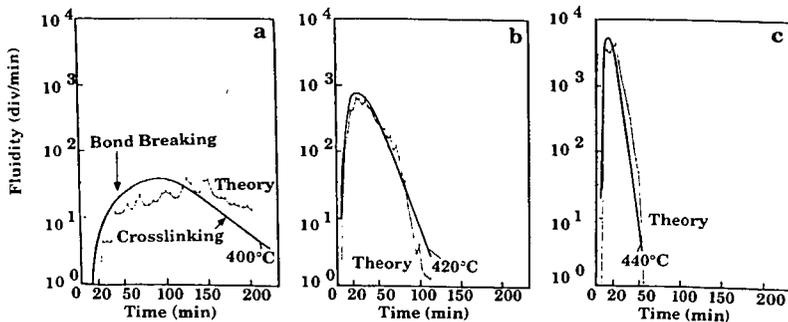


Figure 7. Comparison of Experiment and Theory for Fluidity of a High Rank Coal at Constant Temperatures of a) 400°C, b) 420°C and c) 440°C. The Experiment is for a Coal which has 30% Volatile Matter Content (47) and Theory is for Upper Freeport Coal.

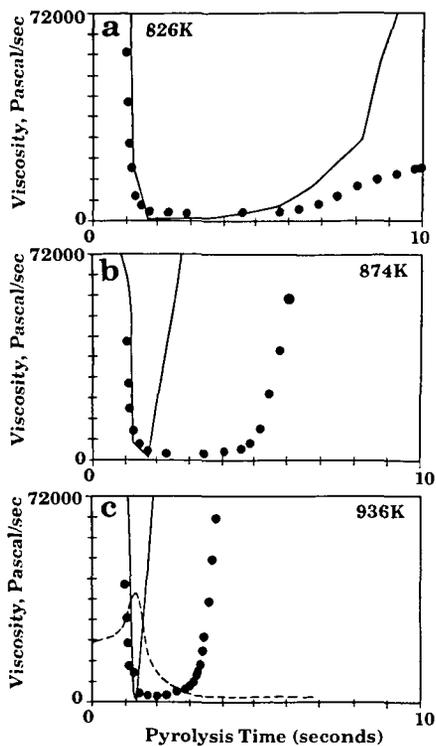


Figure 9. Viscosity at High Temperatures. Symbols are Data of Fong et al. (15).

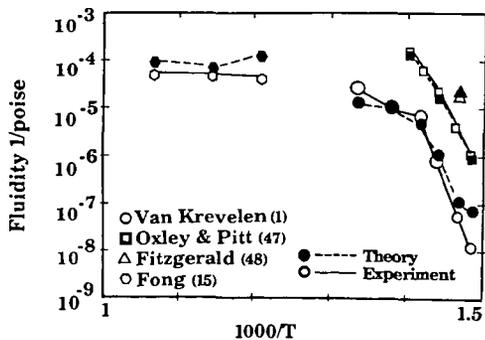


Figure 10. Maximum Fluidity for Four Experiments.