KINETIC MODELS FOR COAL LIQUEFACTION

Introduction:

During the past decade numerous efforts have been made to evaluate and model the kinetics of coal liquefaction. Donor solvent liquefaction of coal occurs through a series of steps that start with the scission of weaker bonds within the coal structure, resulting in the formation of very reactive fragments. Hydrogen transfer from the donor solvent and the hydroaromatic portions of the coal stabilizes these reactive fragments. Additional bond rupture and hydrogen transfer causes these intermediates to react further to form molecules with a wide range of molecular weights.

The process of coal liquefaction depends not only on operating parameters such as the nature of solvent, temperature, and pressure but also on the nature and rank of the feed coal. Therefore, the models developed for a particular coal do not have universal applicability. In attempting to model the kinetics of coal liquefaction, we need information on the possible reaction networks and associated rate constants and products. In this report, we will briefly summarize the information on product characterization and reaction networks before presenting the relevant lumped kinetic or statistical models for coal liquefaction.

Product Characterization:

One of the major difficulties associated with coal liquefaction studies is the characterization of the products of liquefaction. As coal is a heterogeneous mixture, its liquefaction gives numerous compounds. Since the stoichiometric relationships are not well understood, kinetic modeling involving individual reaction steps is impossible.

In the past, kinetic modeling of petroleum refinery processes has been carried out based on lumped fractions containing chemical species of similar

activities. The approach in kinetic studies of coal liquefaction has been to group the products into "kinetically similar" classes based on separation techniques. Most of the studies (Neller et al., 1951; Falkum and Glenn, 1952; Pelipetz et al., 1955; Ishii et al., 1965; Hill et al., 1966; Curran et al., 1967; Struck et al., 1969; Liebenberg and Potgieter, 1973; Yoshida et al., 1976; Squires, 1976; Farcasiu et al., 1976; Brooks et al., 1976; Cronauer et al., 1978; Shalabi et al., 1979; Abichandani et al., 1982) have classified the products by their solubilities or the extractive fractions. The commonly used definitions

Oils:	Soluble in pentane (or hexane)
Asphaltenes:	Soluble in toluene (or benzene)
	Insoluble in pentane (or hexane)
Pre-asphaltenes:	Soluble in tetrahydrofuran (or pyridine)
	Insoluble in toluene (or benzene)
Unreacted Coal	Insoluble in tetrahydrofuran (or pyridine)

In this characterization technique, no distinction is made between the solvent initially present and the pentane-soluble products. In the literature, there is no uniformity in the definition of the various lumped groups. For example, the unreacted coal is defined as benzene insoluble by Weller et al. (1951) and Hill et al. (1966), as xylenol insolubles by Curran et al. (1967), and as tetrahydrofuran insolubles by Shalabi et al. (1979). In addition, the product characterization has also been done on the basis of chromatographic analysis (Whitehurst et al., 1976, 1977; Prather et al., 1977; Hathaway et al., 1978; Petrakis et al., 1983,b) and distillation fractions (Shah et al., 1978 and Brunson, 1979). The reaction products are distilled under vacuum and cuts are taken between different temperatures. Shah et al. (1978) have grouped the products as light gases (C_1-C_4), naptha (C_4-477K),

furnace oil (477-616K), heavy oil (616+K), and solvent refined coal (non-distillables). Recently, Petrakis et al. (1983 a, b) have analyzed the SRC-II heavy distillate fractions using liquid chromatography. They separated the SRC-II heavy distillate into nine fractions, each consisting of chemically similar compounds. These fractions are labeled as strong, weak, and very weak bases; strong, weak, and very weak acids; neutral oils; neutral resins; and asphaltenes. They characterized these fractions in detail by elemental analysis (HNMR at 80 and 600 MHZ, ^{13}CNMR, IR, mass spectrometry, vapor phase osmometry, and other techniques). The results were used to postulate the molecular structures of each fraction. Some investigators (Farcasiu, 1977 and Knudson et al., 1977) have also used gel permeation chromatography for this purpose.

In addition to the differences in the method of characterizing products, there is an added problem that even data obtained by apparently identical methods may not be comparable. Ruberto and Cronauer (1979) have shown that the sequence in which the various solvents are used affects the final weight fraction of the products. In light of these differences, agreement in the kinetic data reported by various authors seems unlikely. If the chemical composition of oils, asphaltenes, and preasphaltenes as reported by the various investigators is not the same then the comparison of kinetic data or any kinetic model developed therefrom are meaningless.

These questions were partly answered by the work of Aczel et al. (1976), who analyzed various SYNTHOIL products using the same analytical techniques such as solvent extraction, liquid chromatography, and various spectroscopic techniques. Their results indicate that when a coal is liquefied by a particular process and the products are analyzed by the same technique the quality of corresponding lumped fractions (oils, asphaltenes, preasphaltenes,

and unreacted coal) is very similar. Therefore, these lumped fractions can be used to model liquefaction reactions and estimate rate parameters.

Mechanism of Coal Liquefaction:

Numerous efforts have been made to obtain an insight into the mechanism of coal liquefaction. Whitehurst et al. (1977) have postulated a conceptual picture of coal dissolution wherein weak bonds (activation energy < 210 KJ/mol) are broken at low temperatures (< 573K), and extracts up to 40 - 50% of bituminous coals are obtained. As the temperature is increased, free radicals are formed. If hydrogen is available, these free radicals combine with hydrogen to yield stable species with molecular weights in the range of 300 to 1000. If hydrogen is unavailable, retrogressive reactions occur resulting in the recombination of radicals to form higher molecular weight compounds and coke. Solvent, coal, solvent refined coal, residue, and hydrogen gas can donate the hydrogen to free radicals. Whitehurst et al. (1977) have suggested that molecular hydrogen cannot directly supply hydrogen to free radicals, and its chief role is to rehydrogenate the spent donor solvent. Solvent, coal, solvent refined coal, and residue can contribute hydrogen through hydroaromatic dehydrogenation, aromatic substitution, and char formation.

Han and Wen (1979) have provided a mechanism which depends on the reaction time. In the initial step, coal produces free radicals by undergoing fast thermal reactions. These free radicals are stabilized by the hydrogen present in the coal itself. In a few minutes this reaction stage is completed, and preasphaltenes are produced as the main product. This process is called autostabilization. Preasphaltenes are light molecular weight compounds containing polar functional groups. Asphaltenes and oils are formed in the second stage, which requires a long residence time. Asphaltenes are

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mostly mono-and di-aromatics whereas the oils are mostly saturated
hydrocarbons.

Tschamler and DeRuiter (1963) have proposed that coal is a matrix of
large, strongly linked micelles that contain intimately associated, smaller,
less strongly bonded micelles that are normally trapped within the coal matrix
unless it is swollen by a solvent. Both types of micelles are a continuous
series instead of single discrete classes and can be progressively dispersed
in a suitable solvent by an increase in temperature. Thus, dissolution occurs
by removal of colloidal size units directly from the coal matrix.

The process of direct coal liquefaction is affected by various parameters
such as, (i) physical properties of coal, (ii) coal rank and petrography,
(iii) coal pretreatment, (iv) solvent, (v) hydrogen pressure, and (vi)
catalytic effects. These effects are considered in a separate report, "Role
of catalysts and hydrogen donor solvents in direct coal liquefaction." This
present report specifically deals with the kinetic models proposed for the
direct liquefaction of coal.

Kinetic Models for Donor Solvent Coal Liquefaction:

Most of the studies reported in the literature evaluate kinetic models
using different types of reacting species. A summary of relevant kinetic
studies reported in the literature is shown in Table I-4. Kinetic models
proposed in the literature can be grouped into three classes:

1. Rate models

2. Lumped models

3. Correlation models

Historically, all the initial models proposed for coal liquefaction can
be termed as rate models. These models correlate the fractional conversion of

coal with concentrations of unconverted coal, kinetic parameters, and time. Table I-4 also includes a summary of the rate models.

The models of Oele et al. (1951), Hill et al. (1962, 1966, 1974), Wiser and coworkers (1968, 1971), and Curran et al. (1966) are all simple models, and they represent the primary reactions of coal dissolution in the presence of excess donor solvents. These models fail to provide information about the effect of operating variables on the yields of various molecular weight fractions from primary as well as secondary reactions.

Neavel (1976) reported that when a highly volatile bituminous coal is rapidly heated 90% of the coal is converted to pyridine solubles in the presence of tetralin. He also found that the initial conversion of feed coal to asphaltene is high when naphthalene and dodecane are used as solvents. In addition, at longer times, some of the asphaltenes (benzene solubles) were reconverted back into benzene insolubles. This is probably due to retrogressive reactions. On the basis of these results, Neavel (1970) postulated the following mechanism for donor solvent liquefaction. At very short times, the coal structure is fragmented due to the scission of weak bonds leading to the formation of lower molecular weight products. The fragmented particles are then subsequently dispersed in the solvent vehicle and undergo further reaction. At short contact times, the nature of the solvent does not have an effect on the coal liquefaction product as hydrogen can be transfered from the hydroaromatic portions of the coal to locations of bond rupture. At larger residence times, a good donor solvent acts as a free radical terminator and does not allow the retrogressive reactions. Although Neavel (1970) did not provide a kinetic model, his study at short contact times has provided critical experimental evidence of the mechanisms operating during donor solvent liquefaction of coal. Whitehurst and coworkers (1976,

1976, 1977) have studied coal liquefaction with several coals in a variety of solvent mixtures at a wide range of contact times both in the presence and absence of gaseous hydrogen. Guin et al. (1976), Kang et al. (1976), Langanbach et al. (1976), Mitchell et al. (1976), Anderson and Kang (1978), and Walker et al. (1977) have reported the occurrence of retrogressive reactions under certain conditions of liquefaction.

All these studies have guided coal liquefaction reaction modeling from the simple rate models to the lumped kinetic models. The basic features of this development are:

1. At any given temperature, the conversion of coal to pyridine-soluble products reaches a maximum value. Although the reaction is not considered to be truly reversible, this maximum conversion has some of the characteristics of an equilibrium value. This value increases with increasing temperature until a certain temperature is reached. Above this temperature, retrogressive reactions are dominant. In addition, with increasing temperature, the time necessary to reach this equilibrium value decreases.

2. At very short reaction times, there are a large number of intermediates formed. The formation of these intermediates is independent of whether or not there is any gaseous hydrogen present and is also independent of the nature of the solvent. This indicates that these intermediate forming reactions are wholly thermal in nature. During this step, it is only necessary for the solvent to be capable of transferring hydrogen to the hydrogen-lean from the hydrogen-rich parts of the coal. This hydrogen transfer is necessary when direct interaction between

hydrogen-accepting and hydrogen-donating coal fragments is not possible.

3. At intermediate and long contact times, the nature of the solvent becomes important because the intermediate species formed attempt to stabilize themselves by combining with other free radicals or atoms; this results in the termination of their free radical state. The quality of the donor solvent affects the relative rates of the progressive and retrogressive reactions. Good donor solvents such as tetralin enhance the relative rates of the progressive reactions while poor donor solvents such as napthalene promote retrogressive reactions.

Based on these facts, efforts were made in the past to propose lumped kinetic models based on different reaction schemes. These lumped kinetic models are discussed in detail in the next section.

Lumped Kinetic Models:

One of the earlier attempts at lumped parameter modeling was by Weller et al. (1951). On the basis of their studies in the absence of a solvent or liquid vehicle, they proposed the following mechanism for coal liquefaction:

$$Coal \rightarrow Asphaltenes \rightarrow Oils$$
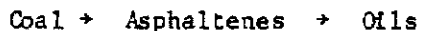
They monitored the product solubilities in benzene and hexane to measure the conversions of the reacting species. The two reactions (Coal → Asphaltenes and Asphaltenes → Oils) were found to be first order with respect to coal and asphaltenes, respectively. This model did not take into account all possible reaction paths and oversimplified the problem by classifying the wide range of molecules into only three separate groups. Although the assumption of oil being only a secondary product of coal liquefaction was later shown to be incorrect by Neavel (1976), the above model provided a direction for lumped

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kinetic modeling of donor solvent liquefaction. Since then, many attempts have been made at similar types of modeling, as shown in Table I-4. Some of the most recent studies are discussed below.

Cronauer and Ruberto (1979) have reported kinetic data on the liquefaction of a Belle Ayr mine subbituminous coal and Burning Star mine bituminous coal (seam number 6) using hydrogenated anthracene oil (HAO), hydrogenated phenanthrene (HPh), and anthracene oil (AO) as solvents. They found that for the Belle Ayr coal the percentage solvation of coal as well as the yield of oils increased with the increasing hydrogen content of donor solvent. Due to retrogressive reactions, they observed a negative yield of oils at low space times when unhydrogenated anthracene oil is used as a solvent at 723 K. Very little reaction to form oil is indicated by the high yield of asphaltenes and preasphaltenes at all space times. At long space times, the liquefaction of Belle Ayr coal with hydrogenated anthracene oil at 743 K resulted in the formation of coke, indicating dominant retrogressive reactions. For Burning Star coal, the percentage solvation is lower at 733 K than at 723 K in the presence of hydrogenated anthracene oil. The yield of oils at 733 K is again negative at short space times using hydrogenated anthracene oil. As explained before, this is due to the retrogressive reactions resulting in the formation of polymeric material. Cronauer and Ruberto (1979) correlated their data for the liquefaction of Belle Ayr coal in the presence of hydrogenated anthracene and hydrogenated phenanthrene and presented the following kinetic model
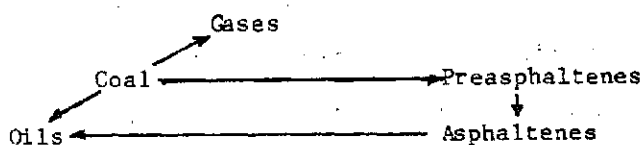
Assuming all reactions to be first order, the above model was found to fit the data well for all space times in the temperature range of 673-723 K and for short space times at 733 K and 743 K. Cronauer and Ruberto (1979) have also reported good agreement for the various lumped fractions in the reaction network. The model proposed by Cronauer and Ruberto (1979) is incapable of predicting negative oil yields. Figure I-9 indicates that the soluble portion of coal varies with the nature of the solvent. For a given coal-solvent system (at a fixed pressure and temperature), an equilibrium concentration of insoluble organic matter seems to exist. Morita et al. (1976) have reported the inhibition of solvent by coal during liquefaction for some Indonesian, Japanese, and Australian coals. Though the ranks of the various coals and nature of the solvent are not well characterized, the above authors indicate that during the reaction of coal in the presence of a H_2MoO_4 catalyst at a temperature at 723 K the amount of oil present dropped to half its initial value, after which it began to increase. The formation of coke and resin type material exhibited a maximum during this time. These authors have proposed the following model to explain their data:

$$C \nearrow C_1 \longrightarrow A \longrightarrow O_I \longrightarrow D \longrightarrow E$$
$$C \searrow C_2 \longrightarrow O_{II}$$
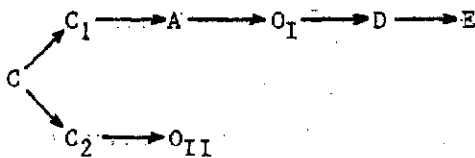
where C, A, O, D, and E represent the coal, asphaltene, oil, resin, and coke fractions, respectively. This mechanism is a modified version of a model put forth by Cronauer et al. (1978). The reactions oils → resins → coke are additionally included in the reaction network proposed by Cronauer et al.

(1978). When the direct formation of oil from coke is negligible, the model

simplifies to an extension of the model of Weller et al. (1951).

Recently, Abichandani et al. (1982) have proposed a more sophisticated

model and have fitted the data reported by Cronauer et al. (1978). On the

basis of the observed behavior of coals during thermal liquefaction, the
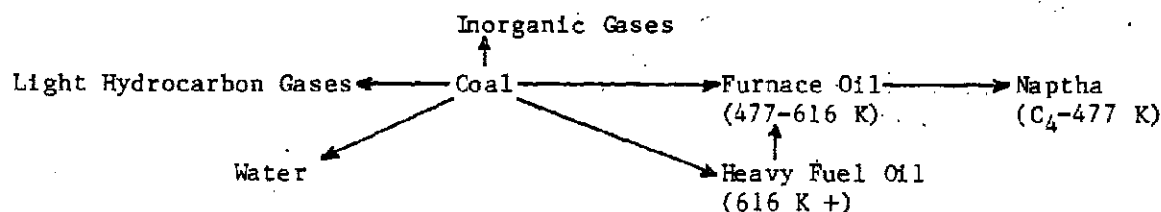
following model is proposed:

Coal (C) + Oil → Coal (C*)

Oils → Gases
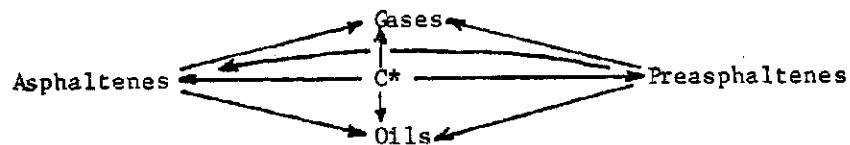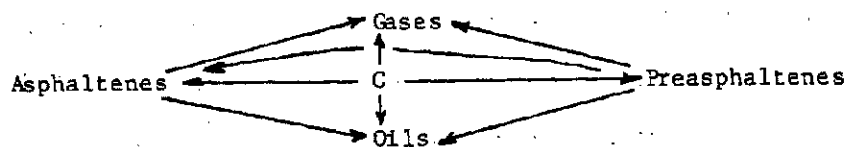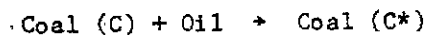
In this model, a retrogressive reaction (coal + oil → more reactive coal) is

assumed, and it accounts for the negative yields of oils in the initial stage

of dissolution. Apart from preasphaltenes, they assume one more product of

liquifaction which is insoluble in pyridine (or tetrahydrofuran). Due to the

lack of a suitable solvent, this reactive coal cannot be experimentally

isolated and is therefore grouped with the less reactive coal. With the

assumption of such a reaction, swelling of coal at low space times and a

sizable increase of the viscosity of the reaction slurry during the initial stages of liquefaction can be explained. In addition, the existence of a retrogressive reaction explains the increase in the yield of oil when solvents of increasing hydrogen donor capacity are used.

Shalabi et al. (1979) tested four reaction networks to fit their experimental data obtained for a highly volatile type-A bituminous coal from the Madisonville #9 seam, Fies Mine, Kentucky in the temperature range of 623-673 K. They concluded that a six parameter model best fitted their data. However, three of these rate parameters did not follow Arrhenius-type temperature profiles. This model is essentially a modification of the mechanism of Cronauer et al. (1978), and it contains the reaction of preasphaltenes to oils and gases.

Shah et al. (1978), have taken a somewhat different approach to the modeling of the reactions. The products of coal liquefaction are classified according to their boiling range as shown below:

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                              Inorganic Gases
                                    ↑
                                    |
Light Hydrocarbon Gases ◄───── Coal ─────────────► Furnace Oil ───────► Naptha
                              ╱      ╲                (477-616 K)          (C₄-477 K)
                             ╱        ╲                    ↑
                        Water ◄        ► Heavy Fuel Oil
                                            (616 K +)
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This model was shown to correlate the data well for the liquefaction of subbituminous Wyoming coal. This model assumed that water, light hydrocarbon gases, and inorganic gases come directly from coal. This model ignored the chemical identity of the molecules and classified the reactive species on the basis of the physical property. Though this is not a true kinetic model, such models have been successfully employed in modeling the cracking of petroleum fractions (Weekman and Nace, 1970). These reactions were thermal in nature as

indicated by the high activation energies obtained for various primary reactions (Shah et al., 1978).

Recently, Singh et al. (1982) have proposed a lumped kinetic model for the liquefaction of coal in the SRC-II coal liquefaction reactor, and they identify important reaction pathways. They assumed the liquefaction reactions to occur in two stages as proposed by Han and Wen (1979). In the first stage, coal is assumed to dissolve instantaneously in the solvent to yield molecules of different sizes belonging to various components. In the second stage, these reactive components undergo slow conversion.
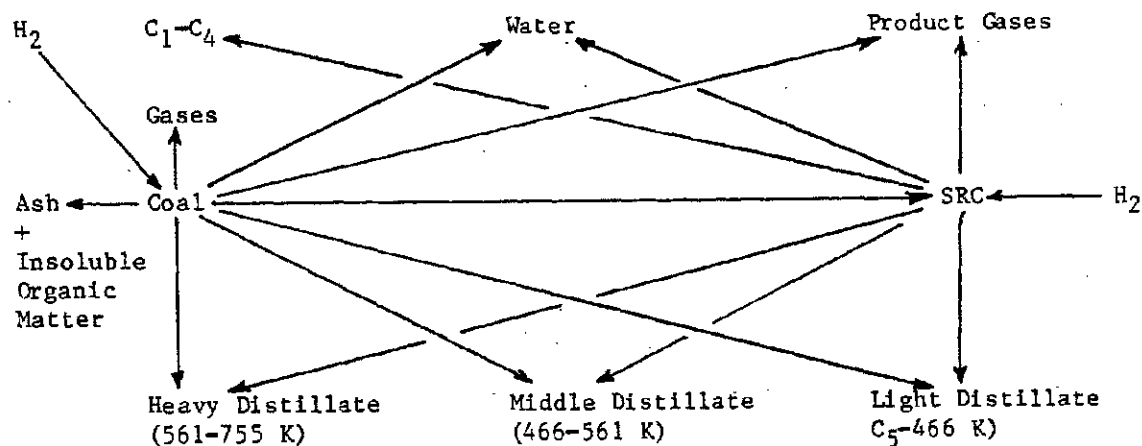
The best overall reaction scheme can be represented by the above network. This network is conceptually similar to the one proposed by Weller et al. (1951) for catalytic liquefaction of coal in the absence of a solvent vehicle. This network differs from one proposed by Weller et al. (1951) in that the model proposed by Weller considers asphaltene to be a major intermediate product which is very different from solvent refined coal. Weller et al. (1951) reported the rate of conversion of coal to products to be 20-30 times larger than that for the conversion of asphaltene to lighter

products. According to the above network proposed by Singh et al. (1982), coal dissolves instantaneously within the preheater, before the liquefaction reactor, yielding several products. Only one of the dissolution products, solvent refined coal (SRC), reacts further yielding lighter components. Based on the studies reported by Reuther (1977), Singh et al. (1982) proposed a linear relationship between the rate of reaction of solvent refined coal to the mass fraction of ash in the coal. They have given the following expression to evaluate the rate of reaction of solvent refined coal.

$$-r_{SRC} = 1.567 \times 10^5 \exp(-79.16/RT) \, P_{H_2}^{0.28} \cdot X_{ASH} \, (\frac{kg}{L.h})$$

They claim that overall error in the analysis yielding the reaction scheme was less than ±4%.

Based on the modification of a model proposed by Liebenberg and Potgieter (1973), Shah (1979) proposed a conceptual model. This model is particularly relevant to the design of coal liquefaction reactors where the primary reactions commence in the preheater and then proceed to completion, along with secondary reactions, in the reactor. He recommends that the preasphaltenes and asphaltenes be separated into two fractions each, PA* and PA, and A* and A, where the "*" represents the active part of each fraction. The proposed reaction network is:

$$PA^* \rightarrow A^* + A$$
$$A^* \rightarrow oils + gases$$
$$PA^* \rightarrow oils + gases$$
$$oils \rightarrow gases$$
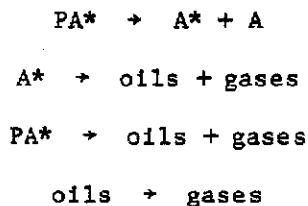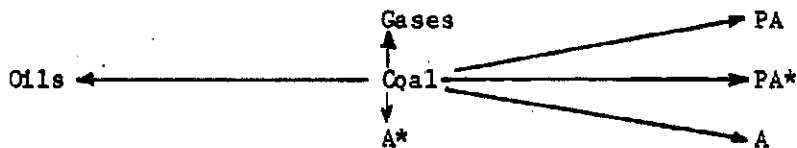
The application of above reactor network requires considerable data at all residence times.

A similar concept in the kinetics of coal liquefaction considers the coal to be made up of two parts with different reactivities. The first is a fraction of high reactivity composed of loosely held bonds that break easily under liquefaction conditions and therefore yield products obtained at short times. The second fraction is one of lower reactivity, which may be due to more stable structures that decompose slowly, and is responsible for the majority of the products formed at long residence times. It is difficult to apply this model as it is difficult to quantitatively identify the two fractions as a function of reaction conditions.

Another method of modeling the coal liquefaction reactions is based on the free radical mechanism. It consists of three steps: a) initial reactions that form free radicals; b) propogation reactions that have no effect on the number of the radicals; and c) termination processes that consume free radicals. Attar (1978) has proposed one such model. Although experimental verification of such models is not complete, it may be an alternative to the lumped kinetic or statistical models.

Statistical Models:

Extreme caution should be taken before applying any kinetic model to a particular process. Most of the models are based on limited data and a particular coal. Even the most complex lumped parameter model could not be applied for a coal liquefaction process using a different rank and nature of feed coal. In this phase of the report, we are concentrating on the SRC-II process. During the development of the SRC-II process, many studies were carried out at the three pilot plants (Ft. Lewis (Dupont, Washington), P-99 at Gulf Research and Development Corporation (Harmarville, PA), and Merrian

(Merrian, KA)). In addition, some SRC-II work has been carried out at the Hydrocarbon Research Institute (HRI). Jones and Carr (1982) at Gulf Research and Development Company have used all this pilot plant data to give SRC-II process yield correlations. These correlation models do not give any information regarding reaction networks and kinetics; however, they are a consistent model relating the product yield with important process variables.

These correlation models are based on the studies of yield, process, and coal property data from 145 runs from the three pilot plants and 10 runs from the Hydrocarbon Research Institute; 34 runs were conducted in SRC I made with no recycle solids. A total of 21 coal sources belonging to Powhattan or Kentucky bituminous classifications were used. This study showed that coal source had a strong influence on the process yields. Precisely, iron in ash or total sulfur, carbon to hydrogen ratio or percent volatile matter, and a maceral variable such as maximum mean reflectance of vitrinite were found to be the most important coal properties. Apart from the coal type, pressure and slurry residence time were shown to be the most important process variables influencing the yield distribution for SRC-II reactors. As the pressure and slurry residence time are increased, more heavy distillate is formed; however, hydrogen consumption is also increased. Temperature seemed to increase the fraction of middle distillates. If the temperature is much higher than $860^{\circ}F$, the undesired reactions might become predominant. Use of higher pressures and slurry residence times are suggested for more productive operation.

These correlation models are a tool for analyzing the present data and identifying the major process variables; however, these models cannot replace the lumped kinetic models. Therefore, one should use a kinetic model based on a wide range of data using the same coal type.

Nomenclature:

a   Maximum weight fraction of coal that can be converted at a given temperature (from kinetic expression given by Wiser (1968)).

a_1 Reciprocal of the maximum liquefiable coal fraction at a given temperature (from kinetic expression given by Hill (1966).

A   Asphaltenes (benzene soluble, pentane insoluble).

b   Initial weight fraction of tetralin that could potentially react (=1.0) (from kinetic expression given by Wiser (1968)).

BP   By products (from model given by Shah et al. (1978)).

C   Coal, moisture and ash free.

C   Weight percent of coal decomposed (from kinetic expression given by Curran (1967)).

C_T Maximum weight percent coal which can be decomposed (from kinetic expression given by Curran (1967)).

C_1, C_2 Two reactive parts of coal

C*   More highly reactive coal (from kinetic scheme given by Abichandani (1982)).

C^1 Solvent refined coal.

E   Ethers.

G   Gases (CO, CO_2, H_2S, NH_3, H_2O, and light hydrocarbons C_1-C_4)

H   Hydroxyls

IOM   Insoluble organic matter (from kinetic scheme given by Singh et al (1982)).

k, k^1 Forward and reverse reaction rate constants

k_o Psuedo 2nd order rate constant (from kinetic expression give by Hill (1966)).

k_1, k_2 1st and 2nd order reaction rate constants

K_I, K_{II} 1st order rate constants with Arrhenius temperature dependence (from kinetic expression given by Curran (1967)).

M   Multifunctionals (from kinetic scheme given by Mohan and Silla (1981)).

N   Nitrogens

O   Oils (pentane solubles)

O_1, O_2, O_3 Oils - heavy, middle, and light distillates

O_I, O_{II} Oils (from kinetic scheme given by Morita et al. (1976)).

P   Preasphaltenes (pyridine soluble benzene insoluble)

W   Water

x_1, x_m Conversion of coal to benzene soluble products: $x_1 = 0$ at $t = 0$; $x_1 = x_m$ as $t \to \infty$ (from kinetic expression given by Kang et al (1979)).

x   Fraction of coal liquefied

α Fraction of maf coal extracted (from kinetic expression given by Oele et al (1951)).

γ Fraction of coal which decomposes at faster rate (from kinetic expression give by Curran (1967))

ν Volatile portion of coal (from kinetic scheme given by Brunson (1979))

ω Unreactive portion of coal (from kinetic scheme given by Brunson (1979)).

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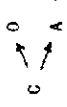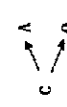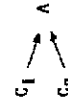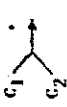
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Table 1-4: Rate Models

Reference	Kinetic Expression	Solvent	Coal Type	Catalyst	Temperature (K) Pressure (MPa)	Rxn time (hr.)	Reactor Type
Oele et al. (1951)	$\frac{d\alpha}{dt} = k - k'\alpha$	Anthracene Oil and β-napthol	Bituminous Dutch	None	T: 523-623 P: NA	NA	NA
Hill (1966)	$\frac{dx}{dt} = k\,(1-x)$ where $k = k_o\,(1-ax)$	Tetralin	Utah Spring Canyon high volatile Bituminous	None	T: 623-723 P: 34.47	25-30	1 liter batch autoclave
Kang et al. (1979)	$\frac{dx_1}{dt} = k_1(x_m-x_1)+k_2(x_m-x_1)^2$ $x_1 = 0$ at $t = 0$ $x_1 = x_m$ at $t = \infty$	Tetralin	Utah high volatile B Bituminous Kentucky high volatile B Bituminous	None	T: 673 P: 10.35	.5	Differential recycle
Wiser (1968)	$\frac{dx}{dt} = k_2\,(a-x)\,(b-x)$ short times $\frac{dx}{dt} = k_1\,(a-x)$ long times	Tetralin	Utah high volatile Bituminous	None	T: 623-723 P: NA	20	NA
Curran (1967)	$C_1-C = Y\,C_1 e^{-k_1 t} + (1-Y)\,C_1 e^{-k_2 t}$	Tetralin, Decalin other solvents	Pittsburgh Seam bituminous from Ireland Mine WV) Pittsburgh Seam bituminous from Ireland Mine (northern WV)	None	T: 597-714 P: NA	.04-2	Microautoclave ~ 30 ml Autoclaves .3 l

TABLE I-4: Lumped Models

Reference	Kinetic Scheme	Solvent	Coal Type	Catalyst	Temperature (K) Pressure (MPa)	Reaction Time (hr)	Reactor Type
Weller et al. (1951)	$C \rightarrow A \rightarrow O$	None	Pittsburgh Seam bituminous from Bruceton Mine	SnS, NH_4Cl	T: 673-713 / P: 41	3	1-liter batch autoclave
Yoshida et al. (1976)	$C \rightarrow A \rightarrow O$ (with O)	decrystallized anthracene oil	Taiheiyo and Oyobari (Hokkaido, Japan)	red mud, sulfur	T: 673 / P: 19.6-21.6	.1-2	.5 liter batch autoclave
Liebenberg and Potgieter (1973)	$C \rightarrow A \rightarrow O$	Tetralin	Bituminous	None	T: 653-713 / P: 16-20	5	Batch autoclave
Pelipetz et al. (1955)	$C \rightarrow A + O$	None	Bituminous C from Rock Springs Bed, WY	None	T: 673 / P: 3.4-27.6	.5-3	1.2 liter batch autoclave
Struck et al. (1969)	$C_1 \rightarrow A + O$, C_2	Tetralin	Pittsburgh Seam Ireland Mine Extract	$ZnO/ZnCl_2$	T: 644-700 / P: 10.34-24.13	.67	.3 liter rocking autoclave
Falkum and Glenn (1952)	$C_1 \rightarrow A + O$, C_2	None	Spitsbergen	Ca-Cu-Cr	T: NA / P: NA	NA	NA
Shalabi et al. (1979)	$O \rightleftharpoons P$, C	Tetralin	High Volatile bituminous from Pres Mine KY	None	T: 623-673 / P: 13.79	3	.3 liter batch autoclave
Morita et al. (1976)	$C \rightarrow C_2$, C_{II}, C_I, $A \rightarrow C_T$, $D \rightarrow E$	Unhydrogenated and hydrogenated solvents	Japanese, Indonesian, Australian	Mixture of Fe hydroxides and Mo oxides	T: 623-723 / P: 0.69	2	.3 l and .5 l batch autoclaves

Reference	Scheme	Solvent	Coal	Catalyst	Conditions	Space time	Reactor
Cronauer et al. (1978)	C → A → O, C → P	Hydrogenated phenanthrene anthracene oil	Subbituminous from Belle Ayr Mine, WY	None	T: 673–743, P: 13.79	1	.3 liter CSTR
Brunson (1979)	C + O	Hydrogenated recycle solvent	Illinois #6	None	T: 644–756, P: 10–17	NA	Tubular Flow
Shah et al. (1978)	$O_2 \rightarrow O_3$, BP, C, G, W, O_1	Recycle solvent, hydrogenated anthracene oil	Subbituminous from Big Horn Mine, WY	$CoMo/Al_2O_3$	T: 686, P: 24.13	2 (space time)	Segmented bed
Mohan and Silla (1981)	H, C, N, E, A	Tetralin	Illinois #6	None	T: 603–723, P: Up to 7.1	.08–1	1 liter batch
Singh et al. (1982)	G, W, C', H_2, O_3, O_2, O_1, H_2, C, Ash + IOM	SRC-Recycle Solvent	Pittsburgh Seam Powhattan #5	None	T: 717–739, P: 10.4–20.8	.54–1.62	1 liter CSTR
Abichandani et al. (1982)	C + O → C*, C/P/A/O scheme	Anthracene oil, hydrogenated anthracene oil, Hydrogenated phenanthrene	Belle Ayr Sub-bituminous, Burning Star bituminous	None	T: 723, P: NA	.08 –1	.3 liter CSTR