Dynamics of the Extract Molecular-Weight Distribution in Supercritical Thermolysis of Coal: Continuous-Mixture Kinetics

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Introduction

In this paper experimental molecular-weight distribution data for coal thermolysis at 340 °C and 360 °C in a differential flow reactor are interpreted by assuming that decomposition reaction rate expressions are continuous with molecular weight. Three groups of chemical species, representing polyaromatic compounds bound in the coal network by one, two, or more chemical linkages, are extracted simultaneously during the thermolysis reaction. The three groups are gamma distributions in molecular weight (Darivakis et al., 1990). The data support the hypothesis that the first-order rate coefficient is independent of molecular weight, and that as a consequence the MWD has a similar shape during the time of extraction.

When the number of chemical species involved in a chemical process reaches a large number, e.g., 10^2-10^3, it is convenient to consider a property of the components to be a continuous variable. For example, the molecular weight, the number of carbon or oxygen atoms, or the boiling point of the different species can be considered a continuum of values, rather than discrete numbers. One line of inquiry is to formulate and solve the equations governing the chemical kinetics, or thermodynamics, of the continuous mixture, and to test the theory by experimentally measuring the frequency of occurrence of the continuous variable (e.g., the molecular weight distribution). Another possible program is to average the governing equations to obtain relations for lumped variables that can be measured experimentally for the bulk mixture. Both these approaches have been explored for continuous-mixture thermodynamics. The theoretical issues of continuous mixture and lumping kinetics for chemical reactions have been addressed in numerous mathematical studies, but their use to interpret experimental data has been limited. In the present work we wish to apply concepts from continuous-mixture kinetics to thermolytic coal extraction.

Some essential ideas of continuous-mixture kinetics provide a framework for the theoretical analysis of the data given below. The averaging, or lumping procedure shows how the kinetics governing the MWDs can lead to overall, lumped rate expressions used in most earlier studies of coal thermolysis. The overlapping groups of extractable compounds in the coal matrix present, in some cases, complications for lumping mathematics. The low temperature data ($T \leq 360$ °C) are readily explained by first-order expressions with rate coefficients that are independent of molecular weight and identical for the three groups of extractable compounds. The lumping in this case provides overall first-order rate expressions with the same rate coefficient.

Theory

In the present continuous-mixture approach the MW is considered to be a continuous variable. If x is the MW then the MWD is $c_i(x,t)$, where at time t, $c_i(x,t)dx$ is the concentration in the MW interval (x, x+dx). The integral over all x is the lumped concentration, expressed in units of mass (kg) of extractables per mass (kg) of coal sample.

A central question of continuous-mixture kinetics is whether the reaction order is preserved by the lumping procedure. We follow Aris (1989) in answering this question for kinetics that describe coal thermolytic extraction when secondary reactions are negligible. For the flow reactor used here the residence time is too short for further (secondary) reactions of the extract molecules to occur. We generalize the earlier development by considering that several groups of chemical species are extracted simultaneously from the coal. If the process consists of parallel reactions of nth-order at each molecular weight, x, then the governing differential equation for the differential coal batch is

$$dc_i(x,t)/dt = -k_i(x)\ [c_i(x,t)]^n \qquad (1)$$

with initial condition $c_i(x,t=0) = c_{io}(x)$. The rate coefficient is $k_i(x)$ and the subscript i refers to the ith group of compounds that react. The solution is

$$c_i(x,t) = c_{io}(x)\ [1 + (n-1)\ c_{io}(x)^{n-1}\ k_i(x)t]^{1/(n-1)} \qquad (2)$$

where in the limit as n --> 1, $c_i(x,t)$ approaches an exponential. The averaged, or lumped, concentration is given by

$$C(t) = \Sigma_i \int_o^\infty c_i(x,t)dx \qquad (3)$$

and

$$C_o = \Sigma_i \int_o^\infty c_{io}(x,t)dx \qquad (4)$$

The lumped nth-order kinetics equation corresponding to this system,

$$dC(t)/dt = -K\ [C(t)]^n \qquad (5)$$

with initial condition $C(t=0)=C_o$ has the solution

$$C(t) = C_o[1 + (n-1)\ C_o^{n-1}\ Kt]^{1/(n-1)} \qquad (6)$$

where K is the rate constant. The solutions for C(t) and the lumped expression of $c_i(x,t)$ are identical when

$$c_{io}(x)^{n-1}\ k_i(x) = K\ C_o^{n-1} \qquad (7)$$

Thus for first-order kinetics (n=1) we must have $k_i(x) = K$, independent of molecular weight, for the lumped expression to be first-order. If the rate coefficient is not constant with x, then the resulting lumped kinetics can be other than first-order.

Ho and Aris (1987) showed how lumping first-order continuous-mixture kinetics can lead to any reaction order between one and two, depending on the initial condition. We apply their reasoning here to the chemical groups extracted from coal. Consider that the rate coefficient is proportional to MW, i.e., $k_i(x) = k_{1i}x$, where k_{1i} is independent of x. A general initial MWD that covers many possible forms for $c_{io}(x)$ is the gamma distribution (or Pearson Type III distribution; see Abramowitz and Stegun, 1968),

$$c_{io}(x) = m_{oi}\, y_i^{\alpha i-1} \exp(-y_i)/\beta_i\, \Gamma(\alpha_i) \qquad (8)$$

where $y_i = (x-x_{io})/\beta_i$. The zero moment of the distribution is m_{oi}. The average position of the peak, $x_{ai} = x_{oi} + \alpha_i\beta_i$, and its variance, $\sigma_i^2 = \alpha_i\beta_i^2$, are the first and second moments. The position of the peak maximum is $x_{pi} = x_{oi} + \beta_i(\alpha_i-1)$. The distribution is equivalent to that used by Ho and Aris (1987) if $\beta=1/\alpha$ and $m_{oi}=1$. In the limit as $\alpha_i \to \infty$, $c_{io}(x) = m_{oi}\delta(x-x_{io})$, so that only components having a single molecular weight are reacting, and the rate coefficient has a constant value at that MW.

With the solution for $c_i(x,t)$, i.e., the case when n=1 in Eq. (2) above, we can integrate to obtain the lumped concentration,

$$C(t) = \Sigma \int_0^\infty c_{io}(x)\exp(-k_{1i}xt)dx = \Sigma\, C_i(t) \qquad (9)$$

with

$$C_i = m_{oi}(1 + \beta_i k_i t)^{-\alpha i} \qquad (10)$$

The rate expression is obtained by differentiation,

$$dC/dt = \Sigma\, dC_i/dt \qquad (11)$$

where

$$dC_i/dt = -m_{oi}\alpha_i\beta_i k_{1i}(C_i/m_{oi})^{(\alpha i+1)/\alpha i} \qquad (12)$$

In the special case that only one species group is reacting, this last equation simplifies to a power-law rate expression,

$$dC/dt = -\, KC^{\phi} \qquad (13)$$

where $\phi = (1 + \alpha)/\alpha$. As α increases from one to infinity, the order of the lumped kinetics expression decreases from two to one. For the more general case when several groups react independently, however, no simple kinetics expression appears. One can perform the lumping operation numerically, and determine a reaction expression empirically.

For our experimental procedure, the extractable component MWD and concentration of coal, $c(x,t)$ and $C(t)$, are not measured directly. Rather, the concentrations of solubilized <u>extract</u> (both MWDs and lumped concentrations) in the solvent leaving the reactor are monitored with time. The time evolution of these concentrations is described by mass balances written for the reactor. The use of a differential bed of fine coal particles allows the reactor analysis to be simplified considerably. The convective term in the mass balance can be approximated as the volumetric flow rate multiplied by the gradientless concentration in the fixed bed. For the experimental conditions the residence time in the heated zone of the reactor is much less than the characteristic reaction time (reciprocal of the rate coefficient). Thus the accumulation term can be neglected, and the mass balance becomes simply

$$u_i(x,t) = k_i(x)\; f[c_i(x,t)]/Q \qquad (14)$$

where $u_i(x,t)$ is the MWD of extract in the solvent, Q is the volumetric flow rate of solvent, and $f[c_i(x,t)]$ represents the rate expression. The lumped extract concentration is

$$U(t) = \Sigma \int_0^\infty u_i(x,t)dx \qquad (15)$$

Various rate expressions can be hypothesized for f[] and substituted into the equation for U(t). Similar to the discussion above of the coal batch extraction, one concludes that only for special cases

will simple lumped mass balance expressions be found for U(t). For example, at temperatures 360 °C and below, the rate is first-order with rate coefficients, k_o, independent of x and identical for the extractable groups. For this case it is straightforward to demonstrate that the lumped rate is first-order with rate coefficient equal to k_o; thus,

$$u(x,t) = k_o\ c_o(x)\ \exp(-k_o t)/Q \tag{16}$$

and

$$U(t) = k_o\ C_o\ \exp(-k_o t)/Q \tag{17}$$

which can be compared with the lumped reactor exit concentration.

Experiments

The experimental apparatus and procedure have been described previously (Zhang et al., 1992). Supercritical fluid thermolysis of Illinois No. 6 coal is conducted in a fixed-bed reactor with flowing solvent. The lumped, reactor-exit concentration is measured by spectrophotometric absorbance in a flow cuvette. Thus we select t-butanol as the solvent, since it does not interfere with the uv absorbance of aromatic coal extraction products. The thermolysis process is carried out at constant pressure, 6.8 MPa, and constant flow rate, 0.17 cm^3/sec. Coal particles are small enough that intraparticle diffusion resistance is not significant, and the solvent flow rate is large enough that external mass transfer resistance is negligible (Zhang et al., 1992). The coal is pretreated by supercritical extraction at 300 °C to remove physically extractable constituents. Coal extract samples of 100 ml were collected during the thermolysis process, and concentrated by evaporation of t-butanol under vacuum. The MWDs of these samples, based on polystyrene molecular-weight standards, are determined by gel permeation chromatography with the uv detector set at 254 nm (Bartle et al. 1984).

Discussion of Results

The time evolution of extract MWDs for the temperatures 340 and 360 °C are provided in Figures 1. The two temperatures show MWDs whose shapes are similar at the different times, i.e., the ratio of peak heights, the position of peaks, and the average molecular weight are invariant with time. Such behavior can be described by assuming that the rate coefficient for the MWDs is independent of MW. The values of the first-order rate coefficients at the two temperatures, displayed in Table 1, give an energy of activation E_1 = 58 kJ/mol. The gamma distribution parameters, provided in Table 2, show that increasing the temperature changes only the zero moments. The concentrations for each group of extractable compounds, m_{oi}, shift due to the greater extraction at the higher of the two temperatures.

The comparison of the calculated and experimental MWDs is shown in Figure 2 for two samples. Only time changes during the course of the evolution of the MWDs; the parameters for the initial MWD in the coal and the rate coefficients are constant. The agreement between the experimental data and the model calculations is consistently good for <u>all</u> samples during the course of a run.

Figure 3 shows experimental data for total, lumped extract concentrations for the thermolytic extractions at two temperatures. The lumped concentrations are determined by the flow-through spectrophotometer at the reactor exit. The model calculations shown in Figure 3 are based on Eq. (17) and the same rate constant values (Table 1) determined from the time evolution of the MWDs. The

satisfactory agreement between theory and experiment, for both the lumped and MWD data, supports the validity of the explanation of coal thermolytic extraction that we have proposed.

Conclusion

A continuous-flow thrmolysis reactor, in which supercritical t-butanol contacts a differential bed of coal particles, provides sequential coal-extract samples that are analyzed by HPLC gel permeation chromatography to obtain time-dependent MWD data. The coal thermolysis experimental data support an interpretation of the results based on considering the molecular weight of extraction products as a continuous variable. This continuous-mixture theory suggests that three groups of coal components are extracted independently. At temperatures 340 °C and 360 °C the MWDs maintain a similar shape during the semibatch extraction. This indicates that first-order kinetics dominate, and that the rate coefficient is independent of molecular weight. The lumped extract concentration is monitored at the reactor exit by continuous uv-absorbance spectrophotometry. Both MWD and lumped concentration data are described by consistent expressions based on the same rate coefficient.

Acknowledgements

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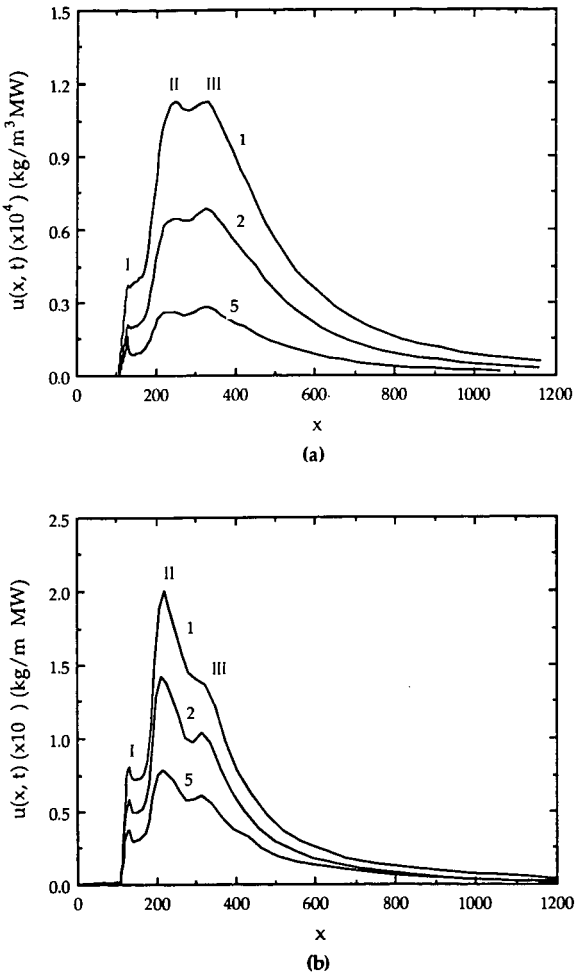

Figure 1. Time evolution of MWDs for thermolytic extractions of coal at 340 °C (a) and 360 °C (b). Samples 1, 2, and 5 were collected at the reactor effluent at times 30 , 56, and 145 min for runs at 340 °C and 10, 30, and 70 min for runs at 360 °C.

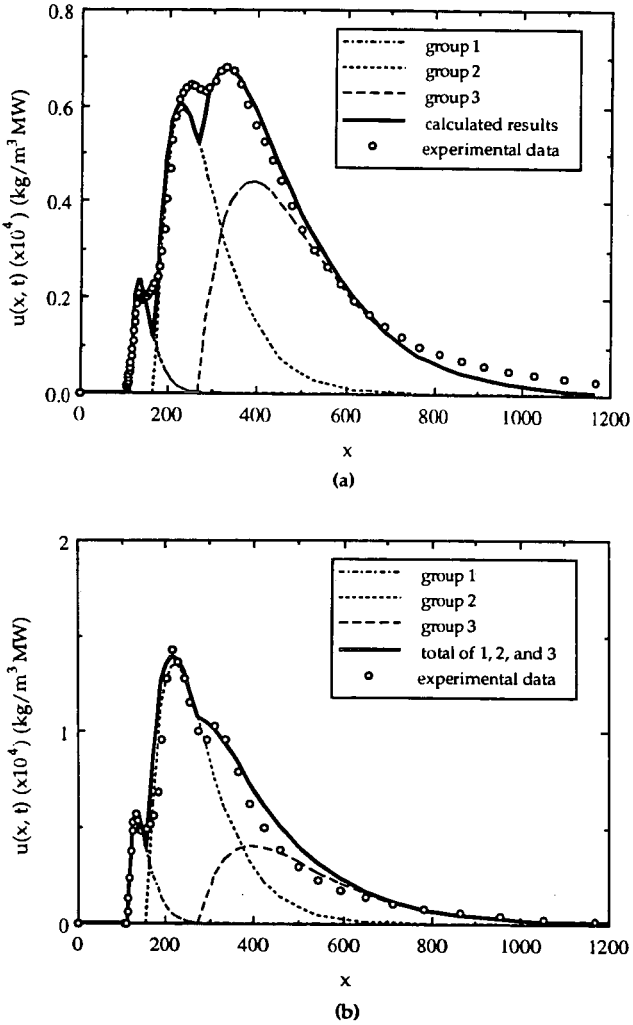

Figure 2. Comparison of model calculations and experimental data for MWDs for Sample 2 of runs at 340 °C (a) and 360 °C (b), respectively.

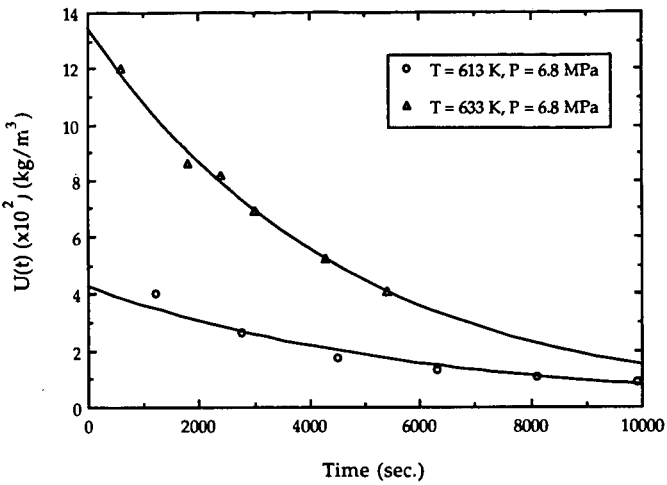

Figure 3. The experimental data of total extract concentrations at 613 K and 633 K and their exponential fit based upon kg of initial coal sample mass.

Table 1. The values of the first-order rate constants from the model

Temperature (K)	Rate Constant, k_i, sec^{-1}	Activation Energy, kJ/mol
613	0.00015	58
633	0.00022	

Table 2. The parameter values for the gamma distributions

		$\alpha = 2$	
	$m_{o1} = 0.0033$ kg/kg coal	$\beta_1 = 20$	$x_{o1} = 120$
T = 613 K	$m_{o2} = 0.032$ kg/kg coal	$\beta_2 = 62$	$x_{o2} = 170$
	$m_{o3} = 0.029$ kg/kg coal	$\beta_3 = 120$	$x_{o3} = 275$
		$\alpha = 2$	
	$m_{o1} = 0.0080$ kg/kg coal	$\beta_1 = 20$	$x_{o1} = 120$
T = 633 K	$m_{o2} = 0.049$ kg/kg coal	$\beta_2 = 62$	$x_{o2} = 170$
	$m_{o3} = 0.041$ kg/kg coal	$\beta_3 = 120$	$x_{o3} = 275$