RATE LIMITATIONS IN COAL/ORGANIC SOLVENT INTERACTIONS

George H. Zieminski* and Edward A. Grens II (Ph.D. thesis)*

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ABSTRACT

Rate limitations in the extraction of tetralin-soluble material from Wyodak subbituminous coal were investigated at temperatures below those of coal pyrolysis. Intimate coal/tetralin contacting was conducted at 150 to 300°C in a stirred batch contactor vessel at contacting times from 1/2 minute up to 24 hours, and in a high pressure Soxhlet apparatus at contacting times up to 725 hours. The yield of extracted coal material as a function of contacting time was determined from the amount of dissolved material in samples of the extract solution; total yields of up to 30% by weight of dry, ash-free (daf) coal were obtained. The extraction process could be well represented by a model based on three groups of soluble materials, in which each group was treated as a pseudo-single component. The first group (1.5-5.0% wt daf coal) extracts within the first minute of contacting, apparently unhindered by kinetic or mass transfer processes. Diffusion and weak bond breaking dominate the extraction of the second, intermediate rate, extract group (1.5-5.0% wt daf coal). The rate of extraction of the third group (5-24% wt daf coal) is kinetically controlled.
The activation energies (0-10 kcal/mol) and rate coefficients (0.001-0.3 min\(^{-1}\)) calculated from this model are well within the range that might be expected for the phenomena involved.
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Many aspects of coal liquefaction, a rapidly expanding technology in coal conversion, are still far from being fully understood. One important feature of the functioning of coal liquefaction processes is the interaction of the coal with the organic liquids with which it comes in contact during the processing. In most coal liquefaction processes, a stream of recycle solvent is added to the feed coal to participate in conversion of the coal and facilitate handling of the coal. Chemical and physical interactions occur during the intimate coal/solvent contacting. A knowledge of the rate of extraction of coal materials and the influence of contacting parameters on this rate is necessary to the understanding of these important coal/solvent interactions and thus is essential for a sound development of coal liquefaction processes.

Although most current processes operate at temperatures above the pyrolysis temperature of coal, where considerable thermal bond-breaking reactions occur, recent developments at lower temperatures offer the possibility of more efficient routes to liquid fuels. In this work, the kinetics of the interaction of coal with an organic liquid, representative of recycle solvents, was investigated at temperatures below coal pyrolysis temperature.

Most current catalytic and non-catalytic coal liquefaction processes, such as Exxon Donor Solvent, H-Coal, SRC-I and SRC-II, require temperatures above the pyrolysis temperature of coal (~325°C), high pressures (10-20 MPa) and large amounts of hydrogen [1]. These
processes recycle a fraction of the coal liquefaction products to slurry the feed coal [2]; this recycle solvent facilitates pumping the coal into high pressure reaction zones, prevents agglomeration and sticking of the coal particles and enhances heat transfer to the reaction slurry. Additionally, typical recycle solvents dissolve some of the coal material, which frequently changes the structure of the coal and renders the coal more accessible to further conversion by thermal or catalytic methods. Solvents can also stabilize thermally or catalytically produced radicals by transfer or donation of hydrogen and act as carrier for removal of reaction products from the coal.

As an alternative, coal liquefaction processes at lower temperatures (200-300°C) and pressures (2-7 MPa) may offer a more efficient route to the desired product, a liquid fuel or oil that can be processed further to transportation or heating fuels. At these lower temperatures, a homogeneous catalyst that can act upon the solid coal structure is necessary to promote bond cleavage in the coal, and a solvent is necessary to terminate catalytically created reactive species and to remove the reaction products. Some recent work on low temperature catalytic coal liquefaction processes has been carried out at Lawrence Berkeley Laboratory [3,4,5,6]. In that work, coal was treated with molten ZnCl$_2$, a homogeneous catalyst, in combination with organic solvents that were either immiscible in the catalyst melt or completely soluble in the melt. Extensive conversion of the coal to cyclohexane soluble products (up to 50% by weight on a dry ash-free coal basis) and
to pyridine soluble products (up to 85% wt daf basis) was obtained with treatment at 300°C for one hour [7].

The rational development of low temperature processes involving contact of coal with solvents, as well as catalytic media, requires an improved characterization of coal/solvent interactions under these conditions. The overall rate and extent of coal conversion are influenced by the dissolution of coal materials in the solvent. The accessibility of the coal structure to the catalyst and the availability of dissolved material for further interaction with the catalyst are affected by the rate of dissolution and removal of the coal material from the pores of the coal particles. Thus, an understanding of coal/solvent interactions, sought in this investigation, is valuable in the design of a viable coal liquefaction process.

Three basic phenomena are associated with the extraction of coal in a solvent; they govern the movement of material from within the coal particle to the bulk solution. First, the material must dissolve in the solvent present in the extended pore structure of the coal; this step may involve molecules that are present in, but not bonded to the coal structure or may require reaction such as bond-breaking to free the material. Soluble material can be bound to the coal structure by relatively weak hydrogen bonds or surface adsorption or stronger covalent bonds, typically heteroatom linkages but also much stronger carbon-carbon bonds such as methylene bridges [8,9,10,11]. Second, this dissolved material must diffuse through the pore structure of the coal particle to the exterior of the particle. This pore structure of coal
generally consists of macropores and micropores; macropores are commonly referred to as those pores with diameters greater than about 200 Å (0.02 micron), micropores less than about 12 Å (0.0012 micron). Characterization of the internal physical structure of the coal used in this study indicates that almost all of the available surface area is contained in the micropore structure of the coal particle [12,13,14]. The macropore structure primarily serves as the major transport system through which the solvent and the dissolved material move within the coal particle. Diffusion through the micropores may be accompanied by adsorption and desorption on the pore wells. Finally, the material is transported to the bulk solution from the exterior of the particle. Convection of solvent past the particle dominates transport of the dissolved material to the bulk. If the saturation limit of the dissolved material in the solvent is approached, the transport phenomena are inhibited. These three phenomena can be generally classified as reaction/dissolution, internal mass transfer, and external mass transfer, respectively. The phenomena that are expected to be of most importance in the interaction of coal with an organic solvent are the rate of dissolution and the rate of diffusion of the dissolved coal material within the coal particles.

**Previous Work**

A considerable volume of literature has been published that is related to coal/solvent interactions. However, much of the early information suffers from a failure to comprehend fully the complexity
of coal dissolution and to maintain constant the important contacting parameters. Early work mainly dealt with the characterization of coals and attempts to optimize the coking property of coals. Solvent extractions of coal with many organic solvents at their normal boiling points were conducted to obtain fractions of the coal for characterization. Later, many studies of the interactions of bituminous coals with organic solvents, and the influence of contacting parameters, have been reported for many solvents at the normal boiling point and at temperatures above coal pyrolysis temperatures. Recent work includes more sophisticated methods of characterization of coal and coal derived products, further studies on the coal/solvent interaction at temperatures above coal pyrolysis temperature, and attempts to model the kinetics of these coal/solvent interactions. Recognition of the importance of fundamental studies have been indicated in several recent reports [15,16]. The emphasis of an increasing number of studies is on basic, fundamental chemistry and physics of coal (and representative model compounds) and its conversion to fuels and chemicals.

Early Studies

General reviews of the early studies of coal/solvent interactions have been presented by Lowry [17] and by van Krevelen [18]. Most of the work was conducted with bituminous and subbituminous coals. The earliest studies dealt primarily with the characterization of coal fractions generated by solvent extraction of coal at atmospheric pressure in boiling solvents, giving a relatively nondestructive, but shallow, extraction of the coal. Elaborate extraction schemes were
developed by Wheeler and by Bone as summarized by van Krevelen in an attempt to separate the coal into various types of compounds for characterization [19]. It was determined that few, if any of these fractions consisted of a single type of compound; furthermore, certain experimental factors (such as traces of oxygen and moisture), on which the solubility of coal in solvents and the stability of the resulting extracts depend, were not understood. Not until the 1930's was much effort made to study the factors involved in the extraction of coal.

In 1945 Lowry reviewed the influence of the particle size of the coal, the temperature and the time of extraction, and the nature of the solvent on the extraction of bituminous coal. The ultimate (or long time) yields showed only a slight dependence on the particle size. Extraction yields for particle sizes decreasing from 16 mesh to 200 mesh increased only slightly over that range; however, extraction yields for finely ground coal (particles about one micron in diameter) were significantly higher [20,21]. The behavior of the yield of extract with increasing time indicated the existence of two fractions, one which was very easily and rapidly removed and the other which was much less soluble and only slowly removed from the coal [22]. The time required to obtain the "ultimate" extraction was recognized as longer than practical to carry out conveniently [23]. Asbury obtained an ultimate yield by calculating the slope of the line from a plot of time as a function of yield divided by time; this empirical approach proved successful for the coal/solvent contacting conditions of a Soxhlet-type of extraction [24]. An increase in extraction yield with temperature
was observed for temperature increases up to the decomposition temperature of the coal at which temperature a rapid evolution of gas (mostly methane) took place when the coal was heated under special conditions [25] and above which temperature extraction yield began to decrease. It was concluded that the temperature of extraction should lie just below the decomposition temperature of the coal (about 390°C for the coal used) in order to produce the greatest yield, and that it was unnecessary and even detrimental to exceed this temperature [25,26].

Many extractions with solvents of different chemical nature were conducted; since most of the extractions were performed at widely varying temperatures, corresponding to the normal boiling points of the solvents, a comparison or analysis of the results is difficult. Kiebler [27] and Asbury [28] conducted extractions at several temperatures (150, 200, 250 and 300°C) with various solvents on a Pittsburg seam coal. An attempt was made to correlate the yield of extract with physical properties of the solvents, but no significant correlation was obtained. Other work seemed to indicate that the yield of extract was not governed by the chemical nature of the solvent [29]. Experimental error and inadequate procedures prevented a firm statement of conclusions.

Subsequently, Dryden published a series of articles in 1950 and 1951 reviewing the action of solvents on bituminous coal and presenting results of the action of nitrogen-containing solvents on various British coals [30]. Characterization of coal was the primary goal of those works; the use of solvents capable of extracting a considerable fraction
of many coals was desirable in order to obtain an extract that was as representative of the whole coal as possible. The greatest solvent power was exhibited by compounds with a nitrogen or oxygen atom containing an easily accessible unshared pair of electrons; these included compounds containing primary amine groups such as ethylene diamine and certain heterocyclic bases, such as pyridine. The influence of contacting conditions on the yield of extract was also presented; conclusions concerning the influence of particle size and temperature concur with those discussed earlier by Lowry. Dryden recommended that the time of extraction for comparison of yields be the shortest time necessary to ensure that the greater part of the dispersible material was extracted, typically 48 hours in a Soxhlet apparatus [31]. Atmospheric oxygen and moisture were found to be detrimental to the yield of extract in several cases. The influence of many other factors were discussed; physical properties and chemical structure of the solvent, chemical interaction of coal and solvent, rank of coal and the petrological constitution of coal among others. Evidence of the strong adsorption (incorporation) of solvents, such as pyridine, in the coal residue and extract led to the conclusion that many organic liquids may chemically interact with the coal in addition to their action as a solvent. The solubility of three petrographic constituents of coal, vitrain, durain, and fusain, showed marked differences in several solvents (pyridine, benzene, and anthracene oil) indicative of the importance of the constitution of the coal in the coal/solvent interaction.
Oele and coworkers, in 1951, classified organic solvents into four categories dependent on their action on coal: non-specific extraction, specific extraction, extractive disintegration, and extractive chemical disintegration [32]. Later, Wise renamed these classifications, labeling the solvents as non-specific, specific, degrading and reactive, and added a fifth, highly reactive [33]. This simple classification seemed at the time to organize adequately solvents for comparison of extraction results reported in the literature. Non-specific solvents are characterized by their ability to dissolve only a small fraction of the coal at the normal boiling point, and include benzene, ethanol and acetone. Degrading solvents are capable of providing a medium at high temperatures (higher than 400°C) where the coal is thermally disintegrated into small, soluble fragments. High-boiling, aromatic hydrocarbons, such as phenanthrene, are typical degrading solvents. Reactive solvents, typically used at high temperatures (300-450°C) interact chemically with coal in addition to providing a medium for dissolution of the coal material. Hydrogen-donor solvents, typically hydroaromatic compounds such as tetralin (tetrahydronaphthalene) can be classified as reactive solvents. At temperatures or conditions under which no hydrogen transfer occurs (below about 320°C for tetralin) these reactive solvents can act more like non-specific solvents. Specific solvents are characterized by their ability to dissolve significant amounts of coal even at relatively low temperatures. Pyridine and ethylenediamine are representative specific solvents. Since these specific solvents interact strongly with coal, incorporate into the coal residue and extract, and
typically degrade beyond easy recovery, the use of these solvents is impractical for commercial processes.

In 1963 Lowry updated the earlier review of coal literature [34]. The effect of the physical and chemical properties of solvents, the influence of rank and petrological constitution of the coal and the influence of contacting conditions on the degrees of extraction were discussed. In addition to the effects of the contacting conditions mentioned above, the effect of the nature of the contacting was also recognized; extraction was much more rapid when the coal and solvent were shaken together than when extraction was conducted in a Soxhlet apparatus [31]. Furthermore, the use of ultrasonic vibrations in conjunction with typical contacting apparatus was found to increase the rate of extraction of coal [35].

Coal Interaction with Tetralin and Related Solvents

The nature of solvents and their mode of action on coal has been of interest for many years. The importance of hydrogen transfer from the solvent medium to coal material in the conversion of coal was recognized as early as 1933 by Pott and Broche; tetralin acted as the hydrogen carrier in that process [36]. In 1951, Oele et al. concluded that hydrogen transfer was important in the prevention of condensation reaction of pyrolytically-generated extract molecules [32]. The study of the action of hydrogen donor solvents on coal has been extensive. Coal conversion process solvents are usually a recycle stream of the coal-derived liquids. These liquids typically contain tetralin and other related hydrogen-donor species [37]; additional hydrogenation of
the recycle stream renders it particularly effective in hydrogen
donating and coal conversion ability [38]. Tetralin is one of the
solvents that is readily available, of convenient boiling point, and
representative of coal recycle liquids.

Many investigators have studied the conversion of various types of
coal, from lignites to low volatile bituminous, by contact with tetralin
in a variety of apparatuses at temperatures ranging from 47-450°C for
times from 1/2 minute to 1000 hours. Most of the studies were carried
out at temperatures greater than 320°C. Hydrogen donor activity of
tetralin generally occurs at or above this temperature [39,40]; extrac­
tions conducted below this temperature dissolve a relatively small frac­
tion of the coal. Two types of contacting equipment have been used, an
autoclave or a Soxhlet-type apparatus.

Hill et al. conducted dissolution experiments of Utah high volatile
bituminous coal (ground to -200 mesh and dried in a vacuum oven at 100°C
for 4 hours) in tetralin at temperatures between 350 and 450°C in a
stirred autoclave [41,42]. Preliminary experiments indicated that a
solvent-to-coal ratio of 8:1 or greater was necessary to ensure adequate
solubility of extract. The fraction of coal extracted, as determined by
weight difference of original coal and coal residue, after tetralin
contact and benzene extraction, showed an increase with temperature and
with time. The extraction approached 95%, 70% and 12% conversion of
dry, ash-free coal for temperatures of 450, 350 and 250°C, respectively,
after 10 hours of contact with tetralin. Several years later, Anderson
et al. using the same coal with tetralin obtained conversion yields of
9.5% and 8.5% for temperatures of 87 and 47°C, respectively [43]. The effect of particle size on total percentage of coal dissolved at these temperatures was negligible, however, the initial rate of dissolution was higher for the smaller coal particles.

About 1965 Curran et al. conducted coal/solvent contacting experiments in a shaken microautoclave with two size fractions of a Pittsburg seam bituminous coal, -100 +200 mesh and -28 +48 mesh, and a hydrogen donor solvent at a temperature between 325 and 440°C [39]. Identical results of rate and yield were obtained for both fractions. Neavel in 1974 also observed negligible influence of coal particle size on extraction at 400°C [44]. This behavior may be attributed to rapid thermal disintegration of the coal particles at these temperatures, as observed by Guin et al. [45].

In 1974 Severson et al. contacted two subbituminous and two bituminous coals with tetralin and also with anthracene oil at 400°C for 2 hours [46]. The bituminous coals gave extractions approximately 10% higher, on a dry, ash-free coal basis, than did the subbituminous coals (80% and 70%); tetralin generally gave higher yields (by up to 5%) than did the anthracene oil solvent. Differences in the extraction yields between the same rank coals were generally small but differences of approximately 3% were typical.

Short contacting time experiments were conducted by Ross and Seth in 1976-77 at temperatures from 325 to 430°C with Illinois #6 bituminous coal and tetralin, naphthalene, phenanthrene and phenanthrene/tetralin mixtures [47]. Conversion of the coal was determined by pyridine
solubility of the extract and coal residue. At 430°C and 1/2 minute contact time, pyridine solubility of 80% (daf coal basis) was obtained. Conversion of Illinois #6 coal at temperatures from 325 to 430°C after about 2 minutes of contact yielded 19% to 94% pyridine solubles. Naphthalene and phenanthrene were considered poorer solvents and exhibited a maximum in pyridine solubility at approximately 400°C of 44% and 38%, respectively. Phenanthrene/tetralin mixtures were less effective at short reaction times (about 2 minutes) than pure tetralin; at long times (2 hours and 20 hours) conversion to pyridine soluble material was greater with the mixture than with either pure tetralin or phenanthrene [48]. As reported above, variation in reactivity even of two bituminous coals from the same region were observed [49].

Draemel and Grens reported solubilities of a Wyoming subbituminous coal (Wyodak, Roland Seam) in tetralin and other aromatic solvents at temperatures from 150 to 350°C in a Soxhlet apparatus, usually for contacting times of 4 hours [40]. Coal extraction by tetralin (daf coal basis, determined by evaporation of solvent from the extract solution) increased with temperature, doubling the yield from 16% to 32% for a temperature change from 300 to 350°C; yields at 150, 200 and 250°C were 5.7%, 6.5% and 8.7%, respectively. A few results were presented indicating an increase in conversion with longer contacting times.

Other reports concerning the solubility of many coals in tetralin and other hydrogen donor solvents under various contacting conditions also exist; the trends cited here persist. However, the direct
application of results from one coal to the next or from one set of contacting conditions to the next is, at best, uncertain.

**Models for Coal Extraction**

Attempts to explain, correlate or model the action of solvents on coal have been made for at least 40 years. Thermodynamics of the solubility of a solid in a liquid has been applied to the extraction of coal in various solvents in an attempt to explain the effectiveness of these solvents as a function of their physical properties. Kiebler [27] and van Krevelen [50] were generally unsuccessful in their attempts to explain coal solubility by physical or thermodynamic properties of solvent alone. Recently Hombach attempted to determine the solubility parameters of various coals and solvent mixtures [51]. Theoretically a solvent with a solubility parameter equal to the coal solubility parameter should be an effective solvent for that coal. Ideally, an effective solvent could be found for any coal if its solubility parameter could be determined, even before solvent contacting. Hombach met with limited success in describing the solubility of coal in the few solvents he observed.

One of the earliest models of coal and coal extracts was proposed by Kreulen as summarized by van Krevelen [52]. A mechanism of solution based on a similar model was developed by Dryden [53]. Coal was considered as a matrix of large and strongly linked micelles interspersed with smaller, less strongly bonded micelles. During extraction, solvent penetrates and swells the matrix, permitting the escape of the small micelles into the bulk solvent, then forming a colloidal solution.
Storch et al. [54], Lahiri [55] and van Krevelen [56] advanced the concept of coal extracts being large molecules of a very wide molecular weight distribution (300 to greater than 1000) frequently occurring in solution weakly held together as aggregates; the structure of solid coals was expected to be similar in nature to the aggregates, only more strongly bound.

Kinetics of Extraction

In an attempt to elucidate the processes involved in deriving liquids from coal, various investigators have studied the kinetics of coal dissolution in organic solvents. Because of the complexity of this process, which involves many reaction steps with numerous chemical species, even a broad understanding of the reaction mechanism is far from being realized. The approach in kinetic studies has been to describe the behavior of the overall coal conversion, with little or no knowledge of the kinetics of individual reactions or the mechanisms of the reactions, by combining various reactant and product species into groups. These groups are determined by various analytical techniques such as solubility in solvents, distillation, or chromatographic separation. Early studies of coal/solvent contacting frequently used massive batch reactors requiring long heat-up and cool-down times during which significant reactions could occur. Meaningful kinetic studies, however, require techniques that minimize these nonisothermal times. Two common approaches have been to use small reactors constructed from thin tubing that can be heated and cooled rapidly or to first heat up
the solvent in the contactor to the reaction temperature and then inject
the coal or a coal slurry into the contactor.

The work of Oele et al. in 1951 proposed one of the earliest and
simplest models [32]. They assumed that the dissolution proceeded with a
zero-order forward step and a first order reverse step (precipitation).
Hill et al. in 1966, based on some experimental observations, concluded
that very little, if any, reverse reactions were involved in their system
[57]. They proposed a simple dissolution mechanism and derived a rate
expression to fit a first order dependence with respect to coal and a
rate constant that varied with extent of conversion. The hydrogen trans­
fer reaction from solvent (tetralin) to coal was regarded as first order
in coal and first order in solvent, and at a sufficiently high solvent­
to-coal ratio any solvent dependence could be eliminated. Because of the
dependence of the rate constant on the extent of conversion, a pseudo­
second order rate expression was obtained; this expression fit the
kinetic data well for most conversions except fairly high ones. Activa­
tion energies were also obtained from the derived rate constants for
temperatures from 100 to 450°C [58]. At low temperatures the average
apparent activation energy calculated was low, 7 kcal/mol, and indicated
that the process could be attributed to diffusion-limited dissolution of
interstitial material in the coal with no or very little hydrogen trans­
fer reactions occurring. A larger apparent activation energy, 19-32
kcal/mol, was obtained at temperatures above 250°C for the initial stages
of conversion. The apparent activation energy increased with conversion
at high temperatures (350-400°C) to values as high as 85 kcal/mol at 90%
conversion. It was concluded from these high apparent activation energies that the dissolution process involved thermal decomposition with chemical bonds of increasing strength being broken at progressively higher temperatures and conversions.

Later work by Anderson et al., on the same system as that of Hill et al., resulted in the conclusion that two different reaction regime exist during the high temperature (higher than 350°C) dissolution process [59]. During the first several minutes, dissolution and thermal decomposition proceed rapidly with minimal transfer of hydrogen. Then the overall rate of dissolution decreased but the rate of hydrogen transfer from tetralin increased.

Curran et al. represented coal conversion in tetralin by a model involving two constituents of coal, one of higher reactivity than the other [39]. These two constituents are converted to soluble material by parallel first order reactions. Rate constants and apparent activation energies were calculated from the rate data obtained at three temperatures, 324, 354 and 388°C. Rate expressions for hydrogen-transfer to coal and to extract were also derived, and rate constants and apparent activation energies were calculated. The experimental data were adequately represented by the model and the expressions developed.

The determination of coal conversions in recent times has often been by Soxhlet extraction of the treated coal and coal derived materials in several organic solvents [4,5,6,60,61,62]. The most easily soluble material (the lowest boiling, least viscous, and typically of lowest average molecular weight) is the fraction soluble in hexane,
cyclohexane, or pentane, and is called "oil". Recycle solvents in a commercial process would be primarily comprised of compounds classified as oils. The next classification is "asphaltenes" (or asphalts); these are removed from the cyclohexane insoluble portions of the coal-derived material by Soxhlet extraction with benzene or toluene. They are typically of higher boiling point, viscosity, and molecular weight than the oils. The compounds in the third and last category, considered important only in the last several years, are called "preasphaltenes" (or asphaltols); these are the cyclohexane- and benzene-insoluble, pyridine- or tetrahydrofuran-soluble fraction of the treated coal. These compounds are even more viscous and of higher molecular weight than the asphaltenes. These three solubility fractions of coal are the basis of several kinetic model developments of coal extraction presented in the literature, in which they are frequently treated as pseudo-single components in a postulated kinetic mechanism.

Liebenberg and Potgeiter presented the following two alternative mechanisms and attempted to fit them to their experimental data obtained at temperatures of 380 to 400°C with a bituminous coal contacted with tetralin [63]:

\[
\begin{align*}
&k_1 \quad k_2 \\
&\text{coal} \rightarrow \text{asphaltene} \rightarrow \text{oil} \quad (1-1) \\
&k'_1 \\
&\text{coal} \rightarrow \text{asphaltene} \quad (1-2) \\
&k'_2 \\
&\text{oil}
\end{align*}
\]
These mechanisms failed to represent the observed data, and a more elaborate mechanism was proposed for further investigation:

\[
\begin{align*}
\text{coal} & \xrightarrow{k_1} \text{asphaltene} \quad \text{oil} \\
\text{coal} & \xrightarrow{k_3} \text{preasphaltene} \\
\text{asphaltene} & \xrightarrow{k_2} \text{oil}
\end{align*}
\]  

(1-3)

Given et al. presented the following model, which does not separate the asphaltene from the oil, but incorporates the preasphaltene fraction into the mechanism [64]:

\[
\begin{align*}
\text{coal} & \xrightarrow{k_1} \text{asphaltene} + \text{oil} \\
\text{coal} & \xrightarrow{k_3} \text{preasphaltene}
\end{align*}
\]  

(1-4)

They postulated that steps 1 and 2 represented cleavage of ether bonds, disproportionation of hydrogen, and stabilization of free radicals by the hydrogen donor solvent, and that step 3 represented hydrogenolysis of oxygen functional groups and slight hydrogenation of the preasphaltenes. Rate expressions were derived and first-order rate constants and apparent activation energies calculated from the data reported by Wiser [65] and by Hill [66] at 350, 375 and 400°C. The proposed model was reported as fitting the data well.

A relatively complicated kinetic model was proposed by Cronauer et al. to represent the liquefaction of a Wyoming subbituminous coal (Belle Ayr Mine) in hydrogenated anthracene oil and hydrogenated phenanthrene at temperatures from 400 to 470°C for contact times of 5
to 55 minutes [67]. The following reaction mechanism of irreversible first-order reactions was proposed:

\begin{equation}
\begin{align*}
\text{coal} & \xrightarrow{k_g} \text{gas} \\
& \xrightarrow{k_a} \text{asphaltene} \\
& \xrightarrow{k_p} \text{preasphaltenes} \\
\text{oil} & \xrightarrow{k_o} \text{coal} \\
\text{asphaltene} & \xrightarrow{k_{ao}} \text{oil} \\
\text{preasphaltenes} & \xrightarrow{k_{pa}} \text{asphaltene}
\end{align*}
\end{equation}

The rate constants for all reactions were found to be generally of the same order of magnitude. The values of the apparent activation energy were dependent on the solvent that was used; for the hydrogenated anthracene oil runs the apparent activation energy varied from 13 to 22 kcal/mol, and for the hydrogenated phenanthrene run the apparent activation energy varied from 4 to 34 kcal/mol. Correlation of the distributions of preasphaltenes, asphaltenes, oil and gases in the coal conversion was reasonably good by this model. Development of a more sophisticated kinetic model which takes into account the effects of the solvent-to-coal ratio, pressure and hydrogen donor solvent was recommended for a better representation of the observed phenomena.

Baldwin et al. studied the rates of formation of oils, asphaltenes and preasphaltenes during conversion of a Kentucky high volatile A bituminous coal (Fies Mine) in tetralin at temperatures from 350 to 400°C for times from 10 minutes to 3 hours [10]. Mathematical models for the following three proposed mechanisms of coal liquefaction to preasphaltenes, asphaltenes and oils plus gases were applied to the experimental data:
The final mechanism (1-8), very similar to the one proposed by Cronauer et al. (mechanism (1-5)), was found to fit the data best of the three but not exceptionally well. It was concluded that models incorporating more fundamental chemistry were needed.

In work presently under way at Sandia National Labs, Thomas and Bickel report some results on the liquefaction of Illinois #6 high volatile bituminous coal (Burning Star Mine) in SRC-II heavy distillate between 275 and 475°C [68]. The heavy distillate is typical of an actual recycle solvent that would be used in a commercial process. Development of a process kinetic model for coal liquefaction that would enable process designers to make sound technical decisions is sought.

A simple kinetic model was proposed which involved the solvent (distillate) in the reaction mechanism:
Rate constants, activation energies and stoichiometries of the postulated reaction were calculated. Reasonable agreement between the experimental data and the concentration derived from the model was obtained.

A new approach to product analysis for application to kinetic models was developed recently by Silla and Mohan [69]. Separation of the liquid products from coal by liquid solid chromatography on alumina was used to obtain classes of compounds consisting of mixtures of aromatics, ethers, nitrogen-containing compounds, hydroxyl-containing compounds and multifunctional compounds. The following kinetic reaction schemes were proposed:

\[
\text{hydroxyls(OH)} \\
\text{coal(C)} \rightarrow \text{multifunctionals(M)} \rightarrow \text{nitrogens(N)} \rightarrow \text{ethers(E)} \\
\text{aromatics(A)}
\]

\[
\text{C} \quad \text{OH} \\
\text{M} \quad \text{N} \\
\text{A} \quad \text{E} 
\]

\[
\text{C} \rightarrow \text{OH} \rightarrow \text{N} \rightarrow \text{E} \rightarrow \text{A}
\]
The second model (1-11) was found to give a reasonably good fit for the experimental data from Illinois #6 bituminous coal (River King Mine) conversion in a tetralin (75%)/decalin (25%) solvent over the entire temperature range from 330 to 450°C and reaction times from 5 to 60 minutes. The other models did not perform as well over the temperature range studied. A somewhat empirical method for combining the five chromatographic fractions was also proposed to approximate the solubility fractions of preasphaltenes, asphaltenes and oils; kinetic models similar to the one proposed by Cronauer were applied to these groupings. Representation of the experimental data was as good by these models as the models using chromatographic separations. The superiority of either separation technique was not established.

Szladow and Given recently discussed the methods of studying the kinetics of coal liquefaction [70]. The fact that kinetic expressions, derived with little knowledge of the mechanisms of the reactions, may be able to correlate the experimental data would not necessarily imply the ability to apply the derived rate expressions to commercial reactor design. In the article, reference was made to Luss and Golikeri who showed that if a particular grouping of compounds (e.g., asphaltenes, preasphaltenes) contains species of different reactivities, the rate expressions derived from experiments in one reactor are not, in general, applicable to the same process in another reactor [71]. Furthermore, many kinetic models correlate the same set of coal conversion data equally well; therefore, the order of the derived rate expressions for the appearance of coal derived material may not necessarily be the same
as the order of the actual reactions occurring. Application of the principles of chemical reaction engineering to these rate expressions could lead to significant errors.

Szladow and Given also reported results obtained in coal/tetralin contacting experiments at temperatures between 340 and 400°C for times from 2 to 32 minutes. Coal conversion was calculated by weight difference of the original coal and coal residues, after tetralin contact in a batch microautoclave and exhaustive pyridine extraction in a Soxhlet apparatus. Contacting of a Pennsylvania bituminous coal (Middle Kittanning Seam) with tetralin at 400°C for 20 minutes yielded 89% pyridine-soluble material on a dry coal basis; this represented approximately 100% of the potentially soluble coal after taking into account the mineral matter (8%) and fusinite (highly inert organic fraction of coal, possibly present in low concentrations in this coal). Lower conversions were observed at the lower temperatures for the same contact time. A kinetic model was postulated that involves two initial groups of coal compounds that are converted by parallel mechanisms to pyridine-soluble materials:

\[
\begin{align*}
\text{coal}_1(C_1) & \xrightarrow{k_1} \text{oil} + \text{asphaltene} + \text{preasphaltene} \\
\text{coal}_2(C_2) & \xrightarrow{k_2} \text{oil} + \text{asphaltene} + \text{preasphaltene}
\end{align*}
\]

Rate constants were calculated for various fractions of the total amount of potentially reactive material that constituted \( C_1 \) and \( C_2 \), such that their sum was equal to the total. Evaluation of the behavior of
the experimental and predicted apparent activation energies led to a choice of the best set of kinetic parameters resulting in a reasonably good fit of the data. In general, the apparent activation energies increased with conversion, consistent with the result of Hill et al. [57,58] and with the expectation that the more reactive species are consumed (dissolved and/or reacted) first and the more refractory materials consumed as the coal conversion progresses. It was concluded that a better knowledge of the kinetic behavior of the liquefaction reactions and the effect of reactor dynamics on yield and type of liquefaction products must be developed for improved models of coal conversion.

Scope

The subject of this investigation has been the interaction of subbituminous coal with tetralin, a hydrogen donor solvent representative of recycle solvents, at temperatures below the coal pyrolysis temperature. A better understanding of the mass transfer and kinetic phenomena involved was sought by study of the rates of extraction of coal materials and the influence of contacting parameters upon these rates. By appropriate variation of these parameters the importance of the dissolution step, the internal mass transfer within the coal particles, and the external mass transfer from the coal particles on the overall rate of extraction was assessed.
A temperature range of 150 to 300°C, contacting time range of approximately 1/2 minute to 500 hours and coal particle size range of 30 to 270 mesh were examined. Batch treatments of coal with excess solvent were conducted in a stirred vessel or a high pressure Soxhlet extraction apparatus.

**Nature of Results**

Based upon measurements of extraction yields as a function of time and contacting parameters for the coal/tetralin system a kinetic model was derived. This model involves grouping compounds of similar extraction characteristics together and treating them as pseudo-single components in a kinetic mechanism to represent the phenomena in coal/solvent interactions. Rate constants and apparent activation energies appropriate to the proposed model were calculated from the experimental data. The value of these kinetic parameters were used to interpret the observed phenomena and to substantiate the proposed model.
II. EXPERIMENTAL EQUIPMENT AND PROCEDURE

The experimental program was designed to determine the influence of time, temperature and coal particle size on the kinetics of extraction in coal/solvent interactions. An investigation of kinetics requires satisfaction of certain criteria in order to obtain meaningful rate data. Constant temperature during an experiment is essential for the determination of the temperature dependence of the rate. Well-defined initiation and termination of coal/solvent contacting are necessary for establishing the actual rate of extraction at the given temperature; contacting of the coal with the organic solvent prior to achieving the desired temperature, as in typical batch autoclaves requiring significant heat-up and cool-down periods, introduces uncertainties in the rate data. In order to study the effect of particle size on the kinetics of extraction, not only must the initial particle size distribution be known to a certain extent, but also the particle size distribution should remain approximately constant.

A better understanding of coal/solvent interaction at subpyrolysis temperatures was sought by starting the measurement of the rate of extraction at times as short as possible. Also, the development of the kinetics of extraction required the determination of "ultimate" yields; thus, coal/solvent contacting experiments at sufficiently long times to approach maximum extraction for a given temperature were also conducted. Therefore, coal/solvent contacting was carried out in two types of reactors to meet the requirements of this investigation, one for relatively short contacting times and the other for long times. For
experiments of relatively short duration (the majority), the coal and organic solvent were contacted in a stirred batch vessel. In order to establish accurately the initiation of contacting, the solvent and coal were preheated separately to the desired temperature before mixing. Termination of contacting was accomplished by rapid filtration of samples of the coal/solvent slurry withdrawn from the contactor at predetermined times. Because of considerable mechanical degradation of the coal particles at long contact times (longer than 6 hours) and the necessity of continuous surveillance, the stirred batch contactor was only appropriate for relatively short times.

For longer contact times a high-pressure Soxhlet extractor was used; this is a device in which the coal is contacted with pure solvent that is vaporized from the solvent/extract mixture and condensed in a reflux condenser. Temperatures other than the atmospheric boiling point of the solvent could be used by control of the pressure in the apparatus. The disadvantage of a Soxhlet-type contactor is that mixing is less vigorous than with a stirred batch contactor, in which the coal and solvent are mixed together, and initial heat-up periods are much longer. Thus the Soxhlet contactor is not appropriate for short contact times. However, this apparatus caused minimal degradation of the coal particles and could be run unattended.
Stirred Extractor System

The apparatus used for most of the experiments in this study consisted of a stirred batch contactor equipped with a solvent preheat vessel and a coal/solvent slurry sampling system as shown in Figure 2-1. At the start of an experiment preheated solvent from the preheat vessel was transferred to the preheated contactor vessel which contains the coal. After a predetermined time of contacting, samples of the slurry were removed from the contactor and filtered to separate the coal from the extract solution.

Both the solvent preheat vessel and the contactor vessel were fabricated by the University of California, College of Chemistry, Machine Shop from type 304 stainless steel 2-1/2 in. schedule 40 pipe. The maximum capacity of the vessels was approximately 350 mL. Both vessels were sealed to a mating head by a flange joint with 3-1/4 in. OD replaceable Varian copper gaskets. A dip tube, extending to the bottom of the solvent preheat vessel, was connected to the transfer line to the contactor vessel. Transfer of all but about 5 mL of the solvent was accomplished by application of nitrogen pressure to the solvent preheat vessel and opening the transfer valve. Both vessels were equipped with 0-600 psig (0-3.4 MPa) pressure gauges, thermocouple wells, inert gas (N₂) inlet lines and vent lines, and were protected against over-pressure by rupture discs (1/2 in. standard Ni or Au-Ni-Au from Continental Disc Corp.) vented to a fume hood. All lines were 1/4 in. OD 304 stainless steel tubing, except for the rupture disc lines, which
Figure 2-1. Coal/solvent contacting apparatus for short contacting times.
were 1/2 in. OD 304 SS tubing (to allow for minimal pressure drop while venting in case of disc rupture), and the N₂ supply lines upstream of inlet valves, which were constructed of 1/4 in. copper tubing. A stirring assembly, manufactured by Parr Instruments, with two impellers was mounted on the contactor. The stirrer seal cooling jacket was supplied with cool water from a closed loop water circulation system. The stirrer was powered by a D.C. Servo Motor controlled by a Motor Speed Control (Series E600 by Electrocraft Corp.) capable of 0-3000 rpm at 0-3 in. lb. torque. Two sets of six radially oriented baffles, attached to the thermocouple probe sheath and the slurry sampling dip tube, approximately 1 cm high with one set above and one set below the top impeller, improved the mixing and eliminated formation of vortices in the slurry within the contactor vessel. (This improvement was observed directly by use of a clear Plexiglas model of the vessel.) For the later runs of this study, coal was introduced into the contactor vessel through a glass funnel that was attached to a port on the contactor flange with a short section of clear plastic tubing.

The contactor was equipped with a sample tube extending to within 4 cm of the bottom of the vessel. Samples of the coal/solvent slurry were removed through this tube and transferred to the filtering apparatus. A 1/4 in. bore Dynaseal 310 ball valve (W-K-M Valve Group, ACF Industries, Inc.) fitted with high-temperature filled-TFE seats was installed in the sample line to provide rapid actuation with minimal flow restriction for the slurry.
Each vessel was heated by a 600 watt heating mantle and insulated with fiberglass insulation. The contactor vessel was also equipped with a 144 watt high temperature heating tape wrapped around the flange to ensure that the flange was adequately heated. The transfer line and the sample line were wrapped with 288 watt and 144 watt heating tapes respectively. The heating tapes were powered by variable transformers precalibrated for the desired temperature. One LFE Model 232 proportioning temperature controller was used for temperature control of the two vessels; the temperature of the vessel being controlled was recorded on a Sargent Model MR strip chart recorder. During a run the temperature controller was first used to control the heat-up of the solvent preheat vessel. Once the desired temperature in the solvent preheat vessel was attained and stabilized, and the heat load necessary to maintain the temperature was determined by timing the on-off cycle of the heater, the temperature controller was switched to control the temperature of the contactor vessel heater and the solvent preheat vessel heater switched to a variable transformer set to the appropriate setting. Copper-constantan thermocouples connected to an Omega Model 175 digital meter were used to monitor the temperatures of the vessels, the vessel top flanges, the transfer line, the sample line, the contactor rupture disc (by monitoring the rupture disc temperature, small pinhole leaks - more common than catastrophic leaks - could be detected by a rise in temperature from escaping gases) and the stirrer seal cooling water. Three timers, registering minutes to 1/100 of a minute, were used to keep track of run time and time between samples.
This equipment was designed to operate, with a considerable safety margin, at temperatures up to 300°C and pressures to 3.4 MPa.

**Sample Filtering System**

The filtering system was designed to separate the slurry rapidly into a solid fraction of undissolved coal and a liquid fraction of solvent and dissolved coal material, and to cool these fractions sufficiently after separation to prevent excessive flashing of the solvent. The slurry was filtered through filter holders fabricated from short sections of appropriately machined 1/2 in. schedule 80 stainless steel pipe with removable filter inserts as shown in Figure 2-2. The filter inserts included a support disc of 1/8 in. thick sintered porous stainless steel (E porosity, 12 micron nominal, 35 micron absolute particle size retention, from Pall Trinity Micro Corporation), a glass fiber filter disc (Toyo GA200, 0.8 micron retention, from Nuclepore Inc.), and two stainless steel screen discs of 200 and 100 mesh, which were provided for removal of the larger particles of coal and for protection of the glass fiber filter from the rapid impingement of the slurry upon the filters. Each filter assembly (pipe section and filter discs) was sealed with copper gaskets between two VCR Cajon fittings within a stainless steel holder. Eight filters were constructed allowing for as many as eight samplings of the slurry throughout the course of a single run. Liquid samples were collected in 20 mL scintillation vials.
Figure 2-2. Coal/solvent slurry sample filtering assembly.
High Pressure Soxhlet Apparatus

The high pressure Soxhlet apparatus shown in Figure 2-3 was designed and constructed for work conducted by Draemel and Grens, and was used with only minor modifications [40]. Coal contained in a wire screen basket (200 mesh stainless steel) was contacted with relatively pure refluxed solvent, which had been vaporized from the bulk of the solvent/extract solution. The basket of coal was held in a cup that collected the condensed solvent; this cup filled with solvent to a fixed level and then dumped the solvent back into the solvent/extract solution by overflow through a siphon. Samples of this liquid in the solvent vessel were periodically removed through the same filter assembly as used with the stirred batch contactor. The filter removed any fines that may have washed through the screen basket into the liquid.

The apparatus consisted of a heated 2-liter vessel for boiling the solvent, a water cooled condenser and a 4-liter vapor surge volume for pressure control. The apparatus was constructed of 304 or 316 stainless steel including all associated tubing. The exterior of the solvent vessel was clad with a thin layer of copper to promote even heating of the vessel.

The contacting cup, and the solvent vessel flange head to which it was attached, are shown in greater detail in Figure 2-4. The stainless steel cup was of 200 mL capacity with a 150 mL siphon overflow level. Coal was contained in the 200 mesh stainless steel wire basket with a close fitting lid. Samples of the liquid in the solvent vessel of the vessel of the contacting cup were removed through the sample lines.
Figure 2-3. High pressure Soxhlet apparatus for long contacting times.
Figure 2-4. Detail of coal/solvent contacting cup and solvent vessel flange for high pressure Soxhlet apparatus.
The solvent vessel was sealed to the top flange with a replaceable copper gasket.

The control of the coal/solvent contacting temperature was accomplished by controlling the system pressure, since the boiling point of the liquid is a direct function of the pressure. Short term pressure stability was improved by the 4-liter surge volume above the reflux condenser and long term pressure control was provided by feedback control on the exit stream of a nitrogen bleed through the surge volume. The control system consisted of a strain gauge pressure transducer (Teledyne Taber Model 2801-A-0200-0, 0-200 psia range) which provided a 4 to 20 mA signal to a recording pressure controller (Robertshaw Microsen Model 221 recorder and Model 321 controller), and an electro-pneumatic transducer (Robertshaw Microsen Model 445B7, 4 to 20 mA converted to 3 to 15 psia) to vent the system through a pneumatic valve (Cashco Type 563). The apparatus was protected against excessive pressures by a rupture disc assembly and vent line on the top flange of the vapor surge volume.

Heat was supplied to the solvent vessel by a 0-750 watt hot plate and a 850 watt heating mantle controlled by a variable transformer. The entire solvent vessel and heaters were insulated with fiberglass insulation. Temperature of the solvent vessel, the contacting cup, the condenser inlet and outlet cooling water, the bottom of the surge volume and the solvent vessel flange were monitored with iron-constantan
thermocouples and continuously recorded on a Leeds and Northrup multi-point recorder (Speedomax H-AZAR).

An emergency shutdown system was used for extended unattended operation. This system provided automatic shutoff of the solvent heaters if either of two temperature sensor switches opened because of a temperature rise. These bimetallic thermally-activated switches were attached to the tube between the condenser and surge volume above the condenser and on the rupture disc vent line, and set to open at temperatures greater than 175°C as in the event of condenser coolant loss or rupture disc blowout.

Materials

Coal

The coal used in this investigation was from the Roland Seam of the Wyodak Mine in Gillette, Wyoming. This coal has an apparent rank of subbituminous C; its proximate and elemental analysis are shown in Table 2-1. Several physical parameters of raw coal reported by Petersen et al. are also shown [12,14]. The coal, shipped as large chunks (up to 15 cm in diameter), required considerable size reduction for use in the experiments. In order to assure an evenly mixed slurry (complete uniformity of suspension) in the contacting vessel, solid particles with settling velocities of less than 3 cm/sec were required [72]. This requirement was met by grinding the coal to particles smaller than 30 mesh. Care in handling of the coal was required to prevent excessive atmospheric oxidation, which has been shown to affect
Table 2-1. Analysis and Physical Properties of Wyodak coal.

<table>
<thead>
<tr>
<th>Proximate Analysis(^a)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>As received</td>
<td>Dry basis</td>
<td></td>
</tr>
<tr>
<td>% Moisture</td>
<td>23.43-23.83</td>
<td>23.43-23.83</td>
</tr>
<tr>
<td>% Ash</td>
<td>10.40-11.49</td>
<td>13.64-15.08</td>
</tr>
<tr>
<td>% Volatile Matter</td>
<td>29.04-35.52</td>
<td>37.94-46.59</td>
</tr>
<tr>
<td>% Fixed Carbon</td>
<td>30.16-36.17</td>
<td>39.60-47.23</td>
</tr>
<tr>
<td>BTU</td>
<td>8,226-8,392</td>
<td>10,800-10,934</td>
</tr>
<tr>
<td>% Sulfur</td>
<td>0.70-0.94</td>
<td>0.92-1.23</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Elemental Analysis(^b)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry basis</td>
<td>daf basis</td>
<td></td>
</tr>
<tr>
<td>% Carbon</td>
<td>62.5</td>
<td>72.3</td>
</tr>
<tr>
<td>% Hydrogen</td>
<td>5.1</td>
<td>5.9</td>
</tr>
<tr>
<td>% Nitrogen</td>
<td>0.93</td>
<td>1.08</td>
</tr>
<tr>
<td>% Sulfur</td>
<td>0.56</td>
<td>0.65</td>
</tr>
<tr>
<td>% Chlorine</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>% Ash</td>
<td>13.6</td>
<td></td>
</tr>
<tr>
<td>% Oxygen (by difference)</td>
<td>17.3</td>
<td>20.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Physical Properties([12,14])</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Apparent Density</td>
<td>1.29 g/cc</td>
<td></td>
</tr>
<tr>
<td>Helium Density</td>
<td>1.55 g/cc</td>
<td></td>
</tr>
<tr>
<td>Pore Volume</td>
<td>0.13 cc/g</td>
<td></td>
</tr>
<tr>
<td>Porosity</td>
<td>0.167</td>
<td></td>
</tr>
<tr>
<td>Surface Area (by CO(_2) adsorption, on daf coal basis)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-28 mesh</td>
<td>106 m(^2)/g</td>
<td></td>
</tr>
<tr>
<td>-28 +150 mesh</td>
<td>99 m(^2)/g</td>
<td></td>
</tr>
<tr>
<td>-150 mesh</td>
<td>170 m(^2)/g</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Commercial Testing and Engineering Co. (Denver, Colorado)

\(^b\) Micro-Analytical Laboratory, College of Chemistry, University of California
the coal's liquefaction characteristics; it has been proposed that oxygen incorporated into the coal will cause polymerization of coal material through oxygen radical chain polymerization rendering the coal much less soluble [73,74,75]. Another consideration in coal processing has been presented by Gavalas et al.; they found upon coal analysis a higher ash content in smaller particles, attributed to differential classification during the grinding and sieving process [76]. This same observation was made by Newell et al. [77]. Draemel, however, on analysis of a -30 +150 mesh fraction and a -150 mesh fraction of the coal used in this study found negligible differences in the ultimate or proximate analyses [40].

The bulk coal as received was crushed to -3/4 in. by a jaw crusher and further processed by a roll crusher to -1/16 in. Fines removal (at this stage removal was not considered critical since most coal was greater than 30 mesh and the fines were most likely oxidized) was accomplished by sieving this coal, leaving a -4 (-1/16 in.) +30 mesh fraction, which was stored under nitrogen in plastic bags placed in friction-lid metal cans. This coal fraction was used for the experiments in this study after further size reduction. All subsequent operations with the coal were conducted in a glove box flushed with dry nitrogen to minimize the atmospheric oxidation of the coal. Representative samples from the -4 +30 mesh fractions were obtained with a riffler and repetitively ground in a ball mill and sieved to the desired fraction. The following fractions were generated, each from a separate
portion of the -4 +30 mesh coal stock, and stored in pint size friction-lid metal cans under nitrogen: -30, -50, -70, -100, -200, -30+40, -50+70, -100+140, and -200+270.

**Solvent**

Reagent grade (99%) tetralin (1,2,3,4-tetrahydronaphthalene) was obtained from Aldrich Chemical in 5 gallon lots. Vapor pressure, viscosity and density of tetralin were taken from reported values and correlations; these properties are presented in Appendix B. Recovery of a significant fraction of the tetralin was possible after each run. The contaminated tetralin was distilled at atmospheric pressure in a glass helice packed column. The first 10-15% distilled over and the bottoms (10-15% of the original charge) were discarded. This procedure yielded 98+% purity tetralin as determined by gas chromatography. Dry nitrogen gas (99.999% purity) was obtained in gas cylinders from Pacific Oxygen.

**Procedures**

Dried coal was used for the experiments in this study. The removal of moisture from coal has been conducted in many ways and has evoked considerable discussion. The definition of what constitutes water in coal is difficult because water is released from normal evaporation of free surface water, and from thermal decomposition of oxygen-containing functional groups in the coal and water of hydration from minerals in the coal. This thermal decomposition can commence at temperatures well below 100°C [78]. In lieu of a universally accepted and satisfactory drying procedure, a room temperature drying procedure was adopted so
that all coal samples would have approximately the same water content, and so minimal thermal decomposition would occur.

Before each run, approximately 40 grams of coal were placed in two preweighed glass bottles. These bottles of coal were then placed in a desiccator kept at room temperature, with 8 mesh indicating Drierite as the desiccant, and the desiccator was evacuated to progressively higher vacuum over a 24 hour period according to the schedule shown in Table 2-2. Gradual application of vacuum was found to be necessary to prevent the coal from "bubbling" out of the bottles into the desiccator because of the rapid release of moisture and gases at pressures below approximately 24 in. Hg vacuum. Moisture removal by this method varied from 14% to 19% by weight of the original coal sample charged (17 to 23% of the dried coal). For comparison, coal that was dried in a vacuum oven at 105°C for 24 hours lost 20% of its original weight (25% of the weight of the dry coal).

**Short Contact Time Procedure**

The procedure described here is the final version arrived at after many modifications that were made throughout this investigation. An effort was made to maintain exactly the same procedure for sets of experiments that were to be compared.

Before each run, approximately 240 grams (for 250°C runs) of tetralin were added to the solvent preheat vessel, which had been purged with nitrogen. The amount of tetralin charged to the vessel was determined so that at the desired run temperature the volume of tetralin was no more than 350 mL, the maximum capacity of the vessels. The
Table 2-2. Coal Drying Procedure

<table>
<thead>
<tr>
<th>Time (hr)</th>
<th>Vacuum (in. Hg)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>24</td>
</tr>
<tr>
<td>1</td>
<td>26</td>
</tr>
<tr>
<td>3</td>
<td>28</td>
</tr>
<tr>
<td>7</td>
<td>29</td>
</tr>
<tr>
<td>23</td>
<td>29+</td>
</tr>
</tbody>
</table>

* Coal was held in a vacuum desiccator with 8 mesh indicating Drierite as the desiccant.
density at elevated temperatures, and thus the amount of tetralin
needed, was calculated by a corresponding-states correlation according
to the method of Chueh and Prausnitz as outlined in Reid et al., [79];
these calculations are presented in Appendix B. The preheat vessel was
then sealed and pressurized with nitrogen to 300 psig (2.1 MPa). Once
the heating mantle and insulation were in place, the vessel was heated
to the desired run temperature under control of the temperature
controller. The empty contactor vessel was also sealed, purged with
nitrogen, and its heating mantle, flange heater and insulation
installed; then, heating of the vessel, flange, and sample and transfer
lines, controlled by variable transformers set to precalibrated
settings, was begun.* As soon as the solvent preheat vessel
temperature had stabilized, control of the heating mantle of the
contactor vessel were exchanged between the temperature controller and
the variable transformer. The stirring motor was started to help
distribute the heat within the contactor vessel. When the contactor
vessel achieved thermal stability at the desired temperature, coal was
fed to the preheated contactor vessel from a covered glass funnel
through a port in its top flange. This port was then sealed as quickly
as possible and the stirrer motor turned up to the desired run speed
(600-1000 rpm). The run timer was started at the beginning of transfer
of the preheated solvent from the pressurized solvent preheat vessel

*For coal/solvent contacting runs prior to Run 62, the dried coal was
charged to the contactor vessel before sealing and was preheated with
the vessel.
through the heated transfer line into the contacting vessel. Transfer of solvent was complete in less than 10 seconds.

The first sample of the coal/solvent slurry was taken as soon as solvent injection was complete, the contactor vessel pressurized to 300 psig (2.1 MPa) with nitrogen, and the sampling system prepared, typically between 1/2 and 1 minute after the start of injection. Samples of the slurry were pressured from the contactor vessel to the filtering assembly by the 300 psig pressure maintained in the vessel. After transfer of approximately 8 mL of slurry to the filtering apparatus, a nitrogen stream was backflushed through the sample valve into the contactor vessel, clearing the slurry remaining in the sample draw-off tube and thus ensuring that the next sample would be representative of the slurry in the contactor vessel. Filtering of the sample, still held in the filtering apparatus under pressure, was then completed by releasing the liquid into an attached glass sample bottle. The filter apparatus was flushed with nitrogen to remove as much of the liquid from the coal residue deposited on the filter as possible. Some longer contact time samples (6-24 hours) required as much as an hour to obtain a reasonable flow of nitrogen through the filter; this was attributed to clogging of the filter by the fines generated from mechanical degradation of the particles at long times in the stirred contactor. The liquid sample bottles and the filter were then removed and the filter holder was cooled to approximately room temperature by dipping it in liquid nitrogen. A clean filter with two copper gaskets and a clean sample bottle were then put into place for the next sample. Samples of
the slurry were removed from the contactor at selected times during the run. After the final sample, the heaters were removed from the contactor and the high temperature extraction terminated by submerging the vessel in cool water. The rest of the apparatus was allowed to cool for at least 1-2 hours before venting the pressure in the contactor. Subsequently, the contactor vessel was removed and the remaining slurry poured into a filter, set on a vacuum flask. The filter, which collected the coal residue during the vacuum filtration, consisted of a glass fiber filter (Toyo GA200) supported on a Buchner-type fritted disc funnel (Pyrex 350 mL medium porosity).

Long Contact Time Procedure

The Soxhlet apparatus was used for two long time contacting experiments, one at 250°C, the other at 300°C. Prior to the runs, the apparatus was flushed with a low flow of nitrogen overnight. The preweighed stainless steel mesh basket was filled with -30 +40 mesh coal, dried according to the procedure described above, weighed again, placed in the contacting cup and attached to the top flange of the solvent vessel. Small, non-reactive, highly resistant granules (Tamer Tabs by Northwest Products) were placed in the solvent vessel to promote boiling and the solvent vessel was then mounted to the top flange. The apparatus was purged with nitrogen for one hour. A preweighed amount of tetralin (about 500 gm) was drawn into the solvent vessel through a tube attached to the solvent sample line by application of a slight vacuum to the apparatus. The heaters were put in place, the apparatus insulated and the cooling water through the condenser started. The hot plate and the
variable transformer for the heating mantle were then set to the appropriate settings and the emergency shut-off system was activated. The pressure of the system, as controlled by the pressure controller, was set to match the vapor pressure of tetralin at the desired temperature, and a low flow of nitrogen through the surge volume was established. The vessel and contacting cup attained the desired temperature in less than 2 hours, and steady dump cycle of approximately 7 dumps per hour (about 15 mL/min) was established after 3-5 hours. Samples of the liquid in the solvent vessel were taken at selected times (up to 725 hr at 250°C and 500 hr at 300°C) during the run through the sample filtering apparatus. A nitrogen backflush of the sample line after sampling insured that the next sample was representative of the solvent/extract mixture. The run was terminated by turning the heaters off, removing the insulation and heaters, increasing the pressure in the system to stop boiling and allowing the apparatus to cool overnight. Any liquid that remained in the contacting cup was removed through the contacting cup sample line. The gas in the system was also vented through the contacting cup sample line followed by a liquid nitrogen trap. The solvent vessel was then removed and the solvent mixture vacuum filtered through a glass fiber filter (Toyo GA200) supported on a fritted glass filter to remove the fines.

Determination of Extract Yield and Characterization of Products

The primary object of the analysis of the experimental samples was the determination of the extract yield of coal material into the solvent as a function of time. The separation of the extract (or dissolved coal
material) and coal residue was accomplished to establish the amount of each of these fractions. An examination of the character of these fractions, and of recovered solvent, was conducted on samples from a few selected runs by gel permeation chromatography, proton nuclear magnetic resonance, elemental analysis, and microscopy.

Coal residue samples collected in the sample filters, as obtained from the filtering apparatus, were weighed and then placed in a vacuum oven (Thelco Model 19 by Precision Scientific Company) at 105-110°C and 12-26 in. Hg vacuum for approximately 48 hours to evaporate the solvent remaining on the coal residue. The oven was flushed with a low flow of dry nitrogen to carry away the evaporating tetralin and to prevent the oxidation of the coal residue as it was drying. After drying, the coal residue samples were placed in a vacuum desiccator under nitrogen to cool for at least 1 hour and then weighed. The coal residue filter cake obtained from filtration of the slurry that remained in the contacting vessel at the end of each run (or the coal that remained in the screen mesh basket from the Soxhlet experiments) was also weighed, then dried by the above method and weighed again. A considerable amount of tetralin (up to as much as the weight of the dried coal residue) was evaporated from the solid samples.

**Determination of Extract Yield**

Liquid samples, and the solvent/extract solution recovered at the end of each run, were weighed and then analyzed for the amount of dissolved coal material (typically about 1% or less by weight in solution). Five milliliter aliquots of each of the liquid samples were
pipetted into labeled preweighed stainless steel dishes (7.5 cm diameter, 1 cm lip). These samples were weighed and then placed in a 105°C vacuum oven for 48 hr under continuous dry nitrogen purge. For the first 24 hrs, the vacuum ranged from 12 to 26 in. Hg; for the last 24 hrs, vacuum was maintained at 29+ in. Hg. Further drying was found to remove only negligible amounts of tetralin. After drying, the hot dishes were removed from the vacuum oven and placed in a desiccator for at least 1 hour to cool before the final weighing was made. From the amount of extract in each of the oven-dried samples, the total amount of extract in each liquid sample, and consequently the amount in the reactor at the time of sampling was determined.

These gravimetric measurements were used to determine overall mass balances on the coal (and extract), and the extent of coal extraction at each sampling and at the end of each run. The weighed amount of tetralin and dried coal charged to the contactors established the initial solvent-to-coal ratio. The extraction yield (on a dry coal basis) is equal to the product of the solvent-to-coal ratio and the extract-to-solvent ratio for the sample in question. This value, divided by the fraction of ash-free material in dry coal (about 15% ash content as determined by coal analysis), is the extraction yield on a dry, ash-free basis (daf). This calculation is appropriate provided that there was a reasonably high uniformity of mixing in the vessel and that the sampling system was able to remove a representative sample of the slurry. The solvent-to-coal ratios for each of the samples taken from the batch contactor, which were calculated from the amounts of tetralin and the
amounts of coal residue and extract removed during a sampling were usually within 10% of the initial value of the solvent-to-coal ratio, as reported in Appendix A. These values of solvent-to-coal ratios established the uniformity of mixing and representativeness of the samples.

The sum of the amounts of liquid samples, filtrate obtained after filtration of the final slurry in the contactor at the end of each run, and solvent removed in the vacuum oven, as determined by difference of coal residue weights before and after drying, was usually more than 95% of the amount of tetralin charged to the system. A coal balance was obtained by summation of the amounts of the dried sample residues, the dried filter cake, the total amount of extract, and the coal or coal residue collected during clean-up of the apparatus after a run; this sum was usually about 3-5% less than the coal charged.

**Characterization of Extract**

The elemental composition, the molecular weight distribution, and the aromatic/aliphatic character of the extract was investigated by elemental analysis, gel permeation chromatography and proton nuclear magnetic resonance, respectively. Dried extract was removed from the stainless steel evaporation dishes by dissolution/suspension in chloroform and transferred to 2-dram (7.4 mL) sample vials; the chloroform was then evaporated from the mixture leaving the extract in the vials.

Elemental analysis provided hydrogen, carbon, nitrogen and ash content of the extract material. Several samples of the dried extract were submitted to the Micro-Analytical Laboratory in the College of Chemistry at the University of California, Berkeley, for elemental
analysis. Carbon, hydrogen, and nitrogen analyses were carried out using a Perkin-Elmer Model 240 automated elemental analyzer. Ash content was determined from the residue weight after combustion of the sample in pure oxygen at 800°C.

Proton nuclear magnetic resonance (NMR) analysis was conducted on extract material to give an indication of the aromatic/aliphatic character of the material being analyzed. Preparation of the samples for NMR analysis involved addition of 0.5 to 1.0 mL of pyridine-d$_5$ (99.93% atomic purity from Prochem Co.) to the dried extract contained in the 2-dram vials. The vial was heated for a short time to accelerate the dissolution of the material. A few samples required filtration to remove undissolved material; these samples were filtered through a 2 mL medium porosity (10-15 microns nominal maximum pore size) fritted glass filter into a clean vial. Hexamethyldisiloxane (HMDS), a reference material for NMR, was added to the solution, which was then transferred to a 5 mm NMR tube. The sample was analyzed on a 60 MHz Varian Model T60 NMR Spectrometer over the chemical shift range of 0 (as determined by HMDS, actually 0.03 chemical shift with respect to tetramethyl siloxane, the customary reference compound; this slight difference is inconsequential for this investigation) to 10 ppm on the $\delta$ scale. Comparison of the integrated peak areas of the NMR spectrum yielded qualitative determination of the aliphatic/aromatic nature of the dissolved material [80]. The NMR analysis is reported in Appendix A.

Gel permeation chromatography (GPC) was employed to obtain an indication of the molecular weight distribution of the dissolved coal
material. A Waters Associates ALC/GPC 201 Liquid Chromatograph, which had three μ-Styragel columns (100Å, 500Å and 1000Å) in series for separation based on size exclusion, was used with pyridine as a carrier solvent. Detection of the separated fractions of the samples was by ultraviolet absorbance at two wavelengths (313 and 365 nm). An approximate calibration of molecular weight of coal-derived compounds as a function of elution volume was made by Davis [81]. Liquid samples in tetralin, as collected from the sampling apparatus, were filtered through a Millipore Teflon filter (0.5 micron particle retention size) before injection into the GPC. The GPC results are reported in Appendix A.

Characterization of Solid Samples

An investigation of the changes in the particle size, one aspect of the physical character, of the solid samples generated in this study was conducted. Visual inspection of the coal and coal residue was made to assess the change in coal particle size with increasing contact time of solvent and coal. In addition to direct visual observation, a Reichert Zetopan Research Microscope was used; examination under reflected light and green-filtered bright field at low magnification (28 and 56 power) was conducted to observe the general size changes in the coal particles. The sample of the coal or dried coal residue particles was placed between a glass slide and a small glass cover plate for observation. These results are reported in Appendix A.
III. RESULTS AND DISCUSSION

Since the phenomena involved in coal/solvent interactions, which can generally be classified as dissolution (or possibly reaction), internal mass transfer and external mass transfer, depend in different ways on the conditions of the contacting, they can be investigated by examination of the influence of several experimental parameters on the rate of interaction. Thus, through appropriate control of stirring speed, particle size, temperature and duration of contact a study of the rate limiting phenomena in coal/solvent interactions is possible. The stirring speed influences the rate of external mass transfer by affecting the extent of suspension of particles and the solvent velocity past any unsuspended coal particles, thereby influencing the mass transfer of dissolved coal material from the surface of the particles to the bulk solution. Coal particle size primarily affects the rate of internal mass transfer in the coal/solvent interactions by changing the length of the diffusion path of the dissolved material from within the particle; it also affects both internal and external mass transfer through particle surface area. The internal mass transfer and especially the dissolution/reaction phenomena are influenced by the temperature of the coal/solvent slurry, since diffusion, reaction and dissolution can have significant temperature dependence. A range of the experimental parameters was used in this investigation that was consistent with those expected in coal liquefaction studies being conducted in related work at Lawrence Berkeley Laboratory.
Experiments Conducted

The investigation of the coal/solvent interactions involved the examination of the influence of stirring speed, particle size, temperature and duration of contact on the extraction of Wyodak coal into tetralin in the stirred contactor described in Chapter 2. By sampling of the coal/solvent slurry at selected times during the runs, the rates of extraction were evaluated over periods from 1/2 minute to up to 24 hours. The effects of stirring speeds from 400 to 1000 rpm, particle sizes of -50, -30 +40, -50 +70, -100 +140, and -200 +270 mesh, and temperatures of 150, 200, 250 and 300°C were investigated within the framework of the procedure previously described. The primary results obtained from the experiments were the yields of extracted coal material as a function of contacting time, as calculated from the amount of dissolved material in the liquid samples.

Stirring Speed Effects

Prior to the study of the effects of stirring speed on the coal/solvent interaction, it was necessary to determine that an adequate mixing pattern was established in the contactor vessel. For this purpose, a clear Plexiglass model of the vessel was constructed and used to visualize the flow pattern within the contactor. Visual inspection indicated that the baffles greatly helped to eliminate formation of vortices, enhanced turbulence and reduced gas entrainment. Observation of a -30 mesh coal particle suspension was difficult at solvent-to-coal ratios of approximately 30 (on a weight basis), since the solution was not transparent. At a solvent-to-coal ratio of approximately 60,
stirring was adequate at 400 rpm with only minor particle suspension limitations. At lower solvent-to-coal ratios, typical of the experiments, inadequate suspension of coal particles at low stirring speeds may be expected to prevent intimate and vigorous coal/solvent contacting.

The rate of extraction was investigated as a function of stirring speed in the stirred contactor apparatus. The coal used in the study of stirring speed effects was -50 mesh Wyodak. The solvent-to-coal ratio varied from 6 to 8 on a weight basis. These hour-long runs were conducted at 250°C and at stirring speeds of 400, 600, 800 and 1000 rpm under a nitrogen gas blanket. The amounts of the coal extracted, calculated on a dry, ash-free, weight percent basis (daf), at the various sampling times for these runs are tabulated in Appendix A. The rate of extraction was observed to increase significantly with increasing stirring speed over the range of 400 to 800 rpm, as shown in Fig. 3-1. At a stirring speed of 1000 rpm, no further increase in the rate of extraction was observed for contacting times up to 1 hour. This seemed to indicate that all particles were suspended at stirrer speeds greater than 800 rpm. However, this behavior would not necessarily indicate the absence of external mass transfer limitations. Therefore, an approximate external mass transfer coefficient was calculated from available correlations, known physical properties of the solvent and the coal, measured properties of the extract and several assumptions, to compare with the observed behavior. Details of these calculations are presented in Appendix C. For spherical particles (approximately 60 mesh)
Figure 3-1. Extract yield as a function of contacting time for selected stirring speeds. Experiments were conducted at 250°C with -50 mesh Wyodak coal.
travelling at their gravitational settling velocity with respect to the bulk solvent, the estimated value of the external mass transfer coefficient was 0.00016 g mol/cm²-s or 14,000 min⁻¹ (on the basis of extract with 400 average molecular weight, 20% wt daf coal). This is so high that extraction of all of the soluble material would occur much sooner than the first sample could be taken, if this were the rate limiting effect. This is the case even though turbulence caused by the vigorous stirring was neglected in the calculation. Since these calculations of an effective external mass transfer rate coefficient were made under the simple assumption of gravitational settling of all particles, the reduced rates of extraction at 400 and 600 rpm are probably not due to simple external mass transfer limitations. Considering the relatively low solvent-to-coal ratio in these runs, inadequate suspension of the coal particles at lower stirring speeds is probably responsible for the low rates; many particles would be settled on the bottom of the vessel resulting in inadequate coal/solvent contact and very low extraction rates.

The initial rapid extraction (up to the time of the first sample, typically between 1/2 and 1 minute) may be external mass transfer limited; however, the observed rate of extraction was so rapid that this could not be investigated. The extract yield at the time of the first sample was as much as 50% of the amount of extraction at 60 minutes. Sampling at contact times less than 1/2 minute, in order to ascertain the rate of extraction and the rate limiting step at these times, was not possible with the apparatus used. In any case the rate limiting
phenomena should not be external mass transfer at contacting times within the limits of the sampling capabilities of this system, at least when stirring is adequate to maintain particle suspension (that is, 800 rpm or more).

A minimum stirring speed of 800 rpm was necessary to attain adequate suspension as evidenced by the lower dissolution at decreased stirring speeds. Higher stirring speeds may increase the turbulence within the contactor, but do not increase the rate of extraction as evidenced by the concurrence of the plots of extract yield for 800 and 1000 rpm. Furthermore, increased stirring speeds contribute to accelerated mechanical degradation of the coal particles. Preservation of the initial coal particle size distribution throughout the run, to the extent that it was possible, was desirable in order to study the effects of temperature and particle size on the coal extraction, without the complicating factor of changing particle size during a single run. The degradation of coal particles was minimized, adequate slurry suspension provided, and external mass transfer limitations eliminated by conducting the succeeding experiments at a stirring speed of 800 rpm.

Particle Size Effects

The investigation of particle size effect on the rate of extraction of coal material into tetralin was conducted at 250°C and a solvent-to-coal ratio from 9.5 to 13.5 on a weight basis. Narrow cut particle sieving yielded four particle size ranges for this part of the investigation: -30 +40, -50 +70, -100 +140, -200 +270 (U.S. Series mesh designation). Grinding and sieving were performed in a manner such that each
size fraction was as representative of the whole coal as possible. This was done by starting with a representative sample of the coal when preparing each fraction and repeatedly performing slight grinding followed by sieving to the size desired to minimize total grinding exposure and avoid further grinding of particles already in the desired size range. The initial rate of extraction was noticeably influenced by the coal particle size, being higher for smaller particles. Up to approximately 40 minutes, the level of extraction for the smaller particles was higher than for the larger particles. After this time the extraction yields for all runs approached the same value. This behavior can be seen in the plot of the extract yield as a function of time for the various size ranges in Fig. 3-2.

The individual curves show generally the same behavior for all particle sizes. The initial extraction was very rapid, especially for the smaller particle sizes. The initial rate of extraction increased with decreasing particle size. After approximately 60 minutes, all curves converge. Assuming that the particle size distribution does not change significantly during an experiment, the convergence of the curves is indicative of a change from a particle size dependent extraction process to a particle size independent rate limiting process. If particle size degradation was considerable, this behavior would also be expected. However, comparison under a microscope of the particles at the beginning of a run to the particles recovered after 60 minutes of contacting showed very little change in particle size distribution, as tabulated in Appendix A. Implicit in the examination of the effect of
Figure 3-2. Extract yield as a function of contacting time for selected coal particle sizes. Experiments were conducted at 250°C.
particle size is also the assumption that the pore structure of the coal particles is essentially the same for all coal particle sizes. Ideally, ball milling and sieving should have no influence on the pore structure of the coal. Furthermore, since the coal preparation was conducted to obtain representative size fractions and to minimize the particle degradation, the pore structure differences between fractions should be at a minimum.

Temperature Effects

The effect of temperature on the rate of dissolution was a critical aspect of the examination of extraction mechanisms. Most of the previous experiments were conducted at 250°C; in this sequence, experiments at temperatures of 150, 200 and 300°C were also performed. Since an improved coal injection procedure was implemented for these experiments, the runs at 250°C were repeated. The Wyodak coal used for each of these experiments was a narrow particle size fraction, -30 +40 mesh. This relatively large coal particle size was used since this coal underwent minimal pre-run treatment and thus was most representative of the coal. Furthermore, the effect of temperature on the rate of extraction could be more easily observed, since of all the particle size ranges studied in the previous set of experiments, the -30 +40 mesh particle size had the slowest rate of extraction. This coal was introduced into the preheated contactor vessel only several minutes prior to solvent injection. The solvent-to-coal ratio for these runs varied from 10 to 17 on a weight basis.
The influence of temperature on the rate of extraction of coal into tetralin was considerable. The extraction for a given contacting time increased with increasing temperature, especially at longer times; after 2 hours of contacting, the extraction at 300°C was more than three times the extraction at 150°C. A plot of extract yield as a function of contacting time for the four temperatures is shown in Fig. 3-3. These curves all follow the same pattern of rapid, essentially instantaneous, initial extraction with a slower rate of extraction during the subsequent contacting time. This leads to the speculation that the rate controlling processes are the same at approximately the same contacting times, regardless of temperature. Further analysis of these rates can lead to better indications of the rate controlling phenomena.

After 2 hours of contacting, the observed rate of extraction was low but not zero at all of the temperatures used. In order to determine whether the extraction approached a common limit for this coal/tetralin system, independent of temperature, a study was initiated to conduct longer contacting experiments. A common limit of extraction may be expected if there is a total amount of soluble material that can dissolve in the tetralin at any temperature. Since there is a large excess of tetralin present for all runs, the solubility limit of these materials should not be reached. This common limit would be an ultimate extent of extraction for this coal and be independent of temperature (below pyrolysis temperature). Variations from a common limit may be expected if the dissolution of coal material at high temperatures is preceded by high energy processes, such as bond breaking, which processes proceed slowly, if at all, at low temperatures.
Figure 3-3. Extract yield as a function of contacting time for selected temperatures. Experiments were conducted with -30 +40 mesh Wyodak coal.
Several relatively long runs were conducted at 250 and 300°C in the stirred contactor. The extraction yields did increase considerably even after 2 hours at these temperatures as shown in Fig. 3-4 and tabulated in Appendix A under Runs 67 and 68. After 12 hrs at 250°C, the extract yield was still increasing; after 24 hrs at 300°C, the rate of extraction did not appear to be zero, although the experimental scatter in the final points makes it difficult to state any definite conclusion. It appeared that the extraction yield continues to increase for some time beyond the contacting times of any of the previous runs but at a very low rate.

The effect of long contacting times on the particle size distribution was also investigated. An examination under a microscope of the coal particles from the 300°C, 24 hour experiment showed noticeable degradation of the particles after 12 hours and extensive degradation of the particles after 24 hours; initial coal particles averaged approximately 500 microns in diameter and the final coal particles less than 100 microns. Tabulation of the results of the microscopic observation of coal treated for various lengths of time and different temperatures are contained in Appendix A. Since the coal particles were significantly degraded at these long times, the stirred contactor was found to be inappropriate for study of the rate of dissolution if the initial coal structure was important to preserve.

The total amount of soluble material can conceivably be determined by running an experiment until the amount of dissolved material ceases to increase with longer contacting time. Accurate values for the total
Figure 3.4. Extract yield as a function of contacting time at 250 and 300°C for extended contacting in the stirred contactor vessel. Experiments were conducted with -30 +40 mesh Wyodak coal.
amount of extractable material, or "ultimate" yield, at several temperatures were needed for the calculations of rate coefficients and other kinetic parameters, as their values were dependent on the choice of ultimate yield. Very long contacting time experiments were conducted in the high pressure Soxhlet apparatus, by the procedure outlined in Chapter 2, to determine ultimate yields at 250 and 300°C. Values at 150 and 200°C were estimated from data obtained by Draemel [40]. Several complications arose in the determination of extract yield for these long time experiments. Although samples were filtered as they were removed from the apparatus, some fines passed through the filter with the liquid samples. These fines may be small pieces of undissolved coal; they may also be dissolved material that has undergone some reaction or change and has precipitated from the solution. Adjustments to the values of ultimate yield were made to compensate for the fines but resulted in some uncertainty in the values. Furthermore, during the course of a run, the amount of relatively pure tetralin in the contacting cup fluctuates from as much as 150 mL (immediately prior to siphoning of the tetralin from the contacting cup into the solvent vessel) to as little as 15 mL (immediately after siphoning); thus, the concentration of the solvent/extract solution in the solvent vessel fluctuates during the run, being most concentrated when there is the maximum amount of tetralin in the contacting cup. Since it was not possible to determine the level of the tetralin in the contacting cup during sampling of the extract solution, the calculation of the extract yield from the amount of extract in the sample of the solvent/extract solution had to
compensate for the fact that the extract solution in the solvent vessel was concentrated by the absence of from 15 to 150 mL of tetralin. A range of values was then obtained for ultimate yield as reported in Table 3-1.

General Observations

Only a small percentage of the coal was extracted in the stirred contactor under the conditions used, with a maximum of 21% by weight (daf) at 300°C and 24 hours (the most severe conditions); typical extract yields between 3 and 12% wt. daf were observed within the first hour of contacting. The initial extraction (first 10 - 20 minutes) accounts for a large percentage of the total extracted material. Unfortunately, a significant fraction of the soluble material is extracted before the first minute (before the first sample) and makes analysis of this initial rate difficult, if not impossible. The rates of extraction between 1 minute and 2 hours were well documented and contain valuable information on the coal/solvent interactions at these times and conditions.

Particle size distribution remained approximately the same during this time, so that any changes in coal particle pore structure would be minimal and the assumption of approximately constant pore structure throughout a single short contacting time experiment was appropriate for analysis of the extraction.

The values of "ultimate" yields presented in Table 3-1 showed a marked dependence on temperature of extraction. Although these values are the results of very long contacting time experiments, they may not
Table 3-1. Ultimate yield as a function of temperature.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Ultimate Yield (wt. % daf)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>27 - 33</td>
</tr>
<tr>
<td>250</td>
<td>16.5 - 19</td>
</tr>
<tr>
<td>200</td>
<td>8 - 15</td>
</tr>
<tr>
<td>150</td>
<td>7 - 12</td>
</tr>
</tbody>
</table>
be equal to the total amount of extractable coal material, as higher extractions may be achieved at even longer contacting times, especially for the lower temperature runs. The determination of an absolute maximum in extraction is probably not possible at these temperatures, within a reasonable length of time.

Duplicate runs that had been conducted for several sets of conditions were generally in agreement with each other. The results of the experiments were sensitive to some conditions that were not recognized immediately. Coal introduction into the contactor vessel was found to be an important consideration. Comparison of the rates of extraction for experiments with the same conditions of particle size (−30 +40 mesh) and temperature (250°C) but different coal pretreatment, shown in Figures 3-2 and 3-3, exhibit dissimilar rates. Higher extract yields were obtained for the later runs (Figure 3-3), in which the coal was injected into the contactor immediately prior to solvent injection and not preheated along with the contactor vessel, as was the case for the earlier experiments. Extended preheating probably caused vaporization of lighter compounds and possibly crosslinking or polymerization of some compounds within the coal, rendering them insoluble in tetralin.

Model Development

The extraction of coal material can be expected to be a complicated process. The complex chemical and physical nature of coal contributes to the complicated nature of coal/solvent interactions and the observed rate of extraction. An analysis of these rates was conducted to establish the simplest model that reasonably fits the data. From such a
model, kinetic parameters, such as rate coefficients, kinetic order of
the process(es), and apparent activation energies could be determined.
Interpretation of these parameters can then lead to a better under-
standing of coal/solvent interactions.

The simplest extraction model that could be proposed to fit the
observed data would involve a single mechanism with a first or second
order dependence on unextracted tetralin-soluble coal material. First
and second order expressions can be stated in terms of the extract
yield, ultimate yield and contacting time:

First order: \[ \ln(D_{ult} - D) = -k(1) t \] \hspace{1cm} (3-1)

Second order: \[ \frac{1}{(D_{ult} - D)} = k(2) t \] \hspace{1cm} (3-2)

where,

- \( D_{ult} \) - total amount of extractable material in the coal,
  ultimate yield
- \( D \) - experimentally determined extract yield at time, \( t \)
- \( k(1) \) - first order rate coefficient
- \( k(2) \) - second order rate coefficient.

Values of the ultimate yield were obtained from the long contacting time
experiments. At 250°C, the expected limits of the total amount ranged
from 16.5 to 19% wt daf. Regardless of the exact choice of \( D_{ult} \), the
plot of the logarithm of the unextracted material (amount of extracted
material subtracted from the ultimate yield) was not a linear function
of the contacting time, which would have been expected for a first order dependence. Additionally, the plot of the inverse of the amount of unextracted material was not a linear function of the contacting time as would have been expected for a second order dependence. To attempt to fit the rate data to a higher order expression or a fractional order expression, besides probably being unsuccessful, would have little significance and would serve only as an empirical correlation at best. Rather, it was necessary to examine the behavior of the rates of extraction measured for indications of the mechanisms involved.

As noted earlier, the extraction appears to proceed in several separate stages: an extremely rapid, essentially instantaneous, extraction; an intermediate rate extraction; and a very slow extraction. For the development of a kinetic model, association of each of these separate stages with a different extracted material would permit use of individual mechanisms for each stage. Although compounds that dissolve from coal are certainly a large assortment of different chemical structures, for analysis of coal/solvent interactions these compounds can be grouped according to their reactivity or ease of solubility. These groups can then be treated as pseudo-single components in the proposed kinetic model. The stages of extraction were here thus attributed to the extraction of three groups of coal compounds, the first group completely extracted within the first minute of contacting, the second group largely extracted within the first 30 or 40 minutes and the third group incompletely extracted even after 24 hours. Any reaction involving any of these groups was assumed to be first order in the unextracted
material; this is the most reasonable simplification as the rates of
dissolution should depend directly on the concentration of the compounds
dissolving as long as there is excess solvent. A model could then be
constructed involving parallel mechanisms, each of which represented one
of the groups proceeding from its unextracted state in the coal struc­
ture to material dissolved in the bulk solvent. A rate expression with
a corresponding rate coefficient could be associated with each of these
mechanisms.

The first group (designated by index 1) of compounds extracts
extremely rapidly, essentially instantaneously; the determination of a
rate coefficient for the extraction of this group was not possible since
the extraction appeared to be complete before or as the first sample was
taken. As far as this investigation is concerned, no rate limitation
seems to exist for this group. External mass transfer may limit the
extraction; however, since the rate of external mass transfer is so
rapid, external mass transfer limited extraction would also be complete
before the first sample was taken. The extraction of this first group
can then be represented by a simple rapid extraction step for which no
rate coefficient is determinable.

The extraction of compounds that are contained in the two more
slowly soluble groups (designated as 2 and 3) proceeds by cleavage
reaction, if necessary, from the coal structure, dissolution into the
solvent in the coal pores, and diffusion to the exterior of the coal
particle. Since external mass transfer was found to be not limiting,
the transport of the compounds to the bulk solvent proceeds unhindered.
The rate of extraction of these two groups then must be limited by kinetic (reaction or dissolution) and/or internal mass transport processes. Although the two groups comprise two different sets of compounds, the molecular size of these would not be expected to differ greatly, at least not significantly enough to affect the effective diffusivities within the coal pore structure. Thus for approximately equal diffusivities and similar distribution within the coal, the rates of extraction of both groups, if both were under internal mass transfer control, would be approximately the same. Since the intermediate rate of extraction appears to be much faster than the long time rate, the extraction of both groups would not be expected to be diffusion limited.

The other possible rate limiting step is the reaction/dissolution step. This kinetic step has a broad expected range of rates, as it is related to the chemistry of the compounds, which can be very diverse. It is possible that both the rates of the intermediate and slowly extracted groups can be kinetically limited, by different reaction/dissolution steps having unequal rates.

From these observations, a simple model can be constructed, incorporating the various steps into a proposed mechanism. The parallel extractions of the three groups showing the potential rate limiting steps are given in Fig. 3-5. The instantaneous extraction of the first group can be represented by the unhindered extraction of coal material from the solid state to the dissolved state in the bulk solution. The extraction of the second group can be limited by the kinetic step or the diffusion step. The rate of reaction/dissolution of the solid coal
Figure J-5. Proposed three group extraction mechanism.
material of group 2, A₂, to the dissolved state, designated B₂, is characterized by the rate coefficient, k₂'. The species, B₂, representing the coal material dissolved in the solvent in the pore structure at the site of original attachment, then diffuses to the exterior surface of the coal particle. The effective diffusivity, \( \text{eff} \) is associated with the diffusion of the material from within the coal particle to the exterior surface. B₂ is then rapidly transported to the bulk solution, designated D₂ in that state. The extraction of the third group is expected to be kinetically controlled; the reaction/dissolution rate coefficient, k₃', governs the extraction of this group and is expected to be smaller than k₂'.

The continuity equation describing this extraction of the second and third groups is written,

\[
\frac{\partial B_i}{\partial t} = \mathcal{D}_\text{eff} \nabla^2 B_i + \frac{\partial A_i}{\partial t} \quad i = 2, 3 ,
\]

where, for first order reaction/dissolution kinetics of a uniformly distributed component, A₁,

\[
\frac{\partial A_i}{\partial t} = \frac{dA_i}{dt} = -k_i A_i .
\]

If the extraction of the second group is assumed to be limited by only one step, the reaction/dissolution step or the diffusion step, Eq. (3-3) can be reduced to a simpler expression. If the kinetic step proceeds much faster than the diffusion step (internal mass transfer
control), $A_2$ will rapidly dissolve to $B_2$, and the extraction of the second group will reduce to a transient diffusion problem* defined by

$$\frac{3B_2}{3t} = D_{\text{eff}} \nabla^2 B_2.$$  \hspace{1cm} (3-5)

If the diffusion step proceeds much faster than the reaction/dissolution step, the rate of extraction of the second group will be equal to the rate of reaction/dissolution of $A_2$ to $B_2$.

In the case of the third group, the kinetic step is expected to proceed slowly, so that the diffusion term in Eq. (3-3) is negligible. Then the rate of extraction is equal to the rate of reaction/dissolution of $A_3$.

Overall rate expressions for the appearance of the individual group can be derived that are appropriate to this proposed mechanism. Since the measured quantities are the amounts of extract in the bulk solution as a function of time, rate expressions will be expressed in terms of $D$ and $D_i$ ($i = 1, 2, 3$). Then the experimental data can be fit to these expressions to determine how well the mechanism represents the behavior of the coal/solvent interactions.

Prior to coal/solvent contacting, the extractable material of the individual groups is part of the solid coal structure; the initial amount of this material in each group is defined:

$$A_i^0 = A_i(t=0) \quad \text{for} \quad i = 1, 2, 3.$$  \hspace{1cm} (3-6)

*This will be the case if all of $A_2$ can dissolve into the solvent in the pores, without any solubility restrictions. If the solubility of $A_2$ is limited, the problem is more appropriately described by a shrinking core model. Both of these models are developed and solved in Appendix E.
At any given time, \( t \), during the coal/solvent contacting, the total amount of extracted material dissolved in the bulk solution is equal to \( D(t) \), or simply \( D \), which is the sum of the amounts of extracted material of the individual groups, \( D_i(t) \) (or \( D_i \)), for \( i = 1, 2, 3 \):

\[
D = \sum_{i=1}^{3} D_i(t) = D_1 + D_2 + D_3 .
\]  

(3-7)

Similarly, upon complete extraction of all groups, the total tetralin soluble material in the coal, the ultimate yield, is equal to the sum of the total amount of extracted material in the individual groups, \( D_i^f \); this sum is also equal to the sum of the amounts of extracted material present initially in the coal:

\[
D_{ult} = \sum_{i=1}^{3} D_i^f = \sum_{i=1}^{3} A_i^o .
\]  

(3-8)

The extraction of the first group is essentially instantaneous so that after the start of contacting the amount of \( D_1 \) is constant at its final value, that is,

\[
D_1 = D_1^f = A_1^o \quad \text{for} \quad t > 0 .
\]  

(3-9)

The rate of extraction of the second group in the case of kinetic control can be expressed in terms of the first-order rate coefficient, \( k_2' \),

\[
\frac{dD_2}{dt} = - \frac{dA_2}{dt} = k_2' A_2 .
\]  

(3-10)
It is also possible to obtain an overall rate coefficient that is appropriate in the case of diffusion control. By solution of Eq. (3-5) for the concentration of dissolved material in the coal particle and determination of the rate of transport from the particle, a simple overall rate coefficient can be defined,

\[ k_2 = \frac{r_2}{s_2} \quad (3-11) \]

where,

\[ r_2 = \text{instantaneous rate of extraction, } \frac{dD_2}{dt} \]

\[ s_2 = \text{total amount of extractable material remaining in particle} \]

\[ = D_2^f - D_2. \]

Details of the derivation of this rate coefficient can be found in Appendix E for two diffusion models, the transient diffusion model and the shrinking core model. Then, an overall rate expression can be derived from Eq. (3-10) or (3-11) for the extraction of the second group

\[ D_2 = D_2^f \left( 1 - e^{-k_2t} \right), \quad (3-12) \]

where \( k_2 \) is equal to \( k_2' \) in the case of kinetic control and equal to the expressions derived in Appendix E in the case of diffusion control.

The rate expression for the extraction of the third group is similarly derived:

\[ D_3 = D_3^f \left( 1 - e^{-k_3t} \right), \quad (3-13) \]
where, under the expected reaction/dissolution rate limiting conditions, the rate coefficient, \( k_3 \), will be equal to \( k_3' \).

The sum of the rate expressions, in terms of the overall rate coefficients, according to Eq. (3-4), is equal to the total amount of extracted material at any given time, \( t \), greater than 0:

\[
D = D_1^f + D_2^f (1 - e^{-k_2 t}) + D_3^f (1 - e^{-k_3 t}) .
\]  

(3-14)

Then values of \( D_1^f \) and \( k_1 \) for the mathematical expression of the proposed model can be determined from the experimental data.

The experimental data that were available were simply the amounts of extract dissolved in the bulk solvent as a function of time. A range of values for the ultimate yield was available as a function of temperature as listed in Table 3-1. Although the total amount of extractable material (ultimate yield) is comprised of the ultimate yields of the individual groups, as per Eq. (3-5), since it is not possible to distinguish the three separate groups from each other in the tetralin/extract solution obtained in the experiments, the ultimate yields of extract from each group, \( D_1^f \), were not directly resolvable by the experiments.

From the observed overall rates of extraction, it appears reasonable to assume that extraction of coal material at long contacting times is controlled entirely by the extraction of the third group; the first group is completely extracted and the extraction of the second group is nearly complete after 30 to 40 minutes of contacting. The overall rate expression appropriate at long times is then:
\[ D = D_1^f + D_2^f + D_3^f (1 - e^{-k_3t}) = D_{ult} - D_3^f e^{-k_3t}. \] (3-15)

A plot of the logarithm of the amount of unextracted material (experimental value of extract yield, \( D \), subtracted from the ultimate yield, \( D_{ult} \)) as a function of contacting time for data points at times greater than 20 or 30 minutes (typically the last two or three samples taken during an experiment) should then yield a straight line. The intercept and slope of this line, determined by a least squares fit, yield the total soluble material in the least easily soluble group, \( D_3^f \), and the first order rate coefficient for this group, \( k_3 \), respectively. The value of \( (D_1^f + D_2^f) \) can then be determined as \( D_{ult} - D_3^f \).

For shorter times (experimental contacting times between approximately 1-2 minutes and 20-30 minutes) the contribution to the overall rate of extraction by the slowest group can be calculated from the values of \( D_3^f \) and \( k_3 \). The experimental rate data can then be adjusted for the extraction of the slowest group, so that the adjusted extract yield, \( D^* \), can be represented by the kinetic parameters of the extraction of the intermediate group. The rate expression for these shorter times is obtained from Eq. (3-14):

\[ D = D_1^f + D_2^f (1 - e^{-k_2t}) + D_3^f (1 - e^{-k_3t}) \]

\[ = D_{ult} - D_2^f e^{-k_2t} - D_3^f e^{-k_3t}. \] (3-16)
By rearrangement, an expression for the adjusted extract yield is obtained:

\[ D^* = D_{ult} - D - D_3^f e^{-k_3t} = D_2^f e^{-k_2t} . \]  \hspace{1cm} (3-17)

As with the previous calculation, a plot of the logarithm of \( D^* \) as a function of contacting time can be fit to a straight line by a least squares method. From the values of the intercept and slope of this line, the total amount of soluble material in the intermediate group, \( D_2^f \), and the rate coefficient of its extraction, \( k_2 \), can be determined. The total amount of extract in the instantaneously extracted group can then be determined by difference:

\[ D_1^f = D_{ult} - D_3^f - D_2^f . \]  \hspace{1cm} (3-18)

\textbf{Kinetic Parameters}

Before calculations of the kinetic parameters could proceed, a choice of \( D_{ult} \) was necessary. From the long contacting time experiments, values for \( D_{ult} \) at 250°C within the range of 16.5 to 19% wt daf were obtained. A value of 16.5% was used for the experiments conducted with different particle sizes at 250°C. The actual value of \( D_{ult} \) chosen for these experiments was not very critical, since the highest extract yields obtained (approximately 7%) were sufficiently lower than \( D_{ult} \).
The choice of $D_{ult}$ for the set of experiments conducted at different temperatures could not be made so easily. From the long contacting time runs conducted in the Soxhlet apparatus, values for $D_{ult}$ were obtained at various temperatures and as seen in Table 3-1 appear to be a function of the temperature. However, if $D_{ult}$ is interpreted to be the total amount of tetralin soluble coal material in the Wyodak coal (not a function of temperature), the highest value of $D_{ult}$ could be used as the maximum or ultimate yield attainable for all temperatures. This implies that the extractions at temperatures below 300°C were not complete for the times used, and would be expected to continue to rise over a very long time.* On this basis, kinetic parameters were calculated from the experimental data collected at the various temperatures with a high value of $D_{ult}$ of 27%, the extraction limit at 300°C. For comparison, values of $D$ obtained at the end of the long contacting time experiments as reported in Table 3-1 were also used for $D_{ult}$ in the calculations.

Values of the kinetic parameters determined for experiments that were conducted to study the effects of particle size and temperature are shown in Tables 3-2 and 3-3. In general, the rate coefficients follow the expected trends, with the rate coefficients for the intermediate

*The extraction yield at 300°C and 500 hours also may not be the maximum amount of tetralin soluble material in the coal. However, the ultimate extraction of soluble material can not be determined by application of higher temperatures, as conversion at higher temperatures are likely to be a result of excessive thermal decomposition and considerable hydrogen transfer, more than just the extraction of soluble material.
Table 3-2. Kinetic Parameters from Three Group Model for Particle Size Study. These experiments were conducted at 250°C.

<table>
<thead>
<tr>
<th>Part. size (US series)</th>
<th>( D_{\text{ult}} )</th>
<th>( D_{1}^{f} )</th>
<th>( D_{2}^{f} )</th>
<th>( D_{3}^{f} )</th>
<th>( k_{2} )</th>
<th>( k_{3} )</th>
<th>( s )</th>
</tr>
</thead>
<tbody>
<tr>
<td>-30 +40</td>
<td>16.5</td>
<td>2.3</td>
<td>2.2</td>
<td>12.0</td>
<td>0.235</td>
<td>0.00196</td>
<td>0.07</td>
</tr>
<tr>
<td>-50 +70</td>
<td>16.5</td>
<td>2.8</td>
<td>2.0</td>
<td>11.7</td>
<td>0.215</td>
<td>0.00145</td>
<td>0.03</td>
</tr>
<tr>
<td>-100+140</td>
<td>16.5</td>
<td>3.3</td>
<td>1.5</td>
<td>11.7</td>
<td>0.181</td>
<td>0.00151</td>
<td>0.08</td>
</tr>
<tr>
<td>-200+270</td>
<td>16.5</td>
<td>3.7</td>
<td>1.5</td>
<td>11.3</td>
<td>0.146</td>
<td>0.00089</td>
<td>0.06</td>
</tr>
</tbody>
</table>

Units: \( D_{\text{ult}}, D_{1}^{f}, D_{2}^{f}, D_{3}^{f}, s: \% \text{ wt daf}; k_{2}, k_{3}: \text{ min}^{-1} \);
\( s \), standard deviation of fit of experimental data to model extraction performance.

Table 3-3. Kinetic Parameters from Three Group Model for Temperature Study. These experiments were conducted with -30 +40 mesh Wyodak coal.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>( D_{\text{ult}} )</th>
<th>( D_{1}^{f} )</th>
<th>( D_{2}^{f} )</th>
<th>( D_{3}^{f} )</th>
<th>( k_{2} )</th>
<th>( k_{3} )</th>
<th>( s )</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>8</td>
<td>1.6</td>
<td>1.9</td>
<td>4.5</td>
<td>0.114</td>
<td>0.00052</td>
<td>0.33</td>
</tr>
<tr>
<td></td>
<td>27</td>
<td>1.6</td>
<td>1.9</td>
<td>23.5</td>
<td>0.114</td>
<td>0.00010</td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>12</td>
<td>2.4</td>
<td>1.6</td>
<td>8.0</td>
<td>0.177</td>
<td>0.00131</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>27</td>
<td>2.4</td>
<td>1.7</td>
<td>22.9</td>
<td>0.175</td>
<td>0.00040</td>
<td></td>
</tr>
<tr>
<td>250</td>
<td>16.5</td>
<td>3.8</td>
<td>2.2</td>
<td>10.5</td>
<td>0.158</td>
<td>0.00156</td>
<td>0.26</td>
</tr>
<tr>
<td></td>
<td>27</td>
<td>3.8</td>
<td>2.2</td>
<td>21.0</td>
<td>0.157</td>
<td>0.00075</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>30</td>
<td>5.0</td>
<td>4.9</td>
<td>20.1</td>
<td>0.109</td>
<td>0.00177</td>
<td>0.46</td>
</tr>
<tr>
<td></td>
<td>27</td>
<td>5.0</td>
<td>4.8</td>
<td>17.2</td>
<td>0.110</td>
<td>0.00215</td>
<td></td>
</tr>
</tbody>
</table>

Units: \( D_{\text{ult}}, D_{1}^{f}, D_{2}^{f}, D_{3}^{f}, s: \% \text{ wt daf}; k_{2}, k_{3}: \text{ min}^{-1} \);
\( s \), standard deviation of fit of experimental data to model extraction performance.
material, \( k_2 \), much greater than the rate coefficients for the slowly
dissolving material, \( k_3 \). The values of the total amounts of soluble
material for any one group at a given choice of \( D_{ult} \) are approximately
the same for all runs; values of \( D_1^f \) and \( D_2^f \) are approximately
equal and much smaller than the amount of soluble material in the slowly
dissolving group, \( D_3^f \), and are independent of the choice of \( D_{ult} \).

Since the two sets of experiments, particle size study and temperature
study, were conducted under slightly different coal pretreatment condi-
tions (the coal was preheated for a considerably longer time in the
particle size experiments), comparison between the two sets of kinetic
parameters is not justified.

The overall rate expression for the proposed model, Eq. (3-14), with
the values of the kinetic parameters was used to generate values of
extract yields to compare with the experimental data. For each run the
following standard deviation calculation was made to determine the fit of
the rate expression to the observed data:

\[
s = \frac{\sum (D_{calc}(t)-D_{obs}(t))^2}{N - 4} \]

(3-19)

where,

\( D_{calc}(t) \) = extract yield calculated from rate expression for a
given time, \( t \)

\( D_{obs}(t) \) = extract yield from experimental data

\( N \) = number of data points
The calculation of the kinetic parameters, model extraction performance, and the standard deviations were performed by a FORTRAN computer program, which is listed in Appendix C.

The fit of the proposed model to the experimental data was reasonably good as indicated by the values of the standard deviation which were typically about 0.1%. The curves drawn through the experimental points in Figures 3-2 and 3-3, shown previously, were generated by the proposed model with the kinetic parameters in Tables 3-2 and 3-3. Those figures also indicate a reasonably good fit for almost all of the experiments.

Interpretation of Kinetic Parameters

The value of $D_1^f$ is the amount of soluble material that is extracted from the coal instantaneously. The amount of this very rapidly dissolving material increases with decreasing particle size as shown in Figure 3-2 and reported as $D_1^f$ in Table 3-2. This general behavior is predicted by several possible models of the extraction phenomena. If the extraction of this material were a surface dissolution phenomena, the extent of extraction of this material would be proportional to the ratio of the surface area-to-volume of the coal particles. For the same amount of coal, the smaller particles would have a larger exterior surface area available* and the instantaneous extraction would be higher than for

*The surface area available for extraction from a porous particle will also include internal pore surface area near the exterior of the particle. Although this supplemental area can surpass in magnitude the exterior surface area of a particle, the effective surface area available will still be larger for the same amount (i.e., weight) of small particles as large particles.
larger particles. Since the surface area-to-volume ratio is proportional to the reciprocal of the diameter, a proportionality of $D_1^f$ to the inverse of the particle diameter would indicate that surface dissolution was the dominant mechanism of extraction for this group. Diffusion of material from within the particle to the bulk solution is also another possible mechanism of transport. Two models were examined for diffusion of soluble material from spherical particles; equations for a transient diffusion model and a shrinking core model are presented in Appendix E and their predictions are essentially the same for diffusion limited extraction at extract fractions up to approximately 0.8, as shown in Figure E-1. For either diffusion model, the effective overall rate coefficient is proportional to the inverse of the square of the particle diameter after a short initial period (less than 5 seconds for typical parameter values) as expressed by Eqs. (E-11) and (E-23). Since the rate of extraction of the first group could not be measured, only the extent of extraction at approximately one minute can be compared with the extent of extraction at one minute as predicted by the transient diffusion model. For an effective diffusivity of $1 \times 10^{-6}$ cm$^2$/s, the extraction of material from all particles except the largest, will be complete by the end of the first minute of contacting, as shown in Figure E-3 in Appendix E, and thus will not be a function of particle size. For a lower (perhaps less realistic) value of the effective diffusivity, $1 \times 10^{-7}$ cm$^2$/s, the extent of extraction shows a slight particle size dependence.
A logarithmic plot of $D_{1f}$ as a function of average particle diameter indicates that there is only a slight dependence of $D_{1f}$ on particle size, as $D_{1f} \propto D_p^{-0.26}$. This indicates that the dissolution of the instantaneously soluble material is not a surface area effect. In addition, since $D_{1f}$ does increase with decreasing particle size over the entire particle size range, it does not appear that internal mass transfer is controlling during the first minute of coal/solvent contacting (if the effective diffusivity is on the order of $1 \times 10^{-6}$ cm$^2$/s); although in the absence of any measured rates in this period, this can not be determined conclusively. The instantaneous dissolution of material, essentially independent of particle size, suggests the presence of a very soluble material in the coal structure that was readily accessible to the solvent. The slight dependence of $D_{1f}$ on the particle diameter may be attributed to differences in exposure of this soluble material at the surface of the particles.

Very soluble coal materials, such as those observed here, have been noted by Hershkowitz and labeled "natural oils" [6]. These materials readily dissolve from undried coal in weak solvents such as cyclohexane to as high an extent as 4% by weight of daf coal [82]. A hexane Soxhlet extraction (at 69°C) conducted on the dry Wyodak coal used in this work yielded almost 1% soluble material (wt daf).* It appears likely that

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*Higher extraction may be attained with undried coals. The effect of drying seems to have a significant influence on the yields of the Soxhlet extractions. One theory advanced by Levine at Exxon proposes that the removal of water from coal collapses the pore structure rendering it less easily extracted [83]. This effect would be noticeable at the low temperatures of the Soxhlet extraction, but would not necessarily be of consequence at the relatively higher contacting temperatures employed in the experiments conducted in this work.
these materials represent a highly soluble coal maceral such as certain exinites that have a waxy or resinous nature and are extremely fluid when heated [84]. These macerals comprise more or less homogeneous regions in the coal structure. There are several macerals that make up the exinite group; these include sporinite, cutinite, alginite and resinite, derived from spore coats, cuticles, algae and resins, respectively. These macerals, especially sporinite, seem to have higher solubility than the other macerals found in coal [84]. No coal maceral analysis was conducted on the coal used for this investigation; however, a maceral analysis of a Western subbituminous coal (Blue Seam, New Mexico) by Given showed an exinite fraction on a mineral-matter-free basis of between 1 and 5% [84]. This range of values may be expected to be typical of subbituminous coals, although large variations would not be unusual. The values obtained for $D_1^f$ in this study fall within this range.

The ease of solubility of these macerals is dependent on the exposure of the macerals to the solvent phase. For sufficiently large maceral size relative to the coal particle size, a large fraction of the macerals will be exposed to the solvent and dissolve rapidly. Microscopic inspection of thin sections of coal by Wen and Lee [85] and Van Krevelen [18], indicate that the size of typical exinite macerals is in the range of 50 to 500 microns. Except for the smallest macerals and the largest coal particle size used, the macerals would be largely accessible to dissolution for all particle sizes used in this investigation. This was determined by estimating the fraction of macerals exposed
to the exterior of the coal particles by the following method. The coal particles and macerals were assumed to be spherical. For a uniform, low density (nonintersecting) maceral distribution throughout the coal structure, those macerals that are exposed to the exterior of the coal particle must have their centers within the spherical shell defined by the exterior of the particle and of one maceral radius thickness. This fraction is expressed mathematically:

\[
E = \frac{(1/6)\pi \left( D_p^3 - (D_p - D_m)^3 \right)}{(1/6)\pi D_p^3} = 1 - (1-D_m/D_p)^3, \tag{3-20}
\]

where,

\[ D_p = \text{average coal particle diameter} \]
\[ D_m = \text{maceral diameter.} \]

A tabulation of $E$ for typical maceral sizes and coal particle sizes is given in Table 3-4. The slight inaccessibility of the maceral in the larger coal particles may account for the slight particle dependence of the value of $D_1^f$.

The values of $D_1^f$ obtained for runs at the four different temperatures studied increase significantly with increasing temperature. The amount of the very rapidly extractable group thus seems to have a temperature dependence, which may be associated with the possible
Table 3-4. Fractional Exposure of Maceral for Selected Particle Sizes and Typical Maceral Sizes.

<table>
<thead>
<tr>
<th>Particle Size</th>
<th>US series mesh avg. diameter $D_p$ (cm)</th>
<th>$D_m$</th>
<th>50 μm</th>
<th>100 μm</th>
<th>250 μm</th>
<th>500 μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>-30 +40</td>
<td>0.05</td>
<td>0.27</td>
<td>0.49</td>
<td>0.88</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>-50 +70</td>
<td>0.025</td>
<td>0.49</td>
<td>0.78</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>-100+140</td>
<td>0.0125</td>
<td>0.78</td>
<td>0.99</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>-200+270</td>
<td>0.00625</td>
<td>0.99</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>
temperature dependence of the total extent of dissolution in this system. An alternative explanation of the observed temperature dependence is that the rate of the dissolution of the rapidly dissolved group is a function of temperature and the values of $D_1^f$ do not account for the entire group; some of the material could be included in the next most soluble group.

After a very short period of contacting, coal material extracts more slowly, being dominated by the extraction of the second group. The amount of material in the second group, $D_2^f$, is on the order of 2% by weight for all particle sizes and temperatures except 300°C. The values of $D_2^f$, as shown in Table 3-2, decrease slightly with decreasing particle size. This is not an expected trend, but can probably be attributed to the incomplete extraction of the first group from the larger particles, with the remaining material in the first group then being included with the second group. Similarly, incomplete extraction of the second group from the larger particles at times greater than 30 minutes can reduce the amount of material in the second group, thus increasing the calculated amount of material in the third group. Furthermore, some of the second group may extract very rapidly from the smaller coal particles and may be included in the value of $D_1^f$. The exact resolution of the individual extract groups is not possible by the calculation method (or the experimental methods) used here, since it cannot take all of these considerations into account for different particle sizes. More detailed data would be required to resolve the ambiguities.
Reasonable approximations to these values, however, appear to be possible by these calculations.

The values of $k_2$ for both studies are in the range of 0.1 to 0.25 min$^{-1}$. No significant dependence of $k_2$ on temperature is indicated; however, the values of $k_2$ for the various particle sizes decrease slightly with decreasing particle size. This trend is not compatible with either an internal mass transfer controlled mechanism (which would predict that the overall rate coefficient would be inversely proportional to the square of the particle size, as discussed previously and shown in Appendix E) nor a reaction/dissolution controlled mechanism (which would predict that the rate coefficient of extraction would be independent of the particle size). An examination of the experimental data suggested a method that would represent the data and provide values of the kinetic parameters consistent with the proposed model.

A single set of kinetic parameters, excepting $k_2$, was estimated from the experimental data and then used with the data from each of the particle size study experiments to obtain a separate value of $k_2$ for each experiment. Since the coal used for all particle size experiments was the same except for the size of the coal particles (since the grinding and sieving was conducted to preserve the composition of the coal) the total amounts of the three extract groups in the proposed model, $D_1^f$, $D_2^f$, and $D_3^f$, should have the same values for all particle sizes. Furthermore, since all curves converge after approximately 40 minutes, one value of $k_3$ should be appropriate for all of these experiments. The values of $k_3$ and $D_3^f$ were determined from an
average of the experimental data after 40 minutes. The value of $D_1^f$ was an average of all values of $D_1^f$ calculated previously. Then, $D_2^f$ was calculated by difference. The values of $k_2$ were determined from the slope of the logarithm of $D^*/D_2^f$ (see Eq. 3-17 for $D^*$) plotted as a function of contacting time for each experiment. By this method, $k_2$, as shown in Table 3-5, was found to be inversely proportional to the 0.44 power of the particle size. Although, the particle size dependence still does not agree with a diffusion controlled mechanism nor a kinetic controlled mechanism, the overall rate coefficient increases in a regular manner with decreasing particle size. A further examination for the mechanisms of extraction of group 2 material is required to account for the particle size dependence observed.

If the extraction of the second group were internal mass transfer limited, the diffusion of dissolved material from within the particle would be described by the transient diffusion model (or the shrinking core model, which has the same behavior over most of the range of extract fraction) described in Appendix E. In this case, the overall rate coefficient is related to the effective diffusivity by,

$$ k = \frac{4\pi^2 D_{eff}}{D_p^2} \quad \text{or} \quad D_{eff} = \frac{k D_p^2}{4\pi^2} $$

(3-21)

where,

- $k = \text{overall rate constant, s}^{-1}$
- $D_{eff} = \text{effective diffusion coefficient, cm}^2/\text{s}$
- $D = D/\omega$
- $D = \text{molecular diffusion coefficient, cm}^2/\text{s}$
Table 3-5. Revised Kinetic Parameters from Three Group Model for Particle Size Study.

<table>
<thead>
<tr>
<th>Particle Size Independent</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$D_1$</td>
<td>3.0% wt daf</td>
</tr>
<tr>
<td></td>
<td>$D_2$</td>
<td>2.0% wt daf</td>
</tr>
<tr>
<td></td>
<td>$D_3$</td>
<td>11.5% wt daf</td>
</tr>
<tr>
<td></td>
<td>$k_3$</td>
<td>0.00115 min$^{-1}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Particle Size Dependent</th>
<th>Rate Coefficient $k_2$ (min$^{-1}$)</th>
<th>Std. deviation of fit to data, s (% wt daf)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-30 +40</td>
<td>0.105</td>
<td>0.29</td>
</tr>
<tr>
<td>-50 +70</td>
<td>0.158</td>
<td>0.06</td>
</tr>
<tr>
<td>-100+140</td>
<td>0.171</td>
<td>0.15</td>
</tr>
<tr>
<td>-200+270</td>
<td>0.281</td>
<td>0.29</td>
</tr>
</tbody>
</table>

$k_2 \propto D_p^{-0.44}$
\( \omega \)  = tortuosity of coal particle pore structure, dimensionless
(values typically in the range: 3-10)

\( D_p \)  = diameter of coal particle, cm

With values of \( D_{\text{eff}} \) (approximately 1 x 10^{-5} to 1 x 10^{-6} cm²/s), estimated by the Wilke-Chang method [86] as described in Appendix C for a typical coal compound of 400-800 MW at 250°C in tetralin with allowance for tortuosity and hindered diffusion, the values of the overall rate coefficient, \( k \), are on the order of 0.01 to 0.1 s⁻¹ (or 0.5 to 10 min⁻¹) for a particle size of 0.05 cm (-30 +40 mesh). The overall rate coefficients in Table 3-5, are one to two orders of magnitude lower than these values, indicative of complicating factors not attributable to diffusion alone.

The extraction of the second group does not appear to be simply diffusion limited nor reaction/dissolution controlled, since the dependence on particle size of the overall rate coefficient for the extraction of this material falls between the values expected for these two limiting cases. This could indicate a situation for which the rates of reaction/dissolution and diffusion are of the same order of magnitude. In this case, no simplification of the continuity equation, Eq. (3-3), can be made. This equation describes the diffusion, from a spherical porous particle, of material generated by a first order reaction/dissolution uniformly throughout the particle. The solution is presented in Appendix F. By varying the values of the effective diffusivity and the reaction rate coefficient (the dimensionless variable, \( \Omega \), represents the ratio of these two parameters multiplied
by the square of the particle radius), the dependence of the overall rate coefficient on the particle size can be varied from a power of -2 (high reactivity relative to diffusivity \(\Omega + \infty\), internal mass transfer control) to 0 (high diffusivity relative to reactivity \(\Omega + 0\), reaction/dissolution limited).

A plot of normalized extract yield of group 2 material as a function of contacting time is shown in Fig. 3-6.* Values of a reaction/dissolution rate coefficient, \(k_d\) (analogous to \(k_2'\)), and an effective diffusivity, \(D_{eff}\), were obtained for this plot so that the overall rate of extraction of the second group, as predicted by the mathematical model, was a reasonable approximation to the experimental data represented in Fig. 3-6. The values of these two coefficients were \(1.5 \times 10^{-7} \text{ cm}^2/\text{s}\) for the diffusivity and \(0.0045 \text{ s}^{-1}\) (or \(0.27 \text{ min}^{-1}\)) for the rate constant. This value of effective diffusivity might be expected for the hindered diffusion of large coal-derived molecules within a tortuous pore structure. The reaction/dissolution step proceeds at a not-unreasonable rate of 95% dissolution in 11 minutes. The plot of the curves generated from the mathematical model with these coefficient values for the average diameters of the four coal particle sizes used in the experiments is shown in Fig. 3-7. Overall rate coefficients were

\[
\frac{D_2}{D_2^f} = \frac{1}{D_2^f} \left[ D(t) - D_1^f - D_3^f(1-e^{-k_3 t}) \right]
\]  

*The values of \(D_1^f, D_2^f, D_3^f\), and \(k_3\), as given in Table 3-6, were used to obtain the values of \(D_2^f\) from the experimental data:
Figure 3-6. Normalized extract yield of second extract group as a function of contacting time for particle size experiments. Kinetic parameters used for normalization of experimental data: $D_1^f = 3.0\%$ wt daf, $D_2^f = 2.0\%$ wt daf, $D_3^f = 11.5\%$ wt daf, $k_3 = 0.00115\ min^{-1}$. 
Figure 3-7. Theoretical extraction of second extract group as a function of contacting time under simultaneous reaction/dissolution and diffusion control. Reaction/dissolution rate constant, $k_d$: $0.0045 \text{ s}^{-1}$; effective diffusion coefficient, $D_{eff}$: $1.5 \times 10^{-7} \text{ cm}^2/\text{s}$. 

<table>
<thead>
<tr>
<th>PARTICLE SIZE</th>
<th>RADIUS (CM)</th>
<th>RANGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>0.00313</td>
<td>-200+270</td>
</tr>
<tr>
<td>b</td>
<td>0.00625</td>
<td>-100+140</td>
</tr>
<tr>
<td>c</td>
<td>0.0125</td>
<td>-50+70</td>
</tr>
<tr>
<td>d</td>
<td>0.025</td>
<td>-30+40</td>
</tr>
</tbody>
</table>
also calculated at various extract conversions for the four particle sizes from the mathematical model by the method described in Appendix F. For the above values of diffusivity and reaction rate constant, the overall rate coefficient was inversely proportional to the 0.3 to 0.4 power of the particle diameter, which is essentially the same dependence as observed for \( k_2 \) from analysis of the experimental data.

Additional information can be obtained from the temperature dependence of the rate constants. By assuming an Arrhenius relationship, \( k = A \exp(-E_a/RT) \), an apparent activation energy, \( E_a \), of the extraction process can be determined from the slope of the plot of the logarithm of the rate coefficient as a function of the reciprocal of the temperature. Since the temperature dependence of \( k_2 \) is slight, as shown in Table 3-3, the slope of an Arrhenius plot is small and consequently a low apparent activation energy (less than 1 kcal/mol) is associated with the rate controlling step (or steps, in this case) of the extraction of the second group. A low activation energy is typical of the diffusion process and low energy dissolution processes, such as desorption of molecules held by van der Waal forces.

Despite the complicated nature of the coal/solvent interaction and the limited experimental data, the mathematical model for simultaneous diffusion and reaction/dissolution represents the trends in the data reasonably well. The extraction of the second group appears to be controlled by both the reaction/dissolution and diffusion of the soluble material. The extraction of the second group may best be described as the dissolution of relatively large (high molecular weight) compounds.
that are present in, but only loosely bound to the coal structure; the hindered diffusion of these compounds from within the coal particle proceeds at approximately the same rate as the dissolution.

The rates of extraction after approximately 40 minutes are independent of particle size and very slow at all temperatures studied. The rate constants, \( k_3 \), are as a result, very low; they are typically two orders of magnitude smaller than \( k_2 \). The values of \( k_3 \) and the total amount of material in group 3, \( D_{3f} \), are influenced to a large extent by the value used for the ultimate yield, \( D_{ult} \); \( D_{3f} \) and \( k_3 \) decreases with increasing values of \( D_{ult} \). In contrast, the kinetic parameters of the first two groups are not significantly influenced by the choice of \( D_{ult} \), as shown in Table 3-3. By using a single value of \( D_{ult} \) for the experiments at all temperatures, the rate constant, \( k_3 \), represents the extraction of a large group of material present in the coal, the amount of which is independent of temperature. The influence of temperature on \( k_3 \) can then be used with the Arrhenius relation to determine an apparent activation energy of the rate controlling process of the extraction of this group of material.

A relatively low apparent activation energy of 9.5 kcal/mol was obtained for the extraction of the third group, as shown in Fig. 3-8. Arrhenius plots of literature data from similar coal dissolution studies are also shown [39,41,42]. The values of the rate coefficient for the extraction of the third extract group, the largest group of soluble material in this model of coal extraction are consistent with the
Figure 3-8. Arrhenius plots of third group extraction and of several literature studies.
reported literature values. The general trend of the data shown is an increasing activation energy with increasing temperature. This indicates that at higher temperatures the breaking of stronger bonds is a major influence on the overall rate coefficient of the extraction of coal.

Curran et al. extracted an Ireland Mine Pittsburgh Seam coal from Northern West Virginia with tetralin at temperatures above 300°C; the data was fit to a two group model with two parallel first-order reactions. The rate constants for the dissolution of the first approximately 30% of the coal at three temperatures between 300 and 400°C exhibit a high temperature dependence and an activation energy of 30 kcal/mol. Hill et al. report rate constants for extraction of a Utah high volatile bituminous coal in tetralin at temperatures below 275°C, for which an average activation energy of 7 kcal/mol was determined, and above 350°C, an average activation energy of approximately 32 kcal/mol.

The low temperature activation energy is typical of low energy processes (diffusion, desorption or weak bond breaking). Hill et al. concluded that at low temperatures diffusion was controlling for the extraction of interstitial material in the coal. However, since the magnitude of rate coefficients are so low (and thus the effective diffusivity would be much lower than expected for the dissolved material, as discussed previously, according to Eq. (3-21)) it is more likely that the rate limiting step at the low temperature is weak bond breaking, such as weak hydrogen bonding or van der Waal bond breaking rather than internal mass transfer. Van der Waal forces are weak and very short range; for non-polar molecules, only molecules that are in close contact
interact. Typical, non-polar, high molecular weight, coal-derived molecules have large external surface areas, so that enhanced intermolecular forces can result between them and the surrounding coal structure. Activation energies for van der Waal adsorption/desorption are usually less than 5 kcal/mol for small molecules [87]; higher values are expected for larger molecules. At the high temperatures (greater than 300°C), high activation energy processes, such as thermal decomposition and hydrogen transfer reactions, are the predominant rate controlling steps.

The extraction of the third group in the present model of coal extraction is likely to be limited by considerably lower energy reaction processes than the high temperature extractions and slightly stronger bond breaking than those occurring at the lower temperatures. Reaction processes such as the breaking of strong hydrogen bonds (average energies of about 5 kcal/mol [88]) or weak chemical desorption (that is, the reverse reaction of chemisorption, which can typically have energies of from 10 to 100 kcal/mol [87]) may be limiting. The presence of complex multifunctional compounds, typically found in coal, and the relatively high fraction of oxygen in Wyodak coal, both capable of strong molecular interactions, help to justify this interpretation.

Thus it appears that for the extraction of Wyodak coal in tetralin at temperatures below 300°C, a three extract group model represents the tetralin-soluble coal material adequately and can be used to explain the coal/solvent interactions. From an analysis of the kinetic parameters derived from the experimental data, the rate limiting step(s) in the extraction of each of the individual extract groups have been deduced and a mechanism of extraction forwarded.
The extraction of the first group proceeds so rapidly that for most of the experiments, this extraction appeared to be complete before the first sample was taken. This group is composed of a highly soluble material, perhaps an exinite maceral, most of which is readily accessible for solvent extraction. Approximately 2-4% of the coal is contained in this group. The material in the second extract group dissolves and diffuses from the coal particles at a much slower rate than the first group, and the extraction is essentially complete after 20 - 40 minutes of contacting, depending on the run conditions. The breaking of very weak bonds to free the extract from the coal structure accompanied by relatively slow, hindered diffusion from within the particle to the exterior, appears to occur during this extraction. The overall rate coefficients for this extraction, typically on the order of 0.1 min⁻¹, is inversely proportional to a small power (0.3-0.5) of the particle size and only very slightly dependent on the temperature. These trends can be explained by approximately equal rates for the two steps in the extraction mechanism, that is the reaction/dissolution step and the diffusion step. The slowest extracting and the largest group of extract material belongs to the third group in the proposed model. The breaking of weak bonds, such as in chemical desorption, in the extraction of this group appears to be the rate limiting step, as indicated by the magnitude of the overall rate coefficient (in the range of 0.001-0.003 min⁻¹, too low for a diffusion limited extraction) and its temperature dependence (an average apparent activation energy of about 10 kcal/mol). The extraction of this last group continues for a very long time (at least 500 hours) at the temperatures used in this investigation.
IV. CONCLUSIONS AND RECOMMENDATIONS

The investigation of coal/solvent interactions at temperatures below pyrolysis has led to the development of a model of the extraction mechanism and the identification of rate limiting processes in the mechanisms. The phenomena involved in coal/solvent contacting are complicated, and alternative explanations or mechanisms to those proposed here are possible; no explanation involving only a few compounds, or groups of compounds, and simple mechanisms can completely represent the process. However, the observed behavior of the rate of extraction of Wyodak coal in tetralin is consistent with the relatively simple three-group model developed in this work.

At all conditions, the extraction was found to proceed at a very rapid rate initially and then at progressively slower rates, perceptible even after times often thought sufficient to achieve total extraction. The extraction of most of the tetralin-soluble material, the first 10-15% of the dry, ash-free coal, is accomplished with little physical degradation of the coal particles. The initial rapid extraction, about 3% of the coal, involves the removal of a highly soluble material that is easily accessible to the solvent. The rate behavior of the next stage of the extraction, consisting of about another 2% of the coal, indicates that the breaking of weak bonds to free large molecules and the hindered diffusion of these molecules from the coal particle are limiting steps in this part of the extraction mechanism. A very low activation energy (less than 1 kcal/mol) and a diffusion coefficient on the order of $1.5 \times 10^{-7}$ cm$^2$/s are representative of this stage. As the extraction
proceeds and most of the weakly bound molecules are removed, the extraction of the remaining, more strongly bound molecules (activation energy on the order of 10 kcal/mol) dominates and the rate is substantially reduced.

The model of coal/organic solvent interaction that is presented here is relatively simple; the development of more detailed models would require considerably more investigation of many aspects of the coal/organic solvent system. An investigation of the extraction at very short times, requiring the development of very rapid contacting and sampling techniques, would clarify the initial mechanism of extraction, left unresolved by this investigation. A detailed chemical characterization of the dissolved coal material successively extracted at increasing times could resolve groups of similar compounds and the influence of temperature and time on the appearance of these groups. From this information and an investigation of the solubility characteristics of the dissolved coal material, an explanation of the temperature dependence of the ultimate yield could be sought.

A complementary investigation involving the use of other solvents should indicate the influence of the solvent on the mechanisms of extraction. Other nonreactive solvents capable of removing a comparable amount of coal material, such as toluene, would be appropriate for comparison. An investigation of the influence of reactive solvents, such as pyridine, on the extraction mechanisms, should give additional insight into the behavior of coal-derived recycle solvents, typically used in coal liquefaction processes, which can be comprised of both nonreactive and reactive components.
APPENDIX A

Detailed Experimental Results

This appendix contains the detailed results of the important experiments and analyses conducted as a part of this research. Table A-1 includes the experimental coal/solvent contacting conditions. Table A-2 lists the extract yield, duration of contact, and solvent-to-coal ratio for each sample taken during these experiments. The recovery of coal plus coal-derived material and the recovery of tetralin is also tabulated for each run as a percentage of the original material charged to the contactor. Table A-3 contains the microscopic analyses of coal and several tetralin-treated coal samples. Table A-4 includes the elemental analyses of several representative extract samples. Figure A-1 shows the gel permeation chromatograms of extract solutions from an early coal/solvent contacting experiment with an indication of the approximate molecular weight of these compounds. Figure A-2 shows the proton nuclear magnetic resonance spectrums of samples of the extract from a 300°C tetralin/coal contacting experiment.
Table A-1. Treatment Conditions for Coal/Solvent Contacting Experiments.

<table>
<thead>
<tr>
<th>Run #</th>
<th>Temperature (°C)</th>
<th>Particle Size (US series mesh)</th>
<th>Stirring Speed (rpm)</th>
<th>Maximum Contact Duration (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stirred Batch Contactor*</td>
<td>18</td>
<td>300</td>
<td>-100</td>
<td>900</td>
</tr>
<tr>
<td>38</td>
<td>250</td>
<td>-50</td>
<td>400</td>
<td>240</td>
</tr>
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<td>49</td>
<td>250</td>
<td>-50</td>
<td>800</td>
<td>60</td>
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<td>1440</td>
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<td>High Pressure Soxhlet</td>
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<td>-30 +40</td>
<td>-</td>
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<tr>
<td>70</td>
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* Runs 18-61: coal preheated with contactor vessel; Runs 62-68: coal injected into preheated contactor approximately 1 min prior to start of run.
Table A-2. Extract Yields and Solvent-to-Coal Ratios for Coal/Solvent Contacting Experiments.

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<td>10.7</td>
<td>10.1</td>
<td>13.1</td>
<td>10.3</td>
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<tr>
<td>time</td>
<td>0</td>
<td>0.85</td>
<td>3.08</td>
<td>12.0</td>
<td>30.0</td>
<td>90.0</td>
<td>240.</td>
<td>420.</td>
<td>720.</td>
<td>-</td>
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<tr>
<td>67</td>
<td>extract</td>
<td>3.55</td>
<td>4.67</td>
<td>5.89</td>
<td>6.66</td>
<td>7.18</td>
<td>7.83</td>
<td>8.55</td>
<td>9.42</td>
<td>97.9</td>
<td></td>
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<tr>
<td>S/C</td>
<td>14.6</td>
<td>11.3</td>
<td>12.2</td>
<td>13.0</td>
<td>15.5</td>
<td>19.2</td>
<td>17.6</td>
<td>15.6</td>
<td>15.1</td>
<td>13.1</td>
<td></td>
</tr>
<tr>
<td>time</td>
<td>0</td>
<td>0.85</td>
<td>3.00</td>
<td>30.0</td>
<td>90.0</td>
<td>180.</td>
<td>720.</td>
<td>1200.</td>
<td>1440.</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>68</td>
<td>extract</td>
<td>5.24</td>
<td>6.90</td>
<td>10.95</td>
<td>13.78</td>
<td>15.35</td>
<td>20.67</td>
<td>20.85</td>
<td>21.77</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>S/C</td>
<td>13.5</td>
<td>14.1</td>
<td>12.5</td>
<td>14.1</td>
<td>14.0</td>
<td>14.6</td>
<td>14.4</td>
<td>13.4</td>
<td>12.9</td>
<td>13.2</td>
<td></td>
</tr>
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</table>
Table A-2. (Continued)

<table>
<thead>
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<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>time(hr)</td>
<td>100</td>
<td>147</td>
<td>217</td>
<td>259</td>
<td>406</td>
<td>500</td>
<td>600</td>
<td>725</td>
</tr>
<tr>
<td>69</td>
<td>extract(min)*</td>
<td>12.5</td>
<td>14.5</td>
<td>15.7</td>
<td>16.1</td>
<td>15.5</td>
<td>17.2</td>
<td>16.1</td>
<td>16.7</td>
</tr>
<tr>
<td></td>
<td>extract(max)+</td>
<td>14.3</td>
<td>16.7</td>
<td>18.2</td>
<td>18.8</td>
<td>18.1</td>
<td>20.2</td>
<td>19.0</td>
<td>19.8</td>
</tr>
<tr>
<td></td>
<td>time(hr)</td>
<td>1.5</td>
<td>3.5</td>
<td>9</td>
<td>24</td>
<td>50</td>
<td>107</td>
<td>200</td>
<td>500</td>
</tr>
<tr>
<td>70</td>
<td>extract(min)</td>
<td>10.5</td>
<td>15.1</td>
<td>20.7</td>
<td>24.0</td>
<td>27.5</td>
<td>26.9</td>
<td>25.2</td>
<td>27.0</td>
</tr>
<tr>
<td></td>
<td>extract(max)</td>
<td>12.3</td>
<td>17.8</td>
<td>24.5</td>
<td>28.6</td>
<td>34.4</td>
<td>38.9</td>
<td>39.4</td>
<td>36.0</td>
</tr>
</tbody>
</table>

* Calculations based on 110 mL tetralin in high pressure Soxhlet contacting cup.
+ Calculations based on 35 mL tetralin in high pressure Soxhlet contacting cup.
<table>
<thead>
<tr>
<th>Initial Particle Size Range</th>
<th>Run #</th>
<th>Temperature (°C)</th>
<th>Sample #</th>
<th>time(min)</th>
<th>Observed Particle Size (mm) *</th>
<th>R indicates coal solids filtered from slurry remaining in reactor at the end of a run.</th>
</tr>
</thead>
<tbody>
<tr>
<td>-200+270</td>
<td>61</td>
<td>250</td>
<td>1</td>
<td>0.65</td>
<td>0.07</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>R 60</td>
<td>0.07 0.04</td>
</tr>
<tr>
<td>-50 +70</td>
<td>63</td>
<td>250</td>
<td>1</td>
<td>1.05</td>
<td>0.25</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>R 60</td>
<td>0.25 0.2</td>
</tr>
<tr>
<td>-30 +40</td>
<td>64</td>
<td>200</td>
<td>1</td>
<td>0.84</td>
<td>0.7</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>R 120</td>
<td>0.7 0.1(25%)</td>
</tr>
<tr>
<td></td>
<td>65</td>
<td>150</td>
<td>1</td>
<td>1.16</td>
<td>0.7</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>R 120</td>
<td>0.7 0.1(15%)</td>
</tr>
<tr>
<td></td>
<td>68</td>
<td>300</td>
<td>1</td>
<td>0.85</td>
<td>0.7</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>6 720</td>
<td>0.7 0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>R 1440</td>
<td>0.1</td>
</tr>
</tbody>
</table>

* Performed on a Reichert Zetopan Research Microscope with: universal condenser "POLYHOS"; objective: 3.5 x; eyepiece: 16 x; field of view: approx. 2mm diameter. (% ) indicates approx. percentage of particles of given size.

+ R indicates coal solids filtered from slurry remaining in reactor at the end of a run.
Table A-4. Elemental Analysis of Extract Samples

<table>
<thead>
<tr>
<th>Run #</th>
<th>64</th>
<th>67</th>
<th>68</th>
<th>68</th>
<th>68</th>
<th>68</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>200</td>
<td>250</td>
<td>300</td>
<td>300</td>
<td>300</td>
<td>300</td>
</tr>
<tr>
<td>Sample #</td>
<td>1</td>
<td>8</td>
<td>1</td>
<td>3</td>
<td>3</td>
<td>6</td>
</tr>
<tr>
<td>Contacting Time (min)</td>
<td>0.84</td>
<td>720</td>
<td>0.85</td>
<td>30</td>
<td>720</td>
<td></td>
</tr>
<tr>
<td>% Carbon</td>
<td>77.39</td>
<td>78.90</td>
<td>78.40</td>
<td>76.81</td>
<td>78.76</td>
<td></td>
</tr>
<tr>
<td>% Hydrogen</td>
<td>10.62</td>
<td>9.84</td>
<td>10.10</td>
<td>9.44</td>
<td>8.43</td>
<td></td>
</tr>
<tr>
<td>% Nitrogen</td>
<td>0.33</td>
<td>0.35</td>
<td>0.31</td>
<td>0.47</td>
<td>0.62</td>
<td></td>
</tr>
<tr>
<td>% Ash</td>
<td>N.D.</td>
<td>N.D.</td>
<td>N.D.</td>
<td>0.6</td>
<td>N.D.</td>
<td></td>
</tr>
<tr>
<td>H: C</td>
<td>1.65</td>
<td>1.50</td>
<td>1.55</td>
<td>1.47</td>
<td>1.28</td>
<td></td>
</tr>
</tbody>
</table>

N.D. - not determined
Figure A-1. Gel permeation chromatograms of tetralin extracts of Wyodak coal. Wyodak coal (-100 mesh) was treated with tetralin (S/C = 38) at 300°C (Run 18). Chromatography was conducted with pyridine carrier using 100, 500 and 1000 Å µ-Styragel columns in series and 313 nm UV detection. Tetralin (solvent) absorbance was subtracted from the chromatograms.
Figure A-2. Proton nuclear magnetic resonance spectra of tetralin extracts of Wyodak coal. Wyodak coal (-30+40 mesh) was treated with tetralin at 300°C in the high pressure Soxhlet apparatus (Run 70). Dried extract was dissolved in pyridine-\(d_5\) (99.93%). Reference compound is hexamethyldisiloxane (HMDS).
APPENDIX B
Solvent Properties

Since tetralin has been used extensively as a coal liquefaction solvent, many of its physical properties have been measured and are reported in the literature. Those values of interest to this investigation are listed in Table B-1. However, the viscosity and density at elevated temperatures (above the boiling point) have not been measured and require the use of generalized correlations.

The corresponding states correlation that was used for estimating the liquid density of tetralin was developed by Chueh et al. and presented in Reid et al. [79]:

\[
\rho = \rho_s \left[ 1 + \frac{9 Z_N (P - P_{vp})}{P_c} \right]^{1/9},
\]  

(B-1)

where,

- \( \rho \) = liquid density, g/cm\(^3\)
- \( \rho_s \) = saturated liquid density at the desired temperature, g/cm\(^3\)
- \( P_{vp} \) = vapor pressure, atm
- \( \dot{P} \) = system pressure, atm
- \( P_c \) = critical pressure, atm
- \( Z_c \) = critical compressibility factor, dimensionless.
Expressions for \( N \) and \( \rho_s \) are:

\[
N = (1.0 - 0.89\omega) \left[ \exp(6.9547 - 76.2853 T_r + 191.3060 T_r^2 - 203.5472 T_r^3 + 82.7631 T_r^4) \right] \quad (B-2)
\]

\[
\rho_s = \frac{\rho_c}{v_r^{(0)} + \omega v_r^{(1)} + \omega^2 v_r^{(2)}} \quad (B-3)
\]

where,

\[
\omega = \text{acentric factor, dimensionless}
\]

\[
T_r = \text{reduced temperature, dimensionless}
\]

\[
= \frac{T}{T_c}
\]

\[
\rho_c = \text{critical density, gm/cm}^3
\]

\[
v_r^{(i)} = a_i + b_i T_r + c_i T_r^2 + d_i T_r^3 + e_i \frac{T_r}{T_c} + f_i \ln(1 - T_r) \quad (B-4)
\]

The values of the coefficients in Eq. (B-4) are given in Reid [79].

Since the value of \( \rho_c \) is not an easily determined nor accurate value, the reference value, \( \rho^R \), at 20°C (293°K) can be used to determine \( \rho_s \) by dividing \( \rho_c \) out of the calculations. The values of \( \rho \) were then calculated by Eq. (B-1) at a system pressure of 300 psig and are listed in Table B-2 for temperatures from 150 to 300°C along with the molal volumes at those temperatures and pressure.

Two methods were employed to estimate the viscosity of tetralin at elevated temperatures. The simplest method is presented by Riddick and Bunker [90]:

\[
\frac{1}{\mu} = \phi = A \exp \left( -\frac{B}{RT} \right) \quad , \quad (B-5)
\]
where,

\[ \mu = \text{viscosity, P(g/cm-s)} \]
\[ T = \text{temperature, °K} \]
\[ R = 1.987 \text{ cal/gmol - °K} \]

The values of the constants for tetralin are given by Riddick and Bunger [90]:

\[ A = 9.8 \times 10^3 \text{ cm-s/g} \]
\[ B = 3.112 \times 10^3 \text{ cal/gmol.} \]

The corresponding-states correlation from Reid et al. for the viscosity is as follows [92],

\[ \eta_L \xi = (\eta_L \xi)^{(0)} + \omega (\eta_L \xi)^{(1)}, \quad (B-6) \]

where

\[ \eta_L = \text{viscosity, cP} (= \mu \times 10^2) \]
\[ \xi = T_c^{1/6}/(M^{1/2} P_c^{2/3}) \]
\[ (\eta_L \xi)^{(i)} = r_i + s_i T_r + t_i T_r^2 \quad (B-7) \]

\[ M = \text{molecular weight of tetralin, g/gmol.} \]

The coefficients in Eq. (B-7) for \( T_r \geq 0.76 \) are given in Reid [92].

The values of the viscosity, calculated by both methods, at temperatures from 150 to 300°C, as shown in Table B-2, are in close agreement.
Table B-1. Physical Properties of Tetralin [89,90,91]

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular Structure</td>
<td>![Molecular Structure Image]</td>
</tr>
<tr>
<td>Molecular Formula</td>
<td>C_{10}H_{12}</td>
</tr>
<tr>
<td>Molecular Weight</td>
<td>132.2 g/gmol</td>
</tr>
<tr>
<td>Density (20°C)</td>
<td>0.973 g/cm³</td>
</tr>
<tr>
<td>Molal Volume (20°C)</td>
<td>135.9 cm³/gmol</td>
</tr>
<tr>
<td>Acentric Factor</td>
<td>0.303</td>
</tr>
<tr>
<td>Viscosity (20°C)</td>
<td>2.202 cP</td>
</tr>
<tr>
<td></td>
<td>(25°C) 2.003 cP</td>
</tr>
</tbody>
</table>

**Critical Constants**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>T&lt;sub&gt;c&lt;/sub&gt;</td>
<td>719°K</td>
</tr>
<tr>
<td>P&lt;sub&gt;c&lt;/sub&gt;</td>
<td>44.69 atm</td>
</tr>
<tr>
<td>ρ&lt;sub&gt;c&lt;/sub&gt;</td>
<td>0.309 g/cm³</td>
</tr>
<tr>
<td>V&lt;sub&gt;c&lt;/sub&gt;</td>
<td>428 cm³/gmol</td>
</tr>
<tr>
<td>Z&lt;sub&gt;c&lt;/sub&gt;</td>
<td>0.251</td>
</tr>
</tbody>
</table>

**Vapor Pressure**

\[
\ln P_s (\text{mm Hg}) = 16.2805 - \frac{4009.49}{T(\text{°K}) - 64.89} \quad 365°K < T < 500°K
\]

\[
\log P(\text{kPa}) = -\frac{2549}{T(\text{°K})} - 1.022\times10^{-3} T + 7.804 \quad 473°K < T < 716°K
\]
Table B-2. Density, Molal Volume, and Viscosity of Tetralin at Elevated Temperatures

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Density (g/cm³)</th>
<th>Molal Volume (cm³/gmol)</th>
<th>Viscosity (cP) by Eq. B-5</th>
<th>Viscosity (cP) by Eq. B-6*</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>0.788</td>
<td>168</td>
<td>0.41</td>
<td>0.33</td>
</tr>
<tr>
<td>200</td>
<td>0.749</td>
<td>176</td>
<td>0.28</td>
<td>0.26</td>
</tr>
<tr>
<td>250</td>
<td>0.710</td>
<td>186</td>
<td>0.20</td>
<td>0.21</td>
</tr>
<tr>
<td>300</td>
<td>0.660</td>
<td>200</td>
<td>0.16</td>
<td>0.16</td>
</tr>
</tbody>
</table>

* Pressure (P) = 300 psig (2.2 MPa)
APPENDIX C

Estimation of the External Mass Transfer Coefficient for Spherical Particles in a Fluid

The determination of an external mass transfer coefficient for the extraction of material from coal particles suspended in a solvent in a well-stirred contactor involves many variables such as contactor geometry (including type of impellers and baffles), impeller rotation speed, and particle size, size distribution, shape, density and loading. The problem can be simplified by considering a single spherical particle (of diameter equal to the average diameter of the coal particles) falling at its gravitational settling velocity through the liquid. By this approach a minimum external mass transfer coefficient can be calculated; a higher mass transfer coefficient would be expected if acceleration and turbulence were included in the determination.

The mass transfer correlation for forced convection around a sphere can be written for constant composition and small mass transfer rates:

\[ Nu = 2 + 0.6 \text{Re}^{1/2} \text{Sc}^{1/3} \]  

where the dimensionless groups are defined:

\[ \text{Nu} = \frac{k_x D}{c D} = \text{Nusselt number for mass transfer} \]
\[ \text{Re} = \frac{D v p}{\mu} = \text{Reynolds number} \]
\[ \text{Sc} = \frac{\mu}{\rho c D} = \text{Schmidt number} \]
and where,

\[ k_x = \text{mass transfer coefficient, } \text{g/mol/cm}^2\text{-s} \]

\[ D = \text{particle diameter, cm} \]

\[ c = \text{molar concentration of solution, } \text{g/mol/cm}^3 \]

\[ = (\text{molar volume of solvent}^{-1}) \text{ for dilute solution} \]

\[ \rho = \text{density of fluid, g/cm}^3 \]

\[ \mu = \text{fluid viscosity, g/cm-s} \]

\[ \mathcal{D}_{AB} = \text{diffusivity of solute, A, in solvent, B, cm}^2\text{/s} \]

\[ v = \text{relative velocity of fluid past particle, cm/s.} \]

The values of the physical parameters for tetralin, \( c, \rho, \) and \( \mu \) are reported in Appendix B. An estimate of the diffusivity of the dissolved coal material was obtained by use of the Wilke-Chang correlation [86]. The values of \( v \) were estimated by calculating the gravitational settling velocity of the particles. Once these values were obtained, a value for \( k_x \) was calculated.

The Wilke-Chang correlation for diffusivity is:

\[ \mathcal{D}_{AB} = 7.4 \times 10^{-8} (\phi M_B)^{1/2} T/\eta_B v_A^{0.6}, \quad (C-2) \]

where

\[ M_B = \text{molecular weight of solvent, g/gmol} \]

\[ T = \text{temperature, } ^\circ\text{K} \]

\[ \eta_B = \text{solvent viscosity, cP (} = \mu x 10^2) \]}
\[ V_A = \text{molal volume of dissolved coal material at its normal boiling point, cm}^3/\text{gmol} \]

\[ \phi = \text{association factor of solvent B, dimensionless} \]

\[ \approx 1 \text{ for nonassociating solvents.} \]

From the extract analyses reported in Appendix A, an approximate molecular weight, structure, and formula can be assigned to a typical dissolved coal molecule. The information is necessary for calculation of molal volume by Schroeder's additive-volume increment method [93]. From gel permeation chromatography results, the molecular weight of the instantaneously extracted group may be expected to be about 400-800. From the elemental analysis, a hydrogen-to-carbon ratio of approximately 1.5 yields a molecular formula of C\(_{30}\)H\(_{44}\). The proton nuclear magnetic resonance results indicated relatively low aromaticity. These results were used to construct a representative molecular structure, from which the Schroeder additive-volume increment calculation was made, as tabulated in Table C-1.

Diffusion coefficients of the dissolved material were then calculated according to Eq. C-2 with the appropriate physical parameters from Table C-2:

\[ D_{400 \text{ MW}} = 5 \times 10^{-5} \text{ cm}^2/\text{s} \]

\[ D_{800 \text{ MW}} = 3 \times 10^{-5} \text{ cm}^2/\text{s} \]
Table C-1. Schroeder Additive-Volume Increment Calculation for a Typical Coal-Derived Molecule.

<table>
<thead>
<tr>
<th>Molecular Weight: 400 g/gmol</th>
<th>Increment (cm$^3$/g mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular Formula: C$<em>{30}$H$</em>{44}$</td>
<td>74 x 7</td>
</tr>
<tr>
<td>Molecular Structure</td>
<td></td>
</tr>
<tr>
<td>1 anthracene ring</td>
<td>1 x -7</td>
</tr>
<tr>
<td>1 naphthalene ring</td>
<td>1 x -7</td>
</tr>
<tr>
<td>6 double bonds</td>
<td>6 x 7</td>
</tr>
<tr>
<td>$V^A_{400 \text{ MW}} = 550 \text{ cm}^3/\text{g mol}$</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Molecular Weight: 800 g/gmol</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$V^A_{800 \text{ MW}} = 1100 \text{ cm}^3/\text{g mol}$</td>
<td></td>
</tr>
</tbody>
</table>
Table C-2. Physical Parameters for External Mass Transfer Coefficient Calculation.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T )</td>
<td>( 523^\circ K ) (250°C)</td>
</tr>
<tr>
<td>( g )</td>
<td>981 cm/s²</td>
</tr>
<tr>
<td>tetralin:</td>
<td></td>
</tr>
<tr>
<td>( M_B )</td>
<td>132.2 g/gmol</td>
</tr>
<tr>
<td>( \rho_L \rho^* )</td>
<td>0.71 g/cm³ @ 250°C</td>
</tr>
<tr>
<td>( \mu(n_B)^* )</td>
<td>( 0.2 \times 10^{-2} ) g/cm·s (0.2 cP) @250°C</td>
</tr>
<tr>
<td>( c )</td>
<td>0.0054 g mol/cm³</td>
</tr>
<tr>
<td>coal:</td>
<td></td>
</tr>
<tr>
<td>( \rho_s^+ )</td>
<td>1.3 g/cm³</td>
</tr>
<tr>
<td>extract:</td>
<td></td>
</tr>
<tr>
<td>( M_A )</td>
<td>400 - 800 g/gmol</td>
</tr>
<tr>
<td>( (H:C)_A )</td>
<td>1.5:1</td>
</tr>
<tr>
<td>( c_0 )</td>
<td>0.05 g/g coal</td>
</tr>
<tr>
<td>( D_{400 \text{ MW}} )</td>
<td>( 5 \times 10^{-5} ) cm²/s @ 250°C</td>
</tr>
<tr>
<td>( D_{800 \text{ MW}} )</td>
<td>( 3 \times 10^{-5} ) cm²/s @ 250°C</td>
</tr>
<tr>
<td>( Sc_{400 \text{ MW}} )</td>
<td>56</td>
</tr>
<tr>
<td>( Sc_{800 \text{ MW}} )</td>
<td>94</td>
</tr>
</tbody>
</table>

* from Appendix B
+ from Table 2-1
# from Appendix A
The gravitational settling velocity of spherical particles in a fluid is determined by equating the drag force to the gravitational force:

\[ \frac{\pi}{4} D^2 \cdot \frac{1}{2} \rho v^2 f = (1/6) \pi D^3 (\rho_g - \rho) g \]  

which becomes

\[ v^2 = \frac{4g(\rho_g - \rho)D}{3pf} \]  

where,

- \( g \) = gravitational acceleration, 981 cm/s²
- \( \rho_g \) = density of coal particles, g/cm³
- \( f \) = friction factor, dimensionless.

The friction factor is correlated as a function of Re and expressions are available for several ranges of Re. For the system parameters used in this investigation it was determined that the intermediate Re law for the friction factor is appropriate [94]:

\[ f = \frac{18.5}{Re^{0.6}} \quad (2 < Re < 500) \]  

The expression for the gravitational terminal velocity then becomes:

\[ v = \left[ \frac{g D^{1/6}(\rho_g - \rho)}{13.875 \rho^{0.4} \mu^{0.6}} \right]^{5/7} \]  

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Equation (C-1) was rearranged to obtain an expression for the external mass transfer coefficient:

$$k_x = \frac{D}{D} (2 + 0.6 \text{Re}^{1/2} \text{Sc}^{1/3})$$  \hspace{1cm} (C-7)

In order to obtain an external mass transfer coefficient comparable to the coefficients calculated from the experimental data discussed in Chapter III, a conversion of $k_x$, which is based on moles, to an equivalent first order rate coefficient, $k$, is necessary. The transformation can be described by:

$$k = k_x \frac{M_A \, a_{ext}}{c_0}$$  \hspace{1cm} (C-8)

where,

$$a_{ext} = \text{external surface area of the particles in a gram of coal},$$

$$\text{cm}^3/\text{g} = 6/(\rho_s D).$$

Values of the parameters, as listed in Table C-2, were then used in the calculation of the relative velocity, Re, and external mass transfer coefficients according to Eqs. C-6, C-7, and C-8 as a function of the particle size and the molecular weight of the solute. These results are tabulated in Table C-3.
Table C-3. External Mass Transfer Coefficients for Selected Particle Sizes.

<table>
<thead>
<tr>
<th>Particle Size</th>
<th>US series</th>
<th>avg. diameter (D_p) (cm)</th>
<th>Velocity (v) (cm/s)</th>
<th>Re</th>
<th>(k_x \times 10^4) (g mol/cm(^2)-s)</th>
<th>(k_x \times 10^4) (g mol/cm(^2)-s)</th>
<th>(k) (s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>-30 +40</td>
<td>0.05</td>
<td>7.4</td>
<td>131</td>
<td></td>
<td>1.5</td>
<td>1.1</td>
<td>110/160</td>
</tr>
<tr>
<td>-50 +70</td>
<td>0.025</td>
<td>3.4</td>
<td>30</td>
<td></td>
<td>1.6</td>
<td>1.1</td>
<td>230/320</td>
</tr>
<tr>
<td>-100+140</td>
<td>0.0125</td>
<td>1.52</td>
<td>6.7</td>
<td></td>
<td>1.7</td>
<td>1.2</td>
<td>500/700</td>
</tr>
<tr>
<td>-200+270</td>
<td>0.00625</td>
<td>0.69</td>
<td>1.6</td>
<td></td>
<td>2.1</td>
<td>1.4</td>
<td>1200/1600</td>
</tr>
</tbody>
</table>
APPENDIX D

Kinetic Parameter Calculations

A FORTRAN computer program, shown in Table D-1, was written to perform the calculations of the kinetic parameters, model extraction performance, and the standard deviation. The kinetic parameters were calculated according to the method described in Chapter III by Eqs. (3-15), (3-17), and (3-18). The extract yield predicted by the model at a given time was then calculated according to Eq. (3-14). These values were compared to the experimental values by calculating the standard deviation according to Eq. (3-19).

The least squares method used for calculating the values of the kinetic parameters is of the general form (for equation of the form: 
\[ y = kt + b \] with \( n \) data points):

\[
k = \frac{\sum_{i=1}^{n} t_i y_i - \left( \sum_{i=1}^{n} t_i \right) \left( \sum_{i=1}^{n} y_i \right) / n}{\sum_{i=1}^{n} t_i^2 - \left( \sum_{i=1}^{n} t_i \right)^2 / n} \tag{D-1}
\]

\[
b = \frac{\left( \sum_{i=1}^{n} y_i - k \sum_{i=1}^{n} t_i \right) / n}{n} \tag{D-2}
\]

The following parameter assignments were made:

- **RN**: run number
- **N**: number of data points
- **TU**: flag for time units (minutes: 0; hours: #0)
- **TEMP**: run temperature, °C
- **MM,MP**: particle mesh size (-MM +MP)
- **TIME**: contacting time, min
EXTR - $D_1D_{obs}$, extract yield, % wt daf

T1 - time at which all of the first group is assumed to be
extracted (typically 0, that is, instantaneous extraction), min

T2 - time at which essentially all of the first two extract groups
are assumed to be extracted (typically 20 or 30 min), min

DULT - $D_{ult}$, ultimate yield, % wt daf

K2,K3 - $k_2,k_3$, overall rate coefficients, min$^{-1}$

DF1,DF2,DF3 - $D_1^f$, $D_2^f$, $D_3^f$, total extract yields of the
individual extract groups, % wt daf

EXTRC - $D_{calc}$, extract yield calculated from rate expression
with kinetic parameters, % wt daf

S - s, standard deviation of fit of experimental data to model
extraction performance

INDEX - control flag:

0 - read new data set
1 - read new Dult
2 - end calculations

A typical printout is shown in Figure D-1.
Table D-1. FORTRAN computer program for calculating three group model kinetic parameters, extraction performance and standard deviation of fit of data to model.

```
PROGRAM ZRCALC1 INPUT, OUTPUT, TAPE5=INPUT, TAPE6=OUTPUT
INTEGER R, RN, TU
REAL K, K21, K31, LN5, LN6, TIME, DF3, DF12, DF21, DF2(R), DF1(R)
*EXTR(R*I) = DF1(R) + DF2(R) * (1. - EXP(-K2(R) * TIME(R,I)))
  * = DF3(R) * (1. - EXP(-K3(R) * TIME(R,I)))
  EXTR(R*I) = EXTR(R*I) - EXTRC(R*I)
DO 20 I = 1*N
  SUMD = SUMD + (EXTRD(R*I) ** 2)
```

S2 = SUMD/(NN-4)*
S(R) = SQRT(S2)
I = IFIX(TMP)
PRINT821, RN + I  * MM, MP
PRINT822
PRINT803
PRINT810
PRINT 804+ (T+TIME(R+1)+EXTR(R+1)+EXTRC(R+1)+EXTD(R+1)+I+1+N)
PRINT 81C
PRINT812, T1, T2
PRINT805
PRINT806, DF1(R)
PRINT807, DF2(R), K2(R)
PRINT808, DF3(R)+K3(R)
PRINT89, DULT
PRINT811, S(R)
2-2 READINDEX
ID = INDEX + 1
GO TO (120+20+I+ID
8-1 FORMAT(1, '14X*RUN ', '12x4**TEMP ', '13x', 'C COAL - ', '13x', ' +', '9819, 1299)
8-2 FORMAT(1, '14X**EXPERIMENTAL DATA *** CALCULATED DATA**', '9819, 1299)
8-3 FORMAT(1, '8X', **SAMPLE **TIME **EXTRACT ***EXTRACT **DIFFER-', '9819, 1299)
8-4 FORMAT(1, '8X', '*8X**9X***9X', '9819, 1299)
8-5 FORMAT(1, '12X', **RATE PARAMETERS**// **13X**EXTRACT FRACTIONS', '9819, 1299)
8-6 FORMAT(1, '11X', **INTEGRAL(DT)**, '5X', 'F6.2')
8-7 FORMAT(1, '11X', 'INTRMID(DT) ', '5X', 'F6.2', '6X', 'K2 = (**F7.5**, / MIN')
8-8 FORMAT(1, '12X', 'SLOW', 'DF3**', '5X', 'F6.2', '6X', 'K3 = (**F7.5**, / MIN')
8-9 FORMAT(1, '11X', 'TOTAL (ULTIMATE)** F6.2')
9-0 FORMAT(1, '8X', '521*')
9-1 FORMAT(1, '17X', 'T1 = **F6.1', '10X', 'T2 = **F6.1')
9-2 FORMAT(2F10.3)
9-3 FORMAT(11)
1 STOP
END
<table>
<thead>
<tr>
<th>Sample</th>
<th>Time (Min)</th>
<th>Extract</th>
<th>Extract</th>
<th>Difference</th>
<th>Extract</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.89</td>
<td>3.450</td>
<td>3.674</td>
<td>-0.224</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>3.19</td>
<td>4.000</td>
<td>4.013</td>
<td>-0.013</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>7.00</td>
<td>4.540</td>
<td>4.425</td>
<td>0.115</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>12.00</td>
<td>4.810</td>
<td>4.775</td>
<td>0.031</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>20.00</td>
<td>5.390</td>
<td>5.137</td>
<td>-0.153</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>40.00</td>
<td>5.513</td>
<td>5.498</td>
<td>0.015</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>60.00</td>
<td>5.763</td>
<td>5.741</td>
<td>0.022</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

T1 = 0.0, T2 = 30.0

Rate Parameters:

Extract Fractions

<table>
<thead>
<tr>
<th>Extract</th>
<th>Rate Constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Instant(CF1)</td>
<td>3.52</td>
</tr>
<tr>
<td>Intermediate(DF2)</td>
<td>1.48</td>
</tr>
<tr>
<td>Slew(DF3)</td>
<td>11.50</td>
</tr>
<tr>
<td>Total(Ultimate)</td>
<td>16.50</td>
</tr>
</tbody>
</table>

Standard Deviation = 1.472

Figure D-1. Sample output of computer program.
APPENDIX E

Solubility-Diffusion Models for Coal Particle Extraction

A model of the extraction of solute from coal particles into a bulk solvent can be developed by considering an ideal case of a spherical porous coal particle of radius, $R$, with uniform, constant porosity, $\varepsilon$, pore tortuosity, $\omega$, and pore internal surface area, $a$, and a solute with diffusivity, $D$. The initial concentration of solute is assumed to be uniform throughout the coal particle and distributed on the pore walls. The bulk solution concentration is assumed to be 0, which is equivalent to an excess solvent condition. Furthermore, external mass transfer resistance is assumed to be absent. The diffusion of the tetralin-soluble material from within the particle to the exterior of the particle is assumed to be the rate limiting step (that is, the rate of diffusion is much slower than the rate of dissolution).

The solubility of the material in the solvent within the pores determines the appropriate diffusion model. Two limiting cases are considered here. If the solubility of the material in the solvent is sufficiently high, all of the tetralin-soluble material, $c_s$, will dissolve instantaneously into the pores. The diffusion of the material from within the particle is described by a transient diffusion model. The second limiting case to consider is the case for which the solubility of the material in the solvent is much less than the concentration of the dissolved material, if it were all dissolved in the pores. For this situation, the extraction of the coal material from the particle is essentially described by a shrinking core model.
For either case, it is desired to evaluate an effective rate constant, equivalent to an experimentally measured rate constant, that is calculated from the rate of disappearance of material from the particle, \( r_s \), and the amount of material remaining within the particle, \( s \):

\[
k = \frac{r_s}{s}
\]  

(E-1)

where,

- \( k \) = effective rate constant, \( s^{-1} \)
- \( r_s \) = rate of removal of material from particle, \( g/cm^3\cdot s \)
  = \(-ds/dt\)
- \( s \) = amount of tetralin-soluble material remaining in particle, \( g/cm^3 \).

**Transient Diffusion Model**

The symmetrical transient diffusion of dissolved, uniformly distributed, material from within a spherical porous particle is described by:

\[
\frac{\partial c}{\partial t} = D_{eff} r^2 c ,
\]  

(E-2)

This becomes in spherical coordinates with no angular dependence:

\[
\frac{\partial c}{\partial t} = D_{eff} \left( \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \frac{\partial c}{\partial r}) \right) ,
\]  

(E-3)
where,

\[ c = \text{solute concentration in solvent in particle pores, g/cm}^3 \]

\[ \mathcal{D}_{\text{eff}} = \text{effective diffusivity, cm}^2/\text{s} \]

\[ = \frac{\mathcal{D}}{\omega} \]

\[ \mathcal{D} = \text{molecular diffusivity, cm}^2/\text{s} \]

\[ \omega = \text{tortuosity of pore structure in coal particle, dimensionless} \]

(values typically in the range: 3-10)

\[ r = \text{particle radius, cm.} \]

The initial concentration of dissolved material in the coal particles is expressed by,

\[ c(t=0) = \frac{a c_s}{\varepsilon} = \frac{c_0}{\varepsilon} \]

where,

\[ c_s = \text{undissolved solute concentration (per unit internal surface area) g/cm}^2 \]

\[ a = \text{internal surface area per volume of coal, cm}^{-1} \]

\[ \varepsilon = \text{porosity, void volume per volume of coal, dimensionless} \]

\[ c_0 = \text{initial concentration of solute in particle, g/cm}^3 \].

Two other boundary conditions are applicable:

\[ c = 0 \quad \text{at} \quad r = R, \quad t > 0 \]
The following dimensionless parameters are defined,

\[ \xi = \frac{r}{R} \]

\[ \tau = \frac{t}{\tau^*} \quad ; \quad \tau^* = \frac{R^2}{\mathcal{D}_{\text{eff}}} \]

\[ C = \frac{CE}{C_0} \]

Upon substitution of these parameters into Eq. (E-3), the following equation is obtained,

\[ \frac{\partial C}{\partial \tau} = \frac{1}{\xi^2} \left( \frac{\partial}{\partial \xi} \left( \xi^2 \frac{\partial C}{\partial \xi} \right) \right) . \quad (E-4) \]

The boundary conditions are expressed by,

\[ C = 1 \quad \text{at} \quad \tau = 0 \]

\[ C = 0 \quad \text{at} \quad \xi = 1 \]

\[ \frac{\partial C}{\partial \xi} = 0 \quad \text{at} \quad \xi = 0 . \]

This differential equation has the following solution as presented by Carslaw and Jaeger [95]:

\[ C = \frac{2}{\pi \xi} \sum_{n=1}^{\infty} \frac{(-1)^n+1}{n} \sin(n\pi \xi) \ e^{-n^2 \pi^2 \tau} . \quad (E-5) \]
The average concentration of solute over the entire particle at any time is also given:

\[ \overline{c} = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n} e^{-n^2 \pi^2 \tau} . \]  
(E-6)

In order to calculate an effective rate constant, the rate of solute leaving the particle needs to be calculated. This rate is equal to the flux of material across the particle surface,

\[ r_s = -4\pi R^2 D_{\text{eff}} \varepsilon \frac{\partial c}{\partial r} \bigg|_{r=R} = -4\pi R D_{\text{eff}} C_0 \frac{\partial c}{\partial \xi} \bigg|_{\xi=1} . \]  
(E-7)

The amount of material remaining in the particle is expressed by,

\[ s = 4\pi R^3 \overline{c} = 4\pi R^3 c_0 \overline{c} . \]  
(E-8)

Then, the rate coefficient becomes,

\[ k = \frac{r_s}{s} - \frac{3 D_{\text{eff}} \varepsilon \frac{\partial c}{\partial \xi} \bigg|_{\xi=1}}{R^2 \overline{c}} . \]  
(E-9)

The derivative of the concentration evaluated at the exterior surface of the particle is found from Eq. (E-5):

\[ \frac{\partial c}{\partial \xi} \bigg|_{\xi=1} = -2 \sum_{n=1}^{\infty} e^{-n^2 \pi^2 \tau} . \]  
(E-10)

The overall rate coefficient can then be expressed in terms of \( \tau, R \) and \( D_{\text{eff}} \):

\[ k = \frac{\pi^2 D_{\text{eff}}}{R^2} \sum_{n=1}^{\infty} \frac{e^{-n^2 \pi^2 \tau}}{n^2} . \]  
(E-11)
For \( r > 0.05 \), the ratio of the sums in Eq. (E-11) is approximately unity and thus the overall rate coefficient is proportional to the inverse of the square of the particle size.

**Shrinking Core Model**

The extraction of soluble material from a porous spherical particle, for which the solubility limit is reached by the dissolving extract, is best described by a shrinking core model. In this case, the soluble material in the particle dissolves rapidly to the solubility limit, \( c_{sl} \). The rate of extraction of the material then proceeds as a "quasi-steady state" diffusion described by,

\[
\frac{r_s}{v} = -4\pi r^2 D_{eff} \frac{dc}{dr} \quad \text{(E-12)}
\]

This rate is considered to be approximately constant at any time. The following boundary conditions apply,

\[
\begin{align*}
\text{c} &= c_{sl} \quad \text{at} \quad r \leq r_c \\
\text{c} &= 0 \quad \text{at} \quad r = R
\end{align*}
\]

where,

\( r_c \) = radius of the core of unextracted material, cm.

The following parameters are defined, similar to above,

\[
C = \frac{c}{c_{sl}} ; \quad \xi = \frac{r}{R} \quad (\xi_c = \frac{r_c}{R})
\]
and

\[ \gamma = \frac{r_s}{4\pi R_c s_1 e^{\Omega_{\text{eff}}}}. \]

Upon substitution of these parameters into Eq. (E-12), the dimensionless equation results,

\[ dC = -\gamma \frac{d\xi}{\xi^2}. \tag{E-13} \]

With the boundary conditions,

\[ C = 0 \quad \text{at} \quad \xi = 1 \]
\[ C = 1 \quad \text{at} \quad \xi \leq \xi_c, \]

solution of this equation yields,

\[ C = \gamma \left( \frac{1-\xi}{\xi} \right). \tag{E-14} \]

where,

\[ \gamma = \frac{\xi_c}{1-\xi_c}. \tag{E-15} \]

The core of unextracted material decreases in size at the rate of extraction according to,

\[ r_s = -ac_s 4\pi r_c^2 \left( \frac{dr_c}{dt} \right), \tag{E-16} \]

with the boundary condition,

\[ r_c = R \quad \text{at} \quad t = 0. \]
Then, the following dimensionless parameters are defined,

\[ \tau = \frac{t}{T^*} \quad \text{and} \quad \tau^* = \frac{R^2}{\text{eff}} \quad \beta = \frac{c_{s1} \xi}{a c_s} . \]

\( \beta \) is the ratio of the solubility limit of the extract to the total amount of extract present initially in the coal (less than 1 for this shrinking core model). Equation (E-16) becomes:

\[ \xi_c^2 \, d\xi_c = -\gamma \beta \, d\tau . \]  

(E-17)

Combining Eqs. E-15 and E-17 yields,

\[ (\xi_c^2 - 1) \, d\xi_c = \beta \, d\tau , \]  

(E-18)

with the boundary condition,

\[ \xi_c = 1 \quad \text{at} \quad \tau = 0 . \]

Solution of Eq. (E-18) yields,

\[ 6\beta \tau = 1 - 3\xi_c^2 + 2\xi_c^3 . \]  

(E-19)

For given values of the dimensionless time, \( \tau \), and the constant, \( \beta \), this equation can be solved to obtain values of the size of the core, \( \xi_c \).

It is then possible to calculate the amount of solute remaining in the particle for a given value of \( \xi_c \), by noting that,

\[ s = (4/3)\pi R^3 a c_s = (4/3)\pi R^3 a c_s \xi_c^3 . \]  

(E-20)

Since the initial amount of solute in the particle is expressed by

\[ s_o = (4/3)\pi R^3 a c_s , \]  

(E-21)
the fraction of material remaining, \( s/s_0 \), is simply,

\[
\frac{s}{s_0} = \frac{r_s}{R} = \frac{3\beta D_{\text{eff}}}{R^2} \left( \frac{1}{\xi_c^3 - \xi_c^3} \right) .
\] (E-22)

An expression for the overall rate constant can be written in terms of the core radius, \( \xi_c \), from Eqs. (E-15), (E-21) and (E-22),

\[
k_R = \frac{r_s}{s} = \frac{3\beta D_{\text{eff}}}{R^2} \left( \frac{1}{\xi_c^3 - \xi_c^3} \right) .
\] (E-23)

Then, with Eq. (E-19), \( k \) can be determined for appropriate values of the effective diffusivity, particle size, and \( \beta \) as a function of time.

**Comparison of the Two Models**

These two models are compared by plotting the fraction of the solute extracted from the particle as a function of a reduced time parameter, \( \tau/\tau_{0.5} \), where \( \tau_{0.5} \) is the value of \( \tau \) at 50% extraction, as shown in Fig. E-1. For the transient diffusion model, the extracted fraction is equal to \( 1-C \) and \( \tau_{0.5} = 0.0305 \); for the shrinking core model, the extracted fraction is equal to \( 1-(s/s_0) \), and \( \tau/\tau_{0.5} \) is equal to \( (6\beta\tau)/(6\beta\tau_{0.5}) \), where \( 6\beta\tau_{0.5} \) has a value of 0.110. (This method of calculating the reduced time parameter eliminates the necessity of determining the value of \( \beta \).)

Essentially the same extraction behavior is predicted by both models, except at very long times, so that either mathematical model can be used to represent the behavior of diffusion limited extraction from porous spherical particles. Since the mathematics of the shrinking core model require an additional parameter, \( \beta \), which cannot be easily determined, the transient diffusion model was used here.
Figure E-1. Comparison of transient diffusion and shrinking core models.
Model Predictions for Coal Particle Sizes Used in Experiments

In order to predict an extraction profile from the transient diffusion model for real times, values of the particle size and solute diffusivity are needed. An average particle radius was determined for each of the four coal particle size ranges used in the particle size study discussed in Chapter III: -30 +40, 0.025 cm; -50 +70, 0.0125 cm; -100 +140, 0.00625 cm; and -200 +270, 0.00313 cm. Values of solute diffusivity on the order of $1 \times 10^{-5} \text{ cm}^2/\text{s}$ were predicted for tetralin-soluble coal-derived material in Appendix C. Thus, a value of approximately $1 \times 10^{-6} \text{ cm}^2/\text{s}$ is expected for the effective diffusivity. With this value of effective diffusivity, the fraction of solute extracted as a function of time (minutes) is calculated from the transient diffusion model for the four particle sizes. The extraction approaches completion within 1 minute for all particle sizes, except the largest, as shown in Fig. E-2. The effect of particle size on the normalized extract yield at times of 1/2 and 1 minute, as shown in Fig. E-3, indicates that extract yield is not a simple function of the particle size. For comparison, two values of the effective diffusivity were used in plotting Fig. E-3, $1 \times 10^{-6} \text{ cm}^2/\text{s}$ and $1 \times 10^{-7} \text{ cm}^2/\text{s}$. 
Figure E-2. Normalized extract yield as a function of contacting time as predicted by the transient diffusion model. Effective diffusion coefficient, $D_{\text{eff}} = 1 \times 10^{-6}$ cm$^2$/s.
Figure E-3. Normalized extract yield as a function of particle size at $\frac{1}{2}$ and 1 minute as predicted by the transient diffusion model.
APPENDIX F

Mathematical Model of Simultaneous Reaction/Dissolution and Diffusion in a Spherical Particle

The unsteady state dissolution of material within a spherical porous particle and the simultaneous diffusion of the material from within the particle to the surface is expressed by the continuity equation,

\[
\frac{\partial c}{\partial t} = \frac{D_{\text{eff}}}{\varepsilon} \nabla^2 c + \frac{1}{\varepsilon} \frac{\partial c_s}{\partial t},
\]

where,

- \( c \) = solute concentration in the solvent in the pores, g/cm³ pore
- \( D_{\text{eff}} \) = effective diffusivity, cm²/s
  \( = \frac{D}{\omega} \)
- \( D \) = molecular diffusivity, cm²/s
- \( \omega \) = tortuosity of pore structure of coal, dimensionless
- \( \varepsilon \) = porosity, cm³ pore/cm³ particle, dimensionless
- \( c_s \) = solute concentration in solid per unit surface area, g/cm².

The dissolution of material is assumed to be first order in the amount of undissolved material and uniformly distributed so that,

\[
\frac{\partial c_s}{\partial t} = \frac{dc_s}{dt} = -k_d ac_s,
\]

(F-2)
where,

\[
 k_d = \text{first order dissolution rate constant, } s^{-1} \\
 a = \text{internal surface area per volume of coal, } cm^{-1}.
\]

The initial concentration of solute in the particle defines the boundary condition,

\[
 a c_s = c_0 \quad \text{at } t = 0,
\]

where,

\[
 c_0 = \text{initial concentration of solute in particle, } g/cm^3 \text{ particle},
\]

so that

\[
 a c_s = c_0 e^{-k_d t} \quad \text{.} \quad (F-3)
\]

Upon substitution of Eqs. (F-2) and (F-3) into Eq. (F-1), the continuity equation, in spherical coordinates with no angular dependence, becomes:

\[
 \frac{\partial c}{\partial t} = D_{\text{eff}} \frac{1}{r^2} \left( \frac{\partial}{\partial r} \left( r^2 \frac{\partial c}{\partial r} \right) \right) + \frac{k_d c_0 e^{-k_d t}}{\epsilon} \quad . \quad (F-4)
\]

The following boundary conditions apply:

\[
 c = 0 \quad \text{at } t = 0 \\
 c = 0 \quad \text{at } r = R \\
 \frac{\partial c}{\partial r} = 0 \quad \text{at } r = 0 \quad .
\]
Reduction of Eq. (F-4) to dimensionless parameters is accomplished by substitution of the following dimensionless groups:

\[ \xi = \frac{r}{R} ; \ \tau = \frac{t}{\tau^*} ; \ \tau^* = \frac{R^2}{D_{\text{eff}}} ; \ C = \frac{c_c}{c_0} ; \ \Omega = k_d \tau^* , \]

so that,

\[ \frac{\partial C}{\partial \tau} = \frac{1}{\xi^2} \frac{\partial}{\partial \xi} \left( \xi^2 \frac{\partial C}{\partial \xi} \right) + \Omega \ e^{-\Omega \tau} . \quad (F-5) \]

The boundary conditions then become:

\[ C = 0 \ \text{at} \ \tau = 0 \]
\[ C = 0 \ \text{at} \ \xi = 1 \]
\[ \frac{\partial C}{\partial \xi} = 0 \ \text{at} \ \xi = 0 \]

An analogous heat transfer problem, that involved conduction of heat from a sphere with exponential heat generation, was solved by Carslaw and Jaeger [96]. In terms of the variables defined here their solution of Eq. (F-5) is:

\[ C = e^{-\Omega \tau} \left( \frac{\sin \xi \ \Omega^{1/2}}{\xi \sin \Omega^{1/2}} - 1 \right) + \frac{2\Omega}{\xi \pi^3} \sum_{n=1}^{\infty} \frac{(-1)^n}{n(n^2 - \Omega/\pi^2)} \left( \sin n\pi \xi \right) \left( e^{-n^2 \pi^2 \tau} \right) \]

\[ (F-6) \]

For this investigation, the average concentration in the particle is more applicable than the concentration profile within the particle. The average concentration of dissolved solute in the pores of the particle can be determined by integrating the concentration, Eq. (F-6), over the entire particle volume:
The concentration of material remaining in the particle can then be calculated by summing the average concentration of dissolved material within the pores of the structure and the concentration of the undissolved material in the particle:

\[ C_{\text{tot}} = c_o \overline{C} + c_o e^{-\Omega} \quad \text{(F-8)} \]

The fraction of material extracted from the particle can be expressed by:

\[ \text{Extract fraction} = \frac{(c_o - C_{\text{tot}})}{c_o} = \frac{(c_o - c_o \overline{C} - c_o e^{-\Omega})}{c_o} \]

\[ = 1 - (\overline{C} + e^{-\Omega}) \quad \text{(F-9)} \]

This fraction is plotted in Fig. F-1 as a function of \( \tau \) at various values of \( \Omega \).

An effective overall rate coefficient can be calculated from this model by determination of the rate of extraction (that is, the flux of material through the exterior surface of the particle) divided by the total concentration of unextracted material remaining in the particle:
Figure F-1. Normalized extract yield as a function of reduced contacting time as predicted by the simultaneous reaction/dissolution and diffusion model.
The partial differentiation of the concentration of dissolved material with respect to the dimensionless radius, evaluated at the exterior of the particle yields:

\[
\frac{\partial C}{\partial \xi} \bigg|_{\xi=1} = e^{-\zeta \tau} \left( \frac{\zeta^{1/2}}{\tan \zeta^{1/2}} - 1 \right) + \frac{2 \zeta}{\pi^2} \sum_{n=1}^{\infty} \frac{e^{-n^2 \pi^2 \tau}}{n^2 - \zeta^2} .
\] (F-11)

The overall rate coefficient can then be expressed in terms of \( \tau, \zeta, R \) and \( D_{\text{eff}} \):

\[
k_{oa} = -\frac{-4\pi^2 R^2 D_{\text{eff}} \frac{\partial C}{\partial r} \bigg|_{r=R}}{4 \pi R^3 (\zeta C + \alpha c)}
= -\frac{3 D_{\text{eff}} \frac{\partial C}{\partial \xi} \bigg|_{\xi=1}}{R^2 (C + e^{-\zeta \tau})} .
\] (F-10)

The parameter \( \zeta \) indicates the importance of the kinetic process relative to the diffusion process in the extraction of material from the particle. If the extraction is diffusion controlled, the reaction rate coefficient is sufficiently large to ensure rapid reaction/dissolution;
in this case, as $\Omega \to \infty$, Eq. (F-12) reduces to the expression for the overall rate coefficient of the transient diffusion model as presented in Appendix E:

$$k_{oa} = \frac{D_{\text{eff}}^2}{R^2} \sum_{n=1}^{\infty} \frac{e^{-n^2 \pi^2 \tau}}{n} \approx \frac{\pi^2 D_{\text{eff}}^2}{R^2} \quad \text{for } \tau \geq 0.05$$

Thus, for diffusion limited extraction, the overall rate coefficient is inversely proportional to the square of the particle size. For kinetic controlled conditions, the reaction/dissolution proceeds slowly. In this case, as $\Omega \to 0$, Eq. (F-12) reduces to the simple particle size independent identity:

$$k_{oa} = k_d$$

If neither kinetic processes nor diffusion processes are controlling, the overall rate coefficient is time and particle size dependent. The dependence of the overall rate coefficient on the particle size at a given reduced time or conversion level will be between a power of $-2$ and $0$.

Typical values for the parameters in this investigation were estimated and used to plot the fraction of material extracted as a function of time for the range of particle sizes of interest, as shown in Fig. F-2.
Figure F-2. Normalized extract yield as a function of contacting time for typical coefficients as predicted by the simultaneous reaction/dissolution and diffusion model. Dissolution rate constant, \( k_d \): 0.002 s\(^{-1}\); effective diffusion coefficient, \( D_{\text{eff}} \): \( 1 \times 10^{-7} \) cm\(^2\)/s.
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