KINETICS
OF
COAL LIQUEFACTION
TO
PREASPHALTENES, ASPHALTENES AND OILS

by

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To
my lovely wife Hanan
and
adorable daughter Souraya

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ABSTRACT

The kinetics and mechanism of coal liquefaction to preasphaltenes, asphaltenes, and oils plus gases was studied in a 300 cc magnedrive autoclave batch reactor. The reactions were conducted with a ratio of coal to solvent (tetralin) of 1:10 and under a hydrogen blanket at a total pressure of 2000 psi. Three temperatures were investigated; 350, 375 and 400°C.

Three models involving first order irreversible series/parallel reactions were discriminated for the raw data using a non-linear parameter estimation technique. The model that exhibited the lowest value of the determinant of moment matrix of residuals was considered the best in explaining the mechanism of coal dissolution. The mechanism chosen contained six rate constants which were determined at the three temperatures investigated. The coal was converted to two primary products; preasphaltenes and asphaltenes. These two products were also converted in turn to oil and gases, with preasphaltenes converted partially to asphaltenes.

Arrhenius activation energies were calculated for each rate constant. The values ranged between 10-50 K cal/g mole. The high activation energies implied that the reactions of coal hydroliquefaction are kinetically controlled and not controlled by interfacial mass transfer. This finding was reinforced by comparison of results from two runs with a large difference in agitation rate.

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INTRODUCTION

The demand for crude oil and petroleum-derived products is growing at an ever increasing rate, however, the rate of oil discovery has been slowing down. This has led researchers to look for other sources of hydrocarbon fuels which are in abundance i.e. coal, tar sands and shale oil. Solvent extraction of coal has long been used to produce useful hydrocarbon products such as heavy, middle distillate, and light oils from coal. The yield of these products depends on the composition of coal used, the ability of the solvent to donate hydrogen and the conditions of extraction (i.e. temperature, pressure, reaction time). Interest is now increasing in re-examining mechanisms and kinetics for solvent extraction/hydrogenation of coal with the long range goal of process optimization.

The kinetics and mechanism of coal liquefaction and hydrodesulfurization has been studied at the Colorado School of Mines under an Energy Research and Development Administration contract. This study deals with the rate of conversion of coal to preasphaltenes, asphaltenes, oils and gases during dissolution in a donor solvent,

A 300 cc magnedrive autoclave batch reactor was used to study the kinetics and mechanism of coal liquefaction to preasphaltenes, asphaltenes and oils plus gases. Coal of

-200 mesh was mixed with solvent and the slurry was introduced into a Ruska pump. Solvent was heated (inside the autoclave reactor) under a hydrogen blanket to reaction temperature. The slurry was then injected into the reactor and reaction time started. After specified time intervals at reaction conditions, the reactor was cooled rapidly by a high speed air fan. The liquid product was analyzed by solvent extraction.

Rate constants and activation energies of the series/parallel reactions for the formation of preasphaltenes, asphaltenes and oils plus gases, and disappearance of unreacted coal have been determined for the non-catalytic solvent extraction of coal in a hydrogen donor solvent (tetralin). Various mechanisms have been hypothesized leading to different models. The mathematical models were compared to kinetic data obtained from a batch stirred 300 cc autoclave reactor. Models were discriminated using a non-linear parameter estimation technique with the goal of improved parameter estimation for the rate constants as indicated by a minimum error sum of squares. Arrhenius activation energies for the kinetic steps of the most adequate model were then determined by conventional techniques.

LITERATURE SURVEY

Research on conversion of coal to light soluble products has been carried out for years. A large literature survey for solvent extraction of bituminous coal is given by Kiebler (1) and Dryden (2) in which the mechanism and kinetics of coal hydrogenation by solvent extraction to liquid products are discussed. In addition, many of the factors that influence coal extraction have been investigated by researchers, and these findings summarized. Some of the more important aspects of coal conversion by solvent extraction are covered in the following sections.

Factors Influencing Coal Extraction

Coal Particle Size

Yields of extractable material tend to increase as the particle size of the feed coal is reduced. Curran et al, (3) and Kloepper et al. (4) reported that the rate of dissolution is independent of coal particle size. On the other hand, investigations by Ashburry (5) and Jenney (6) showed particle size to be a variable of some significance in coal conversion to liquid products. More research is needed to clarify the effect of particle size on coal extraction.

Coal Rank

There are a number of factors believed to be relevant in determining the liquefaction behavior of coals and the character of the products. These factors include coal rank, petrographic composition, the geological history and the composition of the inorganic constituents. These factors have been studied experimentally by Given et al. (7).

Yields of 80% benzene-soluble material from a medium-volatile bituminous coal containing 88% carbon have been reported (8). As the carbon content increased beyond 88%, the yield of pitch decreased rapidly and became negligible at 94% carbon (8).

Given et al. (7) ran experiments on Interior Province vitrains to determine the effect of coal rank on conversion to liquid products. The results of the seven, three-hour runs (Table 1), show a fairly consistent trend of increasing conversion to liquid products with decreasing rank.

Neavel (9) studied the effect of coal rank on conversion to benzene-soluble liquid products and gases. He observed that the initial reaction rate of the lowest-ranked coal is more rapid than that of the "standard" high-volatile C bituminous coal, but conversion at extended residence time becomes essentially identical to that of the bituminous coal. Coals with ranks higher than high-volatile C bituminous are converted at a lower rate, the low-volatile bituminous coal exhibiting essentially no conversion. These observations of the effect of coal rank are shown in Figure 1.

TABLE* 1. EXPERIMENTS WITH INTERIOR PROVINCE VITRAINS

4 : 1 TETRALIN TO COAL, 400°C, 3-HOUR RUNS

PSOC NO.	SEAM, MINE, STATE	ASTM RANK	CAL. VAL.	M.M., %	% CONVERSION
215	Ky. No. 9, No. 2, Ky.	HVA	14921	16.4	82
284	L DeKoven, Will Scarlette, Ill.	HVA	14888	25.1	84.5
217	Ky. No. 9, Colonial, Ky.	HVB	13993	21.4	86
223	Ky. No. 6, West & West, Ky.	HVB	13916	5.2	75
286	Tebo, Power, Ill.	HVB	13866	34.3	90
290	Ill. No. 4, So. Wilmington, Ill.	HVB	13348	17.1	97
188	Ill. No. 2, Banner, Ill.	HVB	13342	7.7	94.5

*Given, P.H., Spackman, W., Davis, A., Walker, Jr., P.L. and Lovell. H.L., The Relation of Coal Characteristics to Coal Liquefaction Behavior, Report No. 2 Submitted to National Science Foundation, Pennsylvania State University. August (1974).

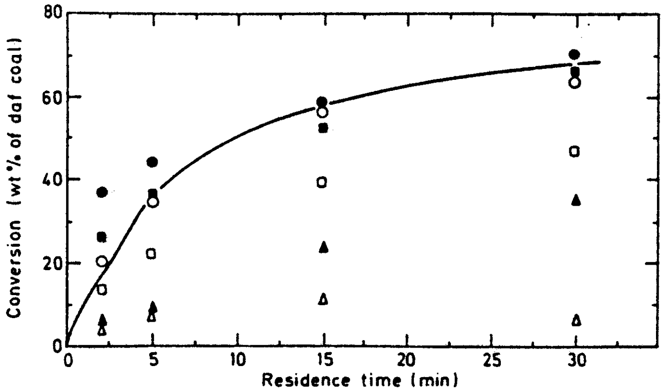


Figure* 1. Effect of Rank on Conversion to benzene solubles and gases, 400°C, hydrogenated creosote oil vehicle.

● Coal a, lignite ■ Coal c, HVC bitum. ▲ Coal f, HVA bitum.

○ Coal b, sub-bitum. □ Coal e, HVB bitum. △ Coal g, LV bitum.

The curve is from coal d/tetralin runs.

*Neavel, Richard C., Liquefaction of Coal in Hydrogen-Donor and Non-Donor Vehicles, Fuel 55, pp. 237-242 (1976).

Solvent Type

The chemical nature of solvents has an important role in determining ease of liquefaction of coal. Orchin and Storch (10) carried out experiments on coal liquefaction by solvents with different chemical nature. Their solvation experiments at 400°C are listed in Table 2. They concluded that solvents can be grouped into three classes; the very good solvents such as 1, 2, 3, 4 tedrahydro-5-hydroxynaphthalene, and O-cyclohexylphenol; moderately effective solvents, like tetralin; and the less effective solvents, such as dicyclohexyl, 2-methoxy-1-cyclohexyl benzene, diphenyl, naphthalene, cresol, and O-phenylphenol. This classification based on solvation effectiveness was shown to be based on chemical structure, and these structures are shown in Figure 2. Thus, the best solvent for coal dissolution was postulated to be hydroaromatic with a hydroxyl group.

Orchin and Storch (10) also experimented with a mixture of solvents. Their results showed that the addition of small quantities of cresol to tetralin or the addition of small quantities of tetralin to cresol resulted in higher liquefaction than that obtained with the pure solvent alone. These results are shwon in Figure 3. Oele et al. (11) divided the solvents into two classes, namely the effective and the less effective or ineffective solvents. They considered solvents to be effective when, after a prolonged extraction carried out at a temperature below 200°C, the liquid was capable of dissolving 20 to 40 percent of a bituminous coal. The effective solvents were classified into groups (Table 3). Group A with nucleophilic properties were active below 100°C, while group B with ampholytic properties had a strong extractive effect only above 100°C.

TABLE* 2. SOLVATION EXPERIMENTS AT 400°C

Experiment No.	Vehicle	Time, Hours	Liquefaction, %
BK-134	1,2,3,4-Tetrahydro-5-hydroxynaphthalene	0.5	85.3 a
G-68, BK-100,143,146	o-Cyclohexylphenol	0.5	81.6 b
BK-111	o-Cyclohexylphenol	1.0	82.8
BK-113	o-Cyclohexylphenol	1.5	82.7
BK-112, 132	Tetralin	0.5	49.4 c
BK-156	Naphthalene, phenol, Tetralin (2:1:2)	0.5	51.3 a
BK-160	U.S.P. cresol	0.5	32.1
BK-152	2-Methoxy-1-cyclohexylbenzene	0.5	30.2
BK-129	Dicyclohexyl	1.0	27.2
BK-141	Naphthalene	0.5	22.2 a
BK-144	o-Phenylphenol	0.5	19.6 a
BK-140	Diphenyl	0.5	19.4 a
BK-162	U.S.P. cresol	0.5	19.2 d
Anthraxylon	o-Cyclohexylphenol	0.5	94.4
Fusain	o-Cyclohexylphenol	0.5	4.2

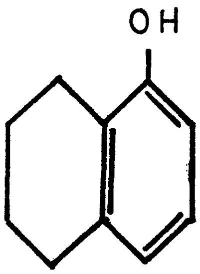
a Transfer to centrifuge bottles made with aid of Tetralin-cresol.

b Average of four determinations; 81.6, 82.7, 81.0, and 81.0%.

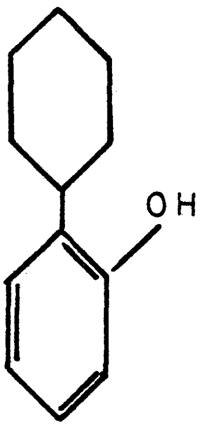
c Average of two determinations; 50.2 and 48.6%.

d In this experiment, 1000 lb./sq. in. initial nitrogen pressure used.

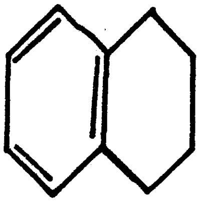
*Orchin, M., and Storch, H.H., Solvation and Hydrogenation of Coal, Ind. Eng. Chem., v. 40, no. 8, pp. 1385-1389 (1948).



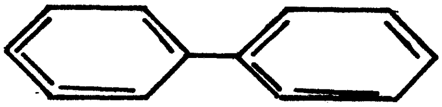
1, 2, 3, 4 - tetrahydro-
5 - hydroxynaphthalene



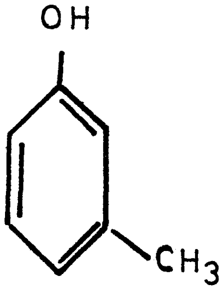
0 - cyclohexylphenol



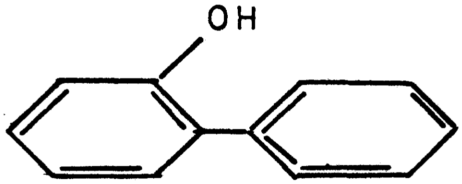
tetralin



diphenyl



m-cresol



0 - phenylphenol

Figure 2. Chemical Structure of Some Solvents.

TABLE* 3. COAL EXTRACTING SOLVENTS

Nucleophilic (A)	Ampholytic (B)
Heterocyclic, tertiary bases,	Phenolic compounds
pyridine, picolines.	phenol, cresols,
Aliphatic amines,	o-phenylphenol,
ethylene diamine.	Carbonyl compounds
	acetophenone, furfural.

*Oele et al., Extractive Disintegration of Bituminous Coals, Fuel 30, pp. 169-178 (1951).

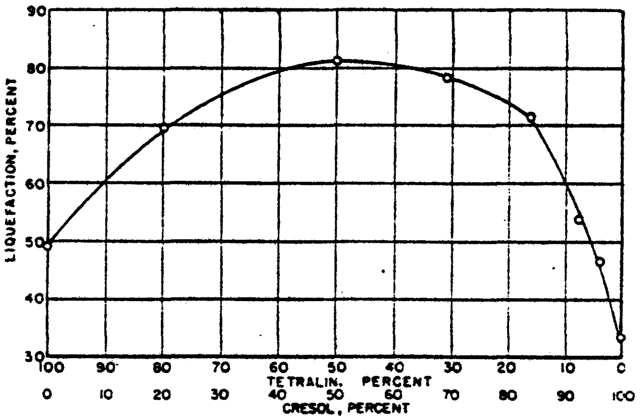


Figure* 3. Solvation Experiments with various Proportions of Tetralin and Cresol.

*Orchin, M. and Storch, H.H., Solvation and Hydrogenation of Coal, Ind. Eng. Chem., v. 40, no. 8, pp. 1385-1389 (1948).

Mineral Matter Content

Given et al. (7) studied the effect of mineral matter content of coal on its conversion to liquid products, using coals with mineral contents up to 27.59%. Their results are shown in Table 4. The data show virtually no differences in conversion with various fractions of differing mineral matter content. Hence, the mineral matter content appeared to have no catalytic effects, positive or negative.

TABLE* 4. EFFECT OF MINERAL MATTER

Conditions in tetralin (4:1), 400°C, 3 Hours

PSOC NO.	M.M., %	ASH %	% CONVERSION
95-A	7.08	6.26	82.5
95-B	6.32	5.81	82.0
95-A	27.59	23.94	78.5
95-B	27.4	24.84	79.5
95	24.17		83

*Given, et al., The Relation of Coal Characteristics to Coal Liquefaction Behavior, Report No 2 Submitted to National Science Foundation, Pennsylvania State Univ., August (1974).

Gas Phase Composition

Usually in coal liquefaction, gaseous hydrogen is used above the reacting coal-solvent slurry. However, little information is known about the relation between hydrogen transfer from a donor solvent vs. that from gaseous hydrogen (12). It is usually assumed that during coal liquefaction, gaseous hydrogen will be consumed to rehydrogenate the solvent. In the case of tetralin solvent, the naphthalene produced may be rehydrogenated back to tetralin.

Temperature

This factor has an immense effect on yields of hydrocarbon liquids during coal extraction. Asbury (5) heated Edenborn coal (85%C) with benzene at 80°C, 160°C, and 220°C, and found respective yields of oil to be 0.1, 0.93 and 8.9 percent. The marked increase of nearly 100:1 over a range of 140°C suggested a chemical rather than a physical change had occurred. Wiser and Hill (13) reported the following data on benzene-soluble products after 50 minutes of dissolution:

At 350°C, 25% extracted
375°C, 40% extracted
400°C, 63% extracted
450°C, 90% extracted

From the above data a high activation energy for coal dissolution was indicated by observing the fraction extracted as a function of temperature. Guin et al, (12) observed drastic changes in coal dissolution with relatively small changes in temperature from 330 to 340°C and from 340 to 350°C. This implied that the disintegration reaction occurred with a relatively high activation energy. They also suggested that this high activation energy seemed to indicate that the coal liquefaction process is more closely related to surface chemical reactions, rather than a purely mass transfer controlled dissolution.

Agitation

At highly turbulent conditions, vigorous mixing of reactants reduces the intraphase mass transfer resistance of hydrogen atoms through solid-liquid boundary so that the rate constant of coal dissolution is increased approaching the regime where chemical reaction is dominating the overall rate. The high activation energy reported in the literature for dissolution in a well stirred reactor suggests that chemical reaction rate is controlling the overall dissolution rate (14).

Agitation is important for disintegration, although further research is needed to determine the exact effect of agitation on particle disintegration.

Coal to Solvent Ratio

A sufficient excess of solvent is required so that solvent concentration does not become rate-determining. Hill (15) carried out a series of extractions at various coal to solvent (tetralin) ratios at 400°C. He plotted the fractions extracted vs. coal to solvent ratio. It was found that at 1:8 of coal to solvent ratio, sufficient solvent was present to prevent solvent starvation.

Liquefaction Mechanism and Kinetics

Hill (15) examined the mechanism and kinetics of coal dissolution in tetralin. He considered a coal particle to be a main structure permeated by both macro and micro pores in which materials are accessible to solvent action. Dissolution of coal with a solvent present was considered to take place in several ways, each with distinct kinetic consequences as listed below by Hill.

1. Dissolving out solvent action on materials in main structure (first or second order).
2. Gross dissolution of coal structure in the presence of a large volume of solvent (first order).
3. Diffusion of dissolved materials out of micro pores in main coal structure (second order).
4. Hydrogen transfer reactions between solvent and main coal structure (second order).
5. Solvent imbibition (absorption) by main coal structure (first or second order).

At the beginning of reaction, the materials which entered the liquid phase first were those that were trapped in the coal pores and which may be weakly bonded to the main coal structure. These require the smallest activation energy to release. The remainder of coal dissolves by breaking chemical bonds which require higher activation energies.

Hill proposed a series of independent first order reactions for the solvent extraction mechanism, where the undissolved residue from a reaction becomes the reactant for a succeeding reaction, forming a liquid and gaseous product. This mechanism may be summarized by the following set of reactions:

$$
\begin{array}{lcl}
\text{Solvent} + \text{Coal} & \xrightarrow{k_1} & R_1 + L_1 + G_1 \\
\text{Solvent} + R_1 & \xrightarrow{k_2} & R_2 + L_2 + G_2 \\
\vdots & & \vdots \quad \vdots \quad \vdots \\
\text{Solvent} + R_n & \xrightarrow{k_{n+1}} & R_{n+1} + L_{n+1} + G_{n+1}
\end{array}
$$

where $k_1 > k_2 \ldots > k_{n+1}$

R = Solid coal of lower molecular weight than parent coal.

L = Coal dissolved or in solution.

G = Gaseous product.

The above model assumes only forward unimolecular reactions are involved, which may be described by the following mathematical model:

$$\frac{dx}{dt} = k\ (1 - x) \tag{1}$$

where x = the amount of coal extracted

k = first order reaction constant

The first order reaction constant was found to be a function of fraction extracted.

$$k = k_o\ (1 - ax) \tag{2}$$

where k_o, a were parameters to be determined experimentally. Therefore, the rate of dissolution was modeled as second order:

$$\frac{dx}{dt} = k_o\ (1 - ax)\ (1 - x) \tag{3}$$

A different view is reported by the work of Wen et al. (16) in that conversion processes studied gave a rate of dissolution which was first order with respect to fraction converted:

$$r_A = k_o \exp(-E/RT) \exp(.000684\ P_{H2})\ (C_{so})\ (1-x)\ (\frac{C}{S})$$

where P_{H2} = partial pressure of hydrogen

C_{so} = wt. fraction of organics in untreated coal

$\frac{C}{S}$ = coal to solvent wt. ratio

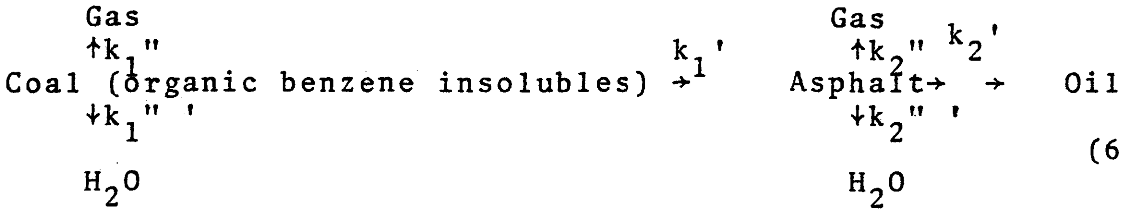
x = fractional conversion

Koltz (17) studied the kinetics of hydrodesulfurization of coal in a solvent in a batch reactor. Hydrogenation and hydrodesulfurization took place on a longer time scale than particle disintegration and these processes may be regarded as occurring in a homogeneous liquid phase rather than a fluid-solid surface reaction. Koltz also was able to model his data as pseudo-second order by fitting the rate constant (k) as a function of conversion.

$$k = k_o (1 - ax) \qquad (5)$$

Gertenbach (18) studied the kinetics of sulfur form removal in coal liquefaction. He fitted the percent desulfurization of total, pyritic and organic sulfur, and the formation of FeS sulfur with first order expressions, and reported activation energies for the organic desulfurization and the FeS formation of 21.9 and 8.1 Kcal/mole, respectively.

Previous work by Weller et al. (19) on the kinetics of coal hydrogenation with catalysts has been conducted. Mathematical models for the dissolution of coal and the formation of asphaltenes as functions of time at four temperatures were developed, and rate constants in the models evaluated. Percentage yields for oils were given, but no model was developed to relate their concentration with time. Dissolution was represented by the following scheme:



$$\begin{array}{c} \text{Gas} \\ \uparrow k_1'' \\ \text{Coal (organic benzene insolubles)} \\ \downarrow k_1''' \\ H_2O \end{array} \xrightarrow{k_1'} \begin{array}{c} \text{Gas} \\ \uparrow k_2'' \\ \text{Asphalt} \\ \downarrow k_2''' \\ H_2O \end{array} \xrightarrow{k_2'} \text{Oil} \qquad (6)$$

The only intermediate in this scheme was asphalt and there was no mention of the products; preasphaltene and asphaltene. The k's were specific rate constants for the first order reactions. To model the concentration of coal and asphalt as functions of time, the following relations were considered:

$$k_2 = k_2' + k_2'' + k_2''' \qquad (7)$$

C = coal (organic benzene insoluble) remaining at time ' t

A = asphalt present at time t

$\alpha = k_1' \mid k_1$

C_o = amount of moisture and ash-free coal present at zero time

The amount of coal and asphalt at time t was then given by:

$$C = C_o e^{-k_1 t} \qquad (8)$$

$$A = \frac{\alpha C_o k_1}{k_1 - k_2} (e^{-k_2 t} - e^{-k_1 t}) \qquad (9)$$

The concentration of oil was determined by;

$$\text{Oil} = \frac{\alpha\ \beta C_o}{k_1 - k_2} \cdot \{k_2 e^{-k_1 t} - k_1 e^{-k_2 t}\} + \alpha \cdot C_o \qquad (10)$$

where $\beta = k_2' / k_2$

Ruether (20) extended the work of Weller et al. by studying the hydrogen consumption in conversion of asphaltenes to oil, gas and water; and in conversion of coal to ashpaltenes, oil, gas and water. He suggested that under the prevalent experimental conditions, the rate of hydrogenation of the asphaltenes was materially faster than the rate of conversion of asphaltenes to oil. The asphaltenes first underwent an increase in chemical hydrogen content of 0.010 g H_2/gram on average, then underwent conversion to oil. He arrived at an empirical equation that preducted the hydrogen consumption in coal conversion to asphaltenes and oil.

$$h = \alpha^{-5} (0.022\ x + 0.024y) + 0.028y \qquad (11)$$

where h = g hydrogen consumed / g of maf coal feed

α = fraction of maf coal converted that goes to asphaltene

x = g of asphaltene in product / g of maf coal feed

y = g of oil in product / g of maf coal feed

Ruether concluded that in heterogeneously catalyzed coal hydroliquefaction, there are two classes of reactions. One involves reaction of molecular hydrogen, and is heterogeneously catalyzed. The other involves conversion of coal to asphaltenes, and is uncatalyzed. The reactions are coupled, since hydrogen donor species are reactants in each; in the hydrogen-poor state in the catalyzed reaction, and the hydrogen-rich state in the uncatalyzed reaction.

Kloepper et al. (4) concluded that hydrogen transfer from the solvent phase was the most important mechanism of free radical termination for the dissolved coal. The presence of a solvent which could transfer hydrogen or a high partial pressure of hydrogen gas in the reaction atmosphere favored the formation of low molecular weight compounds during the dissolution of coal at high temperatures. The application of heat and solvent was found to be sufficient to remove low molecular weight compounds from the coal matrix. The rupture of bonds and free radical formation were shown to become the important kinetic factors at higher temperatures.

The kinetics of hydrogen transfer from tetralin to bituminous coal has been studied by Curran et al. (3), where it was proposed that coal dissolution can be described by two first order reactions occurring in parallel, of which one path was much faster. Hydrogen transfer could be identified with a definite chemical process. Each gram mole of hydrogen transferred could be identified with the dissociation of a specific chemical bond into two free radicals.

Neavel (9) investigated the products of coal extraction by tetralin with mass spectrometry to determine products. The weight concentration of tetralin in the reacting slurry was approximately 66.6% compared to 33.3% coal. At 90% conversion of coal, the reactor contained about 35% tetralin, 30% naphthalene, and the remainder was coal-derived materials plus traces of dihydronaphthalene and decahydronaphthalene. The reactions of the solvent to donate hydrogen and produce its primary unhydrogenated product (naphthalene) are shown in Figure 4. The relative concentrations of tetralin and its derived components as a function of conversion are shown in Figure 5.

Storch et al. (21) studied the relation between oxygen elimination and liquefaction during the hydrogenation of coal. They found that it is possible to liquefy about 20% of the coal under solvation conditions without removing any of the oxygen. Beyond about 20% liquefaction there appeared to be nearly a straight line relationship between liquefaction and oxygen removal. This behavior suggested that the hydrogenolysis of oxygen bonds and the dissociation of oxygen-containing fragments or ether linkages of coal were essential steps during this portion of the liquefaction process.

Solvents having hydroxyl groups are effective in coal liquefaction as explained previously (page 7). The effectiveness of the hydroxyl group is probably related to its hydro-

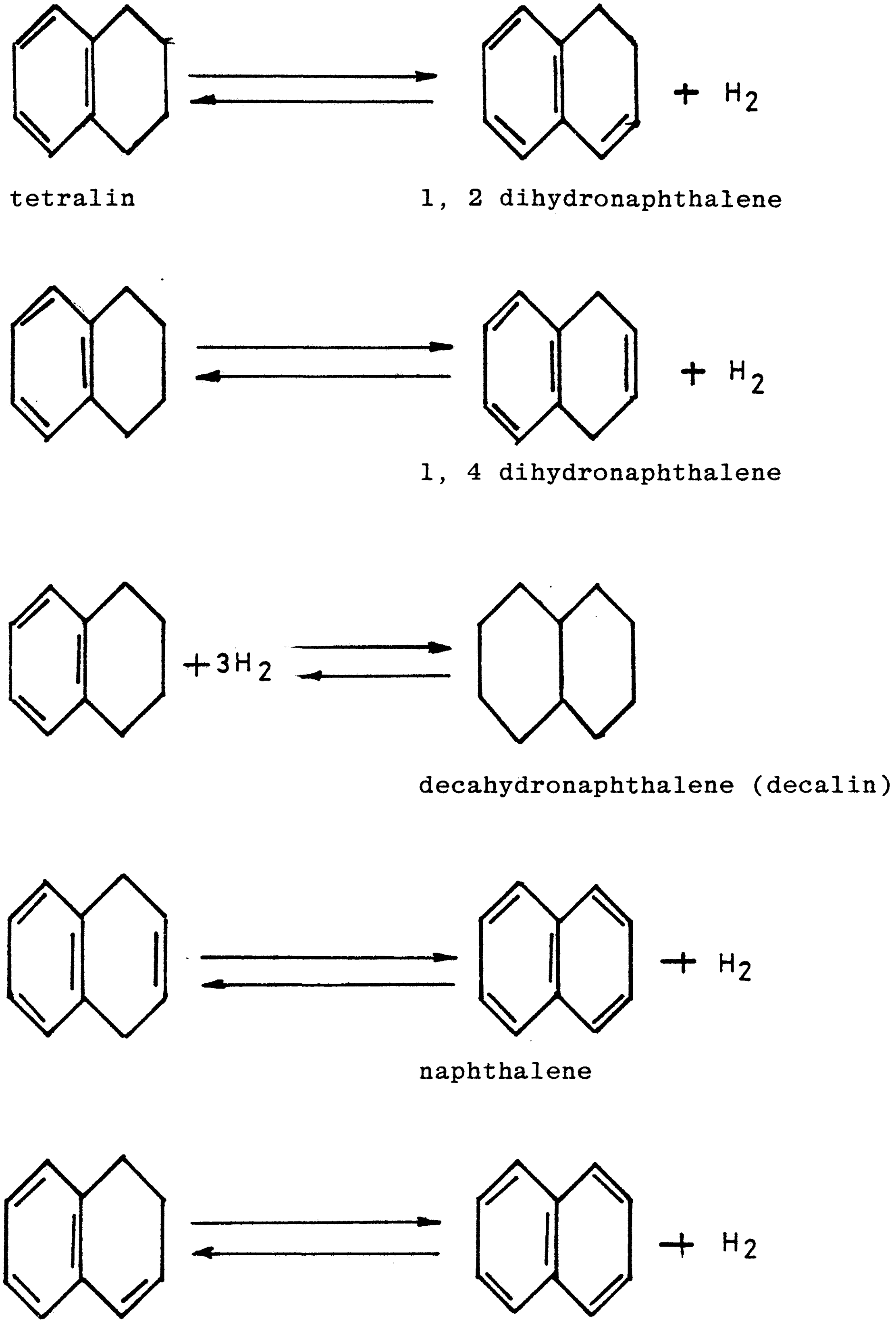


Figure 4. Hydrogen donations and rehydrogenation of tetralin and its products.

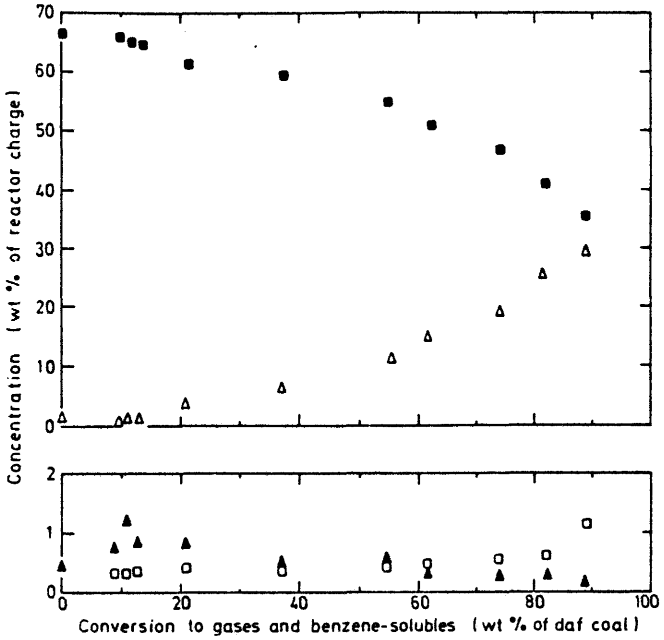


Figure* 5. Tetralin derived Components in Reaction Products, 400°C.

■ Tetralin ☐ decalin ▲ dihydronaphthalene △ naphthalene

*Neavel, Richard C., Liquefaction of Coal in Hydrogen-Donor and Non-Donor Vehicles, Fuel 55, pp. 237-242 (1976).

gen-bonding properties. A hydroxylated solvent would be expected to dissociate a hydrogen-bonded polymer, because the fragments of the polymer could attach themselves to the solvent by hydrogen bonding. An alternate reason for the effectiveness of a hydrogen-bonding solvent may be that the primary liquefaction products obtained by mild hydrogenloysis are themselves hydroxylated and hydrogen-bonded and that an excess of a similar solvent serves to keep these fragments dissociated.

Liebenberg et al. (22) hydrogenated coal without a catalyst in a batch reactor with tetralin. They found that the mechanism expressed by equation (12);

$$\text{Coal} \xrightarrow{k_1} \text{asphalt} \xrightarrow{k_2} \text{heavy oil} \qquad (12)$$

is an oversimplification of the true mechanism of hydrogenation. They suggested a more elaborate mechanism:

$$\text{Coal} \xrightarrow{k_1} \text{asphalt} \xrightarrow{k_2} \text{heavy oil}$$

$$\text{Coal} \xrightarrow{k_3} \text{asphalt} \qquad (13)$$

$$\text{Coal} \xrightarrow{k_4} \text{heavy oil}$$

Research has been conducted by Farcasiu, Mitchell and Whitehurst at Mobil Research and Development Corporation (23) to investigate the chemical nature and structure of soluble coal products, and the kinetics and mechanisms by which they are formed from coal under typical solvent refining conditions. Whitehurst et al. hypothesized that asphaltols are the predominant, primary products (some asphaltenes and oils are formed in parallel from coal), and that asphaltols (preasphaltenes) are then converted in a parallel fashion to asphaltenes and oils, with oil being the preferred product of preasphaltene conversion.

Whitehurst, Farcasiu and Mitchell (24) have reported the yields of various solubility classes as a function of time and this data are shown in Figure 6. The product composition vs. percent conversion to benzene soluble for West Kentucky Coal is shown in Figures 7 and 8.

FIGURE*6.

WEST KENTUCKY SRC COMPOSITION vs. TIME
(800°F, 1000-1300 psi H_2)

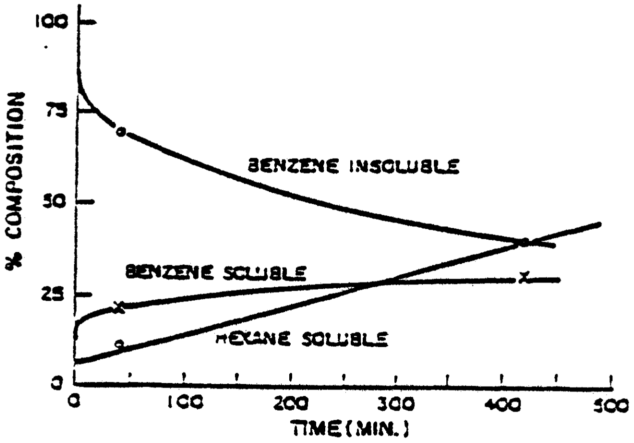


FIGURE*7.

PRODUCT COMPOSITION vs. PERCENT CONVERSION TO BENZENE SOLUBLE WEST KENTUCKY COAL

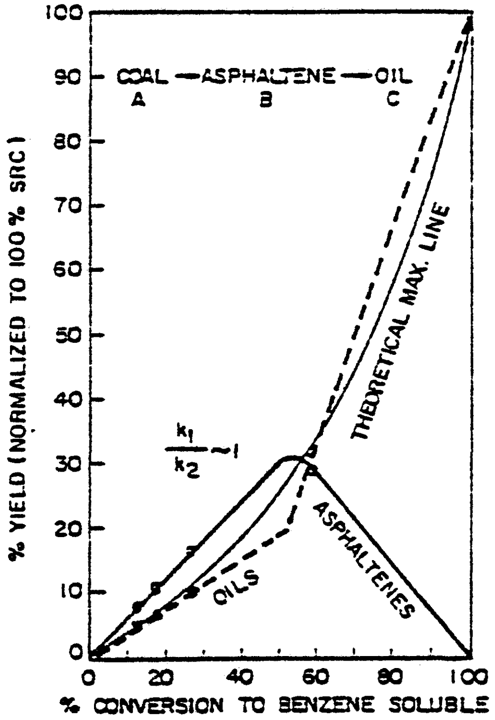
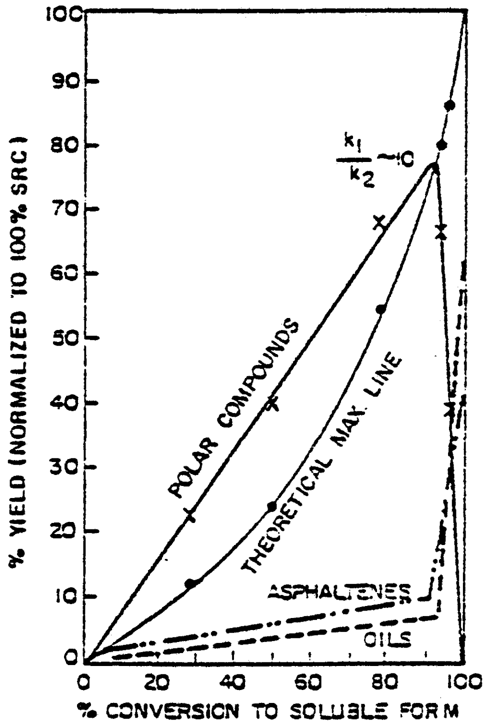


FIGURE*8.

PRODUCT COMPOSITIONS vs. PERCENT CONVERSION TO SOLUBLE FORM
WEST KENTUCKY COAL



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*Whitehurst et al., The Nature and Origin of Asphaltenes in Processed Coals, Mobil Research and Development Corp., Central Research Division, Princeton, N.J., EPRI AF-252, Feb. (1976).

APPARATUS AND EXPERIMENTAL PROCEDURE

Apparatus

The apparatus used to collect the experimental data consisted of a 300 cc magnedrive batch reactor, a slurry pump, a temperature controller and recorder, a gas delivery system, and a high-speed fan. A schematic drawing of the apparatus is shown in Figure 9. Appendix III lists the materials of construction and pressure ratings of all equipment.

The magnedrive reactor was manufactured by Autoclave Engineers, Inc. and was constructed from 316 stainless steel. A sketch of various parts of the reactor is shown in Figure 10. The reactor had an inside diameter of 1 3/16 inches and a depth of 7 inches. A 1200-watt, 115 volt heating jacket was used for heating the reactor to reaction temperature. The stirring head was driven by a 1/4 horsepower, variable-speed, D.C. motor. A 1/4 inch, 316 stainless steel Hoke valve with a soft-seating stem was used for the gas inlet line, and a 1/8 inch, 316 stainless, severe-service, Nupro valve was used for the slurry injection line.

The slurry pump used was a manually-operated 100 ml piston pump, manufactured by Ruska Instrument Corporation. Both the inlet and outlet lines were fitted with 1/4 inch, 316 stainless steel Whitey valves with soft-seating stems. A 12 inch section of 1/4 inch, 316 stainless steel flexible tubing, manufactured by Swagelok, was installed between the slurry pump and the reactor.

A Leeds and Northrup Series 60 controller with a Model 11906-223 SCR final control element was used for temperature control. Temperatures were recorded on a Leeds and Northrup "speedomax" continuous recorder. The input temperature to the controller was from a chromel-alumel (Type K) thermocouple.

A diagram of the gas delivery system is shown in Figure 11. The system consisted of a hydrogen cylinder, a helium cylinder, two pressure regulators, three pressure gauges, two gas reservoirs, a reducing valve, eleven shut-off valves and regulating valves, and other connecting sections such as tees and tubing. The hydrogen and helium bottle pressure regulators were manufactured by Hoke, Inc. Pressure gauges were Ashcraft Maxisafe gauges with a pressure range of 0 to 5000 psig. The reducing valve manufactured by Grove Valve and Regulator Company, was installed in the system to provide the option of maintaining a constant pressure in the range of 0 to 3000 psig. The reservoir and regulator inlet valves and the system vent valve were 1/4 inch, 316 stainless steel Hoke valves. All other shut-off and regulating valves were 1/4 inch,

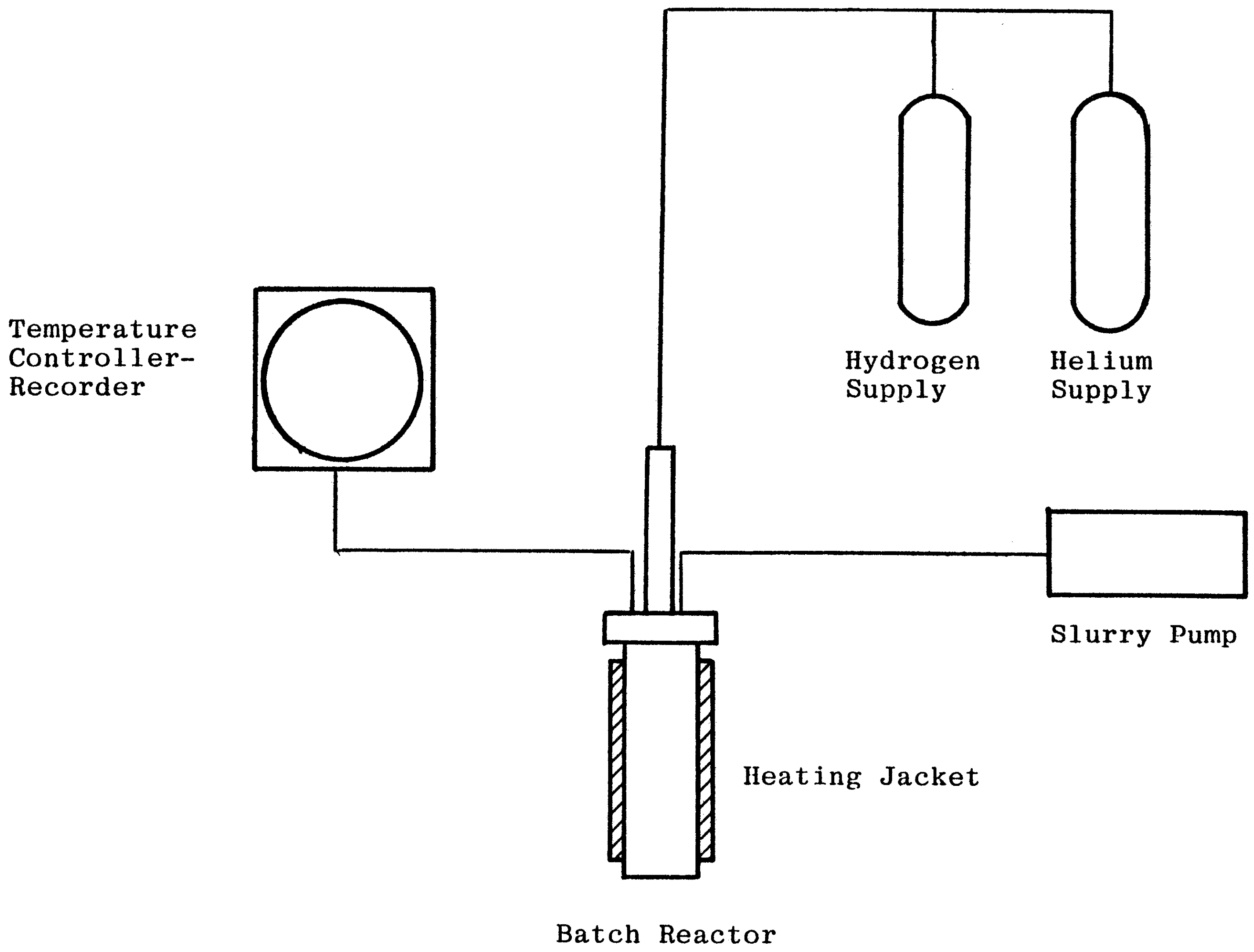


Figure 9. A Schematic Drawing of Experimental System.

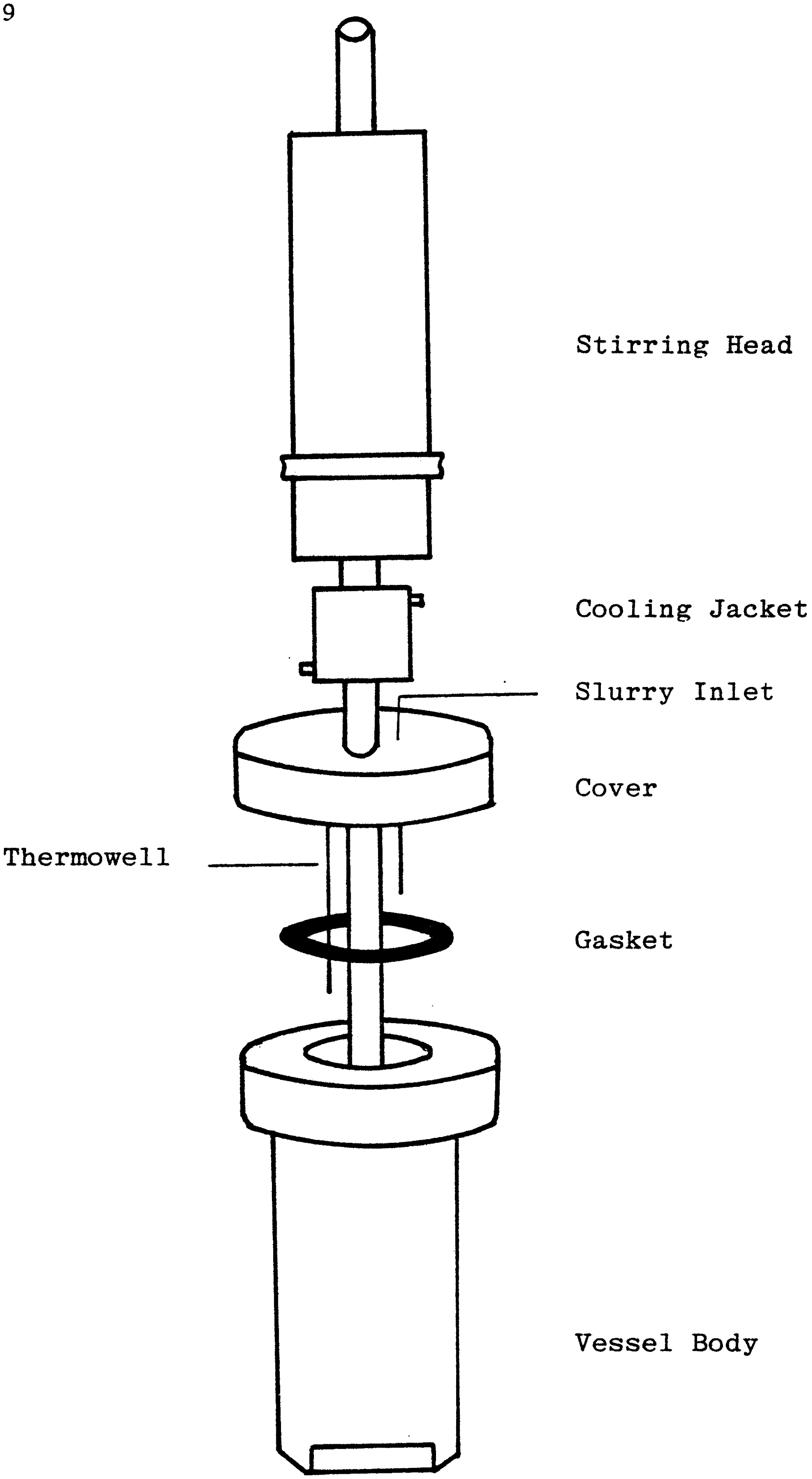


Figure 10. Reactor and Stirring Head Assembly.

316 stainless steel valves manufactured by Autoclave Engineers, Inc. The tubing for the gas delivery system was 316 stainless steel, 1/4 inch O.D. tubing.

A high-speed fan attached to the reactor support was used to rapidly cool the reactor upon completion of a run.

The distillation unit is a Rotavap model RE made by Brinkmann Instruments, Inc. A view of the rotavap with its accessories is shown in Figure 12.

Gaseous products were analyzed with a Carle Model 8001 gas chromatograph. The gas chromatograph was fitted with two eight-foot Porapak Q columns, and one six-foot molecular sieve column in a series by-pass arrangement, and were maintained isothermally at 170°C. Helium carrier gas was used. Vacuum was supplied with a Cenco vacuum pump, with a Heise compound pressure gauge used to measure the system pressure or vacuum. This system is shown in Figure 13.

Experimental Procedure

The preparation of coal was performed once at the start of experimental work generating enough coal for all experimental runs. The remaining procedures were performed for each run.

I. Coal Preparation

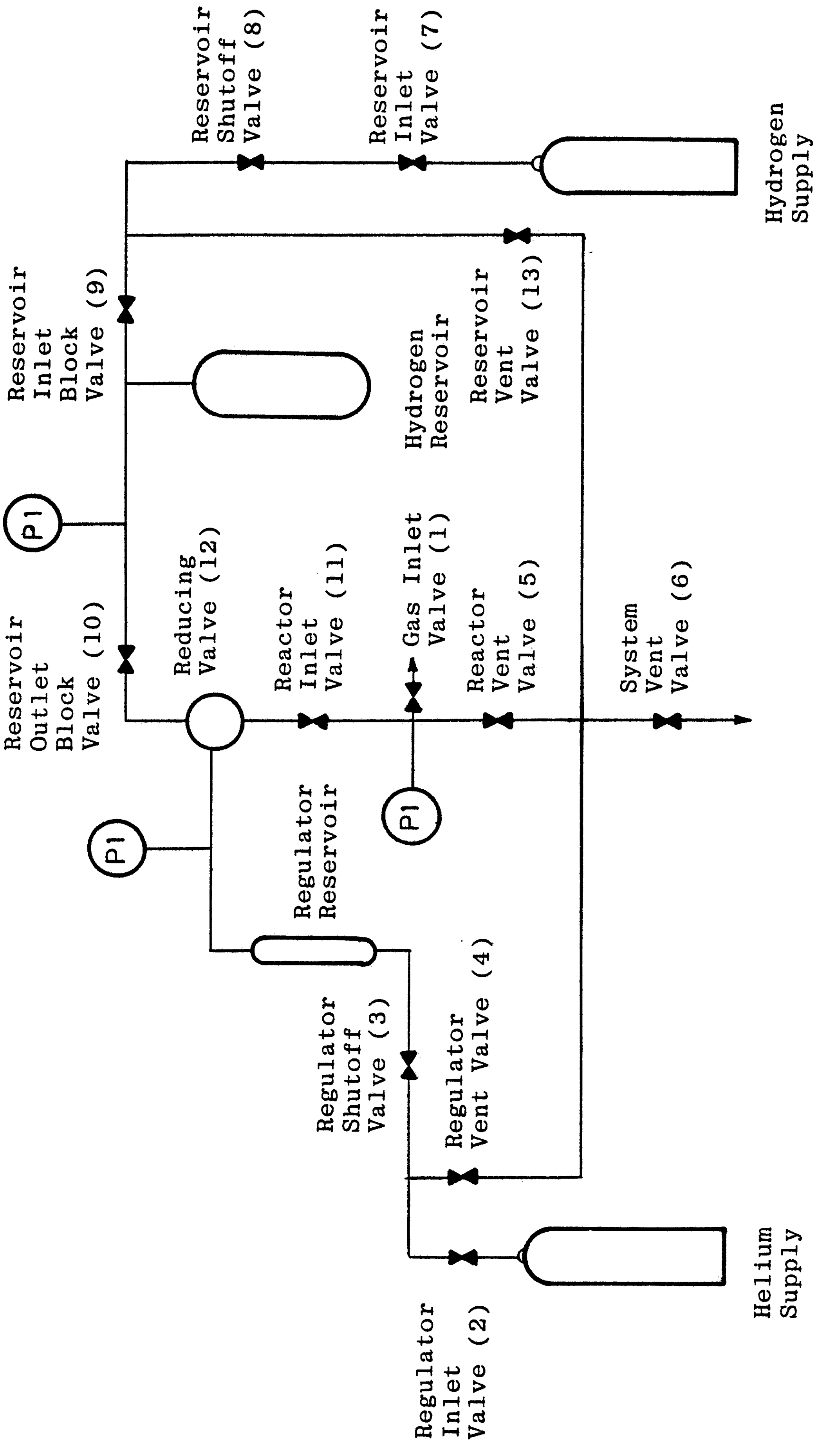


Figure 11. Gas Delivery System.

Coal was pulverized and grounded to pass 200 mesh using a Holms pulverizer located at the Colorado School of Mines Research Institute. A uniform sample was generated by riffling. The coal was stored in a 4 liter glass jar under approximately 5 psig of helium to prevent oxidation in air.

II. Processing

The location of the various numbered valves mentioned in this section can be found in Figure 11.

1. The reactor assembly with the 1/8 inch severe-service valve connected to the dip tube were weighed.
2. 189 cc of tetralin were added to the reactor and the head bolts were torqued to 75 ft.-lb. After few runs it was found that 100 or 125 ft.-lb. was required to seal the reactor.
3. The reactor was reweighed with the solvent.
4. The system was purged with helium gas as follows:
    a) The reactor was connected to the gas delivery system and valve 1 on the reactor was opened.
    b) The regulator reservoir was filled to 1500 psig by adjusting the helium regulator and opening valves 2 and 3.
    c) Valve 2 was closed and valves 4 and 5 were

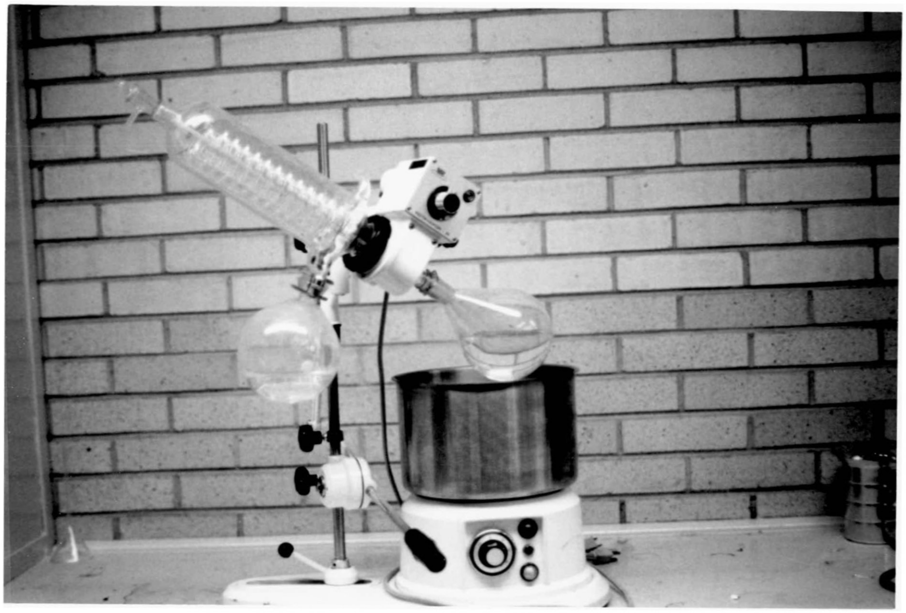


Figure 12. A View of Rotovap.

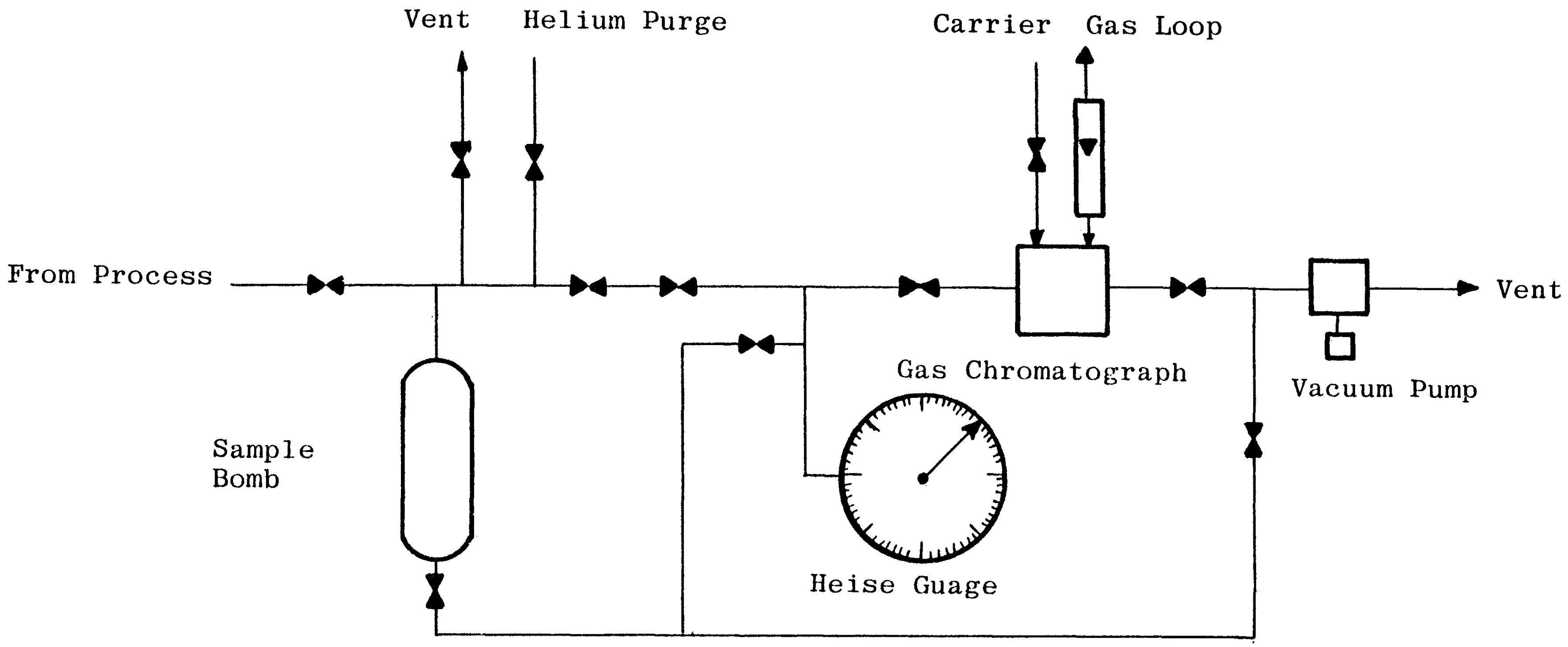


Figure 13. Gas Analysis System.

opened slowly to allow the reactor pressure to increase to 500 psig.

   d) Valves 3 and 4 were closed and valve 6 was opened slowly to allow the reactor to return to atmospheric pressure. Valves 5 and 6 were then closed.

5. The reactor was pressurized with hydrogen to the desired initial pressure as follows:
   a) The hydrogen reservoir was filled to 1200 psig by adjusting the hydrogen regulator and opening valves 7, 8, and 9. These three valves were then closed.
   b) For temperatures of 400°C, 375°C and 350°C, initial hydrogen pressures of 350, 450, and 550 psig, respectively, were used. The reactor was filled to the desired pressure by opening valves 10 and 11. Valves 10, 11, and 1 were then closed.
   c) The pressure in the lines was relieved by slowly opening valves 5 and 6. These valves were then closed and the reactor was disconnected from the gas delivery system.
6. The reactor was reweighed with hydrogen gas and reconnected to the gas delivery system.

7. About 50 g of coal and 42 g of tetralin in a 1:1.2 ratio of solvent to coal were weighed and mixed thoroughly.
8. The slurry pump was charged with slurry and all air was bled from the pump as follows:
   a) The forward valve on the pump was opened and the piston was moved forward to the end. The forward valve was then closed.
   b) The middle valve was opened. The slurry was then charged to the pump by bringing the piston back until all the slurry had been drawn into the pump.
   c) The middle valve was removed and the air was removed from the pump by moving the piston forward until slurry appeared. The cleaning solvent from the previous run was dried by paper towels until the thick slurry persisted. The 1/4 inch middle outlet was covered by restricting swagelok nipple.
   d) The piston was moved forward till the slurry appeared at the outlet of the forward valve.
9. The outlet line from the pump to the reactor was filled with slurry by moving the piston forward until slurry appeared at the end of the outlet line.
10. The outlet line was connected to the reactor and

the outlet valve on the reactor was opened to equalize the pressure between the pump and the reactor.

11. The system pressure was brought back to the initial value by opening valve 1, then slowly opening valves 10 and 11. The latter two valves were then closed.
12. The water lines were connected to the cooling jacket on the stirring head and the water supply was opened.
13. The fan belt was connected between the motor and the stirring head and the motor was turned on.
14. The temperature controller was set at the desired temperature, and the SCR and recorder were turned on.
15. The reactor was brought up to the reaction temperature, and the temperature and pressure were recorded.
16. Approximately 32 ml of slurry were injected into the reactor by bringing the piston on the Ruska pump slowly forward. The temperature and pressure were recorded.
17. The outlet valve between the reactor and the pump was closed, and the pressure in the pump was relieved by moving the piston backward.

18. The system was allowed to react for the specified time.
19. The reactor was quenched by removing the heating jacket and turning on the high-speed fan.
20. When the temperature had dropped below 205°C (400°F), the stirring motor was turned off and the cooling water stopped.
21. When the reactor had reached room temperature, the temperature and pressure were recorded. Valve 1 was closed and valves 5 and 6 were opened to relieve pressure in the gas delivery system.
22. The reactor was disconnected and reweighed.
23. The reactor was connected to the gas chromatograph and the gases in the reactor were analyzed.
24. After completion of the gas analysis, the reactor was vented to atmospheric pressure and reweighed.
25. The reactor was disassembled, and the liquid was mixed well and poured into 250 ml empty jars.
26. The reactor, and connecting lines were cleaned with acetone for the next run.
27. The slurry pump was cleaned by tetralin.

CHEMICAL ANALYSIS

Following an experimental run, after the reactor had reached room temperature, the contents were collected in 250 ml jars. Twenty grams of product were weighed in each of two 200 ml centrifuge tubes, and 150 ml benzene was added to each tube. The tubes were sonicated for 3 minutes and centrifuged for 10 minutes in order to extract the benzene soluble fraction of the product (i.e. asphaltenes, oils and process solvent). The soluble portion was decanted into a 1500 ml flask, and the above procedure repeated three more times using 100 ml benzene portions instead of 150 ml. Benzene insolubles were dried overnight in an oven at 100°C, and were cooled and weighed. Benzene insolubles (solids) were next extracted by 150 ml of tedrahydrofuran (THF), sonicated and centrifuged. THF solubles (preasphaltenes) were discarded into waste solvent containers to be disposed of properly due to the explosive properties of THF. Three more THF extractions were carried out using 100 ml each time. The solids remaining were composed of unreacted coal and ash, and were dried overnight in the oven at 100°C, When dry, the tubes were removed from the oven and weighed, The THF insolubles were transferred to pre-tared crucibles (heated to 750°C and maintained at this temperature for one hour, then cooled inside a desicator to ambient temperature) and the sample was weighed. Ashing of the THF insolubles was carried out in a furnace by heating the crucibles and their contents slowly to a temperature of 700-750°C and maintaining this temperature for one hour. The crucibles were removed and cooled inside a desicator, to room temperature. The crucibles were then weighed to determine ash in the product. The heating, cooling and weighing was repeated as many times as necessary to yield a constant weight with a deviation of ± 0.001 gram or less (25).

The saved benzene solubles were distilled in a rotavap to remove benzene, and the liquid that remained after benzene separation was transferred to centrifuge tubes and extracted with 150 ml pentane, causing precipitation of asphaltenes. The tubes were sonicated, centrifuged and the pentane-soluble portion decanted into a waste solvent drum. The pentane insoluble fraction was extracted twice more using 100 ml aliquots of pentane. Pentane insolubles were dried overnight in an oven at 100°C, then cooled and weighed. A summary of this PERC analysis is shown in Figure 14.

SOLUBILITY CLASSIFICATION AND CHEMICAL NATURE OF COAL LIQUEFACTION PRODUCTS

The products of coal liquefaction are usually classified according to their solubility in certain

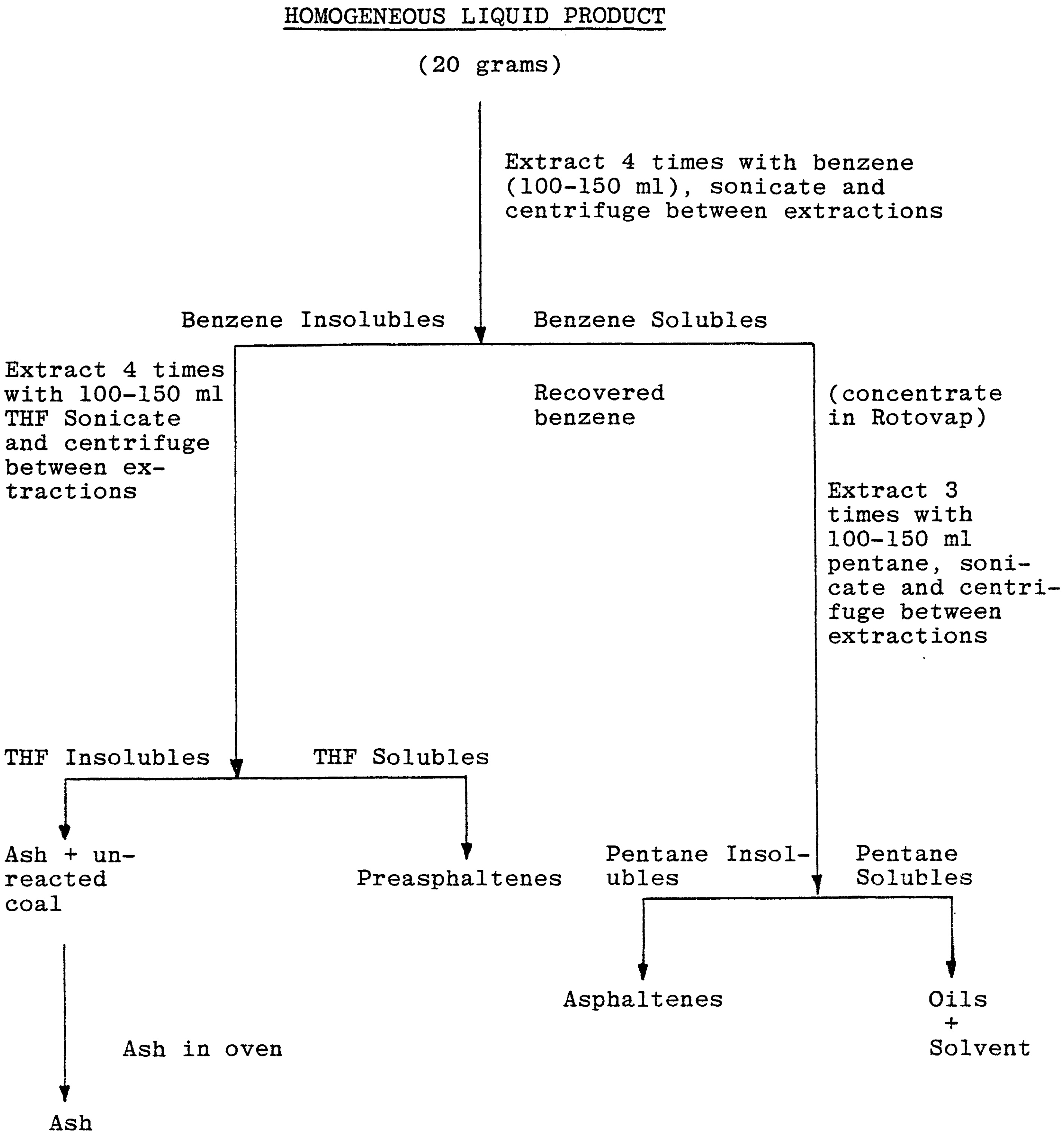


Figure 14. Coal Liquids Characterization Scheme
(PERC Analysis)*.

* Procedure supplied in part by Dr. F.K. Schweighardt, Pittsburg Energy Research Center, Pittsburgh, Pennsylvania.

solvents which indicates the range of their molecular weights.

Preasphaltenes: pyridine soluble-THF soluble-benzene insoluble. This fraction is composed of polyfunctional compounds generally having molecular weights greater than 400 and less than 2000. About 80% of the basic nitrogen compounds in solvent derived coal are located in the preasphaltenes. This explains the higher nitrogen wt. percent in preasphaltenes to that in the parent coal (Table 5). An asphaltene fraction has been isolated from preasphaltenes by breaking the salt-like structure (26). Preasphaltenes contain the highest concentration of heteroatoms and the lowest hydrogen to carbon ratio of all coal product fractions (Table 5). Preasphaltenes are called polar compounds since they contain a large number of polar functional groups such as hydroxyl groups. A view on the chemical structure of preasphaltene is shown in Figure 15.

Asphaltenes:benzene soluble-pentane insoluble. These compounds are predominantly monofunctional having molecular weights in the range of 300-800. Functionality refers to the presence of a hydroxyl group, or a basic or non-basic nitrogen group. Any or all of the molecules can contain oxygen or sulfur as heterocyclic or exocyclic ethers or thioethers. Combinations of functionality can

ANALYTICAL RESULTS

SRC Product	Wt. % Distribution	H/C	Wt. %					Total	$\bar{M}$n Mol. Wt.
			C	H	O	N	S		
Burning Star Mine, 9634	-	0.79	86.90	5.75	5.00	2.00	0.67	100.32	
" , Preasphaltenes	62.8	0.75	85.74	5.39	5.86	2.15	0.66	99.80	870
" , Asphaltenes	27.0	0.95	86.84	6.88	4.78	1.65	0.60	100.75	565
" , Oils	10.2	0.97	88.30	7.10	3.00	0.87	0.48	99.75	350
Total	100.0								

TABLE*5. Elemental Analysis of Illinois No. 6 Solvent Refined Coal Product.

*Burk, Jr., E.H. and Kutta, H.W., Investigations on the Nature of Preasphaltenes Derived from Solvent Refined Coal Conversion Products, Preprints of 1976 Coal Chemistry Workshop, S.R.I., August (1976).

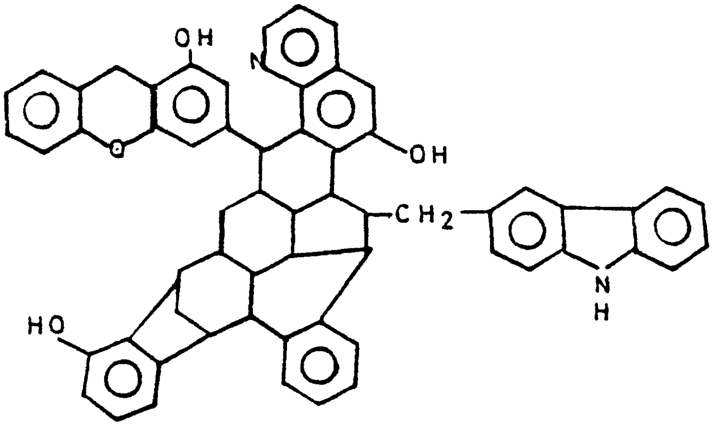


FIGURE*15. AN ASPHALTOL STRUCTURE

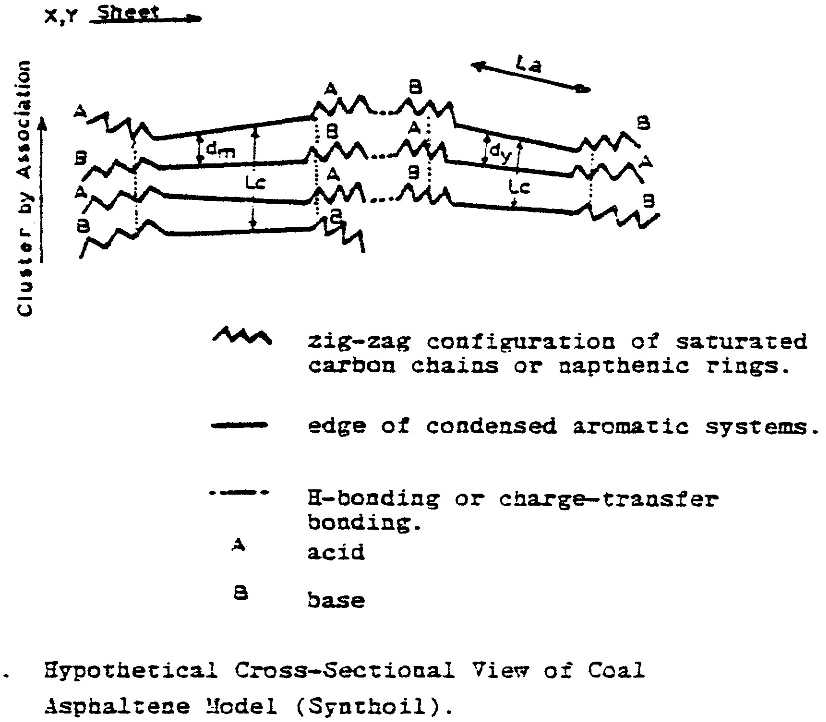


Figure*16. Hypothetical Cross-Sectional View of Coal Asphaltene Model (Synthoil).

*Yen, T.F., Chemistry of Asphaltene in Coal Liquids, Preprints of 1976 Coal Chemistry Workshop, S.R.I., August (1976).

include non-basic nitrogen and a hydroxyl group or perhaps two hydroxyl groups per molecule. Molecules containing both basic nitrogen and a hydroxyl group will generally not be found in this solubility class (24).

The structure of asphaltenes isolated from coal, shale oil and petroleum are quite different. A hypothetical view of the coal asphaltene structure is shown in Figure 16. The bonding within the system is not controlled by only one type of force, rather, it is due to a number of short range and long range molecular interactions which join to form a "functional macro-structure" (27). The chemistry of asphaltenes in coal liquids obviously is a dynamic one and depends on the process variables. The weight percent of sulfur, nitrogen and oxygen in asphaltenes is at a lower level than the parent coal as shown in Table 5.

Oils: benzene soluble-pentane soluble. This fraction is predominately composed of hydrocarbon compounds of molecular weights in the range of 200-400. The fraction is low in sulfur and oxygen content, with these heteroatoms occurring mainly as heterocyclic compounds, or exocyclic ethers or thioethers. This fraction is thought to be free of basic nitrogen as determined by methylation with methyliodide (26). From an elemental analysis of an Illinois No. 6 solvent refined coal product (Table 5), it is apparent that oils have the lowest wt. percentage of oxygen, nitrogen and sulfur. This makes the oil fraction more readily suitable for consumption as a clean fuel.

EXPERIMENTAL DESIGN

The purpose of this work was to investigate the mechanism and kinetics of coal liquefaction to preasphaltenes (asphaltol, polar compounds), asphaltenes, and oils plus gases. Three kinetic models were formulated and tested against the data.

The parent coal used in this study was a bituminous coal from Madisonville No. 9 seam, Fies Mine, Kentucky, supplied by Island Creek Coal Company. The proximate and ultimate analysis of the coal was carried out at the Research Institute of the Colorado School of Mines, and is shown in Table 6. Results of extraction of the parent coal by the PERC method is shown in Table 7.

It has long been recognized that taking kinetic data in a batch reactor implies the problem of imprecise reaction time due to heating and cooling effects. In this study, this problem was overcome by heating the solvent in the reactor to reaction temperature, then injecting a slurry of coal and solvent into the reactor. When the reaction was to be terminated, a high-speed fan was used to rapidly cool the

Table 6

Proximate and Ultimate Analysis of Coal

Proximate Analysis	As Received	Dry Basis
Volatile Matter	31.73%	31.77%
Ash	25.19%	25.23%
Fixed Carbon	42.94%	43.00%
Ultimate Analysis		
Carbon	55.81%	55.89%
Hydrogen	4.29%	4.30%
Sulfur	4.91%	4.92%
Nitrogen	0.87%	0.87%
Oxygen (by difference)	8.79%	8.79%

Table 7

Analysis of Coal by PERC Method
(Ash-free basis)

Unreacted coal = 99.20% wt. percent

Preasphaltene = 0.79% wt. percent

$\left.\begin{array}{l}\text{Asphaltene}\\ \text{Oil}\end{array}\right\}$ = 0.01% wt. percent reactor. The quenching of the reactor from 400°C to 205°C (400°F) took approximately 10 minutes. This improved technique in taking kinetic data helped in defining a precise "reaction time". A temperature profile of a typical run at 350°C is shown in Figure 17.

The kinetic models were to be investigated in the temperature range of 350-425°C, which is a typical range for coal liquefaction. It has been found by Guin, et al. (12) that below 350°C, coal extraction is slowed significantly. On the other hand, at temperatures above 425°C coking of the solvent may occur which renders the data taken of little value since organic carbon and the fixed carbon are difficult to distinguish between analytically.

An evolutionary experimental design was used in which data were taken initially at 400°C, and results at this temperature level used to refine the conditions chosen for the other temperature levels. Data at 400°C were taken at times of 1 hour and 2 hours. This data was plotted and it was conceived that more data had to be taken below 1 hour and at times in excess of 2 hours. Thus, 30 minute, 10 minute, and 3 hour reaction times were carried out. It was determined from the weight fraction of unreacted coal that further experiments at times longer than 3 hours would give an insignificant decrease in the value of unreacted coal.

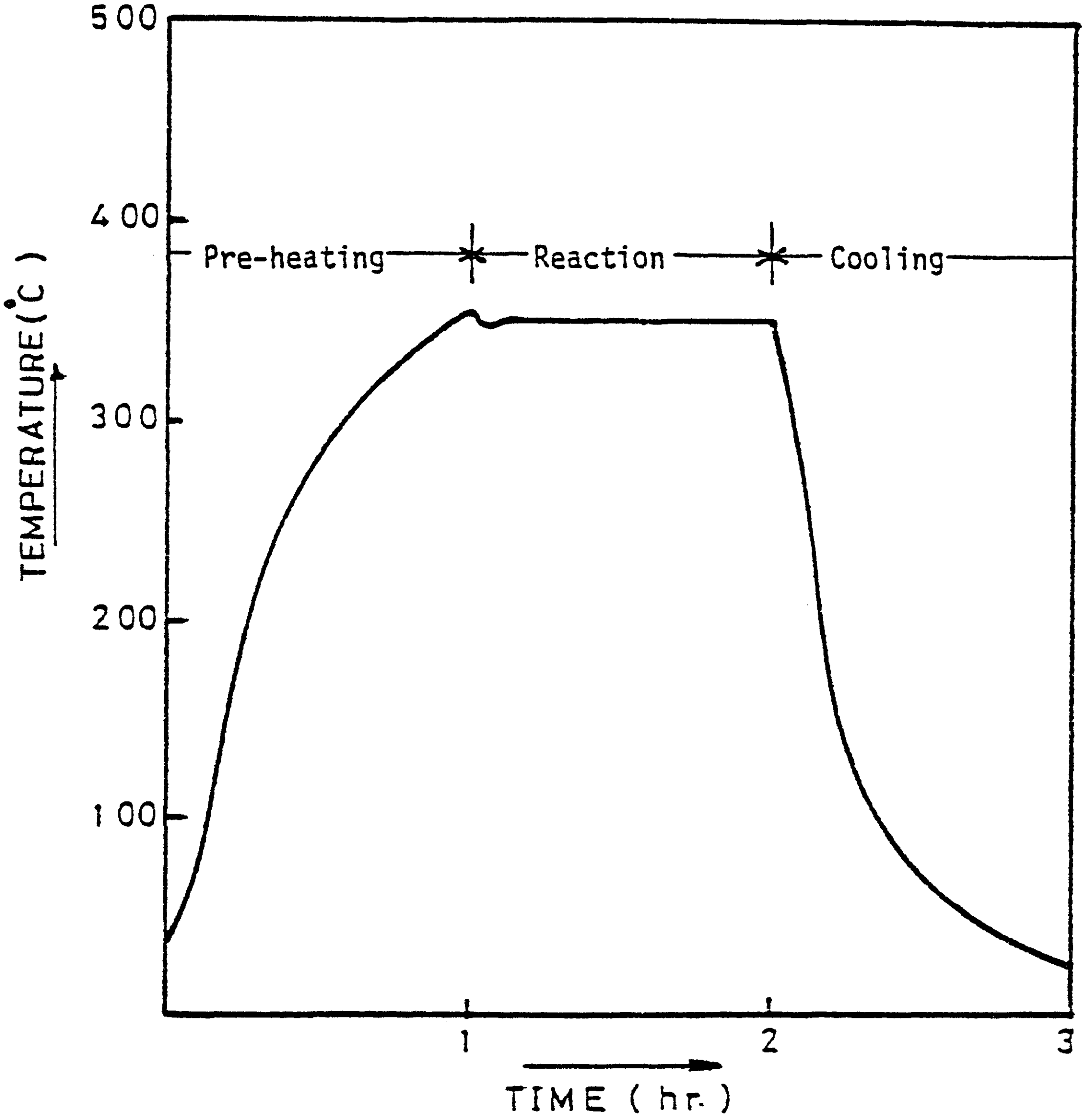


Fig. 17. A Typical Time-Temperature Profile

Another set of data was initially to be taken at 425°C. However, experiments at that temperature level showed the vapor pressure of tetralin to be high enough (i.e. reactor pressure reached 3200 psi) to discourage further study at that temperature for safety reasons. The next two temperatures tried were 375°C and 350°C. Satisfactory operation was secured at these lower temperatures. The reaction times investigated were the five previously tried at 400°C, 10 minutes, 1/2 hour, 1 hour, 2 hours and 3 hours. The sequence of runs as a function of temperature and time is shown in Table 8.

Initial reaction pressure used was approximately 2000 psig. This was accomplished by establishing initial hydrogen pressures before heating of 350, 450, 550 psig for 400°C, 375°C, 350°C runs respectively. The ratio of solvent to coal in the reactor was maintained at 10 to 1, and was established to assure that kinetic effects due to solvent starvation were minimized. This massive excess of solvent also assured that very little temperature drop would be experienced upon injection of reactants.

Table 8

Experimental Design

Temp. (°C)	Time (minutes)				
	10	30	60	120	180
500	4.7*	3	1,6	2	5
375	10	9	8,12		11
350		16	13	14	15

* Run number in order performed.

MATHEMATICAL MODELING AND PARAMETER ESTIMATION

Mathematical Modeling

For many physical systems there exists a precise mathematical and physical representation of all of the phenomena which make up the system. A chemical reaction behaves in the same manner, since it does possess some "true mechanism" which is descriptive of every microscopic detail of the reaction. Analysis of reaction kinetic data requires estimation of parameters such as reaction rate constants, determination of the precision of parameter estimates and evaluation of the adequacy of fit of the theoretical mechanism to the experimental data.

The establishment of systematic procedures for the determination of parameters in non-linear models, and for choosing between alternative models, has assumed considerable importance in the literature. Development and application of both linear and non-linear estimation procedures have been documented and discussed in detail by many authors; Box (28), Hougen and Watson (29), Kittrell et al. (30), and Lapidus and Peterson (31).

Non-linear estimation of several parameters from data ordinarily available for these reaction systems is sometimes difficult. These difficulties usually stem from the lack of sufficient information regarding the reaction system. However, in many reactions a number of reactants, intermediates, and products may be involved and a large amount of information is potentially available if it can be measured.

Models

For this study, reactions of dissolution and conversion of intermediates were assumed to be first order. This assumption can be supported from previous research reported in the literature (23). Three models for the mechanisms of coal liquefaction to preasphaltene, asphaltene, and oil plus gases were investigated and compared to experimental data. These models are illustrated below:

Model 1

The reaction mechanism of this model is represented by the following scheme:

$$\text{Coal} \xrightarrow{k_1} \text{asphaltene}$$

$$\text{Coal} \xrightarrow{k_2} \text{preasphaltene}$$

$$\text{Coal} \xrightarrow{k_3} \text{oil + gases}$$

$$\text{Asphaltene} \xrightarrow{k_4} \text{oil + gases}$$

$$\text{Preasphaltene} \xrightarrow{k_5} \text{oil + gases}$$

$$\text{Preasphaltene} \xrightarrow{k_6} \text{asphaltene}$$

The first three reactions have been shown by Hill (15) to be irreversible, however, at high reaction temperature, intermediate products may polymerize to asphaltenes (32). This polymerization was minimized by maintaining reaction temperatures below 470°C.

To simplify the differential equations representing the rate of disappearance and formation of each group of compounds, the following symbols will be used:

A = Reactive coal
B = Asphaltene
C = Preasphaltene
D = Oil + Gases

The rates of disappearance and formation are then given by:

$$\frac{dA}{dT} = -(k_1 + k_2 + k_3)\ (A) \tag{14}$$

$$\frac{dB}{dt} = k_1\ A + k_6\ C - k_4\ B \tag{15}$$

$$\frac{dC}{dt} = k_2\ A - (k_5 + k_6)\ C \tag{16}$$

$$\frac{dD}{dt} = k_3\ A + k_4\ B + k_5\ C \tag{17}$$

Initial conditions using wt. fractions may be represented by:

at $t = 0$ $A = a$ (ash-free basis)

$B = C = D = 0.$

at any time t

$$A' = 1 - a + A \tag{18}$$

where A' = unreacted coal

1-a = unreactive fraction of coal

a = reactive fraction of coal at time t = 0 (33)

A = reactive fraction of coal at time t

Defining rate constant groupings:

$$\beta = k_1 + k_2 + k_3 \tag{19}$$

$$\gamma = k_5 + k_6 \tag{20}$$

The solutions for the differential equations are then given by:

$$A' = 1 - a + ae^{-\beta t} \tag{21}$$

$$C = \frac{k_2 a}{\gamma-\beta} (e^{-\beta t} - e^{-\gamma t}) \tag{22}$$

$$B = \frac{a}{k_4-\beta} \left[k_1 + \frac{k_2 k_6}{\gamma-\beta} \right] (e^{-\beta t} - e^{-k_4 t}) + \frac{a\, k_2\, k_6}{(\beta-\gamma)\ (k_4-\gamma)} \left[e^{-\gamma t} - e^{-k_4 t} \right] \tag{23}$$

$$D = 1.0 - (A' + B + C) \tag{24}$$

Model 2

This model represents coal dissolution as straight series reactions, with preasphaltenes formed first, then asphaltenes, then oils and gases.

$$A \xrightarrow{k_1} C \xrightarrow{k_2} B \xrightarrow{k_3} D$$

The following differential equations represent the rate of disappearance and formation of reactants and products for this model:

$$\frac{dA}{dt} = -k_1 A \tag{25}$$

$$\frac{dB}{dt} = k_2\ C - k_3\ B \tag{26}$$

$$\frac{dc}{dt} = k_1\ A - k_2\ C \tag{27}$$

$$\frac{dD}{dt} = k_3\ B \tag{28}$$

The solutions of the differential equations are given by:

$$A' = 1 - a + ae^{-k_1 t} \tag{29}$$

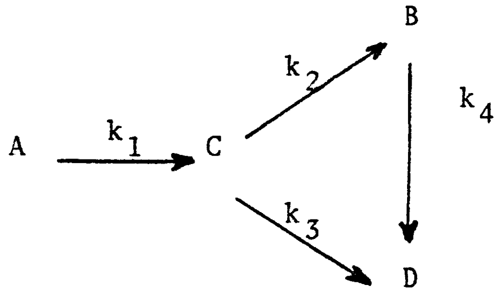
$$B = \frac{a\ k_1\ k_2}{k_2 - k_1} \left[\frac{(e^{-k_1 t} - e^{-k_3 t})}{(k_3 - k_1)} + \frac{(e^{k_3 t} - e^{-k_2 t})}{(k_3 - k_2)} \right] \tag{30}$$

$$C = \frac{a\ k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) \tag{31}$$

$$D = 1.0 - (A' + B + C) \tag{32}$$

Model 3

This model has an extra step which assumes oil and gases to be produced directly from preasphaltenes in addition to being formed from asphaltenes.



The rates of formation and disappearance are then given by:

$$\frac{dA}{dt} = -k_1 A \tag{33}$$

$$\frac{dB}{dt} = k_2 C - k_4 B \tag{34}$$

$$\frac{dC}{dt} = k_1 A - (k_2 + k_3) C \tag{35}$$

$$\frac{dD}{dt} = k_3 C + k_4 B \tag{36}$$

The solutions of these differential equations are given by:

$$A' = 1 - a + ae^{-k_1 t} \tag{37}$$

$$C = \frac{k_1 a}{k_2+k_3-k_1} \left[e^{-k_1 t} - e^{-(k_2+k_3)t} \right] \tag{38}$$

$$B = \frac{k_1 k_2 a}{k_2+k_3-k_1} \left[\frac{(e^{-k_1 t} - e^{-k_4 t})}{(k_4-k_1)} + \frac{(e^{-k_4 t} - e^{-(k_2+k_3)t})}{(k_4-k_2-k_3)} \right] \tag{39}$$

$$D = 1.0 - (A' + B + C) \tag{40}$$

Non-Linear Parameter Estimation Program

A computer program written by Bard (34) on non-linear parameter estimation techniques has been used to estimate the rate constants. The mathematical models or their derived equations attempt to describe the relationships between the physically measured variables (raw data). These models contain parameters (rate constants) whose values are unknown. The object of parameter estimation regression is to find the values of these parameters that cause the proposed equations to give the best possible fit to the data. The measure of fit depends on the residuals, i.e. on the differences between the observed values of certain variables, and the values predicted by the equations. A common measure of this difference is provided by the sum of squares of the residuals, but for models with more than one dependent variable (A, B, C, D), the determinant of moment matrix of residuals is used. The program uses method of maximum likelihood, with variables classified in four categories.

1. Parameters: constants appearing in the model (k's) with unknown numerical values. The vector of parameters is denoted by:

$$\theta = \{\theta_1, \theta_2, \ldots \theta_\ell\} \tag{41}$$

2. Independent variables: variables known precisely for each observation (i.e. time, temperature). The vector of independent variables for the μth experiment is given by;

$$a_\mu = \{a_{\mu 1}, a_{\mu 2}, \ldots . a_{\mu m}\} \tag{42}$$

3. Dependent variables: variables whose values the equations of the model seek to predict (A, B, C).
4. Observed variables: dependent variables which are actually measured in each experiment. Their

vector is given by:

$$y_\mu = \{y_{\mu 1}, y_{\mu 2}, \ldots\ldots y_{\mu k}\} \quad (43)$$

The model relates the observed variables to the dependent variables and parameters. In general,

$$g\ (y_\mu, a_\mu, \theta) = 0 \qquad (\mu = 1, 2, \ldots.\ n) \quad (44)$$

This is called the structural equation. In principle the observed variables can be written in explicit form at each experiment.

$$y_\mu = f\ (a_\mu, \theta) \qquad (\mu = 1, 2, \ldots..\ n) \quad (45)$$

Ideally one would like to find values of θ's that exactly satisfy Eq. (45) at each experiment. Due to errors in measurement and inaccuracies in the model, Eq. (45) must be written in the form:

$$U_\mu = f\ (a_\mu, \theta) - y_\mu \quad (46)$$

where U_μ is a vector representing the departure of the predicted from observed values (the residuals). The task of parameter estimation is then to find values of θ, which minimize or maximize the function,

$$F\ (U_\mu) = F\ (f\ (a_\mu, \theta) - y_\mu). \quad (47)$$

With a_μ and y_μ given, F (U_μ) becomes a function of θ's alone, denoted by G (θ).

It may be assumed that the U's are random variables possessing a joint probability density function P(U, ϕ) of known mathematical form, possibly containing some unknown parameters ϕ. According to the principle of maximum likelihood, we seek those values of θ and ϕ which maximize the likelihood of having made the actual observations, i.e., which maximize P or more conveniently, its logarithm. Thus,

$$G(\theta, \phi) = \log P\,(f\,(a_\mu\,,\,\theta) - y_\mu,\ \phi). \qquad (48)$$

M.L.

The maximum likelihood function G_{ML} is given by;

$$G_{M.L.} = \frac{-kn}{2}\left[\,1 + \log\,(2\pi)\,\right] - \frac{n}{2}\sum_i \log\frac{1}{n}\,Ai \qquad (49)$$

where $$Ai = \sum_\mu U^2_{\mu_i} \qquad (50)$$

U_μ = the residual as given by Eq. (46).

U's are normally distributed.

The maximization of likelihood is provided by two alternative methods;

1. The Gauss-Newton method, with modifications by Greenstadt-Eisenpress (35), Bard (36), and Carroll (37).
2. The Davidon-Fletcher-Powell method (38).

The subroutines used to analyze and estimate parameters from the present data are shown in Figure 18. The following is a list of the subroutines and their functions.

Main Program (deck 01): Calls on subroutine NLMAX.

NLMAX: Reads general input. Finds and prints out maximum of objective function. Calls on ACCUM, EIG, BOUND, OUT.

Deck 02 uses the modified Gauss-Newton method to find the maximum of the objective function.

Deck 09 uses the Davidon-Fletcher-Powell method.

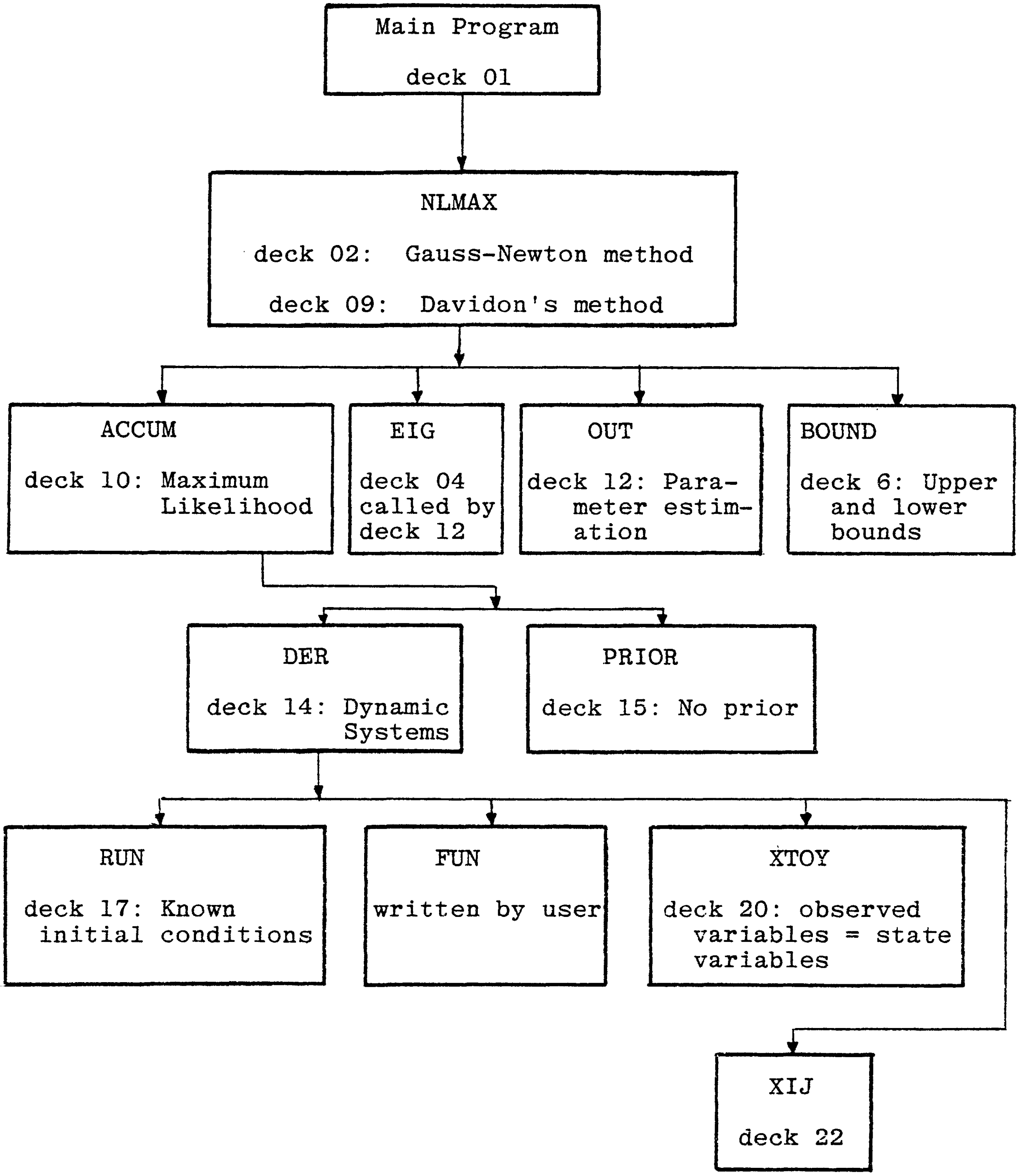
ACCUM: Computes value of objective function and its derivatives. Deck 10 is used for multiple equation weighted least squares, and maximum likelihood estimation with diagonal covariance matrix (i.e. weighted least squares with unknown weights).

EIG: Scales a symmetric matrix, computes eigen values and/or eigen vectors, and then rescales the vectors (uses Threshold-Jacoby method).

OUT: Provides additional detailed output after solution has been found. Deck 12 is used in conjunction with subroutine ACCUM deck 10. Calls on EIG.

BOUND: Computes the constraint penalty functions and their derivatives. Deck 06 is used to specify lower and upper bounds on each parameter.

Figure 18. PROGRAM STRUCTURE



DER: Computes the model equations and their first derivatives. Deck 14 is used for dynamic models (involving solution of differential equations). It calls on RUN, FUN, XTOY, XIJ.

PRIOR: Computes the logarithm of the prior probability and its first and second derivatives. Deck 15 is for a constant prior (i.e. no prior).

RUN: Computes initial conditions and their first derivatives. Deck 17 is used where all the initial conditions are known.

FUN: This subroutine is written for each model separately. It involves the differential equations of the model and their partial differentials with respect to the parameters and the dependent variables.

XTOY: Deck 20 considers the observed variables identical to state variables.

XIJ: Performs some matrix operations for subroutine DER deck 14.

Convergence and Termination

The iterations of the program are terminated when each component of the vector $\lambda\Delta\theta$ is small enough to satisfy the inequality:

$$|\lambda\Delta\theta_i| \leq .0001\,(.001 + |\theta_i^{(0)}|) \qquad (51)$$

where $\Delta\theta$ = a direction for θ to proceed in

λ = a step size.

$\theta i^{(0)}$ = the value of vector θ at the start of the iteration.

This criterion has been suggested by Marquardt (39), and works well in practice.

Analog Computer

The rate constants appearing in Equations 14-17 have also been determined by integrating the differential equation using an analog computer. The circuit of the analog computer simulation used is shown in Figure 19. Potentiometers were adjusted by trial and error until a good fit to the experimental data was obtained. Since an analytical solution of the model is known, the values of k's were used to obtain outputs for unreacted coal (A), asphaltene (B), preasphaltene (C), and oil plus gases (D), by putting these values in Equations 21-24. This approach was imprecise since a visual fit of the data was relied on to determine the rate constants. Once the program on non-linear parameter estimation was obtained, simulation by analog computer was abandoned.

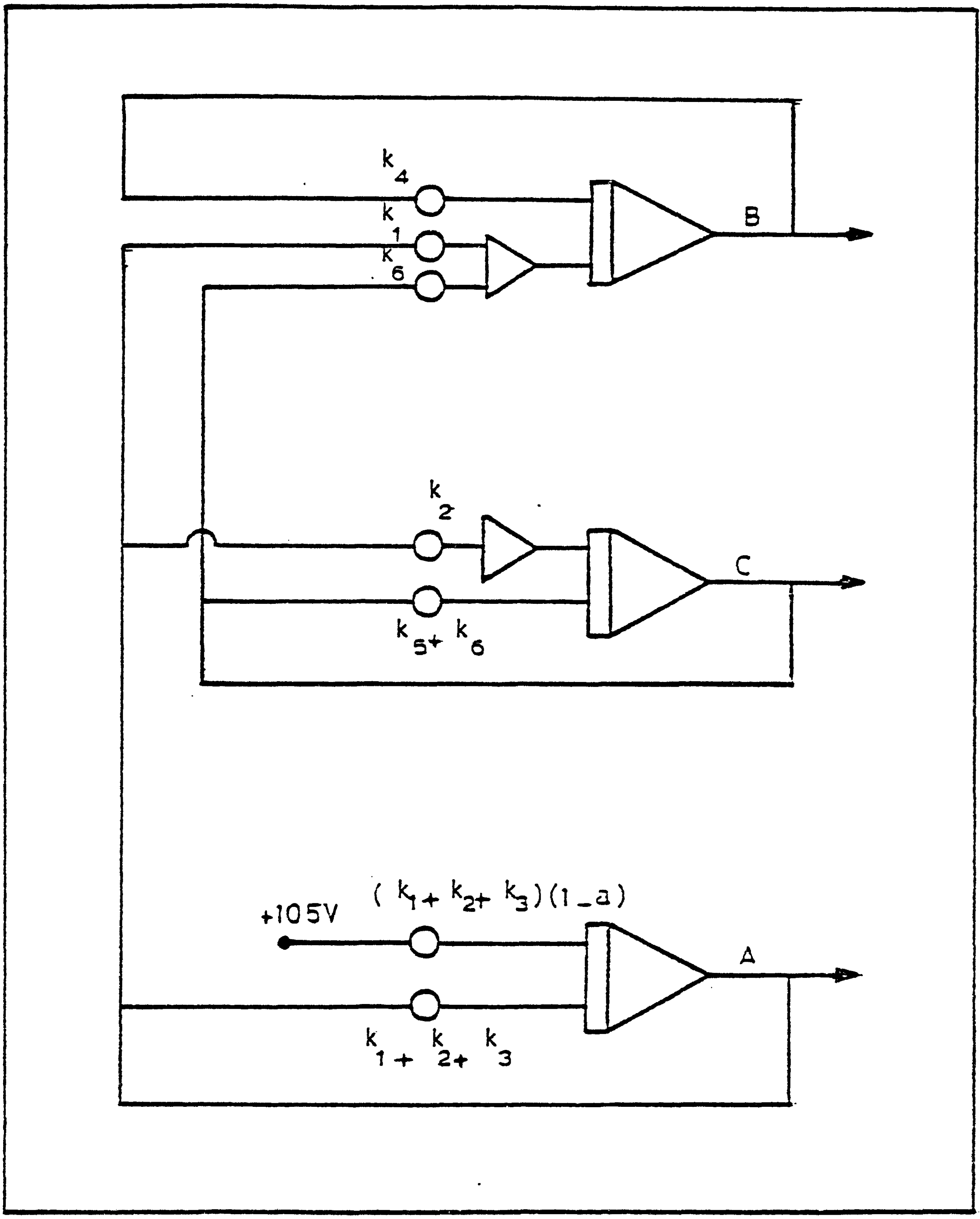


Fig. 19. Analog Computer Circuit

DISCUSSION OF RESULTS

Data Interpretation

Total mass balances and raw data are presented in Appendix I. As can be seen, the weight of slurry injected into the reactor via the Ruska pump was obtained by mass balance. The critical number in analysis of the data is the exact amount of coal injected into the reactor. This number is found by using the principle that the percent ash in the coal injected is equal to that of the parent coal. An estimation of coal injected can be obtained by:

$$\text{wt. of slurry injected} \times \frac{1.2}{2.2} = \text{approx. wt. of coal injected}$$

where 1.2/2.2 is the ratio of coal to coal + solvent in the feed paste charged to the Ruska pump. This gives only an approximation, however, to the exact amount of coal injected, as some coal remains in the dip tube in the reactor and does not enter into the reaction. In addition, some separation of coal and solvent occurs in the Ruska pump before injection, causing the exact ratio of coal to solvent injected to depart from the feed mix of 1.2/1.0. The approximate percent of benzene insolubles in the reaction product was calculated by taking a sample of the well-stirred product slurry, and extracting with benzene as shown previously in the section on chemical analysis. The amount of benzene insolubles was calculated as follows:

$$\frac{\text{wt of benz. Ins. (gm)}}{\text{wt of sample prod (gm)}} \times \frac{\text{wt. of products+solvent}}{\text{approx wt. of coal}} \times 100 = \text{\% benzene insolubles}$$

The benzene insoluble fraction (after drying) was sampled, extracted with THF, and the THF insoluble fraction ashed to determine ash content of the product. Percent ash in the product, relative to the estimated coal charged was then calculated:

$$\frac{\text{wt of ash (gm)}}{\text{wt of sample product (gm)}} \times \frac{\text{wt of products + solvent}}{\text{approx. wt. of coal}} \times 100 = \text{\% ash}$$

If the amount of coal injected has been exactly estimated by mass balance, the percent ash in the product must agree with the percent ash in the parent coal. Any discrepancy indicates that more or less coal was injected than estimated. The exact amount of coal injected is determined by forced ash balance, and the analysis of the product adjusted by normalizing each compound classification with respect to the ash balance. Then, unreacted coal, preasphaltene and asphaltene are recomputed on ash-free basis, Direct determination of oil content in the product is not possible since oil and solvent are not distinguishable by solvent extraction techniques (both are pentane soluble). Thus, the yield of oil plus gas was determined by the difference between the sum of unreacted coal, preasphaltene and asphaltene and 1.0 since, by definition:

$$\Sigma \text{ oil} + \text{gas} + \text{asphaltene} + \text{preasphaltene} + \text{unreacted coal} = 1.0$$

where each compound classification is a weight fraction, normalized as discussed above.

Calculated data for the various liquid products are tabulated in Tables 18-20 as weight fractions of the original coal charged to the reactor on a mineral-matter free basis. These weight fractions have been normalized with respect to ash content in order to put the product conversion on the basis of parent coal initially fed to the reactor. Normalized weight fractions were then converted to a mineral-matter (ash) free basis; thus the reported weight fractions represent yield of oil plus gas, asphaltenes and preasphaltenes from the organic fraction of the parent coal. Sample calculations of results from PERC analysis on one run are shown in Appendix II.

The experimental data and the fit of the various models to the data at temperatures of 400, 375, and 350°C are shown in Figures 20-28. As may be seen from the data, the conversion to preasphaltenes was predominant during the first 30 minutes of reaction time. This trend was observed at all three temperatures examined and can be adequately explained by the mechanism of coal dissolution. Coal with its condensed structure and complicated matrix of high molecular weight is expected to break into lower molecular weight products at the start of thermal cracking. Preasphaltenes have the highest average molecular weight of coal liquefaction products, thus a high concentration of preasphaltenes at the early stages of dissolution is to be expected since thermolysis reactions are predominant at this stage of the conversion. Asphaltenes and oils also were formed at the beginning of coal extraction but their yields were lower than preasphaltenes. As reaction time increased, yields of asphaltenes and oils plus gas continued to rise, while preasphaltenes tended to decline. As thermal cracking and hydrogen transfer from tetralin to coal and the high molecular weight products continued, more low molecular weight compounds were produced. The highest yield of oil and gas (40%) in the liquid product was obtained at 400°C and three-hour reaction time. This run was conducted at the most severe reaction conditions encountered in this study, thus the high yield of oil was expected. Lower temperature extraction did not give extensive thermal cracking of the coal molecular structure, as indicated by the oil yield at 350°C and three-hour reaction time for which a maximum oil and gas yield of only 20 percent was reached.

Asphaltenes yield increased with time and leveled off around 30 percent during reaction at 400°C. However, at lower temperatures the asphaltene yield kept increasing with temperature without leveling off. The unreacted coal concentration decayed in an exponential manner leveling off to a maximum conversion to soluble products of 87 percent, 83 percent, 75 percent at temperatures of 400, 375, and 350°C, respectively. Preasphaltene yield at 400 and 375°C increased to a maximum of approximately 40 percent, then decreased. At 350°C, preasphaltenes behaved like asphaltenes and oils where the three products kept increasing with time with rates slower than the other two isotherms.

Since the emphasis in the present study was on relating the yields of liquid products, gas analysis on the product gas by chromatography gave data of little value in model discrimination for this coal liquefaction process. Percent gasification at the severest conditions studied (400°C and three-hour reaction time) was found to be only 6.2 percent. Weller, et al. (19) in their work on kinetics of coal hydrogenation found gasification at 400°C to reach 5.8 percent. Gasification is expected to be lower as temperature decreases. Therefore, gas analysis at the other two isotherms, 375 and 350°, was not performed. The error of ignoring coal gasification during dissolution is included in oil yield, since the latter is found by difference.

Model Discrimination

Models 1, 2, and 3 were used to fit the experimental data using the non-linear parameter estimation computer program described earlier. This produced estimates of the rate constants and their standard deviations for each of the respective models. These values are shown in Tables 9-11. Since analytical solutions for each of the three models and estimates of the rate constants were known, the values of A', B, C and D were computed and plotted for each model. The plots were compared with the observed data, and the models along with the raw data are shown in Figures 20-28. Model 1 gave the best fit to the experimental data at all three isotherms (Figures 20-22). Model 2 (straight series reactions) exhibited a poor fit to the data (Figures 23-25), except for the concentration of unreacted coal, for which this model fit the data reasonably well. Preasphaltene yield in this model reached a maximum of 60 percent, then decreased to below 5 percent after three hours. The computed oil and gas yields were consistently higher than the experimental data after three hours, with values 50 percent higher predicted by Model 2. This trend was observed at all three isotherms (Figures 23-25) for Model 2. The computed asphaltene yield in Model 2 reached a maximum around 40 percent, then decreased, also in disagreement with the experimental data. This trend was observed at 400°C and 375°C.

Model 3 was a modification of Model 2 to include an extra parameter for conversion of preasphaltenes to oil and gas directly. The model for unreacted coal fitted the experimental data at all three isotherms (Figures 26-28). However, computed preasphaltenes yields at all three isotherms completely missed the data, with the fit at 400°C exhibiting an especially poor fit. The computed oil and gas yields again in this model were higher than the experimental oil and gas yields.

The hypothesized models were discriminated also by their respective values of the determinant of the moment matrix of residuals. This term is analogous to the error sum of squares in models containing only one dependent variable. The model that yields the minimum value for the determinant of moment matrix of residuals is expected to have the best fit to the experimental data. The moment matrix of residuals is defined by the following equation;

$$A_{ij} = \sum_{\mu=1}^{n} U_{\mu i} \, U_{\mu j} = \sum_{\mu=1}^{n} \left[f_i(a_\mu, \theta) - y_{\mu i} \right] \left[f_j(a_\mu, \theta) - y_{\mu j} \right] \qquad (52)$$

where $f_i(a_\mu, \theta)$ = the expression of dependent variable i as a function of independent variables $a\mu$ and parameters θ.

$y_{\mu i}$ = observed value of dependent variables i.

The values of the determinant of moment matrix of residuals for Models 1, 2, and 3 are shown in Table 12. The respective values for Model 1 are clearly lower than those for models 2 and 3. Thus, coal liquefaction in tetralin has been modeled by six irreversible first order series-parallel reactions:

coal $\xrightarrow{k_1}$ asphaltene

coal $\xrightarrow{k_2}$ preasphaltene

coal $\xrightarrow{k_3}$ oil + gas
Asphaltene $\xrightarrow{k_4}$ oil + gas
Preasphaltene $\xrightarrow{k_5}$ oil + gas

Preasphaltene $\xrightarrow{k_6}$ asphaltene

Convergence of the Computer Program

In order to check on the effect of giving the program different starting values on the resulting parameter estimates, the data at 400°C and 375°C for Model 1 was used with two different initial guesses for the rate constants. The program gave the same estimates for all six rate constants at both temperatures to three significant figures.

Activation Energies

The rate constant is related to activation energy by the following expression:

$$k = k_0 \exp \frac{(-E)}{RT} \qquad (53)$$

where k_0 = pre-exponential factor

E = activation energy

R = ideal gas law constant

T = absolute temperature

Equation (53) can be rewritten as:

$$\ln k = \ln k_0 - \frac{E}{RT} \qquad (54)$$

Thus plotting lnk vs. 1/T at the three temperatures studied should yield a straight line with slope of (-E/R) and y intercept of $\ln k_0$. Least square regression lines were drawn for the estimate of rate constants k_1, k_2, and k_3. These Arrhenius plots are shown in Figures 29-31. The last three rate constants had high standard deviations, and activation energies could only be estimated by straight lines whose slope and intercept could change according to the points chosen to represent the data. These plots are shown in Figures 32-34. Thus for k_1, k_2, and k_3, Arrhenius activation energies, pre-exponential factors and correlation coefficient r^2 were determined (Table 13). The value of r^2 is an indication of how good the linear regression fits the data with $r^2 = 1.0$

indicating a perfect fit. For k_4, k_5, k_6 estimates of the activation energies and pre-exponential factors were found according to two fitted straight lines as shown in Figures 32-34. The two lines drawn in Figures 32-34 attempt to illustrate the possible range of activation energies and pre-exponential factors that could be defined for k_4 through k_6.

The activation energies of k_1 (conversion of coal to asphaltene), k_2 (conversion of coal to preasphaltene), and k_3 (conversion of coal to oil) ranged between 20-40 K cal/g mole. The estimates of k_4 (conversion of asphaltene to oil), k_5 (conversion of preasphaltene to oil) and k_6 (conversion of preasphaltene to asphaltene) could vary in the range 10-50 K cal/g mole. These high activation energies for each of the rate constants show a high temperature sensitivity which implies that a true kinetically controlled reaction is being modeled, and not a reaction influenced by interfacial mass transfer.

Analog Computer Simulation

Rate constants in Model 1 were estimated on the analog computer. The values of the rate constants were obtained from potentiometer scales that were adjusted by trial and error until a good visual fit to the experimental data was obtained. Values of the rate constants from analog simulation were used as initial guesses of the parameters when computing the rate constants by regression from Model 1.

Values determined from the analog computer simulation are given in Table 14. The indication is that the rate constant of conversion of coal to preasphaltene k_2 had the highest absolute value of all the rate constants.

When the values of rate constants obtained from analog computer simulation were inserted in the analytical solutions for Model 1, a poor fit to the data was obtained. Thus, rate constant estimation by analog computation was abandoned in favor of estimation by the non-linear parameter estimation computer program.

Reproducibility

Reproducibility of the data was checked at two experimental conditions. The first condition was chosen such that the data was expected to contain the highest degree of uncertainty in temperature and time (400°C, 10 minutes). The values of unreacted coal and yields of preasphaltene and asphaltene as found from PERC analysis on the liquid product was reproducible within 6 percent. Oil and gas yields, however, exhibited a higher variation (40 percent) since errors in analysis were compounded and showed up in the oil and gas yield which was obtained by difference. The second condition was chosen arbitrarily (375°C, 60 minutes). Reproducibility of unreacted coal, preasphaltene and asphaltene were within a maximum of 17 percent, whereas oil and gas yields exhibited a variation of 50 percent. It is not understood why the first condition experiments (potentially high in errors) gave lower variation in concentrations than the second set of experiments. Reproducibility data are shown in Table 15.

Errors in the observed variables could be included in the regression program by reproducing a few more runs and calculating the covariance for each observed variable. The values of the covariance could be utilized in the computer program to generate additional information for construction of a confidence interval on the rate constants.

Mass Transfer Considerations

Mass transfer may play an important role in coal extraction in two ways:

1. Diffusion of solvent or hydrogen into the coal particles before thermolysis (thermal disintegration).
2. Mass transfer resistance due to gas/solid or gas/liquid interfaces.

In the first case, since particles of -200 mesh were used and since the literature reports that disintegration is instantaneous above 350°C, diffusional mass transfer was not expected to have an effect. In the second case, a very high agitation rate (1300 rpm) was maintained to help assure that interfacial mass transfer resistances were minimized. Data on two stirring speeds seems to indicate that this is also not an important parameter in the conversion of coal to soluble products. This data is shown in Table 16.

Interpretation

Model 1 with the six first order irreversible reactions was found to fit the experimental data properly for all four groups of compounds. Rate constant k_2 had the highest value of all rate constants which explains the observed high yield of preasphaltenes at the start of reaction. The model predicts that asphaltene and preasphaltene are products in the preliminary dissolution with preasphaltene being the preferred product. This result is in agreement with literature discussions on the mechanism of coal liquefaction at the beginning of reaction, where thermal cracking is the major contributor to coal dissolution. Other researchers (23) found preasphaltenes to be the preferred product at this early stage of reaction, in agreement with this study. Whitehurst, et al. (24) concluded that at later stages of reaction, preasphaltene was converted to asphaltene and oil with oil being the favored product. However, their experiments were carried out with no solvent. In this study as the reaction proceeded, preasphaltenes were converted to asphaltene and oil plus gases with comparable rates.

The mathematical model arrived at in the present work and the corresponding mechanism associated with it represent the data well from a macroscopic point of view. But the model cannot explain the microscopic mechanism of coal liquefaction which is complex and so far has not been clearly determined. The individual rate constants can be further investigated by using preasphaltenes or asphaltenes as reactants and carrying out the extraction to determine the rate constants more precisely.

The experimental data indicate that stable molecules of both preasphaltene and asphaltene have been formed that would not disintegrate further. In other words, at long reaction times, there still will be finite concentrations of preasphaltene and asphaltene, rather than zero as the mathematical model predicts. It is clear that this model will only apply in the time range studied (0-180 minutes) and extrapolation of the model outside this time frame is not valid.

Examination of Figure 26 and the rates estimated from model 3, leads to the conclusion that perhaps k_3 has been improperly estimated in value leading to the drastic decrease in the predicted value of preasphaltene at 400°C (Figure 26). To check on the effect of changing k_3 on the fit, the computer program was run while k_3 was constrained at two values, .00284, .0265 which were the estimated values of k_5 (preasphaltene to oil) and k_3 (coal to oil) in model 1. The visual fit of the predicted curves to the experimental data as shown in Figures 35-36 is better than the fit shown in Figure 26, although the residuals reported for both of these fits are larger than the residual for the original unconstrained model (Table 17). In Figure 26 both unreacted coal and asphaltene fitted the experimental data throughout the time studied, while in Figures 35-36, the coal extraction products fitted the experimental data only at small values of time. This explains why the visual fit for Figure 26 is worse than for Figures 35 and 36 while the residuals from regression for Figure 26 are considerably lower than for either Figures 35 or 36.

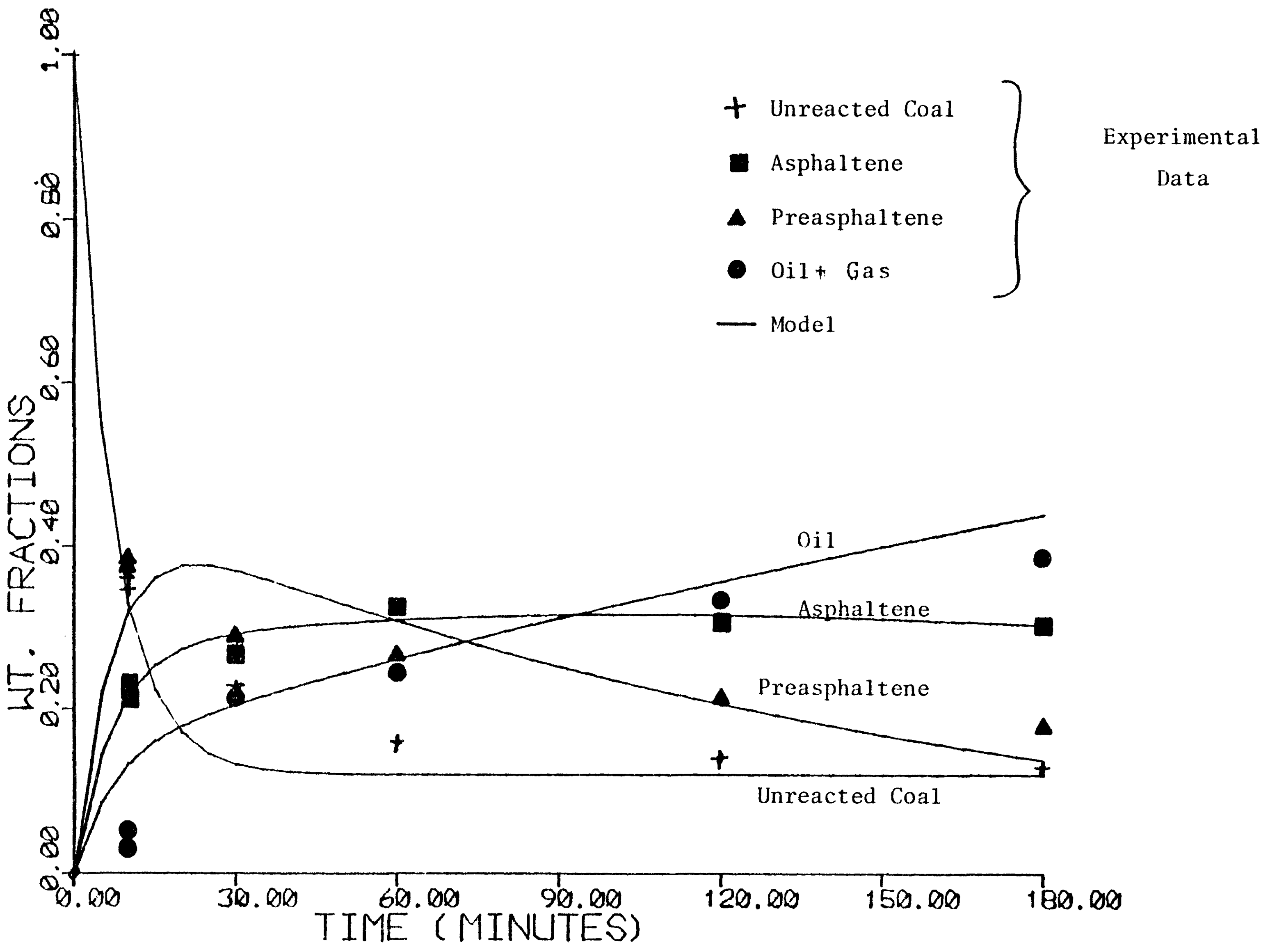


Figure 20. Model 1 at 400°C.

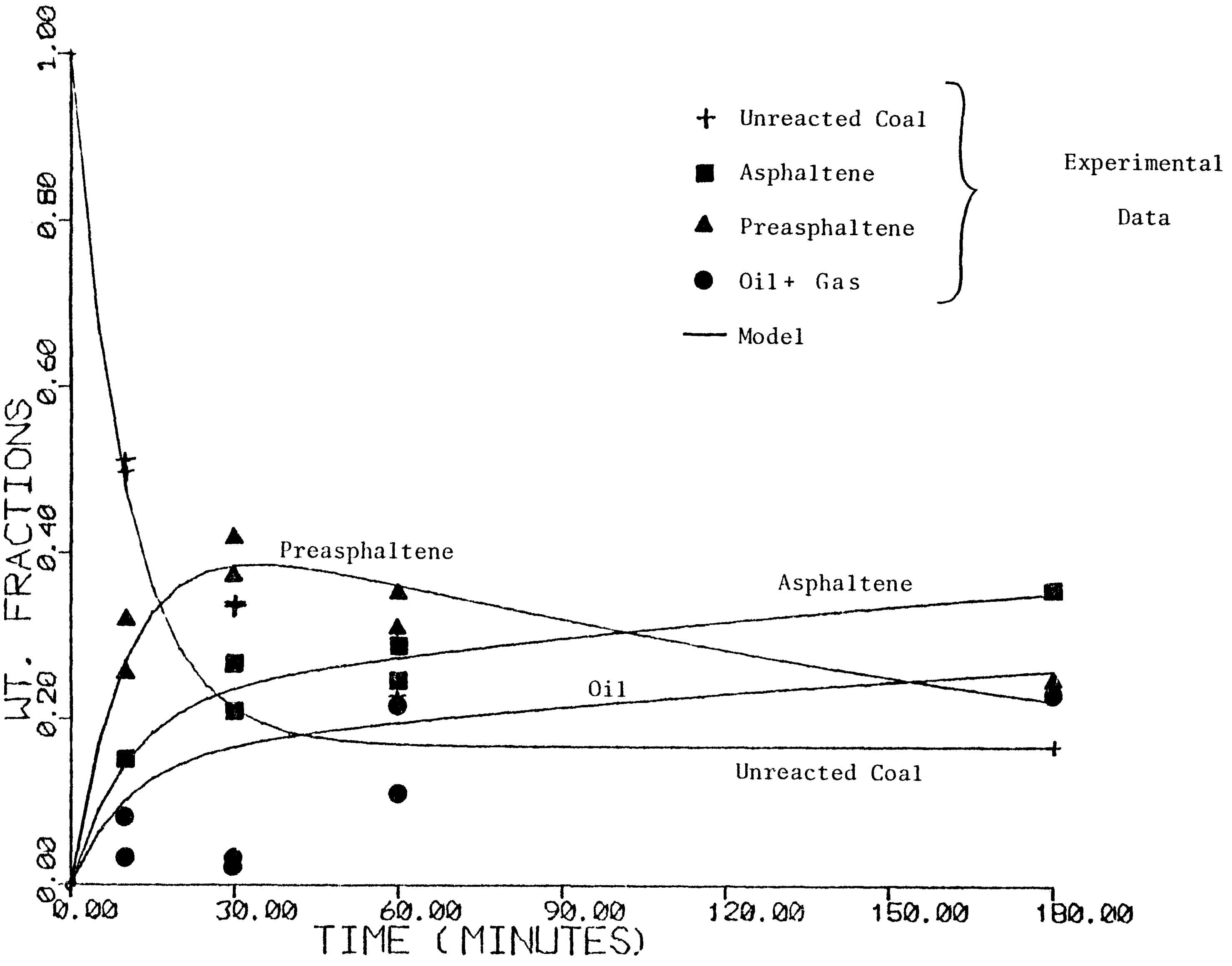


Figure 21. Model 1 at 375°C.

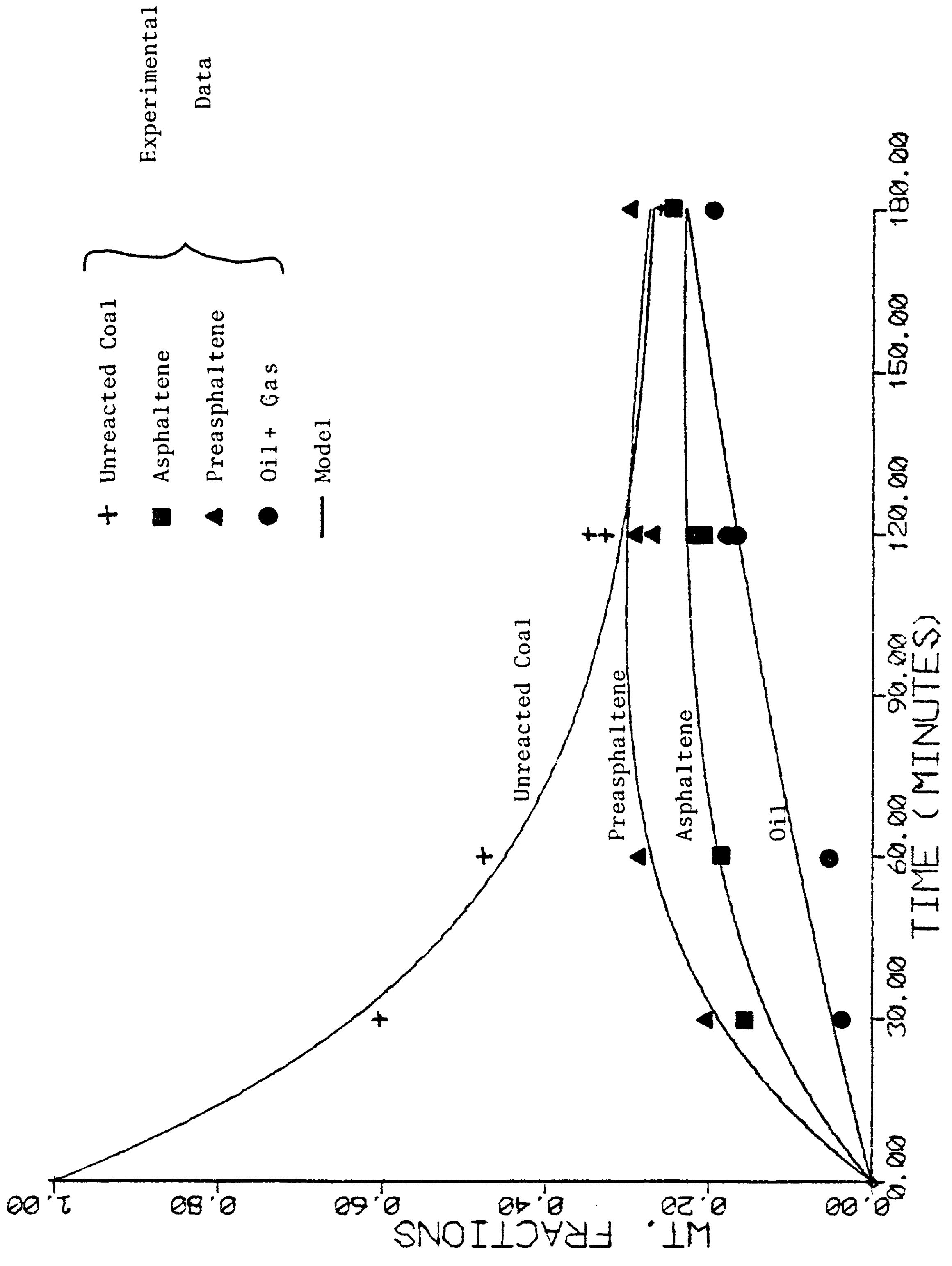


Figure 22. Model 1 at 350°C.

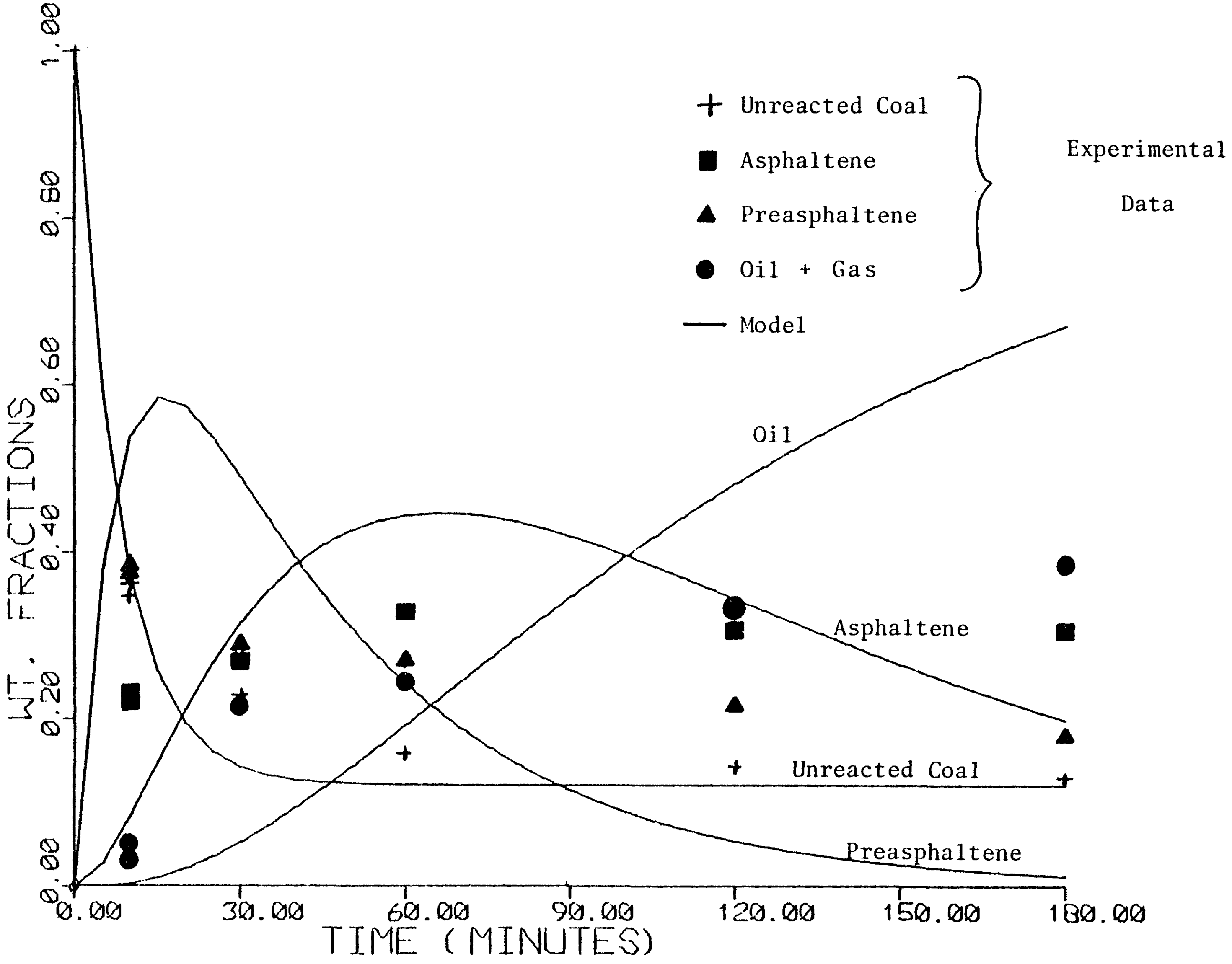


Figure 23. Model 2 at 400°C.

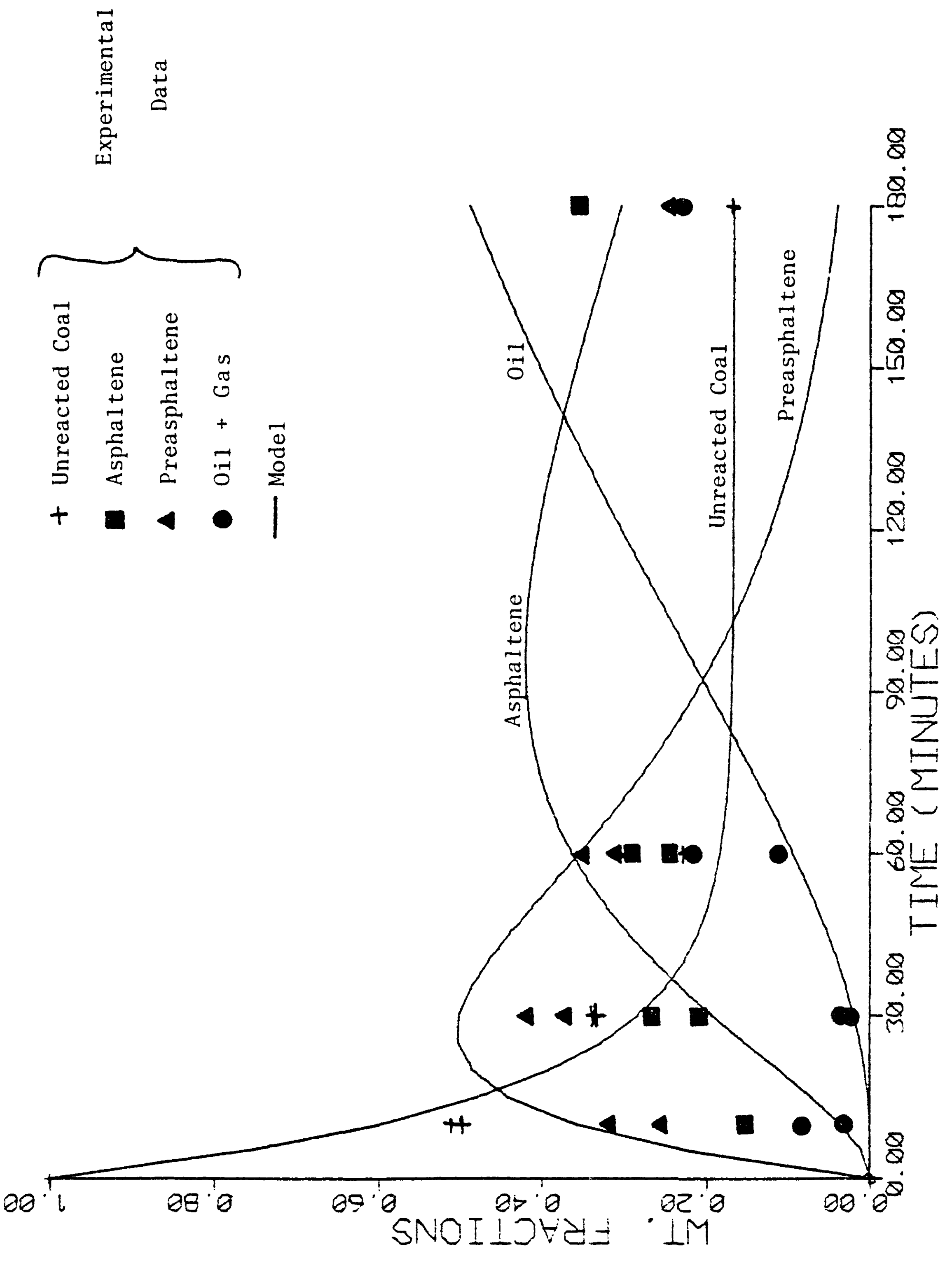


Figure 24. Model 2 at 375°C.

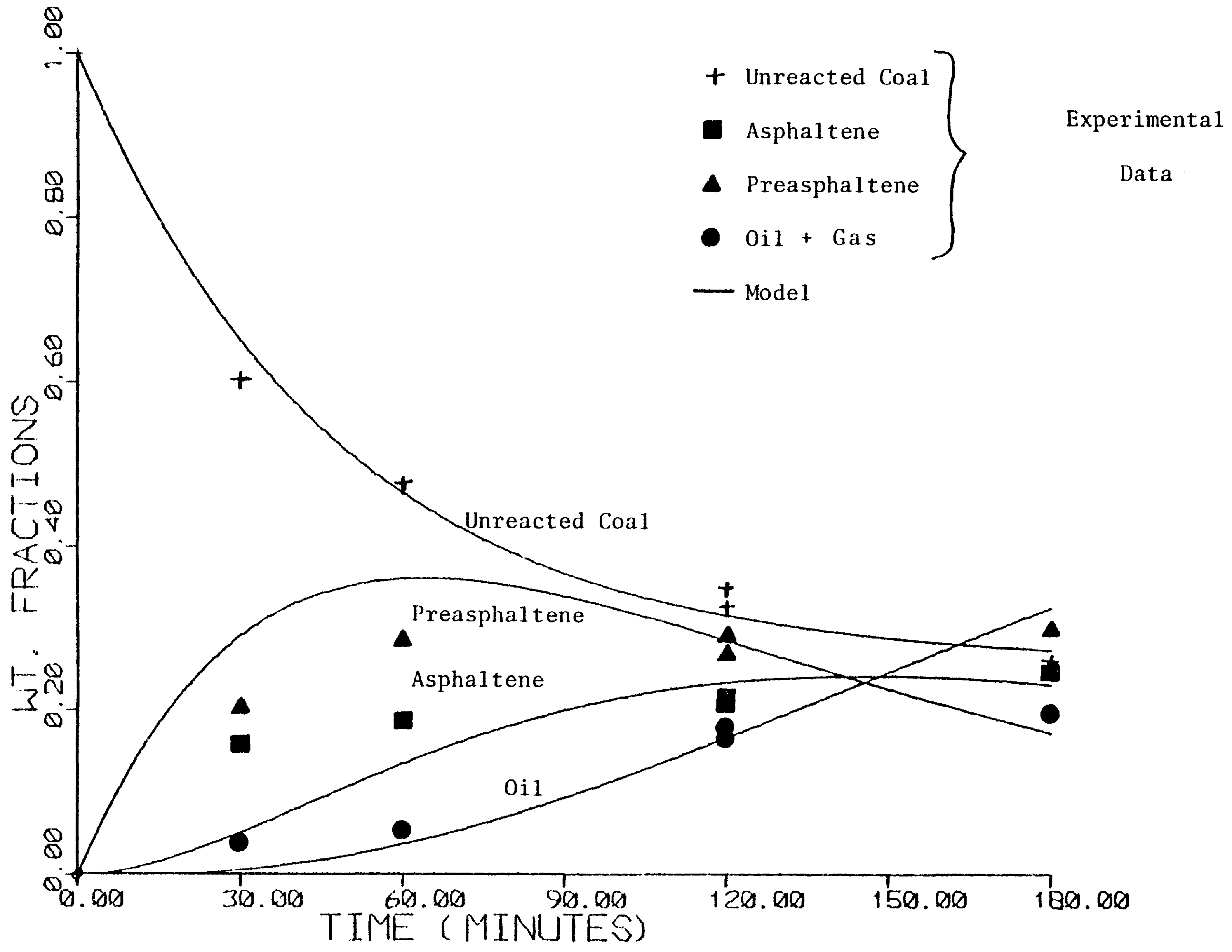


Figure 25. Model 2 at 350°C.

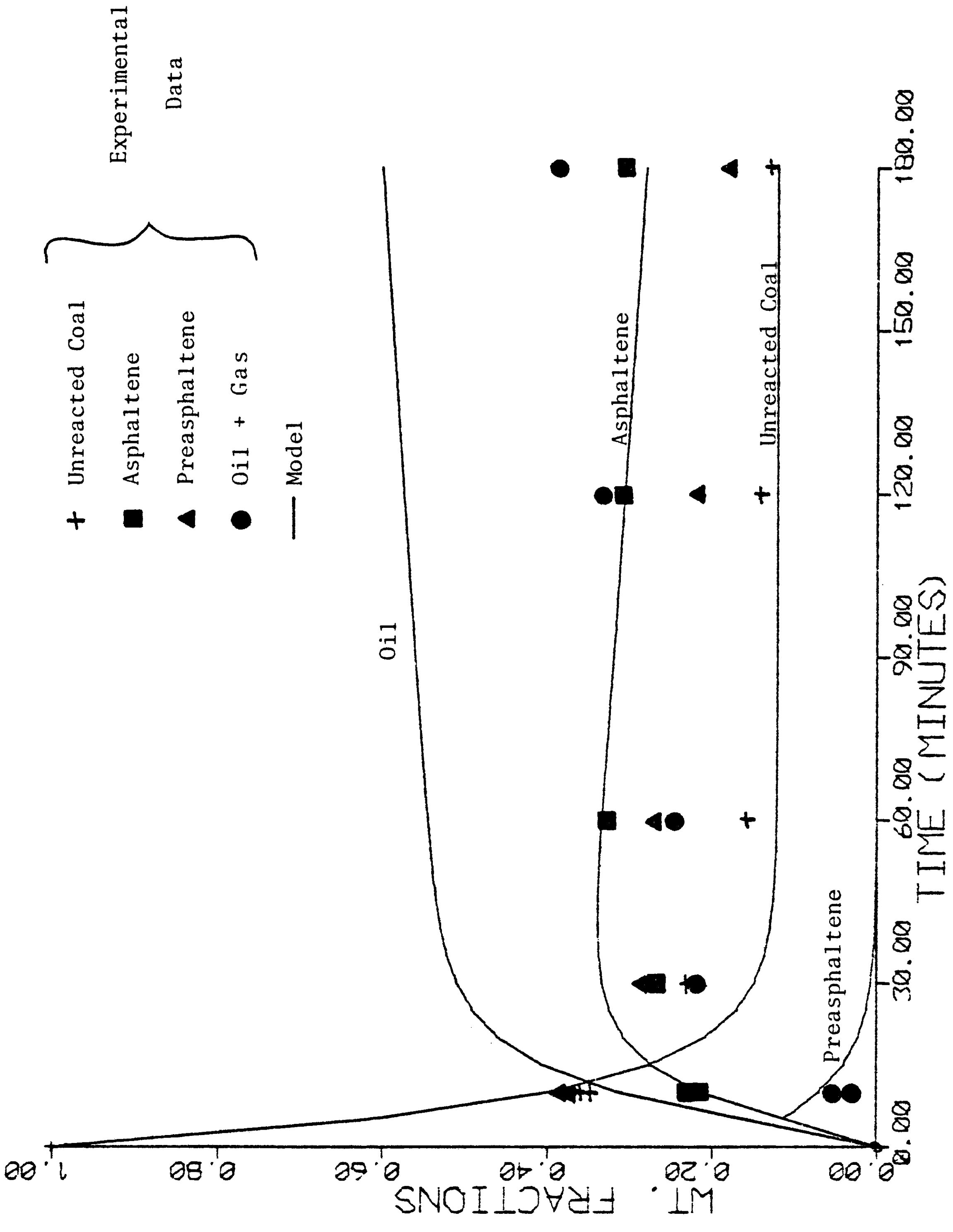


Figure 26. Model 3 at 400°C.

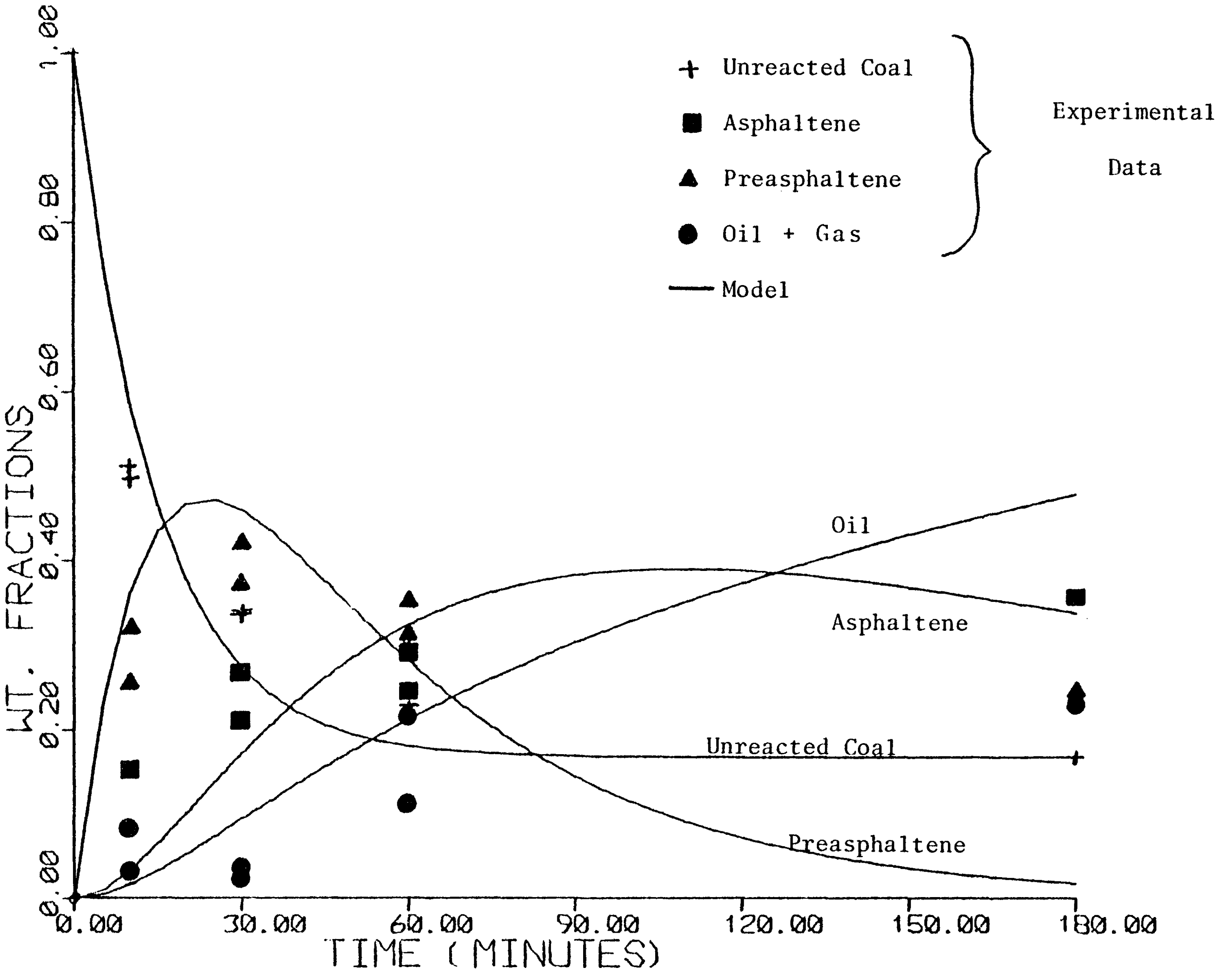


Figure 27. Model 3 at 375°C.

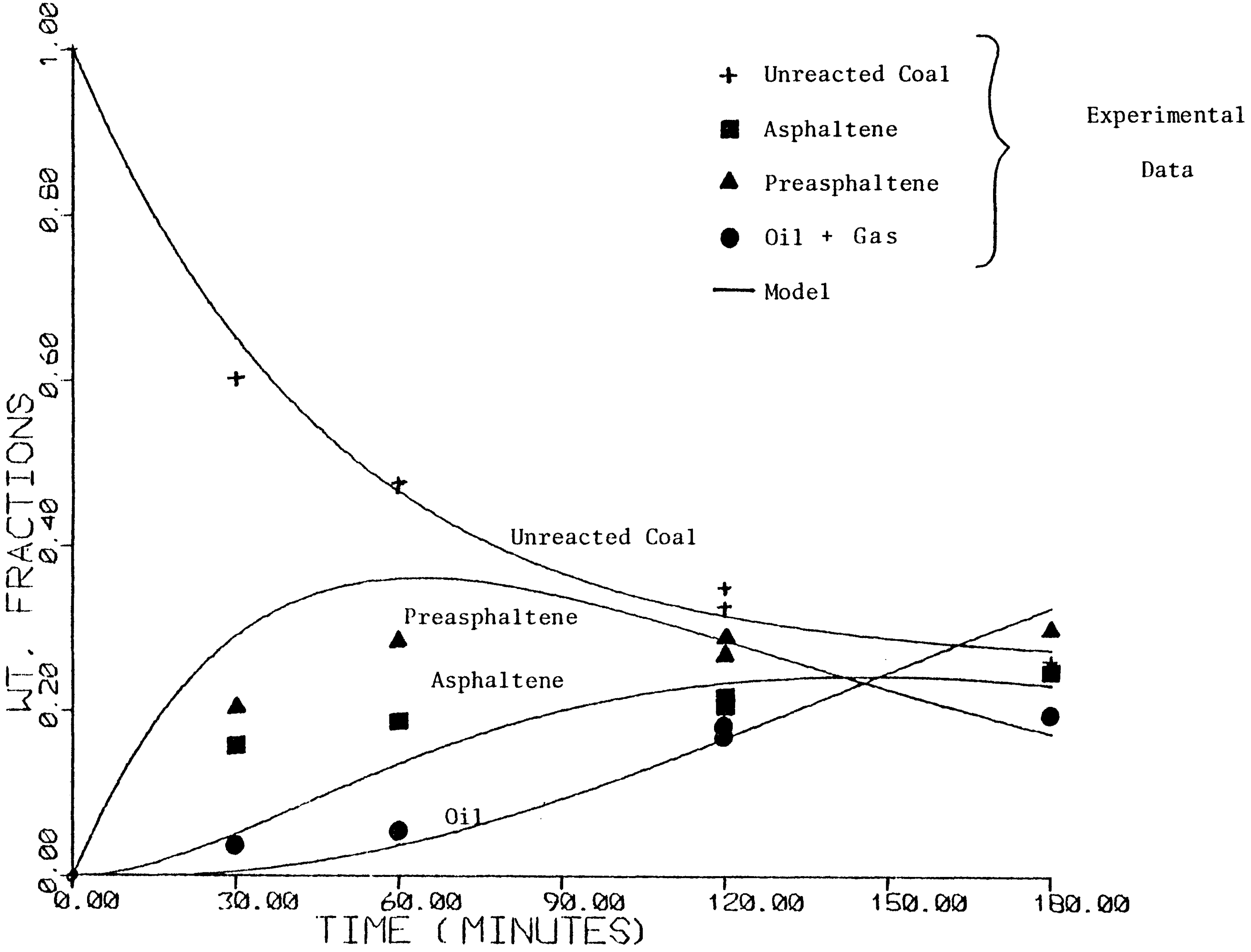


Figure 28. Model 3 at 350°C.

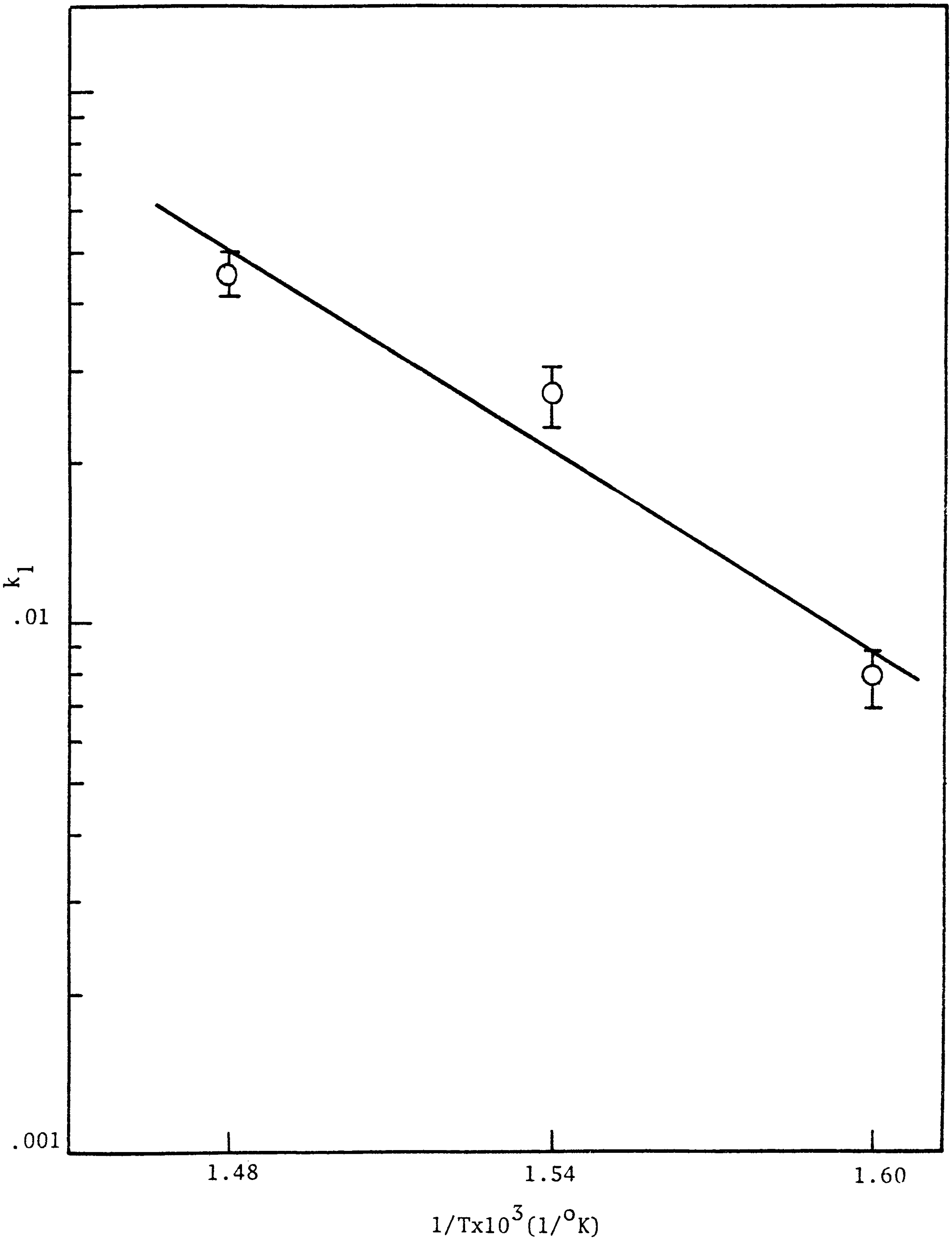


Figure 29. Activation Energy for Conversion of Coal to Asphaltene (k_1).

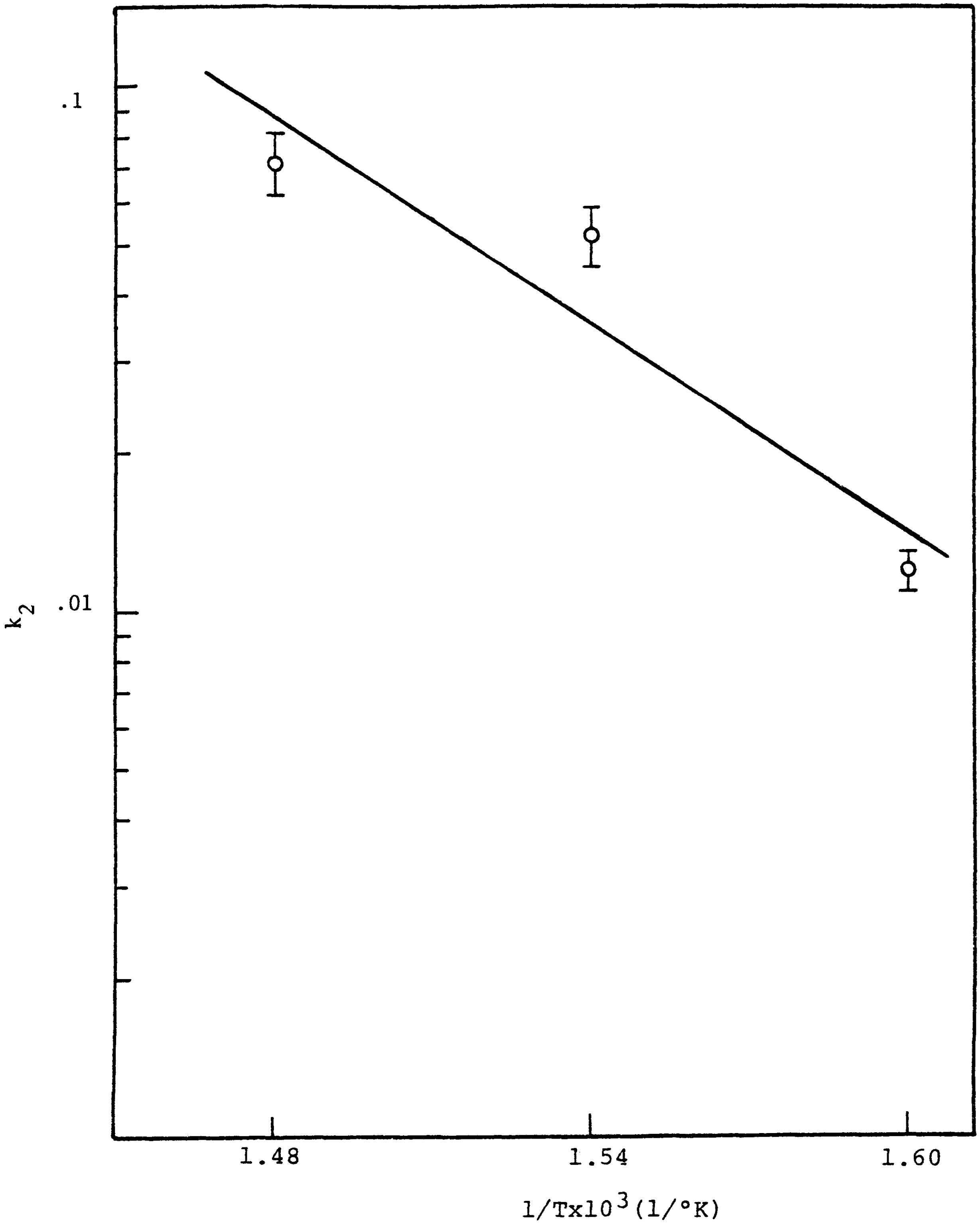


Figure 30. Activation Energy for Conversion of Coal to Preasphaltene (k_2).

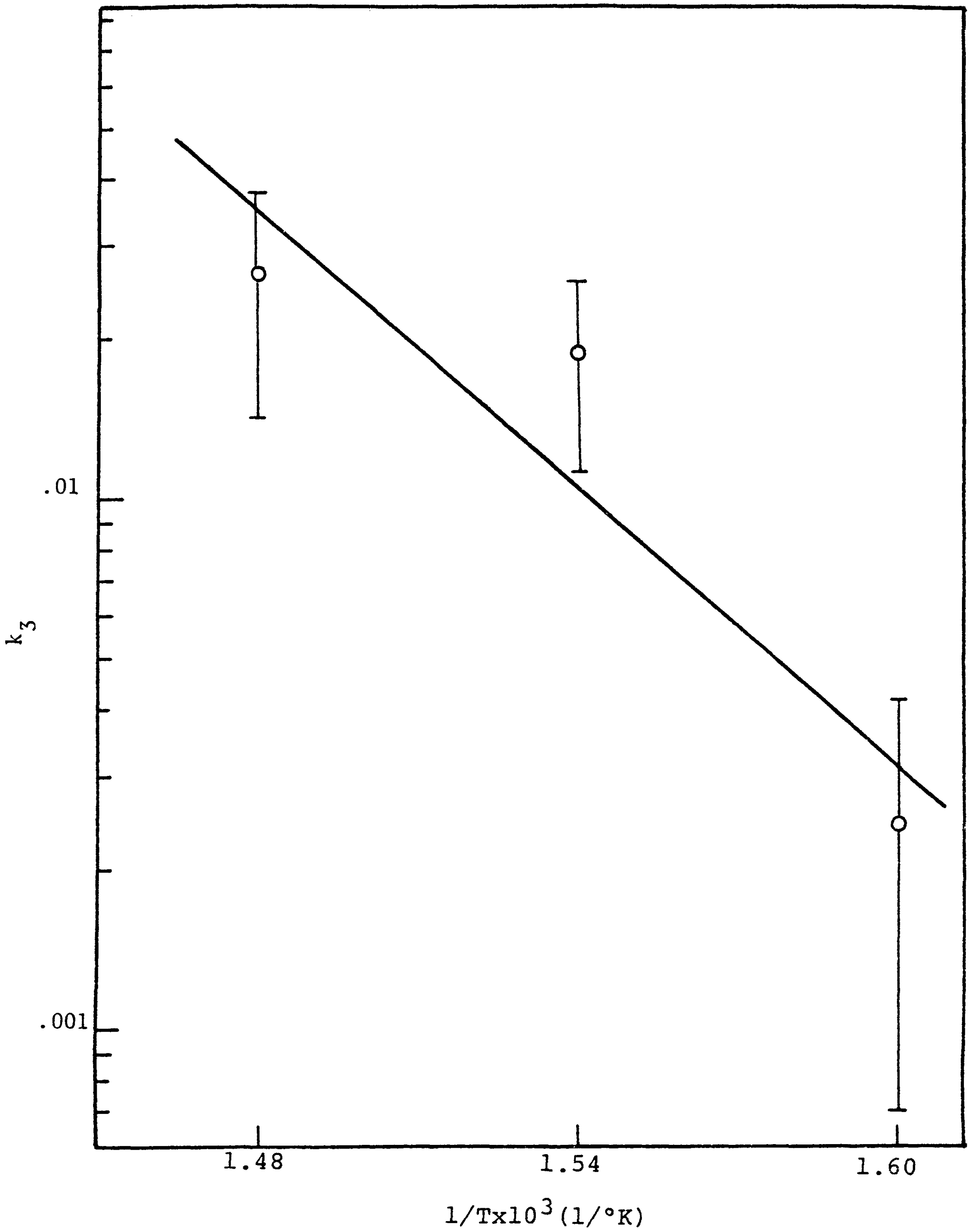


Figure 31. Activation Energy for Conversion of Coal to Oil and Gas (k_3).

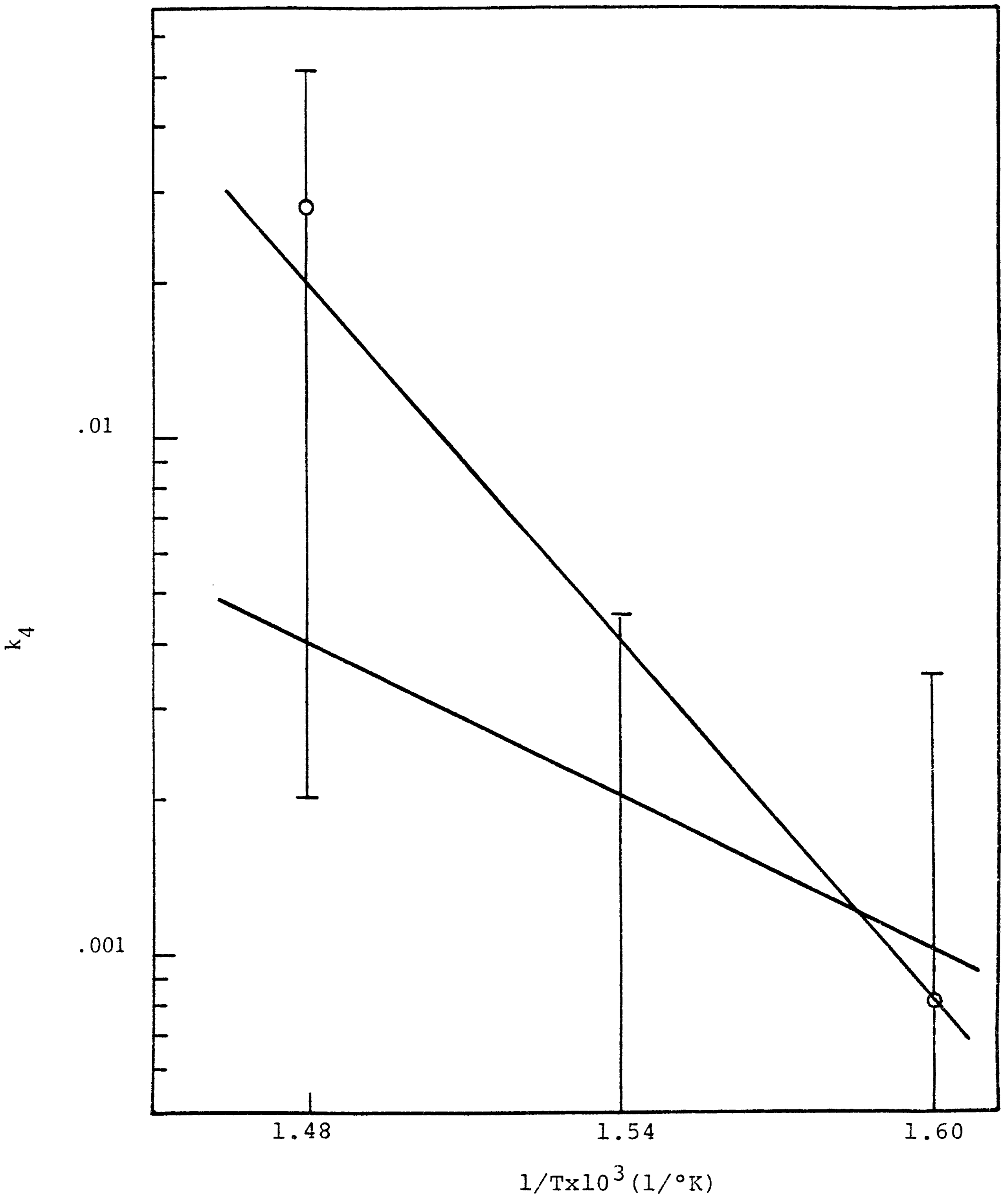


Figure 32. Estimation of Activation Energy for Conversion of Asphaltene to Oil and Gas (k_4).

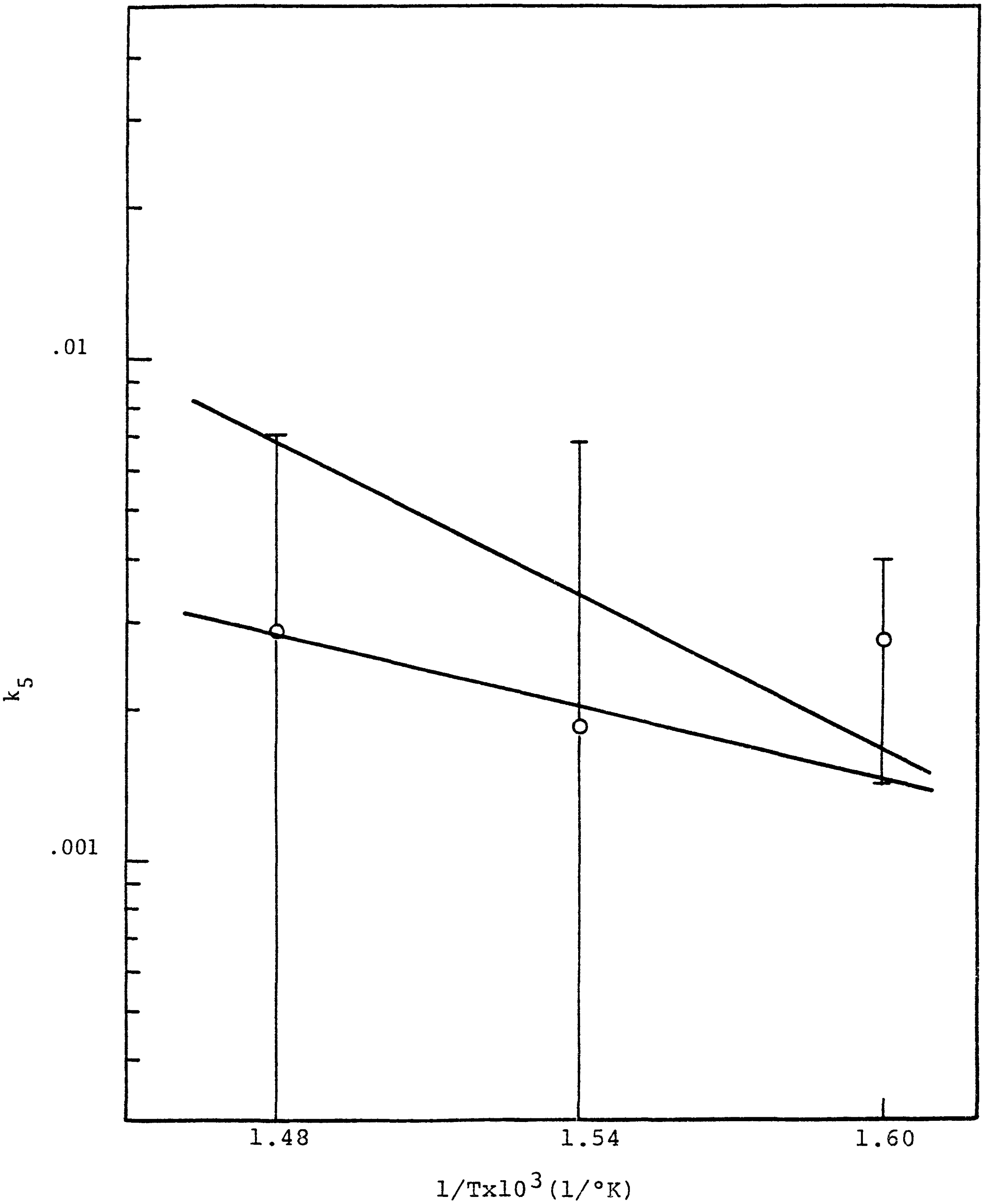


Figure 33. Estimation of Activation Energy for Conversion of Preasphaltene to Oil and Gas (k_5).

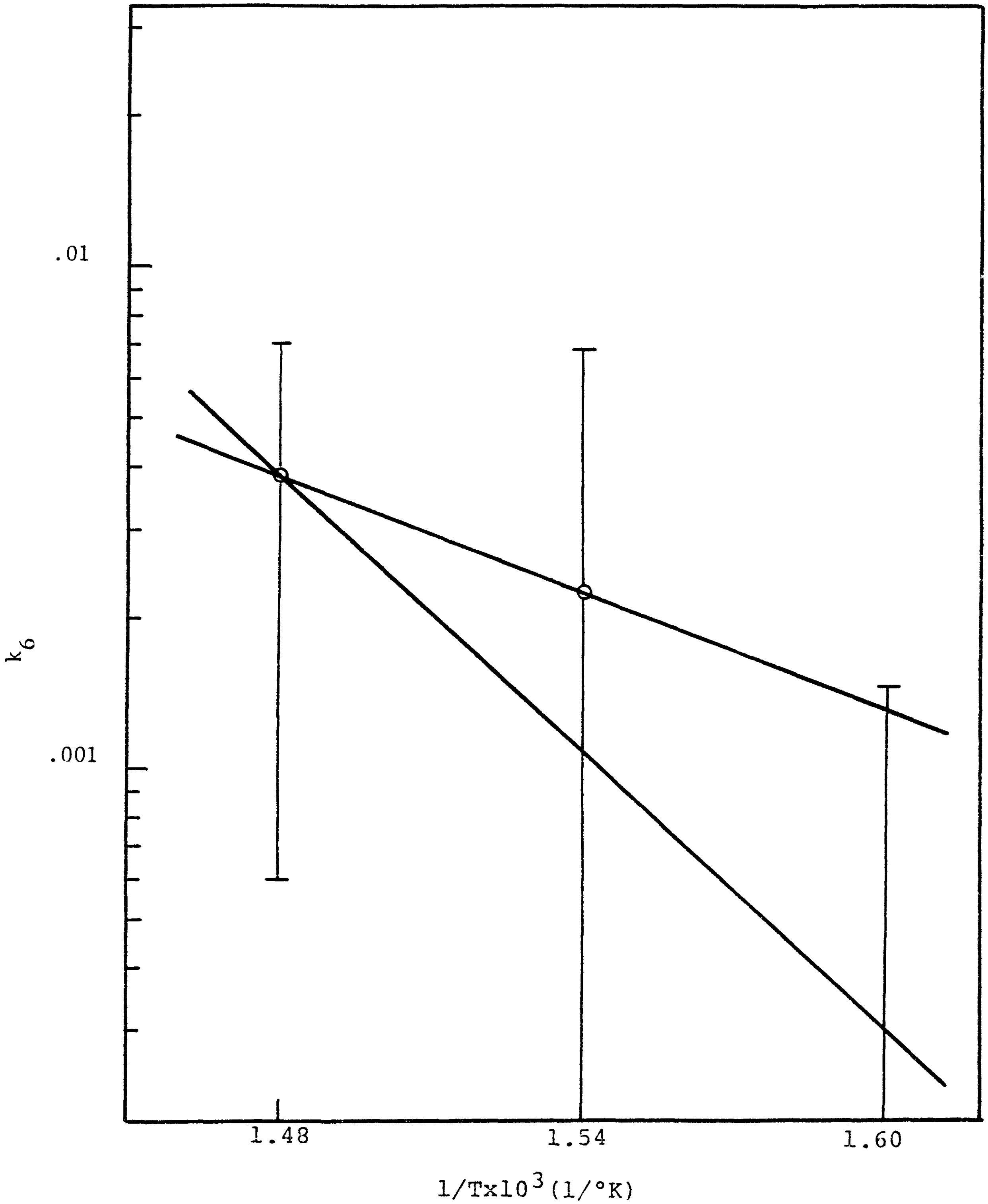


Figure 34. Estimation of Activation Energy for Conversion of Preasphaltene to Asphaltene (k_6).

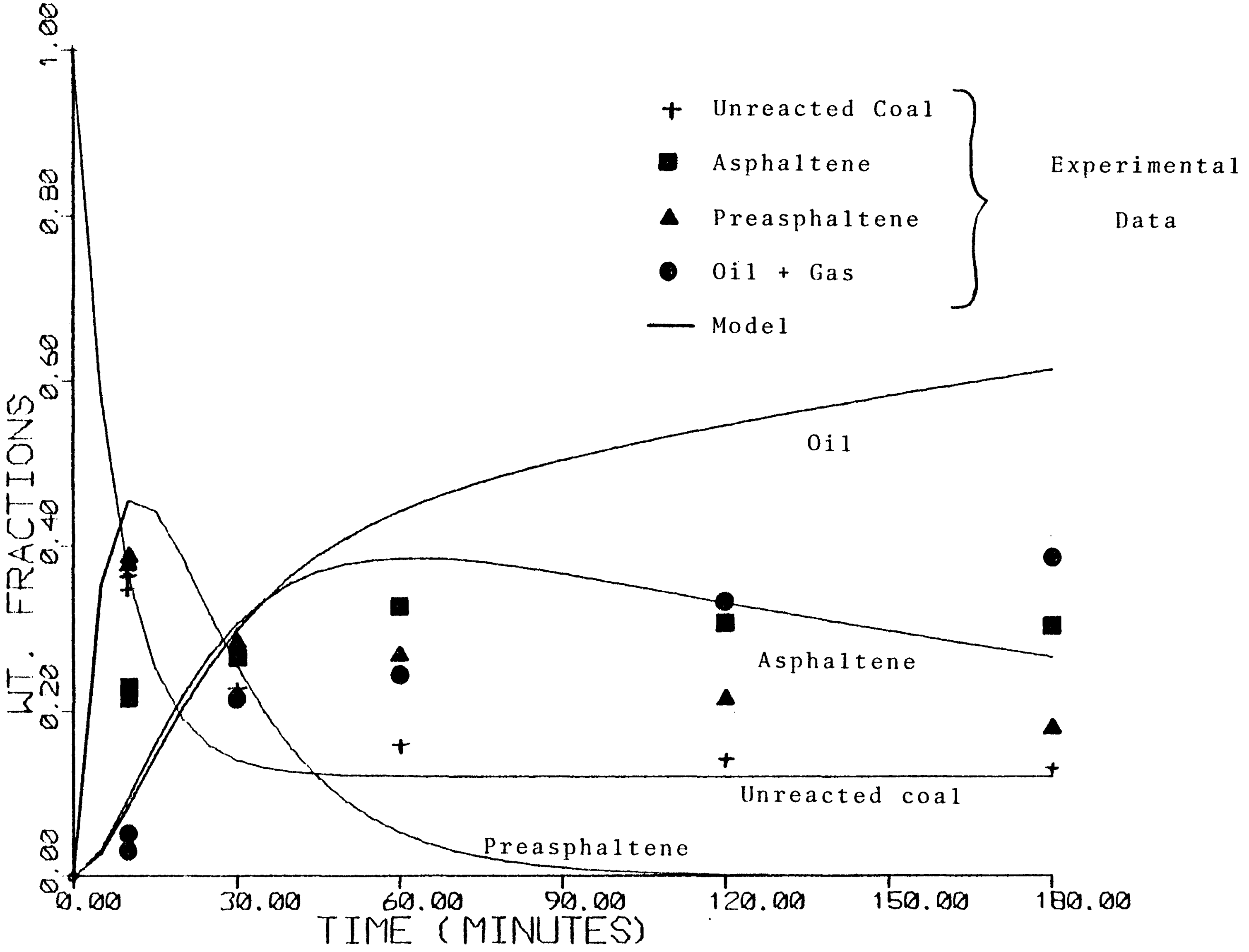


Figure 35. Model 3 at 400°C (k_3 constrained to 0.026).

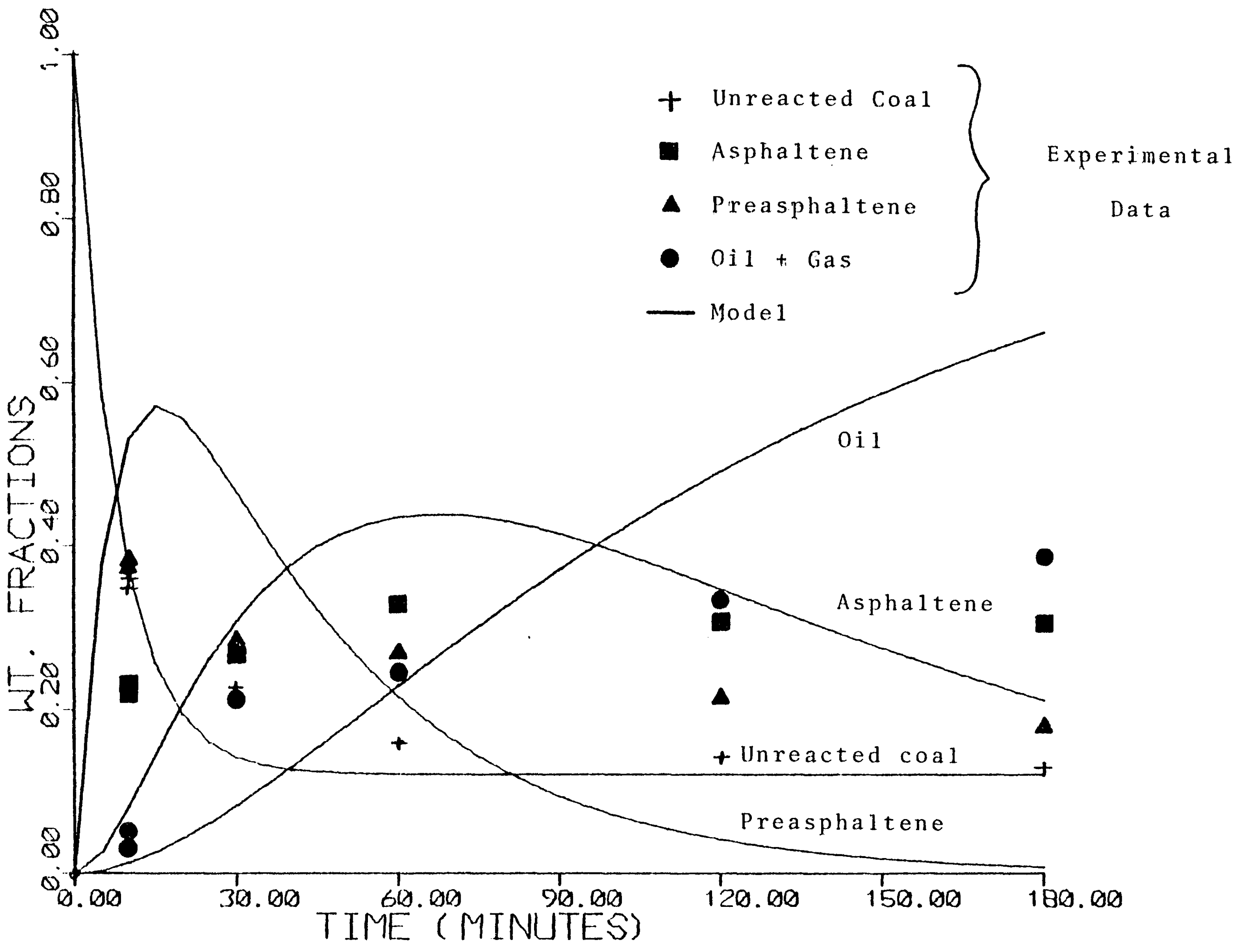


Figure 36. Model 3 at 400°C (k_3 constrained to 0.0028).

Table 9

Rate Constants and Their Standard Deviations Estimated From Computer Program (Model 1)

Temperature	k_1	k_2	k_3	k_4	k_5	k_6
400°C	.04546 ± .00415	.07150 ± .01026	.02646 ± .01212	.00279 ± .00257	.00284 ± .00437	.00385 ± .00328
375°C	.02697 ± .00337	.05202 ± .0070.	.01870 ± .00787	$.76\text{x}10^{-10}$ ± .00454	.00183 ± .00461	.00225 ± .00460
350°C	.00789 ± .00092	.01214 ± .00101	.01214 ± .0017	.00081 ± .00278	.00269 ± .00121	$.45\text{x}10^{-10}$ ± .00148

Table 10

Rate Constants and Their Standard Deviations

Estimated from Computer Program (Model 2)

Temperature	k_1	k_2	k_3
400°C	.12393 ± .01174	.02529 ± .00789	.01174 ± .00288
375°C	.06535 ± .00991	.01877 ± .00384	.00855 ± .00267
350°C	.02116 ± .00158	.01136 ± .002	.01105 ± .00298

Table 11

Rate Constants and Their Standard Deviations

Estimated from Computer Program (Model 3)

Temperature	k_1	k_2	k_3	k_4
400°C	.11508 ± .00074	.23356 ± .00649	.33807 ± .00794	.00148 ± .00103
375°C	.06853 ± .00968	.01632 ± .00364	.00780 ± .00622	.00396 ± .00354
350°C	.02117 ± .00116	.01136 ± .00554	$.45\text{x}10^{-8}$ ± .00528	.01105 ± .00873

Table 12

Determinant of Moment Matrix of Residuals

	400°C	375°C	350°C	
Model 1	.23377 x10^{-6}	.89364 x10^{-6}	.17227 x10^{-7}	
Model 2	.10154 x10^{-3}	.12759 x10^{-3}	.17437 x10^{-5}	
Model 3	.24885 x10^{-4}	.10084 x10^{-3}	.17437 x10^{-5}	

Table 13

Estimation of Pre-exponential Factors and Activation Energies

	ln k_0	E K Cal/g. mole	r^2
k_1	18.9418	29.32	0.95
k_2	19.8093	29.78	0.89
k_3	26.7199	40.22	0.87
k_4	11.73-36.15	23.09-53.62	
k_5	2.31-12.63	10.96-23.59	
k_6	7.95-26.04	18.08-42.30	

Table 14

Estimation of Rate Constants by Analog Computer

Temperature	400°C	375°C
Rate Constants (min.$^{-1}$)		
k_1	.0142	.0058
k_2	.0691	.0622
k_3	.0167	.0146
k_4	.0259	.0229
k_5	.0205	.0166
k_6	.0323	.0272

Table 15

Reproducibility Data

			Yield %			
Run	Time (Minutes)	Temp. °C	A	B	C	D
4	10	400	36.6	22.9	37.5	3.0
7	10	400	34.5	21.7	38.5	5.2
8	60	375	22.6	24.5	30.7	22.2
12	60	375	24.3	29.2	35.2	11.3

Table 16

Mass Transfer Effects

Run no.	5	17
Agitation Speed (R.P.M.)	1300	200
	% Concentration	
Unreacted Coal	12.9	13.5
Asphaltene	30.5	31.6
Preasphaltene	17.8	12.7
Oil (difference)	38.8	42.2

Table 17

Rate Constants and Residuals Estimated from Computer Program (Model 3 with constrained k_3 at 400°C).

k_1	k_2	k_3	k_4	Determinant of Moment Matrix of Residuals
.1241	.0248	.00284	.01003	$.91 \times 10^{-4}$
.1268	.0304	.02646	.00371	$.54 \times 10^{-4}$

Table 18. Calculated Data at 400°C Isotherm, Weight Fractions *

Time, Minutes	10	10	30	60	120	180
Unreacted Coal	.366	.348	.227	.158	.142	.130
Asphaltenes	.229	.217	.270	.328	.308	.305
Preasphaltenes	.375	.383	.283	.268	.215	.179
Oil (by difference)	.03	.052	.22	.246	.335	.386

* Ash-free basis

Table 19. Calulated Data at 375°C Isotherm, Weight Fractions *

Time, Minutes	10	10	30	30	60	60	180
Unreacted Coal	.497	.511	.335	.338	.226	.243	.168
Asphaltenes	.151	.151	.267	.209	.245	.292	.356
Preasphaltenes	.319	.255	.372	.419	.307	.352	.244
Oil (by difference)	.033	.083	.026	.034	.222	.113	.232

* Ash-free basis

Table 20. Calulated Data at $350^{\circ}C$ Isotherm, Weight Fractions*

Time, Minutes	30	60	120	120	180
Unreacted Coal	.602	.475	.327	.348	.258
Asphaltenes	.157	.186	.206	.215	.249
Preasphaltenes	.203	.285	.289	.268	.297
Oil (by difference)	.038	.054	.178	.169	.196

*Ash-free basis

CONCLUSIONS

From this study of coal liquefaction, the following conclusions have been arrived at:

1. Preasphaltenes were the predominant product during the early stages of liquefaction (first 10 minutes).
2. The experimental data indicate that stable molecules of both preasphaltenes and asphaltenes have been formed.
3. Mass transfer resistance was negligible in effecting the rate constants.
4. High activation energies of the individual reaction rates meant that these reactions are kinetically controlled and not influenced by interfacial mass transfer.
5. Six first order reaction models adequately fit the experimental data.

RECOMMENDATIONS FOR FUTURE WORK

Investigating temperatures outside the range 350°-400°C would be interesting to obtain with different equipment capable of withstanding higher pressures. Using the pressure as a variable is another possible extension of the present work. The distribution and rate of reaction of sulfur and nitrogen in the various products of coal extraction is also worth further examination. If it is possible to have enough material of preasphaltene or asphaltene to start the extraction from these compounds and proceed to obtain oil, this would be another approach in determining the rate of dissociation of these compounds.

Mass transfer effects need to be investigated further in detail. This will be accomplished by conducting several runs at the same conditions except with different rates of mixing and particle sizes. Such an experiment would be best conducted in continous processing equipment.

Further modeling of the process needs to be done in order to incorporate pseudo-reversibility into asphaltenes and preasphaltenes, as was done for unreacted coal. A model that can account for the formation of stable, unreactive species needs to be investigated.

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APPENDIX I

RAW DATA

Run No. 1
Temperature = 400°C
*Wt. of reactor + solvent = 10795
Wt. of reactor + solvent + products = 10816
Wt. of empty reactor = 10613

Reaction time = 1 hour
Final Pressure = 2060 psig

*Product sample I = 22.19
Benzene insol. = .66
Pentane insol. = .26
Sample A benz ins.= .3809
Sample A THF ins. = .2373
Sample B benz ins.= .2296
Sample B THF ins. = .1518
Sample AA ashed = .2283
Ash in sample AA = .1432
Sample BB ashed = .1352
Ash in sample BB = .099

Product sample II = 21.28
Benzene insol. = .62
Pentane insol. = .25
Sample A benz. ins. = .309
Sample A THF ins. = .193
Sample B benz. ins. = .2753
Sample B THF ins. = .182
Sample AA ashed = .1857
Ash in sample AA = .12
Sample BB ashed = .175
Ash in sample BB = .1219

Run No. 2
Temperature = 400°C
Wt. of reactor + solvent = 10822
Wt. of reactor + solvent + products = 10839
Wt. of empty reactor = 10639

Reaction time = 2 hour
Final Pressure = 2200 psig

Product sample I = 24.8
Benzene insol. = .54
Pentane insol. = .25
Sample A benz ins.= .2412
Sample A Thf ins. = .1635
Sample B benz ins.= .2927
Sample B THF ins. = .2024
Sample AA ashed = .3442
Ash in sample AA = .2397
Sample BB ashed =
Ash in sample BB =

Product sample II = 20.78
Benzene insol. = .43
Pentane insol. = .20
Sample A benz. ins. = .2245
Sample A THF ins. = .1553
Sample B benz. ins. = .2114
Sample B THF ins. = .1441
Sample AA ashed = .2841
Ash in Sample AA = .1986
Sample BB ashed =
Ash in sample BB =

*weights in grams

Run No. 3 Reaction time = 1/2 hour
Temperature = 400°C Final Pressure = 2000 psig
Wt. of reactor + solvent = 10731
Wt. of reactor + solvent + products = 10762
Wt. of empty reactor = 10549

Product sample I = 22.95
Benzene insol. = .84
Pentane insol. = .27
Sample A benz ins.= .4693
Sample A THF ins. = .2903
Sample B benz ins.= .3621
Sample B THF ins. = .2421
Sample AA ashed = .25
Ash in sample AA = .1379
Sample BB ashed = .2321
Ash in sample BB = .1425

Product sample II = 21.62
Benzene insol. = .79
Pentane insol. = .25
Sample A benz. ins. = .3702
Sample A THF ins. = .2334
Sample B benz. ins. = .3824
Sample B THF ins. = .2535
Sample AA ashed = .21
Ash in sample AA = .1131
Sample BB ashed = .2472
Ash in sample BB = .1437

Run No. 4 Reaction time = 10 minutes
Temperature = 400°C Final Pressure = 2280 psig
Wt. of reactor + solvent = 10734
Wt. of reactor + solvent + products = 10766
Wt. of empty reactor = 10552

Product sample I = 19.21
Benzene insol. = .90
Pentane insol. = .17
Sample A benz ins.= .3307
Sample A Thf ins. = .2148
Sample B benz ins.= .4918
Sample B THF ins. = .3320
Sample AA ashed = .5223
Ash in sample AA = .25
Sample BB ashed =
Ash in sample BB =

Product sample II = 19.93
Benzene insol. = .93
Pentane insol. = .22
Sample A benz. ins. = .2907
Sample A THF ins. = .1591
Sample B benz. ins. = .5849
Sample B THF ins. = .4306
Sample AA ashed = .5721
Ash in Sample AA = .2747
Sample BB ashed =
Ash in sample BB =

Run No. 5 Reaction time = 3 hours
Temperature = 400°C Final Pressure = 2400 psig
Wt. of reactor + solvent = 10732
Wt. of reactor + solvent + products = 10763
Wt. of empty reactor = 10549

Product sample I =	20.6	Product sample II =	20.51
Benzene insol. =	.56	Benzene insol. =	.54
Pentane insol. =	.29	Pentane insol. =	.28
Sample A benz ins.=	.2391	Sample A benz. ins. =	.2681
Sample A THF ins. =	.1678	Sample A THF ins. =	.1917
Sample B benz ins.=	.2751	Sample B benz. ins. =	.2446
Sample B THF ins. =	.2051	Sample B THF ins. =	.1785
Sample AA ashed =	.3625	Sample AA ashed =	.3525
Ash in sample AA =	.2619	Ash in sample AA =	.2545
Sample BB ashed =		Sample BB ashed =	
Ash in sample BB =		Ash in sample BB =	

Run No. 6 Reaction time = 1 hour
Temperature = 400°C Final Pressure = 2280 psig
Wt. of reactor + solvent = 10731
Wt. of reactor + solvent + products = 10764
Wt. of empty reactor = 10549

Product sample I =	19.77	Product sample II =	20.36
Benzene insol. =	.70	Benzene insol. =	.72
Pentane insol. =	.29	Pentane insol. =	.32
Sample A benz ins.=	.3651	Sample A benz. ins. =	.3327
Sample A Thf ins. =	.2351	Sample A THF ins. =	.22
Sample B benz ins.=	.3406	Sample B benz. ins. =	.3569
Sample B THF ins. =	.2226	Sample B THF ins. =	.2268
Sample AA ashed =		Sample AA ashed =	
Ash in sample AA =		Ash in Sample AA =	
Sample BB ashed =	.2156	Sample BB ashed =	.221
Ash in sample BB =	.1495	Ash in sample BB =	.1473

Run No. 7
Reaction time = 10 minutes
Temperature = 400°C
Final Pressure = 2230 psig
Wt. of reactor + solvent = 10731
Wt. of reactor + solvent + products = 10765
Wt. of empty reactor = 10549

Product sample I = 21.91
Benzene insol. = 1.05
THF insoluble = .65
Pentane insol. = .22
Sample ashed = .6234
Ash in sample = .3111

Product sample II = 22.03
Benzene insol. = 1.07
THF insoluble = .71
Pentane insol. = .21
Sample ashed = .6128
Ash in sample = .297

Run No. 8
Reaction time = 1 hour
Temperature = 375°C
Final Pressure = 1950 psig
Wt. of reactor + solvent = 10733
Wt. of reactor + solvent + products = 10766
Wt. of empty reactor = 10551

Product sample I = 21.9
Benzene insol. = 1.18
THF insoluble = .75
Pentane insol. = .34
Sample ashed = .7207
Ash in sample = .4321

Product sample II = 22.02
Benzene insol. = 1.02
THF insoluble = .79
Pentane insol. = .33
Sample ashed = .7309
Ash in sample = .4361

Run No. 9
Temperature = 375°C
Reaction time = 1/2 hour
Final Pressure = 2000 psig
Wt. of reactor + solvent = 10733
Wt. of reactor + solvent + products = 10765
Wt. of empty reactor = 10551

Product sample I = 21.83
Benzene insol. = 1.03
THF insoluble = .66
Pentane insol. = .27
Sample ashed = .6246
Ash in sample = .3144

Product sample II = 20.43
Benzene insol. = .96
THF insoluble = .62
Pentane insol. = .24
Sample ashed = .5791
Ash in sample = .2893

Run No. 9 (repeated analysis)
Temperature = 375°C
Reaction time = 1/2 hour
Final Pressure = 2000 psig
Wt. of reactor + solvent = 10733
Wt. of reactor + solvent + products = 10765
Wt. of empty reactor = 10551

Product sample I = 20.12
Benzene insol. = .97
THF insoluble = .62
Pentane insol. = .19
Sample ashed = .5871
Ash in sample = .2942

Product sample II = 20.33
Benzene insol. = .96
THF insoluble = .57
Pentane insol. = .18
Sample ashed = .5677
Ash in sample = .282

Run No. 10 Reaction time = 10 minutes
Temperature = 375°C Final Pressure = 1900 psig
Wt. of reactor + solvent = 10733
Wt. of reactor + solvent + products = 10764
Wt. of empty reactor = 10551

Product sample I = 21.11 Product sample II = 22.44
Benzene insol. = 1.26 Benzene insol. = 1.37
THF insoluble = .99 THF insoluble = 1.03
Pentane insol. = .18 Pentane insol. = .18
Sample ashed = .9105 Sample ashed = .9382
Ash in sample = .3621 Ash in sample = .3724

Run No. 10 (repeated analysis) Reaction time = 10 minutes
Temperature = 375°C Final Pressure = 1900 psig
Wt. of reactor + solvent = 10733
Wt. of reactor + solvent + products = 10764
Wt. of empty reactor = 10551

Product sample I = 20.76 Product sample II = 21.68
Benzene insol. = 1.3 Benzene insol. = 1.37
THF insoluble = .94 THF insoluble = .99
Pentane insol. = .17 Pentane insol. = .18
Sample ashed = .899 Sample ashed = .9554
Ash in sample = .3632 Ash in sample = .386

Run No. 11 Reaction time = 3 hour
Temperature = 375°C Final Pressure = 2050 psig
Wt. of reactor + solvent = 10729
Wt. of reactor + solvent + products = 10759
Wt. of empty reactor = 10547

Product sample I	=	20.78	Product sample II	=	20.70
Benzene insol.	=	.67	Benzene insol.	=	.71
THF insoluble	=	.45	THF insoluble	=	.48
Pentane insol.	=	.32	Pentane insol.	=	.33
Sample ashed	=	.4091	Sample ashed	=	.4182
Ash in sample	=	.2731	Ash in sample	=	.2791

Run No. 12 Reaction time = 1 hour
Temperature = 375°C Final Pressure = 1900 psig
Wt. of reactor + solvent = 10729
Wt. of reactor + solvent + products = 10765
Wt. of empty reactor = 10546

Product sample I	=	21.94	Product sample II	=	20.84
Benzene insol.	=	.90	Benzene insol.	=	.85
THF insoluble	=	.57	THF insoluble	=	.52
Pentane insol.	=	.30	Pentane insol.	=	.25
Sample ashed	=	.5616	Sample ashed	=	.4933
Ash in sample	=	.3292	Ash in sample	=	.2837

Run No. 13 Reaction time = 1 hour
Temperature = 350°C Final Pressure = 1750 psig
Wt. of reactor + solvent = 10731
Wt. of reactor + solvent + products = 10767
Wt. of empty reactor = 10549

Product sample I	= 20.98	Product sample II	= 22.88
Benzene insol.	= 1.14	Benzene insol.	= 1.28
THF insoluble	= .86	THF insoluble	= .93
Pentane insol.	= .19	Pentane insol.	= .22
Sample ashed	= .8127	Sample ashed	= .9037
Ash in sample	= .3377	Ash in sample	= .3743

Run No. 14 Reaction time = 2 hour
Temperature = 350°C Final Pressure = 1850 psig
Wt. of reactor + solvent = 10734
Wt. of reactor + solvent + products = 10765
Wt. of empty reactor = 10551

Product sample I	= 21.43	Product sample II	= 20.36
Benzene insol.	= 1.12	Benzene insol.	= 1.06
THF insoluble	= .78	THF insoluble	= .65
Pentane insol.	= .22	Pentane insol.	= .25
Sample ashed	= .7491	Sample ashed	= .6394
Ash in sample	= .3803	Ash in sample	= .3337

Run No. 14 (repeated analysis) Reaction time = 2 hour
Temperature = 350°C Final Pressure = 1850 psig
Wt. of reactor + solvent = 10734
Wt. of reactor + solvent + products = 10765
Wt. of empty reactor = 10551

Product sample I	= 21.96	Product sample II	= 21.92
Benzene insol.	= 1.17	Benzene insol.	= 1.18
THF insoluble	= .84	THF insoluble	= .85
Pentane insol.	= .27	Pentane insol.	= .26
Sample ashed	= .7956	Sample ashed	= .7845
Ash in sample	= .3923	Ash in sample	= .3843

Run No. 15 Reaction time = 3 hour
Temperature = 350°C Final Pressure = 1750 psig
Wt. of reactor + solvent = 10734
Wt. of reactor + solvent + products = 10765
Wt. of empty reactor = 10550

Product sample I	= 21.63	Product sample II	= 22.31
Benzene insol.	= .99	Benzene insol.	= 1.02
THF insoluble	= .66	THF insoluble	= .68
Pentane insol.	= .28	Pentane insol.	= .28
Sample ashed	= .6643	Sample ashed	= .685
Ash in sample	= .3751	Ash in sample	= .3889

Run No. 16 Reaction time = 1/2 hour
Temperature = 350°C Final Pressure = 1900 psig
Wt. of reactor + solvent = 10733
Wt. of reactor + solvent + products = 10768
Wt. of empty reactor = 10552

Product sample I	= 22.55	Product sample II	= 23.27
Benzene insol.	= 1.47	Benzene insol.	= 1.51
THF insoluble	= 1.21	THF insoluble	= 1.24
Pentane insol.	= .21	Pentane insol.	= .2
Sample ashed	= 1.1546	Sample ashed	= 1.1575
Ash in sample	= .4167	Ash in sample	= .4128

Run No. 17 (200 rpm) Reaction time = 3 hour
Temperature = 400°C Final Pressure = 2500 psig
Wt. of reactor + solvent = 10734
Wt. of reactor + solvent + products = 10764
Wt. of empty reactor = 10552

Product sample I	= 22.76	Product sample II	= 23.29
Benzene insol.	= .6	Benzene insol.	= .63
THF insoluble	= .48	THF insoluble	= .49
Pentane insol.	= .3	Pentane insol.	= .35
Sample ashed	= .4197	Sample ashed	= .4697
Ash in sample	= .2979	Ash in sample	= .3366

APPENDIX II

SAMPLE CALCULATIONS

SAMPLE CALCULATIONS FOR RUN NO. 14

Conditions: 1 hour, 350°C.

Two samples I and II were taken from the homogeneous liquid product.

Benzene and THF Extractions

+THF Ins.	= 237.32*	+THF Ins.	= 236.86
+Benz. Ins.	= 237.60	+Benz. Ins.	= 237.21
+Sample	= 257.44	+Sample	= 258.81
Empty tube-I	= 236.46	Empty tube-II	= 235.93

	THF Ins. wt.	= 0.86		THF Ins. wt.	= 0.93
I	Benz. Ins. wt.	= 1.14	II	Benz. Ins. wt.	= 1.28
	Sample wt.	=20.98		Sample wt.	= 22.88

Pentane Extraction

+Pent. Ins.	= 237.13	+Pent. Ins.	= 237.15
Empty tube-PI	= 236.94	Empty tube-PII	= 236.93

Pent. Ins. wt. I = 0.19

Pent. Ins. wt. II = 0.22

(*) All numbers are in grams.

Ashing

+Ash	= 10.5355	+Ash	= 10.6370
+Sample	= 11.0105	+Sample	= 11.1664
Empty crucible I	= 10.1978	Empty crucible II	= 10.2627

Ash wt.	= 0.3377	Ash wt.	= 0.3743
Sample wt.	= 0.8127	Sample wt.	= 0.9037

wt. of reactor + total products = 10767

wt. of empty reactor = $\underline{10549.5}$

wt. of total products = 217.5

wt. of reactor + total products = 10767

wt. of reactor + solvent = $\underline{10731.5}$

wt. of injected coal = $(10767 - 10731.5) \times \frac{1.2}{2.2} = 19.3636$

where the ratio of coal to solvent in the slurry is 1.2 to 1

Benz. Ins. %

$$I = \frac{1.14}{20.98} \times \frac{217.5}{19.3636} = 61.034$$

61.936

$$II = \frac{1.28}{22.88} \times \frac{217.5}{19.3636} = 62.838$$

Coal + Ash % of Benz. Ins.

$$I = \frac{.86}{1.14} = 75.438$$

$$II = \frac{.93}{1.28} = 72.656$$

Ash % of Coal + Ash

$$I = \frac{.3377}{.8127} = 41.553$$

$$II = \frac{.3743}{.9037} = 41.418$$

Ash % of Products

I = 61.034 x .75438 x .41553 = 19.132

19.021

II = 62.838 x .72656 x .41418 = 18.909

Preasphaltene %

I = 61.034 x (1 - .75438) = 14.991

16.086

II = 62.838 x (1 - .72656) = 17.182

Unreacted Coal = (61.936 - 19.021 - 16.086)

= 26.829

Asphaltene %

$$\text{I} = \frac{.19}{20.98} \times \frac{217.5}{19.3636} = 10.172$$

10.486

$$\text{II} = \frac{.22}{22.88} \times \frac{217.5}{19.3636} = 10.800$$

	Calculated	Normalized
Ash	= 19.021	25.19
Unreacted Coal	= 26.829	35.53
Preasphaltene	= 16.086	21.303
Asphaltene	= 10.486	13.887

Final Results (ash-free basis)

Unreacted Coal = 47.49

Preasphaltene = 28.47

Asphaltene = 18.56

Oil + Gas (by difference) = 5.48

APPENDIX III

EQUIPMENT CONSTRUCTION AND RATINGS

EQUIPMENT CONSTRUCTION AND RATINGS

Equipment	Material of Construction	Rating Temp. (^oF)	Working Pressure (psig)
Autoclave Reactor	316 stainless	650	5,400
Ruska pump	" "	"	8,000
Ashcroft gauges	" "	"	5,000
Grove valve	" "	"	3,000
Nupro valve	" "	450	3,000
Hoke valves	" "	"	5,000
Autoclave valves	" "	"	20,000
1/4" flexible tubing	" "	70	2,660
1/4" tubing (.049")	" "	800	7,830
1/4" tubing (high pressure)	" "	"	12,000
Swagelok fittings	" "	100	8,700
Autoclave fittings	" "	72	20,000

APPENDIX IV

COMPUTER PROGRAM LISTINGS

```
C DECK 01
C MAIN PROGRAM
 1     WRITE(6,2)
 2     FORMAT(1H1)
       CALL NLMAX
       GO TO 1
       END
```

```
C DECK 02
C MAXIMIZES FUNCTION USING GAUSS-NEWTON METHOD
       SUBROUTINE NLMAX
       COMMON C(20,20),G1(20,20),PSCA,G(20,20),F(20),Y(20),EGV(20),FF(20)
      1,TITLE(20),CUB(20),CLB(20),PNL(20),NCON,LOUT,F3,NTH,F6,F7,METH,NPH
      2,MD,LS,C1(20)
       DIMENSION W(20)
       EQUIVALENCE(NTH,L)
       METH=1
       READ(5,2000)TITLE
 2000  FORMAT(20A4)
       READ(5,2002)NTH,LOUT,MD
 2002  FORMAT(16I5)
       WRITE(6,2001)TITLE,MD
 2001  FORMAT(1H120A4/6H0MODELI5)
       READ(5,2003)(C1(I),I=1,NTH)
 2003  FORMAT(8E10.5)
       LS=1
       CALL ACCUM(3)
       CALL BOUND(3,H)
       WRITE(6,5000)(C1(I),I=1,L)
 5000  FORMAT(26H0PARAMETER INITIAL GUESSES/(7E16.6))
       IF(LS-3)199,907,199
 199   IPH=2
       NIN=0
       NF=0
       ND=0
       EPS=1.E-4
       EPS1=1.E-3
       DO 906 I=1,L
       FF(I)=C1(I)
 906   Y(I)=-C1(I)
       H=1.
       CALL BOUND(4,H)
       DO 911 I=1,L
 911   Y(I)=C1(I)*H
       NPH=1
       IF(NCON)1,899,1
 899   NPH=2
       GO TO 16
 1     GO TO(212,16),LOUT
212    WRITE(6,1001)
 1001  FORMAT(26H1PENALTY FUNCTION INCLUDED)
 16    II=2
       NRE=1
       ND=ND+1
       GO TO 100
 51    II=1
 100   NF=NF+1
       LS=1
       CALL ACCUM(II)
```

```
      F4=F3
      GO TO(405,68,1003),LS
 405  GO TO(401,499),NPH
 401  CALL BOUND(II,X)
 499  GO TO(48,409),II
 409  DO 408 I=2,L
      DO 408 J=2,I
 408  G(I,J-1)=G(J-1,I)
 48   GO TO(205,110),LOUT
 205  GO TO(208,209),II
 209  WRITE(6,210)ND
 210  FORMAT(10H0ITERATIONI6)
 208  WRITE(6,207)F3,NF,(C1(I),I=1,L)
 207  FORMAT(9H0FUNCTIONE17.7,13H   EVALUATIONI6/11H PARAMETERS/(7E17.7)
     2)
 110  GO TO(101,111,894),II
 101  IF(F2-F3)22,21,21
 22   GO TO(24,16),NPH
 24   GO TO(111,16),NRE
 111  DO 106 I=1,L
 106  FF(I)=C1(I)
      IF(II-1)26,26,25
 26   NRE=2
      GO TO(34,16),NRR
34    Q=0.
      IF(NIN)14,14,16
 14   CONTINUE
      DO 27 I=1,L
 27   Q=Q+F(I)*Y(I)
      H=(Q-2.*(F3-F2))/2./(F3-F2-Q)
      IF(ABS(H)-.1)16,16,30
 30   IF(H+1.)304,304,31
 31   DO 29 I=1,L
 29   Y(I)=H*Y(I)
      GO TO 304
 25   CONTINUE
      DO 800 I=1,L
      DO 800 J=1,L
 800  C(I,J)=G(I,J)
      CALL EIG(L,2)
      LT3=2
      DO 9 I=1,L
      EGV(I)=C(I,I)
      IF(C(I,I))9,13,10
 13   C(I,I)=-1.
      GO TO 9
 10   LT3=1
      C(I,I)=-C(I,I)
 9    CONTINUE
 41   DO 11 J=1,L
      W(J)=0.
```

```
      DO 202 J1=1,L
202   W(J)=W(J)+G1(J1,J)*F(J1)
11    W(J)=W(J)/C(J,J)
      DO 201 I=1,L
      Y(I)=0.
      DO 201 J=1,L
201   Y(I)=Y(I)-G1(I,J)*W(J)
304   NRR=1
      F2=F3
      F6=F7
      H=1.
      CALL BOUND(4,H)
      NIN=NIN/2
      H=H/2.**NIN
      DO 604 I=1,L
604   Y(I)=H*Y(I)
603   J=1
      DO 700 I=1,L
      IF(ABS(Y(I))/(EPS1+ABS(FF(I)))-EPS)700,700,701
701   J=2
700   CONTINUE
      GO TO(33,702),J
33    GO TO(898,16),NRE
898   GO TO(1002,897),NPH
897   IF(H-1.)896,1003,1003
896   CALL BOUND(5,H)
      DO 895 I=1,L
895   C1(I)=FF(I)+H*Y(I)
      CALL ACCUM(1)
      NF=NF+1
      II=3
      GO TO(208,894),LOUT
894   IF(F3-F2)706,1003,1003
702   DO 12 I=1,L
12    C1(I)=FF(I)+Y(I)
      GO TO 51
21    GO TO(2,6),NRE
6     DO 3 I=1,L
3     C1(I)=FF(I)
      GO TO 16
2     Q=0.
      NRR=2
      DO 58 I=1,L
58    Q=Q+F(I)*Y(I)
      H=Q/(Q+(F2-F3))*.5
65    IF(4.*H-1.)59,59,62
59    H=.25
62    J=1
      NIN=NIN+1
      DO 703 I=1,L
      Y(I)=H*Y(I)
```

```
      IF(ABS(Y(I))/(EPS1+ABS(FF(I)))-EPS)703,703,704
 704  J=2
 703  CONTINUE
      GO TO(706,705),J
 705  H=1.
      CALL BOUND(4,H)
      DO 23 I=1,L
      Y(I)=H*Y(I)
 23   C1(I)=FF(I)+Y(I)
      GO TO 51
 706  F3=F2
      F7=F6
      DO 707 I=1,L
 707  C1(I)=FF(I)
 19   GO TO(1002,1003),NPH
 1002 IF(IPH)1004,1004,1005
 1004 NPH=2
      GO TO(121,122),LOUT
 121  WRITE(6,214)
 214  FORMAT(20H0NO PENALTY FUNCTION)
 122  F2=-1.E30
      GO TO 16
 1005 IF(ABS(F3-F4)-,1)1004,1006,1006
 1006 CALL BOUND(6,H)
      IPH=IPH-1
      GO TO(213,16),LOUT
 213  WRITE(6,211)
 211  FORMAT(41H0PENALTY FUNCTION REDUCED BY FACTOR OF 10)
      GO TO 16
 1003 CONTINUE
      WRITE(6,123)F3,(C1(I),I=1,L)
 123  FORMAT(30H0MAXIMUM OF OBJECTIVE FUNCTIONE17.7/11H0PARAMETERS/(7E17
     2,7))
      WRITE(6,9001)NF,ND
 9001 FORMAT(21H0FUNCTION EVALUATIONSI6,25H   DERIVATIVE EVALUATIONSI5)
 407  WRITE(6,920)(F(I),I=1,L)
 920  FORMAT(9H1GRADIENT/(7E17.6))
      WRITE(6,921)
 921  FORMAT(8H0HESSIAN)
      DO 922 I=1,L
 922  WRITE(6,923)(G(I,J),J=1,L)
 923  FORMAT(7E17.6)
      WRITE(6,903)(EGV(I),I=1,L)
 903  FORMAT(30H0EIGENVALUES OF SCALED HESSIAN/(7E17.6))
      WRITE(6,904)
 904  FORMAT(21H0PRINCIPAL COMPONENTS)
      DO 905 I=1,L
 905  WRITE(6,37)(G1(J,I),J=1,L)
  37  FORMAT (/7E17.6/(7E17.6))
      CALL BOUND(7,H)
      CALL OUT
```

```
      GO TO(217,907),LT3
217   WRITE(6,216)
216   FORMAT(36H0SOLUTION IS NOT AN INTERIOR MAXIMUM)
907   RETURN
68    J=1
      DO 71 I=1,L
      Y(I)=.5*Y(I)
      IF(ABS(Y(I))/(EPS1+ABS(C1(I)))-EPS)71,71,925
925   J=2
71    C1(I)=C1(I)-Y(I)
      GO TO(909,926),J
909   WRITE(6,910)
910   FORMAT(45H0FEASIBLE PARAMETER VALUES COULD NOT BE FOUND/45H ******
     2**************************************)
      RETURN
926   CONTINUE
      WRITE(6,924)
924   FORMAT(8H0RESTART)
      IF(II-1)51,51,16
      END
```

```
C DECK 10
C COMPUTES LIKELIHOOD FUNCTION WITH DIAGONAL COVARIANCE
      SUBROUTINE ACCUM(II)
      COMMON C(20,20),G1(20,20),PSCA,G(20,20),F(20),Y(20),EGV(20),FF(20)
     1,TITLE(20),CUB(20),CLB(20),PNL(20),NCON,LCUT,F3,NTH,F6,F7,METH,NPH
     2,MD,LS,C1(20)
      COMMON/BONE/V(5,5),QY(5),YTH(5,20),A(100,10),ICOV,DET,IDER,M,NY,NA
      DIMENSION UI(5,20),QQ(5)
C THE FOLLOWING STATEMENTS MAY BE REMOVED FOR DAVIDON'S METHOD
      DIMENSION ZI(5,20,20)
C END OF REMOVABLE STATEMENTS
      IF(II-3)100,101,100
 101  READ(5,2000)NY,M,NA,ICOV
 2000 FORMAT(16I5)
      AM=M
      IDER=1
      DO 2002 I=1,M
 2002 READ(5,102)(A(I,J),J=1,NA)
      GO TO(106,106,107),ICOV
 106  CONTINUE
      DO 105 I=1,NY
      DO 105 J=1,NY
 105  V(I,J)=0.
      READ(5,102)(C(I,I),I=1,NY)
 102  FORMAT(8E10.5)
      WRITE(6,103)(C(I,I),I=1,NY)
 103  FORMAT(31H0PRESCRIBED DIAGONAL COVARIANCE//(7E16.6))
      DET=1.
      DO 104 I=1,NY
      DET=DET*C(I,I)
 104  V(I,I)=1./C(I,I)
      DET=.5*AM*ALOG(DET)
 107  CALL DER(3,0)
      CALL PRIOR(3)
      GO TO(2001,2003),IDER
 2001 WRITE(6,2004)
 2004 FORMAT(13H0OBSERVATIONS/)
      DO 2005 I=1,M
 2005 WRITE(6,2006)I,(A(I,J),J=1,NA)
 2006 FORMAT(I5,7E16.6/(E21.6,6E16.6))
 2003 RETURN
 100  CONTINUE
      DO 3 I=1,NY
 3    C(I,I)=0.
      GO TO(7,5),II
 5    DO 6 K=1,NTH
      F(K)=0.
      DO 9 I=1,NY
 9    UI(I,K)=0.
C THE FOLLOWING STATEMENTS MAY BE REMOVED FOR DAVIDON'S METHOD
      GO TO(209,6),METH
```

```
 209   DO 201 J=K,NTH
       G(K,J)=0.
       DO 201 I=1,NY
 201   ZI(I,K,J)=0.
C END OF REMOVABLE STATEMENTS
 6     CONTINUE
 7     DO 12 MU=1,M
       CALL DER(II,MU)
       GO TO(42,32),LS
 42    DO 13 I=1,NY
       QQ(I)=QY(I)-A(MU,I)
 13    C(I,I)=C(I,I)+QQ(I)*QQ(I)
       GO TO(12,16),II
 16    DO 17 I=1,NY
       DO 17 J=1,NTH
       UI(I,J)=UI(I,J)+YTH(I,J)*QQ(I)
C THE FOLLOWING STATEMENTS MAY BE REMOVED FOR DAVIDON'S METHOD
       GO TO(202,17),METH
 202   DO 203 K=J,NTH
 203   ZI(I,J,K)=ZI(I,J,K)+YTH(I,J)*YTH(I,K)
C END OF REMOVABLE STATEMENTS
 17    CONTINUE
 12    CONTINUE
       GO TO(53,53,52),ICOV
 52    X1=1.
       DO 35 I=1,NY
       IF(C(I,I))50,50,51
 51    V(I,I)=AM/C(I,I)
 35    X1=X1/V(I,I)
       F3=-.5*AM*ALOG(X1)
       GO TO(32,25),II
 25    AM2=2./AM
 62    DO 26 I=1,NY
       DO 26 J=1,NTH
       F(J)=F(J)-UI(I,J)*V(I,I)
C THE FOLLOWING STATEMENTS MAY BE REMOVED FOR DAVIDON'S METHOD
       GO TO(204,26),METH
 204   DO 205 K=J,NTH
 205   G(J,K)=G(J,K)-ZI(I,J,K)*V(I,I)
C END OF REMOVABLE STATEMENTS
 26    CONTINUE
       GO TO(32,63,65),ICOV
 63    CONTINUE
C THE FOLLOWING STATEMENTS MAY BE REMOVED FOR DAVIDON'S METHOD
       GO TO(206,207),METH
 206   DO 64 I=1,NTH
       DO 64 J=I,NTH
 64    G(I,J)=(G(I,J)+AM2*F(I)*F(J))/X1
C END OF REMOVABLE STATEMENTS
 207   DO 68 I=1,NTH
 68    F(I)=F(I)/X1
```

```
      GO TO 32
 65   CONTINUE
C THE FOLLOWING STATEMENTS MAY BE REMOVED FOR DAVIDON'S METHOD
      GO TO(208,32),METH
 208  DO 66 K=1,NY
      X1=AM2*V(K,K)*V(K,K)
      DO 66 I=1,NTH
      DO 66 J=I,NTH
 66   G(I,J)=G(I,J)+X1*UI(K,I)*UI(K,J)
C END OF REMOVABLE STATEMENTS
 32   F7=F3
      CALL PRIOR(II)
      RETURN
 50   LS=3
      WRITE(6,200)
 200  FORMAT(32H0SINGULAR DIAGONAL MOMENT MATRIX/32H *******************
     2************)
      RETURN
 53   X1=0.
      DO 54 I=1,NY
 54   X1=X1+C(I,I)*V(I,I)
      GO TO(60,61,61),ICOV
 60   F3=-.5*X1
      GO TO(32,62),II
 61   IF(X1)50,50,67
 67   X2=AM*FLOAT(NY)
      AM2=2./X1
      X1=X1/X2
      F3=-.5*X2*ALOG(X1)
      GO TO(32,62),II
      END
```

```
C DECK 14
C SOLVES DIFFERENTIAL EQUATIONS
      SUBROUTINE DER(II,I1)
      COMMON C(20,20),G1(20,20),PSCA,G(20,20),F(20),Y(20),EGV(20),FF(20)
     1,TITLE(20),CUB(20),CLB(20),PNL(20),NCON,LCUT,F3,NTH,F6,F7,METH,NPH
     2,MD,LS,C1(20)
      COMMON/BONE/V(5,5),QY(5),YTH(5,20),A(100,10),ICOV,DET,IDER,M,NY,NA
      COMMON/C/NX,NB,NTH2,NTH1,G(10),P(10),FX(10,10),FTH(10,20),BV(20,10
     5),TIME(100),IA(100),FN(10),XTH(10,20),XTTH(10,20)
      DIMENSION Q0(10),P1(10),XTTH1(10,20),XTH1(10,20),Q1(10)
      GO TO(800,800,801),II
 801  READ(5,500)NX,NBV,NB,NTH2
 500  FORMAT(16I5)
      IDER=2
      NTH2=NTH-NTH2
      NTH1=NTH2+1
      DO 100 I=1,NX
      DO 101 J=1,NX
 101  FX(I,J)=0.
      DO 100 J=1,NTH2
 100  FTH(I,J)=0.
      WRITE(6,48)
 48   FORMAT(47H0RUN   EXP,        TIME            OBSERVATIONS)
      L=1
      DO 13 I=1,NBV
      READ(5,14)J,(BV(I,K),K=1,NB)
 14   FORMAT(I5/(8E10.5))
      L2=L+J-1
      WRITE(6,56)I,(BV(I,K),K=1,NB)
 56   FORMAT(1H0I3,23H            INIT, CCND.E22.6,5E16.6/(E47.6,5E16.6
     2)
      READ(5,501)(TIME(K),K=L,L2)
 501  FORMAT(8E10.5)
      DO 46 K=L,L2
      IA(K)=0
 46   WRITE(6,47)K,TIME(K),(A(K,J),J=1,NA)
 47   FORMAT(I11,E16.6,E20.6,5E16.6/(E47.6,5E16.6))
      DO 49 K=L,L2
      IF(TIME(K))49,49,51
 49   IA(K)=I
      GO TO 13
 51   IA(K)=I
 13   L=L2+1
      READ(5,501)(FN(I),I=1,NX)
      EP2=.3E-5
      EP1=3.*EP2
      CALL RUN(3,0)
      CALL FUN(3,0,0,0.)
      CALL XTOY(3,0,0)
      RETURN
 800  JJ=II
```

```
      IF(NTH2)401,402,401
 402  JJ=1
 401  CONTINUE
      I2=IA(I1)
      IF(I2)201,7,201
 201  IT=1
      I3=I2
      GO TO(600,601),JJ
 601  DO 602 I=1,NX
      DO 602 J=1,NTH2
 602  XTH(I,J)=0.
 600  CALL RUN(JJ,I2)
      DO 202 I=1,NX
 202  Q(I)=BV(I2,I)
      CALL FUN(JJ,2,I3,0.)
      GO TO(300,103),LS
 300  CONTINUE
 250  W=.1*TIME(I1)
 203  V2=W/2.
      T=W
      DO 204 I=1,NX
      Q(I)=BV(I2,I)+P(I)*W
 204  P1(I)=P(I)
      CALL FUN(1,1,I3,T)
      GO TO(301,103),LS
 301  CONTINUE
      DO 205 I=1,NX
 205  Q(I)=BV(I2,I)+(P(I)+P1(I))*V2
      CALL FUN(1,1,I3,T)
      GO TO(305,103),LS
 305  CONTINUE
      SSQ1=0.
      SSQ=0.
      DO 207 I=1,NX
      Q1(I)=BV(I2,I)+(P1(I)+P(I))*V2
      SSQ=SSQ+ABS(Q1(I)-Q(I))
      Q(I)=(2.*Q1(I)+Q(I))/3.
 207  SSQ1=SSQ1+ABS(Q(I))
      A1=SSQ/SSQ1/EP1
      IF(A1-1.)208,208,209
 209  W=W/A1**.666667
      DO 210 I=1,NX
 210  P(I)=P1(I)
      GO TO 203
 208  GO TO(211,212),JJ
 212  CALL XIJ
      DO 213 I=1,NX
      DO 213 J=1,NTH2
      XTH(I,J)=XTH(I,J)+XTTH(I,J)*W
 213  XTTH1(I,J)=XTTH(I,J)
      CALL FUN(JJ,1,I3,T)
```

```
      GO TO(302,103),LS
 302  CONTINUE
      CALL XIJ
      DO 220 I=1,NX
      DO 220 J=1,NTH2
      XTH(I,J)=XTH(I,J)+(XTTH(I,J)-XTTH1(I,J))*V2
 220  XTH1(I,J)=XTTH(I,J)
      CALL XIJ
      V3=W/3.
      DO 231 I=1,NX
      DO 231 J=1,NTH2
 231  XTH(I,J)=XTH(I,J)+(XTTH(I,J)-XTH1(I,J))*V3
      CALL XIJ
 211  CALL FUN(1,1,I3,T)
      GO TO(7,103),LS
 7    T1=T
      IF(TIME(I1)-T)400,400,18
 18   U=W
      GO TO(25,29),IT
 29   IF(SSQ)26,30,26
 30   W=W+W
      GO TO 25
 26   W=(BET2*SSQ1/SSQ)**.333333
      W=AMAX1(W,TIME(I1)*.001)
 25   T=T+W
      IT=2
      A1=TIME(I1)-T
      IF(A1)27,28,28
 27   T=TIME(I1)
      W=T-T1
 28   V2=.5*W
      A1=V2/U
      AV1=-A1*W
      AV=W-AV1
      BET=W/3./(U+W)
      BET1=1.-BET
      BET2=3.*EP2*(U+W)*W**2
      DO 1 I=1,NX
      Q1(I)=Q(I)
      Q(I)=Q(I)+AV*P(I)+AV1*P1(I)
 1    P1(I)=P(I)
      CALL FUN(1,1,I3,T)
      GO TO(303,103),LS
 303  CONTINUE
      SSQ=0.
      SSQ1=0.
      DO 4 I=1,NX
      Q1(I)=Q1(I)+(P1(I)+P(I))*V2
      SSQ=SSQ+ABS(Q1(I)-Q(I))
      Q(I)=BET*Q(I)+BET1*Q1(I)
      IF(ABS(Q(I))-FN(I))4,4,50
```

```
 4     SSQ1=SSQ1+ABS(Q(I))
       CALL FUN(JJ,1,I3,T)
       GO TO(304,103),LS
 304   CONTINUE
       GO TO(7,6),JJ
6      DO 8 I=1,NX
       DO 8 J=1,NTH2
       XTH1(I,J)=XTH(I,J)+AV*XTTH(I,J)+AV1*XTTH1(I,J)
 8     XTTH1(I,J)=XTTH(I,J)
       DO 9 I=1,NX
       DO 9 J=1,NTH2
       A1=XTTH(I,J)+FTH(I,J)
       DO 10 K=1,NX
 10    A1=A1+FX(I,K)*XTH1(K,J)
       A1=XTH(I,J)+A1*V2
C      SSQ=SSQ+((A1-XTH1(I,J))*FN(I))**2
       XTH(I,J)=BET*XTH1(I,J)+BET1*A1
C      SSQ1=SSQ1+(XTH(I,J)*FN(I))**2
 9     CONTINUE
       CALL XIJ
       GO TO 7
 400   CALL XTOY(II,I3,I1)
       RETURN
 50    LS=2
 103   RETURN
       END
```

```
C DECK 17
C KNOWN INITIAL CONDITIONS
      SUBROUTINE RUN(II,IB)
      RETURN
      END
```

```
C      DECK 19
C      THIS IS MODEL 3
       SUBROUTINE FUN(II,JJ,IB,T)
       COMMON C(20,20),G1(20,20),PSCA,G(20,20),F(20),Y(20),EGV(20),FF(20)
      1,TITLE(20),CUB(20),CLB(20),PNL(20),NCON,LCUT,F3,NTH,F6,F7,METH,NPH
      2,MD,LS,C1(20)
       COMMON/BONE/V(5,5),QY(5),YTH(5,20),A(100,10),ICOV,DET,IDER,M,NY,NA
       COMMON/C/NX,NB,NTH2,NTH1,Q(10),P(10),FX(10,10),FTH(10,20),BV(20,10
      5),TIME(100),IA(100),FN(10),XTH(10,20),XTTH(10,20)
         GO TO(1,1,2),II
2        FX(1,2)=0.
         FX(1,3)=0.
         FX(2,1)=0.
         FX(3,2)=0.
         FTH(1,2)=0.
         FTH(1,3)=0.
         FTH(1,4)=0.
         FTH(2,1)=0.
         FTH(2,3)=0.
         FTH(3,4)=0.
         RETURN
1        P(1)=-C1(1)*Q(1)
         P(2)=C1(2)*Q(3)-C1(4)*Q(2)
         P(3)=C1(1)*Q(1)-(C1(2)+C1(3))*Q(3)
         GO TO(3,4),II
4        FX(1,1)=-C1(1)
         FX(2,2)=-C1(4)
         FX(2,3)=C1(2)
         FX(3,1)=C1(1)
         FX(3,3)=-(C1(2)+C1(3))
         FTH(1,1)=-Q(1)
         FTH(2,2)=Q(3)
         FTH(2,4)=-Q(2)
         FTH(3,1)=Q(1)
         FTH(3,2)=-Q(3)
         FTH(3,3)=-Q(3)
3        RETURN
         END
```

```
C DECK 20
C OBSERVED = STATE VARIABLES
      SUBROUTINE XTOY(II,IB,I1)
      COMMON C(20,20),G1(20,20),PSCA,G(20,20),F(20),Y(20),EGV(20),FF(20)
     1,TITLE(20),CUB(20),CLB(20),PNL(20),NCON,LCUT,F3,NTH,F6,F7,METH,NPH
     2,MD,LS,C1(20)
      COMMON/BONE/V(5,5),QY(5),YTH(5,20),A(100,10),ICOV,DET,IDER,M,NY,NA
      COMMON/C/NX,NB,NTH2,NTH1,Q(10),F(10),FX(10,10),FTH(10,20),BV(20,10
     5),TIME(100),IA(100),FN(10),XTH(10,20),XTTH(10,20)
      GO TO(1,1,2),II
 1    DO 3 I=1,NY
 3    QY(I)=Q(I)
      GO TO(2,4),II
 4    DO 5 I=1,NY
      DO 5 J=1,NTH
 5    YTH(I,J)=XTH(I,J)
 2    RETURN
      END
```

```
C DECK 15
C CONSTANT PRIOR DISTRIBUTION
      SUBROUTINE PRIOR(II)
      RETURN
      END
```

```
C DECK 06
C LOWER AND UPPER BOUNDS ON PARAMETERS
      SUBROUTINE BOUND(II,H)
      COMMON C(20,20),G1(20,20),PSCA,G(20,20),F(20),Y(20),EGV(20),FF(20)
     1,TITLE(20),CUB(20),CLB(20),PNL(20),NCON,LCUT,F3,NTH,F6,F7,METH,NPH
     2,MD,LS,C1(20)
      GO TO(1,1,2,3,3,44,43),II
 44   DO 45 I=1,NTH
 45   PNL(I)=.1*PNL(I)
      RETURN
 1    DO 4 I=1,NTH
      AA1=C1(I)-CLB(I)
      AA2=PNL(I)/AA1
      AA3=C1(I)-CUB(I)
      AA4=PNL(I)/AA3
      F3=F3-AA2+AA4
      GO TO(4,5),II
 5    AA2=AA2/AA1
      AA4=AA4/AA3
      F(I)=F(I)+AA2-AA4
C THE FOLLOWING STATEMENTS MAY BE REMOVED FOR DAVIDON'S METHOD
      GO TO(100,4),METH
 100  G(I,I)=G(I,I)+2.*(AA4/AA3-AA2/AA1)
C END OF REMOVABLE STATEMENTS
 4    CONTINUE
      RETURN
 2    READ(5,6)(CLB(I),I=1,NTH)
 6    FORMAT(8E10.5)
      READ(5,6)(CUB(I),I=1,NTH)
      DO 20 I=1,NTH
      IF(C1(I)-CLB(I))21,21,23
 21   IF(C1(I))25,26,27
 25   CLB(I)=100.*C1(I)
      GO TO 23
 26   CLB(I)=C1(I)-1.E10
      GO TO 23
 27   CLB(I)=0.
 23   IF(C1(I)-CUB(I))20,22,22
 22   IF(C1(I))28,29,24
 28   CUB(I)=0.
      GO TO 20
 29   CUB(I)=C1(I)+1.E10
      GO TO 20
 24   CUB(I)=100.*C1(I)
 20   CONTINUE
      DO 8 I=1,NTH
 8    PNL(I)=.0001*AMIN1(.001+ABS(C1(I)),CUB(I)-CLB(I))
      WRITE(6,38)(I,CLB(I),CUB(I),PNL(I),I=1,NTH)
 38   FORMAT(60H0PARAMETER LOWER BOUND      UPPER BOUND   PENALTY COEFFIC
     2IENT/(I6,2E16.6,E22.6))
      NCON=2*NTH
```

```
      RETURN
 3    HY=0.
      DO 7 I=1,NTH
 7    HY=AMIN1(Y(I)/(C1(I)-CLB(I)),Y(I)/(C1(I)-CUB(I)),HY)
      IF(II-5)40,41,43
 40   H=AMIN1(1.,-.5/HY)
      RETURN
 41   H=-1./HY
 43   RETURN
      END
```

```
C DECK 12
C OUTPUT FOR MAXIMUM LIKELIHOOD PROBLEMS
      SUBROUTINE OUT
      COMMON C(20,20),G1(20,20),PSCA,G(20,20),F(20),Y(20),EGV(20),FF(20)
     1,TITLE(20),CUB(20),CLB(20),PNL(20),NCOM,LCUT,F3,NTH,F6,F7,METH,NPH
     2,MD,LS,C1(20)
      COMMON/BONE/V(5,5),QY(5),YTH(5,20),A(100,10),ICOV,DET,IDER,M,NY,NA
      EQUIVALENCE(L,NTH),(N,NY)
 13   DO 5 I=1,NY
      DO 5 J=I,NY
 5    C(I,J)=0.
      WRITE(6,3)TITLE,MD
 3    FORMAT(1H120A4/6H0MODELI5/30H0RESIDUALS (COMPUTED-OBSERVED)/)
      DO 1 I=1,M
      CALL DER(1,I)
      DO 2 J=1,NY
 2    F(J)=QY(J)-A(I,J)
      DO 6 K=1,NY
      DO 6 J=K,NY
 6    C(K,J)=C(K,J)+F(K)*F(J)
 1    WRITE(6,4)I,(F(J),J=1,NY)
 4    FORMAT(I5,7E16.6)
      DO 7 I=2,NY
      DO 7 J=2,I
 7    C(I,J-1)=C(J-1,I)
      WRITE(6,850)
 850  FORMAT(///31H COVARIANCE MATRIX OF RESIDUALS/)
      T=AMAX1(1.,FLOAT(M)-FLOAT(L)/FLOAT(NY))
      DO 852 I=1,N
      DO 853 J=1,N
 853  C(I,J)=C(I,J)/T
 852  WRITE(6,37)(C(I,J),J=1,N)
      DO 854 I=1,N
 854  Y(I)=SQRT(C(I,I))
      WRITE(6,855)(Y(I),I=1,N)
 855  FORMAT(///33H STANDARD DEVIATIONS OF RESIDUALS//(7E17.6))
      ANY=NY*M
      T=T/FLOAT(M)
      X1=F3-F7
      GO TO (81,410,80),ICOV
 410  X=-1.4189385*ANY-DET+F3
      H1=EXP(-2./ANY*F7)/T
      H=ANY*T*H1
      GO TO 82
 81   H=-2.*F7
      H1=H/ANY/T
      X=-.9189385*ANY-DET+F3
      GO TO 82
 80   X=F3-ANY*1.4189385
      H=FLOAT(NY)*ALOG(FLOAT(M))-2.*F3/(FLOAT(M))
      H=EXP(H)
```

```
 82   X2=X-X1
      WRITE(6,102)X,X2,X1
 102  FORMAT(16H1LOG PROBABILITYE17.7/15H0LOG LIKELIHOODE18.7/10H0LOG PR
     2IORE23.7)
      GO TO(84,84,83),ICOV
 84   WRITE(6,85)H,H1
 85   FORMAT(37H0WEIGHTED SUM OF SQUARES OF RESIDUALSE17.7/29H0COVARIANC
     2E MATRIX MULTIPLIERE17.7//)
      GO TO 86
 83   IF(NY-1)87,87,88
 87   WRITE(6,89)H
 89   FORMAT(28H0SUM OF SQUARES OF RESIDUALSE17.7//)
      GO TO 86
 88   WRITE(6,90)H
 90   FORMAT(42H0DETERMINANT OF MOMENT MATRIX OF RESIDUALSE17.7//)
 86   WRITE(6,28)(C1(I),I=1,L)
 28   FORMAT(11H PARAMETERS//(7E17.6))
C THE FOLLOWING STATEMENTS MAY BE REMOVED FOR DAVIDON'S METHOD
      GO TO(300,301),METH
 300  DO 400 I=1,L
      DO 400 J=1,L
      C(I,J)=0.
      DO 400 K=1,L
 400  C(I,J)=C(I,J)+G1(I,K)*G1(J,K)/(ABS(EGV(K))+1.E-20)
      GO TO 303
C END OF REMOVABLE STATEMENTS
 301  DO 302 I=1,L
      DO 302 J=1,L
 302  C(I,J)=G(I,J)
 303  DO 45 I=1,L
 45   Y(I)=SQRT(C(I,I))
      WRITE(6,46)(Y(I),I=1,L)
 46   FORMAT(///34H STANDARD DEVIATIONS OF PARAMETERS//(7E17.6))
      WRITE (6,38)
 38   FORMAT(///32H COVARIANCE MATRIX OF PARAMETERS/)
      DO 39 I=1,L
 39   WRITE(6,37)(C(I,J),J=1,L)
   37 FORMAT (/7E17.6/(7E17.6))
      CALL EIG(NTH,2)
      WRITE(6,200)(C(I,I),I=1,NTH)
 200  FORMAT(//34H0EIGENVALUES OF CORRELATION MATRIX//(7E17.6))
      WRITE(6,201)
 201  FORMAT(//21H0PRINCIPAL COMPONENTS/)
      DO 202 I=1,NTH
 202  WRITE(6,37)(G1(J,I),J=1,NTH)
      DO 500 I=1,NTH
      EGV(I)=0.
      Y(I)=SQRT(C(I,I))
      DO 500 J=1,NTH
 500  EGV(I)=EGV(I)+G1(J,I)*C1(J)
      WRITE(6,501)(EGV(I),I=1,NTH)
```

```
 501  FORMAT(//16H0EXPECTED VALUES//(7E17.6))
      WRITE(6,502)(Y(I),I=1,NTM)
 502  FORMAT(//20H0STANDARD DEVIATIONS//(7E17.6))
      RETURN
      END
```

```
C DECK 04
C COMPUTES SCALED EIGENVALUES AND VECTORS
      SUBROUTINE EIG(N,II)
      COMMON A(20,20),V(20,20),PSCA
      DIMENSION SCA(20)
      PSCA=0.
      IF(N-1)107,107,108
 107  GO TO(103,109),II
 109  V(1,1)=1.
      RETURN
 108  VN=2.
      SUM1=0.
      DO 22 I=1,N
      IF(A(I,I))101,100,101
 100  SCA(I)=1.
      GO TO 22
 101  A1=ABS(A(I,I))
      SCA(I)=1./SQRT(A1)
      PSCA=PSCA+ALOG(A1)
      DO 102 J=1,N
      A(I,J)=A(I,J)*SCA(I)
 102  A(J,I)=A(I,J)
      A(I,I)=A(I,I)*SCA(I)
 22   CONTINUE
      DO 1 I=2,N
      DO 1 J=2,I
 1    SUM1=SUM1+A(I,J-1)*A(I,J-1)
      SUM1=SQRT(2.*SUM1)
      SUME=SUM1/10.E7
      GO TO(30,31),II
 31   DO 32 I=1,N
      DO 50 J=1,N
 50   V(I,J)=0.
 32   V(I,I)=1.
 30   IN=0
      IF(N-1)18,17,18
 18   SUM1=AMAX1(SUME,SUM1/VN)
   16  CONTINUE
      DO 3 J=2,N
      J1=J-1
      DO 3 I=1,J1
      IF(ABS(A(I,J))-SUM1)3,3,4
    4 IN=1
      Y1=-A(I,J)
      Y2=(A(I,I)-A(J,J))/2.
      OMEGA=Y1/SQRT(Y1**2+Y2**2)
      OMEGA=OMEGA*SIGN(1.,Y2)
      Y1=OMEGA/SQRT(2.*2.*SQRT(1.-OMEGA**2))
      BB1=Y1**2
      BB2=1.-BB1
      Y2=SQRT(BB2)
```

```
    9 DO 5 K=1,N
      IF (K-I) 6,5,6
    6 IF (K-J) 7,5,7
    7 Y3=A(K,I)*Y2-A(K,J)*Y1
      A(K,J)=A(K,I)*Y1+A(K,J)*Y2
      A(K,I)=Y3
      A(J,K)=A(K,J)
      A(I,K)=A(K,I)
    5 CONTINUE
      BB3=2.*Y1*Y2*A(I,J)
      Y3=A(I,I)*BB2+A(J,J)*BB1-BB3
      Y4=A(I,I)*BB1+A(J,J)*BB2+BB3
      A(I,J)=(A(I,I)-A(J,J))*Y1*Y2+A(I,J)*(BB2-BB1)
      A(J,I)=A(I,J)
      A(I,I)=Y3
      A(J,J)=Y4
      GO TO(3,20),II
   20 DO 12 K=1,N
      Y3=V(K,I)*Y2-V(K,J)*Y1
      V(K,J)=V(K,I)*Y1+V(K,J)*Y2
   12 V(K,I)=Y3
    3 CONTINUE
      IF (N-2) 17,17,21
   21 IF (IN-1) 14,15,15
   15 IN=0
      GO TO 16
   14 IF (SUM1-SUME)17,17,18
 17   GO TO(103,104),II
 104  DO 105 I=1,N
      DO 105 J=1,N
 105  V(I,J)=V(I,J)*SCA(I)
 103  RETURN
      END
```

```
C DECK 22
C MATRIX OPERATIONS FOR DECK 14
      SUBROUTINE XIJ
      COMMON C(20,20),G1(20,20),PSCA,G(20,20),F(20),Y(20),EGV(20),FF(20)
     1,TITLE(20),CUB(20),CLB(20),PNL(20),NCON,LCUT,F3,NTH,F6,F7,METH,NPH
     2,MD,LS,C1(20)
      COMMON/BONE/V(5,5),QY(5),YTH(5,20),A(100,10),ICOV,DET,IDER,M,NY,NA
      COMMON/C/NX,NB,NTH2,NTH1,G(10),P(10),FX(10,10),FTH(10,20),BV(20,10
     5),TIME(100),IA(100),FN(10),XTH(10,20),XTTH(10,20)
      DO 1 I=1,NX
      DO 1 J=1,NTH2
      XTTH(I,J)=FTH(I,J)
      DO 1 K=1,NX
 1    XTTH(I,J)=XTTH(I,J)+FX(I,K)*XTH(K,J)
      RETURN
      END
```