Modeling of Coal Liquefaction Kinetics Based on Reactions in Continuous Mixtures

Part I: Theory

Based on the concept of reactions in a continuum, a mathematical model has been developed to simulate coal liquefaction kinetics. In an excess hydrogen donor environment, the rate-limiting reactions are considered to be irreversible cracking reactions involving cleavage of carbon and oxygen linkages. Concurrent evolution of a wide spectrum of products, with an initial rapid formation of species of high carbon and oxygen contents, followed by progressively slower reactions leading to lower carbon and oxygen content species is predicted. Simple lumping functions are employed to obtain conventional lumped pseudocomponents (preasphaltenes, asphaltenes, and oils). Parameter analysis has been carried out.

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SCOPE

In reactions that involve numerous species it is often not practical to develop kinetic models that describe the behavior of all the participating species. It is convenient to group together various species and treat them as pseudocomponents. Models based on such an approach have been termed lumped kinetic models. The success of such a model depends upon the kinetic similarity of the species present in a lump. The numerous product species obtained upon liquefaction of coal are usually lumped together into several groups based on solubility criteria. For example, the fraction of coal liquefaction product that is soluble in benzene but not soluble in pentane is given the name asphaltenes.

The lumped models based on such pseudocomponents are essentially correlative in nature and have very little scope for generalization. Hence they cannot be used to predict the liquefaction behavior of coals other than the one used in developing the model. Thus there is a need for a fundamental model that can describe the processes occurring during liquefaction of coal. This work presents one such approach to a fundamental model based on the concept of reactions in a continuum (Aris and Gavalas, 1966). Such a concept is likely to be valid in the presence of a numerous species where the concentrations and kinetic rate constants of the species present in the mixture can be specified by continuous distribution functions. The distribution, which is a statistical measure of composition and reactivity of the species present in the mixture, will depend upon one or more state variables chosen to identify the structure and functionalities of the species present in the mixture. This paper attempts to generalize the reactions that occur during liquefaction of coal, using the continuum approach.

CONCLUSIONS AND SIGNIFICANCE

A fundamental model based on the concept of reactions in a continuum has been developed to simulate the rate processes occurring during liquefaction of coal. The reaction mixture has been described in terms of two state variables, the number of carbon atoms and the number of oxygen atoms per molecule. In an environment of excess available hydrogen the rate-limiting reactions can be considered as thermal cracking reac-

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tions to produce species of lower carbon and oxygen contents.

Reactivity is assumed to depend on both carbon and oxygen contents. Reaction leads to a spectrum of products which can be grouped, on the basis of molecular weight, into lumped pseudocomponents such as preasphaltenes, asphaltenes, and oils. Predicted lumped product profiles are similar to those previously obtained. Product distribution can be varied by adjusting a characteristic "molecular weight" of coal.

Background

Lumped models

In attempting to model the kinetics of coal liquefaction on a limited scale one is confronted with the problems of establishing the reaction networks and the subsequent estimation of a set of optimum rate constants associated with the networks. In coal liquefaction, the presence of a large number of molecular species and the obvious inability to monitor the behavior of individual components have given rise to lumped kinetic models. These can be broadly classified as either using extractive techniques leading to components such as preasphaltenes, asphaltenes, and oils, or boiling-point fractionating techniques leading to components such as furnace oils and distillate oils. Reviews of such lumped models have been recently published elsewhere (Gertenbach et al., 1982; Shah, 1981; Pullen, 1981).

The essential feature of these models is the inherent assumption that lumping leads to kinetically similar fractions which, in conjunction with simple series/parallel reaction networks, can adequately correlate the experimental data. These correlations could then be used for design predictive purposes.

It is imperative to realize that a proper kinetic model can be developed only if the lumped pseudocomponents display similar reactivity (Luss and Golikeri, 1975). The problem with lumped models is not unique to coal liquefaction and indeed is common to many complex reactions involving simultaneous interaction of numerous species (see Weekman, 1979 for a discussion on modeling of fluidic catalytic cracking reactions). The obvious advantage in the lumped-component approach lies in the ease of product analysis, the most expensive part of developing any model.

Mechanistic models

Improved techniques for analysis and characterization of coal products such as proton and carbon-13 nuclear magnetic resonance (Wilson et al., 1982; Yoshida et al., 1982) and Fourier-transformed infrared spectroscopy (Painter and Coleman, 1979) have aided in providing extensive information on the possible mechanistic pathways for liquefaction reactions. This has facilitated the formulation of working models for liquefaction kinetics based on the proposed mechanism.

Gangwer (1980) has presented a unified model for coal dissolution based on the concept of thermal-cleavage/hydrogen-capping mechanism. Coal was envisaged as comprising clusters of chemically bonded organic systems such as preasphaltenes, asphaltenes, oils, and gases on a substratum of coal. Successive cleavage followed by stabilization was interpreted as leading to formation of preasphaltenes, asphaltenes, oils, and gases. A similar reaction pathway has been proposed by Squires (1978).

The fundamental similarity between a complex feed stock such as coal and some complex polymers led Attar (1978) to present a free-radical depolymerization path to describe coal liquefaction reactions. A similar approach was adopted by Gun et al. (1979).

Recently Petrakis et al. (1983) using a high-pressure, high-temperature ESR (electron spin resonance) cavity measured the *in situ* formation and reactions of free radicals during coal liquefaction reactions. Based on the free radical concentrations they reported a kinetic model for a Powhattan No. 5 coal. The important findings of their work include the complex nature of the radical formation rate and its dependency on the reaction temperature and the nature of the solvent.

Work on developing a kinetic model based on detailed investigation of the mechanism of coal liquefaction reactions and model compounds continues to provide a valuable data base. With a sufficiently broad data base it is possible to develop a rigorous mechanistic model along lines similar to those attempted for rapid pyrolysis of coal by Gavalas and coworkers (1981).

Stochastic models

One can adopt a pragmatic view to the modeling problem and view coal liquefaction as being a random process of bond-breaking reactions. The probability of such reactions would be dependent upon the strengths of the bonds involved. In the reactions involving coal, which has a wide distribution of types of chemical bonds, it is conceivable that there is a distribution of bond strengths and hence a corresponding distribution of activation energies involved in the rupture of these bonds.

Anthony and Howard (1976) considered an extreme case of a normal distribution of activation energies and obtained an expression for the formation of volatile products from coal pyrolysis reactions. This, they found, fitted the experimentally observed volatile yields both for a low rank Montana lignite and a high rank bituminous coal.

Szladow and Given (1981, 1983) presented a phenomenological approach based on the theoretical analysis of many parallel reactions in a complex reacting mixture. Based on an extension of the method proposed by Golikeri and Luss (1972), Szladow and Given (1981) calculated the apparent activation energy for coal dissolution reactions producing pyridine solubles. The apparent activation energy was found to increase with conversion. They showed that the use of the apparent activation energy concept reduced the number of possible kinetic structures. Szladow and Given (1983) employed a model discrimination procedure based on Lee's (1978) work on synthesis of kinetic structures. Using these two concepts they arrived at two initial lumps for Colorado B2 seam coal that had different rate constants which can simulate the conversion-temperature-time behavior over a wide range.

These techniques are very useful in understanding the complexity of overall breakdown reactions. In liquefaction processes, however, one is more interested in maximizing yields of

certain grouped species (oils in most cases). This problem cannot be tackled very successfully using the above phenomenological approaches.

Coal is bound to exhibit a wide distribution of reactivities due to the several types of chemical bonds present. The fact that multiple levels of reactivity will exist in reactions involving coal has been long recognized. Curran et al. (1976) modeled the dissolution of coal into xylenol solubles using two levels of reactivity. More recently Brunson (1979) modeled the reactions in the Exxon donor solvent process using an empirical classification of four reactive coal constituents. Agreements with multiple-level reactivity models have shown that these models can better describe the experimentally observed trends than single-reactivity models.

Structure of Coal

Any generalized model for coal liquefaction reactions should be based on the structure of coal. Despite extensive efforts, only a partial representation of coal structure is possible, due principally to its heterogeneous nature. Hence no typical structure of coal can be formulated.

The essential feature of the various models for coal recognize the presence of from two to several condensed ring structures with interconnected heteroatomic or -alkyl and hydroaromatic bridges as well as various functional groups attached to the periphery of ring structures. In addition a considerable amount of layered graphitelike structure exists in high-ranking coals.

Adopting a pragmatic approach we can visualize coal liquefaction reactions as contributing to successive cracking of the different bonds within the coal matrix. In the presence of a very good hydrogen donor solvent the cracked portions would be stabilized rather quickly to yield more stable structures. This view is generally supported by the work of Petrakis and coworkers (1983), who observed a low-transient, free-radical concentration at low temperatures (<450°C) and in the presence of an excess of donor solvent.

If we assume that the bond scission reactions are quite random and the probability of a cleavage occurring is generally dependent upon some index of reactivity of that portion of coal, we can readily visualize a number of such reactions occurring simultaneously until the reactivity of the products thus formed reaches a minimum so that no further reaction takes place. This leads one to picture a continuum of reactions occurring simultaneously, and if a suitable index of reactivity can be chosen we can, in effect, characterize the instantaneous state of the reacting mixture.

Continuous-Reaction Mixture

The rigorous theoretical treatment of reaction in continuous mixtures was presented by Aris and Gavalas (1966). With a complex mixture containing a large number of components it is possible to describe the mixture using continuous variable rather than discrete indices. As pointed out by Aris and Gavalas, such continuous-reaction mixtures can be described by distribution of concentrations and are capable of sustaining an infinite number of reactions. Assumed systematic variations in reaction rate constants and stoichiometry are part of the motivation for the continuous distribution-of-reactions approach.

Syamlal and Wittmann (1985) attempted to model coal liquefaction reactions in an excess of donor solvent using this approach. They visualized coal liquefaction reactions as successive bond cleavage reactions leading to a continuous reduction in the molecular weights of products thus formed. The reactivity for any species was assumed to be dependent upon the molecular weight of the species; the higher the molecular weight, the more reactive is the species. Assuming a characteristic molecular weight for a high volatile subbituminous coal, Syamlal and Wittmann showed that the general trends observed on the transient molecular weight distribution (Franz, 1979) can be simulated using such an approach. Prasad (1982) extended this model using both the number of oxygen atoms and molecular weight as characteristic variables to describe the reaction mixture. A preliminary attempt at lumping the continuous distribution of products into solubility fractions (e.g., asphaltenes, preasphaltenes, and oils) was attempted. This work showed that by assuming simple functions to distribute the continuous spectrum of products into various solubility categories, one can simulate the formation of lumped products.

Here we present a generalized model for coal liquefaction reactions based on the concept of continuous-reaction mixtures. The characteristic variables chosen to identify the instantaneous state of the reacting mixture are the number of carbon atoms and the number of oxygen atoms per molecule. The motivations for choosing these two state variables are twofold. First, in the large scale of molecular species involved in coal liquefaction reactions one would expect a distribution of species containing widely varying numbers of carbon and oxygen atoms; hence these two variables can be considered as essentially continuous. Second, during coal liquefaction there is a gradual decrease in the size distribution of the molecules as well as a decrease in the oxygen content of product species (Foster et al., 1983; Szladow and Given, 1978; Stephens, 1983).

Model Formulation

We consider the cracking of coal and of the products produced on liquefaction as being irreversible in the presence of an excess of donor solvent. Following the notation of Aris and Gavalas (1966) we define $A(x_1,x_2)$ to be a continuous distribution of coal products subject to the conditions ($0 \leqq x_1 \leqq u$) and ($0 \leqq x_2 \leqq v$), where x_1 refers to the number of carbon atoms and x_2 to the number of oxygen atoms contained per molecule. The upper bounds (u and v) on the two state variables x_1 and x_2 indicate the maximum number of carbon and oxygen atoms contained in any species and this, of course, cannot exceed the original coal. The species indices can be thought of as being analogous to symbolic species of form $C_{x_1} O_{x_2}$ in the discrete reaction case.

The cracking reactions can be written as:

$$A(x_1, x_2) \rightarrow A(x_1', x_2') + A(x_1 - x_1', x_2 - x_2') \qquad (1)$$

$$0 \leqq x_1' \leqq x_1 \leqq u$$

$$0 \leqq x_2' \leqq x_2 \leqq v$$

Denote the concentration density of $A(x_1, x_2)$ by $C(x_1, x_2, t)$. Let the total rate kernel for cracking of $A(x_1, x_2)$ be $K(x_1, x_2)$ and let $\upsilon(x_1', x_2'; x_1, x_2)$ be the fraction of $A(x_1, x_2)$ that cracks to $A(x_1', x_2')$. All cracking reactions are assumed to be first-order with respect to reacting species.

As pointed out by Aris and Gavalas the rate kernel $[K(x_1, x_2)]$ and the stoichiometric coefficient distribution

$[\nu(x_1', x_2'; x_1, x_2)]$ are entirely analogous to the rate constant and the stoichiometric coefficient in the discrete reaction case.

Since reaction 1 depicts the formation of product species $A(x_1', x_2')$ as well as $A(x_1 - x_1', x_2 - x_2')$, the symmetry implies that

$$\nu(x_1', x_2'; x_1, x_2) = \nu(x_1 - x_1', x_2 - x_2'; x_1, x_2) \tag{2}$$

The fact that ν is a fraction requires that

$$\int_0^{x_1} \int_0^{x_2} \nu(x_1', x_2'; x_1, x_2)\, dx_2'\, dx_1' = 2 \tag{3}$$

For an isothermal batch reactor of constant volume the appropriate mass balance equation for $A(x_1, x_2)$ is:

$$\frac{\partial C}{\partial t}(x_1, x_2, t) = -K(x_1, x_2) \cdot C(x_1, x_2, t) + \int_{x_1}^{u} \int_{x_2}^{v} [K(x_1', x_2')\, \nu(x_1, x_2; x_1', x_2') \cdot C(x_1', x_2', t)]\, dx_2'\, dx_1' \tag{4}$$

with

$$C(x_1, x_2, t = 0) = C_o(x_1, x_2) = \delta(u - x_1, v - x_2) \tag{5}$$

The first term on the righthand side of Eq. 4 refers to the net rate of consumption of species $A(x_1, x_2)$ to form lower carbon and lower oxygen content species. The second term includes the total rate of formation of species $A(x_1, x_2)$ from all other species of high carbon and oxygen contents.

Equation 5 is a reiteration of our initial assumption that the distribution is originally concentrated entirely at $(x_1 = u, x_2 = v)$, which by our definition is coal itself.

Equation 4 can be made dimensionless by defining the following dimensionless variables:

$$\left.\begin{aligned} y_1 &= x_1/u \qquad y_2 = x_2/v \\ \theta &= \alpha t \\ \bar{K}(y_1, y_2) &= K(x_1, x_2)/\alpha \\ \xi(y_1, y_2, \theta) &= C(x_1, x_2, t)/C_i \end{aligned}\right\} \tag{6}$$

where $\alpha = K(u, v)$ and $C_i = \int_0^u \int_0^v C_o(x_1, x_2)\, dx_2\, dx_1$. Now Eq. 4 becomes,

$$\frac{\partial \xi}{\partial \theta}(y_1, y_2, \theta) = -\bar{K}(y_1, y_2) \cdot \xi(y_1, y_2, \theta) + uv \int_{y_1}^{1} \int_{y_2}^{1} [\bar{K}(y_1', y_2') \cdot \nu(y_1, y_2; y_1', y_2') \cdot \xi(y_1', y_2', \theta)]\, dy_2'\, dy_1' \tag{7}$$

Equation 7 can be solved by Laplace transformation to yield the integral equation:

$$\xi(y_1, y_2, \theta) = \delta(1 - y_1, 1 - y_2) \cdot \exp(-\bar{K}\theta) + uv \exp(-\bar{K}\theta) \int_0^{\theta} \int_{y_1}^{1} \int_{y_2}^{1} [\bar{K}(y_1', y_2') \cdot \nu(y_1, y_2; y_1', y_2') \cdot \exp(+\bar{K}\tau) \cdot \xi(y_1', y_2', \tau)]\, dy_2'\, dy_1'\, d\tau \tag{8}$$

The solution of Eq. 8 will yield the instantaneous state of the reaction mixture at any time.

Numerical Solution

The numerical scheme adopted for solution of Eq. 8 is an extended version of the scheme developed by Syamlal (1981). Briefly, it involves dividing the intervals of y_1 and y_2 (0 to 1) into a finite number of grid points. Numerical integration of Eq. 8 is effected using an iterative procedure similar to the Newton-Raphson method. The converged solution at time θ and $(\theta + \Delta\theta)$ are extrapolated as a first guess to the solution at $(\theta + 2\Delta\theta)$. This guess is improved upon by using a secant method. Syamlal has shown that this iterative method converges uniformly to a unique solution for bounded values of the rate kernels. It was found that convergence was generally slower as one approached $y_1 \to 0$ and $y_2 \to 0$, and hence in the interval of 0 to 0.2 the number of grid points was increased.

The numerical solution of Eq. 8 yields the molar concentration function $\xi(y_1, y_2, \theta)$ at discrete values of y_1 and y_2. A bicubic spline interpolant was used to obtain a smooth, continuous distribution for the molar concentration function. This was converted to a dimensionless mass concentration distribution function using the following relationship:

$$\xi_M(y_1, y_2, \theta) = [\xi(y_1, y_2, \theta)](12uy_1 + 16vy_2)/(12u + 16v) \cdot C_i \tag{9}$$

where $(12uy_1 + 16vy_2)$ is the molecular weight. To satisfy an overall mass balance:

$$uv \int_o^1 \int_o^1 \xi_M(y_1, y_2, \theta) dy_1\, dy_2 = 1 \tag{10}$$

A quadrature routine was used to integrate the smooth distribution obtained from the bicubic spline interpolation. Equation 10 provided a criterion for deciding on the number of grid points for the variables y_1 and y_2. The number of grid points was increased until Eq. 10 was satisfied within 0.5%.

Lumping Analysis

The solution of Eq. 8 provides the instantaneous state of the reaction mixture; that is, a concentration distribution as a function of number of carbon and oxygen atoms is predicted. If one has some method of monitoring such a distribution in a reaction mixture, the validity of the model can be ascertained and the parameters (rate kernels and stoichiometric functions) determined. Such a task requires extensive analysis. It is more useful to formulate a simplified lumped model that can adequately describe the overall behavior of the reaction mixture. We note that a lumped model thus formulated is likely to contain kinetically similar species within each lump.

Theoretical work on lumping of monomolecular reactions has been extensively analyzed, starting with the work of Wei and Kuo (1969). Bailey (1972) extended the analysis to cases of continuous-reaction mixtures. Liu and Lapidus (1973) presented a somewhat different approach whereby an *a priori* knowledge of the complete set of kinetic constants of the reaction mixture is not required to arrive at simple lumped models.

Following the theoretical work of Bailey (1972) one can readily arrive at the necessary and sufficient condition for lumping

the continuous-reaction mixture model prediction into simplified lumped models:

$$uv \int_0^{y_1} \int_0^{y_2} M_n(y_1', y_2') \bar{K}(y_1, y_2) \nu(y_1', y_2'; y_1, y_2)\, dy_2'\, dy_1' - \bar{K}(y_1, y_2) M_n(y_1, y_2) + \hat{K}_n M_n(y_1, y_2) = 0 \quad (11)$$

where $M_n(y_1, y_2)$ is the appropriate lumping function for n lumps to form kinetically appropriate lumped components; $\hat{K}_n$ is the corresponding $n \times n$ kinetic matrix for the equivalent discrete model with linear kinetics.

Due to the problems in formulating kinetically similar lumps, we somewhat adjust our original aim. If we assume certain lumping functions to arrive at conventional lumps such as preasphaltenes, asphaltenes, etc., we can classify the concentration distribution predicted by the continuous-reaction mixture model (CRMM) into the corresponding discrete lumps. These assumed lumping functions may or may not satisfy the necessary and sufficient condition (Eq. 11); however an immediate assessment of the CRMM would be possible. The assumed lumping functions can be treated as model parameters and their validity verified by examining the CRMM predictions for different coals.

The lumping functions chosen to classify the CRMM predicted distributions are:

$$M_n(x_1, x_2) = \gamma_n \cdot (12x_1 + 16x_2)^{-1} \quad (12)$$

where γ_n is a constant multiplier.

Qualitatively this implies that as the species molecular weight increases, the species would tend to dissolve less in a particular solvent. There will be n such lumping functions corresponding to n different solvents, each with a different value of γ_n.

Assumption of lumping function such as Eq. 12 is not altogether arbitrary. A general progression in the molecular weight distribution and the functionalities present in lumped components such as oils, asphaltenes, and preasphaltenes has been reported (Wilson et al., 1982), these lumped fractions being obtained by using progressively stronger solvents.

Recently Snape and Bartle (1984) observed that in addition to molecular weight, the hydroxyl functionality and carbon aromaticity dictated the propensity to be classified as asphaltenes. Further refinements of the CRMM should take into account these observations.

Parameter Selection

The parameters associated with the model are the total cracking rate kernel $\bar{K}(y_1, y_2)$ and the stoichiometric distribution, $\nu(y_1, y_2; y_1', y_2')$. The only constraints on the stoichiometric distribution are given by Eqs. 2 and 3. For simplicity we assume both these functions to be continuous, implying that there are no pockets of material left unreacted. Further, we require the cracking rate kernel to vanish rapidly to zero as y_1 and $y_2 \rightarrow 0$ as more stable, smaller size products are formed.

Bearing in mind the above constraints, the most general forms of kernels for the stoichiometric function and rate kernel function would be periodic functions. A few terms in such a series could easily stimulate even complex cracking patterns.

Aris and Gavalas (1966) have outlined methods to determine kinetic kernels using two approaches: application of functional gradients, and approximation by degenerate kernels. The latter method was illustrated using hexadecane cracking as an example. The pertinent point to note is that even for a well-defined reactant such as hexadecane the process of choosing an optimum kernel is not simple.

For coal liquefaction reactions three functional forms of rate kernels were used in the simulation:

$$K(x_1, x_2) = \frac{(x_1 + x_2)}{(u + v)} \cdot \alpha \quad (13a)$$

$$= \frac{(x_1 + x_2)^2}{(u + v)^2} \cdot \alpha \quad (13b)$$

$$= \exp\{-[(u - x_1) + (v - x_2)]\} \cdot \alpha \quad (13c)$$

There is evidence in the literature (Fabuss et al., 1964; Davis and Farrell, 1973) that cracking rate constants for paraffinic hydrocarbons are proportional to the number of carbon atoms. Similar correlations between the cracking rate constant and the carbon content for a mixture of paraffins have been reported (Van Damme et al., 1981; Van Camp et al., 1984). Szladow and Given (1978) have reported a direct correlation between the loss of oxygen functional groups and the generation of pyridine solubles during liquefaction. All three rate kernels, Eqs. 13a–13c, assume a correlation between rate constant and the carbon and oxygen contents, with the predictions of Eq. 13b lying intermediate between those of Eqs. 13a and 13c.

The choice of a functional form for the stoichiometric distribution is more difficult. Reported data on the molecular weight distribution of tetrahyrofuron (THF) soluble product obtained on coal liquefaction for a subbituminous coal (Franz, 1979) as well as for a black coal (Foster et al., 1983) indicate some sort of distribution of products. Usually there is a maximum reported in the intermediate molecular weight range with a rapid approach to zero at either extreme. There is a tendency for the distribution of molecular weight to move toward a lower mean molecular weight value with increase in reaction time. The stoichiometric function employed here is consistent with such observations:

$$\nu(x_1', x_2'; x_1, x_2) = \beta \cdot [x_1'(x_1 - x_1') + x_2'(x_2 - x_2')] \quad (14)$$

where β is fixed by the constraint Eqs. 2 and 3:

$$\beta = 12/(x_1^3 x_2 + x_1 x_2^3) \quad (15)$$

Having selected the functional forms of the rate kernel and stoichiometric function, the only information required for the model simulation are the characteristic numbers of carbon (u) and oxygen (v) atoms. This amounts to assuming an empirical formula for coal ($C_u O_v$) and hence a characteristic molecular weight. If one assumes a typical molecular weight for coal, as an approximation, the elemental analysis would provide the values of u and v to be used for the particular coal.

Simulation Results and Discussion

The solution of Eq. 8 yields the dimensionless molar concentration function, $\xi(y_1, y_2, \theta)$, using the assumed form of rate and stoichiometric kernels (Eqs. 13 and 14). In the following sections we discuss the results of simulation employing rate kernel Eq. 13b. The results obtained from kernel Eqs. 13a and 13c

show similar trends and hence are not discussed. Since the product distribution is a function of carbon and oxygen contents, this leads to a three-dimensional distribution function. It is convenient to sectionalize this distribution into planes of constant carbon or oxygen contents and observe the variation with time. The following discussion pertains to changes at particular planes of constant carbon or oxygen contents.

The mass concentration distribution of product species $[\xi_M^P(y_1, y_2, \theta)]$ is obtained as the difference between the mass concentration distribution of all the species present in the reaction mixture $[\xi_M(y_1, y_2, \theta)]$ minus the mass concentration distribution of unreacted coal $[\xi_M^C(y_1, y_2, \theta)]$:

$$\xi_M^P(y_1, y_2, \theta) = \xi_M(y_1, y_2, \theta) - \xi_M^C(y_1, y_2, \theta) \qquad (16)$$

Since coal is assumed to contain characteristic numbers of carbon and oxygen atoms ($y_1 = 1; y_2 = 1$), the mass concentration distribution of products $[\xi_M^P(y_1, y_2, \theta)]$ refers to all of the product species of indices, $y_1 < 1$ and $y_2 < 1$.

Figures 1a–1d contain the results from a typical simulation carried out with an assumed molecular weight of 2,040 for coal with carbon and oxygen contents of 150 and 15 atoms, respectively. The carbon and oxygen contents would be typical of a medium-rank coal. For the purpose of comparing the product distribution per unit mass of product, the weight fraction distribution for product species $[w^P(y_1, y_2, \theta)]$ is obtained as:

$$w^P(y_1, y_2, \theta) = \frac{\xi_M^P(y_1, y_2, \theta)}{\int_0^1 \int_0^1 \xi_M^P(y_1, y_2, \theta)\, dy_2\, dy_1} \qquad (17)$$

The denominator in Eq. 17 is the total mass of products formed from coal at any time (θ). The normalization involved in Eq. 17 allows direct comparison of the product composition at different times since

$$\int_0^1 \int_0^1 w^P(y_1, y_2, \theta)\, dy_2\, dy_1 = 1 \qquad (18)$$

Figure 1a and 1b show section planes of $w^P(y_1, y_2, \theta)$ taken at low carbon and oxygen contents, respectively. These plots show that with an increase in time ($\theta = 0.05$ to 20), the model predicts

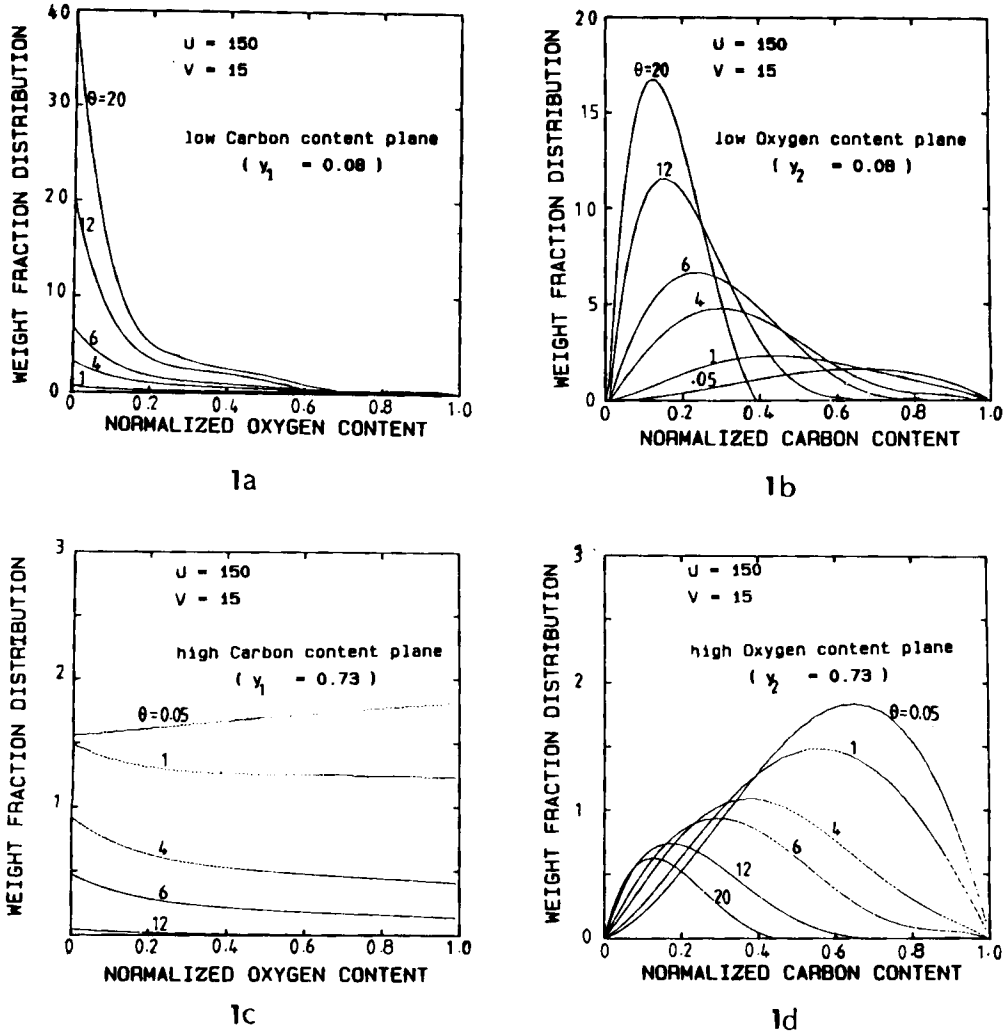

Figure 1. Weight fraction distribution $[w(y_1, y_2, \theta)]$ vs. normalized oxygen and carbon contents at different times (θ) for a typical high-ranking coal.

$u = 150; v = 15$

an increase in the concentration distribution function toward lower mean oxygen content and carbon content. While the concentration distribution shows a maximum in Figure 1b, no maximum occurs in Figure 1a. This is due to the functional form of the stoichiometric kernel (Eq. 13) employed in the simulation. As the ratio of u/v used in the simulation is increased the maximum becomes more pronounced.

Figure 1c and 1d show section planes of $w^P(y_1, y_2, \theta)$ taken at high carbon and oxygen contents, respectively. Here we note that with the progress of time ($\theta = 0.05$ to 20), the concentration distribution function goes through a maximum. As before, Figure 1d shows a clear maximum, once again due to the assumed form of the stoichiometric functions.

The plots in Figure 1 are consistent with our expectations that a whole spectrum of products of varying carbon and oxygen contents is formed simultaneously. As the reactions proceed, the species of high carbon and oxygen contents get preferentially consumed (Figures 1c and 1d) to yield species of low carbon and oxygen contents at longer reaction times (Figures 1a and 1b).

Since the model (Eq. 8) has been written on a dimensionless basis, the concentration distribution function for the same ratio of u/v would yield identical curves when plotted on a normalized scale as in Figure 1. Figures 2a–2d show plots of weight fraction distribution obtained using approximately the same molecular weight for coal (1,980) with carbon and oxygen contents of 125 and 30 atoms, respectively. Such a composition would be typical of a low rank brown coal.

A comparison between corresponding parts of Figures 1 and 2 shows that compounds produced during liquefaction of coals of different elemental composition will be similar. However, the concentrations of the compounds present will be different and will depend upon the composition of coal itself. This prediction is in broad agreement with Whitehurst et al. (1980), who observed that detailed characterization of coal liquids yielded products of varying functionalities whose concentrations were coal-dependent.

Since the composition (carbon and oxygen contents) of a coal are determined by the elemental analysis, the characteristic molecular weight for coal is the only parameter that needs to be chosen to fit the product distribution obtained on coal liquefaction reactions.

The outputs of the simulation were lumped using lumping

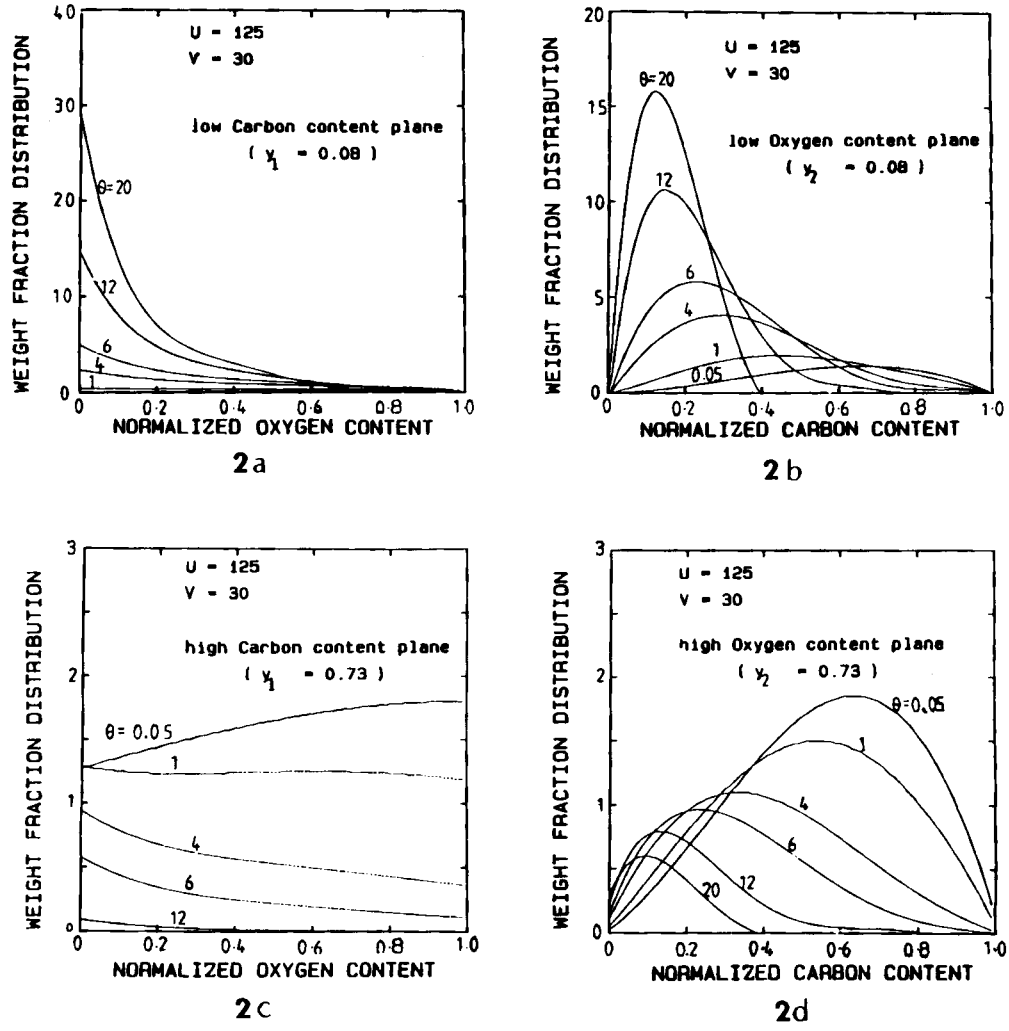

Figure 2. Weight fraction distribution [$w(y_1, y_2, \theta)$] vs. normalized oxygen and carbon contents at different times (θ) for a typical low-ranking coal.

$u = 125$; $v = 30$

function Eq. 12 to arrive at lumped pseudocomponents. Since most of the reported data on coal liquefaction kinetics have employed three lumps (preasphaltenes, asphaltenes and oils, gases and water) to classify the liquefaction products, we require two solubility functions:

$$\left.\begin{aligned} L_1 &= \gamma_1(12x_1 + 16x_2)^{-1} \\ L_2 &= \gamma_2(12x_1 + 16x_2)^{-1} \end{aligned}\right\} \tag{19}$$

with the constraint $\gamma_2 > \gamma_1$ since solvent 2 is stronger than solvent 1 and is able to dissolve all the species soluble in solvent 1.

With two solubility functions we arrive at three lumped pseudocomponents for products:

Oils, gases, and water (OGW) = Soluble in solvent 1 and solvent 2

$$= \int_0^1 \int_0^1 L_1 \cdot \xi_M^P(y_1, y_2, \theta)\, dy_2\, dy_1 \tag{20}$$

Asphaltenes (Asp) = Soluble in solvent 2 but insoluble in solvent 1

$$= \int_0^1 \int_0^1 (L_2 - L_1) \cdot \xi_M^P(y_1, y_2, \theta)\, dy_2\, dy_1 \tag{21}$$

Preasphaltenes (Preasp) = Insoluble in both solvents

$$= \int_0^1 \int_0^1 (1 - L_2) \cdot \xi_M^P(y_1, y_2, \theta)\, dy_2\, dy_1 \tag{22}$$

The weight-averaged molecular weights ($\overline{M}_w$) of each of the lumped product fractions are obtained as:

for OGW fraction,

$$\overline{M}_w = \frac{\int_0^1 \int_0^1 L_1 \cdot \xi_M^P(y_1, y_2, \theta) \cdot (12uy_1 + 16vy_2)\, dy_2\, dy_1}{\int_0^1 \int_0^1 L_1 \cdot \xi_M^P(y_1, y_2, \theta)\, dy_2\, dy_1} \tag{23}$$

for Asp fraction,

$$\overline{M}_w = \frac{\int_0^1 \int_0^1 (L_2 - L_1) \cdot \xi_M^P(y_1, y_2, \theta) \cdot (12uy_1 + 16vy_2)\, dy_2\, dy_1}{\int_0^1 \int_0^1 (L_2 - L_1) \cdot \xi_M^P(y_1, y_2, \theta)\, dy_2\, dy_1} \tag{24}$$

For Preasp fraction,

$$\overline{M}_w = \frac{\int_0^1 \int_0^1 (1 - L_2) \cdot \xi_M^P(y_1, y_2, \theta) \cdot (12uy_1 + 16vy_2)\, dy_2\, dy_1}{\int_0^1 \int_0^1 (1 - L_2) \cdot \xi_M^P(y_1, y_2, \theta)\, dy_2\, dy_1} \tag{25}$$

Figures 3 and 4 contain plots of lumped components obtained from using $\gamma_1 = 200$ and $\gamma_2 = 400$ as constants in Eq. 19. It is apparent from Figure 3 that the reported maxima in preasphaltenes and asphaltenes contents can be simulated using this model. Figure 4 shows a gradual reduction of the weight-averaged-molecular weight of all fractions, with an apparent discontinuity

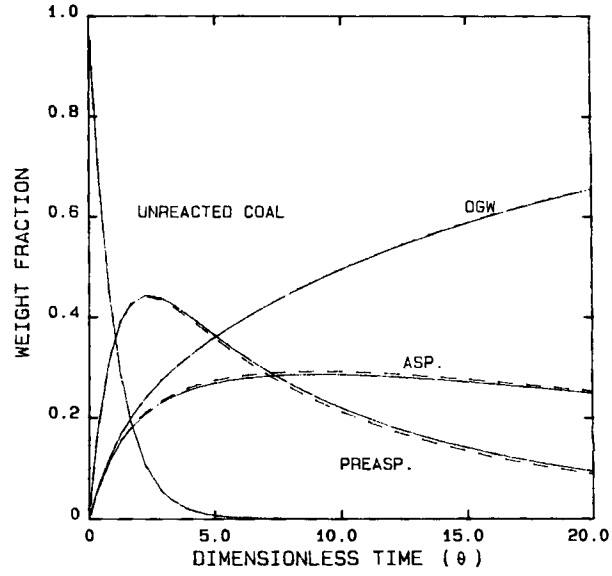

Figure 3. Effect of elemental composition of coal on product yields for $\gamma_1 = 200$, $\gamma_2 = 400$.

—— $u = 150$; $v = 15$
------ $u = 125$; $v = 30$

at zero time due to the absence of the products initially. These plots show that for the same characteristic molecular weight of coal (ca. 2,040), the carbon (u) and oxygen (v) contents do not greatly alter the model predictions. This is due to the lumping functions (Eq. 19) used, which depend upon the molecular weight only. The observations in Figures 3 and 4 are important since it is proposed to use the elemental analysis of coal in choosing the characteristic carbon (u) and oxygen contents (v) of coal based on an assumed molecular weight. The model predictions

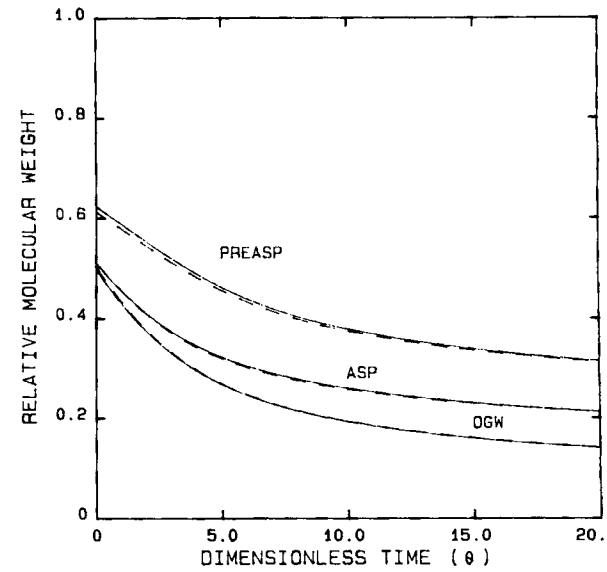

Figure 4. Effect of elemental composition of coal on molecular weight of products for $\gamma_1 = 200$, $\gamma_2 = 400$.

—— $u = 150$; $v = 15$
------ $u = 125$; $v = 30$

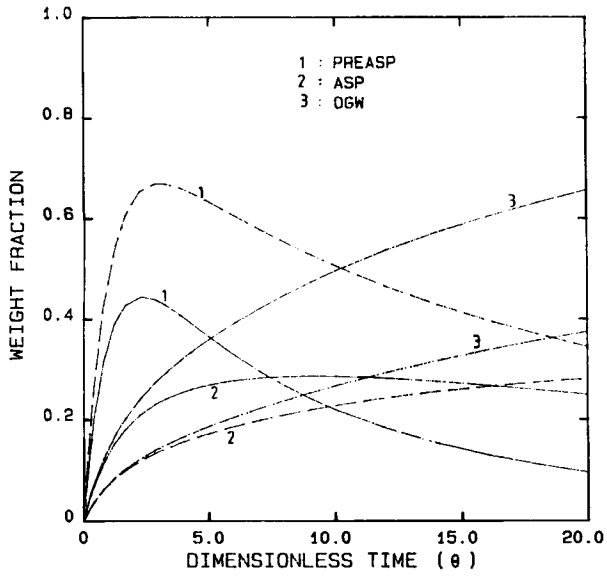

Figure 5. Effect of characteristic molecular weight for coal on product yields for $\gamma_1 = 200$, $\gamma_2 = 400$.

—— $u = 150$; $v = 15$
------ $u = 300$; $v = 30$

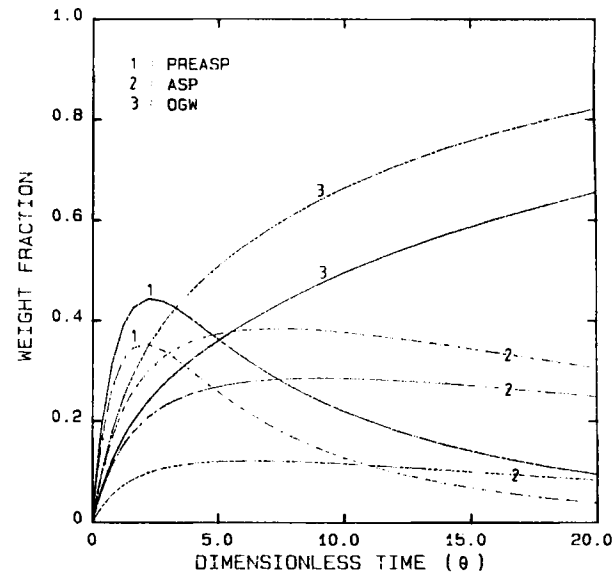

Figure 7. Effect of solvent parameters on product yields for $u = 150$, $v = 15$.

—— $\gamma_1 = 200$; $\gamma_2 = 400$
------ $\gamma_1 = 200$; $\gamma_2 = 500$
····· $\gamma_1 = 300$; $\gamma_2 = 400$

are not greatly altered by variations in elemental composition from 88–80% carbon content.

Figures 5 and 6 show the sensitivity of the model prediction to changes in the characteristic molecular weight parameter for coal. These plots show that doubling the molecular weight for coal (from 2,040 to 4,080), while keeping all other parameters the same, results in a dramatic change in the yield profiles of the products, Figure 5, as well as the molecular weight of each of the factions, Figure 6. The characteristic molecular weight of coal would be a unique function of coal and hence would determine the product yields and composition. Here we note that in this model we have assumed that such a characteristic molecular weight for coal can be described by a very narrow distribution (a Dirac delta function, Eq. 5). Obviously the predictive ability of the model will depend upon how closely the actual molecular weight distribution in coal can be approximated by this function. The alternative description of specifying the molecular weight distribution in coal is considered not justifiable at this stage.

Figures 7 and 8 show the effect of altering either of the solubility function-based parameters γ_1 or γ_2 in Eq. 19. Changing γ_1

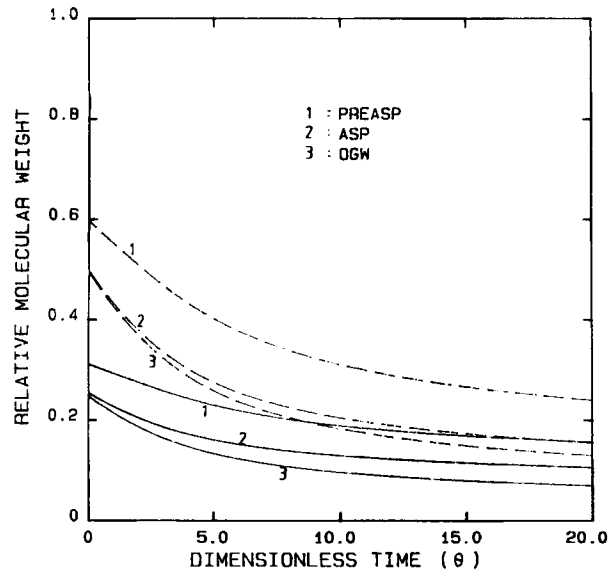

Figure 6. Effect of characteristic molecular weight for coal on molecular weight of products for $\gamma_1 = 200$, $\gamma_2 = 400$.

—— $u = 150$; $v = 15$
------ $u = 300$; $v = 30$

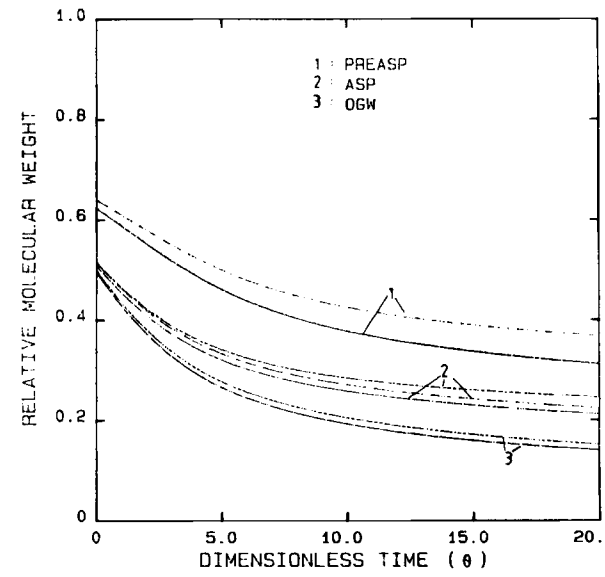

Figure 8. Effect of solvent parameters on molecular weight of products for $u = 150$, $v = 15$.

—— $\gamma_1 = 200$; $\gamma_2 = 400$
------ $\gamma_1 = 200$; $\gamma_2 = 500$
····· $\gamma_1 = 300$; $\gamma_2 = 400$

alters the oils and asphaltenes fractional yields without modifying the preasphaltenes yield. Whereas changing γ_2 alters the asphaltenes and preasphaltenes fractional yields only. Since both γ_1 and γ_2 are solvent-based parameters, they should be kept constant in simulating product distributions for different coals employing similar extraction solvents for product classification. This amounts to assuming that species containing identical carbon and oxygen contents will dissolve to the same extent irrespective of the presence of other species. This is obviously a gross simplification since solubility is known to be affected by the presence of other species that can act as cosolvents. However, we feel that our assumption is no worse than the present system of studying the progress of reaction using models based on solubility criteria. Moreover, in the vast range of species involved, properties such as solubility could conceivably exhibit similar general trends.

With this assumption, we are now in a position to compare the lumped product distribution obtained from liquefying different ranking coals using a characteristic molecular weight of coal as the only parameter.

So far we have not concerned ourselves with the reactivity of different coals. Although Given and coworkers (Yarzab et al., 1980) have attempted to classify reactivity of coals using various parameters, we are far from arriving at general criteria. The rate constant for breakdown of all the species has been expressed as a fraction of the rate of breakdown of parent coal, Eq. 13b. The rate constant for breakdown of coal (α) has to be determined experimentally.

Most of the reported lumped kinetic studies have employed tetrahydrofuran solubility as an indicator of the degree of coal dissolution. If we assume that THF insolubles primarily comprise of unreacted coal, the rate of formation of the THF soluble product will be indicative of the rate of dissolution of coal and hence provide an estimate of (α).

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Notation

$A(x_1, x_2)$ = continuous species of index (x_1, x_2)
C_i = molar concentration of coal initially, mol · m^{-3}
$C(x_1, x_2, t)$ = molar concentration distribution, mol · m^{-3}
CRMM = continuous reaction mixture model
$K(x_1, x_2)$ = reaction rate kernel for species (x_1, x_2), s^{-1}
$\bar{K}(y_1, y_2)$ = dimensionless reaction rate kernel, Eq. 6
K_n = matrix of rate constant for lumped reaction network, s^{-1}
L_1, L_2 = solubility function for 1st and 2nd solvent in Eq. 19
$\bar{M}_w$ = weight-averaged molecular weight of lumped products
$M_n(y_1, y_2)$ = lumping function for nth lump
t = time, s
u = characteristic number of carbon atoms for coal
v = characteristic number of oxygen atoms for coal
$w^P(y_1, y_2, \theta)$ = weight fraction distribution for liquefaction products
x_1 = number of carbon atoms per molecule
x_2 = number of oxygen atoms per molecule
y_1 = normalized number of carbon atoms per molecule
y_2 = normalized number of oxygen atoms per molecule

Greek letters

α = reaction rate constant for disappearance of coal, s^{-1}
β = multiplier in soichiometric kernel, Eq. 15
γ_n = multiplier in lumping function for nth solvent
$\delta(i, j)$ = Dirac delta function = 0, for $i \neq j \neq 0$; = infinite, at $i = j = 0$
$\xi(y_1, y_2, \theta)$ = dimensionless molar concentration distribution
$\xi_M(y_1, y_2, \theta)$ = dimensionless mass concentration distribution
θ = dimensionless time
$\nu(x_1', x_2'; x_1, x_2)$ = stoichiometric kernel
τ = dummy variable for dimensionless time

Subscripts and superscripts

C = coal
i = initial
M = mass
n = nth lumped component
O = evaluated at time = 0
P = products of liquefaction
$'$ = index for dummy variables for x_1, x_2, y_1, and y_2

Literature cited

Anthony, D. B., and J. B. Howard, "Coal Devolatilization and Hydrogasification," *AIChE J.*, **19**, 625 (1976).
Aris, R., and G. R. Gavalas, "On the Theory of Reactions in Continuous Mixtures," *Phil. Trans. Royal Soc.*, London, **260**, 351 (1966).
Attar, A., "The Kinetics of Coal Liquefaction in a Hydrogen Donor Solvent," *ACS Div. Fuel Chem. Prepr.*, **23**, 169 (1978).
Bailey, J. E., "Lumping Analysis of Reactions in Continuous Mixtures," *Chem. Eng. J.*, **3**, 52 (1972).
Brunson, R. J., "Kinetics of Donor-Vehicle Coal Liquefaction in a Flow Reactor," *Fuel*, **58**, 203 (1979).
Curran, G. P., R. T. Struck, and E. Gorin, "Mechanism of the Hydrogen-Transfer Process to Coal and Coal Extracts," *Ind. Eng. Chem. Process Des. Dev.*, **6**, 166 (1967).
Davis, H. G., and T. J. Farrell, "Relative and Absolute Rates of Decomposition of Light Paraffins under Practical Operating Conditions," *Ind. Eng. Chem. Process Des. Dev.*, **12**, 171 (1973).
Fabuss, B. M., J. O. Smith, and C. N. Satterfield, "Thermal Cracking of Pure Saturated Hydrocarbons," *Advances in Petroleum Chemistry and Refining, IX*, Wiley, New York (1964).
Foster, N. R., M. A. Wilson, R. G. Weiss, and K. N. Clark, "Isothermal Studies of Liquefaction of Liddell Coal," *Ind. Eng. Chem. Prod. Res. Dev.*, **22**, 478 (1983).
Franz, J. A., "C-13, H-2, H-1 NMR and GPC Studies of Structural Evolution of a Subbituminous Coal During Treatment with Tetralin at 427°C," *Fuel*, **58**, 405 (1979).
Gangwer, T., "A General Quantitative Model for Coal Liquefaction Kinetics: Thermal-Cleavage/Hydrogen-Capping Mechanism," BNL-27279, Brookhaven Nat. Lab., Upton, NY (1980).
Gavalas, G. R., P. H. Cheong, and R. Jain, "Model of Coal Pyrolysis. 1: Qualitative Development," *Ind. Eng. Chem. Fund.*, **20**, 113 (1981).
Gertenbach, D. D., R. M. Baldwin, and R. L. Bain, "Modelling of Bench-scale Coal Liquefaction System," *Ind. Eng. Chem. Process Des. Dev.*, **21**, 490 (1982).
Golikeri, S. V., and D. Luss, "Analysis of Activation Energy of Grouped Parallel Reactions," *AIChE J.*, **18**, 277 (1972).
Gun, S. R., J. K. Sama, P. B. Chowdhury, S. K. Mukherjee, and D. K. Mukherjee, "A Mechanistic Study of Hydrogenation of Coal," *Fuel*, **58**, 171 (1979).
Lee, H. H., "Synthesis of Kinetic Structure of Reaction Mixtures of Irreversible First-Order Reaction," *AIChE J.*, **24**, 116 (1978).
Liu, Y. A., and L. Lapidus, "Observer Theory for Lumping Analysis of Monomolecular Reaction Systems," *AIChE J.*, **19**, 467 (1973).
Luss, D., and S. V. Golikeri, "Grouping of Many Species Each Consumed by Two Parallel First-Order Reactions," *AIChE J.*, **21**, 865 (1975).
Petrakis, L. W., G. L. Jones, D. W. Grandy, and A. B. King, "Free Radicals in Coal and Coal Conversions. 10: Kinetics and Reaction Pathways in Hydroliquefaction," *Fuel*, **62**, 681 (1983).
Painter, P. C., and M. M. Coleman, "Application of Fourier-Transformed Infrared Spectroscopy to the Characterization of Fractionated Coal Liquids," *Fuel*, **58**, p. 301 (1979).

Prasad, G. N., "Extension and Lumping Analysis of Continuous Reaction Mixture Models for Coal Liquefaction Kinetics," M.Ch.E. Report, Illinois Inst. Tech., Chicago (1982).

Pullen, J. R., "Solvent Extraction of Coal," Report No. ICVTIS/TR16, IEA Coal Research, London (1981).

Shah, Y. T., "Reaction Engineering in Direct Coal Liquefaction," Addison-Wesley, Reading, MA (1981).

Snape, C. E., and K. D. Bartle, "Definition of Fossil Fuel-Derived Asphaltenes in Terms of Average Structural Properties," *Fuel*, **63**, 883 (1984).

Squires, A. M., "Reaction Paths in Donor Solvent Liquefaction," *Appl. Energy*, **4**, 161 (1978).

Stephens, H. P., "Product Distribution and Hydrogen Management in Direct Coal Liquefaction," *Proc. Int. Conf. Coal Sci.* IEA, Pittsburgh, 105 (Aug., 1983).

Syamlal, M., "Continuous Reaction Mixture Models for Coal Liquefaction Kinetics," M. S. Thesis, Illinois Inst. Tech., Chicago (1981).

Syamlal, M., and C. V. Wittmann, "Continuous Reaction Mixture Models for Coal Liquefaction Kinetics," *Ind. Eng. Chem. Fund.*, **24**, 82 (1985).

Szladow, A. J., and P. H. Given, "The Role of Oxygen Functional Groups in the Mechanism of Coal Liquefaction," *ACS Div. Fuel Chem. Prepr.*, **23**, 161 (1978).

———, "Models and Activation Energies for Coal Liquefaction Reactions," *Ind. Eng. Chem. Process Des. Dev.*, **20**, 27 (1981).

———, "Analysis of Coal Dissolution Reaction Engineering," *Chem. Eng. Commun.*, **19**, 115 (1982).

Van Camp, C. E., P. S. Van Damme, and G. F. Froment, "Thermal Cracking of Kerosine," *Ind. Eng. Chem. Process Des. Dev.*, **23**, 155 (1984).

Van Damme, P. S., G. F. Froment, and W. B. Balthasar, "Scaling-up of Naphtha Cracking Coils," *Ind. Eng. Chem. Process Des. Dev.*, **20**, 366 (1981).

Weekman, V. W., "Lumps, Models and Kinetics in Practice," *AIChE Monog. Ser.* **75**(11), (1979).

Wei, J., and J. C. W. Kuo, "A Lumping Analysis in Monomolecular Reaction Systems," *Ind. Eng. Chem. Fund.*, **8**, 114 (1969).

Whitehurst, D. D., T. O. Mitchell, and M. Farcasiu, *Coal Liquefaction—The Chemistry and Technology of Thermal Processes*, Academic Press, New York (1980).

Wilson, M., R. J. Pugmire, A. M. Vasallo, D. M. Grant, P. J. Colin, and K. W. Zilm, "Changes in Aromaticity During Coal Liquefaction," *Ind. Eng. Chem. Prod. Res. Dev.*, **21**, 477 (1982).

Yarzab, R. F., and P. H. Given, "Dependence of Coal Liquefaction behavior on Coal Characteristics. 4: Cluster Analysis for Characterization of 104 Coals," *Fuel*, **59**, 81 (1980).

Yoshida, T., Y. Nakata, R. Yoshida, S. Ueda, N. Kanda, and Y. Maekawa, "Elucidation of Structural and Hydroliquefaction Characteristics of Yallourn Brown Coal by Carbon-13 CP/MAS NMR Spectrometry," *Fuel*, **61**, 824 (1982).

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