CHEMICAL KINETICS AND TRANSPORT PROCESSES IN SUPERCRITICAL FLUID EXTRACTION OF COAL

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FINAL REPORT

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SUMMARY

The overall objective of this project was to study the supercritical fluid extraction of hydrocarbons from coal. Beyond the practical concern of deriving products from coal, the research has provided insights into the structure, properties, and reactivities of coal. Information on engineering fundamentals of coal thermolysis and extraction, including physical and chemical processes, is presented in this final report. To accomplish the goals of the project we developed continuous-flow experiments for fixed-bed samples of coal that allow two types of analysis of the extract: continuous spectrophotometric absorbance measurements of the lumped concentration of extract, and chromatographic determinations of molecular-weight distributions as a function of time.

A kinetic model has been derived for the primary reactions of coal thermolysis both in the presence and absence of excess hydrogen-donor solvent. The model, an extension of previous published mechanisms, is based on a proposed free-radical mechanism following classical free-radical chemistry. First, free-radical reactions are assumed to occur both on the solid surface and in the liquid film around the coal particle. Second, the elementary reactions (initiation, propagation, and termination) are formulated to describe the overall process. The model, based on assumptions of adsorption-desorption equilibrium and stationary-state concentration of free radicals, includes second-order and first-order terms. The second-order term is a measure of the effect of hydrogen transfer on coal conversion. It is important in the initial stage of liquefaction and becomes negligible when donor solvent concentration vanishes.

The supercritical tert-butanol extraction of Illinois No. 6 bituminous coal involves both physical and chemical processes. Extraction rates were estimated by continuously measuring the spectrophotometric absorbance (at 235 nm) of the effluent from a fixed-bed flow reactor. The experiments were conducted in the temperature range of 553-633 K and at 6.8 MPa constant pressure by programmed-temperature techniques. A model for which the extractable compounds in the coal are represented by two groups of components, undergoing parallel first-order reactions, satisfactorily describes the experimental data. The kinetics data indicate that the first group is extracted by a physical process, which occurs below 573 K. The second group is extracted via a thermal decomposition, or thermolytic, reaction (with an apparent average activation energy of 54 kJ/gmol), which is dominant above 573 K.

A kinetic model representing the primary reactions of coal thermolysis is tested with the experimental data of extraction of coal in a flow reactor. The experiments were performed at supercritical conditions (593, 613, 633, 653 K and 6.8 MPa) with a mixed solvent of tetralin and tert-butanol. The coal sample (Illinois No. 6) was pretreated to eliminate the physically-extractable compounds. The kinetic model including first- and second-order terms successfully described the

experimental data. The kinetic parameters, first- and second-order rate constants along with energies of activation, were obtained by regression of the experimental data. For comparison, an experiment at 533 K and 6.8 MPa with pure tert-butanol was performed. The result was interpreted reasonably well by a first-order kinetic model. The results of this study show that the addition of small amount of hydrogen-donor solvent strongly increases coal thermolysis rates and coal conversion. The effect of hydrogen transfer is expressed in the second-order term, which has its largest effect during the initial stage of coal thermolysis.

Thermolysis of coal yields a complex mixture of many extract products whose molecular-weight distribution (MWD) varies with time for continuous-flow, semibatch experiments. The flow reactor with a differential, fixed bed of coal particles contacted by supercritical t-butanol was employed to provide dynamic MWD data by means of HPLC gel permeation chromatography of the extract. The experimental results, time-dependent MWDs of extract molecules, were 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 for one- and two-fragment reaction are determined from the experimental data. The significant effect of temperature on the kinetics of the extraction was explained in terms of one- and two-fragment reactions in the coal. At lower temperatures (613 and 633 K) single product reactions dominate, but at higher temperatures (653 and 673 K) more bonds in the coal are broken and the two-product reactions become significant. The detailed MWDs were 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.

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CHAPTER 1 INTRODUCTION

The existence of large coal reserves in the United States suggests that conversion of coal to liquid hydrocarbons is an attractive alternative to purchasing petroleum abroad (Lumpkin, 1988). The extraction of hydrocarbons from coal by supercritical fluid processes has been proposed by Berkowitz (1985), and by the British National Coal Board (Whitehead and Williams, 1975; Wilhelm and Heddon, 1985). Much research has been performed over the last 25 years on producing liquid chemicals and fuels from coal by a variety of processes. Supercritical fluid extraction of coal (Sunol and Beyer, 1990; Kershaw, 1989; Wilhelm and Hedden, 1985) has received attention because of the greater dissolution power of the supercritical fluid compared to gases in conventional pyrolysis. Supercritical liquefaction typically involves the thermal breakdown of coal and subsequent dissolution of the pyrolysis products in the solvent. Depending on the solvent, supercritical extraction can be successfully performed at relatively low temperatures (593-673 K), moderate to high pressures (6-30 MPa), and in batch or continuous modes. The method shows potential for commercial application, although most studies have been limited to research on thermodynamics, chemical mechanisms, and the structure of the coal and extract. An important feature of supercritical coal extraction that has received limited attention in the literature concerns the kinetics of the dissolution process, especially quantitative interpretation of experimental data.

The research directed specifically to the kinetics of supercritical coal extraction (Slomka and Rutkowski, 1982; Deshpande et al., 1986) is based on the non-polar solvent, toluene. To our knowledge, there is little published information on supercritical extraction with polar or hydrogen-donor solvents, although some research on alcohol extraction of coal (Ross and Blessing, 1979; Makabe and Ouchi, 1981) has been reported. Higher conversions were reported with low molecular weight alcohols than with hydrocarbons under equivalent conditions (Amestica and Wolf, 1984; Vasilakos et al., 1985), possibly due to hydrogen-donor action. Hydrogen-donor solvents may exert a stronger dissociating or depolymerizing action on coal than non-donor solvents, thus increasing the yield of extractable coal material (Vasilakos et al., 1985; Kuznetsov et al., 1990). We found in our earlier work (Zhang et al., 1991) that with Illinois No. 6 coal extraction in supercritical tert-butanol ($P_c=3.97$ MPa, $T_c=506.2$ K), there was some chemical interaction between the coal and the solvent, even at the comparatively low temperature of 573-623 K. Similar results were reported by Makabe and Ouchi (1981) and by Kuznetsov et al. (1990). The chemical reaction kinetics and mechanism for the extraction of coal with alcohols, however, are still unclear, and further research is needed.

A dynamic method using UV spectrophotometry to monitor continuously the extraction processes in a continuous-flow reactor has been successfully used to study kerogen extraction from shale with toluene (Triday and Smith, 1988), and lignin and cellulose extractions from wood with tert-butanol (Goto et al. 1990a and 1990b; Reyes et al., 1989). From such data mathematical models were developed to describe chemical reactions and transport processes during these supercritical processes. The results suggested that the dynamic method may be suitable to investigate quantitatively the kinetics processes for extraction of coal.

In addition to the overall objective to study the supercritical fluid extraction of hydrocarbons from coal, the research has provided insights into the structure, properties, and reactivities of coal, as well as into the practical issue of deriving products from coal. The project provided information on engineering fundamentals of coal treatment, including the physical and chemical processes associated with coal transformations and the products of the transformations. Two monitoring techniques were developed for the continuous-flow experiments for fixed-bed samples of coal: (1) spectrophotometric absorbance, which lumps all extract together, and (2) HPLC gel permeation chromatography to determine molecular-weight distributions. Both methods provide data on coal conversion that can be used to formulate kinetic expressions for the extraction process.

In Chapter 2 we describe the experimental method used in this investigation. Details on sample preparation, extraction procedure, and monitoring techniques are provided.

In Chapter 3 we propose a free-radical mechanism as a basis for determining overall kinetics of the thermolytic extraction. Coal macromolecules are thermally degraded into free radicals, which are stabilized by repolymerization (e.g., char formation) or by being capped off by hydrogen atoms. In our experiments with pure t-butanol as the solvent, conversions are low, since this solvent is but a weak hydrogen donor for the coal conversion. Coal conversion, or liquefaction, is facilitated by using hydrogen-donor solvents, which contribute hydrogen atoms to react with free radicals that result from the thermal degradation. The free-radical mechanism yields a rate expression for hydrogen-donor thermolysis. This expression reduces to nondonor kinetics as the concentration of hydrogen-donor species vanishes.

Chapter 4 presents a simplified kinetics study of supercritical tert-butanol extraction of Illinois No. 6 bituminous coal. Extraction rates were estimated by continuously measuring the spectrophotometric absorbance (at 235 nm) of the effluent from a fixed-bed flow reactor. The experiments were conducted in the temperature range of 553-633 K and 6.8 MPa constant pressure by programmed-temperature techniques. A model for which the extractable material is represented by two groups of components, undergoing parallel first-order reactions, satisfactorily describes the experimental data. This chapter is based on the publication by Zhang et al. (1993a).

Chapter 5 describes an investigation of supercritical thermolysis of coal in the presence of hydrogen-donor solvent. We describe experiments with tetralin, a strong hydrogen donor, mixed with the weak hydrogen donor, t-butanol. Coal conversions are observed to increase dramatically with the fraction of tetralin in the solvent. The extraction rate is satisfactorily explained by the free-radical mechanism. This chapter is based on the publication by Wang et al. (1993a).

In Chapter 6 experimental molecular-weight distribution (MWD) data for coal thermolysis in the temperature range 340-400 °C are interpreted by a mathematical model based on continuous-mixture kinetics (Zhang et al., 1993b; Wang et al. 1993b). 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 is considered to be a continuum of values, rather than discrete numbers for the mixture. The MWDs are quantitatively explained by the continuous-mixture kinetics, and are shown to be consistent with the conventional lumped kinetics data. This chapter is based on the publication by Wang et al. (1993b).

CHAPTER 2

EXPERIMENTS FOR SUPERCRITICAL FLUID COAL EXTRACTION AND THERMOLYSIS

In this study the extraction of coal was carried out dynamically in a semi-continuous reactor, which allows a continuous stream of supercritical fluid to pass through the fixed bed of coal particles. Experimental programmed-temperature runs were conducted in two ways: continuous heating up to a constant temperature, and two-step heating. In the continuous heating method the temperature of the reactor including the coal bed is increased at the rate of 8.4 K/min to the desired temperature, which is maintained until the end of a run. During all runs, flow rate and pressure were held constant. The temperature was in the range of 553-673 K. During the run the cooled liquid extract was directed into a flow-through cuvette of the spectrophotometer, and the absorbance was continuously monitored at 235 nm for the pure tert-butanol runs and 330 nm for the butanol-tetralin runs. Since there is an 8 minute time delay between the reactor and the UV detector in our apparatus, the time of the measured absorbance was corrected for the flow from the point of reactor exit to the absorbance measurement. For an apparatus essentially identical to ours it was found (Triday, 1988) that the effect of dispersion between reactor exit and the spectrophotometer is very small and can be ignored. After each run, the coal sample was vacuum-dried at 343 K to constant weight. The conversion is obtained from the weight measurements, which is defined as (Fong et al., 1983):

$$\% \text{Conversion} = 100 \left(\frac{\text{Dry wt. Coal} - \text{Dry wt. Residue}}{\text{Dry wt. Coal}} \right) \quad (2-1)$$

Experimental runs were conducted at different flow rates, 1.0×10^{-5} and 1.4×10^{-5} m³/min, while the other conditions were unchanged. It was found that the same conversions were obtained with the same extraction time. This indicated that external mass transfer resistance can be ignored when a flow rate of 1.4×10^{-5} m³/min is used. During the high-temperature experimental run (633 K) it was observed that there was a small amount of gas produced. Based on GC-MS analysis, Zhang et al. (1991) found that the gas product is composed mainly of butene from the decomposition of the solvent. At the experimental conditions, gas formation is negligible compared to the liquid product.

In calculations based on the mathematical models the concentration, q , of coal extract in the solvent at the exit of the reactor is at supercritical conditions, while the measured

concentration, q_a , in the cuvette is at 298 K and 0.1 MPa. The measured concentration was converted to supercritical conditions by the expression

$$q = (\rho/\rho_a) q_a \quad (2-2)$$

The flow rate in the reactor was corrected in the same way:

$$Q = (\rho_a/\rho) Q_a \quad (2-3)$$

where ρ_a is the density of the solvent at ambient conditions, equal to 787 kg/m³. The density of the solvent at supercritical conditions is ρ , which was estimated from the generalized correlation of Lee and Kesler (1975). Extract concentrations were always very low in our experiments so that solubility limitations were never an issue.

The most common solvents used in supercritical extraction of coal are toluene, alcohols, and tetralin (Kershaw, 1989). In our system the UV spectra of toluene in a blank-run (solvent only) interfered with the spectra of the extract. For tert-butanol an optimal wavelength was easily chosen by comparing the spectra of a coal-run and a blank-run (solvent only). Thus, tert-butanol was used in most of our experiments. For comparison, several extraction runs were performed at 633 K and 6.8MPa with toluene as the solvent instead of tert-butanol. The other experimental conditions for toluene runs are same as those for tert-butanol runs. The total conversion results showed small differences between tert-butanol runs and toluene runs. The sources of the technical grade solvents used in this research are as follows:

Tert-butanol	Fisher Scientific
Toluene	Fisher Scientific
Tetralin	Fisher Scientific

2.1. APPARATUS

The apparatus, shown in Figure 2-1, consists of four sections: (1) feed and pressurizing section, (2) extraction section, (3) temperature-control section, (4) flowrate-control and sample-collection section. To reduce the dissolution of nitrogen into the solvent, which can cause bubbles in the effluent, two parallel piston-type accumulators with a maximum volumetric capacity of about 8 liters were used. The stainless steel reactor is 0.45 m long and 0.029 m ID with 0.0048 m wall thickness. A preheater coil is wound around the reactor. The preheater-reactor assembly is placed in an electric furnace (1.4 kW maximum power) with a cylindrical cavity of 0.33 m length and 0.06 m ID. The coal particles are supported in the central part of the reactor by a 100 mesh

screen mounted on a hollow stainless-steel plug with a central hole of 0.00635 m ID and 0.18 m length.

A J-type thermocouple with the junction enclosed in a 1.6 mm ID stainless steel sheath is inserted up from the bottom of the reactor. The measuring point is about 2 mm below the lower screen of the coal-particle bed. The specified error limits are 2.2 K between 273 and 550 K and 0.75% in the range of 551 to 1500 K. Pressure is measured with an ASHCROFT gauge having a pressure range of 0 to 5000 psig. The temperature is controlled by a proportional-integral-derivative (PID) controller (Omega Model-2000) and continuously recorded by a Varian Model 9176 recorder.

The solvent flows downward in the bed of coal particles, through a Nupro 60 micron stainless steel filter (8), a pressure-reduction valve (23), and a water-cooling heater exchanger (17). Finally, the extract effluent flows through two rotameters (9, 11) and to the spectrophotometer. The latter instrument is a Perkin Elmer Lambda 4B UV/VIS, which is combined with a Fisher microflow cell to give a continuous recording of the absorbance.

2.2. COAL PROPERTIES AND SAMPLE PREPARATION

The Illinois No. 6 bituminous coal, DECS-2 (PSOC-1539), was used in this work. This coal was provided with the following ultimate analysis:

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

The coal sample was initially prepared by sieving to a particle size range of 5.89×10^{-4} m (20-28 mesh). The particles were then washed with distilled water to remove dust. Whitehead (1980) found that coal-particle sizes smaller than 2.36×10^{-3} m did not significantly affect the conversion. It was reported by Maddocks et al. (1979) that for coal-particle sizes below 1.6×10^{-3} m there was no relationship between the conversion and particle size. Intraparticle-diffusion resistance can thus be neglected for the particle size we chose. The coal samples were stored under water to prevent oxidation, and before extraction were vacuum-dried at 343 K to constant weight. An amount of pure tert-butanol, 1.0×10^{-2} m³/kg coal, was added to the dried coal samples, and after shaking the mixture of the coal and solvent for 40 minutes at 313 K, the solvent was poured out and fresh tert-butanol was added. This procedure, which removes some highly soluble compounds from the coal, was repeated until the absorbance of the solvent that was contacted with coal was below 0.1. The coal samples were vacuum-dried again at 343 K and weighed.

After this pretreatment procedure, which was necessary to achieve reproducible results, the coal samples were ready for extraction in the pure butanol runs.

Zhang et al. (1993a) in this laboratory reported on the supercritical extraction of coal with tert-butanol. They found that the extractable material is represented by two groups of components. A relatively small amount of coal (less than 3% by dry weight) can be extracted physically, and is solubilized at temperatures under 573 K. Most of the extractable material can only be extracted by the thermal decomposition of the coal network and the subsequent dissolution of thermolysis products in the solvent. In the later studies, to focus on the study of supercritical thermolytic extraction of coal, the sieved coal was physically extracted to depletion at 573 K and 6.8 MPa with tert-butanol. The temperature of 573 K was found to give essentially complete extraction of the physically-extractable material in a reasonable time and to minimize the extent of thermal decomposition. The physically-extracted sample was vacuum-dried at 343 K to constant weight. After this treatment the coal samples were stored in brown sample bottles under nitrogen until ready for extraction. The physically-extracted samples were used in the hydrogen donor solvent study and continuous-mixture theory study

2.3. CONTINUOUSLY MONITORING THE EXTRACT.

The composition of coal is so complex that it is impossible to determine the time-dependent concentration of each component in the coal extract. Our method is to measure the total coal extract concentration with time by continuously monitoring the absorbance of the effluent at a wavelength in a flow-through spectrophotometer. We scanned the effluents from blank runs (i.e., when coal is absent) and coal runs in the preliminary experiments. The results showed that: (1) the absorbance spectra (190-900 nm) of the extract do not change with time during a run; (2) the absorbance spectra (190-900 nm) of the extract do change at different temperatures. The first evidence ensures that the absorbance is a measure of the concentration of the extract during a run, and the second one requires that the calibration runs at different temperatures are necessary.

To convert absorbance to extract concentration, calibration based on the total weight loss of coal samples is necessary. The calibration runs were made with a large-size coal sample at different temperatures and constant pressure (6.8 MPa). Before a run the coal samples were pretreated as described previously. After extraction the coal was treated with the same procedure. The fraction extracted is obtained from the coal sample weight before and after extraction. Based on the absorbance of coal extract in the effluent at 235 nm for pure butanol runs and 330 nm for tetralin-butanol runs and the weight loss of the coal samples, a calibration curve for diluted samples of the collected effluent was constructed for each temperature run. The results for pure butanol runs are shown in Figure 2-2. The absorbance was measured at 235 nm for pure butanol runs and 330 nm for tetralin-butanol runs because at that wavelength (1) the absorbance of

solvent effluent is very low for blank runs (i.e. when coal is absent), (2) the coal extract has an absorbance large enough to monitor the concentration history continuously for all the experimental runs, and (3) the relation between concentration and absorbance is linear. The linearity was verified by the calibration runs (Wang et al. 1993a).

For different temperature runs the calibration curves are all straight lines with different slopes. The slope of the calibration curve (concentration versus absorbance) increases with increasing temperature of extraction. A plot of this slope versus temperature (Figure 2-3) for pure butanol runs is consistent with the concept that two groups of components are mixed together in the liquid extract. Lower temperatures produce more physically-extracted compounds, and higher temperatures produce more chemically-extracted compounds. As extraction temperature increases, the contribution of physically-extracted compounds to the absorbance diminishes. A third-order polynomial curve is drawn through the data in Figure 2-3 to illustrate how these two groups of compounds can mix to provide the resultant absorbance. The physically-extracted group gives a larger absorbance at 235 nm although the total weight loss of coal sample in lower temperature runs is small. The low-temperature extract must consist, therefore, of molecules with chromophoric groups that absorb strongly (Sommer, 1989; Bauman, 1962). For the chemically-extracted group, more aromatic compounds are obtained because of the breakdown of the coal macromolecular network. Aromatic compounds have a prominent absorption band at 235 nm (Bauman, 1962). Bartle et al. (1986) also noted that the extract of supercritical fluid extraction of bituminous coal has a maximum absorption around 235 nm. These facts support the concentration measurement method using the absorption of coal extract at 235 nm with the aid of calibration curves.

2.4. 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 mx0.0075 m, of 100 and 500 Å pore size, respectively, packed with 5 mm 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 $1.0 \times 10^{-4} \text{ m}^3$ volume was concentrated to $0.5 \times 10^{-6} \text{ m}^3$ by evaporating excess tert-butanol solvent under vacuum at 323 K. Each concentrated sample then was dissolved in THF solvent for analysis. Since the extracts from our experiments have a relatively small molecular-weight range ($\text{MW} < 1000$), 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 on 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).

Narrow molecular-weight range polystyrene standards ($\text{MW} = 162 - 20,000$) 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 2-4 shows the calibration curve of MW versus 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 ($\text{MW} < 1000$) of coal extract in our experiments, however, Bartle et al. (1984) has 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 GPC software incorporating the polystyrene calibration data.

Figure 2-1 Schematic diagram of the apparatus: 1, solvent supply tank; 2, two pressurized feed tanks; 3, nitrogen cylinder; 4, pressure gauge; 5, electric furnace; 6, extrusion reactor; 7, thermocouple connection; 8, filter; 9, first flow meter; 10, gas-liquid separator; 11, second flow meter; 12, gas sampling tube; 13, water collector; 14, gas burner; 15, spectrophotometer; 16, collection vessel for effluent; 17, water-cooling heat exchanger; 18, collection vessel for pressure relief; 19, temperature controller; 20, vacuum gauge; 21, surge tank; 22, vacuum pump; 23, high-pressure valve.

Figure 2-2. Calibration curves at different temperatures (pressure = 6.8 MPa).

Figure 2-3. Effect of temperature on the slope of the concentration vs. absorbance lines (Figure 2-2).

Figure 2-4. Calibration curve of molecular weight, x , in the range 100 - 10000 based on narrow-MWD standards of polystyrene.

CHAPTER 3

FREE-RADICAL MECHANISM

3.1. INTRODUCTION

The complex kinetics of coal liquefaction result in the formation of numerous compounds. Much research has been devoted to determine liquefaction yields as a function of the rank and type of coal, whether or not a catalyst or solvent is used, and other operating conditions. Many investigators have studied the molecular composition of liquid products to characterize these materials and to make inferences about the structure of coal. Relatively few papers have paid attention to the detailed kinetics of coal liquefaction. Based on the assumption that many of the elementary reactions are similar and result in similar products, a few complex models have been proposed (Lee, 1979; Shah et al., 1981). The products are grouped into a small number of lumps that can be characterized by easily measured dependent variables (Amestica and Wolf, 1985; Weller et al., 1951). The most common groups are oil, asphaltenes, preasphaltenes, and residue, which are characterized by their solubility in different solvents. This approach reduces the complexities involved in product analyses, and thereby facilitates the representation of the actual reactions in terms of lumped kinetic models.

In the absence of strong hydrogen-donor solvent, first-order kinetics usually can describe the formation rate of dissolved product (Krevelen et al., 1951; Deshpande et al., 1986; Zhang et al., 1993a). When a strong donor solvent is used, for example, tetralin, the kinetic reactions are not as simple. Storch and his co-workers (1943) found that their results for a model based on first-order integral equations showed deviations from straight-line relations. Similar observations were also made by Liebenberg and Potgieter (Liebenberg and Potgieter, 1973) in their study on uncatalysed hydrogenation of coal. However, a first-order equation was justified by Weller (1951) on the basis of certain assumptions. By splitting the conversion curve into two straight-line portions on the basis of different reaction rates for the respective portions of coal, Falkum and Glenn (1952) justified first-order rates. Wiser (1968) successfully described experimental data for coal thermolysis by splitting the processes into two portions, of which the first part is second-order and the second part is first-order.

It has been generally accepted to describe coal liquefaction as a free-radical process (Stock, 1985). Curran et al. (1967) initially pointed out the significance of the relationship between the extent of the coal conversion to soluble products and the amount of hydrogen transferred to these products. This concept is supported by the general observation that free-radical reactions control the pyrolysis chemistry of most organic substances. General kinetic features of coal liquefaction have also been used to support this view (Neavel, 1982). A detailed consideration of the chemical

structure of coal and its reaction products also strongly suggests that free-radical reactions control coal chemistry. The aromatic and hydroaromatic units found in coal tars and liquids and presumed to be dominant structures in coal itself are known to be very reactive with free radicals. Moreover, the discovery of free radicals in coal by Uebersfeld et al. (1954) and the experimental results of electron-spin-resonance (ESR) spectrometry (Petrakis and Grandy, 1983) have provided further positive evidence.

Curran et al. (1967) proposed the first free-radical mechanism with five steps. More detailed mechanisms were proposed by Attar (1978) and Gun (1979a,b). In Attar's and Gun's models, the free-radical mechanism is viewed as consisting of three processes: initiation reactions, propagation reactions, and termination reactions. Although direct experimental verification is lacking, the models represent an interesting alternative to the other lumped models, and provide certain mechanistic information about coal liquefaction.

Our objective in this chapter is to develop a kinetic model, through a free-radical mechanism, which describes experimental data from thermolytic and supercritical extraction experiments. The result is a rate expression that includes first- and second-order terms representing parallel reactions of coal. The second-order term, which is mainly due to the hydrogen-transfer processes, is a measure of the effect of hydrogen transfer on coal conversion. An empirical rate equation of the same final form was employed by Kang et al. (Kang et al., 1980) to describe their coal liquefaction data. In Chapters 5, the proposed rate equation is tested with experimental data obtained from supercritical extraction of coal.

3.2. THEORETICAL BACKGROUND

Coal can be viewed as a molecular network of functional groups organized into tightly bound aromatic-ring clusters connected by weaker aliphatic and ether bridges (e.g., ethylene, oxyethylene, and oxymethylene). The basic reactions of coal liquefaction, governed by interrelated physical and chemical phenomena, are believed to involve free-radicals (Wiser, 1978). The types of products produced are determined by the reactions of these free radicals formed by bond breaking as coal is heated. In nondonor processes, or when the free radical has no access to an external hydrogen donor, the radicals may either abstract hydrogen from the already hydrogen-poor coal molecular network or combine with other large free-radical fragments and form a high molecular weight residue. When a hydrogen donor is present, the free radical may abstract hydrogen from the donor and form a relatively low molecular weight product. To establish unequivocally this generally accepted concept of coal liquefaction, many workers over the years have studied free radicals in coal by electron spin resonance (ESR) spectroscopy (Wooten et al., 1976; Petrakis and Grandy, 1983).

The proposed five-step reaction sequence of Curran et al. (1967) focused on the thermolysis of carbon-carbon bonds in coal molecules. In this sequence, the radicals $R_i^\bullet$ produced in the initial reaction, react with other coal molecules or with hydrogen-donor molecules, DH_2 , to form other radicals. A variety of recombination reactions terminate the chain reaction:

Although this mechanism is too simplified to describe the actual coal liquefaction processes, some of the conclusions are very interesting. They postulated the initial step in coal liquefaction to be thermal decomposition. This reaction produces a host of free radicals that are stabilized by capture of hydrogen atoms from donor molecules or from within the coal itself. Thus, if hydrogen donors of sufficient activity are present, stable molecules of lower molecular weight are formed. Although free radical formation is a thermolytic process, experimental results show that hydrogen-donor solvent or hydrogen transfer seems to promote thermal cleavage (Guin et al., 1975). Guin's results show that all the original coal particles physically disintegrate at 400 °C with a hydrogen-donor solvent (tetralin). The same coal at the same temperature with a nondonor solvent (paraffin oil) does not show physical disintegration. This means that thermal degradation is enhanced by the presence of hydrogen-donor solvent.

Gun et al. (1979a, b) developed a useful approach to examine the individual roles of temperature, hydrogen-donor solvent, and catalyst in the mechanism of liquefaction. The following free-radical mechanism was proposed, where P_m represents any material in the benzene solubility class, C_1 is material in the insoluble residue class, $R_m^\bullet$ represents small secondary radicals including $H^\bullet$, and TH is a hydrogen-donor molecule.

Initiation (thermal cleavage, molecular dimensions $m < n-m < n$)

Propagation (intermolecular rearrangement)

Termination

In this mechanism weak bonds in the coal molecular network are decomposed yielding free radicals $R_{n-m}^\bullet$ and $R_m^\bullet$ in the initial process. The free radicals formed in this stage can abstract hydrogen atom from hydrogen-donor molecule TH to form stable products. Products also can be produced through intramolecular and intermolecular rearrangement reactions. The following kinetic expression was derived,

$$\frac{d[P_m]}{dt} = \beta_1 C + \beta_2 C^2 + \beta_3$$

where β_1 , β_2 , and β_3 are functions of hydrogen donor concentration. The zero-order term, β_3 , is much smaller than $\beta_1 C$ and $\beta_2 C^2$. Three aspects of this mechanism can be modified and improved. First, the sites where all the free-radical reactions occur are not specified. Free-radical reactions occurring on the coal surface and in the liquid phase both may play important roles in the coal liquefaction processes (Finseth et al., 1979). Second, not all the processes by which the presence of hydrogen-donor solvent can enhance the thermal degradation of coal thermolysis are represented in this mechanism. Third, since most good hydrogen donors are hydroaromatic compounds (Whitehurst, 1979), the hydrogen-transfer can be described in greater detail. Tetralin, for example, is a model hydrogen donor from which a donor radical can be formed by abstraction of a hydrogen atom. This radical can continue to donate another hydrogen atom to form a stable molecule, dihydronaphthalene. In the free-radical mechanism proposed below these processes are included.

3.3. A MODIFIED FREE-RADICAL MECHANISM

The experimental results from ESR (Electron Spin Resonance) spectroscopy provide useful information for a description of the free-radical mechanism. Petrakis et al. (Petrakis et al., 1982; Petrakis and Grandy, 1983) made a systematic investigation of the free radicals during coal liquefaction. They found coal heated with naphthalene has the highest spin concentration, followed by the coal heated in tetralin, and then with the coal only (pyrolysis). The results agree with the expectation that naphthalene would not tend to quench free radicals as efficiently as

tetralin, which is a good hydrogen donor. But, why is the spin concentration of the coal-only run lower than that of the tetralin run? We reasoned that the presence of solvent can stabilize the free radicals to a certain degree. Thus, radicals formed in the thermal degradation will be more stable in solvent than in the pyrolysis run. This implies that the total concentration of free radicals is higher when a solvent is present. Some free radicals formed on the solid surface of coal particles could dissolve in the stagnant film of solvent after the initiation. Then, radicals both on the coal surface and in the stagnant film of solvent continue to undergo a series of chemical reactions to form stable products. Based on the above explanation the following mechanisms can be proposed.

3.3.1 The Case with Nondonor Solvent

In this mechanism $F_n^\bullet$ is a group of free radicals having molecular weight n , $F_{(n-m)}^\bullet$ is a group of free radicals with molecular weight $n-m$, and $P_m^\bullet$ is a group of free radicals of molecular weight m ; n , $n-m$, and m are not single molecular weights, but represent a range of values. In general, m is much smaller than n . The subscripts s and l denote coal surface and stagnant film of solvent respectively. In the initiation reaction, weak bonds in the macromolecular network are decomposed by thermal cleavage, yielding free radicals. In this stage thermal effects are the main driving force in initiating the extraction process, while subsequent progress will depend on the interaction of the coal-derived radicals. Thus the extent of the reaction, the conversion, is a measure of the primary and secondary formation and stabilization of radicals of such molecular dimensions as will be solvent-soluble. The free radicals formed in the initiation process will either migrate on the coal particle surface or dissolve into the surrounding stagnant film of solvent. Since there is no hydrogen-donor these radicals can be stabilized only through intramolecular or intermolecular rearrangements and lead to a group of products, denoted as P_{ml} and P_{ms} . The postulated reactions on the coal and in the solvent are as follows:

Reactions on coal surface

Initiation reaction (thermal cleavage, molecular dimensions $m < n-m < n$)

Propagation (intramolecular rearrangement)

Termination (intermolecular rearrangement)

Adsorption and desorption between solid surface and stagnant film of solvent

Reactions in the stagnant film of solvent

Propagation (intramolecular rearrangement)

Termination (intermolecular rearrangement)

Reaction between a free radical and coal, (4), is considered to be very important and is not included in some earlier models. The concept of this reaction has its origin in mechanisms for polymerization, where the free radicals readily react with monomers. Curran (1967) used this idea in his simplified mechanism. This type of reaction (H-atom abstraction) is perhaps the most thoroughly studied class of free-radical reactions. Activation energies for H transfer depend on the nature of the radical centers involved. Reactions involving only carbon-centered radicals tend to have intrinsic activation energies of up to 63 kJ/gmol, while for oxygen- and sulfur-centered radicals such activation energies may be distinctly lower (Stein, 1985)

3.3.2. The Case with Strong Donor Solvent

In this case, DH_2 is the hydrogen-donor solvent (e.g., tetralin);

DH• corresponds to a radical produced by abstraction of one hydrogen atom from the solvent molecule; D represents a molecule produced by abstraction of two hydrogen atoms. The free radicals formed in the initiation stage can be stabilized by capture of hydrogen atoms from donor molecules or from within the coal itself. There are three pathways available for such stabilization: (1) H-abstraction from the solvent or from a hydrogen-rich portion of the coal; (2) elimination of part of the radical molecule by associated group migration, or rearrangement to form another more stable structure; (3) a combination reaction such as condensation or alkylation with another molecule in the solvent, which could be a radical. The presence and type of hydrogen donors will determine the preferred reaction path (Whitehurst, 1979). These possible pathways are represented in the proposed mechanism. The coal-derived radicals ($F_n^\bullet$ and $P_m^\bullet$) are large (M.W. 300-3000) and contain several aromatic rings. Therefore they have a small translational motion. The donor molecules and radicals are smaller and much more mobile on the solid surface and in the solution. Hence, the abstraction reaction is more important than the intermolecular rearrangement reactions. Another function of donor solvent is to enhance the intermolecular rearrangement as a hydrogen carrier, that is, to move hydrogen atoms from one coal fragment to another. This is especially important for reaction (4), which is the key reaction through which the initiation reaction is enhanced by the solvent. Without donor solvent as a hydrogen atom carrier it is very difficult to transfer hydrogen atoms from the coal molecular network to $P_m^\bullet$.

Reactions on the coal surface

Initiation reaction (thermal cleavage, molecular dimensions $m < n-m < n$)

Propagation (intramolecular rearrangement)

Termination (intermolecular rearrangement)

Hydrogen abstraction from donor

Adsorption and desorption between coal surface and stagnant film

Reactions in the stagnant film of solvent

Propagation (intramolecular rearrangement)

Termination (intermolecular rearrangement)

Hydrogen abstraction from donor

3.4. RATE EQUATIONS

3.4.1. Assumptions

Based on the above mechanism a detailed kinetic analysis can be developed. To make the analysis tractable, the following assumptions are made:

1. For both free radicals and stable molecules, internal and external diffusion resistances are negligible for the coal particles.
2. Free-radical reactions account for all covalent-bond scission and formation processes and all hydrogen transfer processes.
3. All the elemental reactions except the processes of adsorption and desorption are treated as irreversible reactions
4. The processes of adsorption and desorption between solid surface and stagnant film of solvent are at equilibrium.
5. The stationary-state approximation applies to all free radicals.
6. The solvent is present in large excess. The product formed both on the coal surface and in the stagnant film is totally soluble in the solvent bulk phase.

Several additional assumptions that apply to specific cases are introduced later.

Assumption 4 is a critical assumption which is based on the following arguments. Free radicals in coal chemistry include highly reactive radicals, reactive delocalized radicals, and inert radicals (Stein, 1985). Highly reactive radicals do not possess resonance stabilization energy and are known to be highly reactive in radical-molecule reactions. Small radicals, such as H atom, hydroxyl radical, aryl radical, and alkyl radical, belong to this group. These radicals will be stabilized on the coal surface immediately after its formation. There will be no equilibrium between coal surface and solvent for highly reactive radicals. But this group is expected to constitute a small fraction of the free radicals because of the complex coal structure. Reactive delocalized radicals have a resonance stability resulting from odd-electron delocalization. These radicals are stable and can build up to relatively high concentration. Most coal-related radicals belong to this group. Inert radicals are very stable and can build up to very high concentrations (>0.02 M in coal pyrolysis mixtures Petrakis et al., 1982; Retcofsky et al., 1978) Of the above groups reactive delocalized radicals are probably most important in coal thermolysis. The reactions involving these radicals are relatively slow. For example, the rate constants of these radicals to abstract a H atom

from tetralin at 425 °C is between 100 to 10⁻³ s⁻¹ (Stein, 1985). Kinetic data of adsorption and desorption for free radicals are apparently not available. Based on the data for n-C₄H₁₀ absorbed on silica gel obtained at 50 °C (Schneider and Smith, 1968) a very approximate estimate suggests a rate constant of 10⁵ s⁻¹ at 425 °C. If these results are reasonable the equilibrium assumption, at least for delocalized radicals, seems valid.

3.4.2. Non-Donor Solvent Case

Applying the stationary-stage approximation to the F_n• radical gives

$$\begin{aligned} \frac{d[F_n\bullet]}{dt} = 0 = & k_1[C] - k_2[F_n\bullet]_s - k_3[F_n\bullet]_s + k_4[P_m\bullet]_s - k_5[F_n\bullet]_s[P_m\bullet]_s - k_6[F_n\bullet]_s^2 \\ & - k_{24}[F_n\bullet]_l - k_{25}[F_n\bullet]_l - k_{26}[F_n\bullet]_l[P_m\bullet]_l - k_{27}[F_n\bullet]_l^2 \end{aligned} \quad (3-1)$$

Neglecting second-order terms in the very low free-radical concentrations leads to

$$k_1[C] - k_2[F_n\bullet]_s - k_3[F_n\bullet]_s + k_4[P_m\bullet]_s - k_{24}[F_n\bullet]_l - k_{25}[F_n\bullet]_l = 0$$

Rearranging the above equation and using the adsorption-desorption equilibrium relations to convert free-radical concentrations on the coal surface to concentrations in the stagnant film, we obtain the following equation:

$$(k_2K_F + k_3K_F + k_{24} + k_{25})[F_n\bullet]_l - k_4K_P[P_m\bullet]_l = k_1[C] \quad (3-2)$$

Applying the stationary-state approximation to P_m• gives

$$\begin{aligned} \frac{d[P_m\bullet]}{dt} = 0 = & k_1[C] + k_3[F_n\bullet]_s - k_5[F_n\bullet]_s[P_m\bullet]_s - k_4[P_m\bullet]_s - k'_6[F_{(n-m)}\bullet]_s[P_m\bullet]_s \\ & - k_7[P_m\bullet]_s^2 + k_{25}[F_n\bullet]_l - k_{26}[F_n\bullet]_l[P_m\bullet]_l - k'_{26}[F_{(n-m)}\bullet]_l[P_m\bullet]_l - k_{28}[P_m\bullet]_l^2 \end{aligned} \quad (3-3)$$

Neglecting free-radical second-order terms yields

$$(k_3K_F + k_{25})[F_n\bullet]_l - k_4K_P[P_m\bullet]_l = -k_1[C] \quad (3-4)$$

Combining Eq.(3-2) and (3-4), and solving for [F_n•] and [P_m•] leads to

$$[F_n\bullet]_1 = \frac{2k_1[C]}{k_2K_F + k_{24}} \quad (3-5)$$

$$[P_m\bullet]_1 = \frac{k_1[C]}{k_4K_P} \left(1 + 2 \frac{k_3K_F + k_{25}}{k_2K_F + k_{24}} \right) \quad (3-6)$$

Many reactions in the mechanism contribute to the formation of products, but they are not equally important. In the absence of hydrogen-donor solvent the intermolecular reactions can be neglected due to the difficulty of hydrogen atoms moving from one free radical to another without a hydrogen-donor solvent as a hydrogen carrier. Hence, the formation rate of product can be expressed as

$$\begin{aligned} \frac{d[P_m]}{dt} &= k_2[F_n\bullet]_s + k_4[P_m\bullet]_s + k_{24}[F_n\bullet]_1 \\ &= (k_2K_F + k_{24})[F_n\bullet]_1 + k_4K_P[P_m\bullet]_1 \end{aligned} \quad (3-7)$$

Substituting Eq.(3-5) and (3-6) into Eq.(3-7) gives a first-order rate expression for coal liquefaction in the absence of hydrogen-donor solvent,

$$\frac{d[P_m]}{dt} = k_A [C] \quad (3-8)$$

where

$$k_A = \left\{ 3 + \frac{2(k_3K_F + k_{25})}{k_2K_F + k_{24}} \right\} \quad (3-9)$$

Eq.(3-8) has been used by several prior investigators to treat their experimental data (Krevelen et al., 1951; Deshpande et al., 1986; Zhang et al., 1991). This expression agrees also with Gun's result (Gun et al., 1979a) based on his free-radical mechanism and assumptions.

3.4.3. Strong Donor Solvent Case

Applying the stationary-state approximation to $DH\bullet$ yields

$$\begin{aligned}
\frac{d[\text{DH}\cdot]}{dt} = 0 = & k_{10}[\text{F}_n\cdot]_s[\text{DH}_2]_s - k_{11}[\text{F}_n\cdot]_s[\text{DH}\cdot]_s + k'_{10}[\text{F}_{(n-m)}\cdot]_s[\text{DH}_2]_s \\
& - k'_{11}[\text{F}_{(n-m)}\cdot]_s[\text{DH}\cdot]_s + k_8[\text{P}_m\cdot]_s[\text{DH}_2]_s - k_9[\text{P}_m\cdot]_s[\text{DH}\cdot]_s + k_{29}[\text{P}_m\cdot]_l[\text{DH}_2]_l \\
& - k_{30}[\text{P}_m\cdot]_l[\text{DH}\cdot]_l + k_{31}[\text{F}_n\cdot]_l[\text{DH}_2]_l - k_{32}[\text{F}_n\cdot]_l[\text{DH}\cdot]_l + k'_{31}[\text{F}_{(n-m)}\cdot]_l[\text{DH}_2]_l \\
& - k'_{32}[\text{F}_{(n-m)}\cdot]_l[\text{DH}\cdot]_l
\end{aligned} \tag{3-10}$$

which upon rearrangement may be written

$$\{ k_{10}[\text{F}_n\cdot]_s[\text{DH}_2]_s - k_{11}[\text{F}_n\cdot]_s[\text{DH}\cdot]_s + k_{31}[\text{F}_n\cdot]_l[\text{DH}_2]_l - k_{32}[\text{F}_n\cdot]_l[\text{DH}\cdot]_l \} + \tag{a}$$

$$\{ k_8[\text{P}_m\cdot]_s[\text{DH}_2]_s - k_9[\text{P}_m\cdot]_s[\text{DH}\cdot]_s + k_{29}[\text{P}_m\cdot]_l[\text{DH}_2]_l - k_{30}[\text{P}_m\cdot]_l[\text{DH}\cdot]_l \} + \tag{b}$$

$$\{ k_{10}'[\text{F}_{(n-m)}\cdot]_s[\text{DH}_2]_s - k_{11}'[\text{F}_{(n-m)}\cdot]_s[\text{DH}\cdot]_s + k_{31}'[\text{F}_{(n-m)}\cdot]_l[\text{DH}_2]_l - k_{32}'[\text{F}_{(n-m)}\cdot]_l[\text{DH}\cdot]_l \} = 0 \tag{c}$$

(3-11)

We know that (a) is the net formation rate of $\text{DH}\cdot$ by $\text{F}_n\cdot$ radicals, (b) the net formation rate of $\text{DH}\cdot$ by $\text{P}_m\cdot$ radicals, and (c) the net formation rate of $\text{DH}\cdot$ by $\text{F}_{(n-m)}\cdot$ radicals. From Eq. (3-11) the total formation rate of $\text{DH}\cdot$ is zero. To simplify the mathematical treatment, but without other justification, each of the independent terms (a), (b), and (c) is assumed equal to zero. Then the following relationships are obtained,

$$k_{11}[\text{F}_n\cdot]_s[\text{DH}\cdot]_s + k_{32}[\text{F}_n\cdot]_l[\text{DH}\cdot]_l = k_{10}[\text{F}_n\cdot]_s[\text{DH}_2]_s + k_{31}[\text{F}_n\cdot]_l[\text{DH}_2]_l \tag{3-12}$$

$$k_9[\text{P}_m\cdot]_s[\text{DH}\cdot]_s + k_{30}[\text{P}_m\cdot]_l[\text{DH}\cdot]_l = k_8[\text{P}_m\cdot]_s[\text{DH}_2]_s + k_{29}[\text{P}_m\cdot]_l[\text{DH}_2]_l \tag{3-13}$$

$$k_{11}'[\text{F}_{(n-m)}\cdot]_s[\text{DH}\cdot]_s + k_{32}'[\text{F}_{(n-m)}\cdot]_l[\text{DH}\cdot]_l = k_{10}'[\text{F}_{(n-m)}\cdot]_s[\text{DH}_2]_s + k_{31}'[\text{F}_{(n-m)}\cdot]_l[\text{DH}_2]_l \tag{3-14}$$

Applying the stationary-state approximation to $\text{F}_n\cdot$ radicals yields

$$\begin{aligned}
\frac{d[\text{F}_n\cdot]}{dt} = 0 = & k_1[\text{C}] - k_3[\text{F}_n\cdot]_s - k_2[\text{F}_n\cdot]_s + k_4[\text{P}_m\cdot]_s - k_5[\text{F}_n\cdot]_s[\text{P}_m\cdot]_s - k_6[\text{F}_n\cdot]_s^2 \\
& - k_{10}[\text{F}_n\cdot]_s[\text{DH}_2]_s - k_{11}[\text{F}_n\cdot]_s[\text{DH}\cdot]_s - k_{24}[\text{F}_n\cdot]_l - k_{25}[\text{F}_n\cdot]_l \\
& - k_{26}[\text{F}_n\cdot]_l[\text{P}_m\cdot]_l - k_{27}[\text{F}_n\cdot]_l^2 - k_{31}[\text{F}_n\cdot]_l[\text{DH}_2]_l - k_{32}[\text{F}_n\cdot]_l[\text{DH}\cdot]_l
\end{aligned} \tag{3-15}$$

From the previous discussion, we know that H-abstraction reactions are more important than the intermolecular and intramolecular rearrangement reactions. Hence, the terms involving $[DH\bullet]$ should be treated differently. Neglecting the second-order terms in free-radical concentrations, except for the terms with $[DH\bullet]$, and using Eq. (3-12) to replace $[DH\bullet]$ terms with $[DH_2]$ terms, allows Eq.(3-15) to be simplified to

$$k_1[C] - (k_2 + k_3)[F_n\bullet]_s + k_4[P_m\bullet]_s - 2k_{10}[F_n\bullet]_s[DH_2]_s - (k_{24} + k_{25})[F_n\bullet]_l - 2k_{31}[F_n\bullet]_l[DH_2]_l = 0 \quad (3-16)$$

utilizing the equilibrium relationships in Eq.(3-16) gives

$$\{(k_2 + k_3)K_F + (k_{24} + k_{25}) + 2(k_{31} + k_{10}K_FK_{DH_2})[DH_2]_l\}[F_n\bullet]_l - k_4K_P[P_m\bullet]_l = k_1[C] \quad (3-17)$$

Applying the stationary-state approximation to $P_m\bullet$ radicals yields

$$\begin{aligned} \frac{d[P_m\bullet]}{dt} = 0 = & k_1[C] + k_3[F_n\bullet]_s - k_4[P_m\bullet]_s - k_5[F_n\bullet]_s[P_m\bullet]_s - k_7[P_m\bullet]_s^2 - k_8[P_m\bullet]_s[DH_2]_l \\ & - k_9[P_m\bullet]_s[DH\bullet]_s + k_{25}[F_n\bullet]_l - k_{26}[F_n\bullet]_l[P_m\bullet]_l - k_{28}[P_m\bullet]_l^2 - k_{29}[P_m\bullet]_l[DH_2]_l \\ & - k_{30}[P_m\bullet]_l[DH\bullet]_l \end{aligned} \quad (3-18)$$

If we neglect the terms second-order in free radical concentration except the $DH\bullet$ terms, and use Eq.(3-13), Eq.(3-18) can be simplified to:

$$(k_3K_F + k_{25})[F_n\bullet]_l - \{k_4K_P + 2(k_8K_{DH_2} + k_{29})[DH_2]_l\}[P_m\bullet]_l = -k_1[C] \quad (3-19)$$

Combining Eq.(3-17) and Eq.(3-19), and solving for $[F_n\bullet]_l$ and $[P_m\bullet]_l$ gives

$$[F_n\bullet]_l = \frac{K_{F4} + K_{F5}[DH_2]_l}{K_{F1} + K_{F2}[DH_2]_l + K_{F3}[DH_2]_l^2} [C] \quad (3-20)$$

$$[P_m\bullet]_l = \frac{K_{F6} + K_{F7}[DH_2]_l}{K_{F1} + K_{F2}[DH_2]_l + K_{F3}[DH_2]_l^2} [C] \quad (3-21)$$

where the K_{F4} etc. are defined as follows:

$$K_{F1} = k_4 K_P(k_2 K_F + k_{24}) \quad (3-22)$$

$$K_{F2} = 2[(k_2 + k_3)K_F + (k_{24} + k_{25})](k_8 K_{DH2} + k_{29}) + k_4 K_P(k_{31} + k_{10} K_F K_{DH2}) \quad (3-23)$$

$$K_{F3} = 4(k_{31} + K_{10} K_F K_{DH2})(k_8 K_{DH2} + k_{29}) \quad (3-24)$$

$$K_{F4} = 2k_1 k_4 K_P \quad (3-25)$$

$$K_{F5} = 2k_1(k_8 K_{DH2} + k_{29}) \quad (3-26)$$

$$K_{F6} = k_1[(k_2 K_F + k_{24}) + 2(k_3 K_F + k_{25})] \quad (3-27)$$

$$K_{F7} = 2k_1(k_{31} + k_{10} K_F K_{DH2}) \quad (3-28)$$

Now, applying the stationary-state approximation to $F_{(n-m)}^\bullet$ yields

$$\begin{aligned} \frac{d[F_{(n-m)}^\bullet]}{dt} = 0 = & k_2[F_n^\bullet]_s - k'_6[F_{(n-m)}^\bullet]_s[P_m^\bullet]_s - k'_7[F_{(n-m)}^\bullet]_s^2 - k'_{10}[F_{(n-m)}^\bullet]_s[DH_2]_s \\ & - k'_{11}[F_{(n-m)}^\bullet]_s[DH^\bullet]_s + k_{24}[F_n^\bullet]_l - k'_{26}[F_{(n-m)}^\bullet]_l[P_m^\bullet]_l - k_{27}[F_{(n-m)}^\bullet]_l^2 \\ & - k'_{31}[F_{(n-m)}^\bullet]_l[DH_2]_l - k'_{32}[F_{(n-m)}^\bullet]_l[DH^\bullet]_l \end{aligned} \quad (3-29)$$

We simplify the above equation using Eq.(3-14) and neglect the terms second-order in free-radical concentration. Then

$$(k_2 K_F + k_{24})[F_n^\bullet]_l = 2(k_{10}' K_F K_{DH2} + k_{31}') [DH_2]_l [F_{(n-m)}^\bullet]_l = 0 \quad (3-30)$$

By substitution of Eq.(3-20) in Eq.(3-30), and solving for $[F_{(n-m)}^\bullet]$

$$[F_{(n-m)}^\bullet]_l = \frac{K_{F8} + K_{F9}[DH_2]_l}{K_{F1}[DH_2]_l + K_{F2}[DH_2]_l^2 + K_{F3}[DH_2]_l^3} [C] \quad (3-31)$$

where

$$K_{F8} = \frac{K_{F4}(k_2 K_F + k_{24})}{2(k_{10}' K_F K_{DH2} + k_{31}')} \quad (3-32)$$

$$K_{F9} = \frac{K_{F5}(k_2 K_F + k_{24})}{2(k_{10}' K_F K_{DH2} + k_{31}')} \quad (3-33)$$

The formation rate of product is the contribution of intramolecular and intermolecular rearrangement reactions and abstraction reactions. These three types of reaction influence the rate differently. In the case of strong donor solvent the most important reactions in forming product are the abstraction reactions. Also intermolecular rearrangement reactions are greatly enhanced by the donor solvent. But the probability of two identical free radicals reacting to form product is relatively small. Thus, we neglect the terms with $[P_m^\bullet]^2$, $[F_n^\bullet]^2$, and $[F_{(n-m)}^\bullet]^2$. Then the formation rate of product can be expressed as:

$$\begin{aligned} \frac{d[P_m]}{dt} = & 2k_8[P_m^\bullet]_s[DH_2]_s + 2k_{29}[P_m^\bullet]_l[DH_2]_l + k_2[F_n^\bullet]_s + k_4[P_m^\bullet]_s + k_{24}[F_n^\bullet]_l \\ & + k_5[F_n^\bullet]_s[P_m^\bullet]_s + k_{26}[F_n^\bullet]_l[P_m^\bullet]_l + k'_6[F_{(n-m)}^\bullet]_s[P_m^\bullet]_s + k'_{26}[F_{(n-m)}^\bullet]_l[P_m^\bullet]_l \end{aligned} \quad (3-34)$$

Substituting Eq.(3-20),(3-21), and (3-31) into Eq.(3-34) gives the final rate expression,

$$\frac{d[P_m]}{dt} = k_A [C] + k_B [C]^2 \quad (3-35)$$

where k_A and k_B are complicated functions of donor-solvent concentration and can be defined as follows:

$$\begin{aligned} k_A = & (k_4 K_P + 2(k_8 K_P K_{DH_2} + k_{29})[DH_2]_l) \frac{K_{F6} + K_{F7}[DH_2]_l}{K_{F1} + K_{F2}[DH_2]_l + K_{F3}[DH_2]_l^2} \\ & + (k_{24} + k_2 K_F) \frac{K_{F4} + K_{F5}[DH_2]_l}{K_{F1} + K_{F2}[DH_2]_l + K_{F3}[DH_2]_l^2} \end{aligned} \quad (3-36)$$

$$\begin{aligned} k_B = & (k_{26} + k_5 K_F K_P) \frac{(K_{F4} + K_{F5}[DH_2]_l)(K_{F6} + K_{F7}[DH_2]_l)}{(K_{F1} + K_{F2}[DH_2]_l + K_{F3}[DH_2]_l^2)^2} + \\ & (k'_{26} + k'_6 K_F K_P) \frac{(K_{F8} + K_{F9}[DH_2]_l)(K_{F6} + K_{F7}[DH_2]_l)}{(K_{F1} + K_{F2}[DH_2]_l + K_{F3}[DH_2]_l^2)^2} \end{aligned} \quad (3-37)$$

The rate expression (3-35) is the sum of first-order and second-order terms in coal concentration. This result is in accord with the empirical relation used by Kang et al., which satisfactorily described their experimental results for coal thermolysis. The expressions for k_A and k_B show the effect of hydrogen donor concentration, $[DH_2]$.

3.5. DISCUSSION

3.5.1. Nondonor Solvent Case

Eq.(3-35) is a generalization of the first-order rate expression, Eq.(3-8), for the case with nondonor solvent. In the absence of a donor solvent, the abstraction reactions will be diminished, and the intermolecular rearrangement reactions neglected due to the difficulty for hydrogen atoms transferring from one free radical to another without a hydrogen carrier. The derivation suggests that the second-order term is the contribution of the intermolecular rearrangement reactions. Hence, k_B can be taken as zero.

Now, consider k_A in Eq.(3-36). Substituting $[DH_2]_I = 0$, setting all the rate constants for both abstraction reactions and intermolecular rearrangement reactions equal to zero, and utilizing Eq.(3-25) yields

$$k_A = k_4 K_P \frac{((k_2 K_F + k_{24}) + 2(k_3 K_F + k_{25}))k_1}{K_{F1}} + \frac{2k_1 k_4 K_P (k_{24} + k_2 K_F)}{K_{F1}} \quad (3-38)$$

Applying Eq.(3-22) continues to simplify Eq.(3-38) to

$$\frac{d[P_m]}{dt} = k_A [C] \quad (3-8)$$

which is identical to Eq.(3-8).

3.5.2. The Effect of Solvent on the Rate Constants

It has long been known that the selection of the solvent has a large effect upon the process of coal thermolysis (Whitehurst et al., 1980). In general, the sources of hydrogen in a liquefaction process are H_2 , hydrogen-donor solvent, coal, and coal-derived materials such as hydrogen-rich fragments. A H_2 source is not included in the above mechanism. The demand for hydrogen is a result of free radicals generated during the thermolysis stage. The functions of hydrogen-donor solvent are twofold. First, since donatable hydrogen is available in hydrogen-donor solvent (Bate and Harrison, 1991) the free radicals are "capped" and stable species are produced. This function of the solvent is described in the mechanism for hydrogen abstraction reactions. Second, coal and some of the coal-derived fragments have been reported to be significant sources of hydrogen in themselves during coal liquefaction (Whitehurst, 1979). The presence of donor-solvent can effectively provide a means of hydrogen redistribution from relative hydrogen-rich portions of the

coal structure to hydrogen-lean portions via hydrogenation and dehydrogenation of the donor solvent.

The source of hydrogen is a function of the demand, and in generally follows a hierarchical mechanism with the most active H-donors receiving preference (Whitehurst, 1979). The rate of demand for hydrogen is greatest during the initial stage of liquefaction, when massive thermal fragmentation of the coal structure produces very large numbers of free radicals. From the mechanism, the second-order reaction is due mainly to the effect of hydrogen transfer by means of hydrogen-donor solvent and affects the liquefaction processes in the initial stage. The second-order term may thus be considered a consequence of hydrogen-transfer processes in coal liquefaction.

Since the rate constants are functions of the hydrogen-donor solvent, the kinetic study of coal liquefaction is simplified if the hydrogen-donor solvent concentration is in excess, and therefore unchanging.

3.5.3. The Limitations of the Model

The free-radical hypothesis is the foundation upon which the kinetic model is based. As is the case for most postulated chemical mechanisms, and especially for those in coal chemistry, the free-radical mechanism for liquefaction is based on evidence from numerous investigations. It is the accumulated evidence rather than the result of any one experiment that is conclusive. However, the conclusion that radical mechanisms must be a key factor under liquefaction conditions does not rule out the possibility that other mechanisms may also intervene and under certain circumstances, even become the dominant route to low molecular weight products. Those cases where it is evident that other mechanisms do intervene, for instance, by hydride transfer (Ross and Blessing, 1970), are not included in this model.

The mechanism proposed considers only three types of free radicals, which are in general different from each other in molecular weight. In reality the free radicals formed during thermal cleavage processes are widely distributed in molecular weight. Of the assumptions made perhaps the most critical are the concept of equilibrium between coal surface and solvent and the simplification of Eq.(3-11) for the radical concentration $[DH\cdot]$.

3.6. CONCLUSION

Kinetic equations based on a free-radical mechanism have been proposed for coal thermolysis. The reactions employed to develop the rate equations represent the primary reactions of coal thermolysis in the presence of excess donor solvent. It was shown that:

1. The proposed mechanism is different from previous ones in two aspects. First, all the free-radical reactions are considered to occur in both coal (solid) and in solvent (liquid); second, the

two types of elementary reaction proposed by Curran et al.(1967), which are the reactions between free radicals and coal network and the reactions involving donor radicals, have been combined with the others proposed by Gun et al. (1979a).

2. The proposed mechanism leads to a rate equation which includes second-order and first-order terms. The model is similar to the one proposed empirically by Kang et al. (1980).
3. The second-order rate is a measure of the hydrogen-transfer effect and is significant in the early stages of the coal thermolysis.
4. The rate constants in the model are functions of hydrogen-donor solvent concentration.

3.7. NOMENCLATURE

$[C]$	Concentration of reactive components in coal particles
$[F_n^\bullet]_s$	Concentration of free radicals with molecular weight dimension of n on the coal surface
$[F_n^\bullet]_l$	Concentration of free radicals with molecular weight dimension of n in the stagnant film of solvent
$[P_m^\bullet]_s$	Concentration of free radicals with molecular weight dimension of m on the coal surface
$[P_m^\bullet]_l$	Concentration of free radicals with molecular weight dimension of m in the stagnant film of solvent
$[F_{(n-m)}^\bullet]_s$	Concentration of free radicals with the molecular weight dimension of $n-m$ on the coal surface
$[F_{(n-m)}^\bullet]_l$	Concentration of free radicals with the molecular weight dimension of $n-m$ in the stagnant film of solvent
$[DH_2]_s$	Concentration of hydrogen atom donor solvent on the coal surface
$[DH_2]_l$	Concentration of hydrogen atom donor solvent in the stagnant film of solvent
$[DH^\bullet]_s$	Concentration of radicals produced by abstraction of a hydrogen atom from donor solvent molecules on the coal surface
$[DH^\bullet]_l$	Concentration of radicals produced by abstraction of a hydrogen atom from donor solvent molecules in the stagnant film of solvent
$[P_m]$	Concentration of product dissolved in the solvent
k_A	First-order rate constant
k_B	Second-order rate constant
X_m	Maximum conversion of coal thermolysis
f_A	Pre-exponential factor for the first-order reaction

f_B	Pre-exponential factor for the second-order reaction
$[C]$	Concentration of reactable material in coal based on per gram of coal
K_F	Equilibrium constant for $[F_n^\bullet]_s$ and $[F_n^\bullet]_l$
K_P	Equilibrium constant for $[P_m^\bullet]_s$ and $[P_m^\bullet]_l$
K_{DH2}	Equilibrium constant for $[DH_2]_s$ and $[DH_2]_l$
K_{DH}	Equilibrium constant for $[DH^\bullet]_s$ and $[DH^\bullet]_l$

CHAPTER 4

KINETICS OF COAL THERMOLYSIS

4.1. INTRODUCTION

Much research has been performed over the last 25 years on producing liquid chemicals and fuels from coal by a variety of processes. Supercritical fluid extraction of coal (Sunol and Beyer, 1989; Kershaw, 1989; Wilhelm and Hedden, 1985) has received attention because of the greater dissolution power of the supercritical fluid compared to gases in conventional pyrolysis. Supercritical liquefaction typically involves the thermal breakdown of coal and subsequent dissolution of the pyrolysis products in the solvent. Depending on the solvent, supercritical extraction can be successfully performed at relatively low temperatures (593-673 K), moderate to high pressures (6-30 MPa), and in batch or continuous modes. The method shows potential for commercial application, although most studies have been limited to research on thermodynamics, chemical mechanisms, and the structure of the coal and extract. An important feature of supercritical coal extraction that has received limited attention in the literature concerns the kinetics of the dissolution process, especially quantitative interpretation of experimental data.

The research directed specifically to the kinetics of supercritical coal extraction (Slomka and Rutkowski, 1982; Deshpande et al., 1986) is based on the non-polar solvent, toluene. To our knowledge, there is little published information on supercritical extraction with polar or hydrogen-donor solvents, although some research on alcohol extraction of coal (Ross and Blessing, 1979a,b; Makabe and Ouchi, 1981) has been reported. Higher conversions were reported with low molecular weight alcohols than with hydrocarbons under equivalent conditions (Amestica and Wolf, 1984), possibly due to hydrogen-donor action. Hydrogen-donor solvents may exert a stronger dissociating or depolymerizing action on coal than non-donor solvents, thus increasing the yield of extractable coal material (Vasilakos et al., 1985; Kuznetsov et al., 1990). We found in our earlier work (Zhang et al., 1993a) that with Illinois No. 6 coal extraction in supercritical tert-butanol ($P_c=3.97$ MPa, $T_c=506.2$ K), there was some chemical interaction between the coal and the solvent, even at the comparatively low temperature of 573 - 623 K. Similar results were reported by Makabe and Ouchi (1981) and by Kuznetsov et al. (1990). The chemical reaction kinetics and mechanism for the extraction of coal with alcohols, however, are still unclear, and further research is needed.

A dynamic method using UV spectrophotometry to monitor continuously the extraction processes in a continuous-flow reactor has been successfully used to study kerogen extraction from shale with toluene (Triday and Smith, 1988), and lignin and cellulose extractions from wood with tert-butanol (Goto et al., 1990a,b; Reyes et al., 1989). From such data mathematical models

were developed to describe chemical reactions and transport processes during these supercritical processes. The results suggested that the dynamic method may be suitable to investigate quantitatively the kinetics processes for extraction of coal. In this work our objective was to develop a simple, quantitative kinetics model to describe such experimental data.

4.2. THEORY

Most general models for coal liquefaction are of the lumped-parameter type, where the products are combined into groups characterized by their solubility in different solvents. The most common groups are oil, asphaltenes, preasphaltenes, and insoluble coal. The concentration of these fractions in the liquefaction products can be used to establish reaction networks and estimate rate constants. The typical mechanistic model for coal liquefaction with a donor-solvent is (Angelova et al., 1989):

Deshpande et al. (1986) proposed a model of supercritical extraction of bituminous coal with toluene. It was hypothesized that only part of the coal, including volatiles and non-volatiles, dissolve in the fluid and undergo a liquefaction reaction, forming oils, asphaltenes, gases, and char as products. The following is the reaction scheme in terms of rate constants k_C , k_{C1} and k_A :

Conversion versus time data from a continuous-flow reactor with coal injection was used to estimate the kinetics parameters and the fraction extracted.

Slomka and Rutkowski (1982) proposed a second-order reaction model to describe supercritical toluene extraction of bituminous coal. The second-order rate equation, with respect to

undissolved but potentially extractable coal, closely fits the conversion of a long-time run in a batch system.

It has been proposed (Williams et al., 1987) that coal is composed of two molecular groups, or phases. The mobile phase comprises smaller molecules attached to or held within the network by physical and weak chemical bonds. The insoluble phase of coal is primarily a three-dimensional, cross-linked, macromolecular network or matrix. From the calibration procedure described later, the extract from supercritical tert-butanol extraction of Illinois No. 6 coal in the temperature range of 553 to 633 K likewise can be divided approximately into two groups of components. At low temperature (below 573 K) the absorbance of the effluent versus time exhibited one peak; at higher temperature (above 573 K) two peaks appeared in the absorbance history. In our earlier work of GC-MS analyses for the same system (Zhang et al., 1991), it was found that at low temperature a mixture of aliphatic and aromatic compounds was produced, and as temperature increased, the mixture contained more aromatic components. Presumably, at higher temperature more aromatic materials are produced by thermal decomposition of the macromolecular network. Based on these results a parallel-reaction model is proposed. The first reaction is a physical extraction process to release weakly-bound compounds. The second reaction represents the degradation of the macromolecular network to produce more aromatic compounds.

We assume that the extractable compound concentration is uniform in the coal particle, and each kind of extractable compound follows first-order, irreversible kinetics. Then the reaction scheme may be represented simply as

and the rate equations are

$$-dC_1/dt = k_1 C_1 \quad (4-3)$$

$$-dC_2/dt = k_2 C_2 \quad (4-4)$$

where C_i represents the concentration of solid reactant per gram of coal. The reaction constants, k_i , are expressed in terms of energies of activation, E_{ai} ,

$$k_i = k_{0i} \exp(-E_{ai}/R_g T) \quad (i=1, 2) \quad (4-5)$$

Then, the total reaction rate, R , is represented by

$$R = k_1 C_1 + k_2 C_2 \quad (4-6)$$

Since a very thin coal bed was used and the conversion through the whole fixed-bed was extremely low, the reactor can be assumed to approximate a differential reactor (Levenspiel, 1972). Internal and external particle mass transfer resistance were shown to be negligible, and both fluid and particles are assumed to have uniform concentrations. A dynamic mass balance on the reactor is represented in terms of outlet concentration of extract, $q = q_1 + q_2$, by the expression

$$\alpha V dq/dt + Q q = mR \quad (4-7)$$

where α is the bed void fraction, V is the volume of reactor bed, Q is the flow rate of solvent, and m is coal mass. Initial conditions are:

$$C_1 = C_{01}, \quad C_2 = C_{02}, \quad q_1 = q_2 = 0, \quad \text{when } t = 0. \quad (4-8)$$

where C_{01} and C_{02} are the total concentrations of extractable compounds in coal for the first and second reactions. These values are expected to be dependent on reaction conditions, e.g., temperature and pressure.

The uniform temperature of the bed of coal and the nature of the solid-reactant-based rate equations enable the integration of Equations (4-3) and (4-4) to the form:

$$C_1 = C_{01} \exp(-k_1 t) \quad (4-9)$$

$$C_2 = C_{02} \exp(-k_2 t) \quad (4-10)$$

Equations (4-9) and (4-10) can be substituted into Equation (4-6) to express the total reaction rate in terms of time:

$$R = k_1 C_{01} \exp(-k_1 t) + k_2 C_{02} \exp(-k_2 t) \quad (4-11)$$

With constant temperature and initial conditions, Equation (4-7) combined with Equation (4-11) is a first-order differential equation whose solution is

$$q = \{mk_1 C_{01} / [Q(1 - \alpha \tau k_1)]\} \{ \exp(-k_1 t) - \exp[-t/(\alpha \tau)] \} +$$

$$\{mk_2C_{O2}/[Q(1 - \alpha\tau k_2)]\} \{ \exp(-k_2t) - \exp[-t/(\alpha\tau)] \} \quad (4-12)$$

where the residence time, $\tau = V/Q$, is in the range of 0.01-0.02 min for our experiments (Table 4-1).

The first reaction rate was observed to be faster than the second. At temperatures above 573 K the first reaction is rapidly completed, and the second reaction becomes dominant. Thus, at long times and high temperatures the first reaction term, $\{mk_1C_{O1}/[Q(1 - \alpha\tau k_1)]\} \{ \exp(-k_1t) - \exp[-t/(\alpha\tau)] \}$, can be ignored. Then Equation (4-12) can be written as

$$q = \{mk_2C_{O2}/[Q(1 - \alpha\tau k_2)]\} \{ \exp(-k_2t) - \exp[-t/(\alpha\tau)] \} \quad (4-13)$$

In equation (4-13), $[1/(\alpha\tau)] \gg k_2$, or $\exp(-k_2t) \gg \exp[-t/(\alpha\tau)]$, and $\exp[-t/(\alpha\tau)]$ is negligible. Also, $1 \gg \alpha\tau k_2$, and $(1 - \alpha\tau k_2)$ is nearly equal to 1. Thus, for $t > 0$ the equation (4-13) is reduced to

$$q = [mk_2C_{O2}/Q] \exp(-k_2t) \quad (4-14)$$

Equation (4-14) can be used only in the case that the characteristic time for extraction (i.e., the residence time) is much smaller than the characteristic time for reaction (i.e., $1/k_2$). A plot of $\ln(q)$ vs. time based on Equation (4-14) is linear. The intercept of the line is $\ln[mk_2C_{O2}/Q]$, and the slope is $(-k_2)$. From the slope and intercept of experimental data, k_2 and C_{O2} can be obtained. For the first reaction, $1 \gg \alpha\tau k_1$ and $1/\alpha\tau \gg k_1$, are likewise true.

Since there is a heating period at the beginning of a run, the first reaction occurs in a non-constant temperature range. The parameters k_{O1} , C_{O1} and E_{a1} can be estimated by minimizing the sum of the squares of the difference between the experimental and calculated extraction concentrations during the heating-up period for low temperature runs ($T < 573$ K). For such runs the extract from the second reaction is negligible.

4.3. RESULTS FOR EXPERIMENTAL RUNS

Table 4-1 summarizes the experimental conditions and extraction conversion for the runs when the reactor is heated to one constant temperature. The conversion is defined as the fractional weight loss of the coal sample. The conversion is very low at 573 K and increases to 8.0% at 633 K.

Figures 4-1 to 4-3 show the extraction curves and temperature profiles for different temperatures in the temperature range of 598-633 K at a constant pressure of 6.8 MPa. The plotted points were selected from the continuous data at intervals of 2 minutes at the beginning of the run and 5 minutes at the long time run. During the heating period some components were extracted

rapidly from the coal, so that the extraction rate reached a peak. When temperature went through a certain value of temperature (above 593 K) the extraction rate increased again. At a high temperature (Figure 4-3) two peaks appear: one occurs before temperature reaches the maximum and the second as temperature reaches the maximum. These results are evidence that two kinds of components, which undergo different chemical reactions, exist inside the coal particles. Also, the reaction rates for these two processes are different.

Figure 4-4 shows a temperature-programmed experimental run at a constant pressure of 6.8 MPa. In this experiment, the reactor was first heated to 553 K and held at that temperature until the extraction was nearly complete. Then the temperature was increased from 553 K to 623 K and kept constant to the end of the run. A peak appears corresponding to each temperature step. After the first peak the extraction rate diminishes nearly to zero, suggesting that the first reactant group is depleted. A long tail exists after the second peak, indicating that the second reaction is slower than the first.

A two-step programmed-temperature experiment was conducted at two different temperatures, 563 K and 598 K (Figure 4-5). Because the second-step temperature is lower in Figure 4-5 than in Figure 4-4, the area under the second peak in Figure 4-5 is smaller than that in Figure 4-4. This result indicates that as temperature increases, the extractable concentration, C_{02} , from the second reaction increases. There is little difference in the areas under the first peaks in Figure 4-4 and Figure 4-5. Thus temperature has little effect on the extractable amount, C_{01} , for the first reaction. These experimental results suggest qualitatively that the first reaction has a higher rate constant than the second, and that the total extractable concentration for the first reaction is less than that of the second, which is temperature dependent. Slomka and Rutkowski (1979) and Deshpande et al. (1986), in their mathematical models, also allowed the concentration of extractable compounds to vary with temperature.

4.4. KINETICS PARAMETERS AND MODEL PREDICTIONS

The kinetic parameters were determined according to the estimation methods described earlier. The data at long times for the continuous heating runs (Figures 4-1 to 4-3) were used to determine the second rate constant and extractable concentration, C_{02} . Table 4-2 gives the parameter values for this second group of reactants, which were produced at the higher temperatures. The data of the higher temperature region in the two-step temperature-programmed runs gave k_2 values that agreed within 5% of the values in Table 4-2. The values of k_2 at 553 K and 563 K in Table 4-2 are estimated by means of the Arrhenius equation (Figure 4-6). The activation energy, E_{a2} , is an average value representing a group of reactants. Since C_{02} is temperature dependent, different components are reacting at different temperatures. Thus, it is an

additional simplification to use a single Arrhenius equation. The resultant E_{a2} is therefore an apparent average value.

For the first group of reactants, k_1 and C_{01} were determined by numerically solving the equations (4-3)-(4-8) and minimizing the sum of the squares of the differences between the experimental and calculated concentrations for the low temperature runs. It was found that the total extractable amount, C_{01} , changed little with temperature. The data from 553, 563 and 573 K runs were used to estimate C_{01} , k_{01} and E_{a1} , and the results are also given in Table 4-2. Predicted concentration versus time curves are shown as solid curves in Figures 4-1 to 4-5.

4.5. DISCUSSION

4.5.1. Temperature Effect on Reaction Rates

For the second group of reactants the apparent average activation energy of the second reaction, E_{a2} , is 54 kJ/gmol; for the first reaction, E_{a1} is 8.0 kJ/gmol. At the same low temperature (<573 K) the rate for the second group of reactants, for example, is about 10 times less than the rate for the first group. As temperature increases, the second reaction becomes more important.

An activation energy in the range of 0-40 kJ/gmol is usually regarded as a physical process, and above 40 kJ/gmol as a chemical process (Slomka and Rutkowski, 1982). The value of 8.0 kJ/mol for E_{a1} indicates that the first reaction is a physical process and is dominant at the low temperature. In this low temperature range (553-573 K) the extraction seems mainly to be physical dissolution of interstitial substances from the coal matrix by the solvent tert-butanol. The activation energy for the second reaction, 54 kJ/gmol, indicates that chemical reactions are responsible for the formation of the extract products that are soluble in supercritical tert-butanol solvent.

4.5.2. Relations between Extractable Compound Concentration and Temperature.

Extractable compound concentration is defined as the total extractable amount per gram coal at a certain temperature and pressure. Figure 4-7 shows the relation between extractable concentration, C_{02} , and temperature. Extrapolation to low temperatures shows that the second reaction will be negligible for temperatures below 563 K, as observed in the two-step temperature experiments. The concentration, C_{02} , increases strongly with temperature, implying that more compounds can be extracted when temperature increases. This supports the concept that the second chemical reaction is caused by the thermolytic cleavage of the bonds of the coal macromolecular network.

For the first group of components we assumed that C_{01} is independent of temperature. This assumption was confirmed by the good agreement between the experimental data and predicted results for low temperature runs. It seems reasonable to conclude that these compounds are physically attached or sequestered within the coal matrix, and are easily extracted.

The fractional conversion of coal obtained from experimental runs (Table 4-1) is slightly lower than the value predicted by the model. The reason is that the experimental runs were not taken to total depletion. Our experience is that near the end of extraction, the final 1-2% conversion requires several hours to be completed.

4.5.3. Comparison of Kinetics Data between Tert-Butanol and Toluene Extraction of Coal

Slomka and Rutkowski (1982) proposed a second-order reaction with respect to extractable compound concentration to describe the supercritical toluene extraction of bituminous coal. A first-order liquefaction reaction and a second-order reaction to form char were suggested by Deshpande et al. (1986). The activation energies and pre-exponential factors resulting from these two studies are based on mechanisms different from the present work. In the temperature range of 646-698 K and 9-23 MPa pressure Deshpande et al. determined an activation energy of 79.8 kJ/gmol for the liquefaction reaction forming oils, asphaltenes and gases. Slomka and Rutkowski (1982) obtained an activation energy of 101 kJ/gmol in the temperature range of 627-683 K and 9.8 MPa. In our work the activation energy of the chemical extraction is of the same order of magnitude, 54 kJ/gmol at 6.8 MPa.

The thermolysis of coal is thought to involve the thermal cracking of coal molecules by rupture of chemical bonds within the coal macromolecular network. The cracking or depolymerization reactions produce free radicals (coal fragments) that must be stabilized, or capped, to prevent retrograde, repolymerization reactions. Zhang et al. (1991) found evidence, in the form of branched extract molecules detected by GC-MS, that some tert-butanol reacts with the coal extract. This raises the question of whether the chemical interaction of the tert-butanol increases the extraction. Deshpande et al. (1986) calculated an extractable fraction of 4% for toluene extraction at 647 K and 9.0 MPa by fitting the experimental data with the model. For supercritical tert-butanol extraction of coal the total extractable fraction at 633 K and 6.8 MPa from our work is higher, 8%. However, the extraction processes can be compared only for the same coal under similar conditions. For our system when toluene was used as the solvent instead of tert-butanol, the extraction fraction was 10% at 633K and 6.8 MPa. We conclude that the chemical interaction of tert-butanol with the coal does not strongly affect the extraction process compared with the toluene as the solvent.

4.6. CONCLUSION

The principal conclusions from this investigation are:

1. The experimental approach of dynamic monitoring with a UV spectrophotometer at 235 nm can be used to investigate the physical-chemical process associated with supercritical tert-butanol extraction of bituminous coal.
2. For Illinois No. 6 coal at a constant pressure of 6.8 MPa two extractable fractions can be identified. Below 573 K, a physical extraction process dominates. Above 623 K, the rate of extraction is determined by the thermal degradation of the macromolecular network of coal.
3. At our operating conditions a simplified kinetics model, based on a set of two parallel, first-order reactions, can describe the physical-chemical process of supercritical extraction of coal.
4. The extractable compound concentration in the coal is an increasing function of temperature. At the temperature and pressure employed, total fractions extracted were low (≤ 8 wt%), but comparable to the extraction with toluene as the solvent.

4.7. NOMENCLATURE

c	concentration of extractable compounds in coal, kg/kgcoal
E_{ai}	activation energy, kJ/gmol
k	reaction rate constant, min^{-1}
k_{0i}	pre-exponential factor, min^{-1}
m	mass of initial coal sample, kg
P	pressure, MPa
P_c	critical pressure, MPa
P_r	reduced pressure, P/P_c
q	extract concentration in the effluent in the exit of reactor, $\text{kg/m}^3\text{solvent}$
Q	flow rate of solvent, m^3/min
R	reaction rate, $\text{kg}/(\text{kgcoal} \cdot \text{min})$
R_g	gas constant, $\text{kJ}/(\text{gmol} \cdot \text{K})$
t	time, min
T	temperature, K
T_c	critical temperature, K
T_r	reduced temperature, T/T_c
V	volume of reactor bed, m^3
Greek letters	
α	bed void fraction
τ	residence time, min
ρ	density of solvent, kg/m^3

Table 4-1. Summary Of Experimental Conditions And Conversion

Temperature (K) T_r		Pressure (MPa) P_r		Solvent Density (kg/m ³)	t (min)	Conversion (%)
553	1.09	6.8	1.71	231	0.02	0.4
563	1.11	6.8	1.71	203	0.02	---
573	1.13	6.8	1.71	182	0.02	1.7
598	1.18	6.8	1.71	148	0.02	4.3
623	1.23	6.8	1.71	129	0.01	6.1
633	1.25	6.8	1.71	124	0.01	8.0

Table 4-2. Kinetics Data

1. Relations between temperature and k and c_0				
Temperature (K)	c_{02} (kg/kgcoal)	k_2 (min ⁻¹)	c_{01} (kg/kgcoal)	k_1 (min ⁻¹)
553	-	0.0029*	0.008	0.035
563	-	0.0036*	0.008	0.036
573	0.024	0.0045	0.008	0.037
598	0.065	0.0068	-	0.040*
623	0.081	0.0110	-	0.043*
633	0.087	0.0129	-	0.044*
2. Activation energy and pre-exponential factor				
Activation energy (kJ/gmol)		Pre-exponential factor (min ⁻¹)		
$E_{a1}=8.0$		$k_{01}=2.0 \times 10^{-1}$		
$E_{a2}=54$		$k_{02}=3.5 \times 10^2$		

* estimated by Arrhenius equation.

Figure 4-1. Experimental data and predicted extraction curve at 598 K and 6.8 MPa, extract concentration is based upon kg of initial coal sample mass (— predicted, ○ experimental, — predicted by first or second reaction).

Figure 4-2. Experimental data and predicted extraction curve at 623 K and 6.8 MPa, extract concentration is based upon kg of initial coal sample mass (—predicted, ° experimental, — predicted by first or second reaction).

Figure 4-3. Experimental data and predicted extraction curve at 633 K and 6.8 MPa, extract concentration is based upon kg of initial coal sample mass (— predicted, ○ experimental, — predicted by first or second reaction).

Figure 4-4. Comparison between model predicted curve and temperature-programmed experimental data, extract concentration is based upon kg of initial coal sample mass (— predicted, ° experimental, $Pr=1.71$, $Tr=1.09$ and 1.23).

Figure 4-5. Comparison between model predicted curve and temperature-programmed experimental data, extract concentration is based upon kg of initial coal sample mass (— predicted, ○ experimental, $Pr=1.71$, $Tr=1.11$ and 1.18).

Figure 4-6. Arrhenius plot for second rate constant.

Figure 4-7. Concentration of extractable compounds for the second group of reactants versus temperature (6.8 MPa).

CHAPTER 5

KINETICS OF COAL THERMOLYSIS WITH H-DONOR SOLVENT

5.1. INTRODUCTION

The complex kinetics of coal liquefaction result in the formation of numerous compounds. Much research has been devoted to determine liquefaction yields as a function of the rank and type of coal, whether or not a catalyst or solvent is used, and other operating conditions. Many investigators have studied the molecular composition of liquid products to characterize these materials and to make inferences about the structure of coal. Relatively few papers, however, have paid attention to the detailed kinetics of coal liquefaction. Based on the assumption that many of the elementary reactions are similar and result in similar products, a few complex models have been proposed (Weller et al., 1951; Krevelen et al., 1951). The products are grouped into a small number of lumps that can be characterized by easily measured dependent variables (Deshpande et al., 1986; Zhang et al., 1993a). The most common groups are oil, asphaltenes, preasphaltenes, and residue, which are characterized by their solubility in different solvents. This approach reduces the complexities involved in product analyses, and thereby facilitates the representation of the actual reactions in terms of lumped kinetic models.

In the absence of strong hydrogen-donor solvent, first-order kinetics usually can describe the formation rate of dissolved product (Storch et al., 1943; Liebenberg and Potgieter, 1973; Falkum and Glenn, 1952). When a strong donor solvent is used, for example, tetralin, the kinetic reactions are not as simple. Storch and his co-workers (1943) found that their results for a model based on first-order integral equations showed deviations from straight-line relations. Similar observations were also made by Liebenberg and Potgieter (1973) in their study on uncatalysed hydrogenation of coal. However, a first-order equation was justified by Weller (1951) on the basis of certain assumptions. By splitting the conversion curve into two straight-line portions on the basis of different reaction rates for the respective portions of coal, Falkum and Glenn (1952) justified first-order rates. Wiser (1968) successfully described experimental data for coal thermolysis by splitting the processes into two portions, of which the first part is second-order and the second part is first-order. Later, Kang et al. (1980) studied Kentucky #14 hvBb coal in a differential-recycle reactor. The empirical rate expression used to fit the rate data includes second-order and first-order terms.

Most of the above kinetic studies were carried out in batch reactors. These results are not representations of only the primary reactions of coal liquefaction. A dynamic method using UV spectrophotometry to continuously monitor extraction processes in a semiflow differential reactor

was used in this study. In the preliminary studies of this work the secondary reactions were found negligible in this system. This system has proven useful in the study of kerogen extraction from shale with toluene (Triday and Smith, 1988), lignin and cellulose extraction from wood with t-butanol (Goto and McCoy, 1990), and coal extraction with t-butanol (Zhang et al., 1993a). In the coal extraction work, Zhang et al. studied the kinetics of supercritical extraction of Illinois No. 6 coal. They proposed that the extractable material is represented by two groups of components undergoing parallel first-order reactions. The kinetic data indicate that the first group is extracted by a physical process, which occurs below 573 K. The second group is extracted via a thermal decomposition reaction (with an apparent, average activation energy of 54 kJ/gmol), which is dominant above 573 K.

Our present objective has three aspects. The first is to measure the reaction rates of coal thermolysis at supercritical conditions. The coal samples used in this study have been pretreated at 573 K and 6.8 MPa to remove the physically-extractable material. The data were obtained with and without hydrogen donor (tetralin) in a semi-continuous differential reactor. These data without the effects of secondary reactions represent the kinetic features of the primary reactions of coal liquefaction. Second, the kinetic model which includes second-order and first-order terms is applied to experimental data for the extraction of Illinois No. 6 bituminous coal. The rate constants were evaluated by the least-square regression of the experimental data. Third, experiments at different temperatures are performed to determine the apparent activation energies and preexponential factors. The model provides a fundamental interpretation of the experimental data with reasonable values of parameters.

5.2. REACTION-EXTRACTION MODEL

5.2.1. General Model

The intrinsic rate expression which includes first- and second-order terms is

$$-\frac{d[C]}{dt} = k_A[C] + k_B[C]^2 \quad (5.1)$$

where $[C]$ is the concentration of extractable compounds based on coal mass, and k_A and k_B are rate constants. The above rate equation was originally proposed empirically by Kang et al. (1980). But it is possible to derive the same rate equation by a free-radical mechanism and some assumptions. Integration of the above equation with initial condition $[C](t=0) = [C]_0$ gives

$$[C] = \frac{k_A [C]_0 e^{-k_A t}}{k_A + k_B [C]_0 (1 - e^{-k_A t})} \quad (5-2)$$

where $[C]_0$ is the initial concentration of $[C]$ and is defined as the total expected product yield. This value is dependent on reaction conditions, e.g., temperature, pressure, and solvent and measured by the calibration runs. The rate constants are expressed as

$$k_A = f_A \exp(-E_A/RT) \quad (5-3)$$

$$k_B = f_B \exp(-E_B/RT) \quad (5-4)$$

Since a thin bed of coal sample was used, the reactor can be assumed to be a differential reactor (Levenspiel, 1972). Preliminary experiments in this laboratory suggested that external mass transfer resistance is negligible when flowrate is greater than $1.67 \times 10^{-7} \text{ m}^3/\text{s}$. All experimental data reported here were obtained at the flowrate of about $2.5 \times 10^{-7} \text{ m}^3/\text{s}$. Hence, internal and external mass transfer resistance are neglected as previously mentioned. Both fluid and particles are assumed to have uniform concentration in the reactor. A mass balance on the reactor, expressed in terms of the outlet concentration P of coal extract, is

$$\alpha V dP/dt + QP = m(k_A [C] + k_B [C]^2) \quad (5-5)$$

where α is the bed void fraction, m is the initial coal sample mass, Q is the volumetric flowrate, V is the coal sample volume and $[C]$ is given by Eq.(5-2). Initial condition is:

$$[C] = [C]_0 \quad \text{when } t = 0.$$

The accumulation term in Eq.(5-5) is much smaller than the convection term in our experiments because $\alpha V \ll Q$. Hence, Eq.(5-5) is simplified to the following form:

$$P = (k_A [C] + k_B [C]^2)m/Q \quad (5-6)$$

5.2.2. Density and Dispersion Corrections

The concentration of coal extract was measured in the spectrophotometer at 298 K and 101 kPa, while the model predicts the concentration at reactor exit conditions. The correction accounts for the density change between reactor exit and the spectrophotometer. The generalized correlation of Lee and Kesler and the recommended mixing rules (1975) were used to estimate the densities of

tert-butanol and the mixed solvent (15% tetralin + 85% tert-butanol) in the supercritical region. THERMOPAKTM (Haynes, 1990), a collection of powerful computer programs for calculations in thermodynamics, was used to confirm the calculations. The results of critical points and densities for the mixed solvent at different temperatures are shown in Table 5-1.

The measured concentration at 298 K and 101 kPa was converted to supercritical conditions by the expression:

$$P = (\rho/\rho_a)P_a \quad (5-7)$$

The flowrate in the reactor was corrected in the same way:

$$Q = (\rho/\rho_a)Q_a \quad (5-8)$$

where ρ_a is the density of the mixed solvent at ambient condition, which is equal to 800 kg/m³, and ρ is the density of the mixed solvent at supercritical conditions, listed in Table 5-1.

Triday and Smith (1988) showed that the dispersion effect in the same apparatus is negligible and the space in the tubing between the reactor and the detector contributed only to the time delay for our apparatus. The measured absorbance was corrected for this time delay.

5.3. RESULTS

5.3.1. Experimental Runs

Table 5-2 lists the experimental conditions and conversions for typical runs of three kinds: calibration runs (1, 2, 3, 4, 9*), kinetic extraction runs (5, 6, 7, 8), and pure tert-butanol runs (9*, 10*). The purpose of calibration runs is to measure the maximum conversion and construct the calibration curves. These runs are carried out until the coal samples are completely extracted at the run temperature. The concentration history of the kinetic extraction runs, usually carried out for 200 minutes, is used to determine the kinetic parameters in the model. Conversions for the mixed solvent runs are much larger than those for the pure tert-butanol runs, showing the effect of hydrogen-donor solvent.

Figure 5-1 shows that the maximum conversion is a function of temperature. In the temperature range of this study (590-650 K) there is a linear relationship between conversion and temperature for the mixed solvent runs. The maximum conversion at a given temperature is taken as the initial concentration of the extractable compounds for that temperature so that the initial concentration is temperature dependent. Most kinetic models in coal thermolysis have temperature-dependent initial concentration (Slomka and Rutkowski, 1982; Deshpande et al., 1986).

Figures 5-2 to 5-5 show the extraction curves and temperature profiles for different temperatures at a constant pressure of 6.8 MPa. The experimental points were selected from the continuous data at 2 minute intervals at the first part of the run and at 5 minute intervals thereafter. Figure 5-6 shows the concentration curve and temperature profile for the pure tert-butanol run at 630 k and 6.8 MPa. There is no evidence of two concentration peaks, which was observed in this laboratory when the coal sample was not pretreated (Zhang et al., 1993a). This result shows that the pretreatment eliminated the effect of the physically extractable compounds. Thus, this study represents the results of coal thermolysis instead of the mixed results of physical extraction and coal thermolysis. Since there were no coal extracts formed at $T \leq 573$ K for the pretreated samples, the zero time in the above figures is the time when the reactor reaches 573 K. The nonisothermal part of extraction was fitted by an assumed linear temperature profile.

5.3.2. Model Simulation.

The two adjustable parameters in Eq. (5-6) are the first- and second-order rate constants. They were evaluated by the least-square regression of the experimental data of the extract-concentration history. The objective function minimized is:

$$\Phi(k_A, k_B) = \sum_{i=1}^N (P_{\text{exp}} - P_{\text{simu}})^2 \quad (5-9)$$

where P_{exp} is the experimental concentrations of coal extract at supercritical conditions. The software package of MathematicaTM (Wolfram, 1988) was employed for solving the two sets of the equations. The experimental data were treated differently for the isothermal part and nonisothermal part. The nonisothermal data were fitted by assumed linear temperature profile.

Table 5-3 gives optimal parameter values for the supercritical conditions with the mixed solvent (runs 5-8). Figures 5-2 to 5-5 display simulated and experimental concentration curves of the coal extract. The good agreement lends credibility to the model. The Arrhenius plots of first- and second-order constants are shown in Figure 5-7. The activation energies and preexponential factors are listed in Table 5-4.

5.4. DISCUSSION

5.4.1. Model Simulation of Wiser's (1968) Experimental Data

The concentration vs. time relationship for a batch reactor is obtained by integrating Eq. (5-1) with respect to time. The result is Eq. (5-2). The conversion X is defined as the coal weight loss based on a gram of coal and is equal to $([C]_0 - [C])$.

Wiser (1968) studied thermolysis of Utah high-volatile bituminous coal. Constant temperature data were obtained at eight temperatures ranging from 350 to 450 °C. For illustration, the experimental data of conversion vs. time at four temperatures (350, 375, 400, 450 °C) were simulated by our model. The results are shown in Figure 5-8. The final values of rate constants were determined by a least-squares regression analysis. Both k_A and k_B satisfy the Arrhenius equation, plotted in Figure 5-9. The activation energies and preexponential factors for the first- and second-order rate constants that best fit the data are

$$\begin{aligned} f_A &= 7.20 \times 10^3 \text{ sec}^{-1} & E_A &= 59.8 \text{ kJ/gmol} \\ f_B &= 8.22 \times 10^6 \text{ sec}^{-1} & E_B &= 85.3 \text{ kJ/gmol} \end{aligned} \quad (5-10)$$

where $k_i = f_i \exp(-E_i/RT)$, $i=A, B$.

In Wiser's (1968) paper, the experimental data were split into two parts. The first part was fitted by a second-order rate equation, the second part by a first-order rate equation. This treatment leads to the following parameters.

Second-order region:

$$f = 2.64 \times 10^7 \text{ sec}^{-1} \quad E = 113 \text{ kJ/gmol}$$

First-order region:

$$f = 9.4 \times 10^3 \text{ sec}^{-1} \quad E = 73 \text{ kJ/gmol} \quad (5-11)$$

This treatment suggests that the coal thermolysis process is solely second-order in the initial stage, and solely first-order in the later stages. The present model indicates that the two terms in Eq. (5-10) contribute to the rate during all stages of the coal dissolution process. There is no sharp transition between the two reactions. Since the initial reactant concentration in coal is high, the second-order term is important when t is not large; in the later stages, the decrease in the reactant concentration eventually leads to dominance of the first-order term.

A difference between the kinetic parameters of (5-10) and our values (Table 5-4) is expected since the type of coal is different and because secondary reactions occur in a batch reactor. Secondary reactions among the dissolved fragments are negligible because of the short residence time in our flow reactor.

5.4.2. Kinetic Comparisons of Coal Thermolysis with and without Hydrogen-Donor Solvent

The thermolysis of coal involves thermal cracking of coal molecules by rupture of chemical bonds (Curran et al., 1967). The depolymerization reactions produce free radicals that are stabilized by abstracting hydrogen atoms, either from hydrogen-donor molecules or hydrogen-rich fragments of coal to form products. With nondonor solvent the mechanism leads to a first-order rate expression. With strong donor solvent our mechanism gives a rate expression with first- and second-order terms. For the runs with pure tert-butanol, which is a poor donor solvent (Ross) and

Blessing, 1979; Zhang et al., 1993a), Figure 5-6 shows that the first-order model fits the experimental data reasonably well. Zhang et al. (1992) also reported that a first-order rate expression successfully represented thermolysis of untreated coal with tert-butanol. Figure 5-6 also shows that there is a small difference between the first order fit and the data for extraction with pure tert-butanol. The small difference, which can be corrected by a second-order term, probably caused by the intermolecular rearrangement reactions of coal network at short reaction times. This effect may increase dramatically in a batch system as described by Wiser (1968).

Figures 5-1 to 5-5 show that the experimental data of coal thermolysis with tetralin, a strong hydrogen-donor solvent (Kershaw, 1989), were successfully represented by the model with first- and second-order terms. Comparing Figures 5-4 with Figure 5-6, the effect of the second-order reaction became negligible when there was no hydrogen-donor solvent in our experiments (Figure 5-6). Thus, the second-order reaction could be a measure of hydrogen-transfer effects on coal conversion, and its influence increases with temperature and hydrogen-donor concentration. The hydrogen-transfer processes include hydrogen shuttling reactions and hydrogen-abstraction reactions (Stock, 1985).

Based on the above results, we conclude that the model provides a fundamental interpretation of the coal thermolysis in supercritical conditions with and without hydrogen-donor solvent.

5.4.3. Temperature Effect on Reaction Rates

The apparent, average activation energy is 50.6 kJ/gmol for the first-order reaction and 82.9 kJ/gmol for the second-order reaction. An activation energy in the range of 0-40 kJ/gmol is usually regarded as physical process, and above 40 kJ/gmol as a chemical process (Slomka and Rutkowski, 1982). Thus, both the first- and second-order processes are chemical thermolytic reactions, not physical-extraction processes.

At very low temperatures (less than 573 K) neither reaction is significant because of the relatively large activation energies. In our preliminary experiments a coal sample that was not pretreated was extracted with the mixed solvent at 573 K and 6.8 MPa. The conversion was small (less than 3%) and comparable to the amount of physically-extractable compounds (Zhang et al., 1993a) accomplished with pure tert-butanol. Thus, the presence of hydrogen donor has a negligible effect at temperatures below 573 K, and coal thermolysis does not occur.

Zhang et al. (1993a) studied the coal thermolysis at supercritical conditions with tert-butanol (no tetralin). They reported that the activation energy is 54 kJ/gmol for coal thermolysis, and 8.0 kJ/gmol for physical extraction. The former number agrees with our value of 50.6 kJ/gmol (Table 5-4) for the first-order contribution. Thus, the result of Zhang et al. agrees with

the concept that the first-order contribution represents the thermolysis effect and the second-order contribution describes the effect of hydrogen transfer.

5.4.4. Hydrogen-Donor Solvent and Coal Thermolysis

Our data and that of Canel et al. (1990) and Kershaw and Overbeek (1984) confirm that addition of a hydrogen donor strongly increases extract formation rates and coal conversion. Since the density of the supercritical fluid and its ability to act as a solvent probably are not greatly changed by the addition of tetralin, the observed effects are mainly caused by enhanced hydrogenation of the coal structure. From Figures 5-2 to 5-5, the effect of hydrogen-donor solvent on coal conversion is to introduce second-order kinetics, which is particularly influential during the initial stage of thermolysis. This was effectively explained by the free-radical mechanism. During the initial stage of thermolysis, massive thermal fragmentation of the coal structure produces large numbers of free-radical species. This decomposition process decays with increasing conversion as the remaining bonds become increasingly more difficult to cleave thermally.

5.5. CONCLUSION

From our results of coal thermolysis with a mixed-solvent of 15% tetralin and 85% tert-butanol at different temperatures (593-653 K) and a constant pressure of 6.8 MPa, it is concluded that:

1. The kinetic model proposed in this paper provides a reasonable interpretation of the coal thermolysis data. The values of activation energy imply that both first- and second-order processes are chemical-reaction processes, rather than physical extraction.
2. The addition of a hydrogen donor strongly increases coal thermolysis rates and coal conversion. The effect of hydrogen transfer on the reaction is second-order, and has its largest effect during the initial stage of coal thermolysis.
3. The second-order effect was negligible in a nondonor run (tert-butanol). The experimental data was described reasonably well by a first-order rate expression.
4. The maximum coal conversion increased dramatically by adding hydrogen-donor solvent, and is a linear function of temperature for the investigated conditions.

5.6. NOMENCLATURE

[C]	concentration of extractable compounds in the solid coal particles, kg/kg coal
k_A	first-order rate constant, s^{-1}
k_B	second-order rate constant, s^{-1}
E_A	activation energy for first-order reaction, kJ/gmol
E_B	activation energy for second-order reaction, kJ/gmol

A_A	preexponential factor for first-order reaction, s^{-1}
f_B	preexponential factor for second-order reaction, s^{-1}
P	coal extract concentration in the solvent at supercritical condition, kg/m^3 solvent
P_a	coal extract concentration at room conditions
Q	flow rate of solvent at supercritical conditions, m^3/min
Q_a	flow rate of solvent at room conditions, m^3/min
F	objective function for optimum fitting of the experimental data

Table 5-1. The Densities of the mixed solvent at different temperatures.

Temperature K	593	613	633	653
Pressure MPa	6.8	6.8	6.8	6.8
Density kg/m ³	308.1	227.6	161.8	147.0

Table 5-2. Summary of Experimental Conditions and Conversions.

Extraction Run No.	P MPa	P _r	T K	T _r	m $\times 10^3$ kg	Max. Conversion %	Q $\times 10^6$ m ³ /min
1	6.8	1.75	593	1.11	2.0012	8.3	15.1
2	6.8	1.75	613	1.15	2.0009	14.5	14.8
3	6.8	1.75	633	1.19	2.0023	24.1	15.0
4	6.8	1.75	653	1.22	1.9984	31.1	15.2
5	6.8	1.75	593	1.11	0.9896	-----	15.0
6	6.8	1.75	613	1.15	1.0031	-----	15.1
7	6.8	1.75	633	1.19	1.0017	-----	14.7
8	6.8	1.75	653	1.22	0.5098	-----	14.9
9*	6.8	1.71	633	1.25	4.0087	7.6	15.0
10*	6.8	1.71	633	1.25	2.0012	-----	14.9

* The solvent used in runs 9* and 10* was pure tert-butanol.

Table 5-3. Optimum Parameter Values from the Fit of the Model to the Dynamic Data.

Temperature K	593	613	633	653
$k_A \text{ min}^{-1}$	0.0025	0.0030	0.0047	0.0062
$k_B \text{ min}^{-1}$	0.0072	0.012	0.018	0.035

Table 5-4. Activation Energies and Preexponential Factors.

Reaction	E_A kJ/mol	E_B min^{-1}
First-Order Reaction	50.6	67.8
Second-Order Reaction	82.9	1.39×10^5

Figure 5-1. Maximum conversions ($[C]_0$) at different temperatures (Solvent: 15% Tetralin + 85% Tert-Butanol; Pressure: 6.8 MPa).

Figure 5-2. Experimental data and model simulation at 593 K and 6.8 MPa; extraction concentration is based upon 1 kg of initial coal sample mass; solvent is 15% tetralin + 85% tert-butanol.

Figure 5-3. Experimental data and model simulation at 613 K and 6.8 MPa; extraction concentration is based upon 1 kg of initial coal sample mass; solvent is 15% tetralin + 85% tert-butanol.

Figure 5-4. Experimental data and model simulation at 633 K and 6.8 MPa; extraction concentration is based upon 1 kg of initial coal sample mass; solvent is 15% tetralin + 85% tert-butanol.

Figure 5-5. Experimental data and model simulation at 653 K and 6.8 MPa; extraction concentration is based upon 1 kg of initial coal sample mass; solvent is 15% tetralin + 85% tert-butanol.

Figure 5-6. Experimental data and model simulation at 633 K and 6.8 MPa; extraction concentration is based upon 1 kg of initial coal sample mass; solvent is pure tert-butanol.

Figure 5-7. Arrhenius plot for the kinetic rate constants.
 $A_A = 1.13 \text{ s}^{-1}$ $E_A = 50.6 \text{ kJ/mol}$ $A_B = 2.32 \times 10^3 \text{ s}^{-1}$ $E_B = 82.9 \text{ kJ/mol}$.

Figure 5-8. Model simulation of Wiser's (1969) experimental data; symbol, experimental data; line, model simulation.

Figure 5-9. Arrhenius plot for the kinetic rate constants fitted to Wiser's data (1969)
 $A_A = 7.20 \times 10^3 \text{ s}^{-1}$ $E_A = 59.8 \text{ kJ/mol}$ $A_B = 8.22 \times 10^6 \text{ s}^{-1}$ $E_B = 85.3 \text{ kJ/mol}$

CHAPTER 6. CONTINUOUS-MIXTURE KINETICS

6.1 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 have a polymeric molecular network composed of cross-linked polyaromatic units (Solomon et al., 1992; Green et al., 1982). These multi-ring aromatic units are attached with 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 attention because of advantages over conventional pyrolysis and liquefaction (Kershaw, 1989). Supercritical fluids have high solubilities, liquid-like densities, and viscosity and diffusion coefficients that are near to those of gases. Compared to a gas, the supercritical fluid enhances heat and mass transport as well as solubilities, and thereby reduces the effects of transport limitations and secondary reactions. 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 (i.e., 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. The common 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). The normal lumped groups are oil, asphaltenes, preasphaltenes, and unreacted coal. The advantage of the lumped model is its straight-forward 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, e.g., 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; Sandler and Astarita, 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 were considered. The product molecular-weight distribution (MWD) was lumped into groups representing solubility fractions, e.g., 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 crosslinked polymeric 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 are negligible, is employed.

6.2 THEORETICAL MODEL

6.2.1. 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 crosslinked 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 were characterized:

- End polyaromatic units bonded to the structure by one linkage.
- Regular polyaromatic units connected into the main structure by two linkages.
- Crosslinked 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,

$$c_{oi}(x) = m_{oi} y^{(\alpha_i-1)} \exp(-y) / [\beta_i \Gamma(\alpha_i)] \quad i=1, 2, 3 \quad (6-1)$$

with

$$y = \frac{x-x_{oi}}{\beta_i} \quad (6-2)$$

where subscript i represents the i th 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, s_i , are related to the first and second moments of the gamma distribution, which are given by Abramowitz and Stegun (1968), respectively, as

$$\bar{x}_i = x_{oi} + \alpha_i \beta_i \quad (6-3)$$

and

$$s_i^2 = \alpha_i \beta_i^2 \quad (6-4)$$

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

$$x_{pi} = x_{oi} + (\alpha_i - 1)\beta_i \quad (6-5)$$

6.2.2. 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 sec), 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 $T \leq 633\text{K}$ 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:

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.

6.2.3. 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.

6.2.3.1. 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

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

with initial condition

$$c_i(x,t=0) = c_{oi}(x) \quad (6-7)$$

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

$$c_i(x,t) = c_{oi} \exp[-k_i t] \quad i = 1, 2, 3 \quad (6-8)$$

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

$$\epsilon \tau \frac{\partial u_1(x,t)}{\partial t} + u_1(x,t) = k_1 c_1(x,t)/Q \quad (6-9)$$

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

$$u_1(x,t=0) = 0 \quad (6-10)$$

For our experimental condition, τ is small (10 s) and the accumulation term in Eq.(6-9) is negligible relative to the other terms so that

$$u_1(x,t) = k_1 c_1(x,t)/Q \quad (6-11)$$

Combining Eq. (6-5) and Eq. (6-11) leads to the following solution

$$u_1(x,t) = k_1 c_{o1}(x) \exp(-k_1 t)/Q \quad (6-12)$$

6.2.3.2. 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 products. The two-fragment reaction can be written as:

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 $v(x,x')$ 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

$$v(x,x') = v(x'-x,x') \quad (6-14)$$

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 $v(x,x')$ is a fraction requires that

$$\int_{x_{o1}}^{x'} v(x,x') dx = 1 \quad (6-15)$$

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

$$v(x,x') = Bx(x'-x) \quad (6-16)$$

where B is fixed by Eq.(6-15), by which we obtain

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

Then the stoichiometric distribution is

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

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:

$$k_{ic}(x) = \kappa_{ic} \frac{x - x_{o1}}{\beta_1} \quad i=2, 3 \quad (6-19)$$

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:

$$\frac{\partial c_i(x,t)}{\partial t} = -(k_i + k_{ic}(x))c_i(x,t) \quad i=2, 3 \quad (6-20)$$

with initial condition

$$c_i(x,t=0) = c_{oi}(x) \quad i=2, 3 \quad (6-21)$$

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

$$r(x,t) = \int_x^\infty k_{ic}(x')c_i(x',t)v(x,x')dx' + k_i c_i(x,t) \quad i=2, 3 \quad (6-22)$$

On the right side of Eq.(6-19), 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

$$\varepsilon \tau \frac{\partial u_i(x,t)}{\partial t} + u_i(x,t) = \frac{1}{Q} \left[\int_x^\infty k_{ic}(x') c_i(x',t) v(x,x') dx' + k_i c_i(x,t) \right] \quad i=2, 3 \quad (6-23)$$

where the initial condition is

$$u_i(x,t=0) = 0 \quad (6-24)$$

Again neglecting the accumulation term, Eq.(6-23) becomes

$$u_i(x,t) = \frac{1}{Q} \left[\int_x^\infty k_{ic}(x') c_i(x',t) v(x,x') dx' + k_i c_i(x,t) \right] \quad i=2, 3 \quad (6-25)$$

Eqs.(6-20) and (6-21) can be solved analytically and the solution is

$$c_i(x,t) = c_{oi}(x) \exp[-(k_i + k_{ic}(x))t] \quad i=2, 3 \quad (6-26)$$

which is substituted into Eq.(6-25).

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 extractable polyaromatic units. These rate constants are functions only of temperature, thus,

$$k_i = k_1(T) \quad (6-27)$$

Now combining Eqs. (6-18), (6-19), (6-25), (6-26) and (6-27) 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

$$u(x,t) = u_1(x,t) + u_2(x,t) + u_3(x,t) \quad (6-28)$$

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

$$k_{ic} \approx 0 \quad (6-29)$$

which will be shown to be consistent with the magnitude of the activation energy. Substituting Eq.(6-29) into Eq.(6-25) and Eq.(6-26) gives a result consistent with Eq.(6-12),

$$u_i(x,t) = k_i c_{oi}(x) \exp(-k_i t) / Q \quad (6-30)$$

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

$$u(x,t) = \sum k_i c_{oi}(x) \exp(-k_i t) / Q \quad (6-31)$$

where $c_{oi}(x)$ is given by Eq.(6-1).

6.2.4. 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,

$$C_i(t) = \int_0^{\infty} c_i(x,t) dx \quad (6-32)$$

$$U_i(t) = \int_0^{\infty} u_i(x,t) dx \quad (6-33)$$

Group 1: Group 1 undergoes only one-fragment reactions. It is easy to derive the lumped expression from Eqs. (6-1), (6-8), and (6-12). Thus, when Eq.(6-1) is substituted for c_{o1} , one obtains for the lumped extractable components in the coal,

$$\begin{aligned} C_1(t) &= \int_{x_{o1}}^{\infty} c_i(x,t) dx = \int_{x_{o1}}^{\infty} c_{o1}(x) e^{-k_1 t} dx \\ &= m_{o1} e^{-k_1 t} \end{aligned} \quad (6-34)$$

In the same way, the concentration distribution for solubilized extract products from Group 1 can be obtained with Eq.(6-12). The result is

$$U_1(t) = \frac{k_1}{Q} m_{o1} e^{-k_1 t} \quad (6-35)$$

Groups 2 and 3: The lumped concentrations for Groups 2 and 3 are derived by applying Eqs. (6-26) and (6-32),

$$C_i(t) = \int_{x_{o1}}^{\infty} c_i(x, t) dx = \int_{x_{o1}}^{\infty} c_{oi}(x) e^{-[k_1 + \kappa_{ic}(\frac{x - x_{o1}}{\beta_1})] t} dx \quad i=2, 3 \quad (6-36)$$

Substituting the gamma function for $c_{oi}(x)$, Eq.(6-1), and integrating yields the lumped concentration of extractable species in the coal,

$$C_i(t) = \frac{m_{oi}}{(1 + \kappa_{ic} \frac{\beta_1}{\alpha_i} t)^{\alpha_i}} e^{-[k_1 + \kappa_{ic}(\frac{x_{oi} - x_{o1}}{\beta_1})] t} \quad i=2, 3 \quad (6-37)$$

In the same way, combining Eqs.(6-25) and (6-33) gives for the extract products,

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

$$\frac{1}{Q} \int_{x_{o1}}^{\infty} dx \int_x^{\infty} \kappa_{ic} \left(\frac{x' - x_{o1}}{\beta_1} \right) c_{oi}(x') e^{-[k_1 + \kappa_{ic}(\frac{x' - x_{o1}}{\beta_1})] t} \left\{ \frac{6x(x' - x)}{x'^3 - x_{o1}^2 (3x' - 2x_{o1})} \right\} dx' \quad (6-38)$$

Denoting the first term on the right side of Eq.(6-38) as A and integrating yields

$$A = \frac{k_1 m_{oi}}{Q (1 + \kappa_{ic} \frac{\beta_i}{\beta_1} t)^{\alpha_i}} e^{-[k_1 + \kappa_{ic} (\frac{x_{oi} - x_{o1}}{\beta_1})] t} \quad (6-39)$$

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

$$\begin{aligned} B &= \frac{6\kappa_{ic}}{Q} \int_0^\infty \left(\frac{x' - x_{o1}}{\beta_1} \right) c_{oi}(x') e^{-[k_1 + \kappa_{ic} (\frac{x' - x_{o1}}{\beta_1})] t} \frac{dx'}{x'^3 - x_{o1}^2 (3x' - 2x_{o1})} \int_{x_{o1}}^{x'} x (x' - x) dx \\ &= \frac{\kappa_{ic}}{Q} \int_0^\infty \left(\frac{x' - x_{o1}}{\beta_1} \right) c_{oi}(x') e^{-[k_1 + \kappa_{ic} (\frac{x' - x_{o1}}{\beta_1})] t} dx' \end{aligned} \quad (6-40)$$

after partial integration. When $x' \leq x_{oi}$, we have $c_{oi}(x') = 0$, and the range of integration in Eq.(6-40) is x_{oi} to infinity. Combining Eqs.(6-38), (6-39), and (6-40) leads to

$$\begin{aligned} U_i(t) &= \frac{k_1 m_{oi}}{Q (1 + \kappa_{ic} \frac{\beta_i}{\beta_1} t)^{\alpha_i}} e^{-[k_1 + \kappa_{ic} (\frac{x_{oi} - x_{o1}}{\beta_1})] t} + \\ &\quad \frac{\kappa_{ic}}{Q} \int_{x_{oi}}^\infty \left(\frac{x' - x_{o1}}{\beta_1} \right) c_{oi}(x) e^{-[k_1 + \kappa_{ic} (\frac{x' - x_{o1}}{\beta_1})] t} dx' \quad i = 2, 3 \end{aligned} \quad (6-41)$$

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

$$U(t) = U_1(t) + U_2(t) + U_3(t) \quad (6-42)$$

Since the two-fragment reactions are negligible at low temperatures ($T \leq 633$ K), $U(t)$ based upon Eq.(6-33) is

$$U(t) = \frac{k_1}{Q} m_o e^{-k_1 t} \quad (6-43)$$

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

6.3. RESULTS AND DISCUSSION

6.3.1. 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 6-1. Based on the calibration results with polystyrene standards and naphthalene, the MWDs of coal extract were determined. The MWDs of coal extract at different times for different temperatures (613 K, 633 K, 653 K, and 673 K) are shown in Figures 6-2 to 6-5. 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 sample the weight-average MW was calculated with GPC software; the results are summarized in Table 6-1. It is noted that at low temperatures ($T \leq 633$ K) the average MWs are relatively constant with time; 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, i.e., $k_i(x) = k_i$. 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 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. It was reported (Darivakis et al., 1990) that the range of a is 1.3-3.0, but the most likely value is 2. In our simulations we fixed $a = 2$ for the three gamma functions. Based on Eq. 5 and the shape of experimental MWDs at the four temperatures, the parameters x_{oi} and b_i were estimated (Table 6-2) by minimizing the deviations between MWD data and model computations. The values of a , x_{oi} , and b_i are all independent of temperature.

The relationships between totally lumped extract concentration, $U(t)$, and extraction time at 613 K and 633 K are shown in Figure 6-1. 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 first-order rate constants of one-fragment reactions for 613 K and 633 K are the same for

different extractable polyaromatic units, i.e., $k_i = k_i(T)$, and were determined from the lumped data to be 1.3×10^{-4} and $2.2 \times 10^{-4} \text{ sec}^{-1}$, respectively.

Finally, values of m_{0i} for the three gamma functions were obtained by fitting the model with the time-dependent MWD data at 613 K and 633 K using Eq. 32. The simulation results for 613 K and 633 K are presented in Figures 6-2 to 6-3. Once the parameters are fixed, only time is allowed to vary in these plots.

Since the peak positions and shapes of the three gamma functions for our experimental results are relatively fixed for all temperatures, the x_{0i} and b_i are considered unchanged at higher temperatures ($T = 653 \text{ K}, 673 \text{ K}$). The rate constants of one-fragment reactions at 653 and 673 K were estimated from the values at $T = 613$ and 633 K by the Arrhenius equation. By fitting the model with the experimental results at 653 and 673 K, the constants k_{ic} and the initial concentrations of the three extractable polyaromatic units, m_{0i} , were determined. The values of these temperature-dependent parameters are listed in Table 6-3. Figures 6-4 to 6-5 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.

The above simulation results were compared to experiments by two other methods. The zero moments, m_{0i} , were determined from the MWDs, while the total lumped extract concentration, C_0 , was measured by UV absorbance spectrophotometry of the reactor effluent. The good agreement between $\sum m_{0i}$ and C_0 is shown in Table 6-3. Moreover, the experimental results of extract-concentration history at 653 K and 673 K, which are not fitted well by first-order kinetics, are represented reasonably well in Figure 6-6 by the lumped concentration based on Eqs. 43 and 44. The approach thus satisfies required conditions of internal consistency.

The Arrhenius plot of the rate constants for both one- and two-fragment reactions is presented in Figure 6-7. From the plot the activation energies are estimated:

$$\begin{array}{lll} \text{One-fragment reactions} & E_i = 58 \text{ kJ/mol} & i = 1, 2, 3 \\ \text{Two-fragment reactions} & E_2 = 205 \text{ kJ/mol} & E_3 = 191 \text{ kJ/mol} \end{array} \quad (6-45)$$

where the subscript represents the group number. The results for rate constants summarized in 6-3 imply that one-fragment reactions are always important for the temperature range 613 K - 673 K, whereas two-fragment reactions are negligible at $T \leq 633 \text{ K}$ but become very important at $T = 673 \text{ K}$.

The initial concentrations of the extractable polyaromatic units, m_{0i} , are plotted versus temperature in Figure 6-8. For the four temperatures the three groups demonstrate a linear dependence of m_{0i} 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 $(C_6H_5)_3C-C(C_6H_5)_3$ 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 much 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.

The different groups of products are extractable polyaromatic units representing the composition of coal. From Table 6-1 it is noted that the weight-average MWs of extracts are fairly constant at low temperatures ($T \leq 633$ K) and decrease with time for higher temperatures ($T > 633$ K). This indicates the occurrence of two-fragment, cracking reactions. Figure 6-9 shows 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 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.

6.3.2. The Parameters and Coal Structure

In the present work, fitting the model with experimental data yields three gamma distributions for the coal initial composition. The first gamma function is a narrow and small peak (with smallest β). 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.

1. From the postulated theory (Darivakis et al., 1990), $\bar{x}$ is the average MW of a polyaromatic unit. We consider that the first gamma function represents the end polyaromatic unit, the second the regular polyaromatic unit, and the third the crosslinked 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, $\bar{x}_2 = 284$. For the crosslinked unit, the MW, $\bar{x}_3$, is 517. These results suggest that larger units are more likely to be bonded with other units. The end polyaromatic unit contains fewer rings, and the crosslinked polyaromatic unit has more rings.

2. The variance for the gamma function is $\alpha\beta^2$ (Eq.(6-4)). 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 polymeric 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 crosslinked polyaromatic units, a larger β should be expected. From Table 6-2, it is seen that the third group of polyaromatic units has the largest β . The reason is that the crosslinked units have more linkages, which are of dissimilar bonds. Thus the model results corroborate the Darivakis et al. theory.

3. Table 6-3 and Figure 6-8 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 crosslinked polyaromatic units, and that the average number of linkages, which must rupture to form an extract precursor, is close to two. Our experimental results thus are in general agreement with the Darivakis et al. analysis.

According to Haenel (1992), the average polyaromatic unit in bituminous coal contains between 14 and 20 carbon atoms corresponding to 3 to 5 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 6-1) 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.

6.4. 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 describes well 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.

6.5. NOMENCLATURE

$c_i(x, t)$	concentration distribution of i th group of extractable polyaromatic units in coal, kg/kg coal MW
$C_i(t)$	totally lumped concentration of extractable polyaromatic units for i th group in coal, kg/kg coal
$C(t)$	the summation of $C_i(t)$
k_i	rate constants for one-fragment reactions for i th extractable group, sec^{-1}
k_{ic}	proportional constants for two-fragment reactions for i th extractable group, sec^{-1}
$k_{ic}(x)$	rate constants for two-fragment reactions for i th extractable group, sec^{-1}
m_{oi}	zero moment of gamma function in Eq. 1, kg/kg coal
P	pressure, MPa
Q	flow rate of solvent, m^3/sec
t	time, sec
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
$U(t)$	the summation of $U_i(t)$
x	molecular weight
x_{oi}	the minimum molecular weight for Group i in the gamma function.
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
ϵ	bed void fraction

τ residence time based on reactor volume, sec

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

Temperature (K)	Sample	Time (sec.)	Concentration ($\times 10^2$) (kg/m ³)	M _{w,avg} *
613	1	1800	4.7	307
613	2	3360	2.6	311
613	3	5100	1.7	307
613	4	6900	1.3	304
613	5	8700	1.1	294
613	6	10500	0.91	298
<hr/>				
633	1	600	11.9	261
633	2	1800	8.4	256
633	3	2400	7.9	267
633	4	3000	6.8	260
633	5	4200	5.1	264
633	6	5400	4.2	254
<hr/>				
653	1	1560	7.2	271
653	2	2400	4.9	266
653	3	3600	2.3	254
653	4	5400	1.6	240
653	5	7500	1.1	224
<hr/>				
673	1	1980	14.1	286
673	2	3900	3.3	293
673	3	5100	2.1	222
673	4	6600	1.4	207
673	5	8400	1.2	181

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

Figure 6-1. Plot of $\ln U(t)$ versus time for experimental data of lumped extract concentration for the runs at 613 K and 633 K.

Table 6-2. Temperature-Independent Parameter Values for the Model.

Parameter	a	b ₁	b ₂	b ₃	x ₀₁	x ₀₂	x ₀₃
Values	2	20	62	120	115	170	275

Table 6-3. Temperature-Dependent Parameter Values for the Model.

Temperature (K)		613	633	653	673
k _i	i=1, 2, 3	1.3x10 ⁻⁴	2.2x10 ⁻⁴	3.0x10 ⁻⁴	3.7x10 ⁻⁴
k _{2c}		*3x10 ⁻⁷	*1.7x10 ⁻⁶	5.3x10 ⁻⁶	1.6x10 ⁻⁵
k _{3c}		*5.3x10 ⁻⁷	*1.6x10 ⁻⁶	4.5x10 ⁻⁶	1.2x10 ⁻⁵
m ₀₁		0.0033	0.0080	0.010	0.013
m ₀₂		0.032	0.049	0.064	0.081
m ₀₃		0.029	0.041	0.047	0.056
Σ m _{0i}	i=1, 2, 3	0.064	0.098	0.12	0.15
**C ₀		0.066	0.100	0.11	0.14

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

**The values of C₀ were measured from experimental runs.

Figure 6-2. Comparison of model calculations and experimental data for MWDs at 613 K for Samples 1-5. Sample numbers refer to Table 6-1.

Figure 6-3. Comparison of model calculations and experimental data for MWDs at 633 K for Samples 1-5. Sample numbers refer to Table 6-1.

Figure 6-4. Comparison of model calculations and experimental data for MWDs at 653 K for Samples 1-5. Sample numbers refer to Table 6-1.

Figure 6-5. Comparison of model calculations and experimental data for MWDs at 673 K for Samples 1-5. Sample numbers refer to Table 6-1.

Figure 6-6. Comparisons between the experimental data and the values calculated for lumped extract concentrations at 653 K and 673 K.

Figure 6-7. Arrhenius plot of the rate constants for one- and two-fragment reactions.

Figure 6-8. Plot of initial concentrations of three groups of reactive components at different temperatures (613 - 673 K) and 6.8 MPa.

Figure 6-9. Plot of concentration distributions of extract from one- and two-fragment reactions for group 3 at 673 K and 6.8 MPa.

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APPENDIX

PAPERS AND PRESENTATIONS BASED ON THE PROJECT

Publications:

- Zhang, C. J., M. Wang, and B. J. McCoy, "Extraction of Bituminous Coal with Supercritical Butanol." 2nd International Symposium on Supercritical Fluid Processes, Boston, (1991); pp 332-335.
- Zhang, C. J., J. M. Smith, and B. J. McCoy, "Kinetics of Supercritical Fluid Extraction of Coal: Physical and Chemical Processes." in Supercritical Fluid Engineering Science, E. Kiran, J.F. Brennecke (eds.) ACS Symposium Series **514** (1993); pp 363-379.
- Wang, M., J. M. Smith, and B. J. McCoy, "Kinetics of Coal Thermolysis with a Mixed Solvent of Tert-Butanol and Tetralin." Energy and Fuels, **7**, 78 (1993a).
- Wang, M., C. J. Zhang, J. M. Smith, and B. J. McCoy, "Continuous Mixture Kinetics of Coal Thermolysis in Supercritical Fluid." AIChE Journal, Submitted.
- Zhang, C. J., M. Wang, J. M. Smith, and B. J. McCoy, "Dynamics of the Extract Molecular-Weight Distribution in Supercritical Thermolysis of Coal: Continuous-Mixture Kinetics." Preprint for ACS Symposium on Low-Severity Processing of Coal, April (1993).

Presentations:

- B. J. McCoy, 2nd International Symposium on Supercritical Fluid Processes, Boston. "Extraction of Bituminous Coal with Supercritical Butanol." (February, 1991).
- B. J. McCoy, DOE University Coal Research Contractors Review Meeting, Pittsburgh. "Chemical Kinetics and Transport Processes in Supercritical Extraction of Coal." (June, 1991).
- B. J. McCoy, University of Wyoming, "Supercritical Extractions--Coffee and Coal." (October, 1991).
- B. J. McCoy, AIChE, Los Angeles, "Kinetics of Supercritical Fluid Extraction of Coal: Physical and Chemical Processes." (November, 1991).
- B. J. McCoy, Tsinghua University, Beijing, "Supercritical Fluid Processes." (April, 1992).
- B. J. McCoy, Institute for Coal Chemistry, Taiyuan, Shanxi, "Thermolytic Extraction of Coal." (April, 1992).

- B. J. McCoy, Kumamoto University, "Supercritical Fluid Processes." May, 1992.
- B. J. McCoy, Yamaguchi University, "Supercritical Fluid Extraction Processes." (May, 1992).
- B. J. McCoy, DOE University Coal Research Contractors Review Meeting, Pittsburgh, "Chemical Kinetics and Transport Processes in Supercritical Extraction of Coal." (June, 1992).
- B. J. McCoy, AIChE, Minneapolis, "Lumped and Continuous-Mixture Models for Multicomponent Extraction." (July, 1992).
- B. J. McCoy, Bosphorus University, Istanbul, "Progress in Supercritical Studies." (August, 1992).
- B. J. McCoy, Middle East Technical University, Ankara, "Advances in Supercritical Processes." (August, 1992).
- B. J. McCoy, Gazi University, Ankara, "Coal Thermolysis." (September, 1992).
- B. J. McCoy, AIChE., Miami, "Continuous-Mixture Kinetics of Supercritical Thermolysis of Coal." (November, 1992).
- Ming Wang, Department of Chemical Engineering, UC Davis, "Thesis Research on Supercritical Thermolysis of Coal." (November, 1992).

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