Continuous-Mixture Kinetics of Thermolytic Extraction of Coal in Supercritical Fluid

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Thermolysis of coal yields a complex mixture of many extract products whose molecular-weight distribution (MWD) varies with time for continuous-flow, semibatch experiments. A laboratory flow reactor with a differential fixed bed of coal particles contacted by supercritical tert-butanol was used to provide dynamic MWD data by means of HPLC gel permeation chromatography of the extract. The experimental results, multipeaked, time-dependent MWDs of extract molecules, are interpreted by a novel mathematical model based on continuous-mixture kinetics for thermal cleavage of chemical bonds in the coal network. The parameters for the MWDs of extractable groups in the coal and the rate constants are determined from the experimental data. The effect of temperature on the kinetics of the extraction is explained in terms of one- and two-fragment reactions of the extractable groups in the coal. At lower temperatures (613 and 633 K) single-fragment reactions dominate, but at higher temperatures (653 and 673 K) more bonds in the coal are broken and the two-fragment reactions become significant. Also, the detailed MWDs are related to conventional lumped data for the thermolytic extraction process. The results yield information about the structure of coal, as well as the kinetics and mechanism of supercritical thermolytic reactions.

Introduction

Thermolysis is a fundamental step in the chemical transformation processes of coal for useful purposes, including liquefaction and pyrolysis. Heating coal to temperatures of the order 573 K and higher causes the macromolecular network to thermolyze by rupture of chemical bonds. The progress of the reaction depends on the initial molecular structure of the coal, as well as on the rate. Understanding the chemical kinetics of these thermolytic reactions of coal is relevant to a wide range of coal processes.

The detailed structure of coal is complex, and varies with its rank and source. Coal is believed to be composed of cross-linked polyaromatic units (Solomon et al., 1992; Green et al., 1982). These multiring aromatic units are attached to aliphatic or heterocyclic substituent groups: methylene, ethylene and ether bridges (Darivakis et al., 1990). Thermolysis of the coal macromolecular network occurs by heat-induced scission of the linkages. The rate of thermolysis and release of solubilized products depends on the rate of bond rupture, which allows the polyaromatic units to migrate away from the coal particle and then out of the reactor.

Supercritical fluid extraction of coal has received increasing attention because of advantages over conventional pyrolysis and liquefaction (Kershaw, 1989). Supercritical fluids have the following features: (1) supercritical fluids provide high solubility for nonvolatile components and improved mass-transfer rates, and (2) operation can be manipulated by changing pressure or temperature. The pioneering work in supercritical extraction of coal was carried out by Britain's National Coal Board (Davies, 1978). Studies of supercritical extraction have mainly focused on coal structure and chemical analysis of the extract. Less attention has been directed to kinetics and engineering aspects.

Some kinetics data for supercritical fluid extraction have been obtained in batch reactors (Slomka and Rutkowski, 1982; Deshpande et al., 1986). There is little published information on kinetics of supercritical fluid extraction of coal in flow-through reactors. In a batch reactor, the product species in the extract may further react and degrade to smaller molecular-weight compounds by secondary reactions. In a flow reactor, in contrast, if the residence time is much less than the order of the time for a reaction to occur (that is, the inverse rate constant), then secondary reactions of the solubilized molecules can be neglected. Thus, the instantaneous state of the chemical reaction can be obtained from a continuous-flow reactor.

Since coal liquefaction involves an enormous number of products, it is not feasible to develop a mathematical model to describe each of the individual chemical reactions. Many previous models are of the lumped-parameter type, where the products are combined into groups typically characterized by their solubility in different solvents (Angelova et al., 1989). Recently, more detailed models have been developed for pyrolysis (Niksa and Kerstein, 1986). The normal lumped groups are oil, asphaltenes, preasphaltenes and unreacted coal. The advantage of a lumped model is its straightforward relationship to bulk-concentration experimental data, and its practical use for engineering purposes. An appropriate lumped-kinetics model can be developed when the lumped components display similar reactivity.

The notion of a continuous mixture has proved valuable since the discussion by Aris and Gavalas (1966) treating a complex mixture of components as a continuum undergoing first-order reactions. Both monomolecular (one-fragment) and cracking (two-fragment) reactions were considered. The models of continuous-mixture kinetics take advantage of the complex, multicomponent nature of reaction systems by allowing a property, for example, the MW, to be a continuous variable. Recently, the theory of continuous mixtures has received considerable attention in both academic and industrial settings (Sapre and Krambeck, 1991; Astarita and Sandler, 1991). Continuous-mixture theory has been applied to distillation (Haynes and Matthews, 1991), thermodynamics (Cotterman et al., 1985) and chemical reactions (Ho et al., 1990; Ho, 1991). Some preliminary efforts have applied continuous-mixture kinetics to coal liquefaction.

Prasad et al. (1986a,b) simulated the rate processes of coal liquefaction based on the continuum concept. In his model, two indices, the number of carbon atoms and the number of oxygen atoms, served as continuous variables. Both coal thermolysis and secondary reactions of the thermolysis products were considered. The total product molecular-weight distribution (MWD) was lumped into groups representing solubility fractions, for example, preasphaltenes, asphaltenes and oil. Certain assumptions defined the particular reactions accounted for by Prasad et al. (1986a,b). Thus, every cracking reaction was supposed to yield two product molecules (two-fragment reaction), whose MWs summed to the MW of the reactant molecule. The two-molecule reaction, assumed first-order, required the adoption of a stoichiometric term having symmetry and normalization properties. According to Prasad et al. (1986a,b) several different forms for the dependence of the rate constant on MW provided similar results, such that progressively slower reactions occurred as molecules became smaller. Lastly, the coal was assumed to be composed of large molecules of identical MW. The cascade of thermal cracking reactions reduced the initial MW of coal to a distribution of MWs. This MWD varied with time and, according to the model, eventually yielded a mixture of molecules all having an identical, minimum MW.

Darivakis et al. (1990) applied probability theory to develop a model for coal thermolysis to predict MWDs of primary coal pyrolysis liquids. Coal was assumed to have a cross-linked macromolecular structure in which different polyaromatic units are interconnected with chemical linkages. Rupture of kinetically similar bonds is the preferred pathway for release of these polyaromatic units. The study focused on the MWDs of primary coal pyrolysis products and showed that a gamma distribution function can successfully fit experimental MWD data. Although the model interpreted the MWDs of pyrolysis products, it did not consider rate expressions for the thermolysis reactions.

Here, we present a rate theory based in part upon the concepts presented by Darivakis et al. (1990) and combined with concepts of continuous-mixture kinetics. The model builds on earlier approaches, and introduces the following novel features:

- new rate expressions are developed that describe how the polyaromatic units are thermolytically broken away from the coal macromolecular network through both one- and two-fragment reactions.
- the initial composition of coal is supposed to be represented by molecular-weight distributions of polyaromatic units that can be released from the coal matrix by bond rupture.
- a semi-batch flow reactor, for which secondary reactions of the extract molecules are negligible, is employed.

Experiments

Supercritical extraction of bituminous coal

Illinois No. 6 bituminous coal, DECS-2 (PSOC-1539) with the following ultimate analysis was used:

Carbon	65.49 wt. %
Hydrogen	4.56 wt. %
Nitrogen	1.11 wt. %
Sulfur	4.52 wt. %
Oxygen	8.16 wt. %
Ash	16.16 wt. %

Supercritical fluid extraction with tert-butanol ($T_c = 506.2$ K, $P_c = 3.97$ MPa) was conducted in a fixed-bed reactor through which the solvent flows continuously. The detailed apparatus and the operation procedure were described earlier (Zhang et al., 1992; Wang et al., 1993). The extraction was carried out at constant pressure, 6.8 MPa, and constant flow rate, 1.7×10^{-7} m^3/s. The temperature was continuously increased at a heating rate of 0.14 K/s to 633 K and then held constant until the end of a run. Kershaw (1989) reported that for coal particle size below 1.6×10^{-3} m, there was little effect of particle size on the kinetics data of coal conversion. Thus, coal samples for the bed were prepared by sieving to a particle-size range small enough ($6\text{–}8 \times 10^{-4}$ m) to eliminate significant internal mass-transfer resistance. At the flow rate of the experiment, the external mass-transfer resistance is negligible (Zhang et al., 1992). The coal samples are stored under water to prevent oxidation after sieving and, before extraction, are vacuum dried at 343 K to constant weight. Liquid extract samples are stored under nitrogen for analysis.

Two kinds of processes occur in supercritical extraction: physical and chemical processes. For Illinois No. 6 coal thermolytically extracted with supercritical tert-butanol, the energies of activation for the physical and chemical processes are 8.0 kJ/mol and 54 kJ/mol, respectively (Zhang et al., 1992). The physical process, which extracts less than 3% of the coal mass, takes place at 573 K (Zhang et al., 1992). At higher temperature the conversion of coal is mainly due to the thermolytic (chemical) extraction, that is, the rupture of the linkages to release polyaromatic units as extract. Therefore, we pretreated the coal samples with supercritical tert-butanol solvent in the reactor at 573 K and 6.8 MPa to remove physically-extractable components. Our study thus focuses on the chemical-reaction kinetics of the thermolytic extraction.

Retrogressive (repolymerization) reactions are negligible in this system. Concentration of extract molecules are extremely low due to the low residence time (10 s) in the reactor. Deposits of high molecular-weight substances either on the coal or on the reactor surfaces were never observed. Moreover, we conducted special tests for the influence of secondary reactions by feeding extracted material into the reactor containing depleted coal. For residence times up to 20 min the effluent showed no increase in MWD even at high temperatures, demonstrating that repolymerization reactions were not significant. At higher temperatures and with smaller solvent/coal ratios, repolymerization reactions may be important.

Following the same calibration procedure in earlier work (Zhang et al., 1992), the totally lumped concentration of coal liquid in the extract stream was determined from a calibration curve based on the measured absorbance at 235 nm for the entire extract from a run. Solvent tert-butanol is favorable for this application since it does not interfere with the UV absorbance of the aromatic thermolysis products.

Analysis of coal extract with gel permeation chromatography

The MWDs of the extract, based on polystyrene molecular-weight standards, were determined by using PLgel columns coupled with a Hewlett Packard 1050 HPLC. Two PLgel columns (Polymer Lab), 0.30 m × 0.0075 m, of 100 and 500 Å pore size, respectively, packed with 5 μm cross-linked polystyrene-divinylbenzene copolymer, were used in series. The HPLC reagent-grade tetrahydrofuran (THF, Baker Analyzed) was continuously pumped through the columns at a flow rate of 1.0 mL/min. The injected sample volume was 100 μL at a concentration 0.2% w/v. A variable-wavelength spectrophotometric detector with a wide wavelength range (190–700 nm) was used. The wavelengths of 235, 254 and 280 nm were examined in the preliminary experiments. The wavelength 254 nm was chosen since it gives the maximum absorption for the coal-extract samples. A refractive index detector confirmed the positions of MWD peaks indicated by the UV detector.

The coal extract samples from runs at 6.8 MPa and four temperatures were collected at different times. Each sample of 1.0×10^{-4} m^3 volume was concentrated to $0.5\text{–}1 \times 10^{-6}$ m^3 by evaporating excess tert-butanol solvent under vacuum at 338 K. Each concentrated sample was then dissolved in THF solvent for analysis. Since the extracts from our experiments have a relatively small molecular-weight range (MW < 1,000), THF proves to be a satisfactory solvent. The samples were completely dissolved in THF, and no segregation of components was observed. In the preliminary experiments, the injection-volume range (20–100 μL) of coal-extract sample and the velocity range (0.5–4 mL/min) were tested and no effects of retention time or shape of MWD were observed. This indicates that there were no significant effects of association in solution or of column adsorption (Yau et al., 1979).

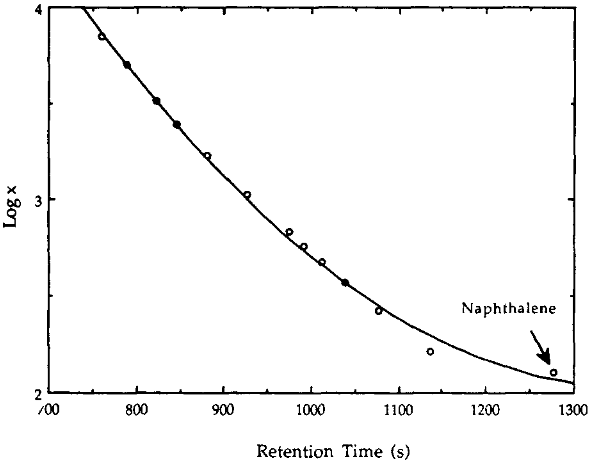


Figure 1. Calibration curve of molecular weight, *x*, in the range 100–10,000 based on narrow-MWD standards of polystyrene.

Narrow molecular-weight range polystyrene standards (MW = 162–20,000) from Polymer Lab were dissolved in THF for calibration. Naphthalene in THF was used to extend the calibration to lower MW. The method of peak position calibration was applied. Figure 1 shows the calibration curve of MW vs. retention time. Use of narrow polystyrene standards requires the application of corrections for analysis of *high* molecular-weight coal-derived materials (Solomon et al., 1992). For the molecular-weight range (MW < 1,000) of coal extract in our experiments, however, Bartle et al. (1984) have shown that the retention behavior of narrow polystyrene standards approximates closely that of coal extracts produced under mild conditions. As our objective is not to identify specific chemical components, but to analyze chemical-reaction kinetics data, shifting of the calibration curve for MWDs will not affect the interpretation. Based on the assessment that such calibration standards are satisfactory for these purposes and conditions, the MWDs were determined with a data acquisition system (Chem Station) and a GPC software incorporating the polystyrene calibration data.

Theoretical Model

Coal structure

A generalized and fundamental model for coal liquefaction reaction should be based on the structure of coal. Although the complete detailed structure is unknown, it is agreed that coal involves a macromolecular network. Green et al. (1982) proposed the existence of largely aromatic and hydroaromatic "clusters" in coal, as suggested by X-ray and chemical degradation studies. The polyaromatic units have a MWD spanning several hundred amu. These units are extensively bonded internally, so that they can be freed from the coal matrix more easily than they can themselves be chemically degraded. Since each unit is polyvalent, the potential for extensive cross-linking exists. Based on these views, Green et al. (1982) described the structure as a network composed of polyaromatic units with one, two or more cross-links. Darivakis et al. (1990) also assumed that coal has a cross-linked structure in which different polyaromatic units are interconnected with chemical linkages.

Each polyaromatic unit contains one or more aromatic rings and a nonaromatic part. The linkage consists of one or more chemical functional groups. Based on the number of linkages, three kinds of polyaromatic units, or groups, were characterized:

- End polyaromatic units bonded to the structure by one linkage.
- Regular polyaromatic units connected into the main structure by two linkages.
- Cross-linked polyaromatic units that are connected into the main structure by three or possibly more linkages.

Our data for the MWDs, as well as that of Syamlal and Wittmann (1985) and Franz et al. (1981), show that multiple, overlapping peaks appear in the product distribution. Oil shale extraction likewise yields multipeak MWDs (Tahiri et al., 1988). We consider that each of the three peaks we observed represents a group of extractable polyaromatic units in the coal network. Following Darivakis et al. (1990), we assume that the MWD of each group of extractable polyaromatic units is described by a gamma distribution,

$$c_{oi}(x) = m_{oi} y^{(\alpha_i - 1)} \exp(-y)/[\beta_i \Gamma(\alpha_i)] \qquad i = 1, 2, 3 \tag{1}$$

with

$$y = \frac{x - x_{oi}}{\beta_i} \tag{2}$$

where subscript i represents the ith extractable group. Since the gamma distribution is defined for $y \geq 0$, we have $c_{oi}(x \leq x_{oi}) = 0$.

The average position, $\bar{x}_i$, and width of a peak, σ_i, are related to the first and second moments of the gamma distribution, which are given by Abramowitz and Stegun (1968), respectively, as:

$$\bar{x}_i = x_{oi} + \alpha_i \beta_i \tag{3}$$

and

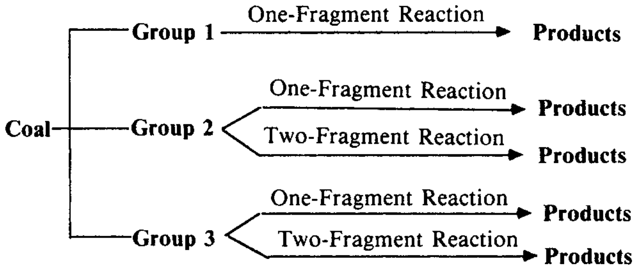
$$\sigma_i^2 = \alpha_i \beta_i^2 \tag{4}$$

The zero moment, m_{oi}, is the total concentration of the reactive components in a particular group. The position of the peak maximum, x_{pi}, is determined by $dc_{oi}(x)/dt = 0$, which yields:

$$x_{pi} = x_{0i} + (\alpha_i - 1)\beta_i \tag{5}$$

Mechanism

The thermolytic extraction of coal is considered to occur by chemical bonds rupturing to release product species. The rate of thermolysis and release of solubilized products will depend on the rate of bond rupture, which allows the polyaromatic units to migrate away from the coal particle. For supercritical extraction, the polyaromatic units from the thermolysis of the coal macromolecular network are readily dissolved because of the solvating strength of the supercritical fluid. Based on the short residence time in the heated reactor (~10 s), we consider that bond rupture within the coal network produces product species that are carried away from the reaction zone before secondary reactions can occur. Two types of reactions are considered, one producing single product species (one-fragment reaction) and the other producing two product species (two-fragment reaction). The reaction scheme is based on the observation that for $T \leq 633$ K the extract MWDs have the same shape during the time of the reaction and both average MW and the ratios of peak heights are essentially constant with time. At higher temperatures, however, the lower MW peaks grow at the expense of the higher MW peaks during the thermolysis. The one-fragment process is hypothesized to dominate over the two-fragment process at low temperatures since fewer bonds are ruptured simultaneously. The two types of reactions considered in the continuous-mixture kinetics are visualized as:



The fragments are the products which dissolve in the supercritical solvent and whose MWD can be determined by HPLC analysis of the extract. The one-fragment reactions occur by breakage of the relatively weak linkages connecting the polyaromatic units in the macromolecular network. This corresponds to scission of one linkage for the Group 1 polyaromatic unit, two linkages to produce the single fragment for Group 2 and 3 or more linkages for the Group 3 polyaromatic unit. These reactions are prominent over the temperature range of our experiments since their activation energy is low. In the two-fragment reactions the relatively stronger bonds connecting the aromatic rings in a group break simultaneously with the linkages. This produces two dissolvable species and results in a distribution of lower molecular-weight products that are observed only at the higher temperatures. The model does not attempt to describe the sequence of events that constitute the two-fragment reaction. As shown below, the average activation energy for producing these products is more than three times that for the single-fragment reactions. Hence, at the high temperatures the rates of the one- and two-fragment reactions can be of similar magnitudes.

Each group, represented as a gamma distribution, is a mixture of extractable polyaromatic units with different average MW and reactivity. Group 1 is composed of relatively small units which can form product species only through one-fragment reactions. Groups 2 and 3 have much larger units that can form products through both one-fragment reactions and two-fragment reactions.

Model formulation

Continuous distributions of molecular weight, x, are used to represent extractable polyaromatic units in coal and its thermolytic-extraction products. The time-dependent concentration distributions of a particular group of extractable polyaromatic units and product species, denoted by the subscript i, are $c_i(x, t)$ and $u_i(x, t)$, respectively. The rate constants for one-fragment reaction and two-fragment reaction are k_i and $k_{ic}(x)$, respectively.

One-Fragment Reaction. At all temperatures in our experiments one-fragment reactions are significant for all three groups of polyaromatic units in coal. The reactions, referred to as monomolecular by Aris and Gavalas (1966), are assumed to be first-order. Thus, in terms of $c_i(x, t)$, the MWD of group i extractable molecules in coal, the rates of one-fragment reactions are:

$$\frac{\partial c_i(x, t)}{\partial t} = -k_i c_i(x, t) \qquad i=1, 2, 3 \tag{6}$$

with initial condition

$$c_i(x, t=0) = c_{oi}(x) \tag{7}$$

This expression can be immediately integrated to give the concentration distribution,

$$c_i(x, t) = c_{oi}\exp[-k_i t] \qquad i=1, 2, 3 \tag{8}$$

For Group 1, which is composed of stable two- and three-ring aromatics or hydroaromatics, only one-fragment reactions occur. Consider that the concentration distribution of reaction products originating from $c_{o1}(x)$ in the differential reactor is $u_1(x, t)$. The average residence time based on the reactor volume of the fixed bed of coal is τ, and the bed void fraction is ϵ. The mass balance equation for the differential flow reactor is written:

$$\epsilon\tau\frac{\partial u_1(x, t)}{\partial t} + u_1(x, t) = k_1 c_1(x, t)/Q \tag{9}$$

where Q is the volumetric flow rate. The initial condition is:

$$u_1(x, t=0) = 0 \tag{10}$$

For our experimental condition, τ is small (10 s) and the accumulation term in Eq. 9 is negligible relative to the other terms so that

$$u_1(x, t) = k_1 c_1(x, t)/Q \tag{11}$$

Combining Eq. 5 and Eq. 11 leads to the following solution:

$$u_1(x, t) = k_1 c_{o1}(x)\exp(-k_1 t)/Q \tag{12}$$

Two-Fragment Reactions. Since at higher temperatures (>633 K) more chemical bonds can be ruptured simultaneously, two-fragment, or cracking reactions (Aris and Gavalas, 1966) become significant. Group 1 itself, composed of very stable two- and three-ring aromatics or hydroaromatics, is unlikely to be cracked to form products. Thus, one-fragment reactions are hypothesized to be the dominant reactions for Group 1. For Groups 2 and 3, composed of four-ring and larger aromatics, both one- and two-fragment reactions are significant at high temperatures. Following the notation of Aris and Gavalas (1966), we define $A(x)$ to be a continuous distribution of coal components. The two-fragment reaction can be written as:

$$A(x') \rightarrow A(x) + A(x'-x) \tag{13}$$

Denote the concentration density of $A(x)$ by $c_i(x, t)$. Let the rate constant for cracking of $A(x)$ be $k_{ic}(x)$ and define $\upsilon(x, x')$ as the fraction of $A(x')$ that cracks to $A(x)$. All cracking reactions are assumed to be first-order with respect to reacting species. The symmetry of the formation of product species $A(x)$ and $A(x'-x)$ implies that:

$$\upsilon(x, x') = \upsilon(x'-x, x') \tag{14}$$

The products of two-fragment reactions are considered to be distributed in the molecular-weight range, x_{o1} to x'. According to our experimental results, the lower molecular-weight limit of extract, x_{o1}, is about 115. The fact $\upsilon(x, x')$ is a fraction and requires that:

$$\int_{x_{o1}}^{x'} \upsilon(x, x')dx = 1 \tag{15}$$

A possible form of the stoichiometric distribution was proposed originally by Syamlal et al. (1986):

$$\upsilon(x, x') = Bx(x'-x) \tag{16}$$

where B is fixed by Eq. 15, by which we obtain:

$$B = \frac{6}{x'^3 - x_{o1}'^2(3x' - 2x_{o1})} \tag{17}$$

Then the stoichiometric distribution is:

$$\upsilon(x, x') = \frac{6x(x'-x)}{x'^3 - x_{o1}^2(3x' - 2x_{o1})} \tag{18}$$

which differs from that of Syamlal et al. (1986), who took $x_{o1} = 0$.

The expression for $k_{ic}(x)$ significantly affects the relation between MWD and time. The rate coefficient used in this model is chosen to increase linearly with MW:

$$k_{ic}(x) = \kappa_{ic}\frac{x - x_{o1}}{\beta_1} \qquad i=2, 3 \tag{19}$$

so that $k_{ic}(x \leq x_{o1}) = 0$. Higher MW reactants are thus preferentially cracked.

For Groups 2 and 3, both one-fragment reactions and two-fragment reactions are included. Thus, the rate equation in the coal particle can be written as:

$$\frac{\partial c_i(x, t)}{\partial t} = -(k_i + k_{ic}(x))c_i(x, t) \qquad i=2, 3 \tag{20}$$

with initial condition

$$c_i(x, t=0) = c_{oi}(x) \qquad i=2, 3 \tag{21}$$

The rate of generation of product species $A(x)$ is:

$$r(x, t) = \int_x^\infty k_{ic}(x')c_i(x', t)v(x, x')dx' + k_i c_i(x, t) \qquad i=2, 3 \tag{22}$$

On the right side of Eq. 22, the first term accounts for the rate of production by two-fragment reactions, and the second term accounts for the rate of production by one-fragment reactions. The mass balance for the flow reactor is:

$$\epsilon\tau \frac{\partial u_i(x, t)}{\partial t} + u_i(x, t) = \frac{1}{Q}\left[\int_x^\infty k_{ic}(x')c_i(x', t)v(x, x')dx' + k_i c_i(x, t)\right] \qquad i=2, 3 \tag{23}$$

where the initial condition is:

$$u_i(x, t=0) = 0 \tag{24}$$

Again neglecting the accumulation term, Eq. 23 becomes:

$$u_i(x, t) = \frac{1}{Q}\left[\int_x^\infty k_{ic}(x')c_i(x', t)v(x, x')dx' + k_i c_i(x, t)\right] \qquad i=2, 3 \tag{25}$$

Equations 20 and 21 can be solved analytically and the solution is:

$$c_i(x, t) = c_{oi}(x)\exp[-(k_i + k_{ic}(x))t] \qquad i=2, 3 \tag{26}$$

which is substituted into Eq. 25.

Based on the experimental evidence that will be discussed later, the rate constant for the one-fragment reactions is independent of MW and identical for all three groups of extactable polyaromatic units. These rate constants are functions only of temperature, thus,

$$k_i = k_1(T) \tag{27}$$

Now combining Eqs. 18, 19, 25, 26 and 27 leads to the solution for the concentration distribution $u_i(x, t)$ for Groups 2 and 3 by numerical integration. The concentration distribution of all products is the summation:

$$u(x, t) = u_1(x, t) + u_2(x, t) + u_3(x, t) \tag{28}$$

If the temperature is low (<633 K), two-fragment reactions are negligible,

$$k_{ic} \approx 0 \tag{30}$$

which will be shown to be consistent with the magnitudes of the activation energy. Substituting Eq. 30 into Eq. 25 and Eq. 26 gives a result consistent with Eq. 12:

$$u_i(x, t) = k_i c_{oi}(x)\exp(-k_i t)/Q \tag{31}$$

Summation over $i = 1, 2, 3$, gives the concentration distribution of products at low temperatures:

$$u(x, t) = \Sigma k_i c_{oi}(x)\exp(-k_i t)/Q \tag{32}$$

where $c_{oi}(x)$ is given by Eq. 1.

Lumped kinetics based on continuous-mixture theory

The lumped rate expressions for the extractable compound and the product concentration distributions are readily deduced for either the one- or two-fragment reactions. One defines the total lump as an integral over all values of MW:

$$C_i(t) = \int_0^\infty c_i(x, t)dx \tag{33}$$

$$U_i(t) = \int_0^\infty u_i(x, t)dx \tag{34}$$

Group 1. Group 1 undergoes only one-fragment reactions. It is easy to derive the lumped expression from Eqs. 1, 8 and 12. Thus, when Eq. 1 is substituted for c_{o1}, one obtains for the lumped extractable components in the coal:

$$C_1(t) = \int_{x_{oi}}^\infty c_i(x, t)dx = \int_{x_{o1}}^\infty c_{o1}(x)e^{-k_1 t}dx = m_{o1}e^{-k_1 t} \tag{35}$$

In the same way, the concentration distribution for solubilized extract products from Group 1 can be obtained with Eq. 12. The result is:

$$U_1(t) = \frac{k_1}{Q} m_{o1} e^{-k_1 t} \tag{36}$$

Groups 2 and 3. The lumped concentrations for Groups 2 and 3 are derived by applying Eqs. 26 and 33:

$$C_i(t) = \int_{x_{oi}}^\infty c_i(x, t)dx = \int_{x_{oi}}^\infty c_{oi}(x)e^{-\left[k_1 + \kappa_{ic}\left(\frac{x - x_{o1}}{\beta_1}\right)\right]t}dx \qquad i=2, 3 \tag{37}$$

Substituting the gamma function for $c_{oi}(x)$, Eq. 1, and integrating yields the lumped concentration of extractable species in the coal:

$$C_i(t) = \frac{m_{oi}}{\left(1 + \kappa_{ic}\frac{\beta_i}{\beta_1}t\right)^{\alpha_i}} e^{-\left[k_1 + \kappa_{ic}\left(\frac{x_{oi} - x_{o1}}{\beta_1}\right)\right]t} \qquad i=2, 3 \tag{38}$$

In the same way, combining Eqs. 25 and 34 gives for the extract products:

$$U_i(t)=\int_{x_{o1}}^{\infty}u_i(x,\,t)dx=\int_{x_{o1}}^{\infty}\frac{k_1}{Q}c_{oi}(x)e^{-\left[k_1+\kappa_{ic}\left(\frac{x-x_{o1}}{\beta_1}\right)\right]t}dx$$

$$+\frac{1}{Q}\int_{x_{oi}}^{\infty}dx\int_{x}^{\infty}\kappa_{ic}\left(\frac{x'-x_{o1}}{\beta_1}\right)c_{oi}(x')e^{-\left[k_1+\kappa_{ic}\left(\frac{x'-x_{o1}}{\beta_1}\right)\right]t}$$

$$\times\left\{\frac{6x(x'-x)}{x'^3-x_{o1}^2(3x'-2x_{o1})}\right\}dx' \qquad (39)$$

Denoting the first term on the right side of Eq. 39 as A and integrating yields:

$$A=\frac{k_1m_{oi}}{Q\left(1+\kappa_{ic}\frac{\beta_i}{\beta_1}t\right)^{\alpha_i}}e^{-\left[k_1+\kappa_{ic}\left(\frac{x_{oi}-x_{o1}}{\beta_1}\right)\right]t} \qquad (40)$$

If we denote the second term as B, interchanging the order of integration gives:

$$B=\frac{6\kappa_{ic}}{Q}\int_0^{\infty}\left(\frac{x'-x_{o1}}{\beta_1}\right)c_{oi}(x')e^{-\left[k_1+\kappa_{ic}\left(\frac{x'-x_{o1}}{\beta_1}\right)\right]t}$$

$$\times\frac{dx'}{x'^3-x_{o1}^2(3x'-2x_{o1})}\int_{x_{o1}}^{x'}x(x'-x)dx$$

$$=\frac{\kappa_{ic}}{Q}\int_0^{\infty}\left(\frac{x'-x_{o1}}{\beta_1}\right)c_{oi}(x')e^{-\left[k_1+\kappa_{ic}\left(\frac{x'-x_{o1}}{\beta_1}\right)\right]t}dx' \qquad (41)$$

after partial integration. When $x'\leq x_{oi}$, we have $c_{oi}(x')=0$, and the range of integration in Eq. 41 is x_{oi} to infinity. Combining Eqs. 39 and 41 leads to:

$$U_i(t)=\frac{k_1m_{oi}}{Q\left(1+\kappa_{ic}\frac{\beta_i}{\beta_1}t\right)^{\alpha_i}}e^{-\left[k_1+\kappa_{ic}\left(\frac{x_{oi}-x_{o1}}{\beta_1}\right)\right]t}+\frac{\kappa_{ic}}{Q}\int_{x_{oi}}^{\infty}$$

$$\times\left(\frac{x'-x_{o1}}{\beta_1}\right)c_{oi}(x)e^{-\left[k_1+\kappa_{ic}\left(\frac{x'-x_{o1}}{\beta_1}\right)\right]t}dx' \qquad i=2,\,3 \quad (42)$$

which can be evaluated easily by numerical integration. The total lumped concentration of extract products is:

$$U(t)=U_1(t)+U_2(t)+U_3(t) \qquad (43)$$

Since the two-fragment reactions are negligible at low temperatures ($T\leq 633$ K), $U(t)$ based upon Eq. 34 is:

$$U(t)=\frac{k_1}{Q}m_oe^{-k_1t} \qquad (44)$$

where m_o is the summation of m_{o1}, m_{o2}, and m_{o3}.

Results and Discussion

Model simulation and parameters

The extract samples for different times during a thermolytic extraction run were first treated by evaporation and then analyzed with gel permeation chromatography. The lumped concentrations are plotted in Figure 2. Based on the calibration results with polystyrene standards and naphthalene, the MWDs of coal extract were determined at different times for temperatures 613, 633, 653 and 673 K, as shown in Figures 3-6. All the MWDs decrease with time as the extractable aromatic units in the coal are removed. For all the samples at different temperatures, the positions of the three peaks in these graphs are essentially fixed. At low temperatures ($T\leq 633$ K) the ratios of peak heights are relatively constant for the samples. At higher temperatures ($T>633$ K), however, the low MW peaks grow at the expense of the higher MW peaks. For each extract

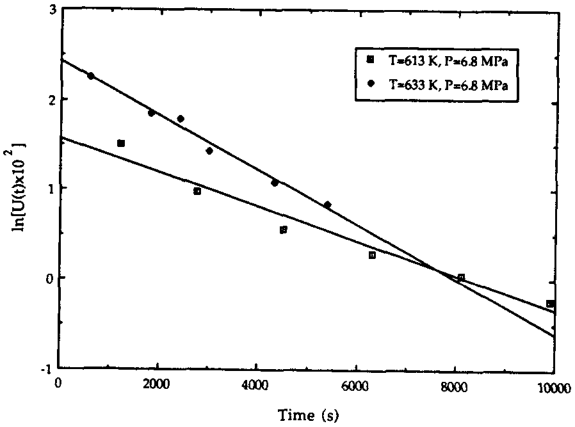


Figure 2. Plot of ln *U(t)* vs. time for experimental data of lumped extract concentration for the runs at 613 and 633 K.

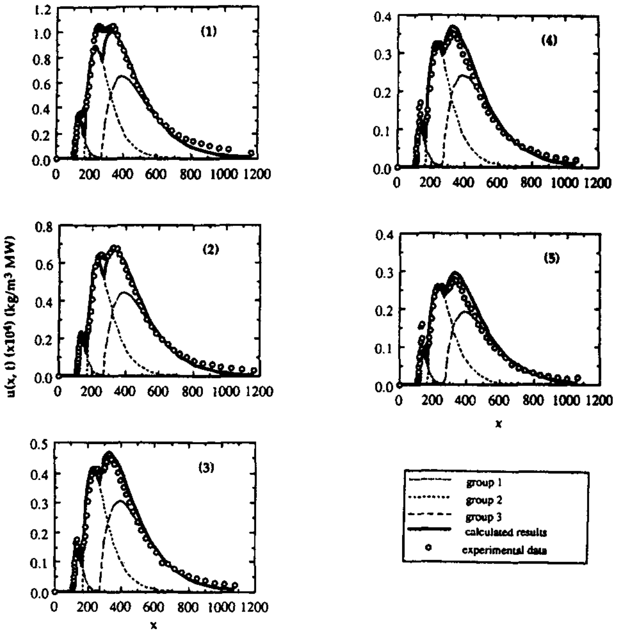


Figure 3. Model calculations vs. experimental data for MWDs at 613 K for Samples 1-5.

Sample numbers refer to Table 1.

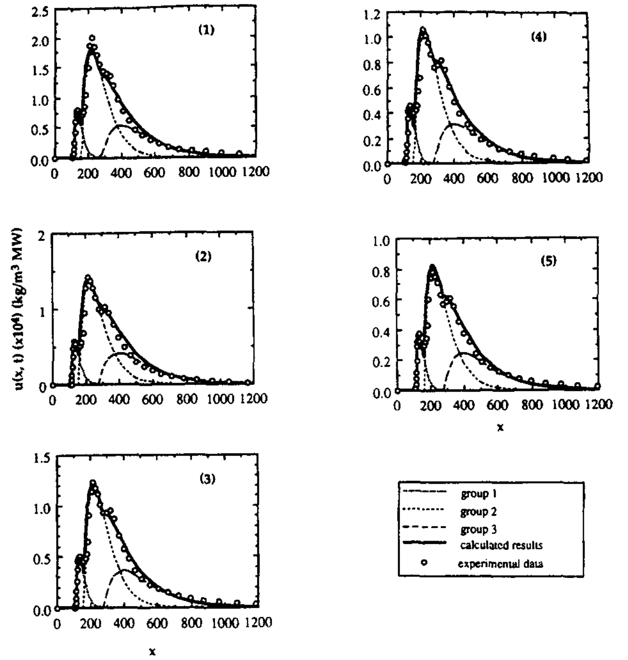


Figure 4. Model calculations vs. experimental data for MWDs at 633 K for Samples 1-5.

Sample numbers refer to Table 1.

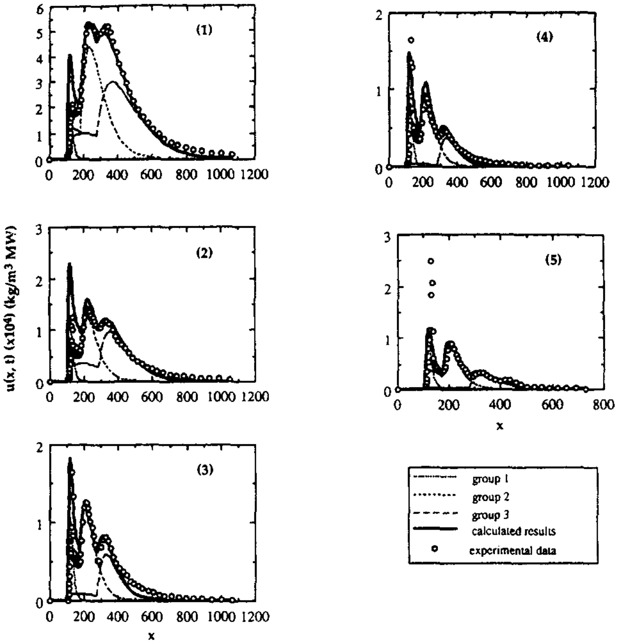


Figure 6. Model calculations vs. experimental data for MWDs at 673 K for Samples 1-5.

Sample numbers refer to Table 1.

sample the weight-average MWs, calculated with GPC software, are summarized in Table 1. At low temperatures ($T \leq 633$ K) the average MWs are relatively constant with time, but at higher temperatures ($T > 633$ K) the weight-average MWs decrease significantly with time. Based on this experimental evidence from our differential flow reactor we infer that at $T \leq 633$ K, two-fragment reactions are not significant. Also, the rate constants of one-fragment reactions are independent of MW, that is, $k_i(x) = k_i$. At $T > 633$ K, both one-fragment reactions and two-fragment reactions are important.

Two types of parameters appear in this model: those in the

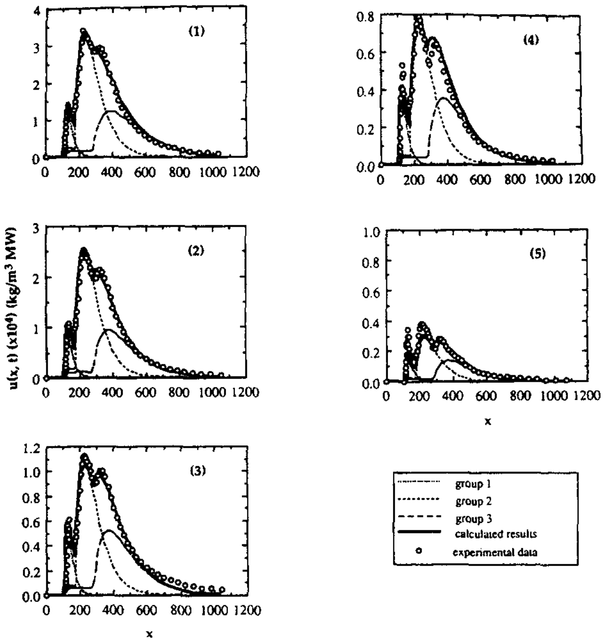


Figure 5. **Model calculations vs. experimental data for MWDs at 653 K for Samples 1-5.**

Sample numbers refer to Table 1.

Table 1. Extract Samples from Thermolysis of Illinois No. 6 Coal at 6.8 MPa

Temp. (K)	Sample	Time (s)	Conc. ($\times 10^2$ kg/m^3)	$M_{w,avg}$*
613	1	1,800	4.7	307
613	2	3,360	2.6	311
613	3	5,100	1.7	307
613	4	6,900	1.3	304
613	5	8,700	1.1	294
613	6	10,500	0.91	298
633	1	600	11.9	261
633	2	1,800	8.4	256
633	3	2,400	7.9	267
633	4	3,000	6.8	260
633	5	4,200	5.1	264
633	6	5,400	4.2	254
653	1	1,560	7.2	271
653	2	2,400	4.9	266
653	3	3,600	2.3	254
653	4	5,400	1.6	240
653	5	7,500	1.1	224
673	1	1,980	14.1	286
673	2	3,900	3.3	293
673	3	5,100	2.1	222
673	4	6,600	1.4	207
673	5	8,400	1.2	181

* Weight-average molecular weight from the experimental results of MWDs.

Table 2. Temperature-Independent Parameter Values for the Model

Parameter	α	β_1	β_2	β_3	x_{01}	x_{02}	x_{03}
Values	2	20	62	120	115	170	275

three gamma functions describing the initial MW distributions of extractable polyaromatic units in coal, and the rate coefficients for the thermolysis of the extractable groups. Darivakis et al. (1990) reported that the range of α is 1.3-3.0, but the most likely value is 2. In our simulations we fixed $\alpha = 2$ for the three gamma functions. Based on Eq. 5 and the shape of experimental MWDs at the four temperatures, the parameters x_{oi} and β_i were estimated (Table 2) by minimizing the deviations between the moments of the MWD data and model computations (Eqs. 3-5). The values of α, x_{oi}, and β_i are all independent of temperature.

To determine $k_i(T)$, the time-dependent concentration data were fitted by an exponential expression based on the lumped expression for $U(t)$, Eq. 44. The relationships between totally lumped extract concentration, $U(t)$, and extraction time at 613 and 633 K are shown in Figure 2. The first-order rate constants of one-fragment reactions for 613 and 633 K are the same for the three extractable polyaromatic units, that is, $k_i = k_1(T)$, and were determined from the lumped data to be 1.3×10^{-4} and 2.2×10^{-4} s^{-1}, respectively.

Finally, values of m_{oi} for the three gamma functions were obtained by fitting the model with the time-dependent MWD data at 613 and 633 K using Eq. 32 (Figures 3-4). Once the parameters are fixed, only time is allowed to vary in these plots. While the model predicts instantaneous MWDs, the experimental MWDs are averaged over the 10 min sampling time, accounting for some of the deviations between theory and experiment.

Since the peak positions and shapes of the three gamma functions for our experimental results are relatively fixed for all temperatures, the x_{oi} and β_i are considered unchanged at higher temperatures ($T = 653$, 673 K). The rate constants of one-fragment reactions at 653 and 673 K were estimated from the values of $T = 613$ and 633 K by the Arrhenius equation. By fitting the model with the experimental results at 653 and 673 K, the constants κ_{ic} and the initial concentrations of the three extractable polyaromatic units, m_{oi}, were determined. The values of these temperature-dependent parameters are listed in Table 3. Figures 5-6 compare the simulated and experimental results and show good agreement. The minimum value of the inverse rate coefficients, 10^4 s, is much greater than the residence time, 10 s, justifying the neglect of secondary reactions of the extract molecules in our continuous-flow differential reactor.

Table 3. Temperature-Dependent Parameter Values for the Model

Temp. (K)		613	633	653	673
k_i	$i = 1, 2, 3$	1.3×10^{-4}	2.2×10^{-4}	3.0×10^{-4}	3.7×10^{-4}
κ_{2c}		3×10^{-7}*	1.7×10^{-6}*	5.3×10^{-6}	1.6×10^{-5}
κ_{3c}		5.3×10^{-7}*	1.6×10^{-6}*	4.5×10^{-6}	1.2×10^{-5}
m_{o1}		0.0033	0.0080	0.010	0.013
m_{o2}		0.032	0.049	0.064	0.081
m_{o3}		0.029	0.041	0.047	0.056
Σm_{0i}	$i = 1, 2, 3$	0.064	0.098	0.12	0.15
C_o**		0.066	0.100	0.11	0.14

* Estimated by extrapolation of values at 653 K and 673 K.

** The values of C_o were measured from experimental runs.

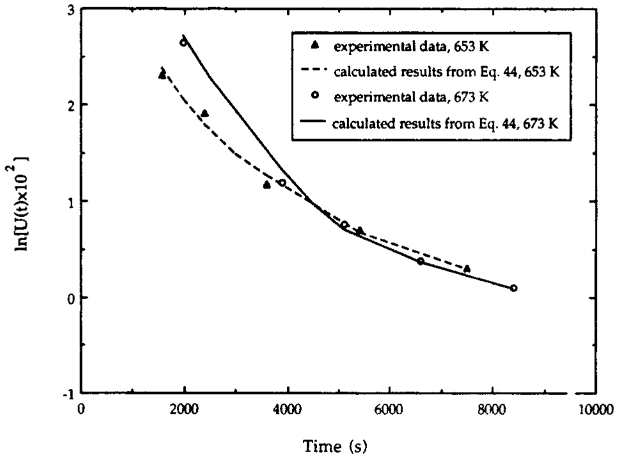


Figure 7. Experimental data vs. values calculated for lumped extract concentrations at 653 and 673 K.

The above simulation results were compared to experiments by two other methods. The initial zero moments, m_{oi}, were determined from the MWDs, while the total lumped extract concentration, C_o, was measured by UV absorbance spectrophotometry of the reactor effluent. The good agreement between Σm_{oi} and C_o is shown in Table 3. Moreover, the experimental results of extract-concentration history at 653 K and 673 K, which are not fitted well by first-order kinetics, are satisfactorily represented in Figure 7 by the lumped concentration based on Eqs. 43 and 44. The approach we have adopted in this study thus satisfies required conditions of internal consistency.

The Arrhenius plot of the rate constants for both one- and

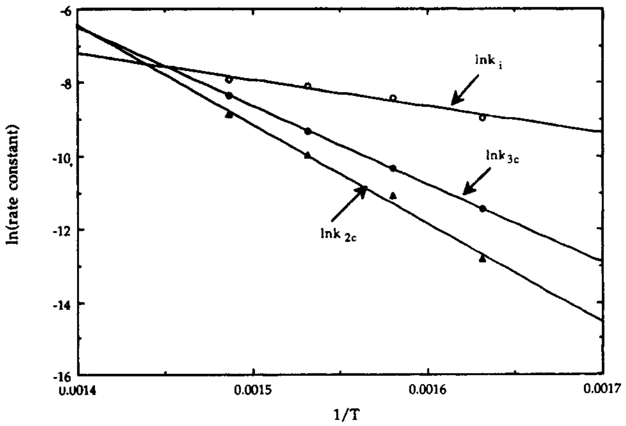


Figure 8. Arrhenius plot of rate coefficients for one- and two-fragment reactions.

The rate constants for the two-fragment reactions are based on average molecular weights for Groups 2 and 3, respectively.

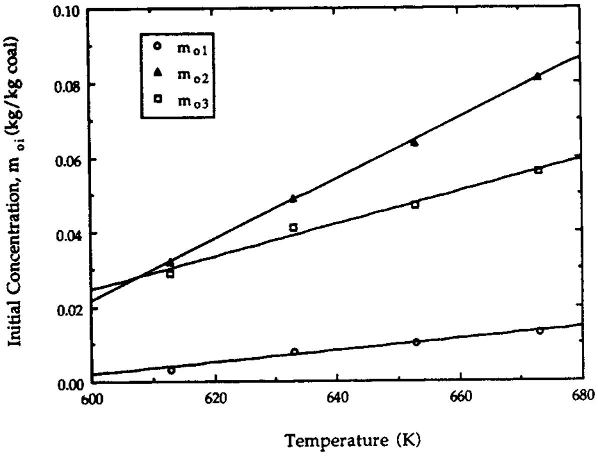


Figure 9. Initial concentrations of three groups of reactive components at four temperatures (613-673 K).

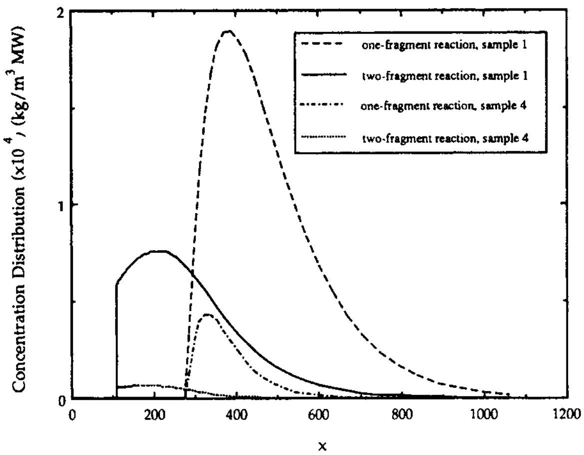


Figure 10. Computed concentration distributions of extract from one- and two-fragment reactions for group 3 at 673 K.

two-fragment reactions is presented in Figure 8. From the plot the activation energies are estimated:

$$\text{One-fragment reactions} \quad E_i = 58 \text{ kJ/mol} \quad i = 1, 2, 3$$
$$\text{Two-fragment reactions} \quad E_2 = 205 \text{ kJ/mol} \quad E_3 = 191 \text{ kJ/mol} \tag{46}$$

where the subscript represents the group number. The results for rate constants summarized in Table 3 imply that one-fragment reactions are always significant for the entire temperature range 613–673 K, whereas two-fragment reactions are negligible at $T \leq 633$ K, but become very important at $T = 673$ K.

The initial concentrations of the extractable polyaromatic units, m_{oi}, are plotted vs. temperature in Figure 9. For the four temperatures the three groups demonstrate a linear dependence of m_{oi} on T.

The first reaction step in any direct liquefaction of coal is thermolysis to smaller units. This usually requires high temperatures to overcome the dissociation energies involved in the rupture of different covalent bonds in the macromolecular structure of coal (Petrakis and Grandy, 1983). Comparing the activation energies from our study with the dissociation energies of coal-network bonds helps to understand the thermolytic extraction process. According to Stein (1981) for model compounds the strongest C-C bond is found in bibenzyl (~255 kJ/mol) and the strongest C-O bond is found in benzyl phenyl ether (~218 kJ/mol). If phenyl rings are replaced by polyaromatic clusters these bonds can be substantially weakened. In coal-derived structures, these effects are expected to reduce the dissociation energy as much as 200 kJ/mol. For example, the dissociation energy for $(C_6H_5)_3C\text{-}C(C_6H_5)_3$ is 46 kJ/mol (Petrakis and Grandy, 1983). This implies that in the one-fragment reactions of our experiments only weak C-C and C-O bonds or other weak bonds are ruptured. In the two-fragment reactions, stronger C-C and C-O bonds or other bonds are ruptured. Since polyaromatic-ring structures are much stronger, they are stable under the conditions of our study.

According to Haenel (1992), the average polyaromatic unit in bituminous coal contains between 14 and 20 carbon atoms corresponding to three to five condensed rings based on the results from solid-state ^{13}C n.m.r., X-ray diffraction, electron microscopy and degradative reactions. The weight-average MWs of extract products in our study (Table 1) range from 181 to 311, which corresponds closely to Haenel's (1992) results for the average polyaromatic unit in bituminous coal. This supports the concept that the MWDs of the extract products represent polyaromatic units in the initial coal.

The weight-average MWs of extracts in Table 1 are nearly constant at low temperature ($T \leq 633$ K) and decrease with time for higher temperatures ($T > 633$ K). This indicates the occurrence of two-fragment, cracking reactions. Model computations in Figure 10 show that the products from one-fragment reactions have gamma distributions of polyaromatic units. The products from two-fragment reactions shift the MWDs of polyaromatic units toward lower MW, which is caused by the rupture of the linkages between polyaromatic units.

The coal composition determined from fitting the model calculations and the experimental data is for one type of coal (Illinois No. 6) and for low (< 14%) conversion. If temperature increases above 673 K, more bonds will be broken. If this occurs, the concentration and proportion of different groups of polyaromatic units will change and rate coefficients will become more complicated functions of MW. It is expected that experimental investigation at higher temperatures can provide more insight into the coal structure and mechanism of coal liquefaction. A study of the effects of pressure and presence of hydrogen-donor solvent should also yield useful information.

Coal structure

The experimental data supports the model of three gamma distributions representing the coal initial composition. The first gamma function is a narrow and small peak (with smallest β and m_{oi}). The second, with the largest concentration, is a moderately wide peak. The third represents a broad MWD function (with the largest β). The discussion of Derivakis et al. (1990) invites an interpretation of the three peaks in terms of the polyaromatic units in the coal macromolecular network based on an average coal molecule. Evidence based on the position (i), width (ii) and size (iii) of the peaks suggests that they represent different groups of polyaromatic units bonded by one, two or more linkages in the initial coal structure.

(i) According to Darivakis et al. (1990), $\bar{x}$ is the average MW of the polyaromatic unit. We consider that the first gamma function represents the end polyaromatic unit, the second the regular polyaromatic unit and the third the cross-linked polyaromatic unit. The weight-average MW for the end unit, $\bar{x}_1$, is 155, near to a two- or three ring MW. For the regular unit $\bar{x}_2 = 292$, and for the cross-linked unit $\bar{x}_3 = 515$. The end polyaromatic unit contains fewer rings, while the cross-linked polyaromatic unit has more rings. These results show that larger units are more likely to be bonded with other units.

(ii) The variance for the gamma function is $\alpha\beta^2$ (Eq. 4). When α is fixed, the value of β denotes the width of the MWD. As Darivakis et al. (1990) pointed out, β is an index of the degree of the chemical heterogeneity in the macromolecular structure of coal. Large β values indicate a higher probability of finding kinetically dissimilar bonds within the coal structure. If the third gamma function represents the cross-linked polyaromatic units, a larger β should be expected. Table 2 shows that the third group of polyaromatic units has the largest β. The reason is that the cross-linked units have more linkages, which are of dissimilar bonds. Thus, the present results corroborate the Darivakis et al. theory.

(iii) Table 3 and Figure 9 show that the proportion of each gamma function, m_{oi}, is different and temperature dependent. The regular polyaromatic unit has the greatest concentration; the end polyaromatic unit has the smallest concentration. This result suggests that a large proportion of regular units and a small number of end units exist in the coal macromolecular network. Darivakis et al. (1990) hypothesized that the concentration of the regular polyaromatic units is higher than the concentrations of end and cross-linked polyaromatic units, and that the average number of linkages, which must rupture to form an extract molecule, is close to two. Our experimental results thus are in general agreement with the Darivakis et al. analysis.

Conclusions

The major intent of this work has been to present an approach that yields fundamental information about the kinetics of thermolytic reactions. The monitoring of molecular-weight distributions as they develop with time gives detailed, dynamic data that can be interpreted with continuous-mixture kinetics. Our results in the temperature range of 613 K–673 K for Illinois No. 6 coal suggest that at $T \leq 633$ K, one-fragment reactions dominate over two-fragment reactions and that the single rate constant for thermolysis is not a function of the MW of extractable polyaromatic units in coal. At $T > 633$ K, both one- and two-fragment reactions are important and the rate constants for two-fragment reactions are functions of MW. The model satisfactorily describes the experimental results for the time evolution of MWDs of extract products from coal thermolytic extraction with supercritical tert-butanol. The parameters, resulting from the fitting of the model with the experimental results, are in general agreement with the existing information about coal structure. Whether the conceptual framework of the mathematical model will apply when temperature and pressure are increased, or for other varieties of coal or in the presence of hydrogen-donor solvent, are questions worthwhile to address in future studies.

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Notation

$A(x)$ = continuous distribution of coal components
$c_i(x, t)$ = concentration distribution of *i*th group of extractable polyaromatic units in coal, kg/kg coal MW
$c_{oi}(x)$ = initial distribution of coal components for Group i
$C_i(t)$ = totally lumped concentration of extractable polyaromatic units for *i*th group in coal, kg/kg coal
$C(t)$ = summation of $C_i(t)$
k_i = rate constants for one-fragment reactions for *i*th extractable group, s^{-1}
κ_{ic} = proportional constants for two-fragment reactions for *i*th extractable group, s^{-1}
$k_{ic}(x)$ = rate constants for two-fragment reactions for *i*th extractable group, s^{-1}
m_{oi} = zero moment of gamma function in Eq. 1, kg/kg coal
m_{o1} = initial zero moment of the gamma function for Group 1
P = pressure, MPa
Q = flow rate of solvent, m^3/s
t = time, s
T = temperature, K
$u_i(x, t)$ = concentration distribution of extract products from *i*th extractable group in coal based on kg dried coal sample, kg/m^3 MW
$U_i(t)$ = totally lumped extract concentration of extract products from *i*th extractable group, kg/m^3
$U(t)$ = summation of $U_i(t)$
x = molecular weight
x_{oi} = minimum molecular weight for Group *i* in the gamma function
y = dimensionless valuable for x

Greek letters

α_i = parameter in the gamma function for *i*th extractable group, Eq. 1
β_i = parameter in the gamma function for *i*th extractable group, Eq. 1
γ^2 = variance of the gamma distribution for Group *i*
ϵ = bed void fraction
τ = residence time based on reactor volume, s
$v(x,x')$ = function of $A(x')$ that cracks to $A(x)$

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