

THE KINETICS OF COAL LIQUEFACTION IN A HYDROGEN DONOR SOLVENT

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1. Introduction

One of the most important liquefaction processes involves the treatment of coal with hydrogen donors (HD). HD solvents are materials that can donate hydrogen at the reaction conditions. The industrially important HD's are those which can be regenerated with molecular hydrogen.

Quantitative data on liquefaction was published by Orchin (1944), Orchin and Storch (1948), Oele *et al.*, (1951), Curran *et al.*, (1966), Hill (1966) and Neavel (1976).

In hydrogen donor, liquefaction is believed to proceed by a free-radicals mechanism (Hill (1966), Curran *et al.*, (1966).) However, because of the complexity of the system coal-HD-ASH and catalyst, (when added), little quantitative work if any has been published on modeling coal liquefaction as a free radical depolymerization process. Several empirical models were published however, e.g., Curran *et al.* (1966), Hill (1966), Oele *et al.* (1951), Wen and Han (1975) and Yoshida *et al.* (1976).

The main objective of the present work is to present a fundamental approach to the modeling of coal liquefaction in hydrogen donors, which will permit predictions relevant to the processing of coals at different conditions. The discussion concentrates on liquefaction to heavy boiler fuel although it could be extended to modeling of liquefaction to gasoline.

2.1 Arguments of Material Balance

Conversion of coal to oils requires production of material with a smaller molecular weight and with a larger ratio of hydrogen to carbon. One hydrogen have to be added per each 3-6 carbon atoms in order to obtain the desired H/C ratio for boiler fuels.

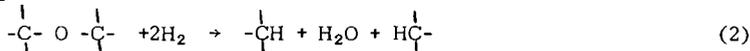
If it is assumed that on the average, each time a bond is broken, two fragments will be formed with approximately equal molecular weights, then each coal molecule will have to be broken 2-4 times to form heavy oil, or 3-6 times to form gasoline.

As an example, consider a "molecule" of bituminous coal with molecular weight of 3000 and ultimate composition of $\text{CH}_{0.88} \text{O}_{0.132} \text{N}_{0.016} \text{S}_{0.0174}$ (MWU= 15.77). Each such coal molecule will have an average of 190 carbon atoms. Typical hydrogenation products may have ultimate composition of $\text{CH}_{1.0} \text{O}_{0.09} \text{N}_{0.016} \text{S}_{0.016}$ (MWU= 14.34) and molecular weight of about 400, and will contain an average of 28 carbon atoms. Such product can be obtained if the original molecule is broken on the average 2.75 times and if 0.32-0.51 hydrogen atoms are added per each carbon atom in the original molecule.

Reduction in the molecular weight can be achieved by elimination of certain "side chained" functioned groups, e.g. OH, C=O, SH etc., or by breaking the HC structure of the main molecule, e.g., by reactions like:



or by



Elimination of side chains can result in a reduction in the molecular weight of the order of 16-32 units/group. Breaking of the main chain could result in a much more significant reduction in the molecular weight. The products of the latter reaction could have half the molecular weight of the original molecules. Opening of rings with or without the elimination of a heteroatom does not change significantly the molecular weight.

Most of the oxygen is present in coal in the form of hydroxylic (-OH) ketonic (C = O), and to a lesser extent heterocyclic or etheric (C-O-C) groups (Dryden (1963), (p. 267)). However, products with significantly reduced molecular weight result only when etheric oxygens or sulfidic sulfur are eliminated. Elimination of an OH group requires two hydrogen atoms but elimination of other groups requires four hydrogen atoms.

Data on the concentrations of etheric and sulfidic sulfur indicate that elimination of the etheric oxygen and the sulfidic sulfur could in some cases be sufficient to produce products with sufficiently low molecular weight. However, some saturation of π and c-c bonds is also required in order to bring the H/C ratio to the desired range. If each coal molecule has to be broken 2-6 times to produce heavy oil, then breaking of 1-3 etheric oxygen (if present) bonds and 2-3 sulfur-carbon or carbon-carbon bonds will result in product with M.W. in the range required for boiler fuel. When low volatile bituminous coal is processed breaking of c-c bonds may occur more than 2-3/ coal molecule.

2.2 Fundamental Assumptions

The most important assumptions of the present model are:

1. each coal consists of an assembly of functional groups or bonds with a given initial distribution which is specific to the particular coal.
2. the kinetic parameters, the activation energy and the frequency factor, for the reaction of each functional group with a given reagent, are function only of the reagent and the group, and are independent of the specific coal involved. Once such parameters are evaluated they can be used to model the kinetics of the reactions of similar groups in every coal.
3. the coal "molecules" are large and therefore have a small translational motion. The donor molecules and radicals are much smaller and much more mobile in the solution.
4. the bonds of each coal molecule break according to the hierarchy of the bond energies in each molecule, the weakest bonds first.
5. the depolymerization proceeds by a free radicals mechanism for which the steady state approximation can be applied.
6. the rate of the chemical reaction controls and not the rate of mass transport.
7. the solvent is present in a large excess.

Several additional assumptions are introduced latter which apply to specific cases.

3. Development of the Kinetic Model

A model is developed which describes the depolymerization in solution of a single high molecular weight compound. Classical chemistry of free radicals reactions is built into the model, and that permits to attribute physical significance to some of the reaction parameters. The rate of change of the average molecular weight of the solution is then discussed, and the model is extended to include the kinetics of the redistribution of the molecular weight of a system which initially contains compounds with different molecular weights.

3.1 Chemistry of Free Radicals Depolymerization in a Hydrogen Donor

A free radicals reaction mechanism consists of three types of processes:

1. initiation reactions - which form more radicals than they consume.
2. propagation reactions - which do not affect the number of free radicals in the system.
3. termination reactions - which consume free radicals.

In the system coal-hydrogen-donor, initiation can proceed by various mechanisms, the most plausible ones are:

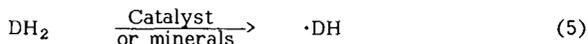
1. decomposition of very weak bonds in the coal macromolecule.



The radicals $1n_1\cdot$ react with the hydrogen donor, DH_2 , and form the donor radical $DH\cdot$.

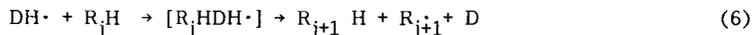


2. interaction between the hydrogen donor molecules, DH_2 , and the mineral matter or catalysts.



The number of weak bonds that can initiate a chain of radicals per unit mass of coal is finite and probably small. Therefore, the rate of initiation, by the decomposition of bonds decreases during the course of an isothermal decomposition. However, since the solvent is usually in a large excess, the rate of initiation by the interaction of the solvent and heterogeneous inorganic minerals is approximately constant.

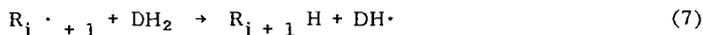
The radical $\cdot DH$ can break carbon-carbon and carbon-oxygen bonds. In the process, the donor molecules are converted into dehydrogenated donor molecules, D. The coal molecules break into smaller molecular fragments; i.e:



This is a propagation reaction.

The index j is used to denote the number of times that the macromolecule has been broken prior to that reaction. All the molecules $R_j H$ and the radicals $R_j\cdot$ are large (M.W. 300-3000) and contain several aromatic rings. It is therefore plausible to assume that they are not very mobile in the solution. Moreover, it is reasonable to assume that the activated complex that is formed in reaction (6), $[R_j HDH\cdot]$ dissociate at the weakest carbon-carbon or carbon-oxygen bond of the macromolecule. Therefore, the weakest bond in the $R_{j+1} H$ product is stronger than that in the parent molecule, $R_j H$. In other words,

the decomposition of the original coal macromolecule, R_0H , proceeds by the hierarchy of the strength of the bonds. The propagation step is completed by the fast reaction:



which replenishes the concentration of the radicals $DH\cdot$.

Since the radicals $R_j\cdot$ are much more bulky than $DH\cdot$, they are less mobile. Therefore, it is reasonable to assume that the dominant termination reaction is:



We were not able to detect the dimer di-tetralin in studies on model compounds. Therefore, reaction (8) describes the dominant mode of termination.

3.2 Modeling of The Depolymerization of a Single Component Macromolecule

Let the initiation reactions proceed at a rate $I = I(t)$, and assume that the steady-state approximation can be applied. Then, the rate of initiation has to be equal to the rate of termination, since the propagation reactions do not change the total concentration of free radicals and because termination is assumed to occur predominantly by binary collisions of $DH\cdot$, then:

$$2k_t [DH\cdot]^2 = I \quad (9)$$

$$[DH\cdot] = \sqrt{\frac{I}{2k_t}} \quad (10)$$

The rate of change of the component R_jH is described by the equation:

$$\begin{aligned} \frac{d[R_jH]}{dt} &= k_{pj-1} [DH\cdot] [R_{j-1}H] - k_{pj} [DH\cdot] [R_jH] = \\ &= \sqrt{\frac{I}{2k_t}} (k_{pj-1} [R_{j-1}H] - k_{pj} [R_jH]) \end{aligned} \quad (11)$$

Denote:

$$\Pi_j = \frac{[R_jH]}{[R_0H]_0} \quad (12)$$

$$d\theta = k_{po} \sqrt{\frac{I}{2k_t}} dt \quad (13)$$

Thus:

$$\frac{d\Pi_j}{d\theta} = \frac{k_{pj-1}}{k_{po}} \Pi_{j-1} - \frac{k_{pj}}{k_{po}} \Pi_j \quad \Pi_j = \beta_{j-1} \Pi_{j-1} - \beta_j \Pi_j \quad (14)$$

where:

$$\beta_j = \frac{k_{pj}}{k_{po}} \quad (15)$$

$$\text{Also: } \frac{d[R_0H]}{dt} = -k_{po} \frac{I}{2k_t} [R_0H] \quad (16)$$

$$\text{or: } \frac{d\bar{\Pi}_0}{d\theta} = -\bar{\Pi}_0 \quad (17)$$

$$\beta_0 = 1 \quad (18)$$

$$\text{Initially, } \bar{\Pi}_j = 0 \quad j > 0 \quad (19)$$

$$\bar{\Pi}_0 = 1 \quad j = 0 \quad (20)$$

Let us assume that an integration constant is chosen so that $\theta(t=0) = 0$. If the process is isothermal, then all the k 's are constant. Thus, it is possible to solve equation (15) by Laplace transform with respect to θ :

$$m \bar{\Pi}_j = \beta_{j-1} \bar{\Pi}_{j-1} - \beta_j \bar{\Pi}_j \frac{\beta_{j-1}}{m+\beta_j} \quad (21)$$

$$\bar{\Pi}_j = \frac{\beta_{j-1} \bar{\Pi}_{j-1}}{m + \beta_j} = \bar{\Pi}_0 \prod_{j=1}^j \frac{\beta_{j-1}}{(m+\beta_j)} \quad (22)$$

$$\text{But: } \bar{\Pi}_0 = \frac{1}{1+m} \quad (23)$$

$$\text{Therefore: } \bar{\Pi}_j = \frac{1}{1+m} \prod_{j=1}^j \frac{\beta_{j-1}}{m+\beta_j} \quad (24)$$

The last equation has poles at every $m = -\beta_j$, and will therefore have slightly different solutions when all the β_j are distinct and different or when some of them are identical. The solutions for the case where all the β_j 's are different and for the case where all the β_j 's $j \geq 1$ are the same as listed in tables 1 and 2.

Table 1: The Kinetics of Isothermal Coal Liquefaction by Successive Depolymerization in Hydrogen Donor Distinct and Different Rates for each Step*

j	$\bar{\Pi}_j$
0	$\bar{\Pi}_0 = e^{-\theta}$
1	$\bar{\Pi}_1 = \frac{1}{1-\beta_1} (e^{-\beta_1\theta} - e^{-\theta})$
2	$\bar{\Pi}_2 = \beta_1 \left[\frac{e^{-\theta}}{(\beta_1-1)(\beta_2-1)} + \frac{e^{-\beta_1\theta}}{(1-\beta_1)(\beta_2-\beta_1)} + \frac{e^{-\beta_2\theta}}{(1-\beta_2)(\beta_1-\beta_2)} \right]$
3	$\bar{\Pi}_3 = \beta_1\beta_2 \left[\frac{e^{-\theta}}{(\beta_1-1)(\beta_2-1)(\beta_3-1)} + \frac{e^{-\beta_1\theta}}{(1-\beta_1)(\beta_2-\beta_1)(\beta_3-\beta_1)} + \frac{e^{-\beta_2\theta}}{(1-\beta_2)(\beta_1-\beta_2)(\beta_3-\beta_2)} + \right]$

$$\left. + \frac{e^{-\beta_3\theta}}{(1-\beta_3)(\beta_1-\beta_3)(\beta_2-\beta_3)} \right\}$$

$$4 \quad \Pi_4 = \beta_1\beta_2\beta_3 \left\{ \frac{e^{-\theta}}{(\beta_1-1)(\beta_2-1)(\beta_3-1)(\beta_4-1)} + \frac{e^{-\beta_1\theta}}{(1-\beta_1)(\beta_2-\beta_1)(\beta_3-\beta_1)(\beta_4-\beta_1)} + \right.$$

$$\frac{e^{-\beta_2\theta}}{(1-\beta_2)(\beta_1-\beta_2)(\beta_3-\beta_2)(\beta_4-\beta_2)} + \frac{e^{-\beta_3\theta}}{(1-\beta_3)(\beta_1-\beta_3)(\beta_2-\beta_3)(\beta_4-\beta_3)} +$$

$$\left. \frac{e^{-\beta_4\theta}}{(1-\beta_4)(\beta_1-\beta_4)(\beta_2-\beta_4)(\beta_3-\beta_4)} \right\}$$

etc.

* $\beta_0=1, \beta_j \neq \beta_i, i \neq j.$

Table 2: The Kinetics of Isothermal Coal Liquefaction by Successive Depolymerization in Hydrogen Donor -

Initial Unique rate followed by steps with an identical rates*

j Π_j

0 $\Pi_0 = e^{-\theta}$

1 $\Pi_1 = \frac{1}{1-\beta} (e^{-\beta\theta} - e^{-\theta})$

2 $\Pi_2 = \frac{\beta}{(1-\beta)^2} e^{-\theta} + \beta e^{-\beta\theta} \left[\frac{\theta}{(1-\beta)} - \frac{1}{(1-\beta)^2} \right]$

3 $\Pi_3 = \frac{\beta^2}{(1-\beta)^3} e^{-\theta} + \beta^2 e^{-\beta\theta} \left[\frac{\theta^2}{2(1-\beta)} - \frac{\theta}{(1-\beta)^2} + \frac{1}{(1-\beta)^3} \right]$

4 $\Pi_4 = \frac{\beta^3}{(1-\beta)^4} e^{-\theta} + \beta^3 e^{-\beta\theta} \left[\frac{\theta^3}{6(1-\beta)} - \frac{\theta^2}{2(1-\beta)^2} + \frac{\theta}{(1-\beta)^3} - \frac{1}{(1-\beta)^4} \right]$

etc.

* $\beta_0 \neq \beta_j, j > 0$

$\beta_j = \beta_1 = \beta, i, j > 0$

3.3 Analysis of Models of the Initiation Reaction

Four models are proposed which describe various modes of initiations:

3.3.1 Decompositions of Unstable Bonds in the Coal:

It is assumed that initially a finite number of labile bonds exist per unit mass, and that these bonds decompose in a first order reaction.

$$I = - \frac{d[ln]}{dt} = 2k_i [ln] \quad (25)$$

Then, if the systems is isothermal:

$$[ln] = [ln]_0 e^{-2k_i t} \quad (26)$$

and:

$$d\theta = k_{po} \sqrt{\frac{I}{2k_t}} dt = k_{po} \sqrt{\frac{2[ln]_0 k_i}{2k_t}} e^{-k_i t} dt \quad (27)$$

$$\theta = \frac{k_{po}}{k_i} \sqrt{\frac{2[ln]_0}{2k_t}} (1 - e^{-k_i t}) \quad (28)$$

(Denoted as Model B)

3.3.2 Catalytic Interaction Between the Donor and Inorganic Materials:

When the minerals can catalyze the decomposition of the donor, the initiation rate constant will depend on the type of mineral matter, its surface area, quantity, and its porosity. The rate of initiation, I, will be more or less constant, since the concentration of donor and the mineral matter remains more or less constant. In such a case:

$$d\theta = k_{po} \frac{I_0}{2k_t} d\theta \quad (29)$$

and

$$\theta = k_{po} \frac{I_0}{2k_t} t \quad (30)$$

since $\theta(t=0) = 0$ (Denoted as Model A)

3.3.3 Combination Models of Initiation:

In reality, initiation can occur both by decomposition of unstable bonds and by catalytic reactions. In such a case, the rate of initiation will have the former:

$$I = I_0 + k_i [ln]_0 e^{-k_i t} \quad (31)$$

and:

$$d\theta = k_{po} \sqrt{\frac{I}{2k_t}} dt = k_{po} \sqrt{\frac{I_0 + 2k_i [ln]_0 e^{-2k_i t}}{2k_t}} dt \quad (32)$$

(Denoted as Model C) $\theta(t=0) = 0$

When the coal contains more than one type of bond that can dissociate and initiate a chain, one obtains:

$$I = 2k_{i_1} [1n]_{10} e^{-2k_{i_1} t} + 2[1n]_{20} k_{i_2} e^{-2k_{i_2} t} \quad (33)$$

and:

$$d\theta = \sqrt{\frac{\rho_0}{2k_t}} (2k_{i_1} [1n]_{10} e^{-k_{i_2} t} + 2k_{i_2} [1n]_{20} e^{-k_{i_2} t})^{\frac{1}{2}} dt \quad (34)$$

and

$$\theta(t=0) = 0 \quad (35)$$

(Denoted as Model D)

3.4 Modification of the Liquefaction Model to Real Coals

Extraction of coals with different solvents yield a given amount of the various fraction, e.g. asphaltenes, hexane solubles etc. If, it is assumed that the molecular weight and the functionality of these fractions are similar to that of the same fractions which are produced by the liquefaction of coal, then they will contribute to the rate of accumulation of the various fractions. To include these effects in the model, the dimensionless initial concentration of each group, Π_i^0 , have to be taken into account. The equations that result are listed in table 3. Note should be made that it has been assumed that each fraction depolymerize with a specific set of parameters which is a function only of the particular fraction. It could be shown (Attar, 1978) that fractions which are isolated by the "solvent soluble/insoluble" method should have molecular volume or weight and functionality in a given range. "Functionality" is defined in this context as the sum $\sum F_i N_i$, where N_i are the number of atoms of the i-th kind and F, the energy parameter as described by Small (1953): Whithurst et. al., (1976) examined SRC fractions and noted that the molecular weight and composition of the various fractions is independent of the conversion, in accord with the semi-theoretical prediction of Attar (1978). Therefore, in the following text it will be assumed that each j group could be identified with a given "solvent soluble/insoluble" fraction.

Table 3: Kinetics of the Depolymerization of Coal

$$\Pi_j^0 \neq 0 \quad \beta_j \neq \beta_i, \quad i \neq j$$

$$\begin{aligned} j & \quad \Pi_j \\ 0 & \quad \Pi_0 = \Pi_0 e^{-\theta} \\ 1 & \quad \Pi_1 = \frac{\Pi_1^0}{1-\beta_1} (e^{-\beta_1 \theta} - e^{-\theta}) + \Pi_1^0 e^{-\beta_1 \theta} \\ 2 & \quad \Pi_2 = \beta_1 \Pi_1^0 \left\{ \frac{e^{-\theta}}{(\beta_1 - 1)(\beta_2 - 1)} + \frac{e^{-\beta_1 \theta}}{(1 - \beta_1)(\beta_2 - \beta_1)} + \frac{e^{-\beta_2 \theta}}{(1 - \beta_2)(\beta_1 - \beta_2)} \right\} + \\ & \quad + \frac{\Pi_1^0 \beta_1}{\beta_1 - \beta_2} (e^{-\beta_2 \theta} - e^{-\beta_1 \theta}) + \Pi_2^0 e^{-\beta_2 \theta} \end{aligned}$$

$$\begin{aligned}
 3 \quad \Pi_3 = & \beta_1 \beta_2 \Pi_0^0 \left\{ \frac{e^{-\theta}}{(\beta_1-1)(\beta_2-1)(\beta_3-1)} + \frac{e^{-\beta_1\theta}}{(1-\beta_1)(\beta_2-\beta_1)(\beta_3-\beta_1)} + \right. \\
 & \left. \frac{e^{-\beta_2\theta}}{(1-\beta_2)(\beta_1-\beta_2)(\beta_3-\beta_2)} + \frac{e^{-\beta_3\theta}}{(1-\beta_3)(\beta_1-\beta_3)(\beta_2-\beta_3)} \right\} + \\
 & \Pi_1^0 \beta_2 \beta_1 \left\{ \frac{e^{-\beta_1\theta}}{(\beta_2-\beta_1)(\beta_3-\beta_1)} + \frac{e^{-\beta_2\theta}}{(\beta_1-\beta_2)(\beta_3-\beta_2)} + \frac{e^{-\beta_3\theta}}{(\beta_1-\beta_3)(\beta_2-\beta_3)} \right\} + \\
 & \frac{\Pi_2^0 \beta_3}{\beta_2-\beta_3} (e^{-\beta_3\theta} - e^{-\beta_2\theta}) + \Pi_3^0 e^{-\beta_3\theta}
 \end{aligned}$$

and so on.

4. Estimation of Parameters

The parameters which are needed are divided into two groups:

1. parameters associated with the propagation - β_j , $j \geq 1$.
2. parameters associated with the initiation and the termination

The kinetics parameters associated with the propagation reaction depend mainly on the structure of the molecules. The kinetic parameters associated with the initiation and the termination depend on the structure of the molecules and will have a different form which depends on which initiation mechanism is assumed.

4.1 Estimation of the Propagation Parameters

The rate limiting step in the propagation is reaction (6)

The corresponding rate parameter is β_j :

$$\beta_j = \frac{k_{pj}}{k_{po}} = \frac{A_{pjo} e^{-\frac{E_{pj}}{RT}}}{A_{po} e^{-\frac{E_{po}}{RT}}} = \frac{A_{pjo}}{A_{po}} e^{-\frac{(E_{pj} - E_{po})}{RT}} \quad (36)$$

It is convenient to evaluate separately the values of A_{pjo}/A_{po} and $E_{pj}-E_{po}$.

4.1.1 Depolymerization of Analogue Bonds.

Application of the polyani relation yield:

$$E_{pj} - E_{po} = \alpha(\Delta H_j - \Delta H_o) \quad (37)$$

If the absolute rate theory is applied to equation (36) and it is assumed that the activated complex is similar to the molecule R_jH , one obtains for the frequency factor

$$A_{po} = A_{pjo} \cong \frac{kT}{hQ_{DH}} \quad (38)$$

The last equation shows that to a first order approximation the frequency factor is independent of j , therefore,:

$$\beta_j = e^{-\frac{\alpha (\Delta H_j - \Delta H_o)}{RT}} \quad (39)$$

4.1.2 Depolymerization by the Hierarchy of the Functional Groups

Following the initial solubilization of the coal, the various functional groups will compete for the hydrogen donors radicals. However, if the heat of reaction of the depolymerization of a particular group is much smaller than that of the other groups it will be eliminated at a much larger rate than the others.

The functional groups which are believed to be present in coal in substantial concentrations can be arranged in the order of increasing stability toward an attack by a hydrogen donor radical. The author calculates that at the initial stages of the liquefaction etheric bonds are broken first and subsequently methelenic bridges are broken at the benzylic position along with sulfidic sulfur. Other groups like -OH, C=O also react, but their elimination will not result in a major decrease in the molecular weight of large coal molecules. If the first bond that is broken is an etheric bond, the second will be either etheric or benzylic and the third, and subsequent bonds that are broken are benzylic bonds. Based on these arguments, the activation energies for breaking the various bonds will probably be $j=0$, 7.8 kcal/mole, $j=1$, 9.0 kcal/mole, $j=2$, 9.9 kcal/mole, $j=3$, 10.5 kcal/mole, $j=4$, 11.1 kcal/mole.

4.2 Estimation of the Initiation and Termination Parameters

The rate of termination was assumed to be diffusion controlled and equal to $2 \cdot 10^9$ lit/mole sec.

The parameters associated with different initiation models are different and can not be estimated by simple assumptions. Two types of parameters are needed: rate constants and initial concentrations. The values of the rate constants for the decomposition of specific bonds is independent of the coal used. However, different values of the initial concentrations are expected to be present in different coals.

The rates of initiation by the decomposition of weak bonds are determined by the thermodynamic bond-dissociation energy and entropy. If initiation occurs by the decomposition of bonds which become unstable around 350°C, for example:



The activation energy of such reactions will be about the same as the bond energy. For reaction (40), $E_a \sim \Delta H \sim 76.4$ kcal/mole. at 400°C. Also, $\Delta S \sim 41.57$ cal/mole°k and by $\log k_o \sim 22.26$. The rate constant for the decomposition at 400°C is $2.87 \cdot 10^{-3}$ sec⁻¹. Since the number of moles of such relatively weak bonds is finite, and depend on the aromaticity of the coal, the number of chains that could be initiated by such a mechanism is finite and depend on the aromaticity of the coal. For coals with an aromaticity of 0.84 and H/C ~ 0.757 the concentration of such groups can not exceed $8 \cdot 10^{-2}$ mole/mole carbon and will probably be no larger than $3 \cdot 10^{-2}$ mole/mole

carbon. The concentration of such groups is in effect smaller since the solvent further dilutes the solution.

The value of the kinetic parameters which determine k_{po} is assumed to be $E_{po} = 7.8$ kcal/mole $A_{po} = 2.2 \cdot 10^7$ (lit./mole sec).

5. Results and Discussion of the Results

In order to apply the model one needs to have data on the initial condition of the coal and on the conditions of the reaction. The data needed on the initial condition of the coal are: 1. the ultimate analysis and the aromaticity. 2. the mineral content and composition; and 3. the distribution of oxygen and sulfur functional groups. Detailed accurate knowledge of the groups distribution is not necessary since the mathematical model lumps many molecules and reduces the sensitivity to the value of β_1 . The data needed on the condition of the reaction are 1. the temperature, 2. the solvent, 3. the pressure and type of gas, and 4. the catalyst.

The concentration of etheric oxygen determine the kinetic parameters chosen for the first and possibly the second propagation step.

The temperature and the solvent determine the values of the rate constants and of the relative rate parameters β_1 . The type of gas and its pressure determine whether solvent regeneration should be included in the model or not. The effect of hydrogen is more important when catalyst is present and/or when deep liquefaction is considered. The catalyst effects mainly the rate of initiation and in a sense, (its effect) is analogous to that of certain components of the mineral matter, e.g. FeS_2 and FeS . Catalysts will permit the liquefaction process to continue after the labile bonds decomposed.

5.1 Case Study: Analysis of the Liquefaction of a Bituminous Coal

The coal is treated in this case study as a single macromolecule so that the relationships among the various fractions will be more clear. The data used are described in table 4. The results of applying the model are described in figures 1 and 2. Figure 1 shows the dimensionless amount of the various fractions in a batch operation, as a function of the dimensionless time parameter θ . To obtain the dependence of θ on the real time t , use Figure 2 which shows the dependence of t on θ for various initiation models. Figure 2 shows also the change in the dimensionless average molecular weight of the SRC as a function of time.

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Note: Because of space limitations, several sections of the manuscript, case studies and calculations have been removed. The complete paper will be published soon. The main sections that were omitted include the rate of desulfurization and deoxygenation, the change in the molecular weight, several case studies, and the references.

Table 4: Case Study: Liquefaction of a Medium Volatile Bituminous Coal in Tetralin at 427°C

Approximate initial ultimate analysis:

$C_{1}H_{0.88}O_{0.132}N_{0.0160}S_{0.174}$ Ash: 14.7 wt.% Pyritic Sulfur: 1.3 wt.%

j	Bond Broken	Initial Conc. of Fractions	Epj Kcal/mole	Apo lit/mole sec)
0	-O- very weak	100	7.8	$2.2 \cdot 10^7$
1	-O- weak	-	9.0	
2	$\phi-CH_2CH_2\phi$	-	9.9	
3	$\phi-CH_2-\phi$	-	10.5	
4	$\phi-CH_2-\phi$	-	11.1	

Initiation and Termination Models:

$$I_0 = 8 \cdot 10^{-6} \quad I = I_0 + k_{i1} [lni]_0 e^{-k_{i1} t} \quad k_{i1} = k_{i10} e^{-\frac{E_{i1}}{RT}} =$$

$$[lni]_0 = 0.01 \quad 2k_t = 2 \cdot 10^9 \quad k_{i10} = 2 \cdot 0 \cdot 10^{22} \text{ sec}^{-1} \quad E_{i10} = 76.4 \text{ kcal/mole.}$$

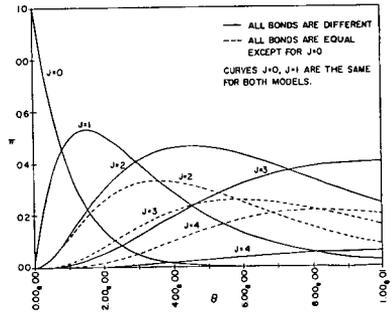
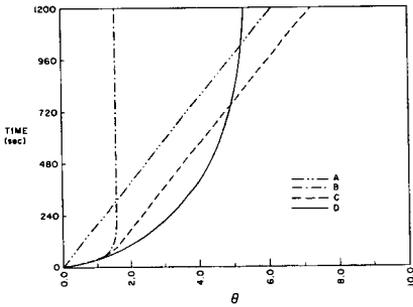


Figure 1: The Kinetics of Coal Liquefaction in Hydrogen Donor