بسم الله الرحمن الرحيم

IN THE NAME OF GOD MOST MERCIFUL
AND MOST COMPASSIONATE

ESTIMATION
OF RATE CONSTANTS FOR
THE COAL LIQUEFACTION
PROCESS

By

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ABSTRACT

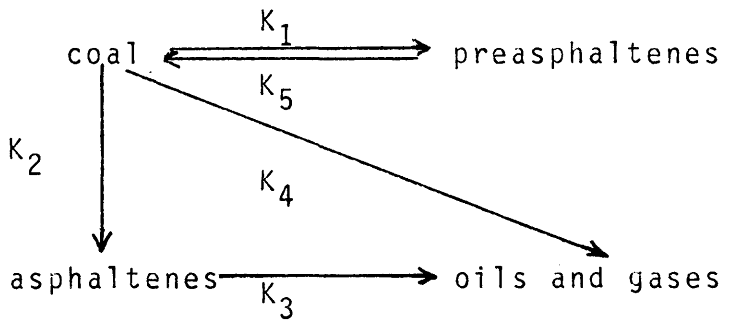
Eleven different reaction networks describing coal liquefaction in terms of oils, asphaltenes, preasphaltenes, and unreacted coal were investigated with the objective of determining the best model that represents the coal liquefaction process. The analysis was made using both integral and differential methods, where the differential method was applied only to the initial rate data.

In the integral analysis method, the parameters (rate constants) were evaluated by a least-squares fit using an available non-linear parameter estimation computer program. The goodness of fit for the parameter estimations was given by the "determinant of the moment matrix of residuals" (dmmr). The model that exhibited the lowest value of this determinant was considered the best in describing the kinetics of the coal liquefaction process.

In the differential (initial rate) method, the parameters were evaluated by multiple linear regression using the available MINITAB library program. The goodness of fit for these parameter estimations was given as the "ratio of sum of squares due to regression to the total sum of squares". The closer this ratio was to one, the better the model.

Both methods of analysis led to the following reaction

network as the best model:



where reactions 1, 2, and 4 are second order in coal.

Arrhenius activation energies of 36.4, 34.3, 7.9, 39.6, and 25.0 K cal/gm mole were calculated using integral analysis method for reactions 1, 2, 3, 4, and 5, respectively. Activation energies of 25.9, 30.4, and 31.1 K cal/gm mole were calculated using differential analysis for reactions 1, 2, and 4, respectively.

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To

My lovely wife, Rabia

and

My two beautiful sons

Rabea and Sirrage

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. One of the alternatives is the conversion of coal to produce useful hydrocarbon products.

This study deals with the rate of conversion of coal to preasphaltenes, asphaltenes, and oils plus gases. Rate constants for the formation of preasphaltenes, asphaltenes, oils plus gases, and disappearance of unreacted coal have been calculated for a variety of different reaction networks. The mathematical models were compared to available experimental data of Furlong (23) and Shalabi (19).

Two completely independent techniques of analysis were employed for the purpose of this study. First, the integral analysis technique which required the analysis to be carried out on the overall reaction was used. Secondly, the differential analysis technique was used, which required the analysis to be done where the change in the rate of reaction was the greatest. Hence, only the initial rate data were employed for the differential technique. Models were discriminated using least-squares fit non-linear parameter estimation for the integral analysis technique, and by using the regression analysis coupled with Lagrangian differentiation of the data to estimate rate constants for the differential analysis technique. Arrhenius activation energies were calculated where data were available at more than one temperature.

Several research groups have investigated the kinetics and mechanism of coal liquefaction. However, most of the work has been quite narrow in scope. Generally, data for coal reactivity in these investigations have consisted of a single number for the total percentage of coal converted at some set reaction time. This number can tell nothing of the rate of reaction of coal, especially since most of the data were taken at long residence times where the change in the rate of reactions may be nearly zero. Also, most of these prior investigations were made on only one or two kinds of coal, and employed very few kinetic models for data analysis. The factors that make this study unique are the use of large sets of data on many different kinds of coals which were carefully chosen from virtually every area of the United States and vary widely in physical and chemical properties. Another unique factor of this study is that many reaction networks, including some new models, have been investigated. Several of these models include additional kinetic steps which have not appeared in previously published work. Finally, this study takes into account the analysis of short residence times where the change in the rate of reactions is the greatest.

LITERATURE SURVEY

Studies of the kinetics and mechanism of coal conversion were started many years ago and these studies continue to this day.

Storch, et al (1940) have successfully modeled liquefaction data for a Pittsburgh coal in tetralin in the form of first-order mechanism with respect to coal remaining.

Oele, et al (1951), in a non-catalytic dissolution study, used anthracene oil and a Limburg bituminous coal. They found that it was useful to use the following equation:

$$\frac{dx}{dt} = K - K' x \qquad (1)$$

Here, zero-order dependence on coal conversions for the thermal disintegration of coal and first-order dependence for coal conversions were assumed.

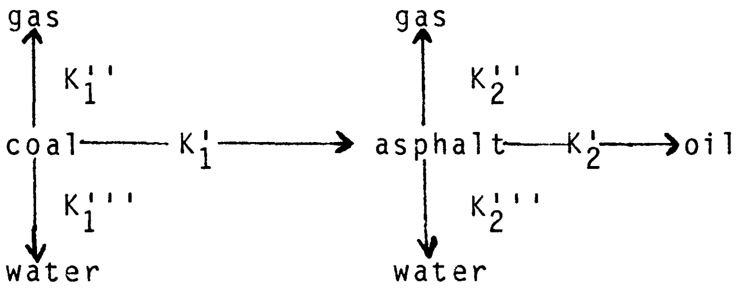
Integration of the above equation and substitution of $K=K'a$ yielded the following expressions:

$$\ln\left(1-\frac{x}{a}\right) = -K't \qquad (2)$$

where "a" represented the equilibrium conversion and K' was the rate constant. Their data were successfully modeled using the last equation.

Weller, et al (1951A,B) have studied the kinetics of coal hydrogenations of Bruceton (Pittsburgh-seam) coal.

Table 1 provides the data obtained for conversion of coal, and Figure 1 represents the plot of coal versus reaction time. Based on these results, Weller, et al proposed the following reaction network of the conversion of coal:



As can be seen, the only intermediate product in this mechanism was asphalt and there was no metion of other products such as preasphaltenes and asphaltenes. The K's were specific rate constants for the reactions indicated. Weller et al (1951A,B) assumed that the conversion of coal was first-order with respect to coal remaining. The following expressions were proposed for the amount of coal and asphalt as a function of time:

$$C = C_o e^{-K_1 t} \tag{3}$$

and

$$A = \frac{\alpha C_o K_1}{K_1 - K_2} \left(e^{-K_2 t} - e^{K_1 t}\right) \tag{4}$$

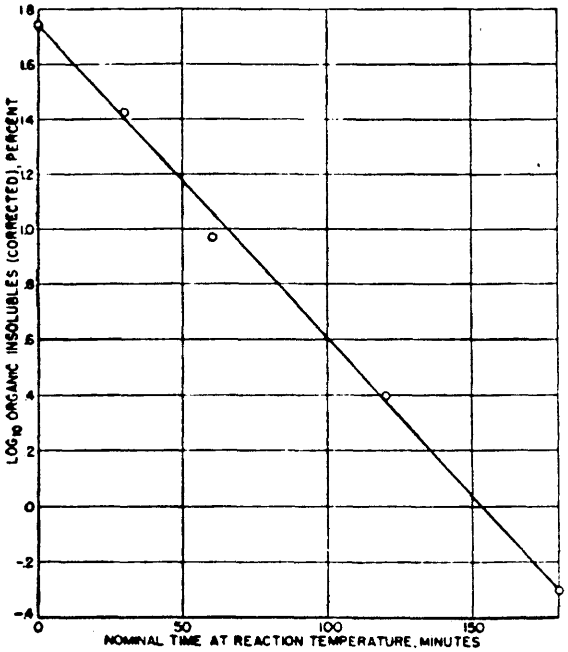


Figure 1. First-Order Plot for Over-All Conversion of Anthraxylon at 400° C.

where

$K_1 = K_1' + K_1'' + K_1'''$

$K_2 = K_2' + K_2'' + K_2'''$

C = coal remaining at time, t

A = asphalt present at time, t

C_0 = amount of moisture and ash-free coal present at time, zero

$\alpha = K_1'/K_1$

Hill (1966) suggested the following mechanism for the dissolution of coal:

$$\text{Solvent} + \text{coal} \xrightarrow{K_1} R_i + L_i + G_i$$

$$\text{Solvent} + R_i \xrightarrow{K_2} R_2 + L_2 + G_2$$

$$\vdots$$

$$\text{Solvent} + R_n \xrightarrow{K_{n+1}} R_{n+1} + L_{n+1} + G_{n+1}$$

where

R_i = solid coal residue

L_i = extract in solution

G_i = gaseous products.

It was assumed that the coal dissolution reaction would be first-order, which may be described by the following mathematical model:

Table 1. Rate constants for the conversion of coal.

Temperature °C	K_1 Min^{-1}	K_2 Min^{-1}
400	.027	.00107
420	.060	.00503
430	.126	.00892
440	.129	.01282

$$\frac{dx}{dt} = K^1 (1-x) \qquad (5)$$

where

x = fraction of extracted coal
K^1 = first-order reaction rate constant.

The relationship between K^1 and x was shown to be linear according to the following equation:

$$K^1 = K (1-ax) \qquad (6)$$

where K and a were parameters that could be determined experimentally. The rate of dissolution was successfully modeled as second order after substituting equation (6) in equation (5) to give:

$$\frac{dx}{dt} = K (1-ax) (1-x) \qquad (7)$$

Curran, et al (1967) have studied the kinetics of hydrogen transfer from tetralin to bituminous coal where two first-order reactions occuring in parallel were proposed to describe coal dissolution to products

$$\text{coal} \overset{K_1}{\underset{K_2}{\rightrightarrows}} \text{products}$$

where $K_1 > K_2$

The rate of coal pyrolysis for the model was given by

$$C_T - C = \gamma C_T \exp(-K_1 t) + (1-\gamma) C_T \exp(-K_2 t) \qquad (8)$$

where:

C_T = coal conversion in percent MAF coal achieved at infinite time

C = coal conversion in percent of MAF coal

γ = the fraction of the coal which decomposes by the faster rate.

K_1 and K_2 were the specific rate constants.

The kinetics of coal hydrogenation without a catalyst in a batch reactor with tetralin has been studied by Liebenberg et al (1973). They proposed the following mechanism to be the best representation of the hydrogenation of coal:

$$\text{coal} \xrightarrow{K_1} \text{asphalt} \xrightarrow{K_2} \text{heavy oil}$$

Unfortunately, the data fit was unsuccessful. However, they suggested a more elaborate mechanism in the form of:

$$\text{coal} \xrightarrow{K_1} \text{asphalt} \xrightarrow{K_2} \text{heavy oil}$$

$$\text{coal} \xrightarrow{K_3} \text{asphalt}$$

$$\text{coal} \xrightarrow{K_4} \text{heavy oil}$$

Koltz (1975) studied the kinetics of hydro-desulfurization of coal in a coal in a batch reactor. Koltz successfully modeled his data according to the following mechanism:

$$\frac{dx}{dt} = K_o (1-ax)(1-x) \qquad (9)$$

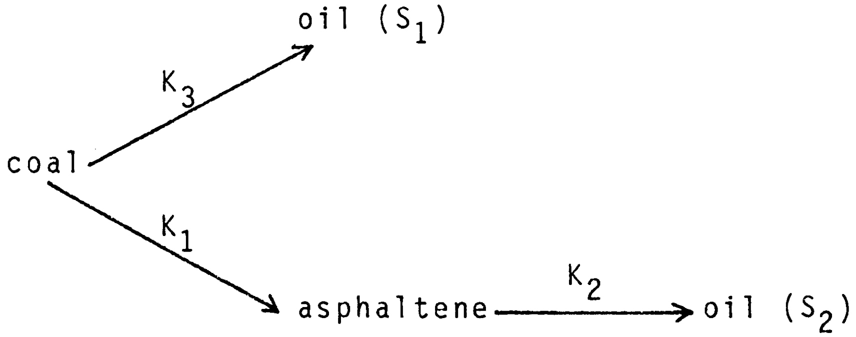
where

K_o was the pseudo second-order rate constant
x was the fractional coversion

Integrating equation (9), the following equation was obtained:

$$\ln\left(\frac{1-x}{1-ax}\right) = K_o t (a-1) \qquad (10)$$

Yoshida et al (1976A,B) carried out a kinetic study on Sumiyoshi brown coal of Hokkaido, and established the following mechanism:



One of their conclusions was that the formation reaction of S_1 (oil) was not recognized in foreign coals. Also, they found that the oil produced directly from coal as the initial reactant was much different in chemical structure than that produced from the asphaltenes.

The calculated rate constants were:

		Min^{-1}		
Coal	K_1	K_2	K_3	K_1+K_3
Taiheiyo	.0037	.0049	.0170	.0207
Oyubari	.0090	.0044	.0046	.0136

Ruether (1977) extended the work done by Weller et al by considering asphaltene to be a hydrogen donor solvent of variable hydrogen composition. He suggested that under the experimental conditions employed, the rate of hydrogenation of asphaltenes was materially faster than the rate of conversion of asphaltenes to oil. According to his work, the asphaltenes first underwent an increase in chemical hydrogen content of 0.010 gm of hydrogen 1 gram on average, then underwent conversion to oil. The empirical equation that predicted the hydrogen consumption in coal conversion to asphaltenes and oil was:

$$h = \alpha^{-5} (0.022\ x + 0.024\ y) + 0.043\ y \qquad (11)$$

where

h = grams of hydrogen consumed/gram of MAF coal feed.

α = fraction of MAF coal converted that goes to asphaltenes

x = gram of asphaltenes in product/gram of MAF coal feed

y = gram of oil in product of MAF coal feed.

Ruether concluded that coal conversion occurred via catalyzed and uncatalyzed reactions, and those two reactions are coupled.

Wen et al (1978) did studies on bituminous coal. They found that the coal dissolution rates seemed to be affected by types of coal. The degree of coal dissolution was measured by conversion based on the fraction of coal that was converted to benzene solubles on a moisture-ash free basis. They proposed rate expressions for coal dissolution that took the following form:

$$-\gamma_A = k\ C_{Ao}\ (X_e - X) \qquad (12)$$

where

X = MAF conversions based on benzene solubles

X_e = equilibrium conversions

C_{Ao} = concentrations of MAF coal in feed stream, gram/cm^3

k = first-order dissolution rate coefficient, hr^{-1}

γ_A = rate of coal dissolution, gram/ln-cm^3

For a plug flow reactor, integration of equation (12) gave the following expressions:

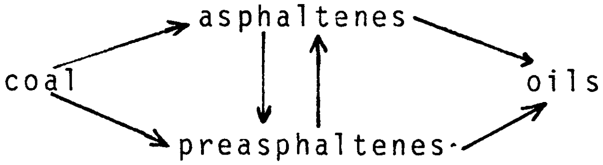
$$\ln (X_e - X) = -k\theta \qquad (13)$$

where

θ = residence time, hr.

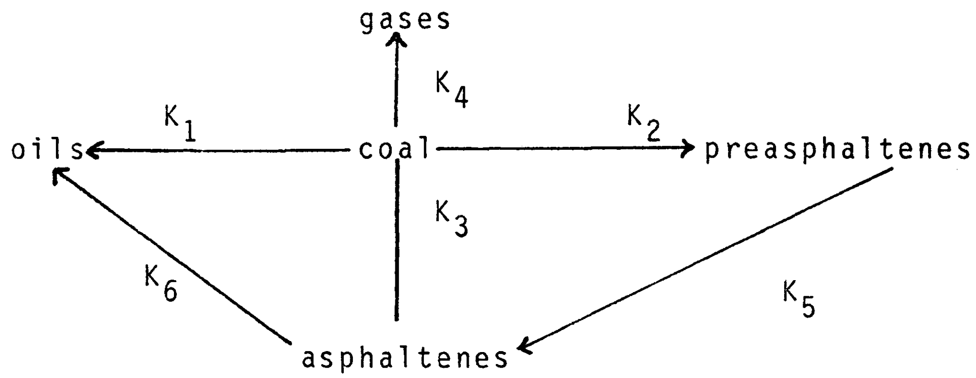
Wen et al also studied the effect of residence time, pressure, and temperature on coal conversions.

Schwager and Yen (1978) reached the conclusion that a reaction mechanism of the following from:



is more probable than that of a straight series mechanism. This was because the H/C ratio in the preasphaltenes was less than that in the parent coal. A parallel series mechanism can account for this.

Cronauer et al (1978) did studies on coal liquefactions using Illinois No. 6 coal in SRC-II heavy distillate. The liquefaction process was described by the following scheme:



Reactions 1, 2, 3, 4, 5, and 6 give activation energies of 14.1, 13.8, 15.6, 21.5, 12.8, and 16.0 K cal/gm mole, respectively.

Shalabi et al (1979) studied non-catalytic coal liquefaction in a donor solvent. Rates of formation of preasphaltenes, asphaltenes, and oil were experimentally determined during solvent extraction of a high-volatile A bituminous coal. They proposed the following mechanism as a best fit to the data:

$$\text{coal} \xrightarrow{K_1} \text{asphaltenes}$$

$$\text{coal} \xrightarrow{K_2} \text{preasphaltenes}$$

$$\text{coal} \xrightarrow{K_3} \text{oil and gas}$$

$$\text{asphaltenes} \xrightarrow{K_4} \text{oil and gas}$$

$$\text{preasphaltenes} \xrightarrow{K_5} \text{oil and gas}$$

$$\text{preasphaltenes} \xrightarrow{K_6} \text{asphaltenes}$$

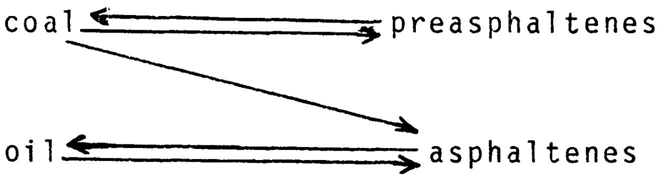
All of the six reactions were assumed to be first-order, irreversible reactions. Reaction conditionswere a pressure of 2000 psig, and a temperature range from 350 to 400 °C. The determined rate constants are given below

hr^{-1}

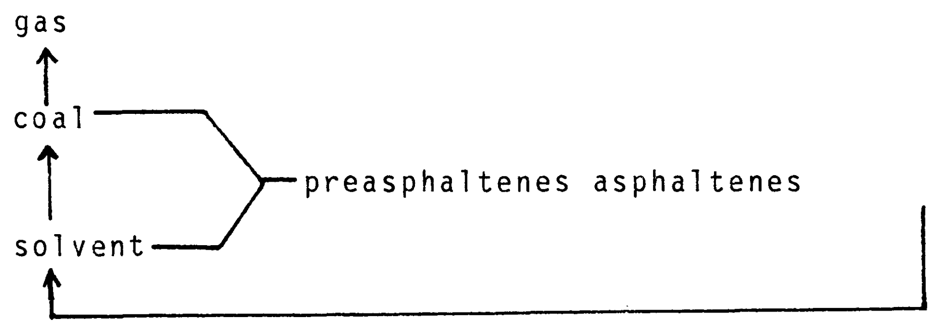
Temp.	K_1	K_2	K_3	K_4	K_5	K_6
400	.04546	.0715	.02646	.00279	.00284	.00385
375	.02697	.05202	.01870	0	.00183	.00225
350	.00789	.01214	.01214	.00081	.00269	$\simeq 0$

A fit of the model to the experimental data was quite good, except for the oil and gas fraction.

Gertenbach (1979) studied the kinetics of continous coal liquefaction processes. Based on previous work done by Shalabi et al (1979), he proposed the following mechanism for coal liquefaction:



Thomas et al (1980) studied the kinetics and mechanism of the hydroliquefaction of Illinois No. 6, and an unreacted SRC-II heavy distillate in a tabular flow reactor. They worked with temperatures from 400 to 475 °C, and a pressure of 2000 psia. The proposed mechanism was:



They also were able to show that the stoichiometries for the reaction at 450 °C were:

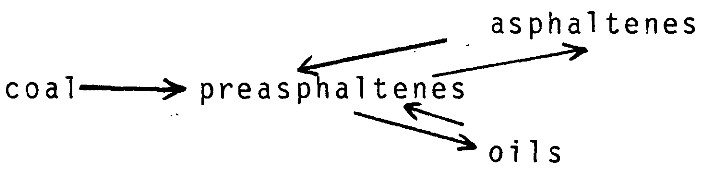
$$\text{coal} + 3\ \text{solvent} \longrightarrow \text{preasphaltenes}$$
$$\text{preasphaltenes} \longrightarrow 2\ \text{asphaltenes}$$
$$\text{asphaltenes} \longrightarrow 3\ \text{oils}$$

Calculated activation energies for the preasphaltene and asphaltene conversion reactions were 15 and 21 K al/gm mole, respectively.

Traeger (1980) liquefied Illinois No. 6 in SRC-II heavy distillate using a bench scale reactor. His research was based on the model proposed by Cronaur et al (1978). He found that the dissolution of coal was rapid, resulting in high preasphaltene content. Traeger also studied the effect of short residence time on product yield, and made a comparison between his bench scale reactor data superimposed on

Cronaur's predictions, and the calculated product distribution using Cronaur's reaction rate constants for a 425 °C isothermal operation (Figure 2). The results were in good agreement at long residence times. According to Traeger (1980), this was to be expected since Cronaur's reactions had long residence times. The major differences were in the early time behaviour of preasphaltenes. As can be seen from Figure 2, bench scale reactor data show a higher preasphaltene content earlier in the reaction than predicted by Cronaur's model.

Mohan, et al (1981) studied the kinetics of coal liquefaction of Illinois No. 6 coal in a batch reactor under non-isothermal conditions from 330 to 450 °C using tetralin as a hydrogen-donor solvent at total pressure of 70 atmosphere and reaction times from 5 to 60 minutes. They were able to fit their experimental data in the low-temperature range and in the high temperature range according to the following model:



All reactions were assumed to be first-order. Figures 3 and 4 represent the fit of experimental data to the above

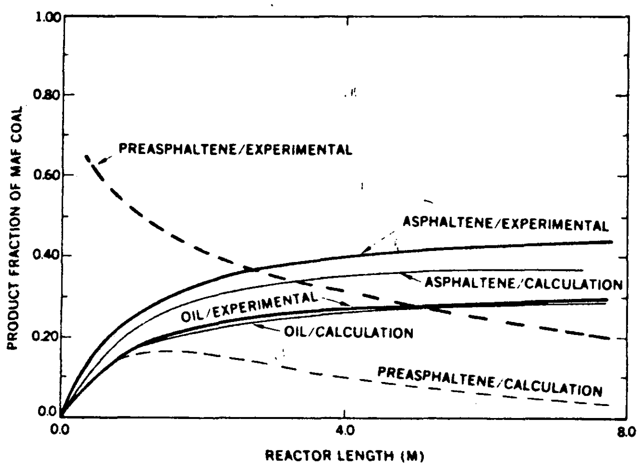


Figure 2. Product distribution comparison for short residence time at 425°C.

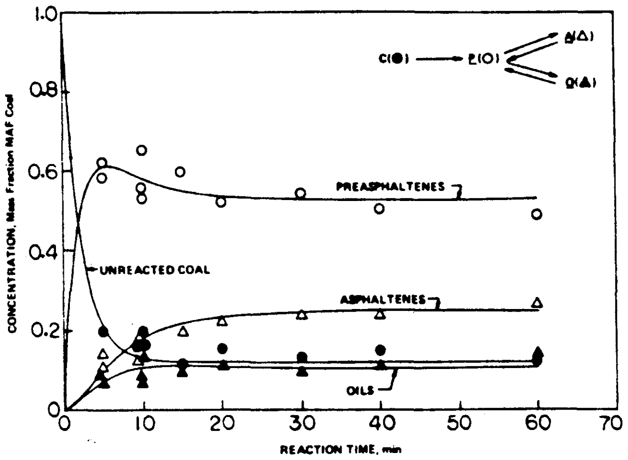


Figure 3. Comparison of Mohan, et al's model with experimental product concentration in the high-temperature range.

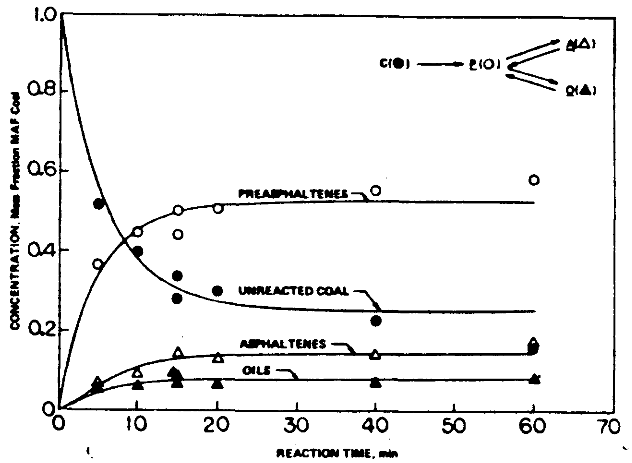


Figure 4. Comparison of Mohan, et al's model with experimental product concentration in the low-temperature range.

model in the high and low temeprature range respectively. Mohan, et al (1981) found that the calculated kinetic parameters differed considerably from literature values.

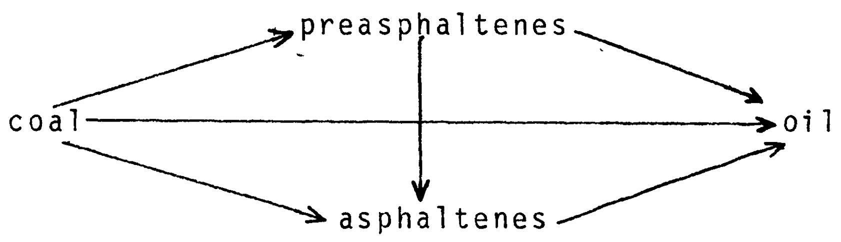
Furlong (1981) studied coal liquefaction in a one-liter semi-batch stirred reactor. Reactions were carried out at 400 °C, and 2000 psig total pressure. He concluded that pseudo second-order rate models may be used to describe coal conversion to THF or to benzene soluble products. The form of equation describing the model was:

$$\frac{dx}{dt} = K\,(a-x)^{2} \qquad (14)$$

where

x = conversion at time, t, min.
a = equlibirium conversion of coal
K = pseudo-second-order rate constant.

Furlong also was able to model his data using the following six parameter mechanism:



Hardy (1981) did studies on the kinetics of coal hydrogenation of a Kentucky No. 9 coal in a continuous flow stirred tank reactor. He concluded that the overall conversion of coal was first-order pseudo irrversible:

$$\frac{dx}{dt} = K\ (1-\frac{x}{a}) \qquad (15)$$

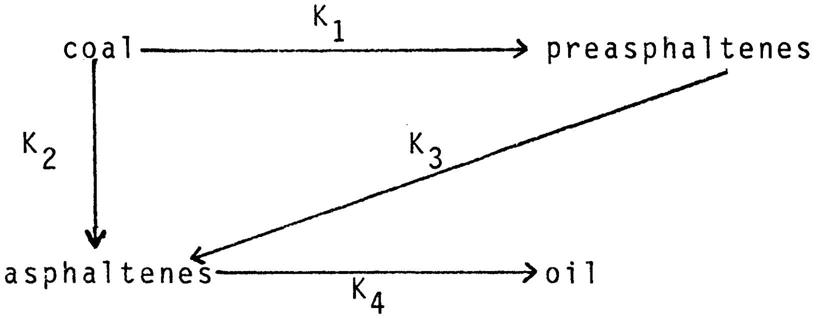
where

x = the coal conversion

a = the equilibrium conversion

K = the pseudo first-order rate constant.

Hardy also concluded that the data on product distributions could be modeled according to the following mechanism.



The calculated rate constants for each reaction were:

Temp. °C			hr^{-1}	
	K_1	K_2	K_3	K_4
350	2.11±.65	3.21±.66	0.014±.87	1.089±.57
390	7.61±1.53	4.97±1.52	-.042±.61	0.833±.88
430	37.9±10.9	15.6±10.8	1.43±1.54	3.13±1.19

DATA ANALYSIS

Many reaction networks can be postulated for coal reacting to form liquefaction products, with the products themselves reacting to form other products. As the objective of this work was to discriminate between a large number of different candidate reaction networks for coal liquefaction, two independent techniques of data analysis were employed in this study. First, the integral analysis technique was used, which required numerical integration of the set of differential equations, and subsequently the parameters (rate constants) were evaluated by least-squares fit nonlinear parameter estimation. Second, the differential analysis technique, which required numerical differentiation of the short residence time experimental data (23), followed by regression analysis to estimate the coefficients (rate constants).

Integral Analysis Technique:

Liquefaction rate data from a comprehensive batch reactor study by Furlong (23) on thirteen coals were employed for integral analysis. All of the experimental data (from time 0 to 60 minutes) were used, since integral analysis deals with the overall reaction. Several reaction networks were proposed and the corresponding batch reactor mass balance equations were written. A non-linear parameter estimation (NLPE) program was obtained from the IBM share library system (30). Many reaction networks could be evaluated for rate constants using the NLPE program. An existing subroutine "driver" program was included with the program which was used directly for different models. The given reaction network was then described by a user-written subroutine. Model discrimination then took place using the Determinant of Moment Matrix of Rsiduals from the NLPE program as an indicator of goodness of fit. Use of existing and user-written "driver" routines is described in Appendix B.

Once kinetic parameters were evaluated for a proposed reaction network, the model and its evaluated parameters were input to a Runge-Kutta program to generate predicted concentration-time profiles for the four reaction components (unreacted coal, preasphaltenes, asphaltenes, and oils plus gases). The Runge-Kutta program is described in Appendix C. For a given reaction network, the fit was visually evaluated by plotting the resulting concentration-time profiles for the four components along with the experimental data from which the parameters were derived. These plots were generated using the available interactive GRAPH library programs.

Since many models were to be proposed and thirteen coals had been run, only two of the coals were used for model discrimination. Coals chosen were those for which the most reliable rate data were available from the study of Furlong (23), PSOC 370 and Fies Mine 9.

Differential Analysis Techniques (Initial Rate Analysis):

The differential method of analysis evaluates the rate of reaction (initial rates) directly by numerical differentiation of the experimental concentration versus time data. The differential analysis technique may be summarized as follows:

1. A reaction network is hypothesized, and from it the rate equations are obtained.
2. The experimental concentration versus time data is plotted.
3. A smooth curve is drawn through these data points for all components.
4. The slopes of these curves at selected concentration values are determined. These slopes are the rates of reaction at these compositions.

Step 4 was done by using Lagrange Interpolation formulas (33). By differentiating five-point Lagrange interpolation formulas, the following differentiation formulas result for equally spaced points.

$$f^1(x_0) = \frac{1}{12h}\,[-25f_0+48f_1-36f_2+16f_3-f_4] + \frac{h^4}{5}\,f^{(v)}\ (\epsilon)$$

$$f^1(x_1) = \frac{1}{12h}[-3f_0-10f_1+18f_2-6f_3+f_4] - \frac{h^4}{20}f^{(v)}(\varepsilon)$$

$$f^1(x_2) = \frac{1}{12h}[f_0-8f_1+8f_3-f_4] + \frac{h^4}{30}f^{(v)}(\varepsilon)$$

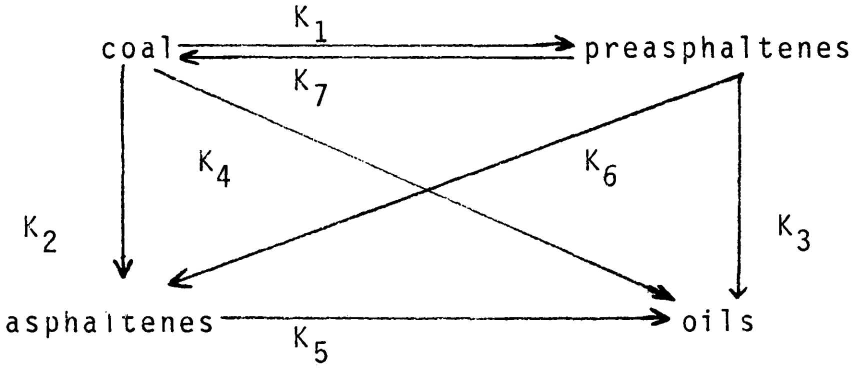
$$f^1(x_3) = \frac{1}{12h}[-f_0+6f_1-18f_2+10f_3+3f_4] - \frac{h^4}{20}f^{(v)}(\varepsilon)$$

$$f^1(x_4) = \frac{1}{12h}[3f_0-16f_1+36f_2-48f_3+25f_4] + \frac{h^4}{5}f^{(v)}(\varepsilon)$$

where x_0, x_1, x_2, x_3, and x_4 were the residence times, f_0, f_1, f_2, f_3, and f_4 were the corresponding concentrations, and h was the interval between two consectuive residence time data points (since the points were equally spaced, h was constant). The last term of each equation represents an error term. Usually numerical differentiation involves errors of considerable magnitude, the errors increasing significantly as derivatives of higher order are computed. However, since this study deals with derivatives of first-order, then neglecting the error terms from the above equations was reasonable.

Because application of the above equations required equidistant points (residence times), and since the residence times of the experimental data at hand were not equally spaced, step 3 (from above) was used to generate equally spaced residence time points, along with the corresponding concentrations. The analysis was done on the portions where the curves were steepest because the differential method is most accurate in this region. In other words, the analysis was made on the portions of the curves of the four components (unreacted coal, preasphaltenes, asphaltenes, and oils plus gases) where the change in the rate of reaction was the greatest (e.g., using initial rate data). Differential analysis should be avoided when the compositions profiles become flat since the change in the rates of reaction are almost zero, leading to large inaccuracies. In this study, the experimental data of Furlong were used only where the change in the rate of reaction was the greatest. As a result, some of the differential analyses was made on data up to a residence time of 10 minutes, and some analyses were made on data up to a residence time of 20 minutes, depending on the significance of the change in the rate of reaction.

As soon as these rates of reaction were obtained for a given experimental data set, the model and its evaluated rates of reaction were input to an interactive MINITAB library program. MINITAB performed multiple linear regression analysis, and the resulting coefficients represented the rate constants for the given model. For an example reaction network;



The equations to be solved are:

$$\frac{dc}{dt} = -(K_1+K_2+K_4)\ C + K_7P$$

$$\frac{dA}{dt} = K_2C - K_5A + K_6P$$

$$\frac{dP}{dt} = K_1C - (K_3+K_6+K_7)\ P$$

$$\frac{dO}{dt} = K_3P + K_4C + K_5A$$

The matrices describing this set of equations using two data points are shown in Figure 5. The Y's in the $\underline{Y}$ matrix represent the rates of reaction, and the X's in the $\underline{X}$ matrix represent the yields of the various components. The K's represent the rate constants to be evaluated.

Model discrimination then took place using the ratio of the sums of squares due to regression to the total sum of squares from MINITAB program as an indicator of goodness of fit. A sample run and data file for MINITAB are shown in Appendix E.

Once rate constants were evaluated for a proposed reaction network, the model and its evaluated parameters were input to a Runge-Kutta program to generate predicted concentration-time profiles for the four components. As was done in the integral analysis, the fit was visually evaluated by plotting the resulting concentration-time profiles for the four components along with the experimental data from which the parameters (rate constants) were derived.

From the most reliable rate data which were available from the study of Furlong (23), only eight coals were found to be suitable for differential analysis technique. However, two of those eight suitable coals were employed for model discrimination. These two coals were PSOC 107 and Fies Mine 9.

Figure 5: Matrices for Least-Squares Analysis

$$\begin{bmatrix} Y_1 \\ Y_2 \\ Y_3 \\ Y_4 \\ Y_5 \\ Y_6 \\ Y_7 \\ Y_8 \end{bmatrix} \quad \begin{bmatrix} -x_{11} & -x_{12} & 0 & -x_{14} & 0 & 0 & x_{17} \\ 0 & x_{22} & 0 & 0 & -x_{25} & x_{26} & 0 \\ x_{31} & 0 & -x_{33} & 0 & 0 & -x_{36} & -x_{37} \\ 0 & 0 & x_{43} & x_{44} & x_{45} & 0 & 0 \\ -x_{51} & -x_{52} & 0 & -x_{54} & 0 & 0 & x_{57} \\ 0 & x_{62} & 0 & 0 & -x_{65} & -x_{66} & 0 \\ x_{71} & 0 & -x_{73} & 0 & 0 & -x_{76} & -x_{77} \\ 0 & 0 & x_{83} & x_{84} & x_{85} & 0 & 0 \end{bmatrix} \quad \begin{bmatrix} K_1 \\ K_2 \\ K_3 \\ K_4 \\ K_5 \\ K_6 \\ K_7 \\ K_8 \end{bmatrix}$$

$$\underline{Y} \quad = \quad \underline{X} \quad \underline{b}$$

DISCUSSION OF RESULTS

As the main objective of this study was to develop the best possible reaction network that represented the kinetics of coal liquefaction, and since there was available a large set of experimental rate data from the study of Furlong (23), two completely independent techniques of data analysis were employed for the purpose of model discrimination. First, the integral method of analysis which dealt with the overall reaction (all of the experimental data from 0 to 60 minutes) was employed, followed by the differential method of analysis which dealt only with the short residence time experimental data.

Integral Analysis Method:

A pure first-order series model (designated Model 1) was first investigated leading to the following reaction sequence:

$$\text{coal} \xrightarrow{K_1} \text{preasphaltenes} \xrightarrow{K_2} \text{asphaltenes} \xrightarrow{K_3} \text{oils}$$

The rates of disappearance and formation of reactants and products in the batch reactor were represented by the following differential equations:

$$\frac{dc}{dt} = -K_1 C$$

$$\frac{dP}{dt} = K_1C - K_2P$$

$$\frac{dA}{dt} = K_2P - K_3A$$

$$\frac{dO}{dt} = K_3A$$

where C, P, A, and O were the mass fractions of unreacted coal, preasphaltenes, asphaltenes, and oils plus gases, respectively. The differential equations were then coded into the NLPE program, and the following rate constants generated:

Coal	K_1	K_2	K_3
PSOC 370	.02884	.03878	.01670
Fies Mine 9	.03894	.04719	.02737

where K_1, K_2, and K_3 have units, minutes^{-1}. Figures 6 and 7 show the computer-generated curves from this model along with the experimental data for the two runs of each coal.

The adequacy of the data fit for different models was given by the NLPE program as the "determinant of the moment matrix of residuals" (dmmr), the "residuals" being the differences between the experimental values for each of the component concentrations and the model predicted value for the variable. The model that yields the minimum value for

Figure 6:Model 1, Integral Method
3 Parameter,Coal:Fies Mine No.9

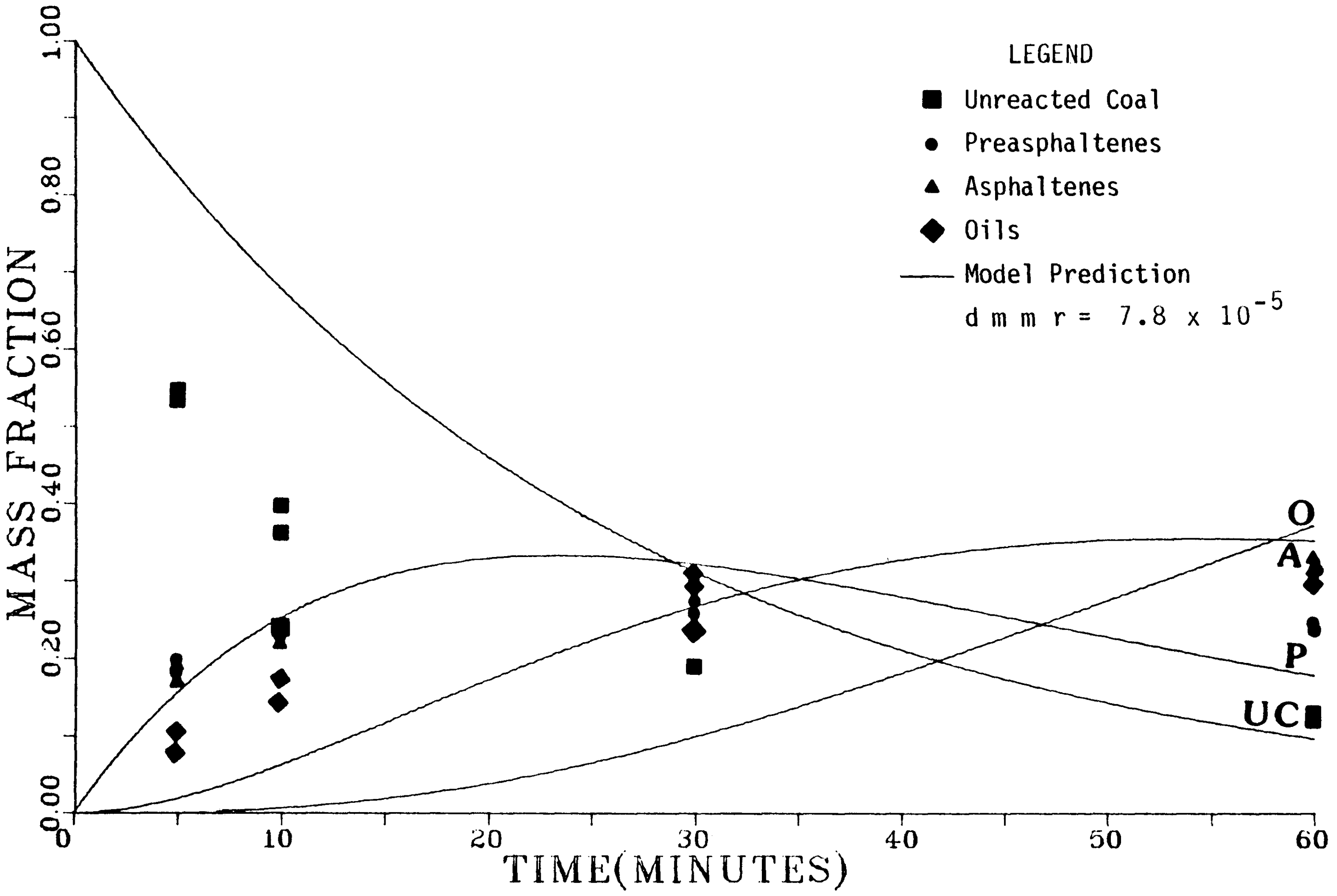
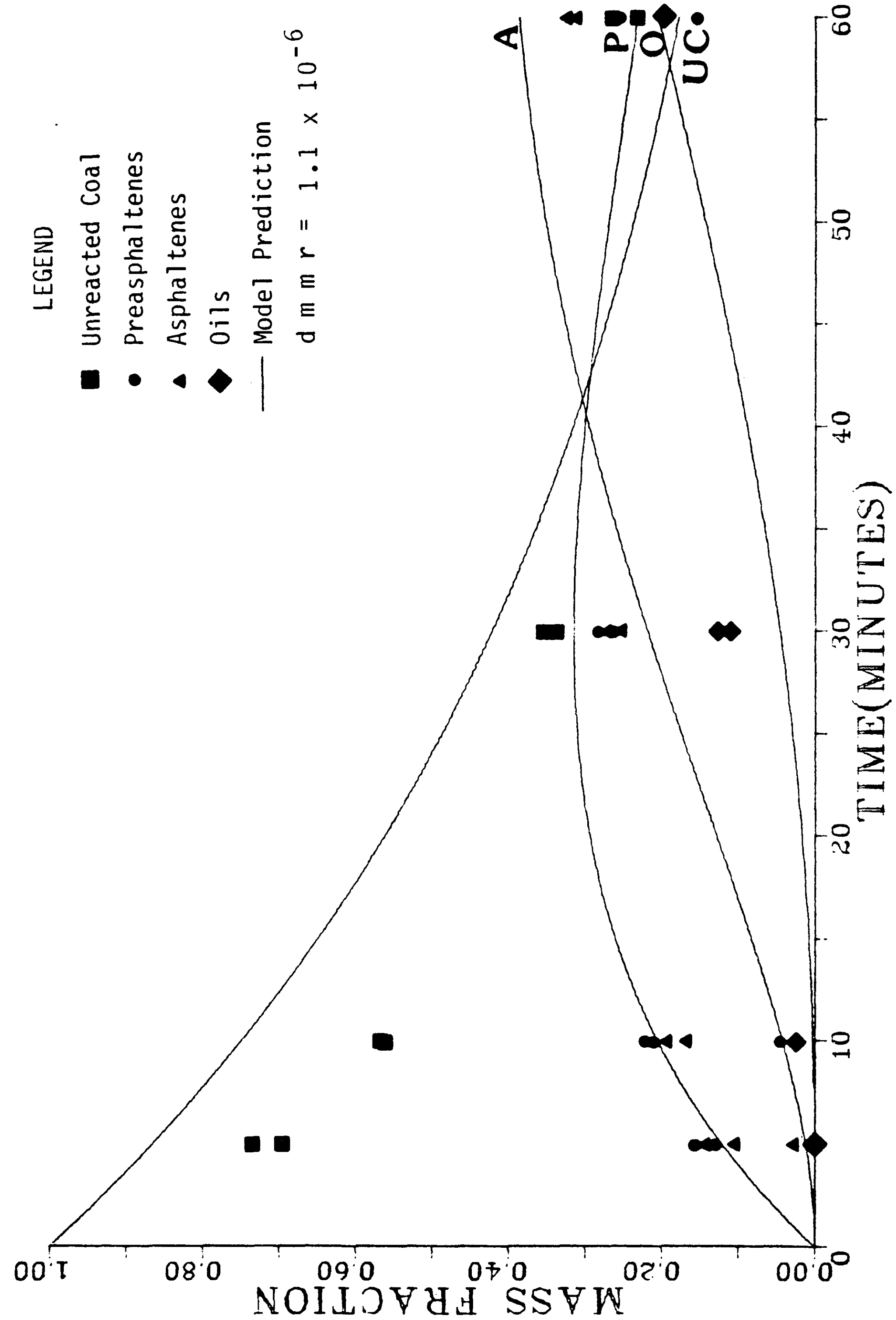
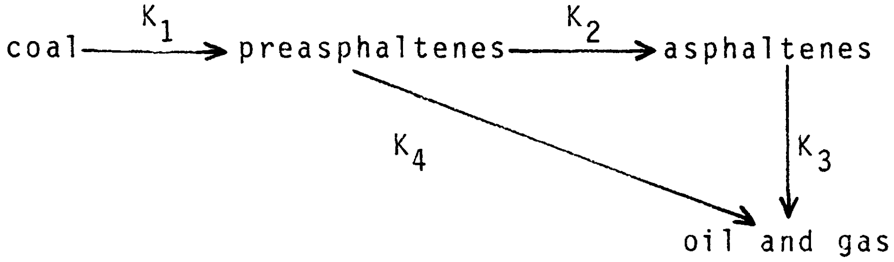


Figure 7:Model 1,Integral Method
3 Parameter, Coal:PSOC No.370



the "dmmr" would be expected to have the best fit to the experimental data. The "dmmr" value for each of the fits is given on each appropriate plot. As can be seen from Figures 6 and 7 the first-order series model with three parameters was inadequate.

Next, a four parameter model was sought, designated Model 2. Model 2 was a modification of Model 1 to include an extra parameter for conversion of preasphaltenes to oil and gas directly in addition to oil being formed from asphaltenes. Model 2 was represented by the following reaction network:



This yielded the following mass balance equations:

$$\frac{dC}{dt} = -K_1 C$$

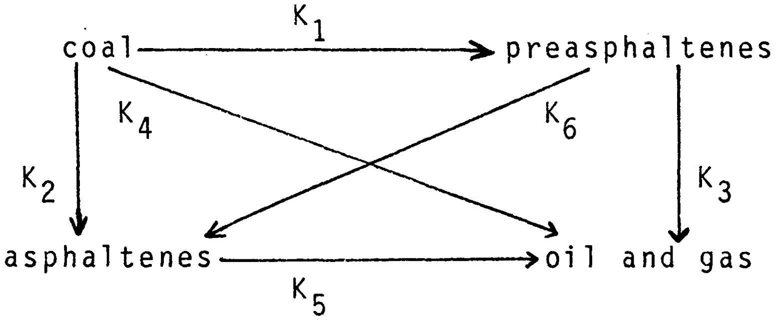
$$\frac{dP}{dt} = K_1 C - (K_2 + K_4) P$$

$$\frac{dA}{dt} = K_2 P - K_3 A$$

$$\frac{dO}{dt} = K_3 A + K_4 P$$

Here C, P, A, and O were defined as before. Although there was a small improvement on the fit to the data as can be seen in Figures 8 and 9, Model 2 was not suitable as an adequate representation for the coal conversion to preasphaltenes, asphaltenes, and oil and gas.

As a result, Model 3 was proposed. This was represented by the following scheme:



Assuming first-order irreversible kinetics for each of the six reactions involved, the following mass balances on the components were developed:

$$\frac{dC}{dt} = -(K_1+K_2+K_4)\ C$$

$$\frac{dP}{dt} = K_1C - (K_3+K_6)\ P$$

$$\frac{dA}{dt} = K_2C - K_5A + K_6P$$

$$\frac{dO}{dt} = K_3P + K_4C + K_5A$$

Figure 8:Model 2,Integral Method
4 Parameter, Coal: Fies Mine No. 9

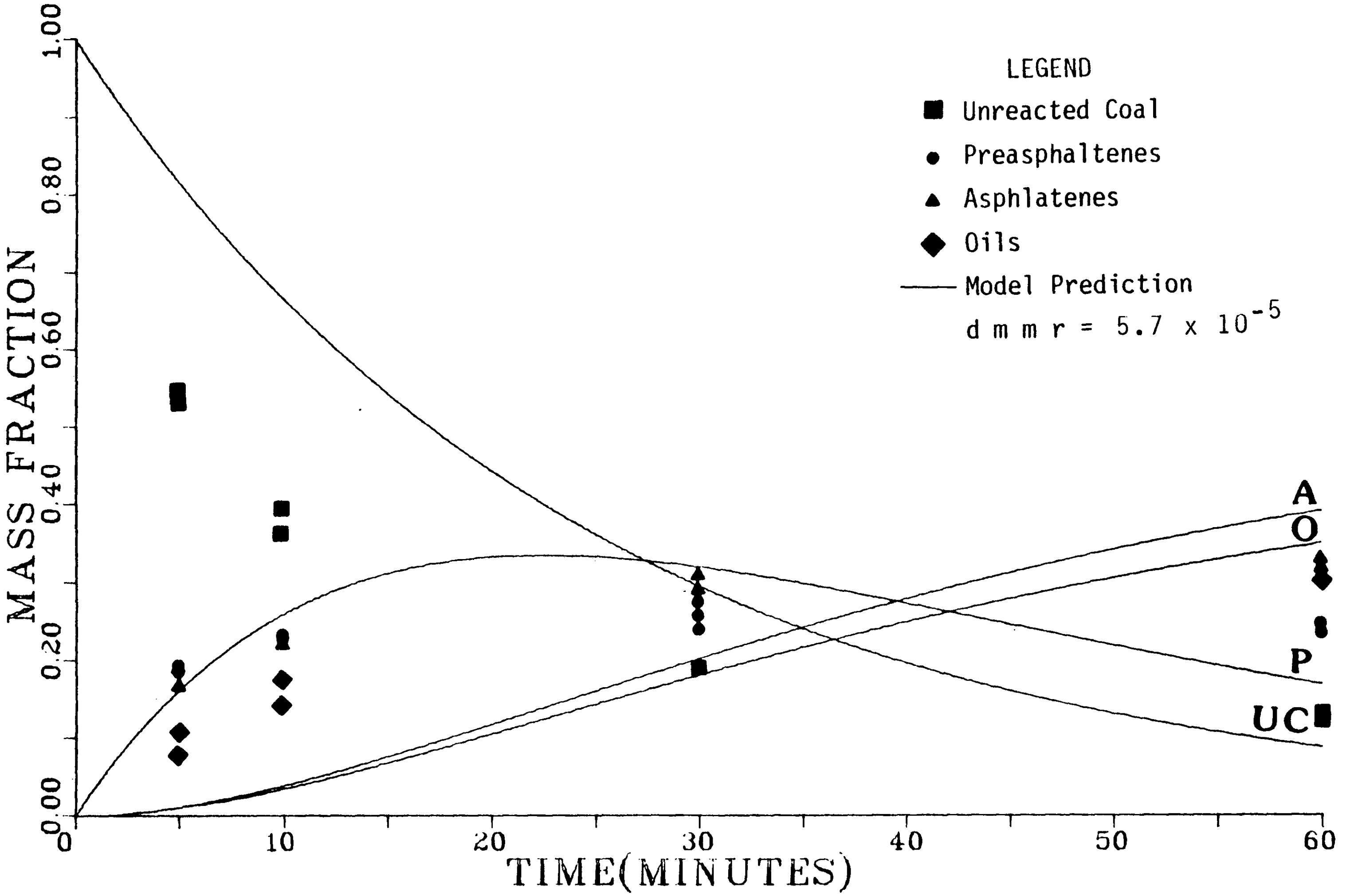
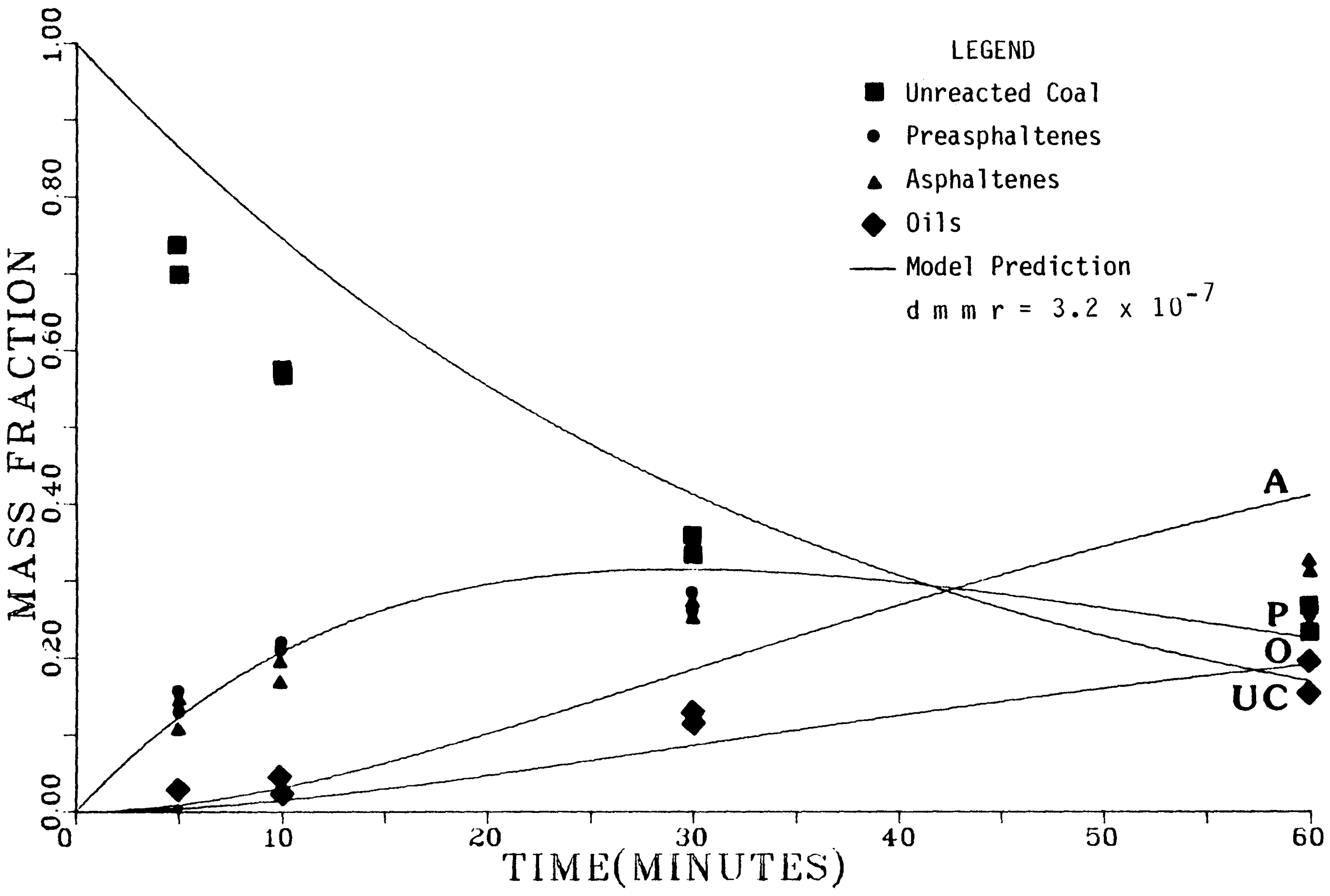


**Figure 9:Model 2,Integral Method
4 Parameter,Coal:PSOC No. 370**



This six-parameter model yielded the fits shown in Figures 10 and 11. As can be seen, the fit was good with respect to the oil and gas, and asphaltene curves for Fies Mine 9 coal, and also was good with respect to the oil and gas, and preasphaltene curves for PSOC 370 coal, but the fit for the other products for both coals was still extremely poor.

Assuming reversibility for reaction 1 of Model 3 led to Model 4 with seven parameters. As can be seen from Figures 10 and 11, the mass fraction of the unreacted coal tends to go to zero as the liquefaction process proceeds, which was undesirable, so the addition of the reversibility step was necessary to eliminate this unwanted result. Figures 12 and 13 represent the fit of Model 4 to the experimental data. As would be expected, the seven-parameter model fits the data better than the previous three models. The calculated rate constants are shown in Table 2.

It is clear from Table 2 that K_3 and K_6 are either very small or zero, which consequently means that the preasphaltenes had nothing to do with the formation of asphaltenes and oil plus gas. To examine the effect of elimination of the reaction of preasphaltenes to oil plus gases, Model 5 was proposed which is represented by the following reaction network:

Figure 10:Model 3,Integral Method
6 Parameter,Coal:Fies Mine No. 9

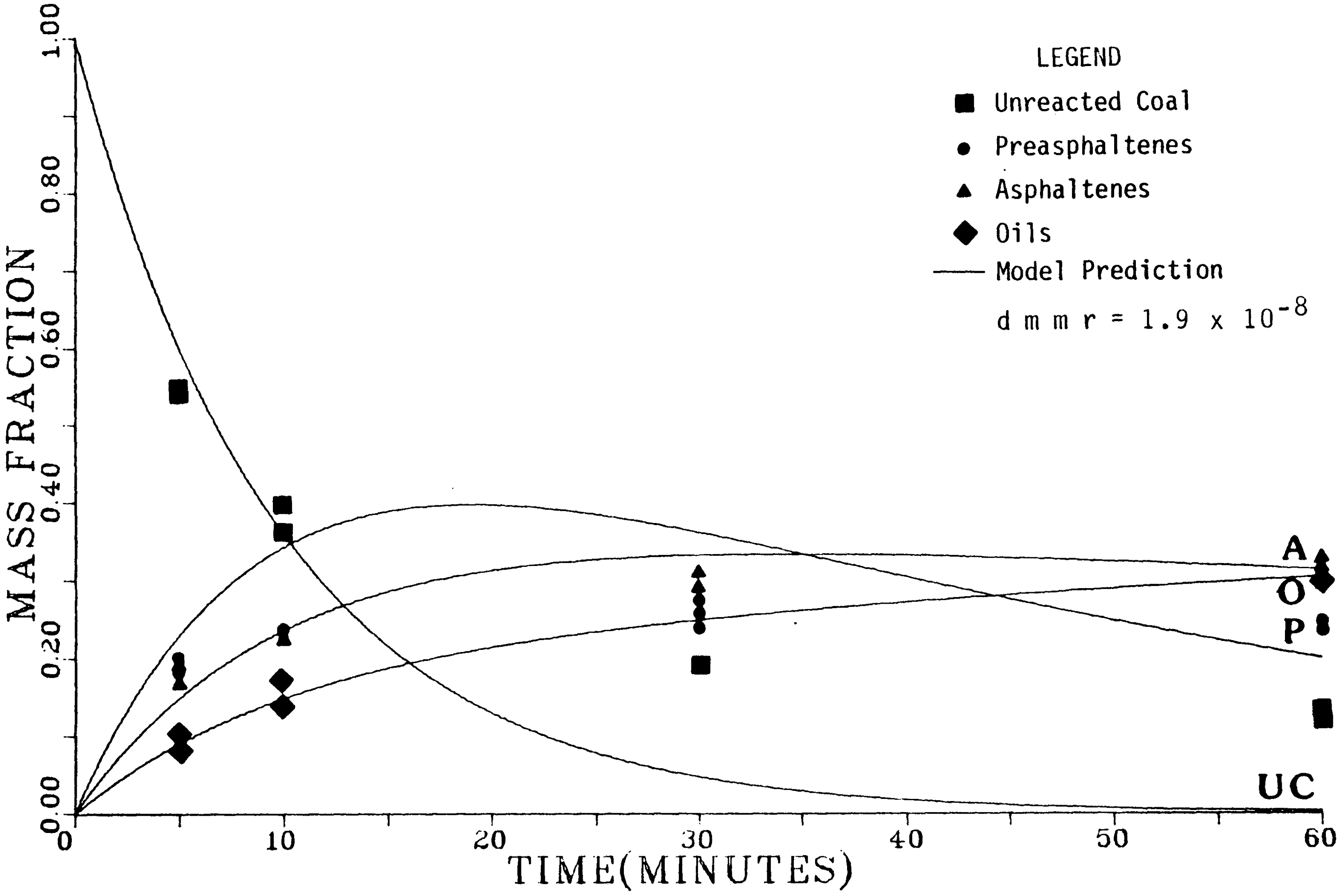


Figure 11:Model 3, Integral Method
6 Parameter,Coal:PSOC No. 370

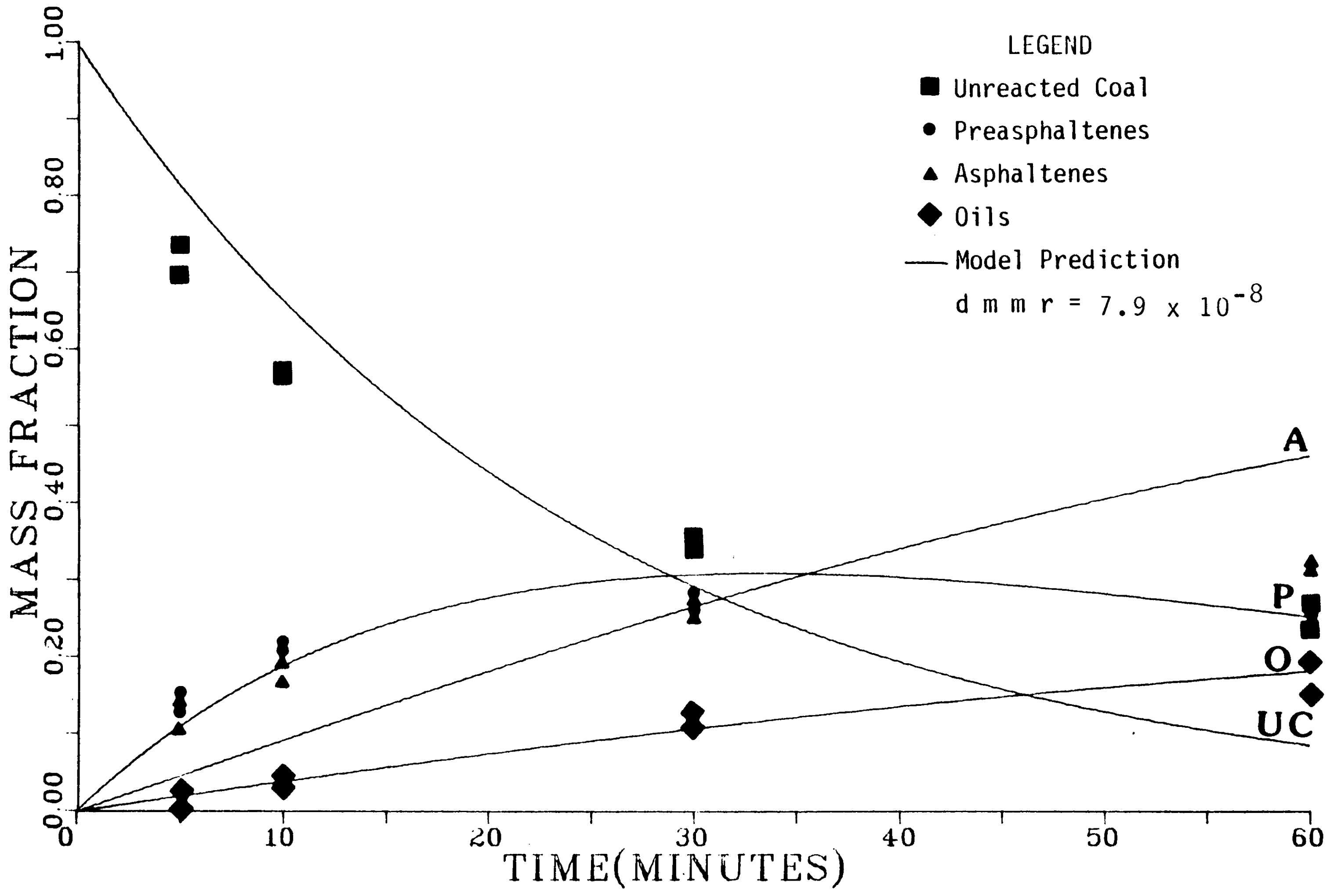


Figure12:Model 4,Integral Method
7 Parameter,Coal:Fies Mine No. 9

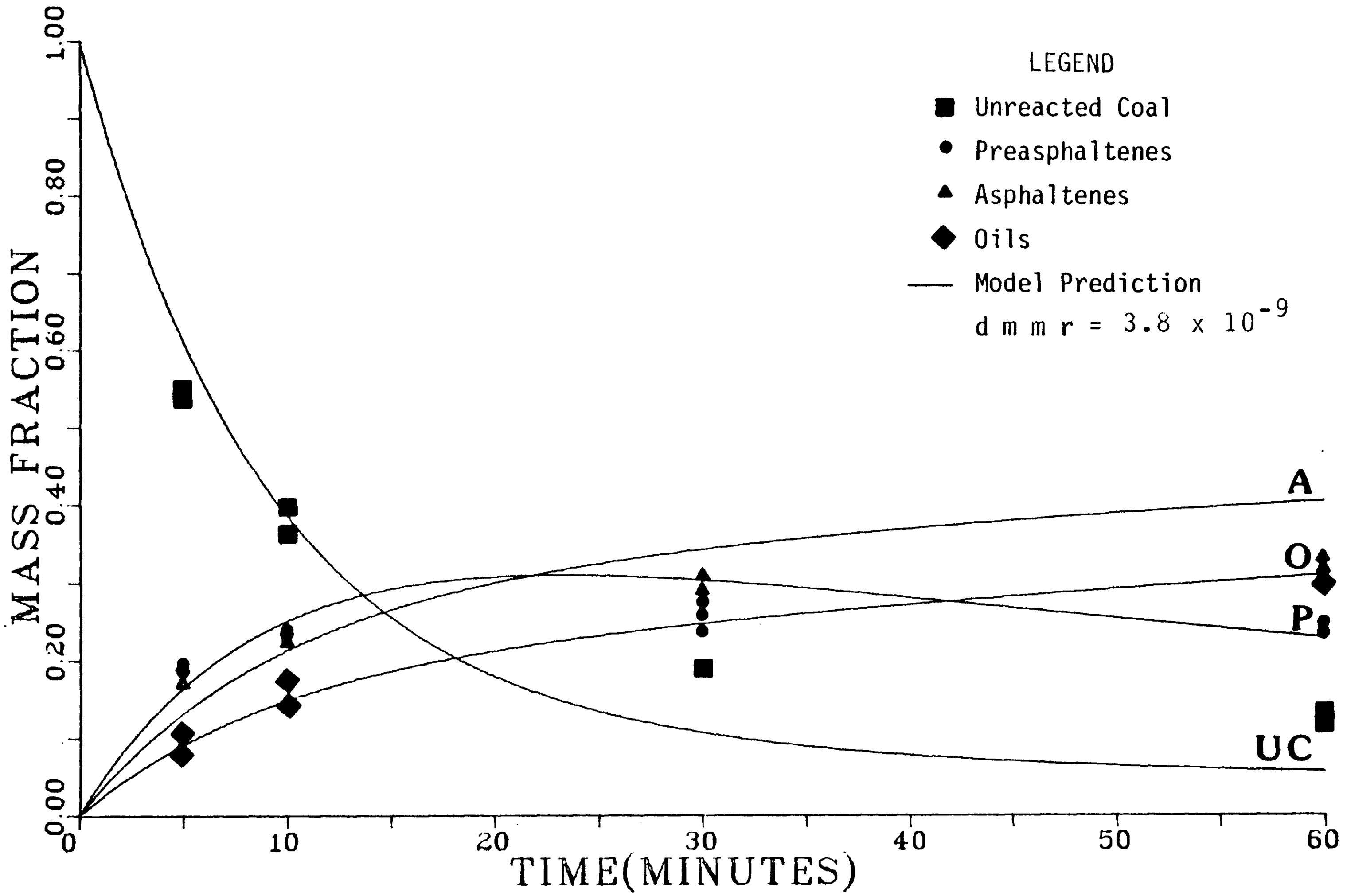


Figure 13: Model 4, Integral Method
7 Parameter, Coal: PSOC No. 370

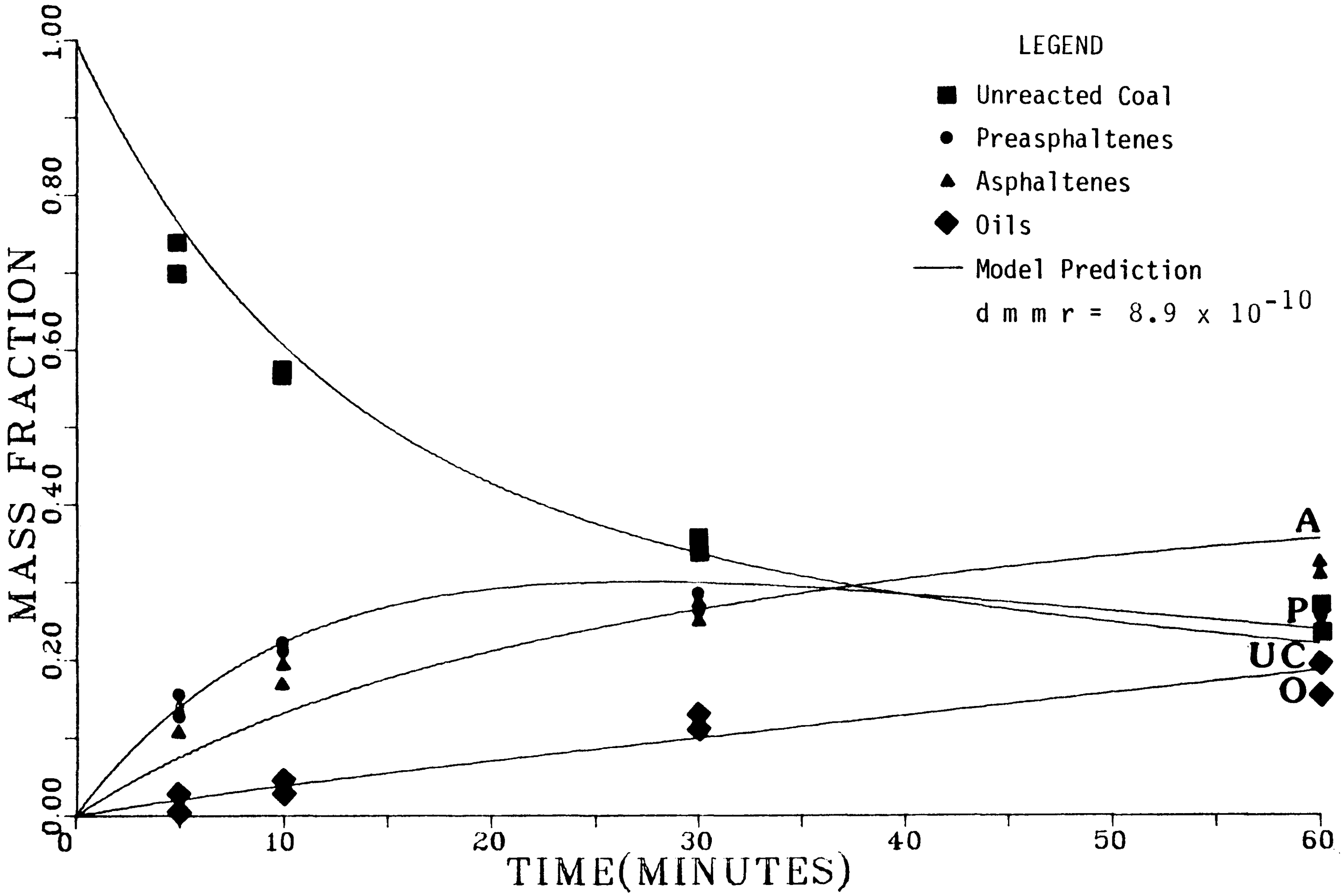
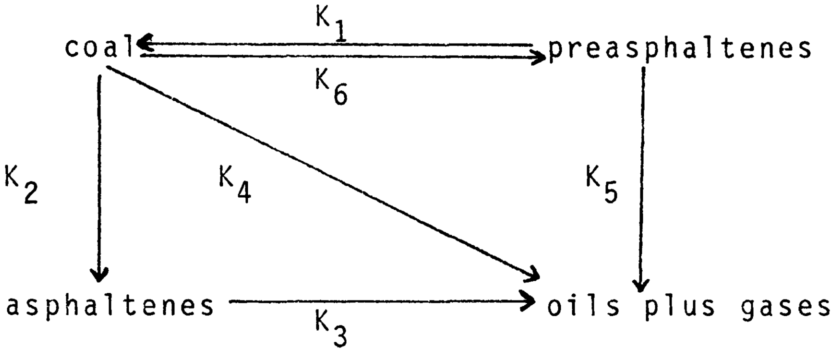


Table 2: Rate Constants of Model 4

Coal	K_1	K_2	K_3	K_4	K_5	K_6	K_7
PSOC 370	.03599	.01753	.000023	.00445	.00531	0.0	.04295
Fies Mine 9	.04464	.02377	0.0	.02317	.00104	.0000028	.0214



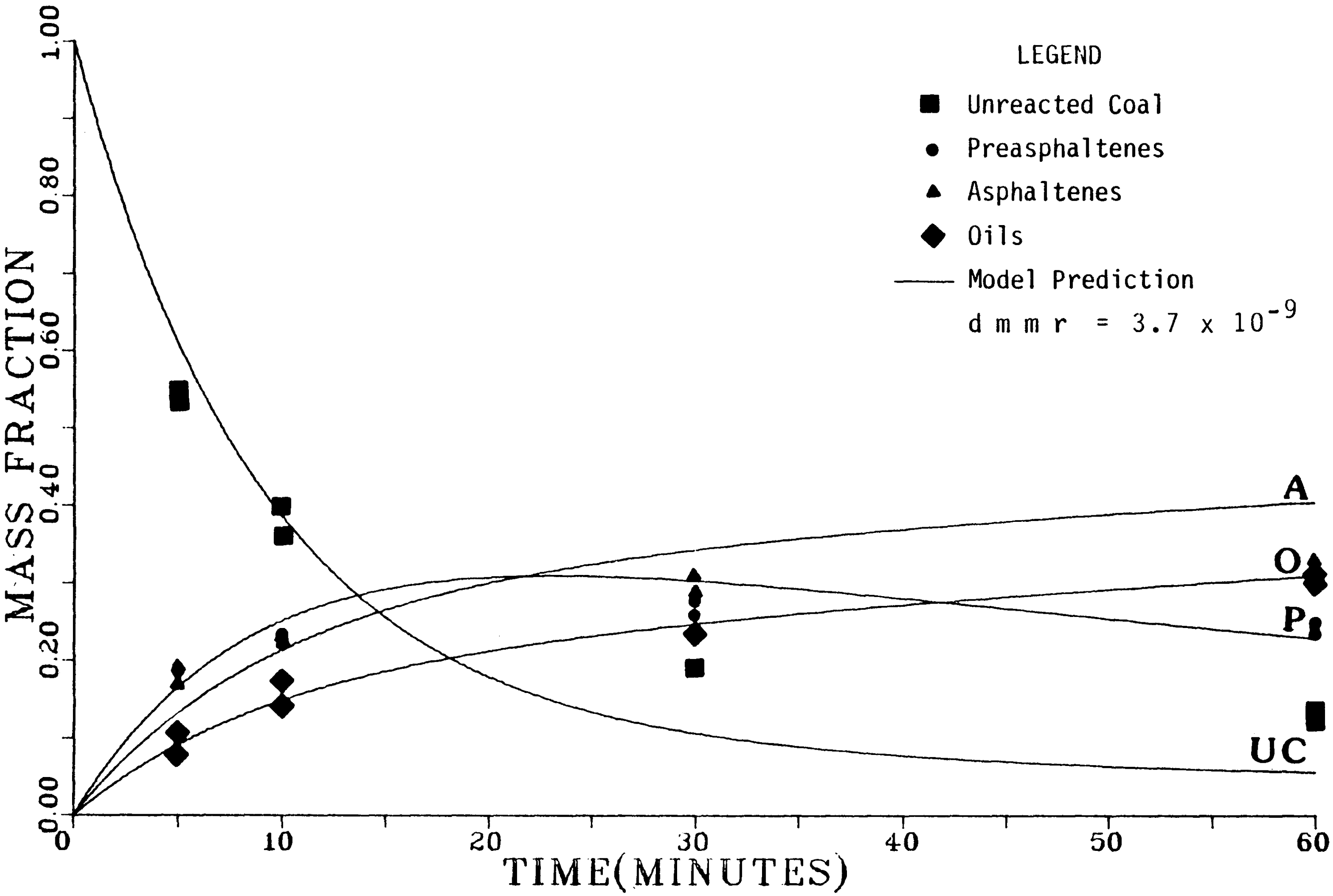
The fit of this model to the data is shown in Figures 14 and 15. Although there was a slight improvement to the data fit, the concern here was to see whether the preasphaltene reacted to from asphaltene or not. The rate constants were calculated and shown below:

Coal	K_1	K_2	K_3	K_4	K_5	K_6
PSOC 370	.04981	.01715	.00505	.00406	0.0	.06495
Fies Mine 9	.04465	.03378	.00103	.02317	0.0	.02146

As can be seen from Model 5, K_5 is zero, thus a conclusion may be drawn that the asphaltenes are produced predominately from coal and not from preasphaltenes.

Thus, to see the effect of elimination of the preasphaltene to asphaltene reaction, the following reaction network (designated Model 6) was introduced.

Figure 14:Model 5,Integral Method
6 Parameter,Coal:Fies Mine No. 9



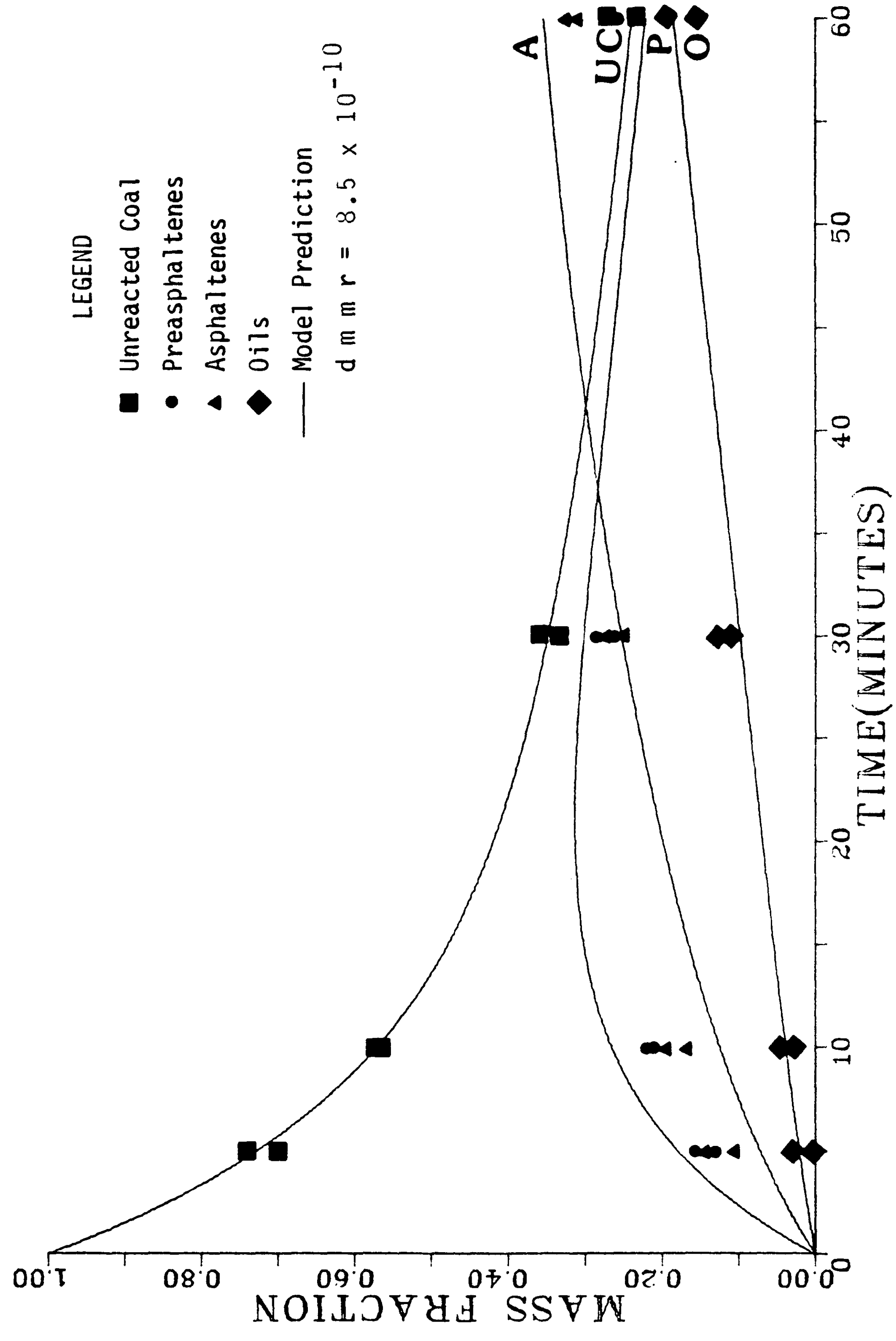
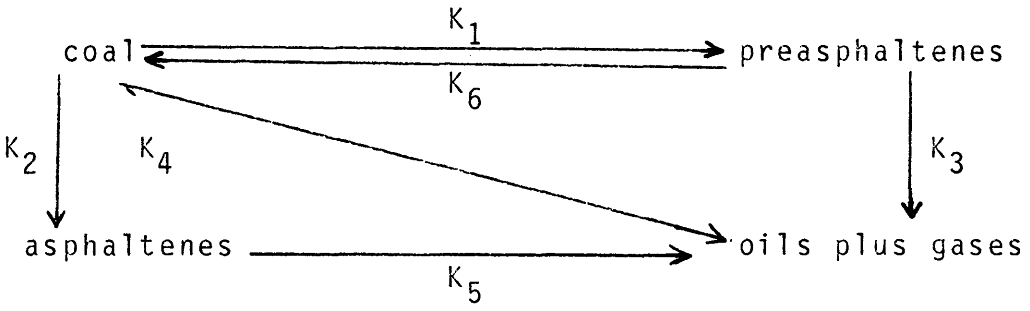


Figure 15: Model 5, Integral Method 6 Parameter, Coal: PSOC No. 370



The calculated rate constants are shown below:

Coal	K_1	K_2	k_3	K_4	K_5	K_6
PSOC 370	.03599	.01754	0.0	.00446	.00534	.04297
Fies Mine 9	.04465	.03378	0.0	.02316	.00103	.02146

It is clear that the preasphaltenes did not react to produce oil plus gas since K_3 is zero. Figures 16 and 17 represent the data fit of Model 6.

Since the previous two models (Models 5 and 6) demonstrated that the preasphaltenes did not react to produce either asphaltenes or oils plus gas, elimination of both these reactions from the reaction network was proposed, resulting in the development of Model 7, which is represented by the following reaction sequences:

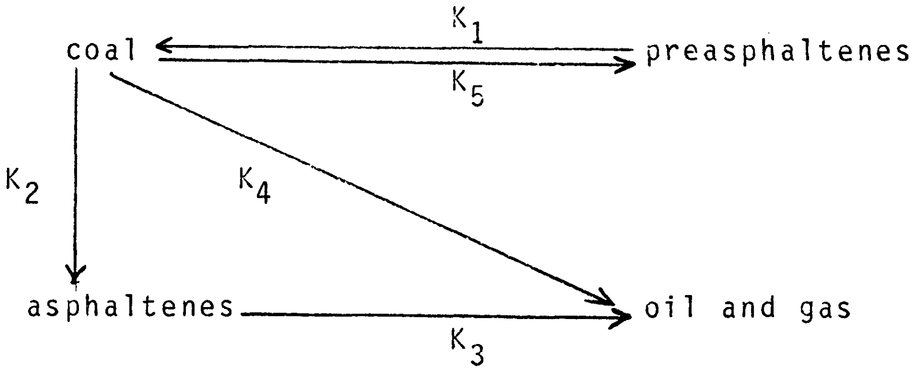


Figure 16:Model 6,Integral Method
6 Parameter,Coal:Fies Mine No. 9

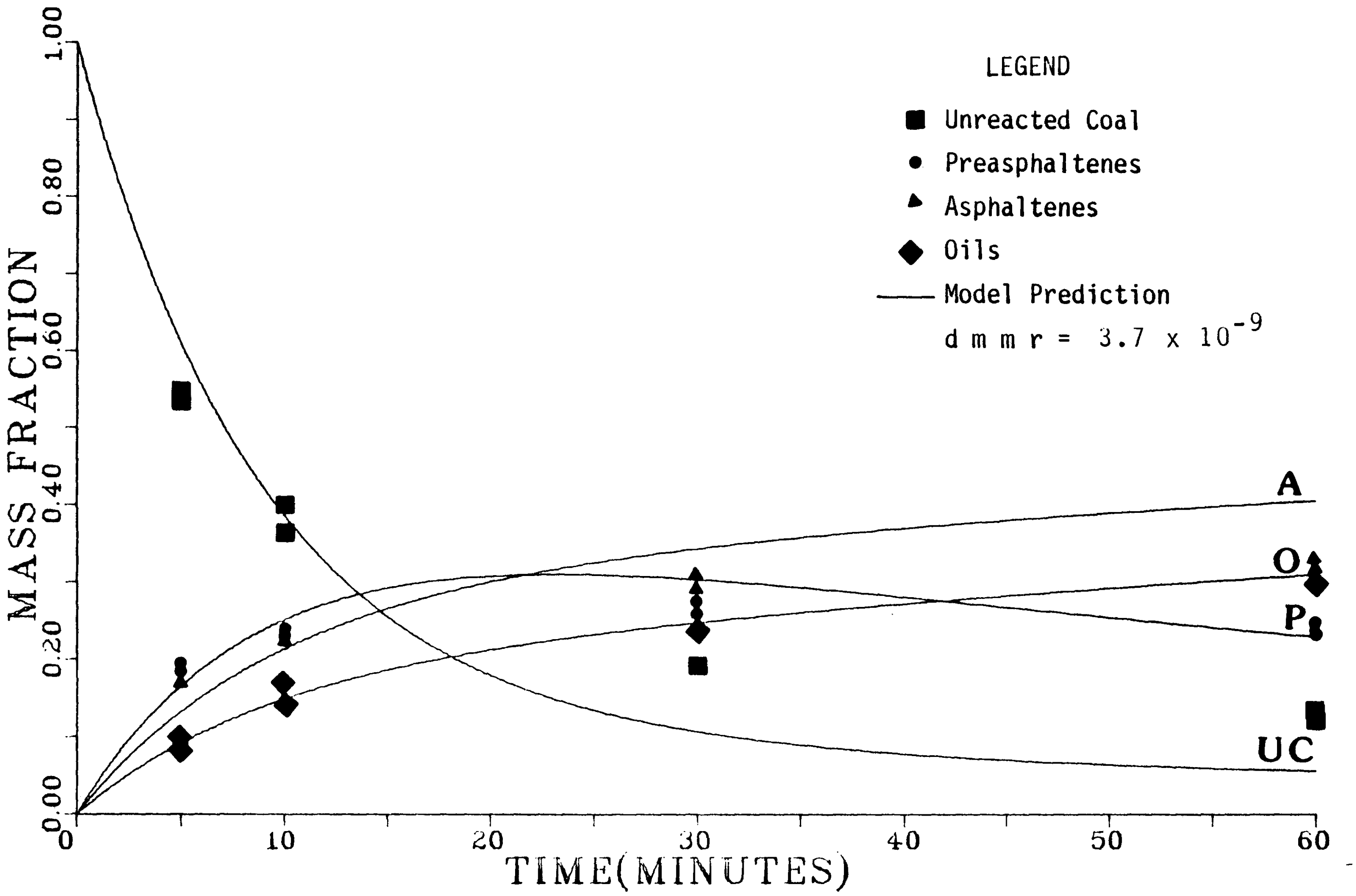
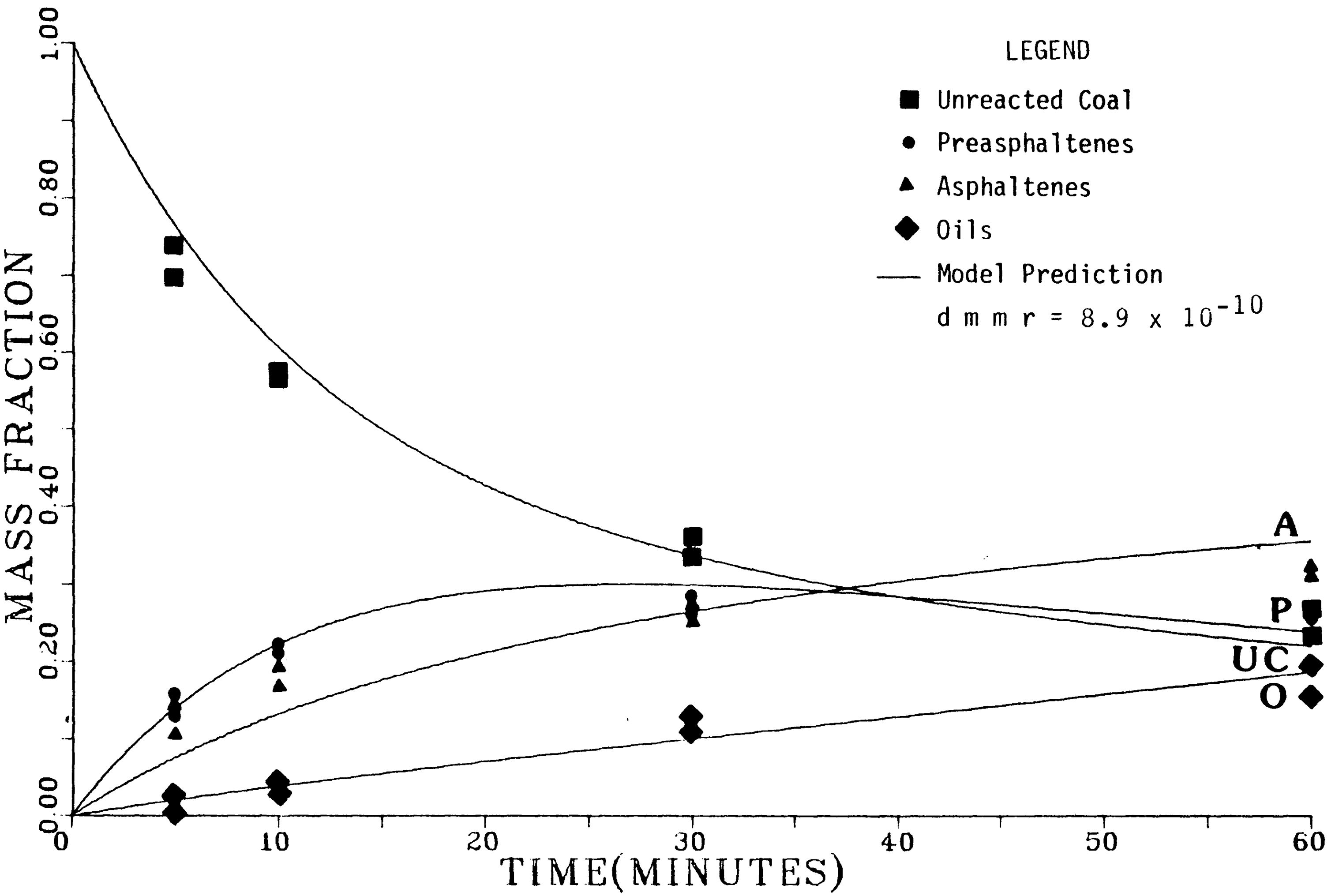


Figure 17:Model 6,Integral Method
6 Parameter,Coal:PSOC No. 370

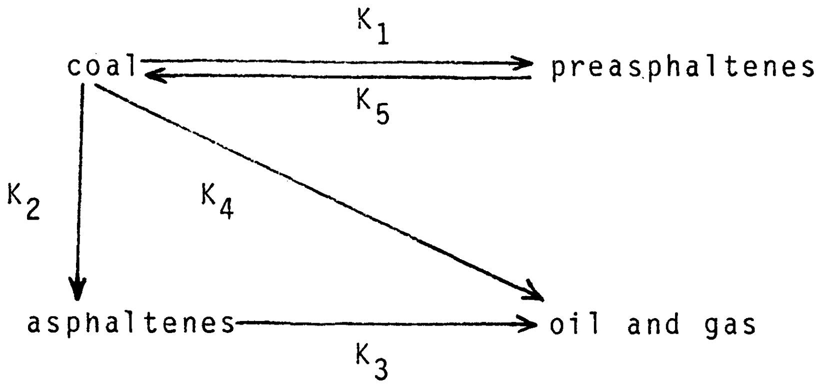


The fit of Model 7 to the data is shown in Figures 18 and 19. The calculated rate constants were:

Coal	K_1	K_2	K_3	K_4	K_5
PSOC 370	.03599	.01754	.00534	.00456	.04297
Fies Mine 9	.04465	.03378	.00103	.02318	.02146

As may be seen, the fit was quite adequate.

Model 8 was next proposed leading to the following reaction scheme:



where all coal reactions (reactions 1, 2, and 4) were second-order in coal remaining.

Model 8 was represented by the following equations:

$$\frac{dc}{dt} = -(K_1+K_2+K_4)\ C^2 + K_5P$$

$$\frac{dP}{dt} = K_1C^2 - K_5P$$

Figure 18: Model 7, Integral Method 5 Parameter, Coal: Fies Mine No. 9

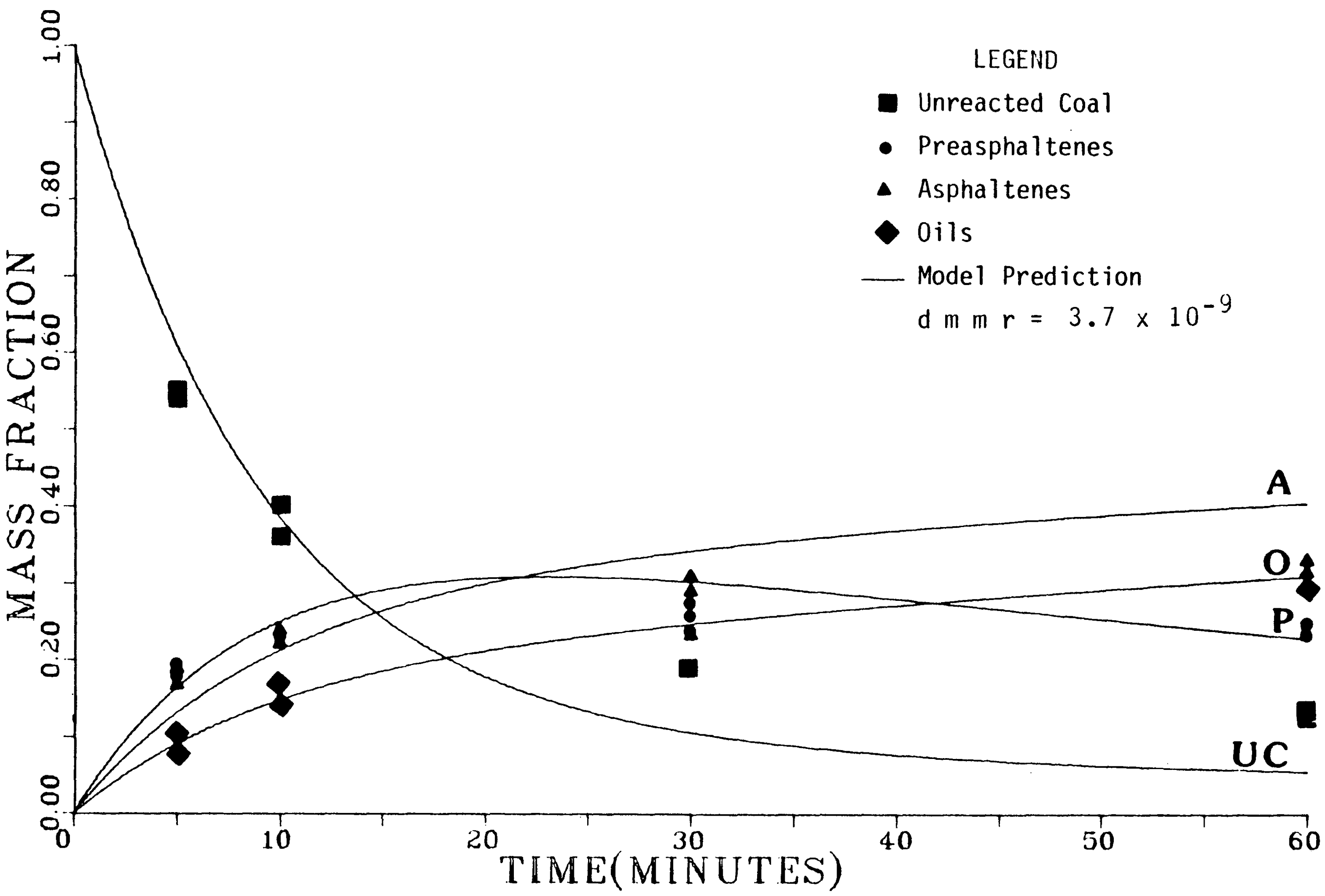
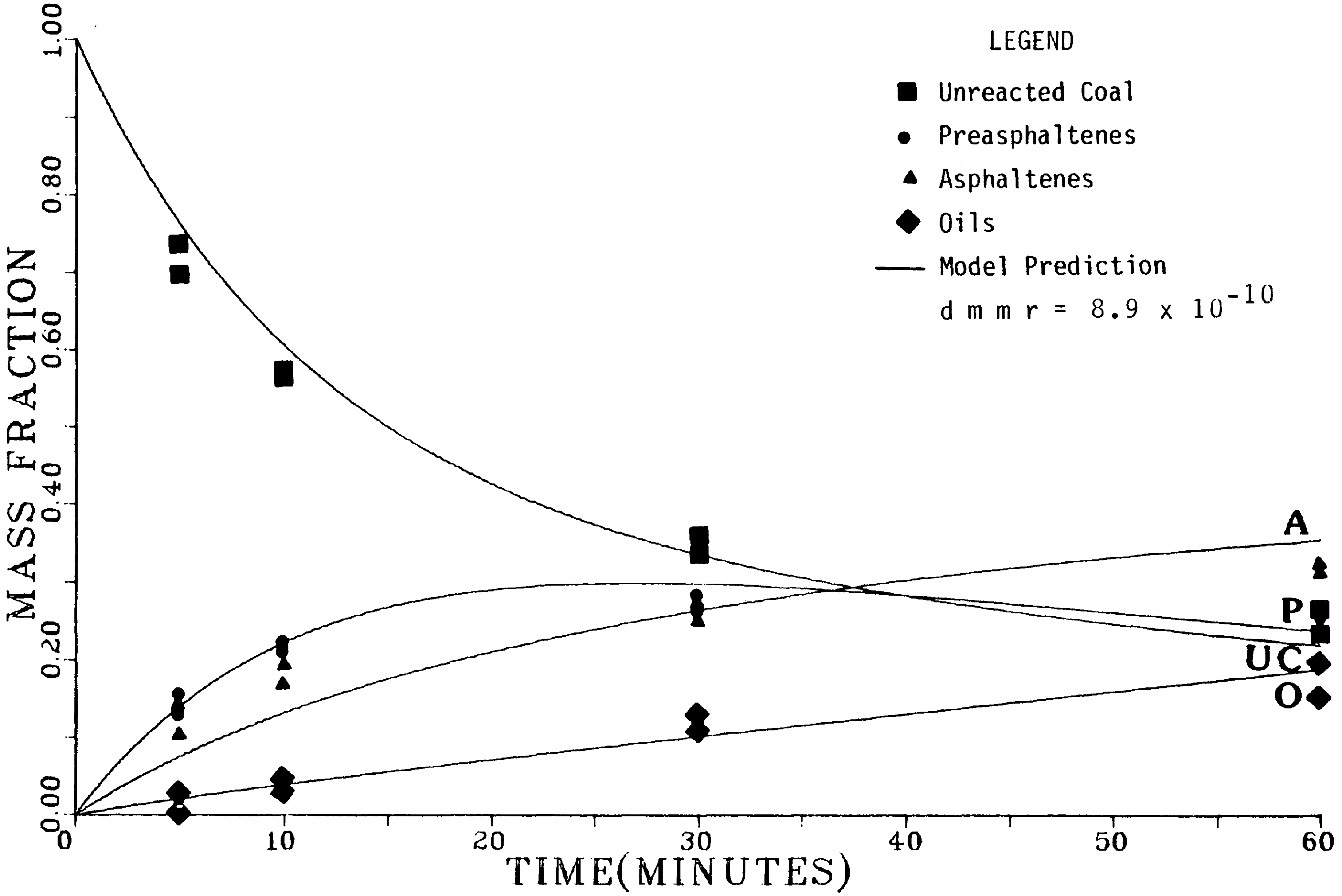


Figure 19:Model 7,Integral Method
5 Parameter,Coal:PSOC No. 370



$$\frac{dA}{dt} = K_2C^2 - K_3A$$

$$\frac{dO}{dt} = K_3A + K_4C^2$$

The calculated rate constants for Model 8 are shown below.

Rate Constants for Model 8, Integral Method

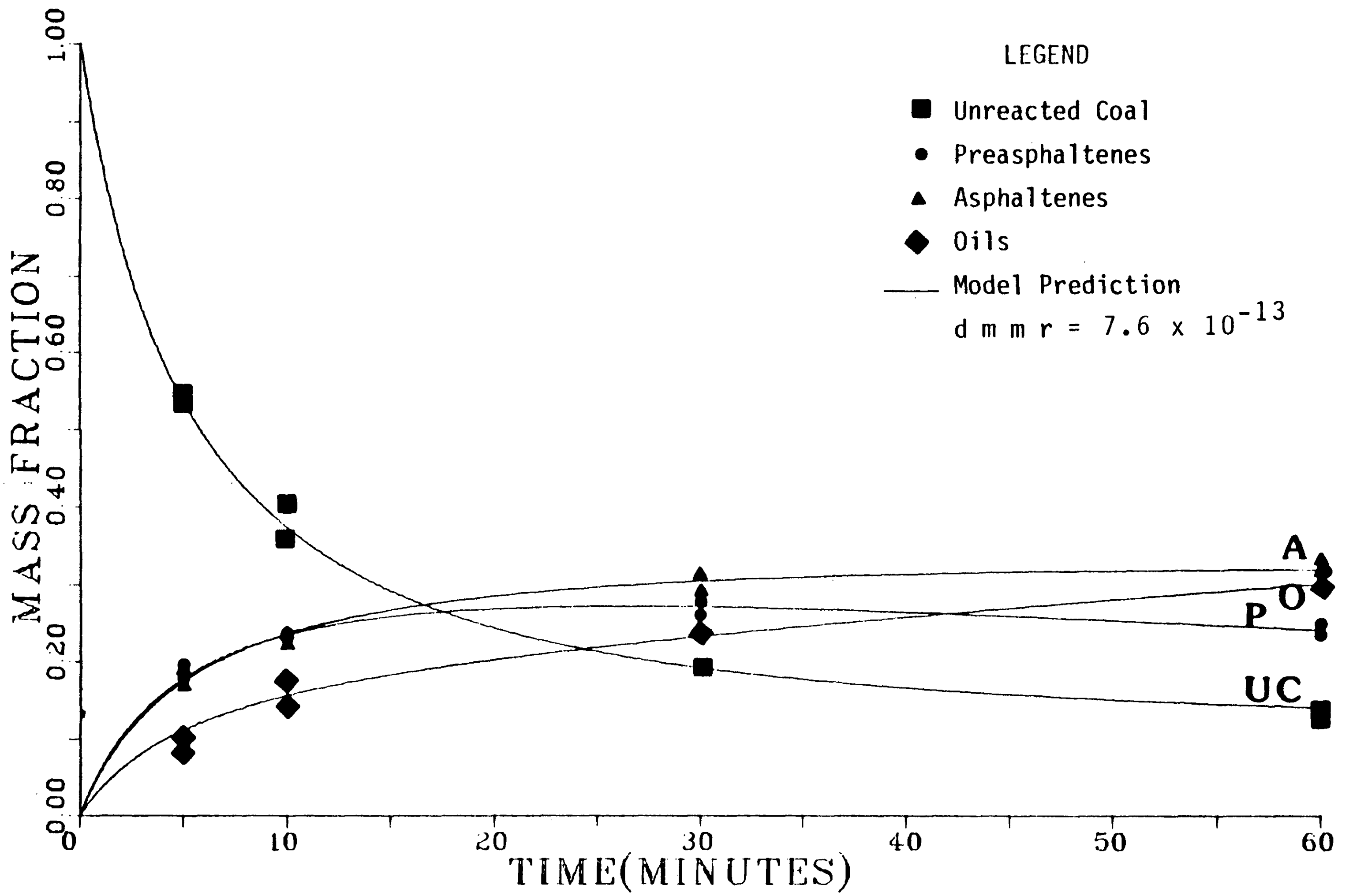
Coal	L_1	K_2	K_3	K_4	K_5
PSOC 370	.0414	.03373	.00606	.00772	.01599
Fies Mine 9	.06886	.06617	.00383	.04101	.01082

As can be noticed from Figures 20 and 21, the fit was adequate to the experimental data.

Three more reaction networks, designated models 9, 10, and 11 were proposed. Based on Model 7, Model 9 assumed the coal reaction to preasphaltenes was second-order. Model 10 assumed the reaction of coal to asphaltenes was a second-order; and Model 11 assumed the coal reaction to oil plus gas was second-order. Figures 22, 23, 24, 25, 26, and 27 represent the fit to the experimental data to Models 9, 10, and 11 respectively.

From the "dmmr" values of the eleven models for PSOC 370 and Fies Mine 9 coals, which are shown on Figures 6 through 27, it was obvious that Model 8 was the best model

Figure 20:Model 8,Integral Method
5 Parameter,Coal:Fies Mine No. 9



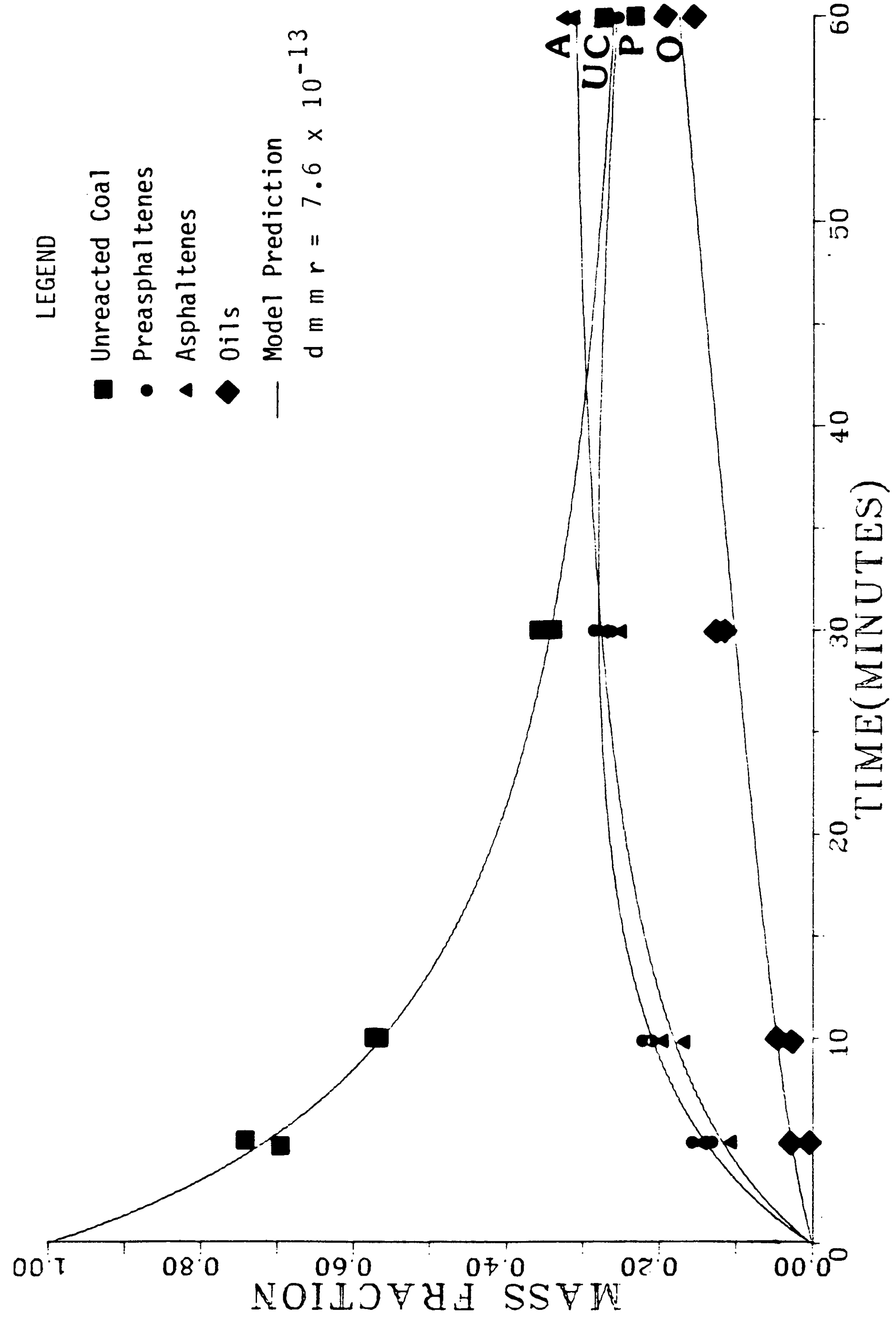


Figure 21: Model 8, Integral Method 5 Parameter, Coal: PSOC No. 370

Figure 22:Model 9,Integral Method
5 Parameter,Coal:Fies Mine No. 9

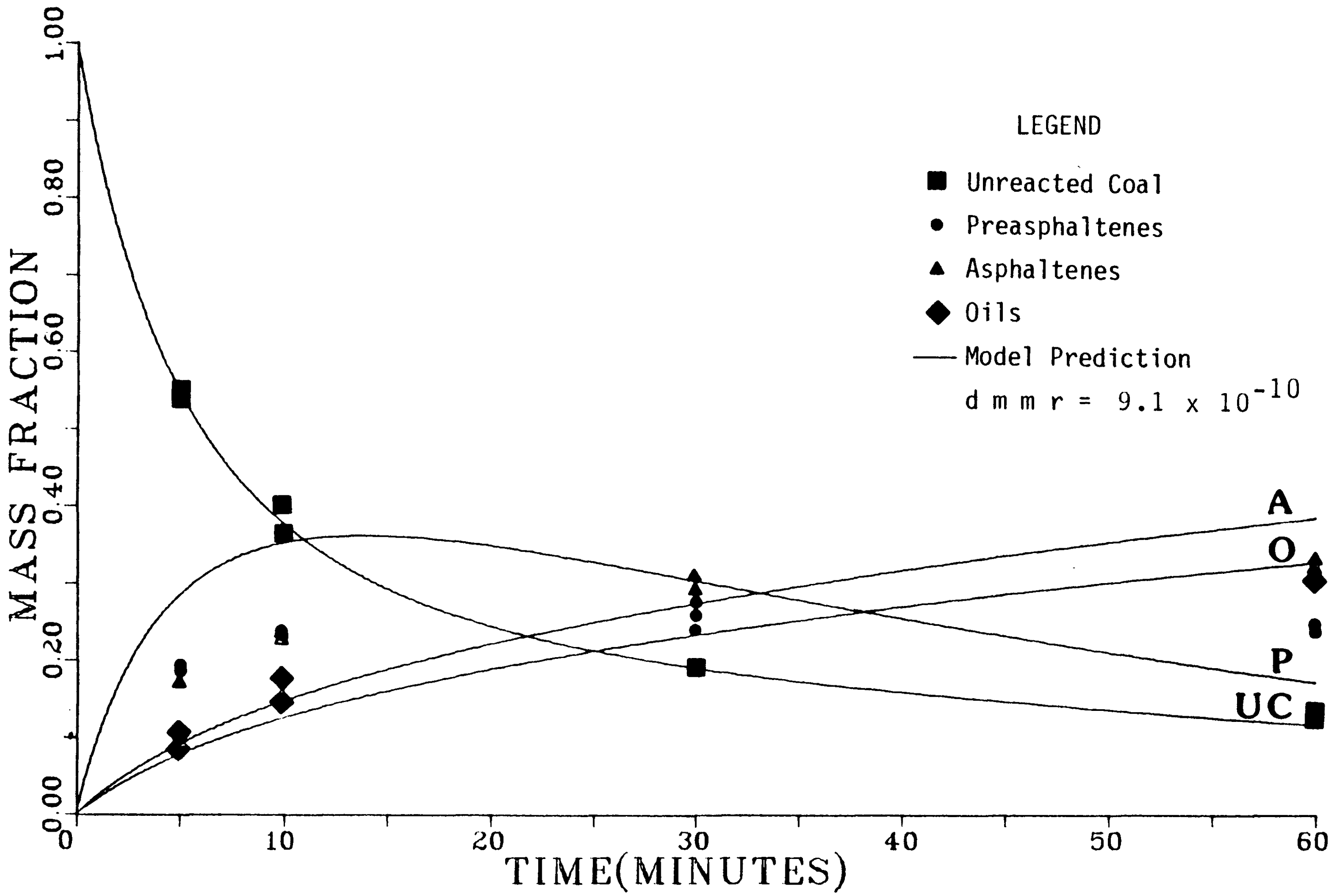


Figure 23:Model 9,Integral Method
5 Parameter,Coal:PSOC No.370

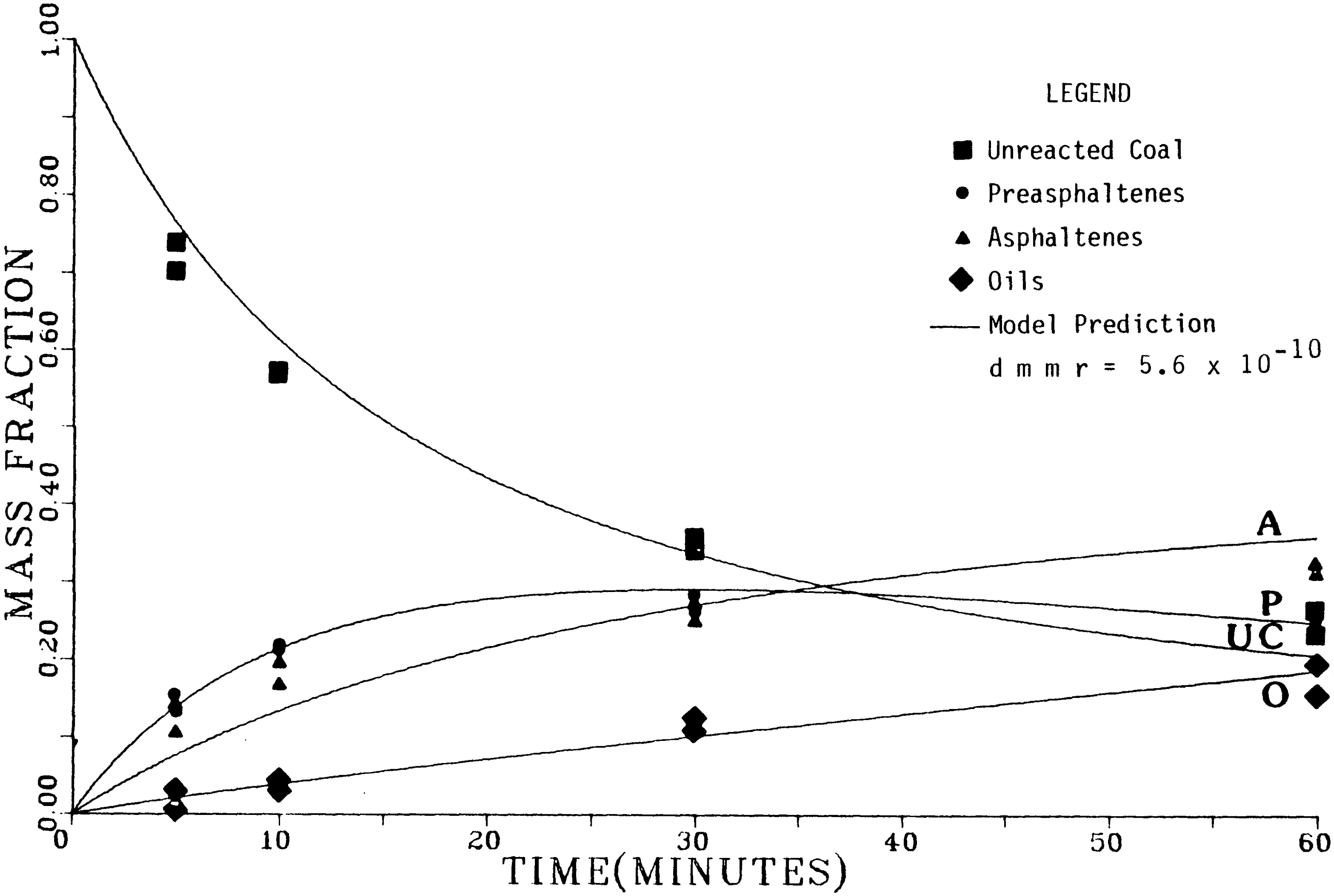


Figure 24:Model 10,Integral Method
5 Parameter,Coal:Fies Mine No. 9

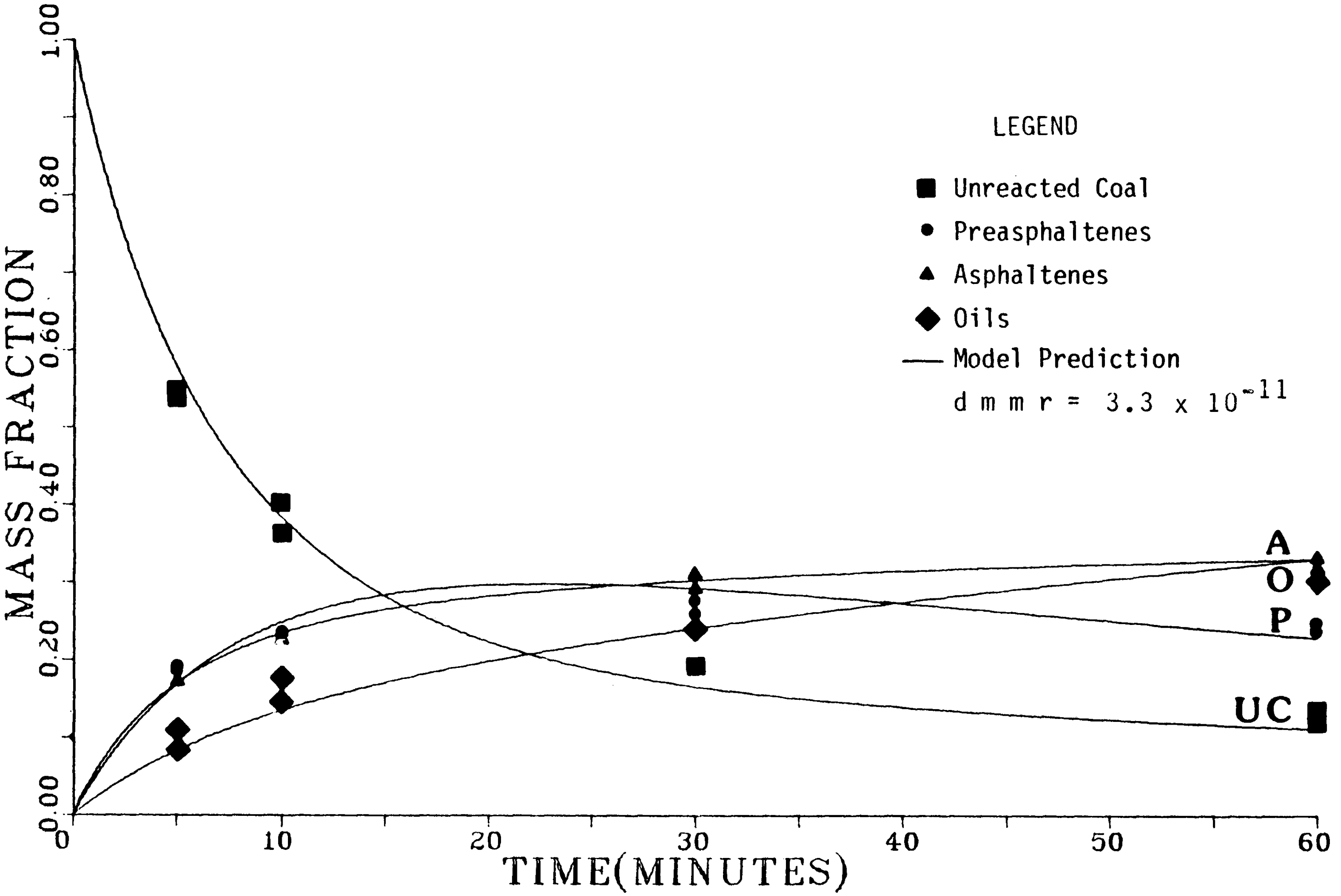


Figure 25:Model 10,Integral Method
5 Parameter,Coal:PSOC No. 370

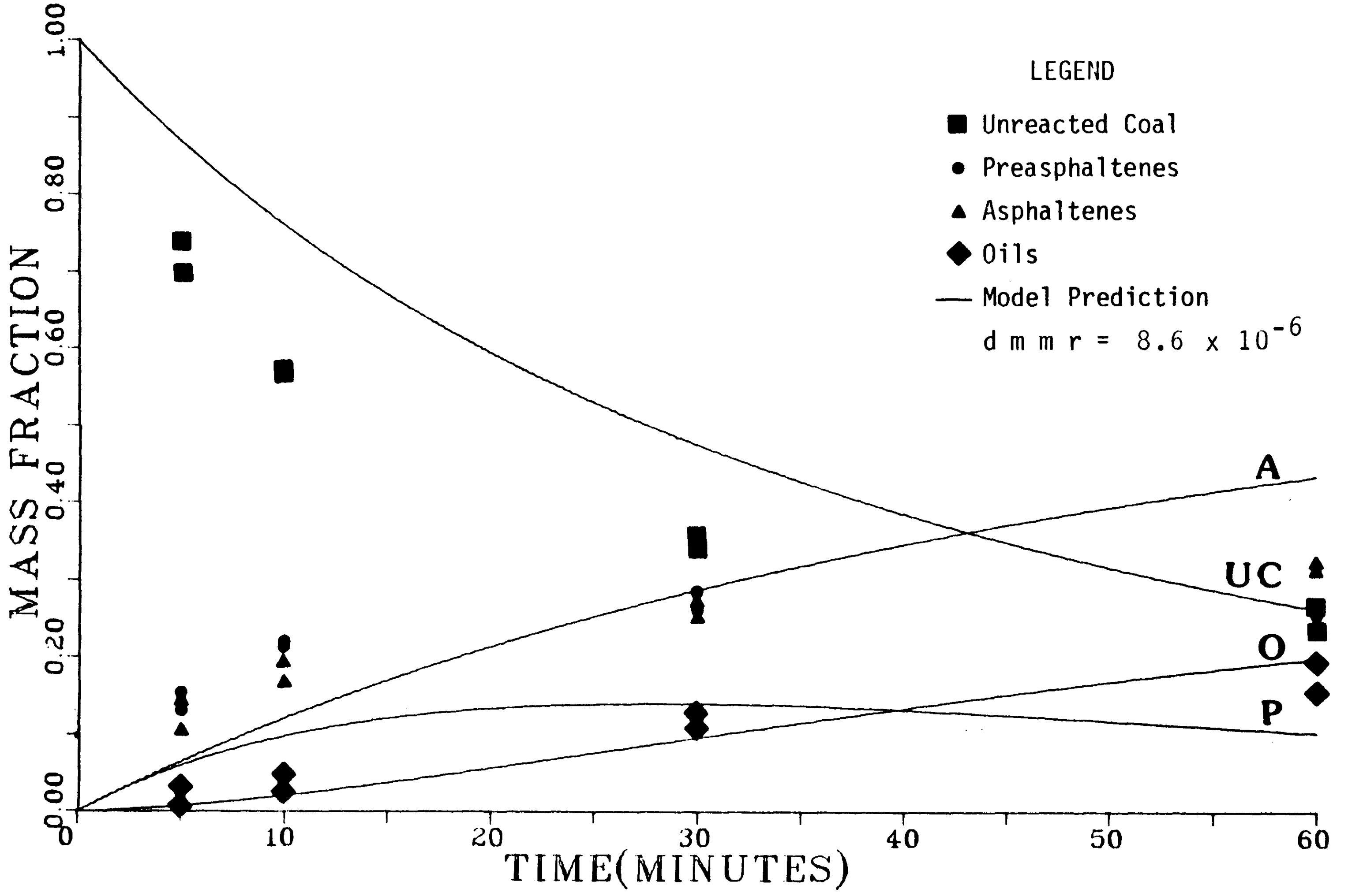


Figure 26:Model 11,Integral Method
5 Parameter,Coal:Fies Mine No. 9

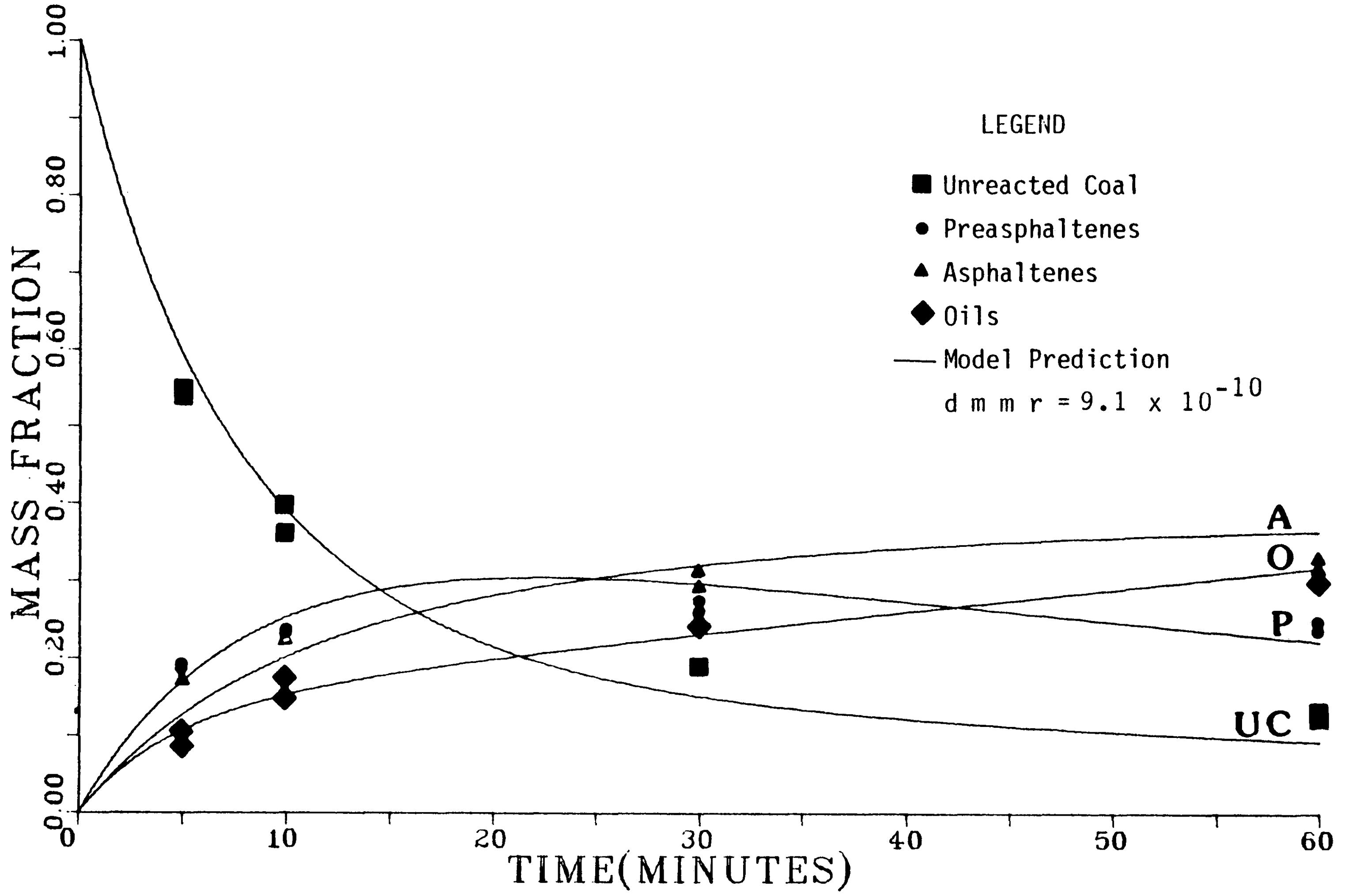
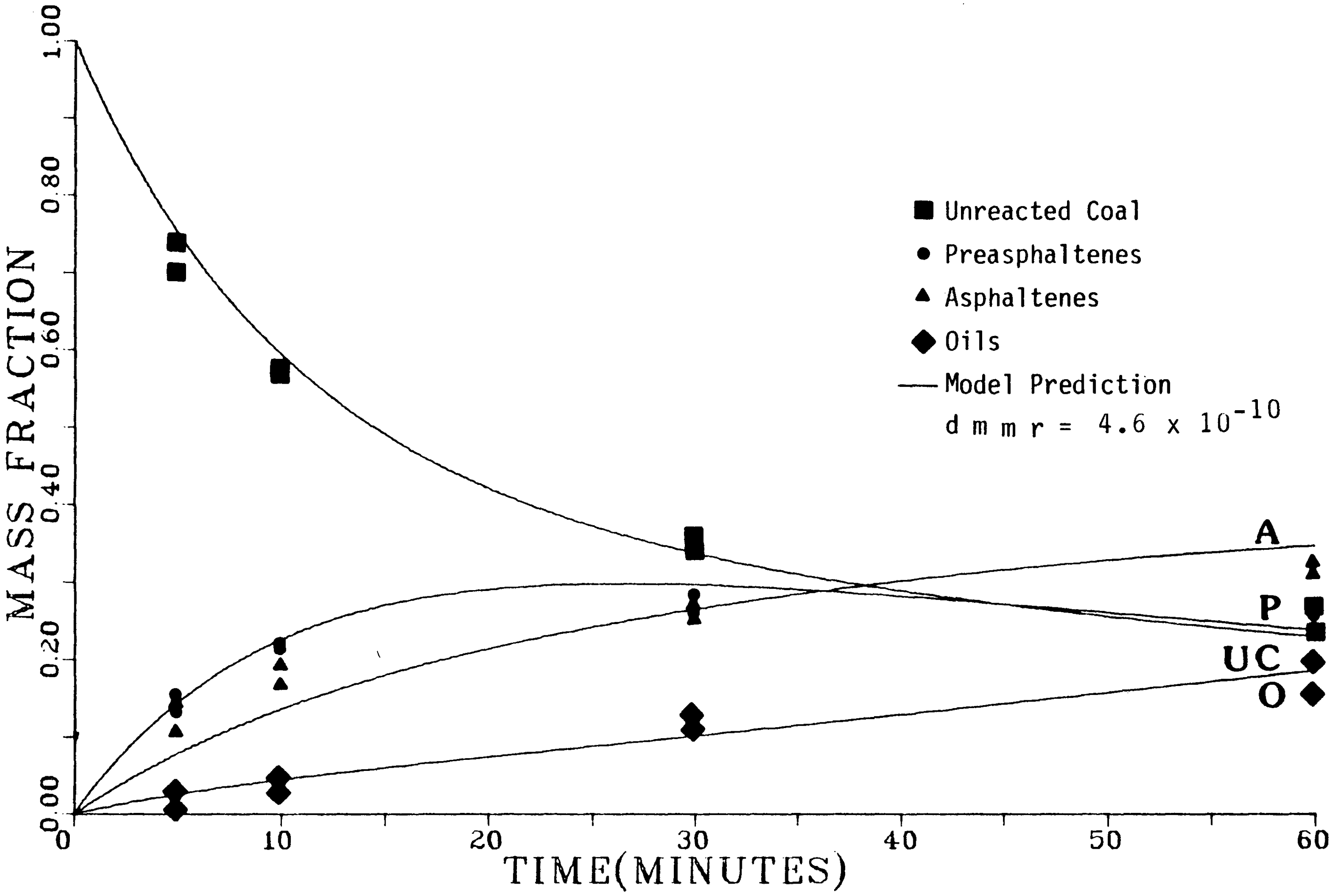


Figure 27:Model 11,Integral Method
5 Parameter,Coal:PSOC No. 370



describing the coal liquefaction process since it exhibited the lowest value of the "dmmr" for both coals tested. Model 8 is shown in Figures 20, 21, and 28 through 38.

Differential Analysis Method:

The same eleven models were investigated using the differential method on the initial rate data. The adequacy of the fit for these models was given by the available MINITAB library program as the "Ratio of the sum of squares due to regression to the total sum of squares". The closer this ratio to one, the better the fit to the data. MINITAB performed multiple linear regression analysis of the matrices representing rates and compositions, and the resulting coefficients represented the rate constants for the given model.

Tables 3 and 4 show the calculated ratios as a discriminator for determining the most adequate fit to the experimental data for PSOC 107 and Fies Mine 9 coals, respectively. As may be seen, Model 8 was found to be the best reaction network to represent the liquefaction process by differential analysis since the corresponding sum of squares ratio was close to one.

In using the sum of squares ratio in the differential method as a discriminator, the objective was to look for a significant difference between these ratios to tell which

Figure 28 Model 8, Integral Method
5 Parameter, Coal: PSOC No. 437

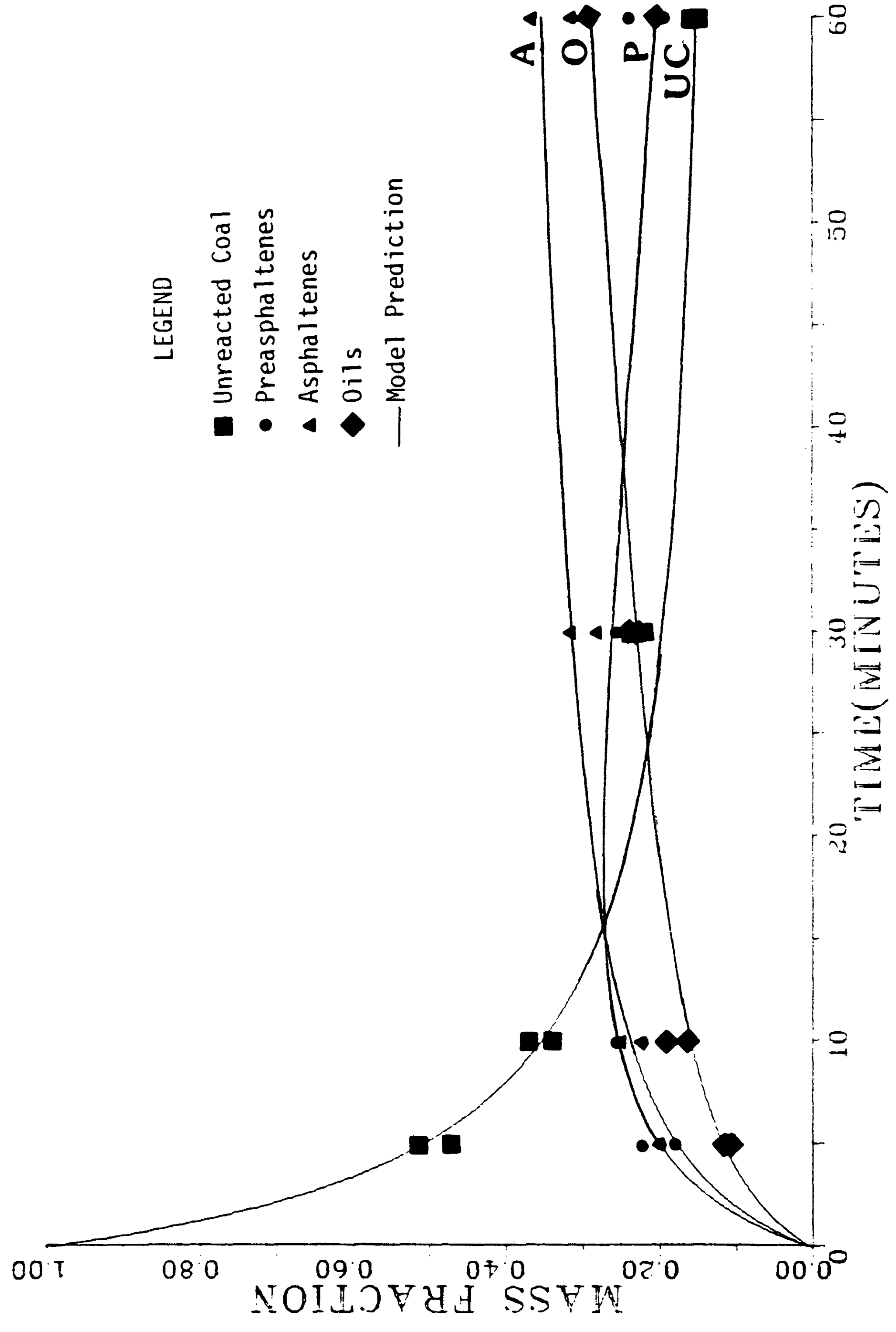


Figure 29:Model 8,Integral Method
5 Parameter,Coal:PSOC No. 444

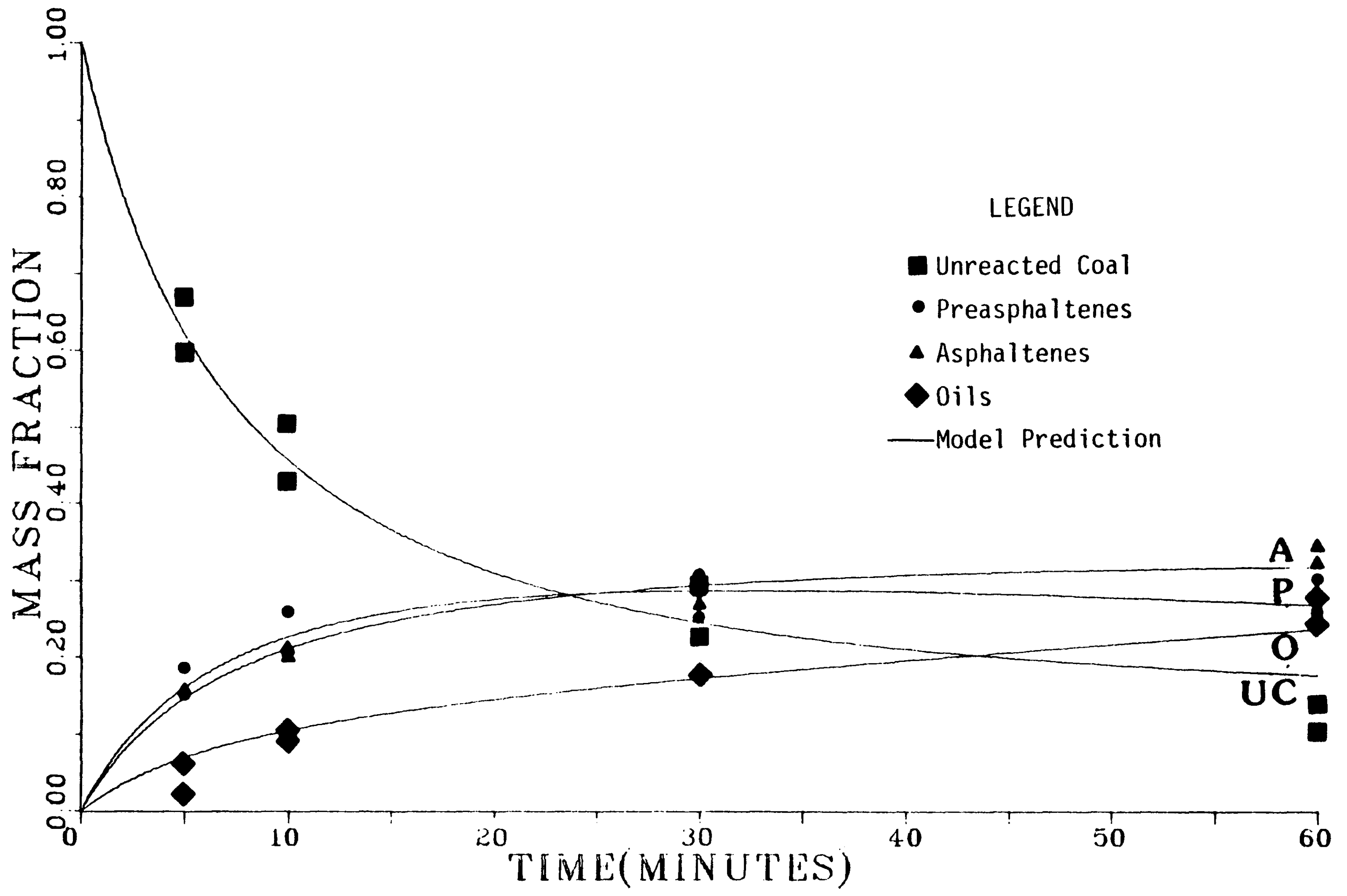


Figure30 :Model 8,Integral Method
5 Parameter,Coal:PSOC No. 151

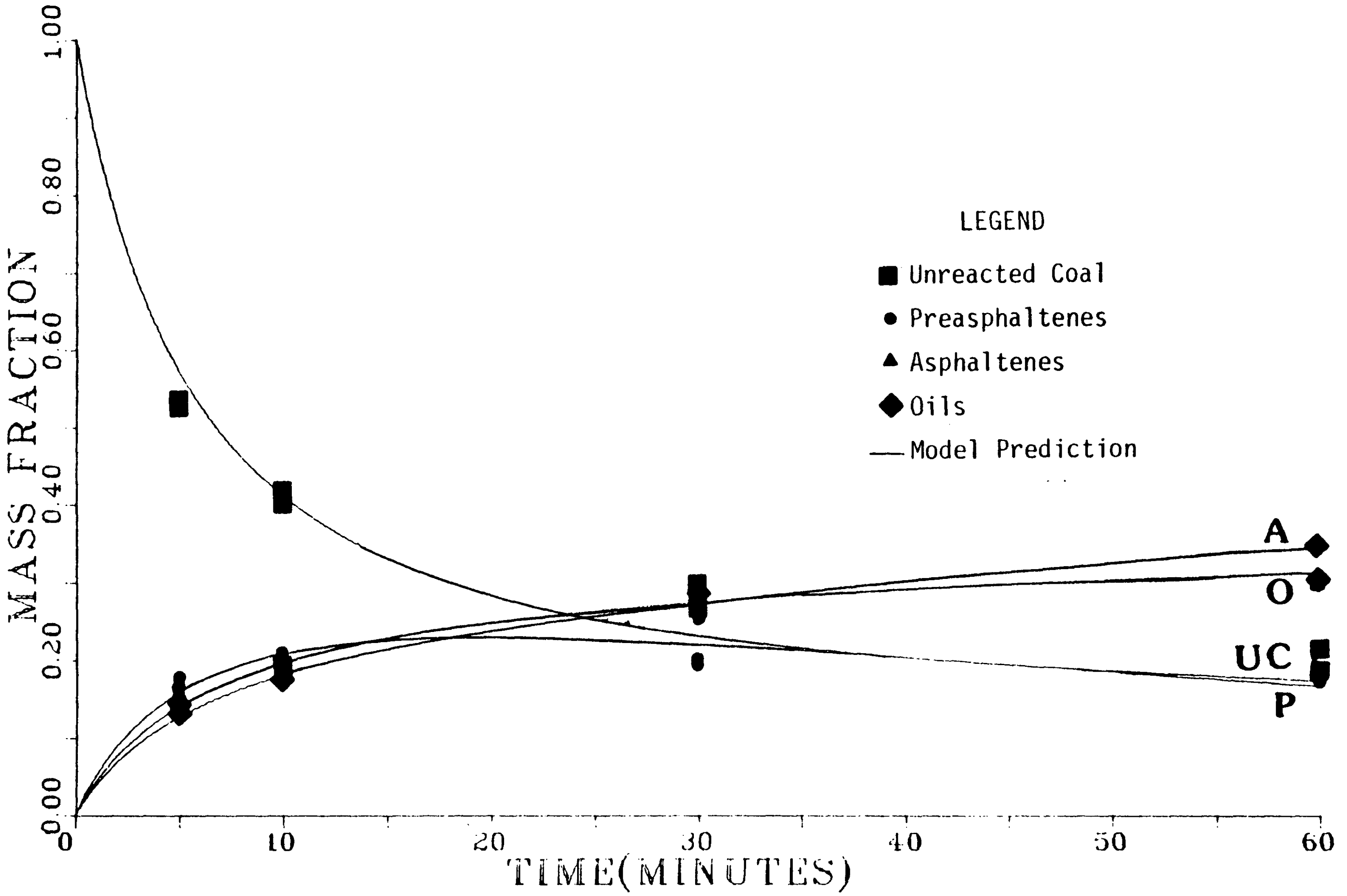


Figure31:Model 8,Integral Method
5 Parameter,Coal:PSOC No. 071

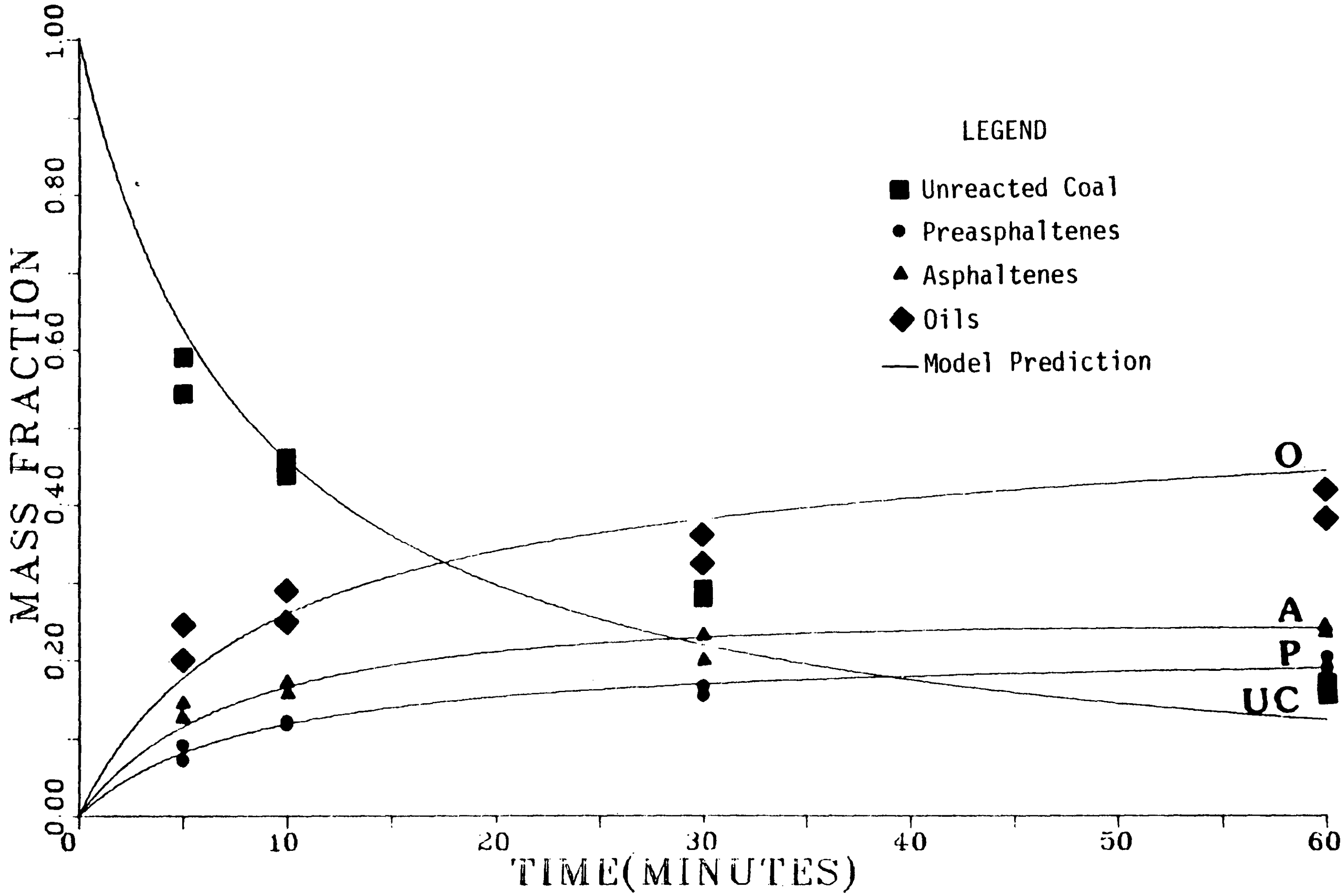


Figure 32:Model 8,Integral Method
5 Parameter,Coal:PSOC No. 107

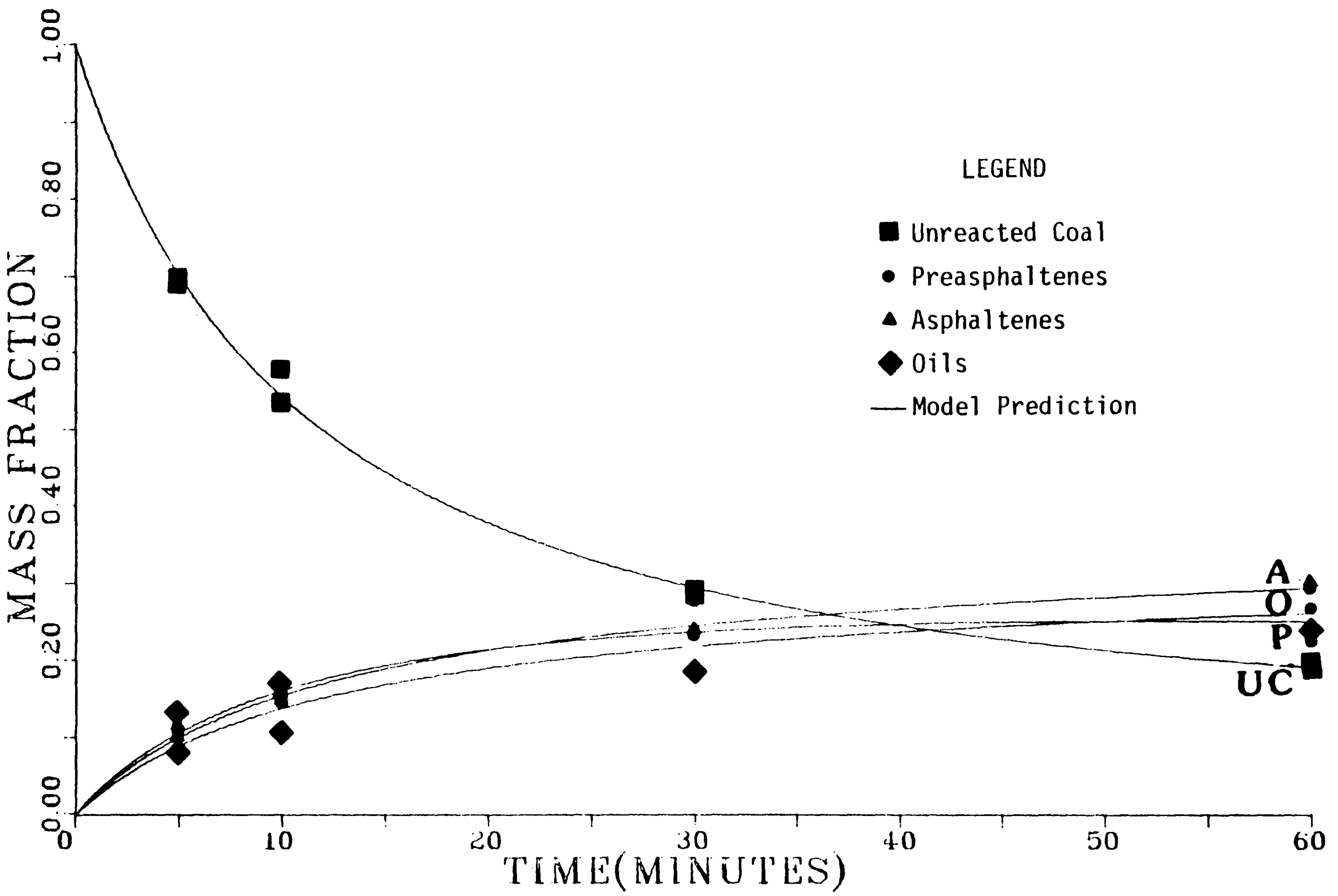


Figure 33: Model 8, Integral Method
5 Parameter, Coal: PSOC No. 056

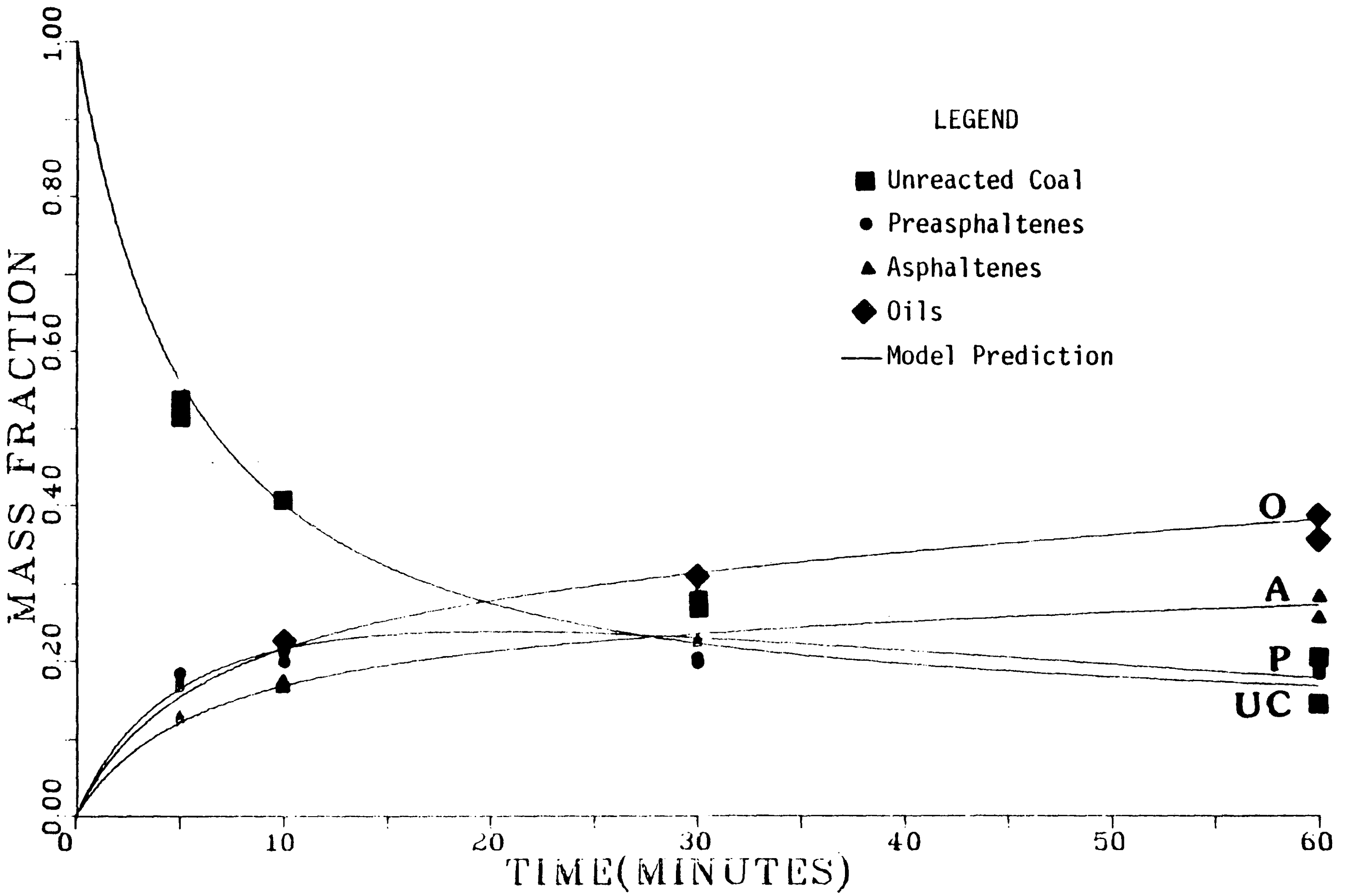


Figure34:Model 8,Integral Method
5 Parameter,Coal:PSOC No. 737

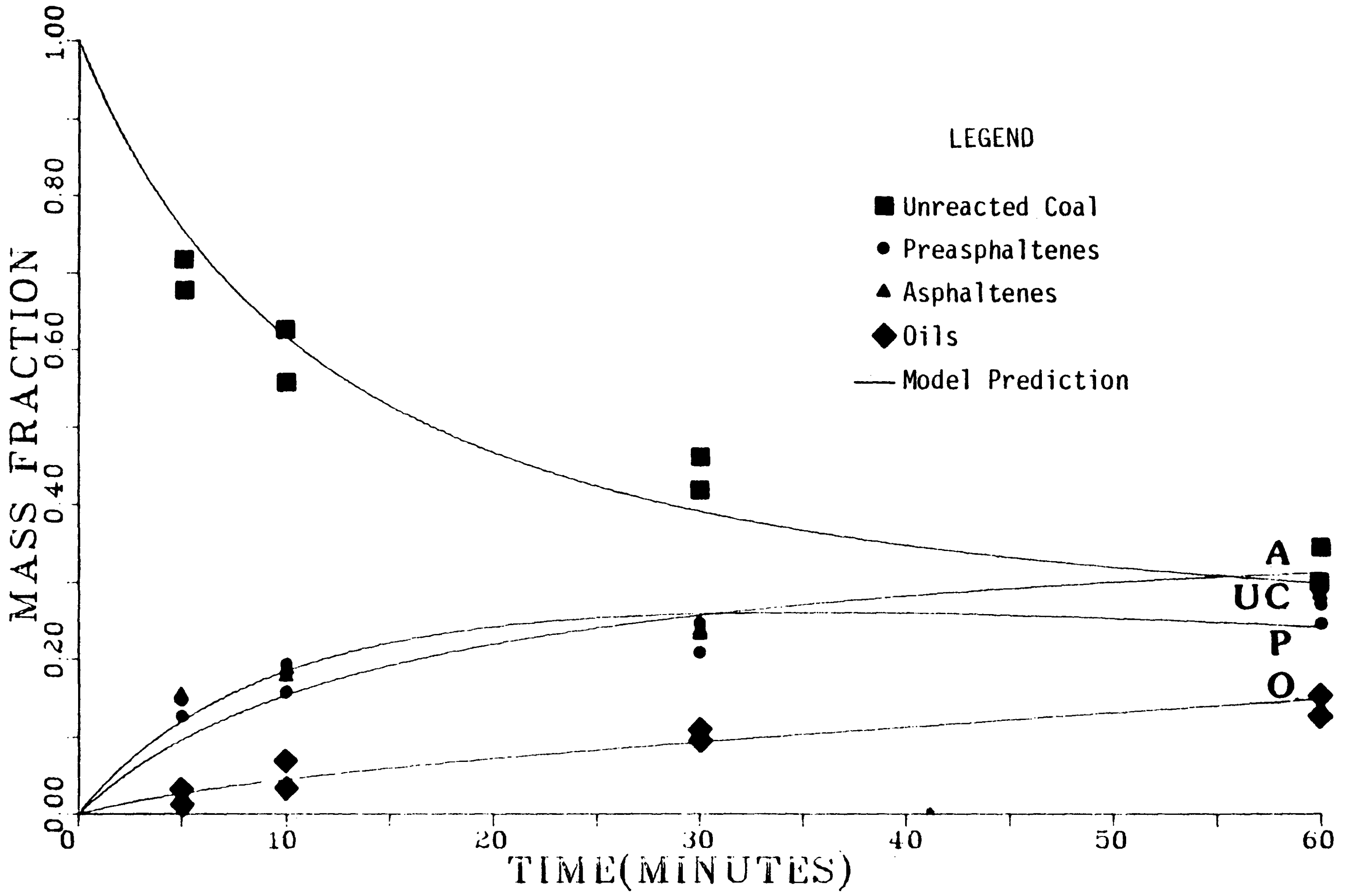


Figure 35:Model 8,Integral Method
5 Parameter,Coal:PSOC No. 577

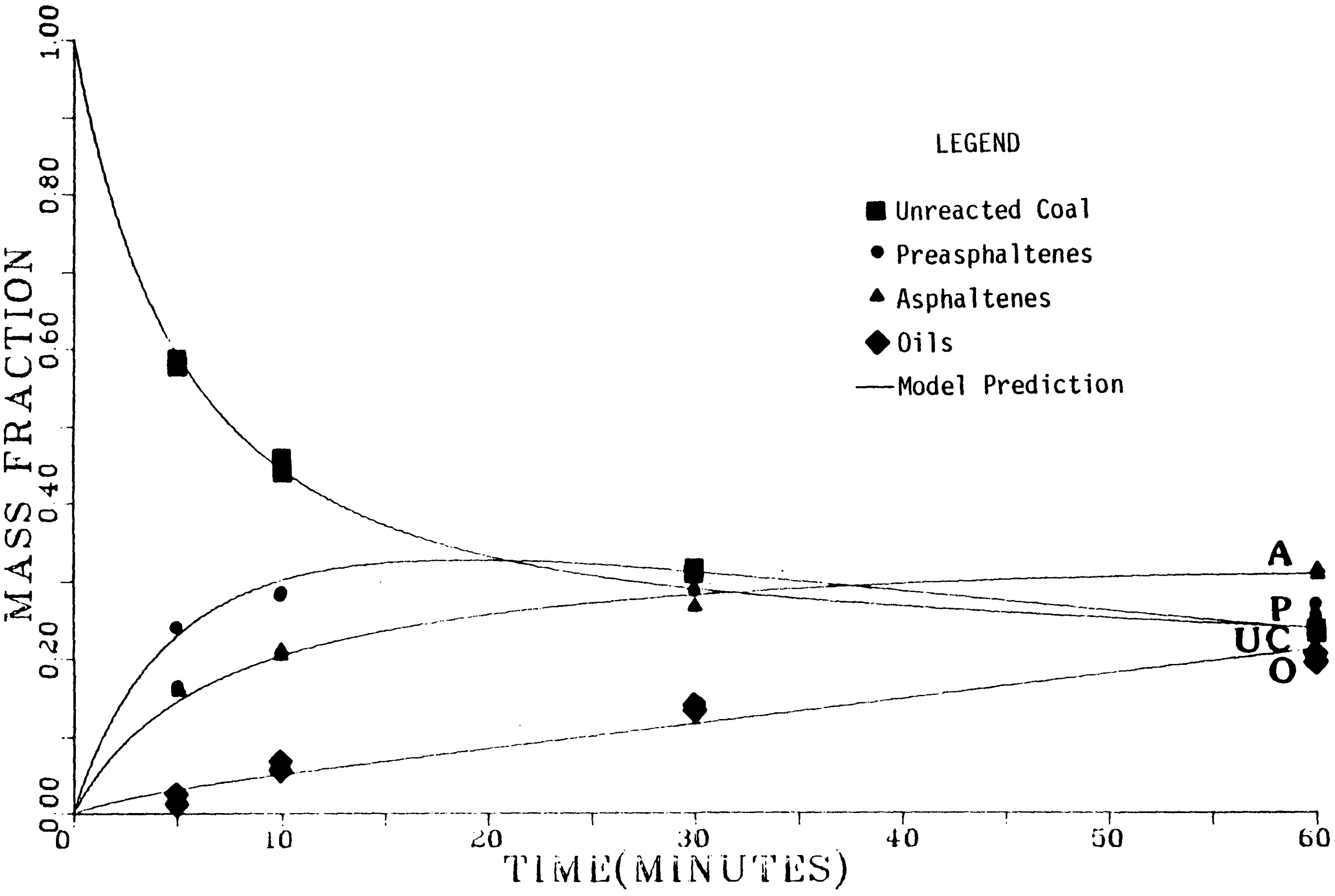


Figure 36:Model 8,Integral Method
5 Parameter,Coal:PSOC No. 456

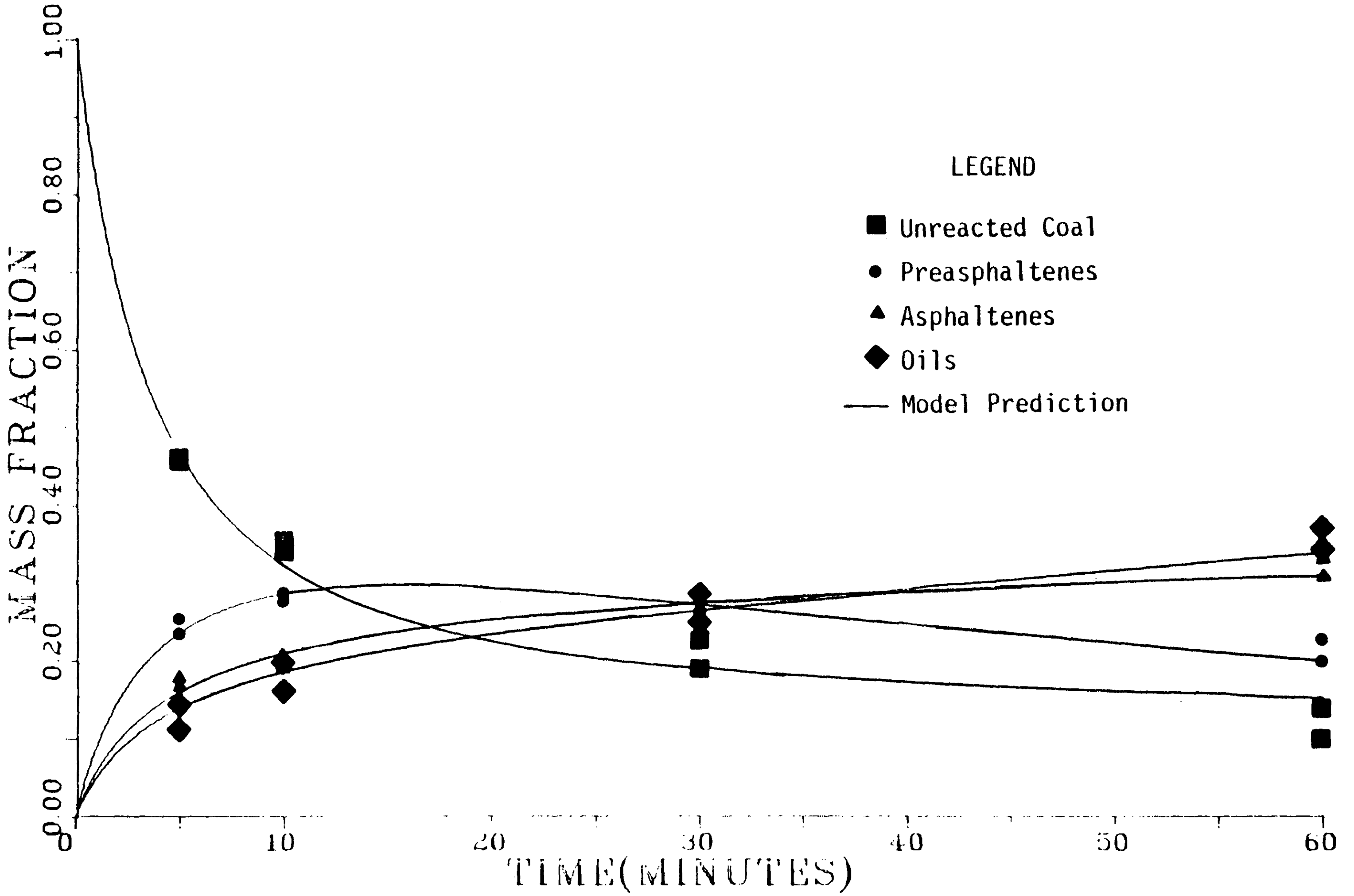


**Figure 37:Model 8,Integral Method
5 Parameter,Coal:Colo. Energy**

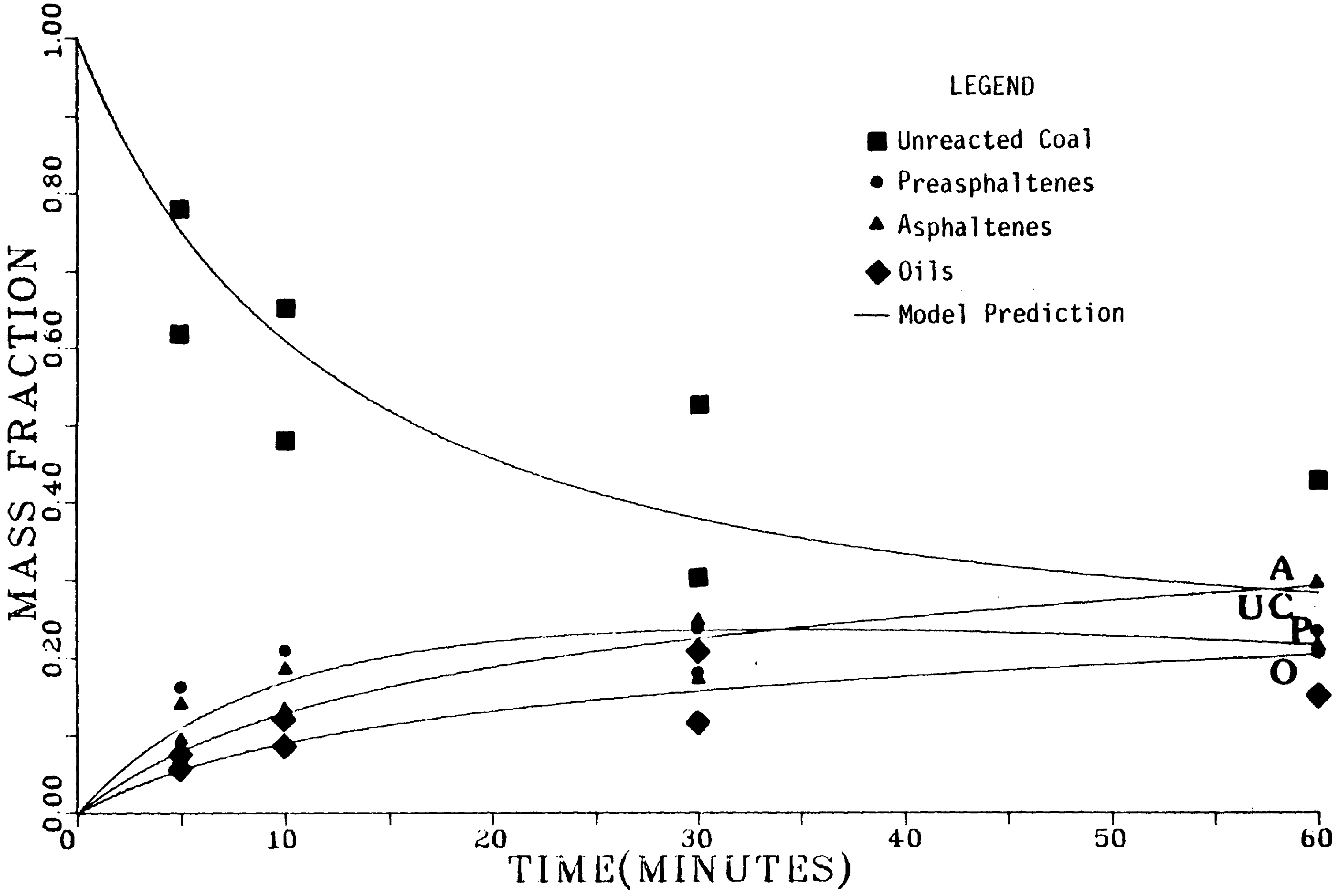
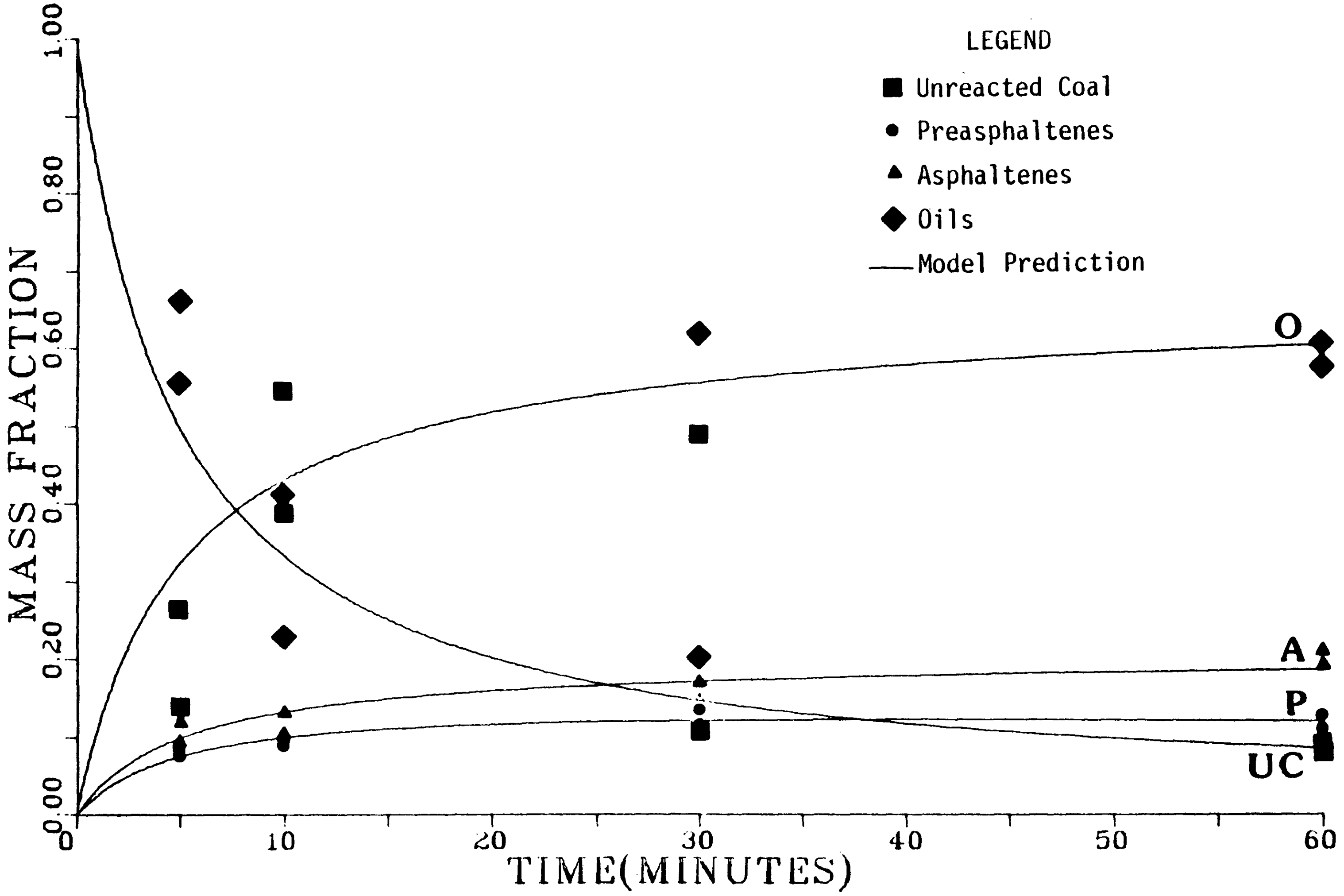


Figure 38: Model 8, Integral Method 5 Parameter, Coal: PSOC No. 130



model was the best. Another objective was also to predict a unified model that represented the liquefaction process by the two methods of analysis and Model 8 was found to meet both of these objectives.

Figures 39 to 46 represent the fit of Model 8 to the experimental data by the differential method.

Eight coals were found to be suitable for the differential method out of the thirteen sets of reliable rate data which were available from the study of Furlong (23). The choice of the coals was based on the calculated initial rates of reaction for each experimental data set for the four components (unreacted coal, preasphaltenes, asphaltenes, and oils plus gases). The given experimental data set was chosen when the change in those rates of reaction for each component was significantly large, otherwise that given experimental data set was rejected as not suitable for differential analysis.

Rate constants for Model 8 which were calculated using both the integral and differential methods for the eight coals were compared and presented in Tables 5 through 12. As can be seen, Tables 5 through 11 show a comparable values of the rate constants for reactions 1, 2, and 4, respectively.

Figure 39:Model 8, Differential Method
5 Parameter,Coal:PSOC No. 071

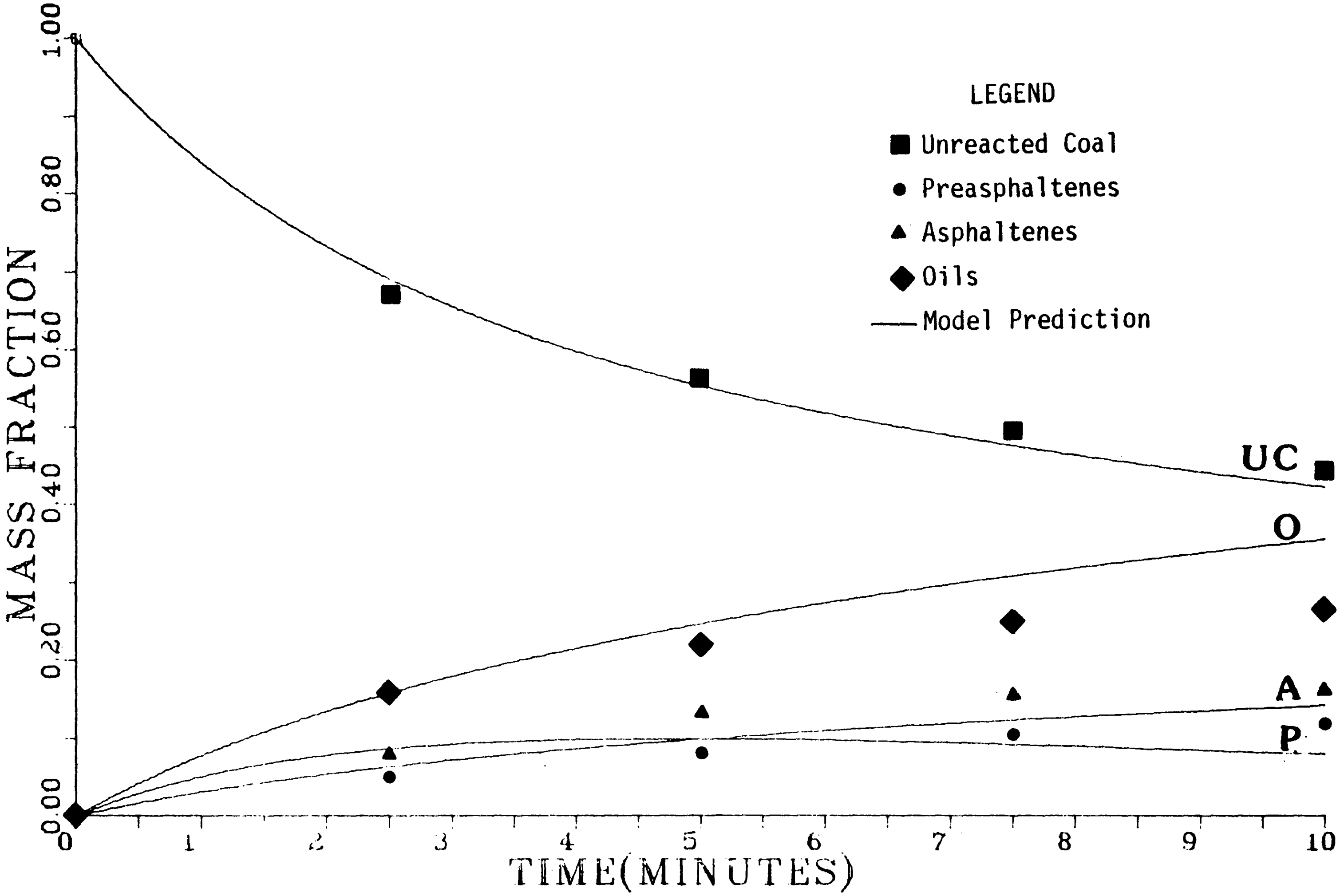


Figure 40:Model 8, Differential Method
5 Parameter,Coal:PSOC No. 107

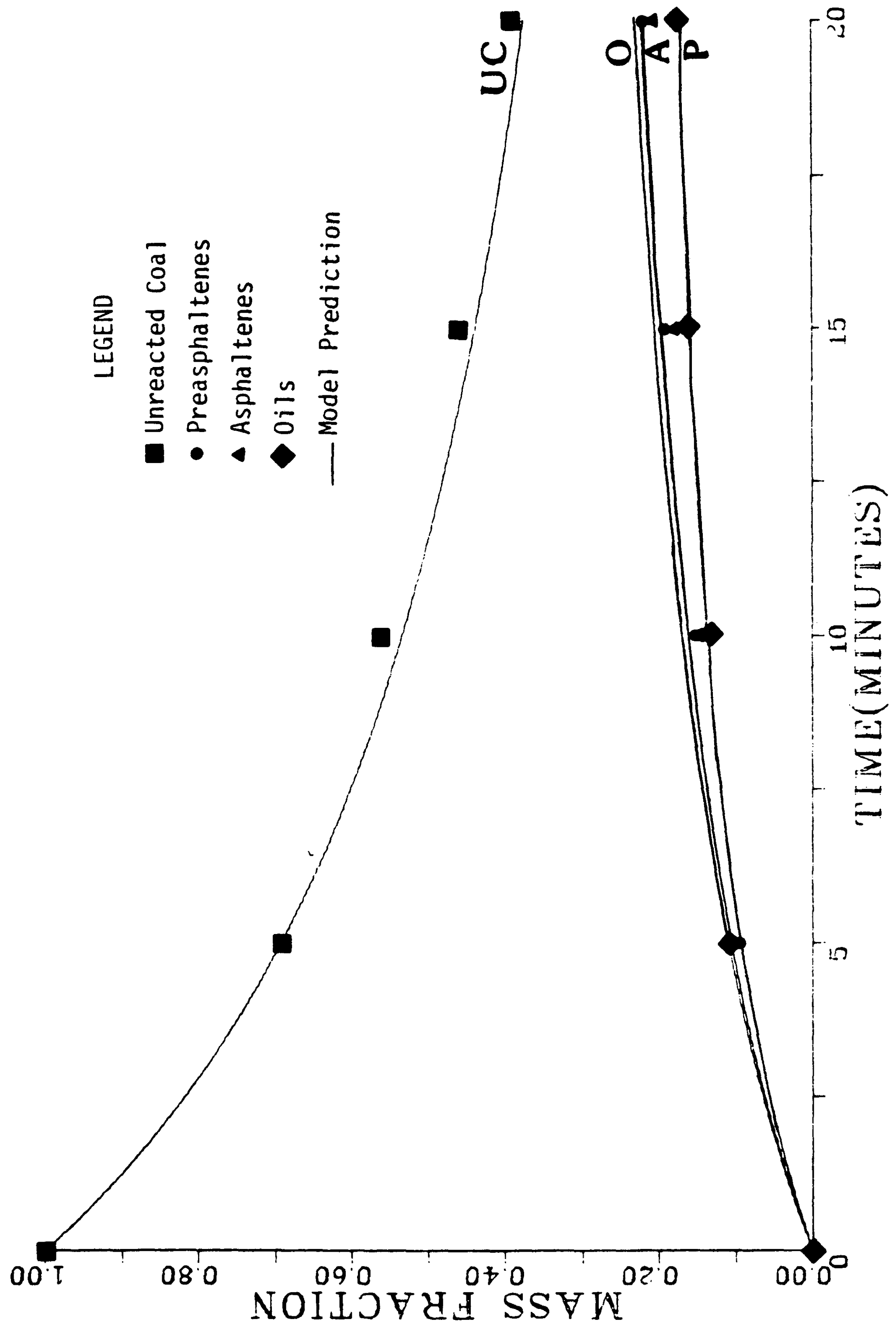


Figure 41:Model 8,Differential Method
5 Parameter,Coal:PSOC No. 456

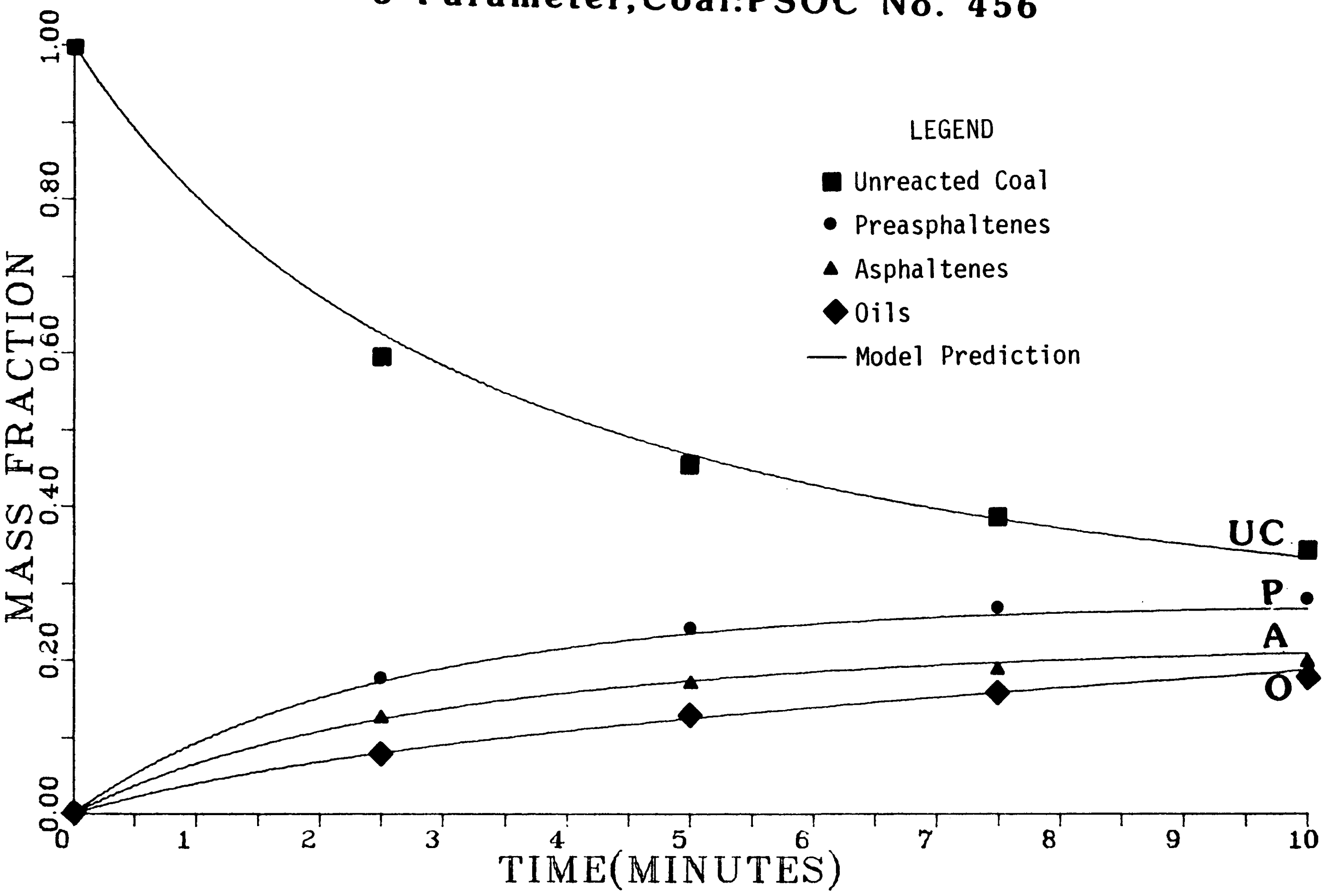


Figure 42:Model 8,Differential Method
5 Parameter,Coal:F. `Mine 9

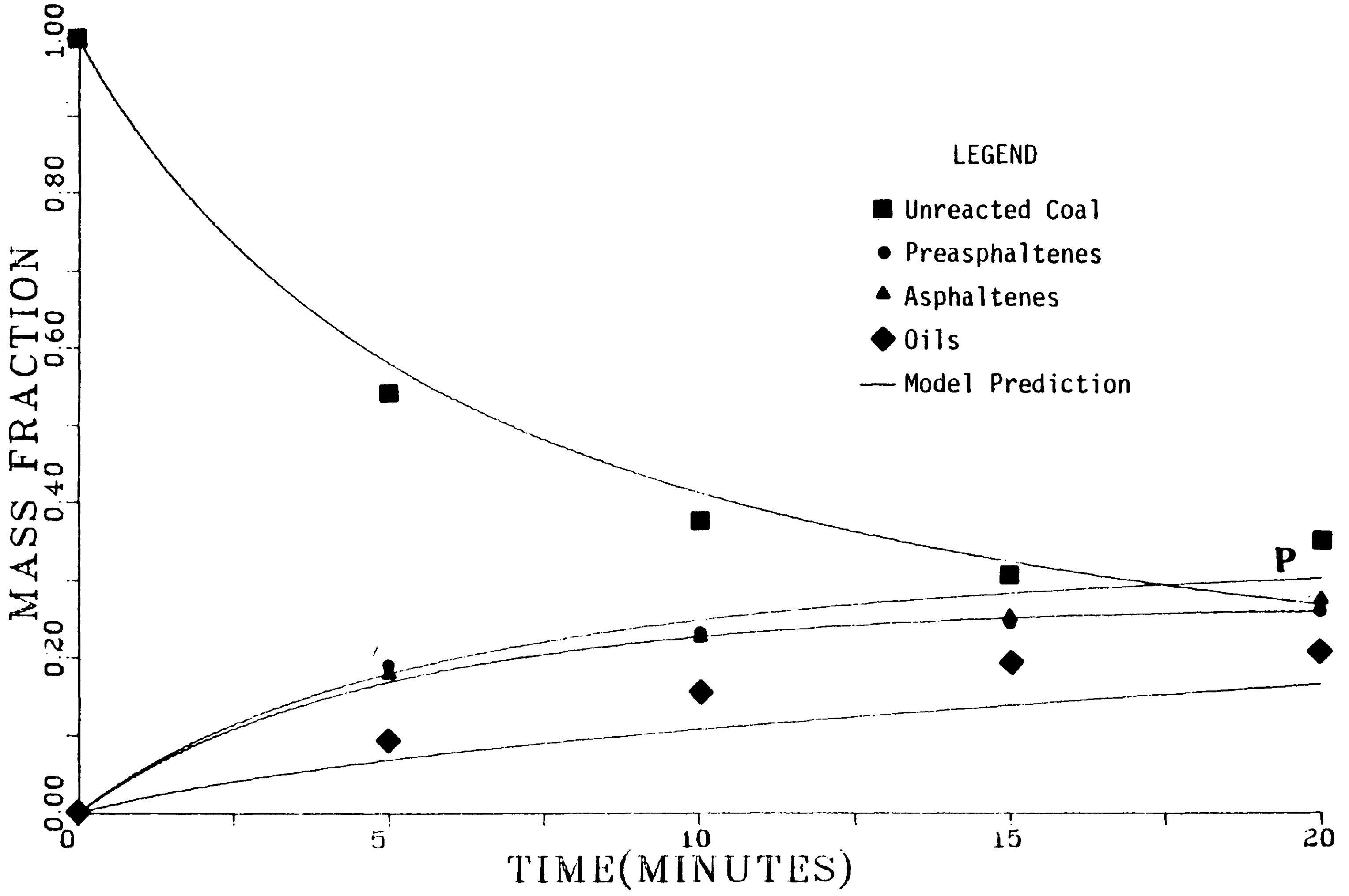


Figure43:Model 8,Differential Method
5 Parameter,Coal:PSOC No. 437

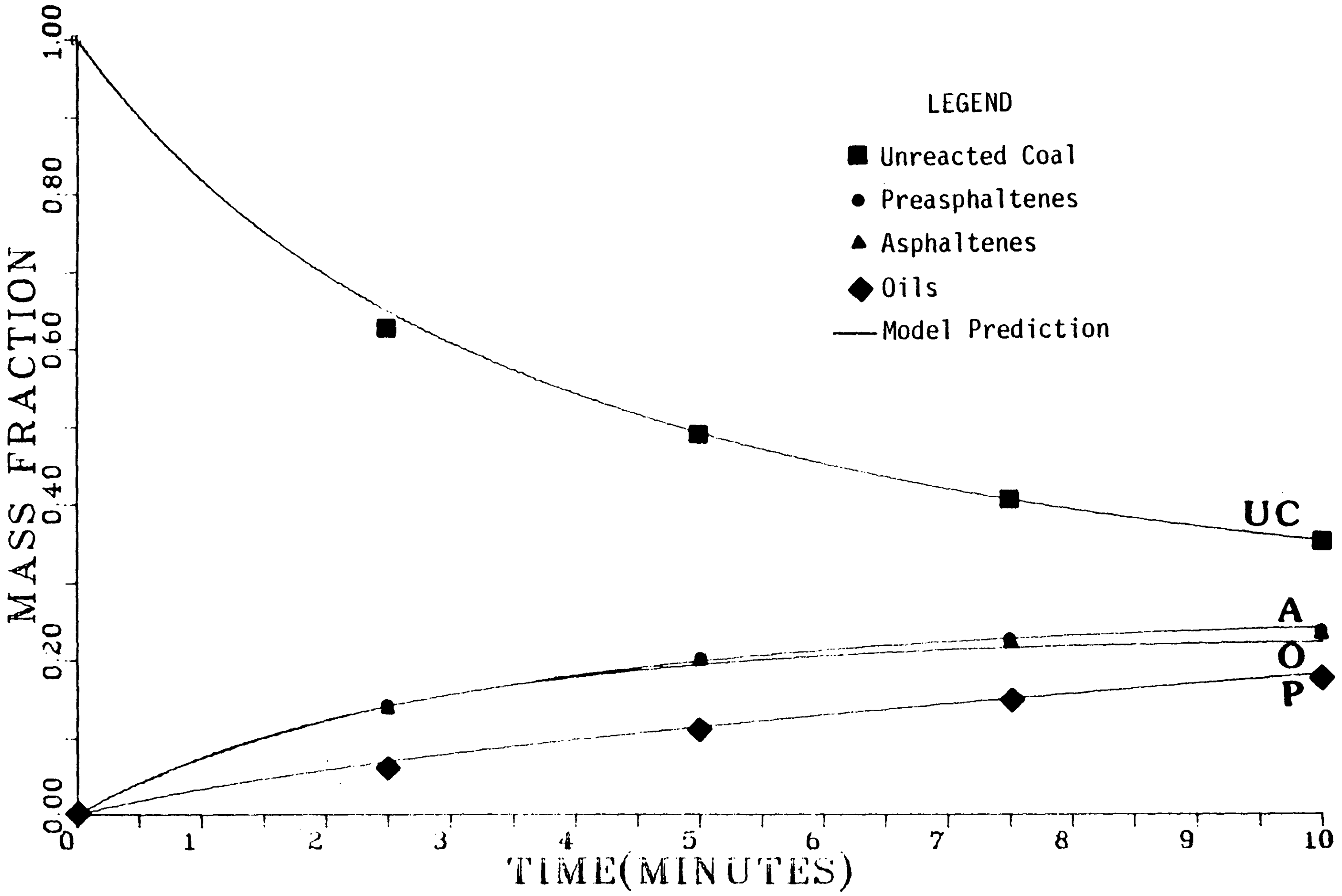


Figure 44:Model 8,Differential Method 5 Parameter,Coal:PSOC No. 151

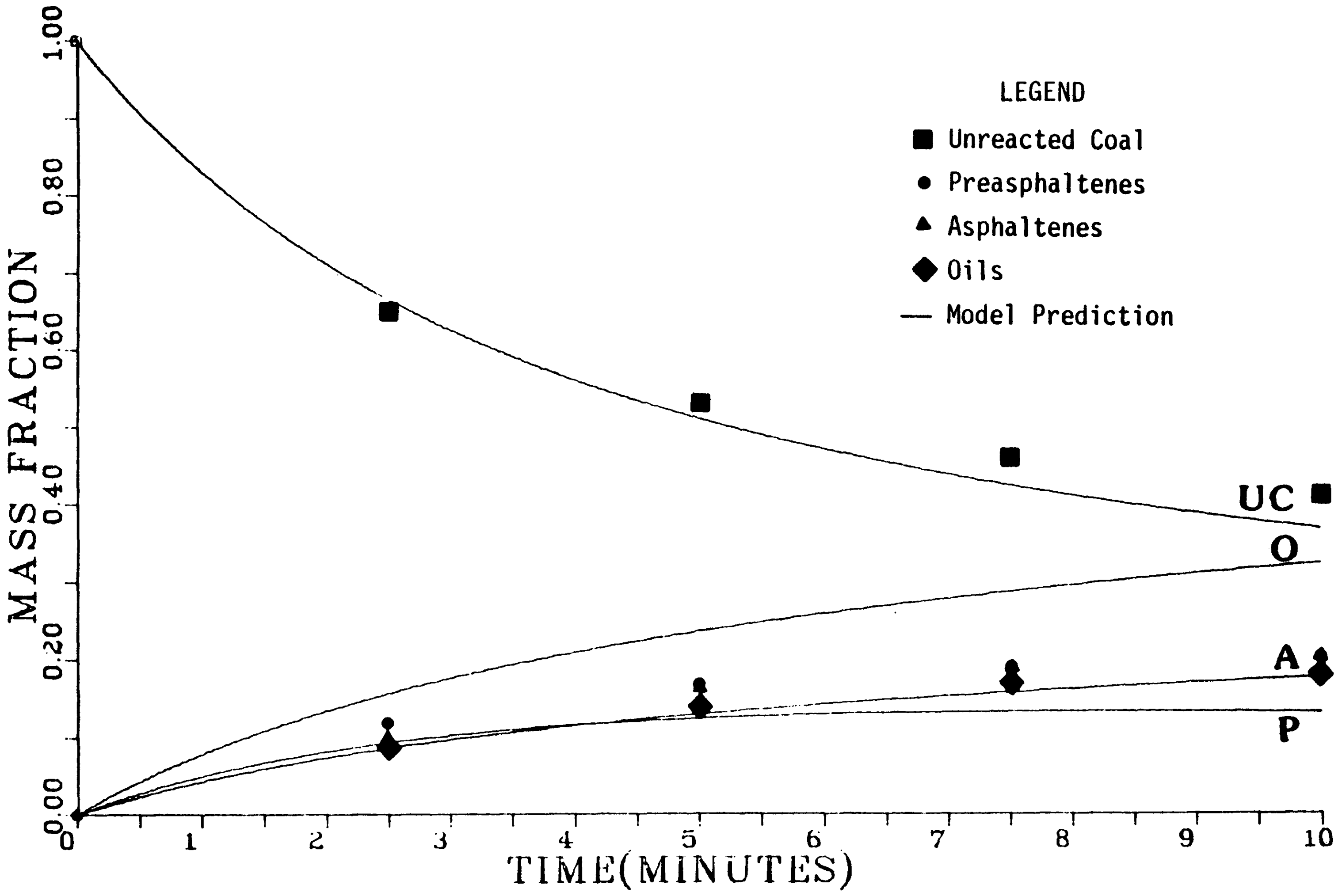


Figure 45: Model 8, Differential Method
5 Parameter, Coal: PSOC No. 056

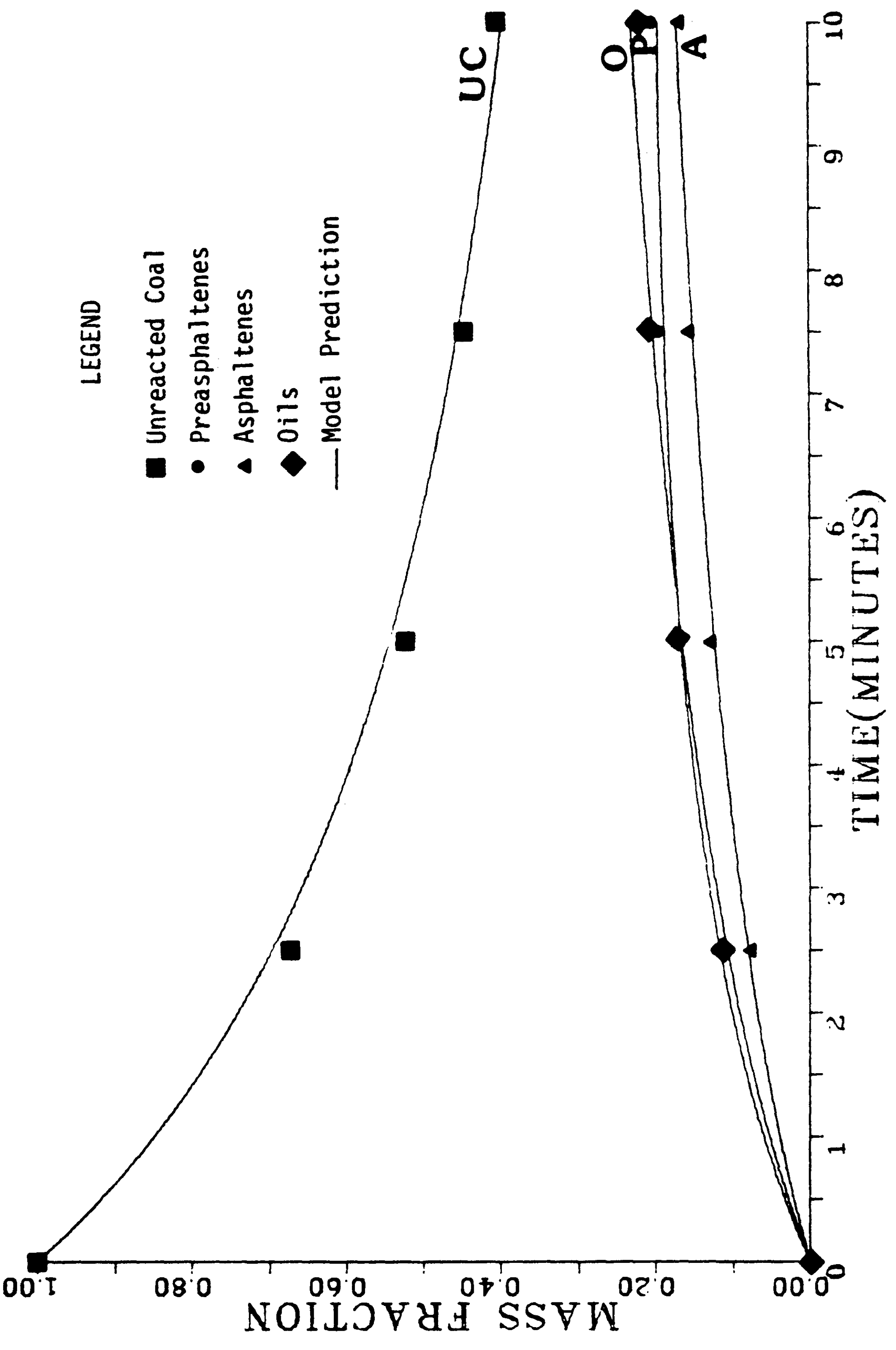


Figure 46:Model 8,Differential Method
5 Parameter,Coal:Co . Energy

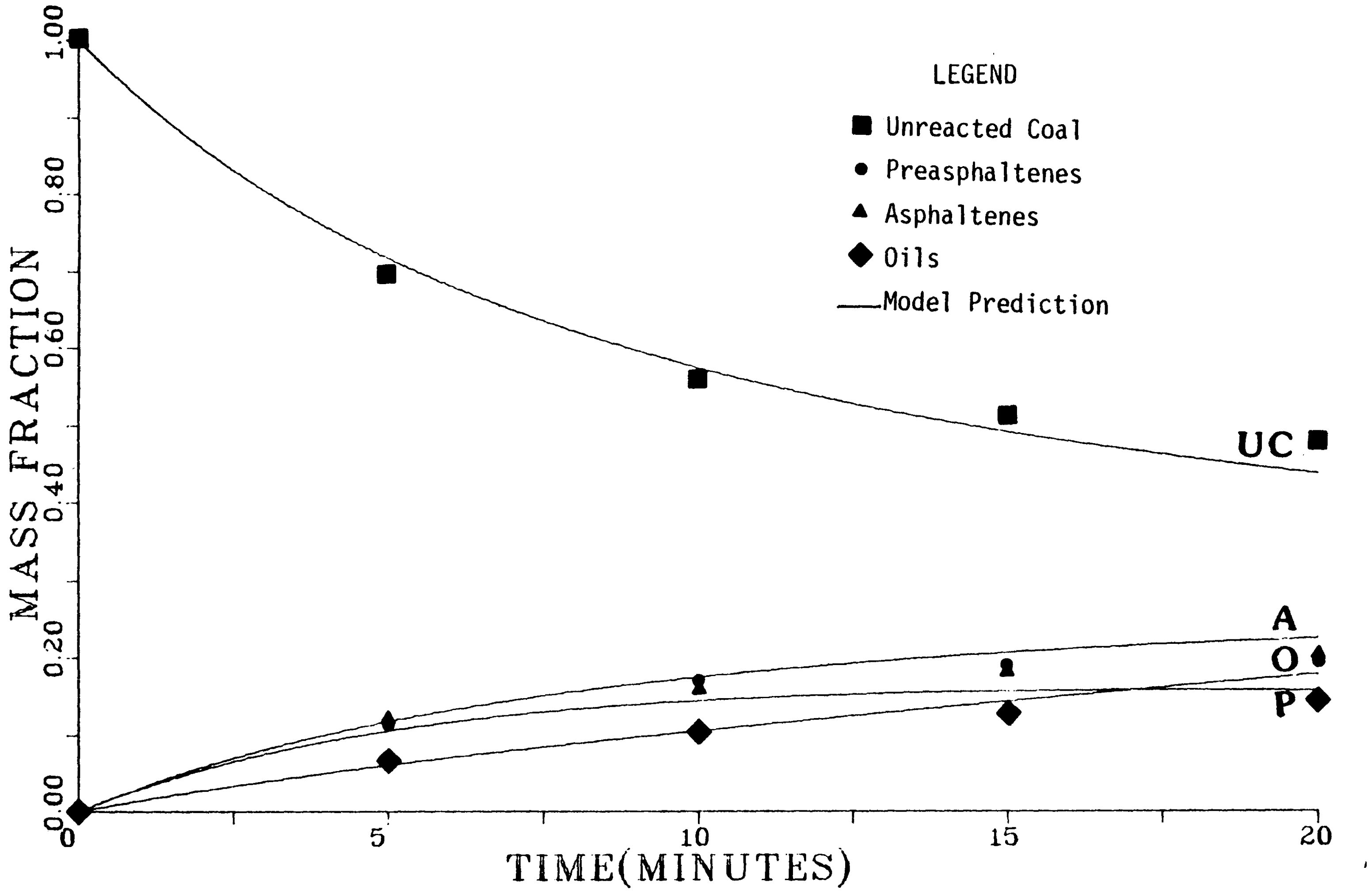


Table 3. "Ratio" Values, Coal: PSOC 107

Model	Ratio
1	0.614
2	0.614
3	0.848
4	0.977
5	0.977
6	0.976
7	0.911
8	0.983
9	0.916
10	0.951
11	0.952

Table 4. "Ratio" Values, Coal: Fies Mine 9

Model	Ratio
1	0.732
2	0.732
3	0.898
4	0.996
5	0.995
6	0.994
7	0.980
8	0.992
9	0.982
10	0.996
11	0.987

Table 5. Parameters Comparison of Model 8

Coal: Fies Mine 9

Method	K_1	K_2	K_3	K_4	K_5
Integral	.06886	.06617	.00383	.04101	.01082
Differential	.0634	.0610	.0139	.0214	.0059

Table 6. Parameters Comparison of Model 8

Coal: Colorado Energy

Method	K_1	K_2	K_3	K_4	K_5
Integral	.03106	.0215	0.0	.01501	.01684
Differential	.0335	.0346	.0172	.0155	.0455

Table 7. Parameters Comparison of Model 8

Coal: PSOC 056

Method	K_1	K_2	K_3	K_4	K_5
Integral	.06264	.04345	.00131	.05501	.01951
Differential	.0724	.0463	0.0	.0620	.0499

Table 8. Parameters Comparison of Model 8

Coal: PSOC 437

Method	K_1	K_2	K_3	K_4	K_5
Integral	.08345	.07031	.00215	.04539	.01829
Differential	.0936	.0909	.0310	.0390	.0487

Table 9. Parameters Comparison of Model 8

Coal: PSOC 456

Method	K_1	K_2	K_3	K_4	K_5
Integral	.1102	.0701	.00262	.0599	.02355
Differential	.119	.0832	.0271	.0482	.0452

Table 10. Parameters Comparison of Model 8

Coal: PSOC 107

Method	K_1	K_2	K_3	K_4	K_5
Integral	.03084	.0288	0.0	.02566	.00501
Differential	.0280	.0305	0.0	.0317	.0134

Table 11. Parameters Comparison of Model 8

Coal: PSOC 071

Method	K_1	K_2	K_3	K_4	K_5
Integral	.02578	.03681	.00237	.05631	0.0
Differential	.0687	.0376	0.0	.0936	.218

Table 12. Parameters Comparison of Model 8

Coal: PSOC 151

Method	K_1	K_2	K_3	K_4	K_5
Integral	.05971	.05004	.00237	.0446	.0212
Differential	.0625	.0519	0.0	.947	.0773

Modeling of Non-Isothermal Data:

The same methods of analysis were employed to investigate the eleven models presented previously for data obtained by Shalabi (19) at temperatures of 400, 375, and 350 °C. Tables 16, 17, and 18 present a summary of the results obtained from the integral method of analysis. All of the three tables indicate that Model 8 was the best in fitting the experimental data, since Model 8 exhibited the lowest "dmmr". Results of differential method of analysis are presented in Tables 19, 20, and 21. Referring to these three tables, it was again concluded that Model 8 gave the best fit to the experimental data. Finally, a comparison between the rate constants for Model 8 from both integral and differential analysis was made, as shown in Tables 22, 23, and 24.

Activation Energies

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

$$K = A \exp\left(-\frac{E}{RT}\right)$$

where

A = frequency factor
E = activation energy
R = ideal gas law constant

T = absolute temperature.

The above expression may be rewritten as:

$$\ln K = \ln A - \frac{E}{RT}$$

Thus, plotting lnK vs $\frac{1}{T}$ at the three available temperatures (19) should yield a straight line with slope of $(-\frac{E}{R})$ and y intercept of lnA. Rate constants from Models 1, 8, and 9 were plotted according to the above expression for the three temperature data of Shalabi. One other method of discriminating between various models involves use of the linearity of the Arrhenius plot as a measure of model adequacy. Thus, models 1, 8, and 9, which are the best and worst data fits for the data of Shalabi were employed to investigate the effect of model on calculated activation energies. Linearity of the Arrhenius plot is the important consideration here. How good the linear regression fits the data is given by the R^2 value in these figures, with a value of R^2=1.00 indicating a perfect fit. The Arrhenius activation energies and their corresponding R^2 values are shown in Tables 13, 14, and 15 for the three given models. Figures 47 through 56 represent the Arrhenius plots of Models 1, 8, and 9.

The activation energies for Model 8 of K_1 (conversion of coal to preashaltenes), K_2 (conversion of coal to asphalt-

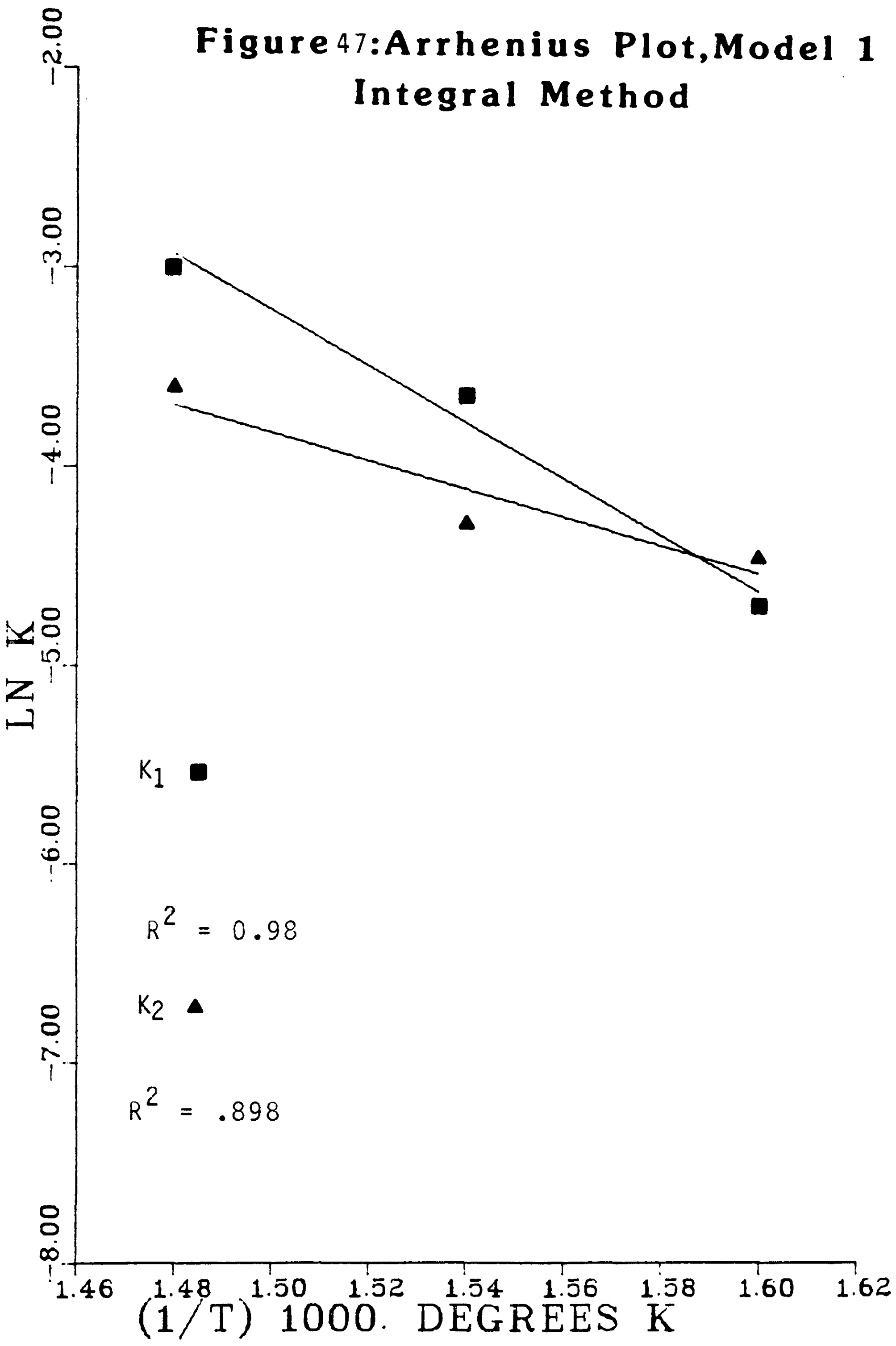


Figure 47: Arrhenius Plot, Model 1 Integral Method

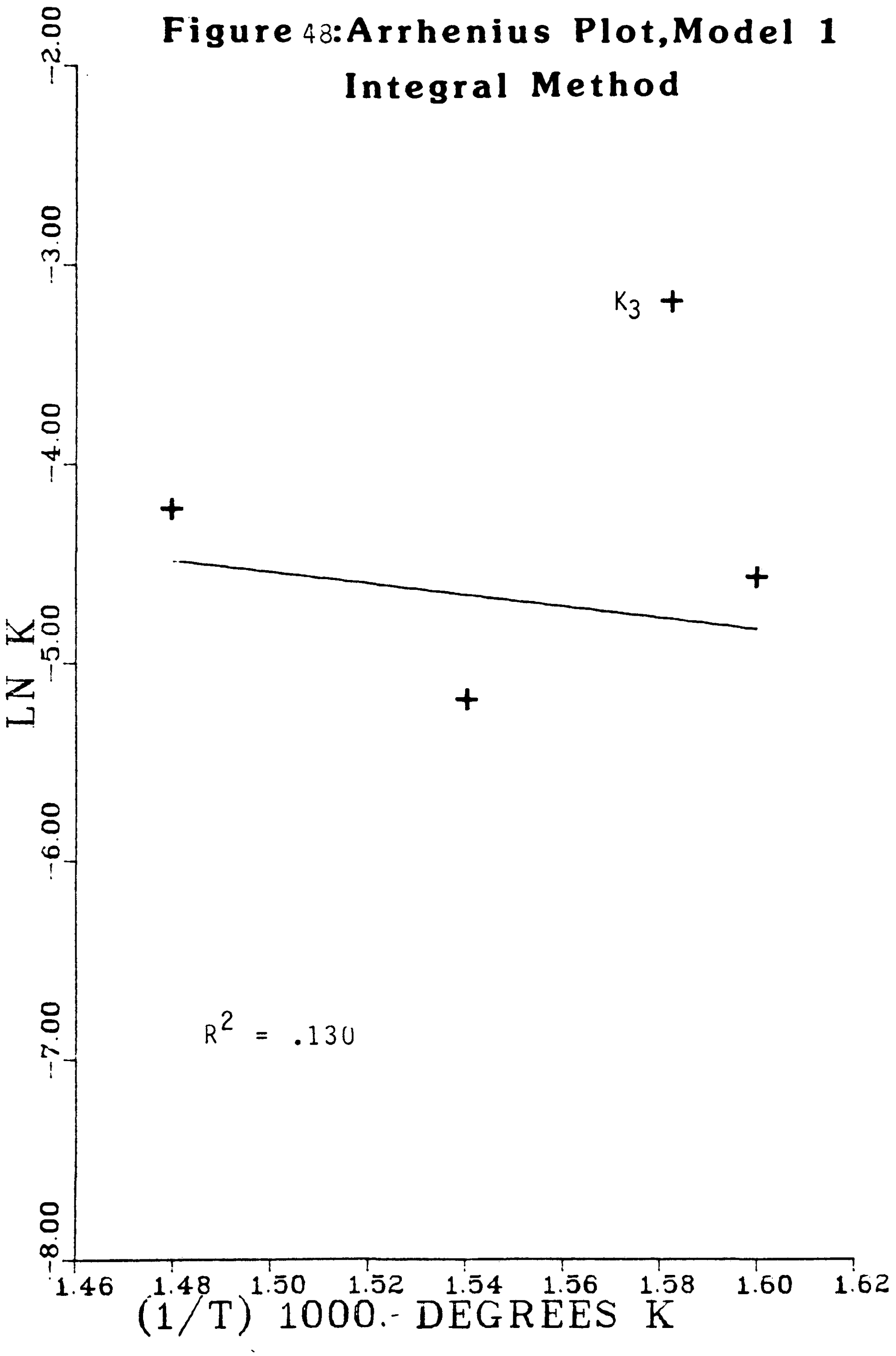


Figure 48: Arrhenius Plot, Model 1 Integral Method

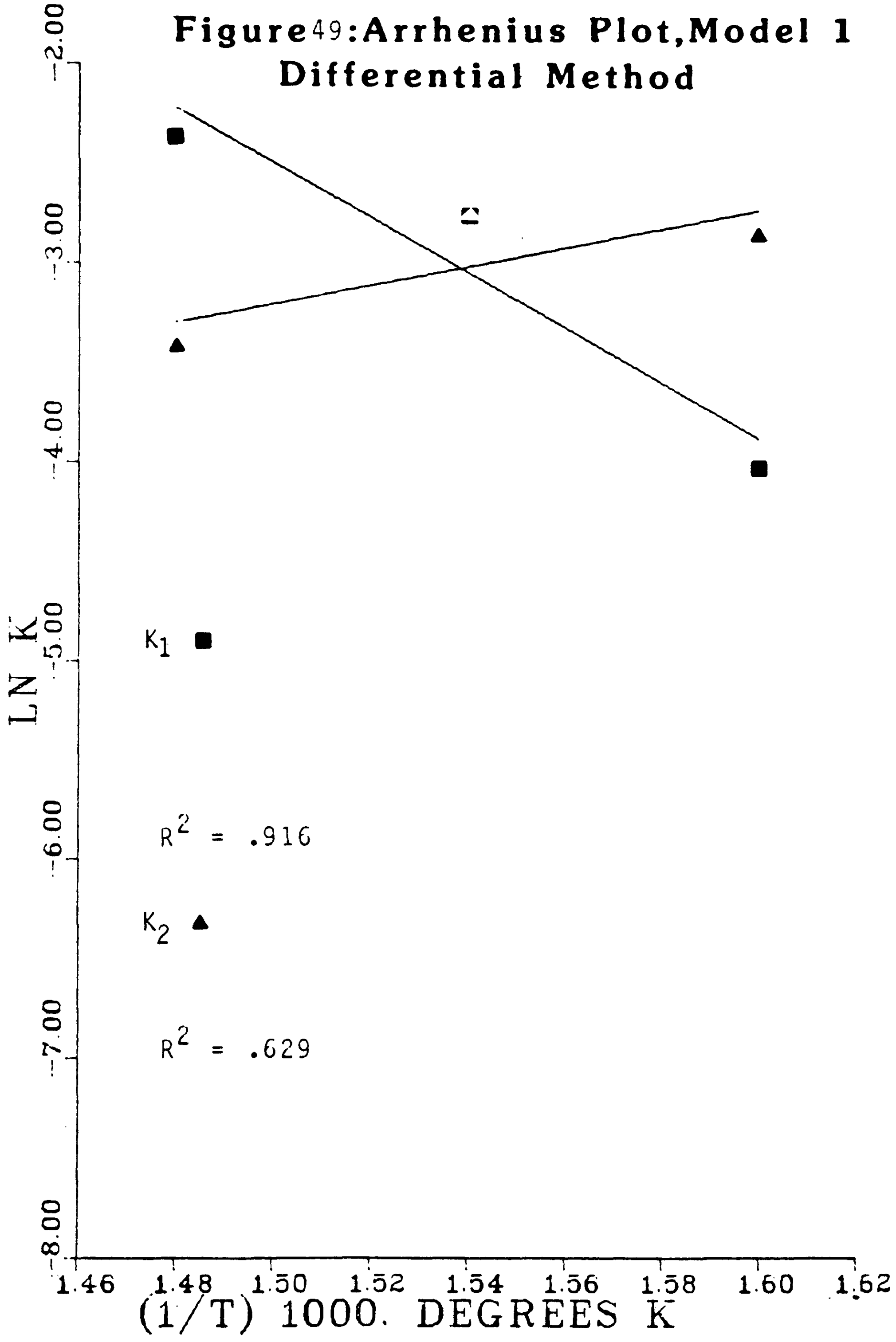
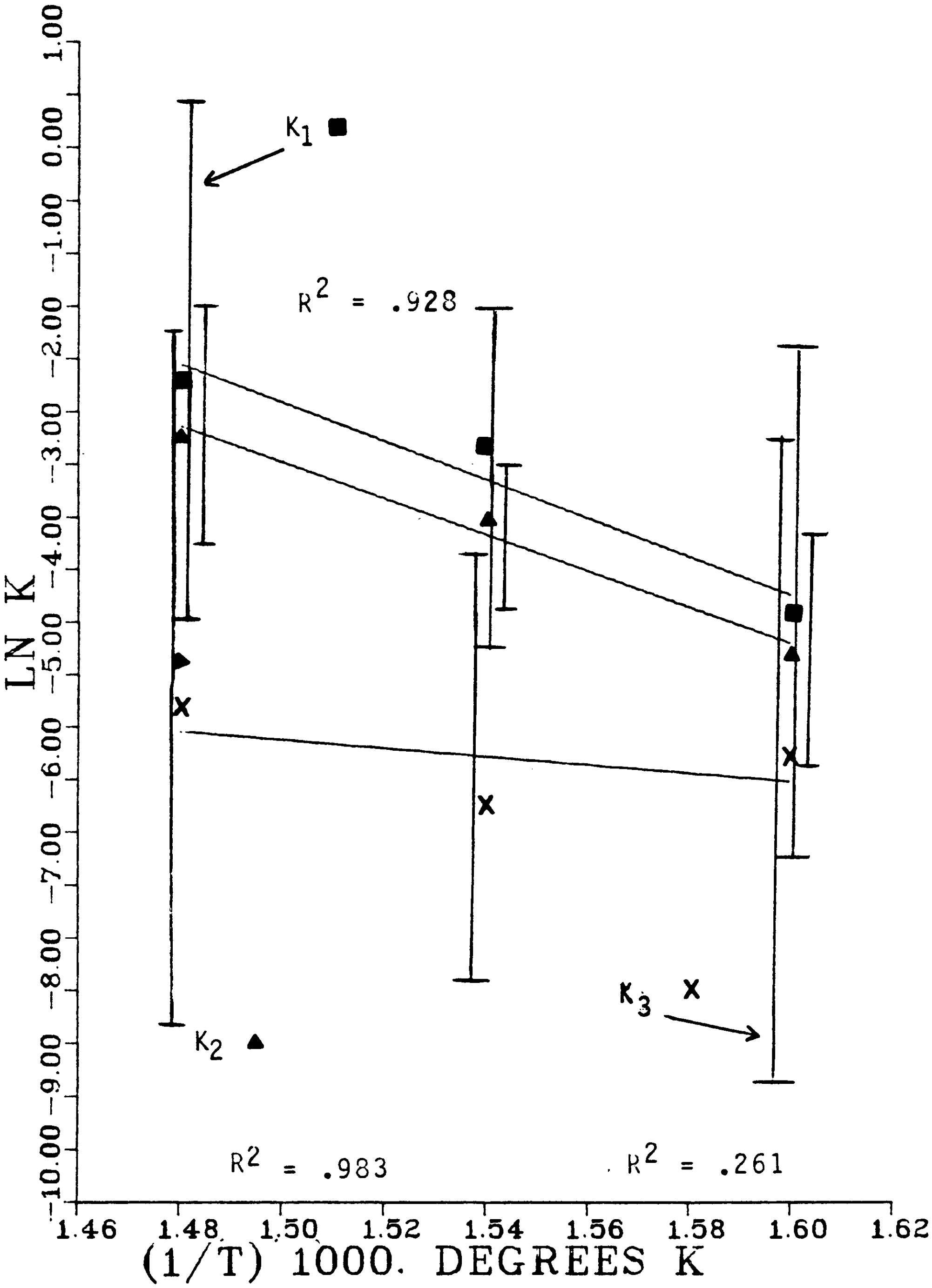


Figure 49: Arrhenius Plot, Model 1 Differential Method

Figure 50: Arrhenius Plot, Model 8
Integral Method



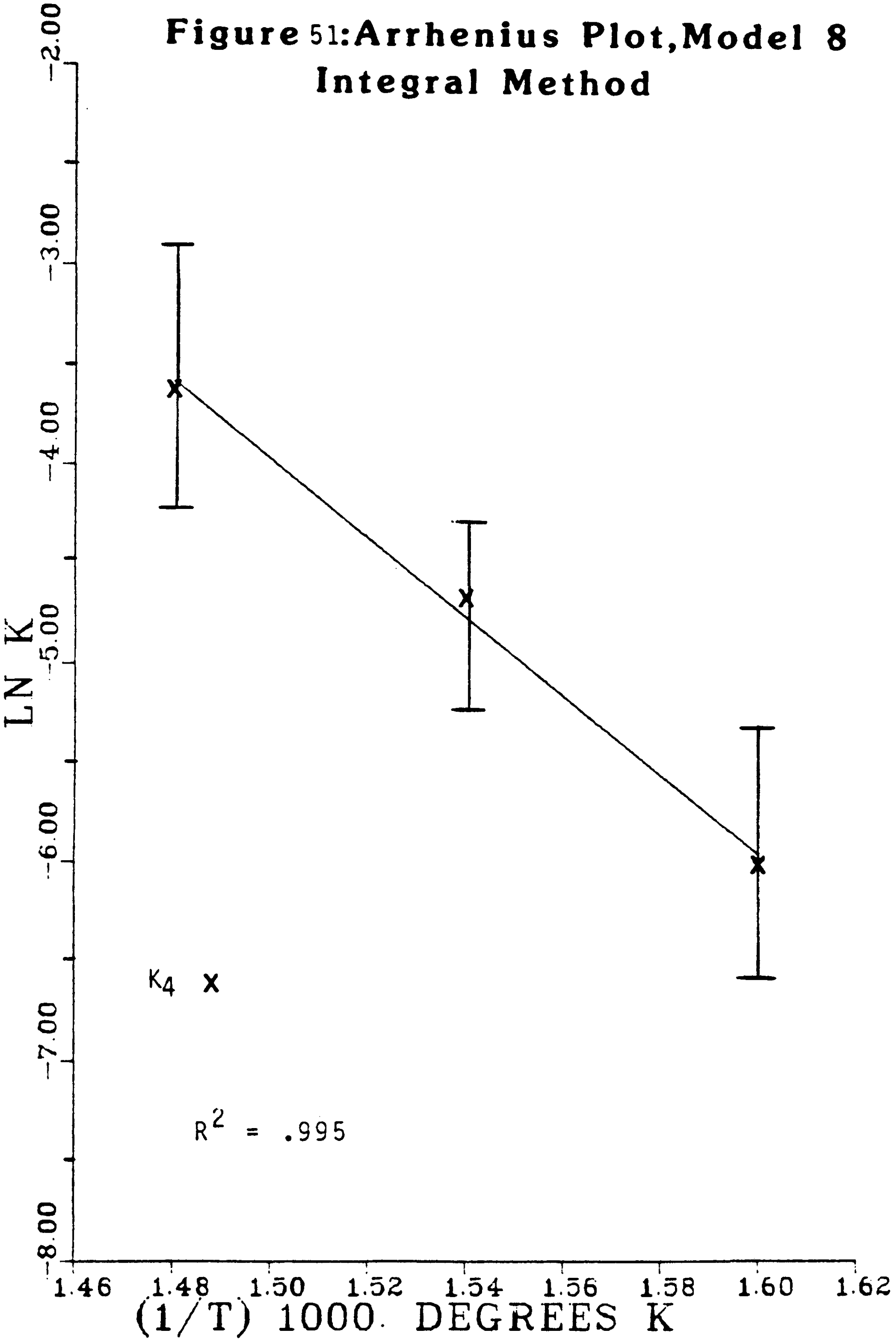


Figure 51: Arrhenius Plot, Model 8 Integral Method

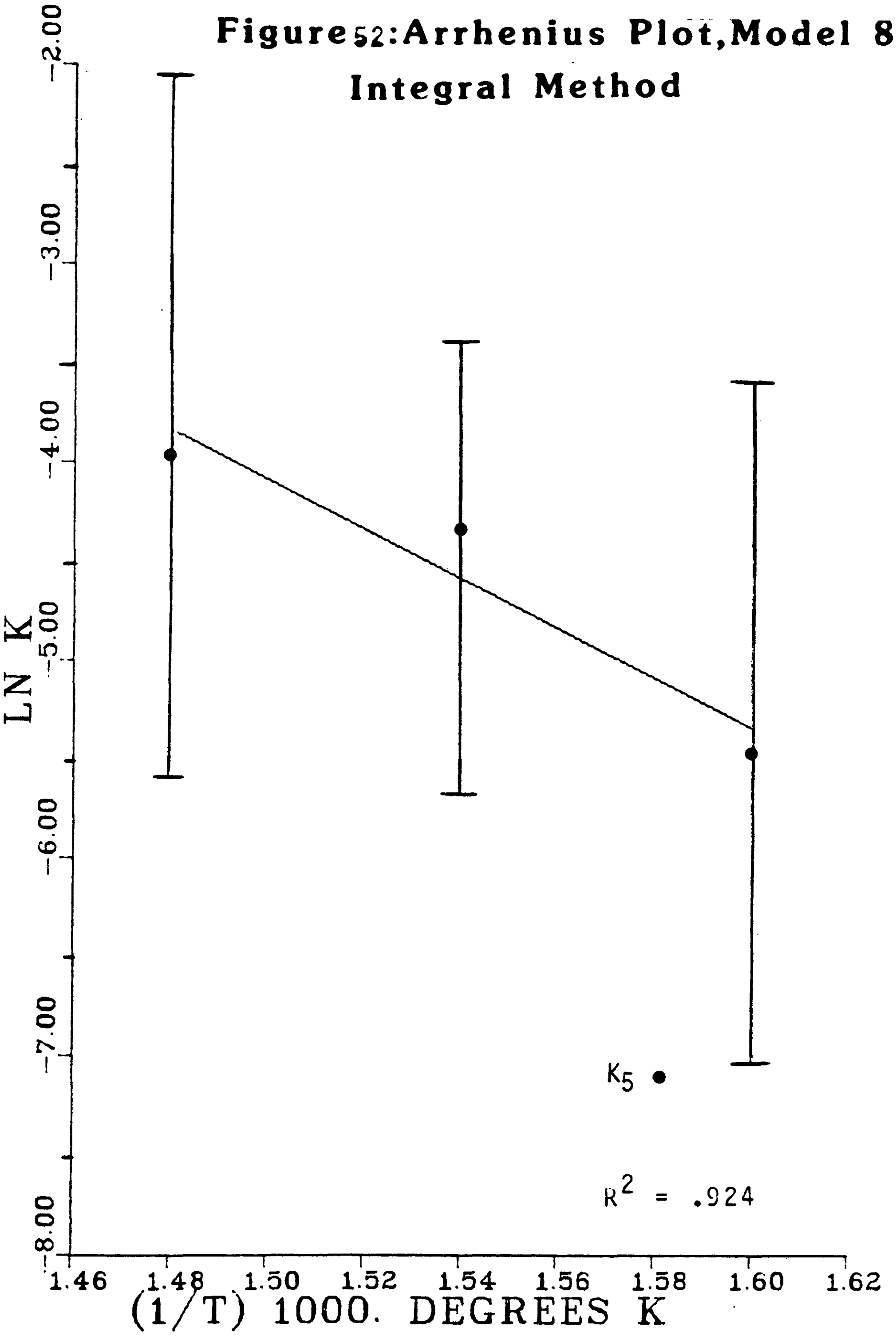
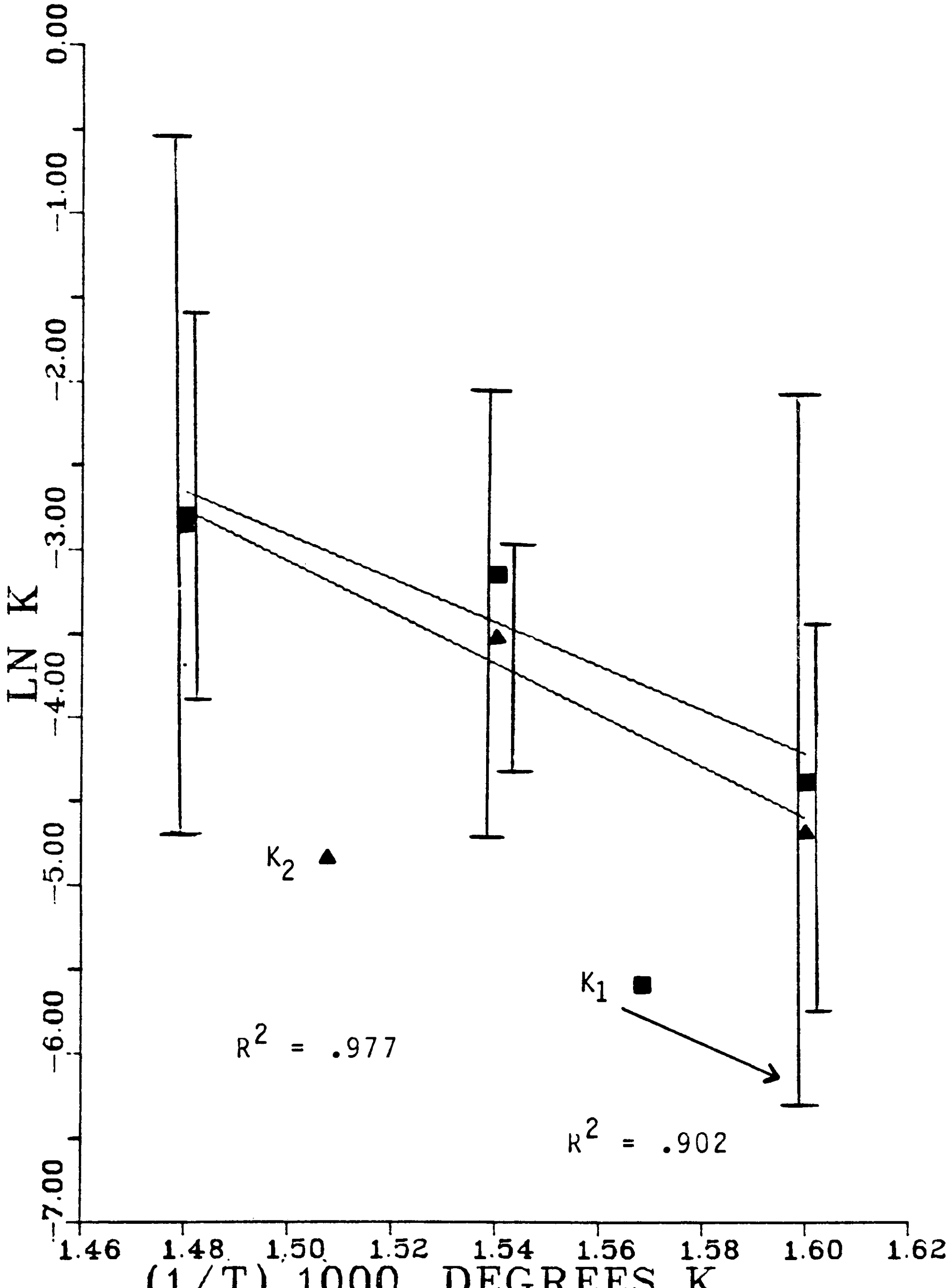


Figure 52: Arrhenius Plot, Model 8
Integral Method

Figure 53: Arrhenius Plot, Model 8
Differential Method



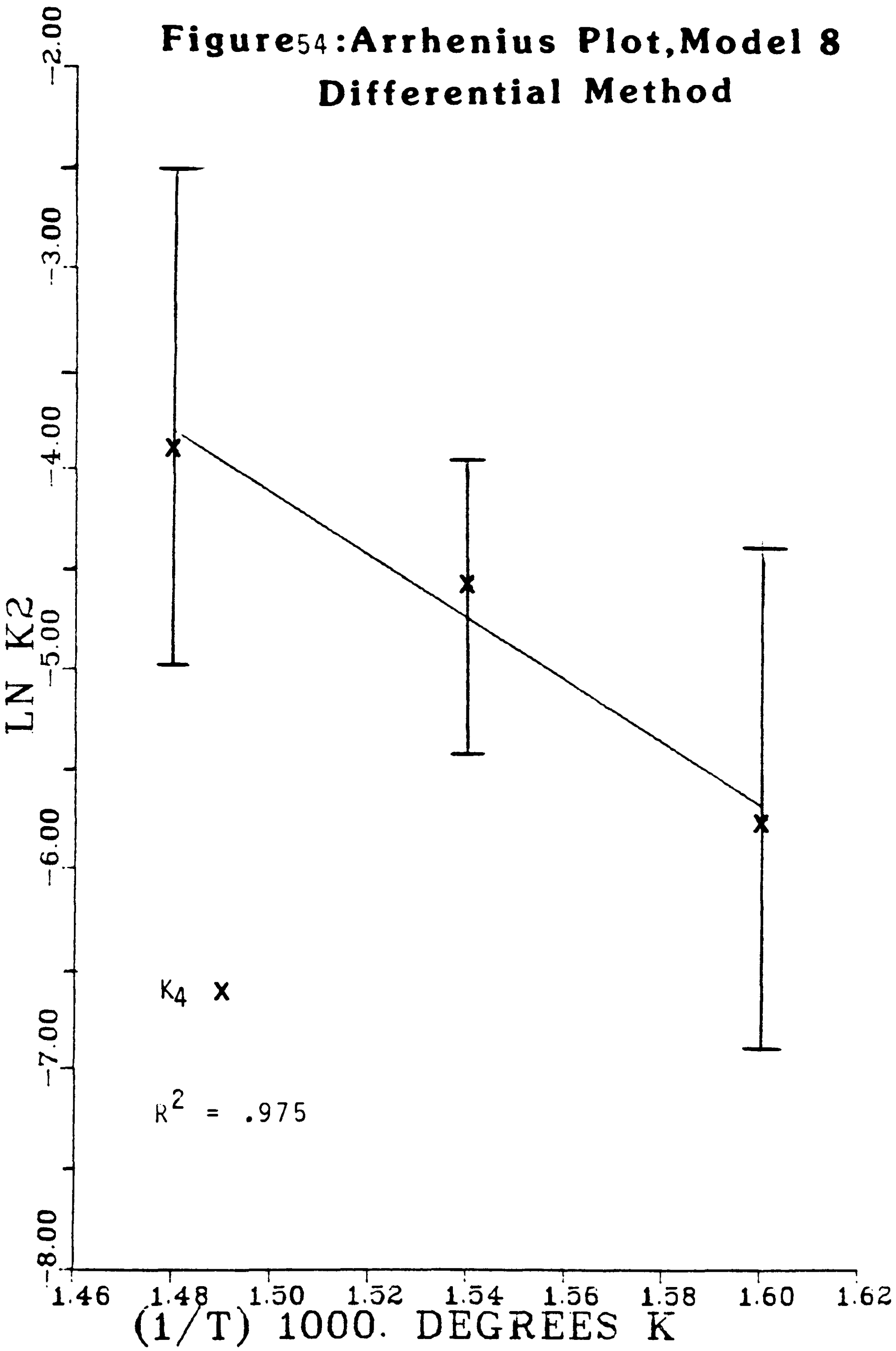


Figure54:Arrhenius Plot,Model 8 Differential Method

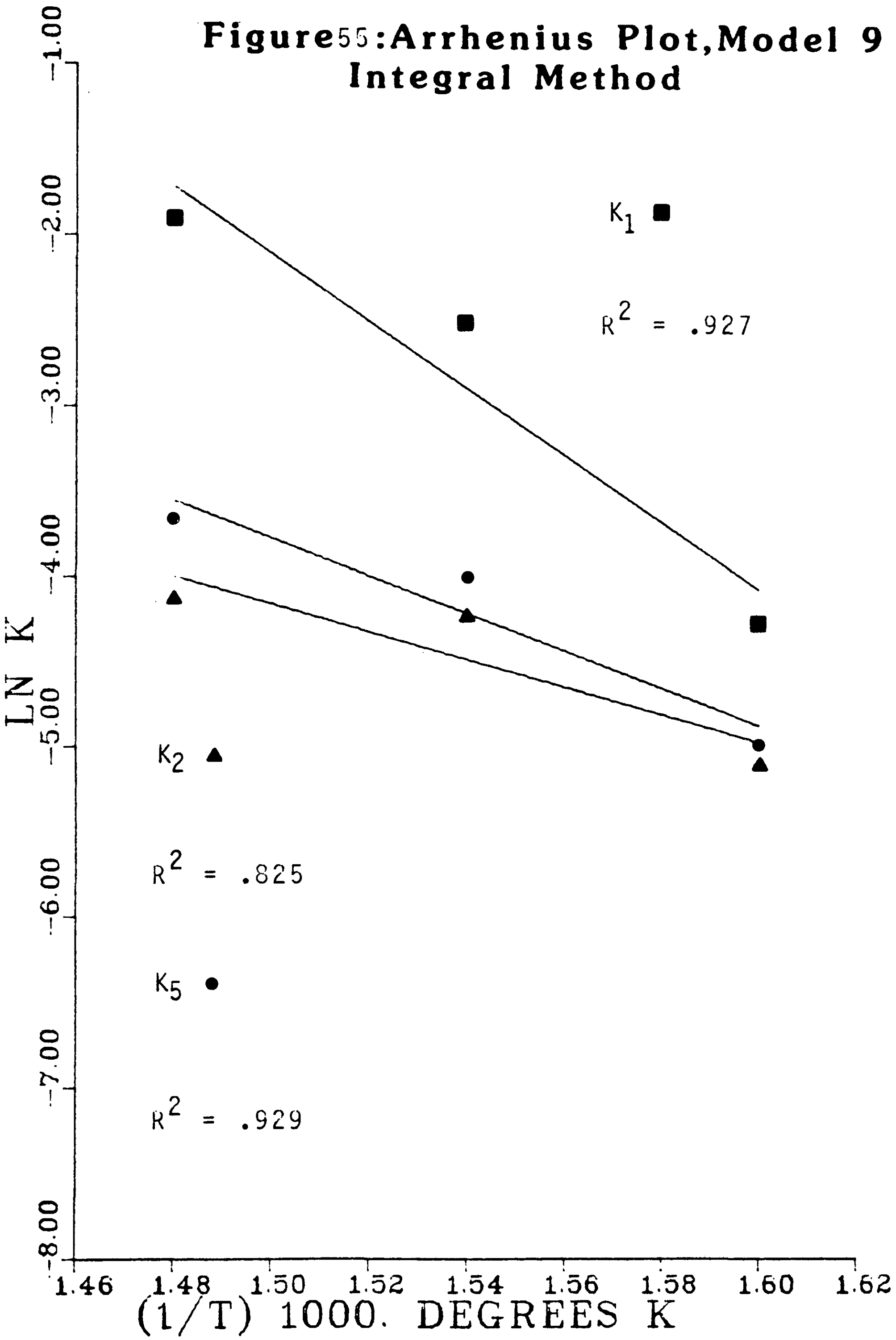


Figure55:Arrhenius Plot,Model 9 Integral Method

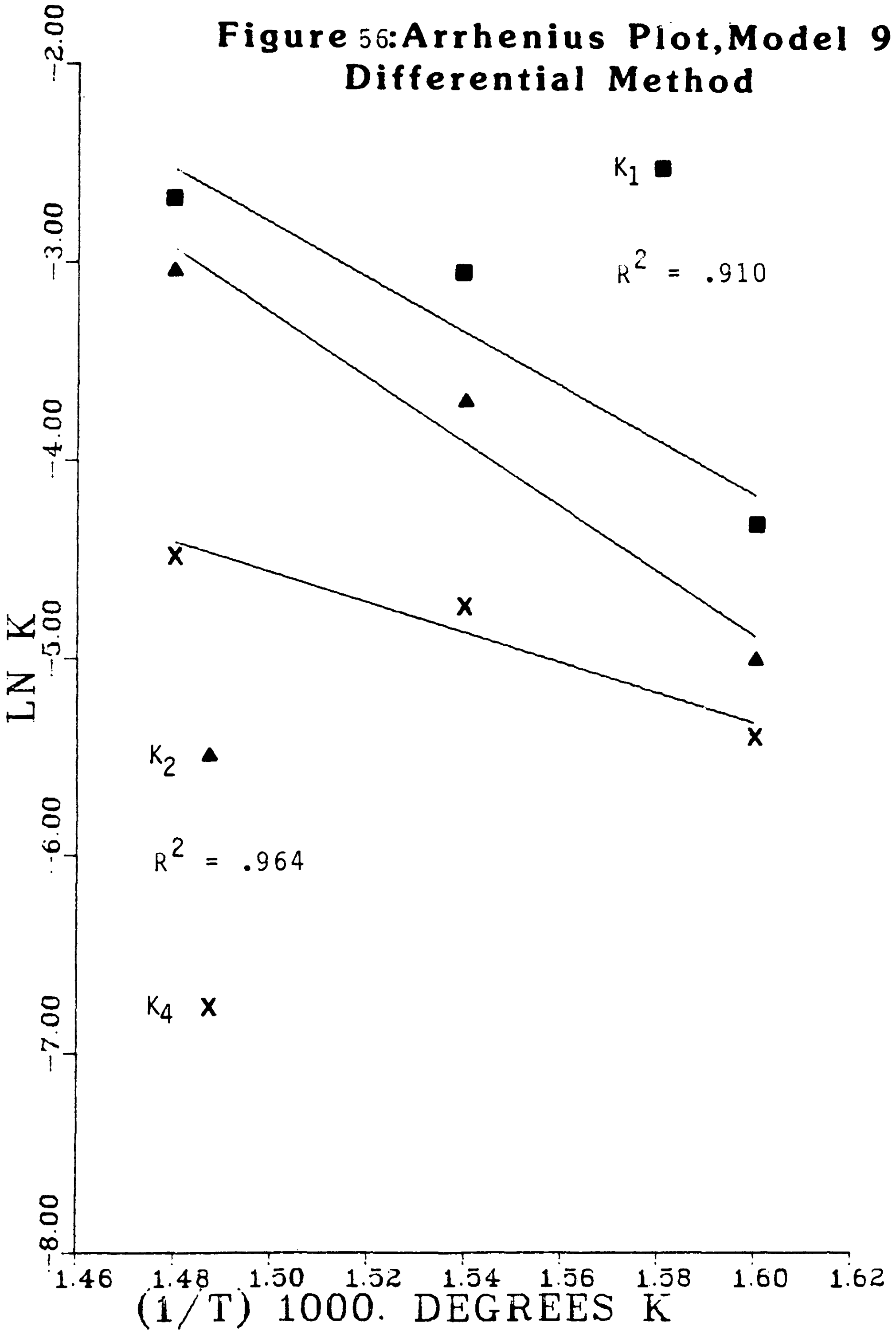


Figure 56: Arrhenius Plot, Model 9
Differential Method

enes), and K_4 (conversion of coal to oil plus gas) ranged from 34.3 to 39.6 K cal/gm mole for the integral method, and from 25.9 to 31.1 K cal/gm mole for the differential method. The activation energy of K_3 (conversion of asphaltenes to oils plus gases) exhibited the lowest value of 7.9 K cal/gm mole for the integral method and 0 K cal/gm mole for the differential method.

Interpretation:

The reaction network represented by Model 8 with five parameters, and with second-order reactions in coal was found to fit the experimental data quite well for all four reaction products. Rate constant K_1 (conversion of coal to preasphaltenes) had the highest value compared to the other rate constants which explains the observed high yield of the preasphaltenes at the start of reaction. The model also predicts that asphaltenes and preasphaltenes are the major products with preasphaltenes being the preferred product. As the reaction proceeded, the asphaltenes converted to oils plus gases with rate constant K_3, which was a low value compared to the other rate constants. This means that the formation of oils plus gases were mainly due to the conversion of coal in these batch hydrogenation systems.

The mathematical model and the corresponding reaction network associated with it, however, represent the experimental data quite well only from a macroscopic viewpoint. The model cannot explain the microscopic mechanism of coal liquefaction which so far has not been clearly determined. Consequently, the individual rate constants should be further investigated by using asphaltenes or preasphaltenes as reactants to determine the rate constants more precisely. In addition, it is clear that this model will only apply in the time range studied (0-60 minutes for Furlong's data, and 0-180 minutes for Shalabi's) and extropolation of the model outside this time range is not reasonable.

Table 13. "dmmr" Values, for 400 °C Temperature.

Model	dmmr
1	3.4×10^{-4}
2	4.8×10^{-4}
3	1.1×10^{-6}
4	2.6×10^{-7}
5	2.6×10^{-7}
6	2.6×10^{-7}
7	2.6×10^{-7}
8	3.4×10^{-10}
9	2.8×10^{-7}
10	2.3×10^{-2}
11	7.5×10^{-8}

Table 14. "dmmr" Values, for 375 °C Temperature.

Model	dmmr
1	1.4×10^{-4}
2	7.5×10^{-5}
3	1.3×10^{-5}
4	1.1×10^{-7}
5	1.1×10^{-7}
6	1.1×10^{-7}
7	1.1×10^{-7}
8	1.2×10^{-9}
9	9.4×10^{-8}
10	1.4×10^{-4}
11	6.0×10^{-8}

Table 15. "dmmr" Values, for 350 °C Temperature.

Model	dmmr
1	3.8×10^{-7}
2	2.4×10^{-7}
3	5.9×10^{-8}
4	3.4×10^{-10}
5	3.3×10^{-10}
6	3.3×10^{-10}
7	3.3×10^{-10}
8	1.0×10^{-10}
9	3.1×10^{-10}
10	6.3×10^{-5}
11	3.0×10^{-10}

Table 16. "Ratio" Values, for 400 °C Temperature

Model	Ratio
1	.771
2	.776
3	.951
4	.967
5	.967
6	.967
7	.940
8	.961
9	.938
10	.961
11	.948

Table 17. "Ratio" Values, for 375 °C Temperature.

Model	Ratio
1	.869
2	.871
3	.979
4	.994
5	.994
6	.994
7	.984
8	.996
9	.985
10	.993
11	.988

Table 18. "Ratio" Values, for 350 °C Temperature.

Model	Ratio
1	.856
2	.649
3	.526
4	.995
5	.995
6	.995
7	.977
8	.995
9	.974
10	.992
11	.987

Table 19. Parameters Comparison of Model 8, 400 °C

Method	K_1	K_2	K_3	K_4	K_5
Integral	.1070	.0658	.0049	.0265	.019
Differential	.0603	.0575	0.0	.0203	0.0

Table 20. Parameters Comparison of Model 8, 375 °C

Method	K_1	K_2	K_3	K_4	K_5
Integral	.06068	.0296	.00193	.00926	.01296
Differential	.0431	.0294	0.0	.0103	0.0

Table 21. Parameters Comparison of Model 8, 350 °C

Method	K_1	K_2	K_3	K_4	K_5
Integral	.01191	.00832	.00306	.00242	.0042
Differential	.0126	.0092	0.0	.0031	.0102

Table 22. Estimation of Activation Energies, Model 1

	Integral Method			Differential Method	
	K_1	K_2	K_3	K_1	K_2
E (K cal/gm mole)	28.2	14.2	5.8	27.7	-9.2
R^2	.980	.898	.130	.916	.629

Table 23. Estimation of Activation Energies, Model 8

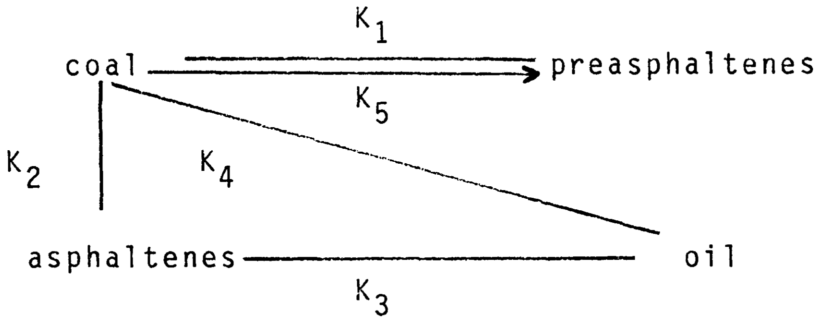
	Integral Method					Differential Method		
	K_1	K_2	K_3	K_4	K_5	K_1	K_2	K_4
E (K cal/gm mole)	36.4	34.3	7.9	39.6	25.0	25.9	30.4	31.1
R^2	.928	.983	.261	.995	.924	.902	.977	.975

Table 24. Estimation of Activation Energies, Model 9

	Integral Method			Differential Method		
	K_1	K_2	K_5	K_1	K_2	K_4
E (K cal/gm mole)	39.4	16.4	22.2	27.4	32.5	15.3
R^2	.927	.825	.929	.910	.964	.935

CONCLUSIONS

1. The experimental data (19,23) on product distribution was modeled successfully with the following reaction network:



where reactions 1, 2, and 4 are second-order in coal.

2. Activation energies of 36.4, 34.3, 7.9, 39.6 and 25.0 K cal/gm mole for reactions 1, 2, 3, 4, and 5 respectively were calculated using integral method, and of 25.9, 30.4, and 31.1 K cal/gm mole using differential method for reactions 1, 2, and 4, respectively.
3. Results of data modeling have indicated that reaction networks which do not incorporate direct reaction of preasphaltenes to asphaltenes and oil plus gas are appropriate for coal liquefaction.
4. The reaction of asphaltenes to oils plus gases was shown to be very slow.
5. In using the differential method, the analysis should be made where the change in the rate of reaction is the

greatest. For coal liquefaction data, it was found that short residence time data had to be used because the compositions of all products are almost at a steady state after 10 to 20 minutes.

6. The rate constants of the reaction network shown above using both integral and differential methods for all the experimental data were comparable.
7. High activation energies calculated indicated that the corresponding reactions are kinetically controlled and not influenced by interfacial mass transfer.

RECOMMENDATIONS

1. Further modeling of the liquefaction process needs to be done in order to obtain a model with the fewest possible parameters (rate constants).
2. The reactivity of the preasphaltenes should be investigated separately.
3. Future investigation should be performed using shorter residence times.
4. Using the pressure as a variable is another possible area of investigation.
5. The causes of the non-linearity of Arrhenius equations should be investigated.

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APPENDICES

APPENDIX A

The experimental data used in the initial rate (differential) analysis

1. Furlong's data (23).

A. 20 minutes residence time data

Coal: Fies Mine 9

Time	0	5	10	15	20
% unreacted coal	100	54.05	37.95	30.75	25.2
% preasphaltenes	0	18.85	23.2	24.7	26.1
% asphaltenes	0	18.0	23.05	25.6	27.7
% oils	0	9.1	15.75	19.2	20.9

Coal: Colorado Energy

Time	0	5	10	15	20
% unreacted coal	100	70	56.6	51.0	48.0
% preasphaltenes	0	11.35	17.05	19.0	19.5
% asphaltenes	0	11.9	15.95	18.4	20.0
% oils	0	6.8	10.35	12.5	14.5

B. 10 minutes residence time data

Coal: PSOC No. 107

Time	0	2.5	5	7.5	10
% unreacted coal	100	69.1	55.8	46.0	39.0
% preasphaltenes	0	9.35	15.1	19.0	22.0
% asphaltenes	0	10.9	15.35	18.0	20.5
% oils	0	10.4	13.75	15.9	17.5

Coal: PSOC No. 151

Time	0	2.5	5	7.5	10
% unreacted coal	100	65.0	52.8	45.75	40.8
% preasphaltenes	0	11.75	16.8	19.0	20.05
% asphaltenes	0	10.0	16.4	19.3	20.25
% oils	0	8.5	14.0	16.9	18.55

Coal: PSOC No. 456

Time	0	2.5	5	7.5	10
% unreacted coal	100	59.5	45.5	38.5	34.4
% preasphaltenes	0	17.75	24.3	26.9	28.05
% asphaltenes	0	12.5	17.15	19.0	19.85
% oils	0	8.9	12.9	15.9	17.75

Coal: PSOC No. 437

Time	0	2.5	5	7.5	10
% unreacted coal	100	62.75	49.1	40.75	35.2
% preasphaltenes	0	13.9	20.05	22.5	23.7
% asphaltenes	0	13.9	20.05	22.4	23.55
% oils	0	6.0	10.75	14.5	17.5

Coal: PSOC No. 071

Time	0	2.5	5	7.5	10
% unreacted coal	100	67.0	56.4	49.6	44.7
% preasphaltenes	0	5.0	8.05	10.5	11.85
% asphaltenes	0	8.0	13.45	15.75	16.4
% oils	0	16.0	22.05	25.0	26.8

Coal: PSOC No. 056

Time	0	2.5	5	7.5	10
% unreacted coal	100	67.5	52.5	45.0	40.55
% preasphaltenes	0	11.75	17.45	19.75	20.5
% asphaltenes	0	8.0	12.85	15.6	17.0
% oils	0	11.0	17.25	20.25	21.9

2. Shalbi's data (19).

No. 400 °C's data

Time (min.)	0	2.5	5	7.5	10
% unreacted coal	100	71.0	54.0	43.1	35.7
% preasphaltenes	0	9.7	19.35	28.85	37.9
% asphaltenes	0	9.0	15.5	19.6	22.3
% oils	0	12.5	24.3	35.0	41.0

No. 350 °C's data

Time (min)	0	2.5	5	7.5	10
% unreacted coal	100	88.7	80.4	73.8	68.4
% preasphaltenes	0	5.0	8.5	12.0	15.1
% asphaltenes	0	4.15	7.5	10.0	12.1
% oils	0	1.25	2.12	2.75	3.30

No. 375 °C's data

Time (min)	0	2.5	5	7.5	10
% unreacted coal	100	81.7	69.0	59.0	50.4
% preasphaltenes	0	9.25	17.25	23.5	28.7
% asphaltenes	0	5.75	9.8	12.9	15.1
% oils	0	2.5	4.25	5.25	5.8

APPENDIX B

Use of Exisiting and User-Written "Driver" Routines for NLPE Program

The NLPE program used in this study (30) included a general kinetic constant evaluation "driver" program. This particular routine allowed the calculation of the kinetic parameters (rate constants) by least-squares methods for appropriate data sets. This "driver" program was used exclusively in this study as it was very nearly as easy to write the driver routine (Deck 19) for each model.

Each model required to be coded in the exisitng subroutine in addition to the data. The required data file is outlined in the following pages. Subsequent to that is an example of the data deck,required to run a user-written subroutine. The example is for the six-parameter model (Model 3) described on page 36. The PSOC 370 is the particular data base used.

Title Card: (Up to 80 characters of information on the model)

Problem Definition (3I): Number of unknowns, LOUT (1 for iteration output, 2 for final output only), model identification number.

Parameter Initial Guesses (8F): An initial guess for each unknown parameter to be evaluated

Problem Size (4I): No. of observed variables (generally 4 in these studies, one for each fraction), number of experiments (number of runs times number of times at which samples were taken), total number of variables (usually 4), ICOV (defines degree of knowledge of covariant matrix. 3 for this study, ie., matrix unknown)

Data (8F): One line of data for each time for each run, each line contains, in order, the fractional quantities of "unreacted coal", "preasphaltenes", "asphaltenes", and "oils" at the given time and run. The first time for each run is given, then the second time for each run, and so forth.

System Definition (4I): Number of state variables (4), number of distinct sets of initial conditions (1), number of state variables plus run variables (4), number of unknown parameters which relate observed to state variables (0)

Run Length (1I): Number of runs times number of times per run.

Initial Conditions (4F): Initial fractional concentrations for each of the four fractions (1.,0.,0.,0.)

Times (8F): The times at which each sample was taken. For two runs at sample times of 5, 10, 30, and 60 minutes this card (line) would be: 5.,5.,10.,10., 30.,30.,60.,60.

State Variable Boundaries (8F): Upper bounds on absolute values of the state variagles (1. for the fractional concentrations)

Lower Boundary Data (8F): Allowable lower boundaries for each of the unknown parameters

Upper Boundary Data (8F): Allowable upper boundaries for each of the unknown parameters.

The "SUBROUTINE", "COMMON", "GOTO", "RETURN", and "END" statements of Deck 19 remain unchanged for each model

The nomenclature which were used is:

P(i) = first derivative of the fraction of component "i" with respect to time (minutes).

Q(i) = fraction of component "i"

Ci(n) = unknown rate constant "n".

Three series of equations must be written for each reaction network:

P(i): = One equation for each reactant, "i", describing the derivative of Q(i) wrt time (minutes).

FX(i,j) = one equation for the derivatives of each P(i) wrt each component, Q(j).

FTH(i,n) - one equation for the derivative of each P(i) wrt each unknown rate constant, Ci(n).

The constant values of FX or FTH (eg. 0) at all times for all values of Q and Ci should be listing from line "2" through the "RETURN" statement just before line "1". The "P" equations for the four components (C, P, A, and O) are given as line "1" through the GOTO statement "GOTO (3,4), IT". The non-constant expressions for FX and FTH are contained from line "4" up to the "3 RETURN" statment.

```
  MODEL 3,WITH 6 PARAMETERS,COAL:PSOC 370
6,2,18
.001,.001,.001,.001,.001,.001
4,8,4,3
.737,.154,.106,.003
.698,.131,.144,.027
.569,.219,.168,.043
.566,.212,.195,.027
.338,.283,.254,.125
.355,.264,.273,.108
.234,.257,.312,.196
.263,.259,.324,.154
4,1,4,0
8
1.,0.,0.,0.
5.0,5.0,10.0,10.0,30.0,30.0,60.0,60.0
1.,1.,1.,1.
0.,0.,0.,0.,0.,0.
100.,100.,100.,100.,100.,100.
```

```
C----   DECK 19-MODEFIED
C---    MODEL 8
C---    ALL COAL REACTIONS ARE 2-ORDER
C
C
         SUBROUTINE FUN(II,JJ,IB,T)
         COMMON C(20,20),G1(20,20),PSCA,G(20,20),F(20),
         1Y(20),EGV(20),FF(20),TITLE(20),CUB(20),CLB(20)
         2,PNL(20),NCON,LOUT,F3,NTH,F6,F7,METH,NPH,MD,LS,
         3C1(20),KIN,KOUT
         COMMON/BONE/V(5,5),QY(5),YTH(5,20),A(100,10),ICOV,
         4DET,IDER,M,NY,NA
         COMMON/C/NX,NB,NTH2,NTH1,Q(10),P(10),FX(10,10),FTH
         5(10,10),BV(20,10),TIME(100),IA(100),FN(10),XTH(10,
         620),XTTH(10,20)
         GO TO (1,1,2),II
2        FX(1,3)=0.
         FX(1,4)=0.
         FX(2,3)=0.
         FX(2,4)=0.
         FX(3,2)=0.
         FX(3,4)=0.
         FX(4,2)=0.
         FX(4,4)=0.
         FTH(1,3)=0.
         FTH(2,2)=0.
         FTH(2,3)=0.
         FTH(2,4)=0.
         FTH(3,1)=0.
         FTH(3,4)=0.
         FTH(3,5)=0.
         FTH(4,1)=0.
         FTH(4,2)=0.
         FTH(4,5)=0.
         RETURN
1        P(1)=-(C1(1)+C1(2)+C1(4))*(Q(1)**2)+C1(5)*Q(2)
         P(2)=C1(1)*(Q(1)**2)-Q(2)*C1(5)
         P(3)=C1(2)*(Q(1)**2)-C1(3)*Q(3)
         P(4)=C1(3)*Q(3)+C1(4)*(Q(1)**2)
         GO TO (3,4),II
4        FX(1,1)=-2.0*(C1(1)+C1(2)+C1(4))*Q(1)
         FX(1,2)=C1(5)
         FX(2,1)=2.0*C1(1)*Q(1)
         FX(2,2)=-C1(5)
         FX(3,1)=2.0*C1(2)*Q(1)
         FX(3,3)=-C1(3)
         FX(4,1)=2.0*C1(4)*Q(1)
         FX(4,3)=C1(3)
         FTH(1,1)=-Q(1)**2
         FTH(1,2)=-Q(1)**2
         FTH(1,4)=-Q(1)**2
         FTH(1,5)=Q(2)
         FTH(2,1)=Q(1)**2
         FTH(2,5)=-Q(2)
         FTH(3,2)=Q(1)**2
         FTH(3,3)=-Q(3)
         FTH(4,3)=Q(3)
         FTH(4,4)=Q(1)**2
3        RETURN
         END
```

APPENDIX C

Use of Runge-Kutta Routine

The computer-generated concentration-time profiles used in this study were generated by the Runge-Kutta routine given in this Appendix. Once the rate constants for the given model had been generated by the NLPE program, they were input to the Rung-Kutta program to generate concentration-time profiles to be plotted afterwards.

The only changes which are necessary in this program when changing reaction networks are the descriptive equations F(1) through F(4) given in subroutine "FUNC". These four equations are analogous to P(1) through P(4) equation used in the user-written driver deck for the NLPE program which was described in the previous Appendix and are the equations for the first time derivatives of each of the weight fractions of the components (coal, preasphaltenes, asphaltenes, and oils plus gases, in that order). In this program, Y(i) represented the designation of the components, and the rate constants as C(n).

The program used a time range of 0 to 60 minutes, number iterations (usually 600), iterations between printouts, and number of variables (4). Variable initial values are also requested (1.,0.,0.,0.).

```
.TY 111.FOR
[14:11:58]
        SUBROUTINE RUNG(X,EK,F,Y,YCAL,N,H,II)
        DIMENSION Y(50),EK(50,3),F(50),YCAL(50),C(10)
        DO 1 I=1,N
1       YCAL(I)=Y(I)
        XCAL=X
        IF(II.NE.1) GO TO 6
        WRITE(4,50)
        WRITE(15,51)X,(Y(I),I=1,N)
6       CONTINUE
        CALL FUNC(YCAL,XCAL,F,II)
        DO 2 I=1,N
        EK(I,1)=F(I)
        YCAL(I)=Y(I)+H*F(I)/2.
        XCAL=X+H/2.
        CALL FUNC(YCAL,XCAL,F,2)
        DO 3 I=1,N
        EK(I,2)=F(I)
3       YCAL(I)=Y(I)+H*F(I)/2.
        XCAL=X+H/2.
        CALL FUNC(YCAL,XCAL,F,2)
        DO 4 I=1,N
        EK(I,3)=F(I)
4       YCAL(I)=Y(I)+H*F(I)
        XCAL=X+H
        CALL FUNC(YCAL,XCAL,F,2)
        DO 5 I=1,N
5       Y(I)=Y(I)+H/6.*(EK(I,1)+2.*EK(I,2)+2.*EK(I,3)+F(I))
50      FORMAT(' SOLUTION, X, Y1, Y2, ...YN'/)
51      FORMAT(5E14.8)
        RETURN
        END

        SUBROUTINE FUNC(Y,X,F,II)
        DIMENSION Y(50),F(50),C(10)
        IF(II.NE.1) GO TO 10
        WRITE(4,30)
30      FORMAT(1X,'WHAT ARE THE RATE CONSTANTS '/)
        READ(4,31) (C(I),I=1,5)
31      FORMAT(5F)
10      CONTINUE
C       INPUT FUNCTIONS BELOW:
        F(1)=-(C(1)+C(2)+C(4))*Y(1)**2+C(5)*Y(2)
        F(2)=C(1)*Y(1)**2-Y(2)*C(5)
        F(3)=C(2)*Y(1)**2-C(3)*Y(3)
        F(4)=C(4)*Y(1)**2+C(3)*Y(3)
        RETURN
        END

C       RUNGE KUTTA MAIN PROGRAM
        DIMENSION Y(50),EK(50,3),F(50),YCAL(50),C(10)
1       WRITE(4,50)
50      FORMAT(' INPUT XMIN,XMAX, NUMBER OF ITERATIONS, ITERATIONS
        1BETWEEN EACH PRINTOUT, NUMBER OF VARIABLES =  /)
        READ(4,51)XMIN,XMAX,NITS,NPT,N
51      FORMAT(2F,3I)
        IF(N.EQ.0) GO TO 3
        ENITS =NITS
        H=(XMAX-XMIN)/ENITS
        WRITE(4,52)
52      FORMAT(' INPUT N INITIAL VALUES, 6 PER LINE ='/)
        READ(4,53)(Y(I),I=1,N)
53      FORMAT(6F)
        X=XMIN
        DO 2 I=1,NITS
        CALL RUNG(X,EK,F,Y,YCAL,N,H,I)
        X=X+H
        IF(I/NPT*NPT.EQ.I)WRITE(15,54)
        1X,(Y(J),J=1,N)
54      FORMAT(5E14.8)
2       CONTINUE
        GO TO 1
3       CONTINUE
        END
```

APPENDIX D

Sample calculation: Using differentiating Lagrangian interpolation formulas to estimate initial rates of reaction.

Coal: PSOC 107

1. Unreacted coal:

x (time) minutes	0	5	10	15	200
f (x) mass fractions	1.0	.691	.558	.460	.390
h=5	f_0	f_1	f_2	f_3	f_4

$$f^1(0) = \frac{1}{12x5}[-25x1+48x.691-36x.558+16x.460-3x.390]$$

$$= -.0955$$

$$f^1(5) = \frac{1}{12x5}[-3x1-10x.691+18x.558-6x.460+.390]$$

$$= -.03727$$

$$f^1(10) = \frac{1}{12x5}[1-8x.691+8x.460-.390]$$

$$= -.02063$$

$$f^1(15) = \frac{1}{12x5}[-1+6x.691-18x.558+10x.460+3x.390]$$

$$= -.0188$$

$$f^1(20 = \frac{1}{12x5}[3x1-16x.691+36x.558-48x.460+25x.390]$$

$$= -4.967x10^{-3}$$

2. Asphaltenes

x	0	5	10	15	20
f(x)	0	.109	.1535	.180	.205

$$f^1(0) = \frac{1}{12x5}\ [-25.0+48x.109-36x.1535+16x.180-3x.205]$$

$$= .03285$$

$$f^1(15) = \frac{1}{12x5}\ [-3x0-10x.109+18x.1535-6x.180+.205]$$

$$= .0133$$

$$f^1(10) = \frac{1}{12x5}\ [0-8x.109+8x.180-.205]$$

$$= 6.05x10^{-3}$$

$$f^1(15) = \frac{1}{12x5}\ [-0+6x.109-18x.1535+10x.180+3x.205]$$

$$= 5.1x10^{-3}$$

$$f^1(20) = \frac{1}{12x5}\ [3x0-16x.109+36x.1535-48x.180+25x.205]$$

$$= 4.45x10^{-3}$$

3. Preasphaltenes

x	0	5	10	15	20
f(x)	0	.0935	.151	.190	.220

$$f^1(0) = \frac{1}{12x5}[-25x0+48x.0935-36x.151+16x.190-3x.22o]$$

$$= .0239$$

$$f^1(5) = \frac{1}{12x5}[-3x0-10x.0935+18x.151-6x.190+.220]$$

$$= .0144$$

$$f^1(10) = \frac{1}{12x5}[0-8x.0935+8x.190-.220]$$

$$= 9.2x10^{-3}$$

$$f^1(15) = \frac{1}{12x5}[-0+6x.0935-18x.151+10x.190+3x.220]$$

$$= 6.717x10^{-3}$$

$$f^1(20) = \frac{1}{12x5}[3x0-16x.0935+36x.151-48x.190+25x.220]$$

$$= 5.33x10^{-3}$$

4. Oils plus gas

x	0	5	10	15	20
f(x)	0	.104	.1375	.159	.175

$$f^1(0) = \frac{1}{12x5}[-25.0+48x.104-36x.1375+16x.159-3x.175]$$

$$= .03425$$

$$f^1(5) = \frac{1}{12x5}[-3x0-10x.104+18x.1375-6x.159+.175]$$

$$= .0109$$

$$f^1(10) = \frac{1}{12x5}[0-8x.104+8x.159-.175]$$

$$= 4.417x10^{-3}$$

$$f^1(15) = \frac{1}{12x5}[-0+6x.104-18x.1375+10x.159+3x.175]$$

$$= 4.400x10^{-3}$$

$$f^1(20) = \frac{1}{12x5}[3x0-16x.104+36x.1375-48x.159+25x.175]$$

$$= 4.830x10^{-4}$$

APPENDIX E

MINITAB Data File and Printout

```
.TY FM903.FOR
[15:02:13]
-.1512,-1,-1,0,-1,0,0
.0402,0,1,0,0,0,0
.039,1,0,0,0,0,0
.0054,0,0,0,1,0,0
-.087,-.710,-.710,0,-.710,0,0
.0312,0,.710,-.090,0,0,.097
.0387,.710,0,0,0,-.097,-.097
.00478,0,0,.090,.710,.097,0
-.053,-.540,-.540,0,-.540,0,0
.0208,0,.540,-.155,0,0,.1935
.0384,.540,0,0,0,-.1935,-.1935
.00463,0,0,.155,.540,.1935,0
-.036,-.431,-.431,0,-.431,0,0
.0126,0,.431,-.196,0,0,.2885
.0374,.431,0,0,0,-.2885,-.2885
.00369,0,0,.196,.431,.2885,0
-.0228,-.357,-.357,0,-.357,0,0
.0102,0,.357,-.223,0,0,.379
.0347,.357,0,0,0,-.379,-.379
.00062,0,0,.223,.357,.379,0


.TY FM904.FOR
[15:02:49]
-.1512,-1,-1,0,-1,0,0,0
.0402,0,1,0,0,0,0,0
.039,1,0,0,0,0,0,0
.0054,0,0,0,1,0,0,0
 .087,-.710,-.710,0,-.710,0,0,.097
.0312,0,.710,0,0,-.090,.097,0
.0387,.710,0,-.097,0,0,-.097,-.097
.00478,0,0,.097,.710,.090,0,0
-.053,-.540,-.540,0,-.540,0,0,.1935
.0208,0,.540,0,0,-.155,.1935,0
.0384,.540,0,-.1935,0,0,-.1935,-.1935
.00463,0,0,.1935,.540,.155,0,0
-.036,-.431,-.431,0,-.431,0,0,.2885
.0126,0,.431,0,0,-.196,.2885,0
.0374,.431,0,-.2885,0,0,-.2885,-.2885
.00369,0,0,.2885,.431,.196,0,0
-.0228,-.357,-.357,0,-.357,0,0,.379
.0102,0,.357,0,0,-.223,.379,0
.0347,.357,0,-.379,0,0,-.379,-.379
.00066,0,0,.379,.357,.223,0,0


.
.
.TY CEOB.DAT
[15:03:26]
-.2364,-1,-1,0,-1,0
.0777,0,1,0,0,0
.0781,1,0,0,0,0
.02683,0,0,0,1,0
-.0843,-.3938,-.3938,0,-.3938,.139
.0370,0,.3938,-.139,0,0
.03687,.3938,0,0,0,-.139
.0213,0,0,.139,.3938,0
-.03707,-.2411,-.2411,0,-.2411,.2005
.0148,0,.2411,-.2005,0,0
.01503,.2411,0,0,0,-.2005
.01683,0,0,.2005,.2411,0
-.0314,-.1661,-.1661,0,-.1661,.225
.005716,0,.1661,-.224,0,0
.0062,.1661,0,0,0,-.225
.01333,0,0,.224,.1661,0
 .00413,-.1239,-.1239,0,-.1239,.237
.004316,0,.1239,-.2355,0,0
.00397,.1239,0,0,0,-.237
.01083,0,0,.2355,.1239,0
```

```
MINITAB RELEASE 81.1 *** COPYRIGHT - PENN STATE UNIV. 1981
MAY 25, 1982 *** Colorado School of Mines * DECsystem-1091
STORAGE AVAILABLE  19800

-- READ 'CE08.DAT'C1,C2,C3,C4,C5,C6

COLUMN        C1           C2           C3           C4           C5           C6
COUNT         20           20           20           20           20           20
ROW
  1    -0.236400     -1.00000     -1.00000     0.000000     -1.00000     0.000000
  2     0.077700      0.00000      1.00000     0.000000      0.00000     0.000000
  3     0.078100      1.00000      0.00000     0.000000      0.00000     0.000000
  4     0.026830      0.00000      0.00000     0.000000      1.00000     0.000000
  .   .   .

-- NOCONSTANT

-- NOBRIEF

-- REGRESS Y IN C1 ON 5 PRED. IN C2,C3,C4,C5,C6

THE REGRESSION EQUATION IS
Y = + .0936 X1 + .0909 X2 + .0310 X3
    + .0391 X4 + .0487 X5

                                         ST. DEV.     T-RATIO =
       COLUMN      COEFFICIENT           OF COEF.     COEF/S.D.
NOCONSTANT
X1     C2             0.093642          0.006872        13.63
X2     C3             0.090879          0.006873        13.22
X3     C4              0.03098           0.01585         1.95
X4     C5             0.039142          0.006873         5.70
X5     C6              0.04875           0.01579         3.09

THE ST. DEV. OF Y ABOUT REGRESSION LINE IS
S = 0.008453
WITH (  20- 5) =  15 DEGREES OF FREEDOM

ANALYSIS OF VARIANCE

 DUE TO      DF            SS      MS=SS/DF
REGRESSION    5    0.08146432    0.01629286
RESIDUAL     15    0.00107193    0.00007146
TOTAL        20    0.08253616

FURTHER ANALYSIS OF VARIANCE
SS EXPLAINED BY EACH VARIABLE WHEN ENTERED IN THE ORDER GIVEN

 DUE TO      DF            SS
REGRESSION    5    0.08146432
C2            1    0.05805213
C3            1    0.01927457
C4            1    0.00109850
C5            1    0.00231777
C6            1    0.00068135

             X1            Y     PRED. Y     ST.DEV.
ROW          C2           C1       VALUE     PRED. Y    RESIDUAL      ST.RES.
  1       -1.00     -0.23640    -0.22366     0.00687    -0.01274      -2.59RX
  2        0.00      0.07770     0.09088     0.00687    -0.01318      -2.68RX
  3        1.00      0.07810     0.09364     0.00687    -0.01554      -3.16RX
  4        0.00      0.02683     0.03914     0.00687    -0.01231      -2.50RX
  5       -0.39     -0.08430    -0.08130     0.00291    -0.00300      -0.38
  6        0.00      0.03700     0.03148     0.00291     0.00552       0.70
  7        0.39      0.03687     0.03010     0.00291     0.00677       0.85
  8        0.00      0.02130     0.01972     0.00291     0.00158       0.20
  9       -0.24     -0.03707    -0.04415     0.00308     0.00708       0.90
 10        0.00      0.01480     0.01570     0.00309    -0.00090      -0.11
 11        0.24      0.01503     0.01280     0.00308     0.00223       0.28
 12        0.00      0.01693     0.01565     0.00309     0.00118       0.15
 13       -0.17     -0.03140    -0.02618     0.00338    -0.00522      -0.67
 14        0.00      0.00572     0.00816     0.00337    -0.00244      -0.31
 15        0.17      0.00620     0.00459     0.00339     0.00161       0.21
 16        0.00      0.01233     0.01344     0.00337    -0.00111      -0.01
 17       -0.12     -0.00413    -0.01615     0.00257     0.01203       1.57
 18        0.00      0.00432     0.00397     0.00356     0.00035       0.05
 19        0.12      0.00397     0.00005     0.00257     0.00392       0.51
 20        0.00      0.01083     0.01214     0.00356    -0.00131      -0.17

R DENOTES AN OBS. WITH A LARGE ST. RES.
X DENOTES AN OBS. WHOSE X VALUE GIVES IT LARGE INFLUENCE.

DURBIN-WATSON STATISTIC = 0.65

(X-PRIME X) INVERSE

               1            2            3            4            5
   1     0.66080
   2    -0.19902      0.66101
   3     0.00000      0.47404      3.51381
   4    -0.19902     -0.23297     -0.47404      0.66101
   5     0.47150     -0.00000     -0.00000      0.00000      3.48776

   STOP
```

APPENDIX F

Statistics for Arrhenius Plots with 95% Confidence Limits.

This Appendix gives the formulas used to estimate the interval limits of the rate constants at three different temperatures. The x-axis represents $(\frac{1}{T})$, and the y-axis represents the rate constants.

The 95% confidence limits of the regression line were:

$$\hat{y}_o \pm (t_{95\%}, n-2) \quad S\sqrt{\frac{1}{n} + \frac{(x_o-\bar{x})^2}{S_{xx}}}$$

where:

$\hat{y}_o$ is a point on the line $y = a+bx$, at x_o

$$S = \left(\frac{S_{yy}-bS_{xy}}{n-2}\right)^{1/2}$$

$$S_{xx} = \sum_{i=1}^{n} x_i^2 - \frac{(\sum_{i=1}^{n} x_i)^2}{n}$$

$$S_{yy} = \sum_{i=1}^{n} y_i^2 - \frac{(\sum_{i=1}^{n} y_i)^2}{n}$$

$$S_{xy} = \sum_{i=1}^{n} x_i y_i - \frac{(\sum_{i=1}^{n} x_i)(\sum_{i=1}^{n} y_i)}{n}$$

b is the slope of the line y=a+bx

$\overline{x}$ is the mean value

n is the number of data points.

n-2 = degrees of freedom