

Inverse Methods and Kinetic Models of Hydrocarbon Generation: III. Case Histories for Autoclave Product Analysis¹

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From a determination of the transformation matrix for three pyrolysis product experimental data sets, an examination is given of both the applicability of the laboratory experimental data to the modeling of oil cracking in a sedimentary basin, and of the appropriateness of an inverse model. The results of the laboratory experimental data sets, which were done under different thermodynamic conditions and using different sources, show that the transformation matrix varies over each data set and also with time. Therefore, it is necessary to check the data sets before applying them to a basin for hydrocarbon modeling. The laboratory experimental data taken at lower temperature and over longer times appear more pertinent for the construction of an oil-cracking kinetic model suitable for geologic conditions.

KEY WORDS: hydrocarbons, kinetics, inverse methods.

INTRODUCTION

In previous papers of this series, we have discussed mathematical inverse procedures for both hydrocarbon generation directly from kerogen degradation based on residual kerogen analysis, and the subsequent changes in composition of the hydrocarbons based on autoclave pyrolysis product analysis experimental results (Lerche, 1989); and have presented case histories and numerical implementation of the inversion model for residual kerogen analysis (Liu and Lerche, 1989).

As well as considering the kinetic model of residual kerogen analysis, a knowledge of hydrocarbon-cracking kinetics is necessary for oil exploration and for application of thermal methods of enhanced oil recovery. There have been investigations of this problem (Tissot and Espitalie, 1975; Sweeney et al., 1986; Ungerer et al., 1988), but difficulties still exist because: (a) individual products

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(e.g., CH_4 , CO_2 , \dots) can depend not only directly on the kerogen degradation but also on the thermocatalytic degradation of products produced by the kerogen (e.g., oil cracking to gas) as well as on transformations among the products themselves; and (b) when data from laboratory chemical experiments are applied to the modeling of the oil-cracking process in a sedimentary basin, we have to determine to what extent the laboratory experimental results pertain to geological conditions—and under what conditions the experimental data can be correctly extrapolated to the modeling of a basin's hydrocarbon history.

In controlled autoclave product pyrolysis experiments, where the products can be measured in situ as temperature increases, we can examine proposed kinetic models for thermal evolution of hydrocarbons and ascertain if the experimental data provide enough information for determination of the correctness of either a kinetic model or of parameters within a model. In this paper, we focus on: (1) the numerical implementation of an inverse method proposed in the first paper of this series (Lerche, 1989); and (2) the application of this inverse model to autoclave pyrolysis products.

MATHEMATICAL MODEL

For a closed system, a kinetic model of primary cracking and secondary cracking of hydrocarbons is written in the vector form (Ungerer et al., 1988a):

$$\frac{dq}{dt} = Cx + Bq \quad (1)$$

where q is the vector of the amounts $q_j(t)$ of products of the fraction j generated at time t , x is the vector of the residual potential $x_j(t)$ of the j^{th} parallel reaction, solution of:

$$\frac{dx_j}{dt} = -A \exp(-E_j/RT)x_j(t) \quad (2)$$

where A , E_j are the pre-exponential factor and activation energy attached to reaction j , R is the gas constant, and T is the temperature; C is a $4 \times n$ matrix with coefficients given by $C_{ij} = a_{ji} A \exp(-E_j/RT)$, where the relative yields a_{ji} are defined in Ungerer et al. (1988a). B is a 4×4 matrix with coefficients

$$b_{ij} = \alpha_{ji} k'_j \text{ for } i = 1-4, j = 1-3, i \neq j$$

$$b_{jj} = -k'_j \text{ for } j = 1-3$$

$$b_{ij} = 0 \text{ for } i = 1-4, j = 4,$$

$k'_j = A'_j \exp(-E'_j/RT)$ are the first-order rate constants of the secondary reactions, the stoichiometric coefficients α_{ij} being defined in Ungerer et al. (1988a).

The free parameters of this model (A'_j , E'_j , α_{ij}) are optimized vs. autoclave pyrolysis data, accounting for conservation of carbon and hydrogen.

The general scheme of this kinetic model is as shown in Fig. 1. The general form of the equations is as follows.

Suppose the amount of the i^{th} product is $q_i(t)$ at time t . This amount may arise because of transformation from other products of source degradation (such as kerogen degradation or oil cracking), then

$$\left(\frac{dq_i}{dt}\right)_{\text{transformation}} = B_{ij}q_j \quad (3)$$

where the Einstein summation convention over repeated Latin indices is used. Here B_{ij} is a transformation matrix, which is *nominally* solely temperature-dependent (Ungerer et al., 1988a).

The amount of the i^{th} product produced can also be generated directly from the source or sources:

$$\left(\frac{dq_i}{dt}\right)_{\text{direct}} = C_{i\alpha}x_{\alpha}(t) \quad (4)$$

where the Einstein summation convention over repeated Greek indices is used, where $C_{i\alpha}$ is a generation matrix, and where $x_{\alpha}(t) (\equiv x(\alpha, t))$ is the source which can be the amount of kerogen of type α or the amount of oil of composition α at time t . In the experimental data we use, taken from Ungerer et al. (1988b), the source material is oil.

Thus, the total generation with time of product i is written

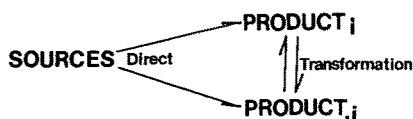
$$\frac{dq_i(t)}{dt} = B_{ij}q_j(t) + C_{i\alpha}x_{\alpha}(t) \quad (5)$$

which has the same meaning and structure as Eq. (1).

Direct inspection of Eq. (5) tells us that the matrices B_{ij} and $C_{i\alpha}$ are *not* uniquely determinable. For suppose that B_{ij} was of the form

$$B_{ij} = B(T)[\delta_{ij} - q_iq_j/q \cdot q] + \epsilon_{ijk}(q_k/|q|)C(T) \quad (6)$$

Fig. 1. General scheme of the model which shows hydrocarbon products arise in two ways: (1) direct production from sources; and (2) transformation from other products.



where $q \cdot q = q_i q_i$, $|q| = (q_i q_i)^{1/2}$, δ_{ij} is the Kronecker δ -function (unity if $i = j$, zero otherwise), and ϵ_{ijk} is the alternating Levi-Civita symbol (+1 if ijk are cyclic, -1 if ijk are anticyclic, and zero otherwise), then

$$B_{ij} q_i \equiv 0 \quad (7)$$

Hence, no components of Eq. (6) survive projection with q . (A similar argument holds for $C_{i\alpha}$ with j replaced by α , and q replaced by x .)

Hence, the only components of B_{ij} which are determinable are those which project along q_i or q_j . Likewise, the only components of $C_{i\alpha}$ which are determinable are those which project along x_α . Fortunately, these are precisely and solely the components which are needed for use in Eq. (5).

A determination of the components of B_{ij} and $C_{i\alpha}$ can be made as follows: Introduce the vector $U(T) = (q(T), x(T))$ and the matrix, D_{ij} , so that

$$B_{ij} q_j + C_{i\alpha} x_\alpha \equiv D_{ij} U_j \quad (8)$$

where D_{ij} is the bulk rate matrix which should be temperature-dependent only if the kinetic scheme proposed by Ungerer et al. (1988a,b) is to hold.

Then Eq. (5) takes on the form

$$\frac{dq_i}{dt} = D_{ij}(T) U_j(T) \quad (9)$$

A solution for Eq. (9) is provided by

$$D_{ij}(T) = dq_i/dt \ U_j(T) / |U_s^P(T) \ U_s^P(T)| \quad (10)$$

where uppercase P means U_s^P is the sum of all U_j except the U_i term when calculating D_{ij} .

Equation 10 completes the inverse solution to the kinetic problem because from a given set of pyrolysis experiments $D_{ij}(T)$ is determined. Then in any other set of experiments [with values $u_j(T)$ replacing the test set U_j ; and Q_i replacing q_i], and on the supposition that $D_{ij}(T)$ is an absolute, kinetic-process determined, fixed functional form so that the same $D_{ij}(T)$ applied to all pyrolysis product measurements, we can write:

$$\frac{dQ_i}{dt} = D_{ij}(T) u_j(T) \quad (11)$$

which provides a predictive measure for autoclave product measurements—if the kinetic description is accurate. By running many such experiments, a best set of values can be determined by averaging the results of D_{ij} determinations from many experiments and the resolution obtained.

The questions we address here are basically simple: (i) Using the inverse scheme given above, does it follow that the matrix D_{ij} is really only temperature-dependent? (ii) Even if the matrix D_{ij} is time-dependent, is it of the same

behavior for all experiments and/or does some average value serve to satisfy the data fields?

INPUT DATA

The inverse procedure has been applied to three sets of pyrolysis product analysis experimental data taken from Ungerer et al. (1988b). The data are taken to be true reflections of the kinetic process of oil cracking (Figs. 2-4). In the experiments reported by Ungerer et al. (1988b), the compositions of the hydrocarbon products are defined by the molecular weight fractions. There are five classes of hydrocarbon fractions in their experimental results (C_{13+} , C_6-C_{13} , C_2-C_5 , C_1 , coke); C_{13+} is taken as the source material in their experiments.

Among the three data sets, data sets 1 and 2 were obtained for the same temperature (450°C) and pressure (≥ 9 MPa) and heating time (7 hr) with different source materials [data set 1: Boscan (aromatic oil); data set 2: Pematang (paraffinic oil)]. Data set 3 is derived from the same source material as data set 1 (Boscan), but with a different temperature (357°C) and heating time (190 hr).

By inverting these data sets, we learn about: (1) the dependence of the experimental results on temperature and heating time; and (2) the influence of different source material on the experimental results, and the influences of these two factors on the modeling results.

MODELING RESULTS

An inverse code was constructed along the lines given in the mathematical section of this paper, and applied to the three data sets.

The kinetic matrix, D_{ij} , is supposedly only temperature-dependent so that, once D_{ij} is determined, the prediction model for oil cracking is also determined. Therefore, we first discuss the behavior of D_{ij} for each data set and then consider the possibility of using an average D_{ij} in the prediction equation.

Behavior of D_{ij}

Data sets 1 and 2 are derived from different source materials but under the same experimental thermodynamic condition (both at $P \geq 9$ MPa, $T = 450^\circ\text{C}$, and time = 7 hr), while data sets 1 and 3 are from same source material but different thermodynamic conditions. Therefore, a comparison of D_{ij} between data sets 1 and 2, as well as between data sets 1 and 3, provides measures of the sensitivity of D_{ij} both to the source material and to the thermodynamic conditions.

Figure 5a-e (data set 1), Fig. 6a-e (data set 2), and Fig. 6a-e (data set 3)

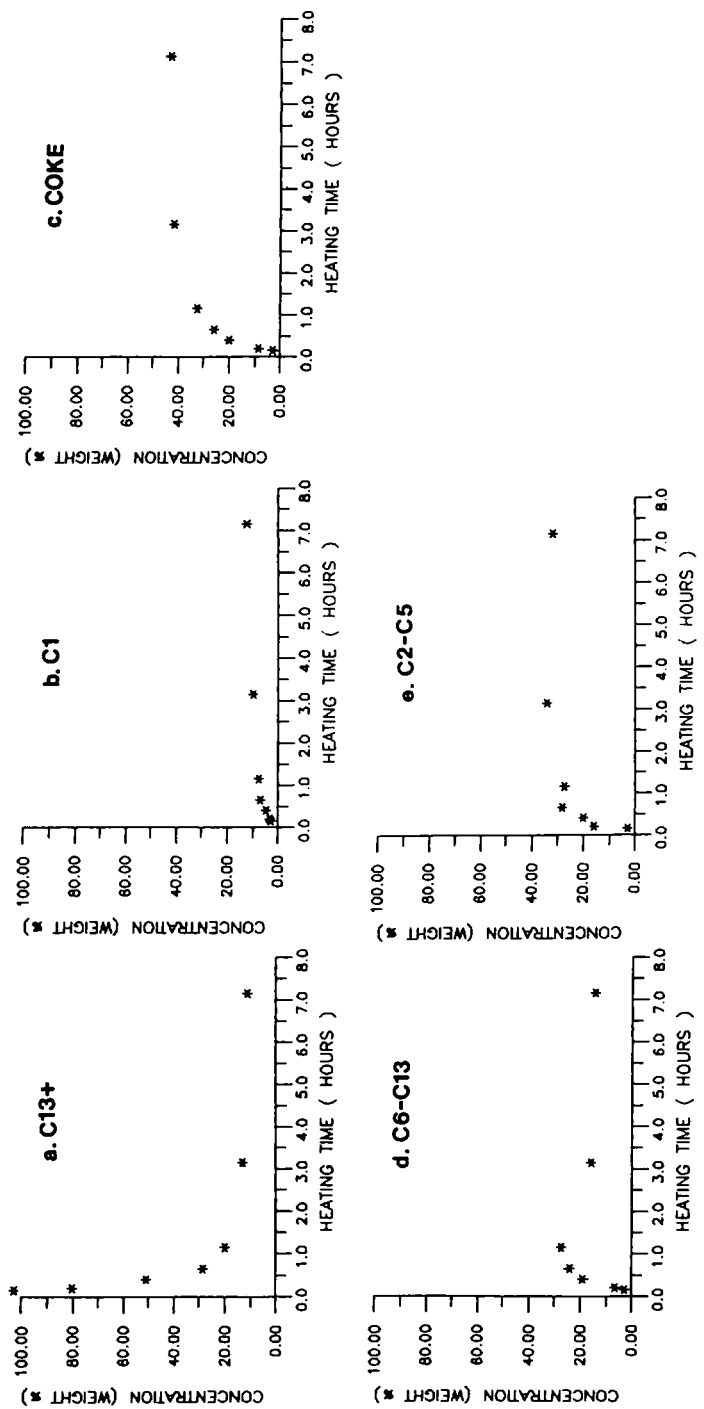


Fig. 2. Measured concentrations of the various fractions from the pyrolysis of the Boscan oil at 450°C (from Ungerer et al., 1988): (a) C13+; (b) C1; (c) coke; (d) C6-C13; (e) C2-C5.

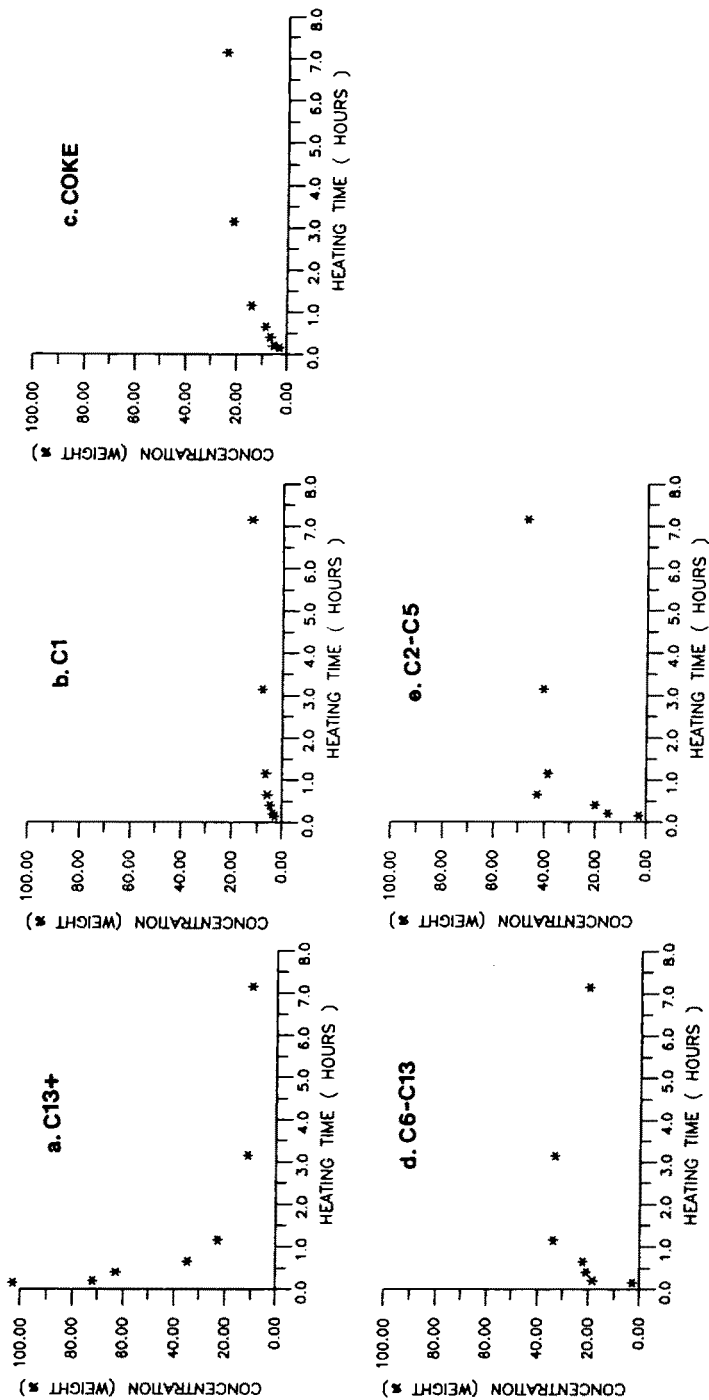


Fig. 3. Measured concentrations of the various fractions from the pyrolysis of the Pematang oil at 450°C (from Ungerer et al., 1988): (a) C13+; (b) C1; (c) coke; (d) C6-C13; (e) C2-C5.

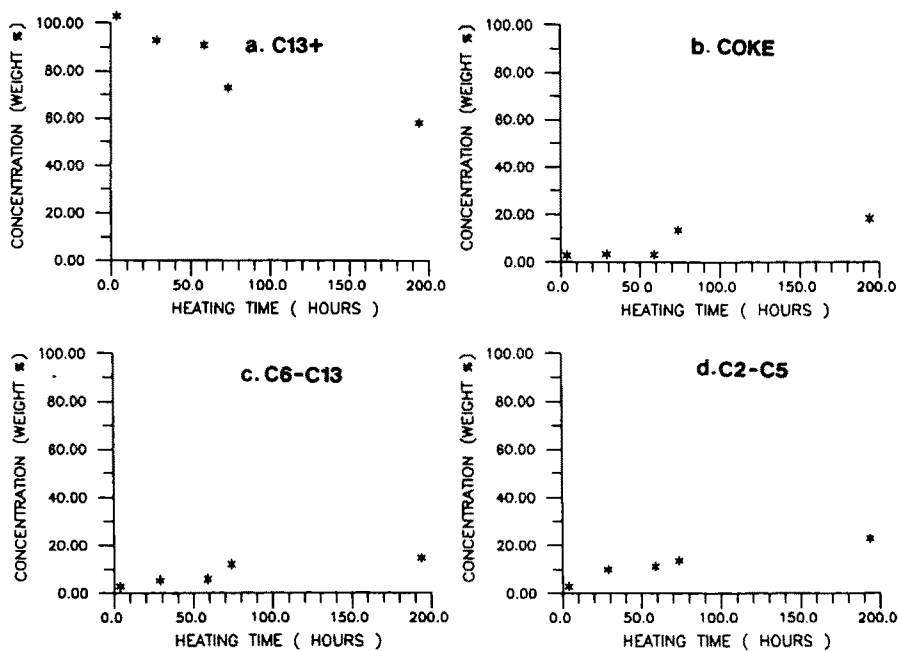


Fig. 4. Measured concentrations of the various fractions from the pyrolysis of the Boscan oil at 357°C (from Ungerer et al., 1988): (a) C13+; (b) coke; (c) C6-C13; (d) C2-C5.

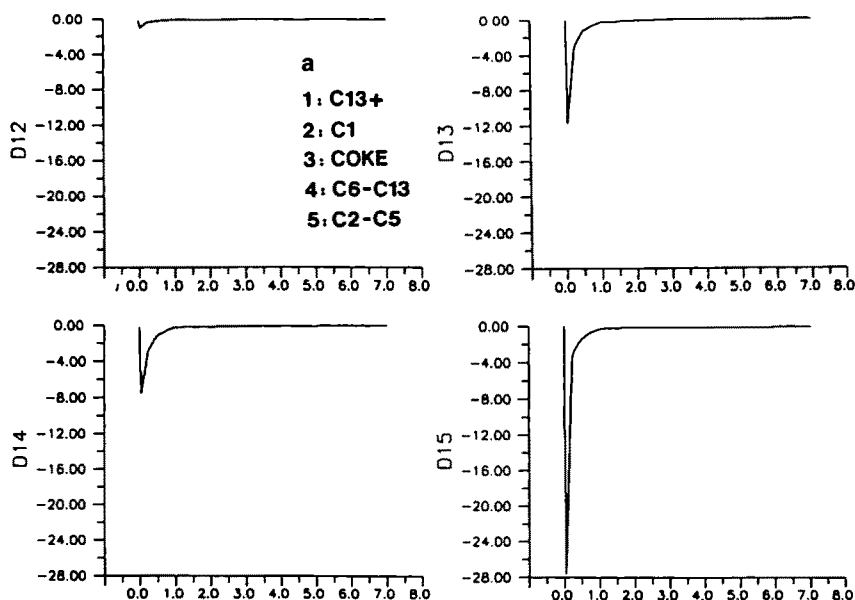


Fig. 5. The variations of the elements of the transformation matrix D_{ij} with heating time for Boscan oil at 450°C: (a) D_{1j} ; (b) D_{2j} ; (c) D_{3j} ; (d) D_{4j} ; (e) D_{5j} .

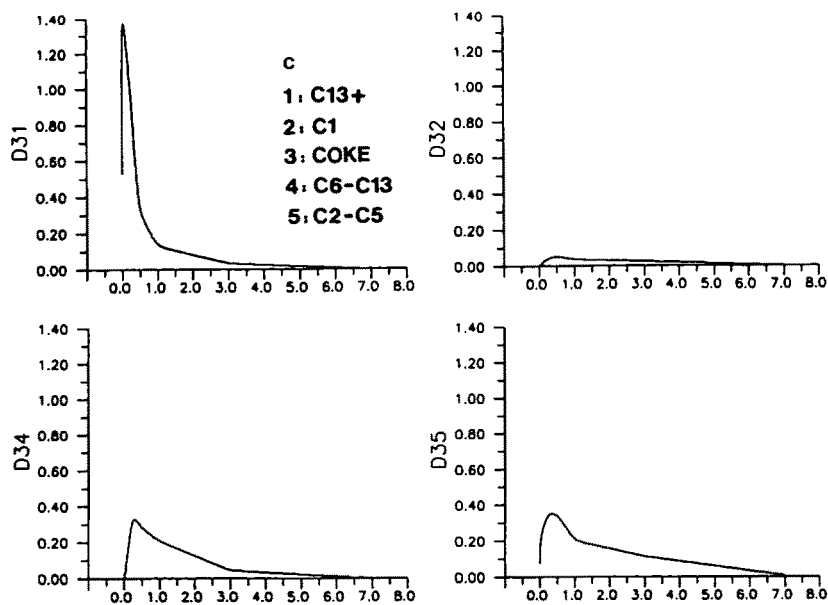
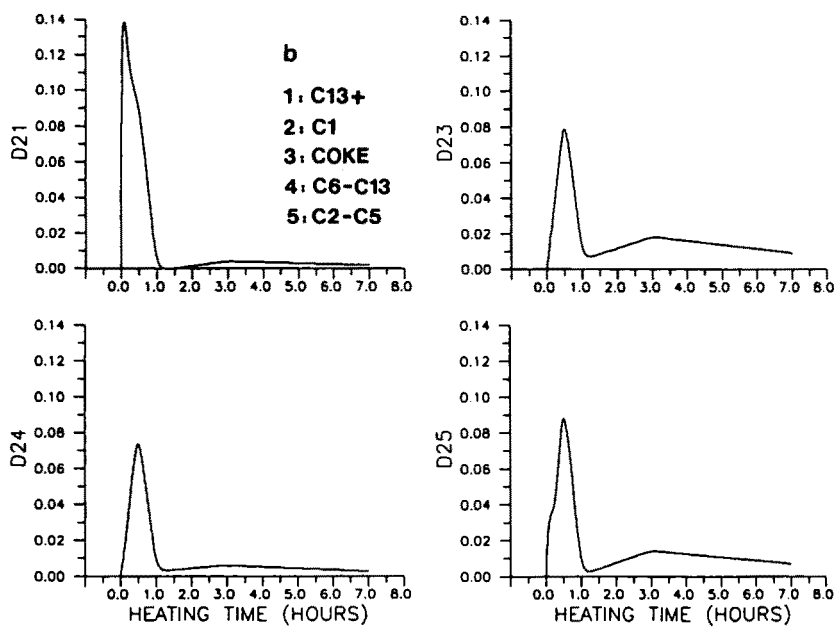


Fig. 5. Continued

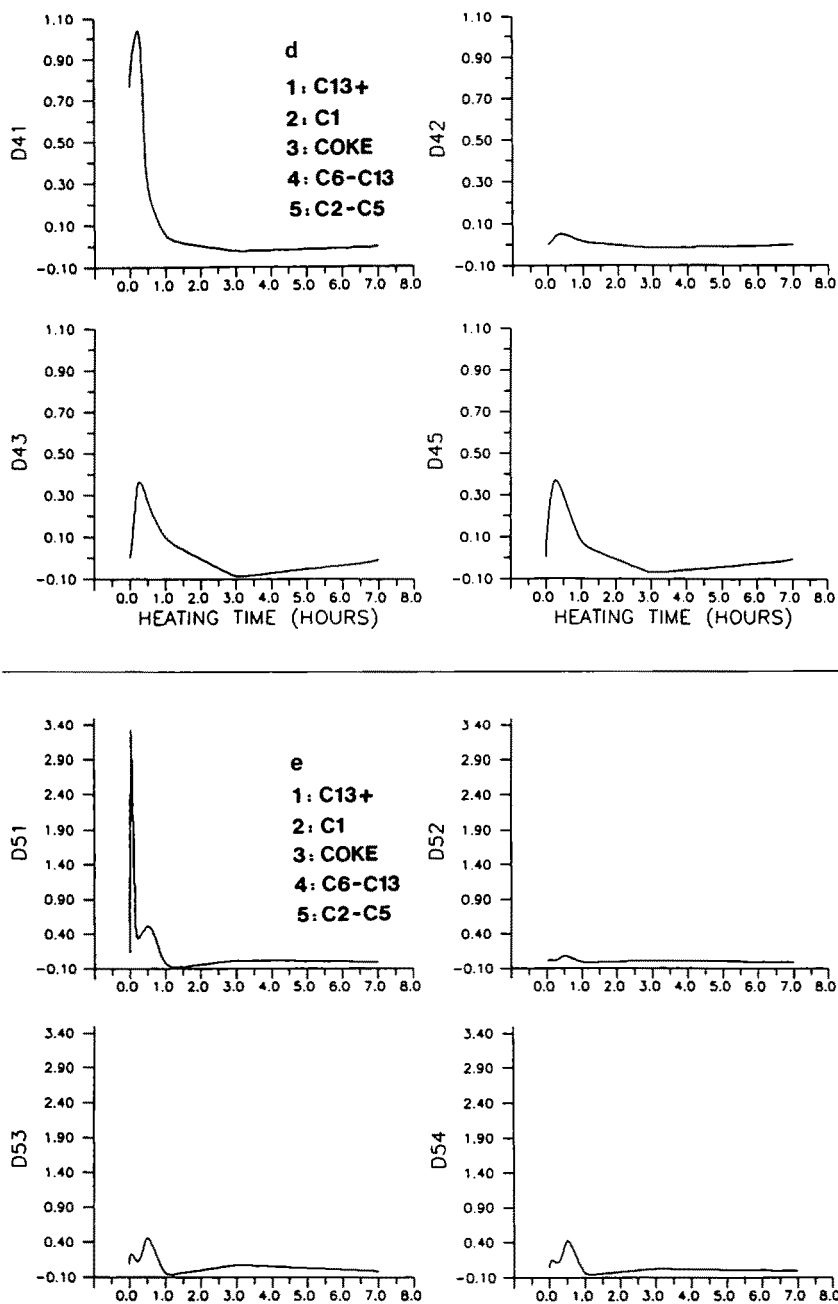


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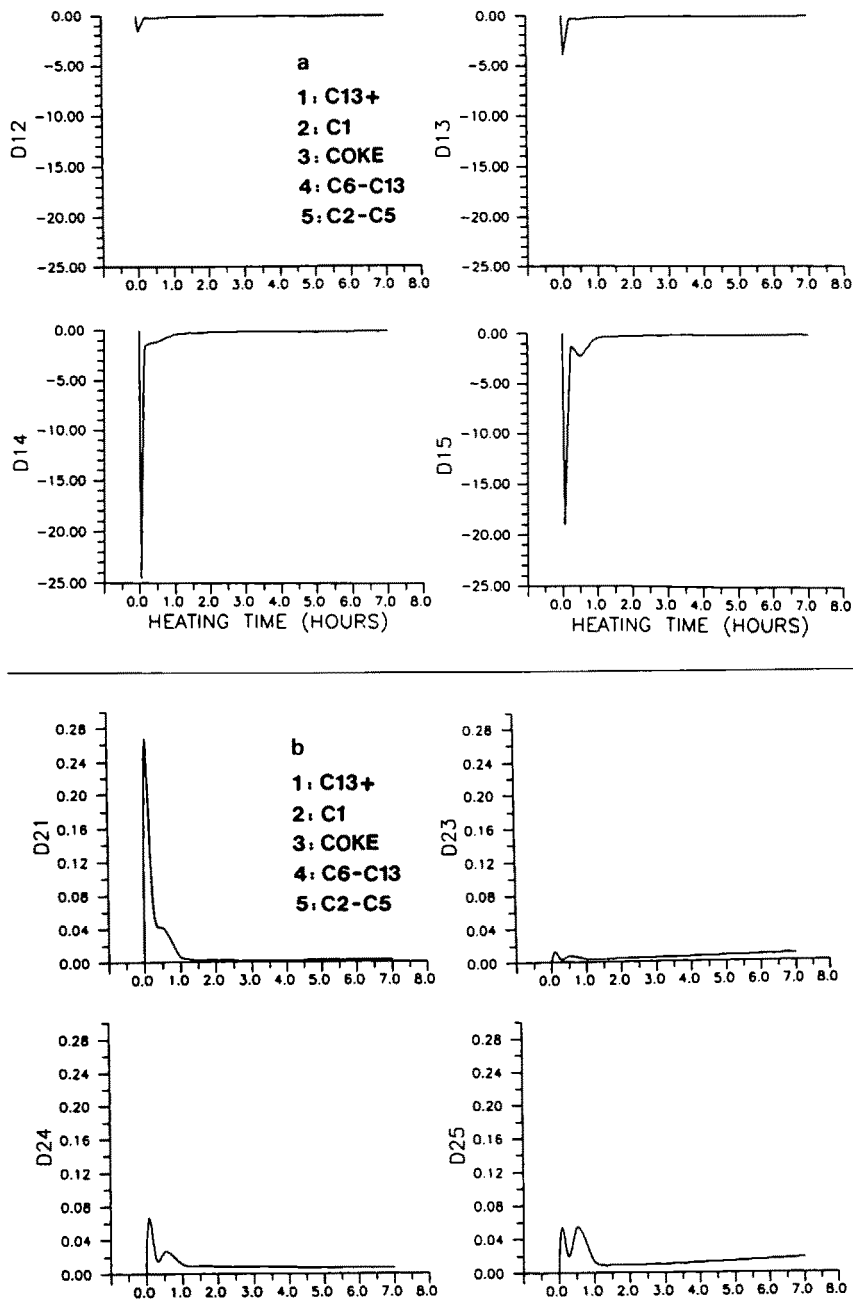


Fig. 6. The variations of the elements of the transformation matrix D_{ij} with heating time for Pematang oil at 450°C: (a) D_{1j} ; (b) D_{2j} ; (c) D_{3j} ; (d) D_{4j} ; (e) D_{5j} .

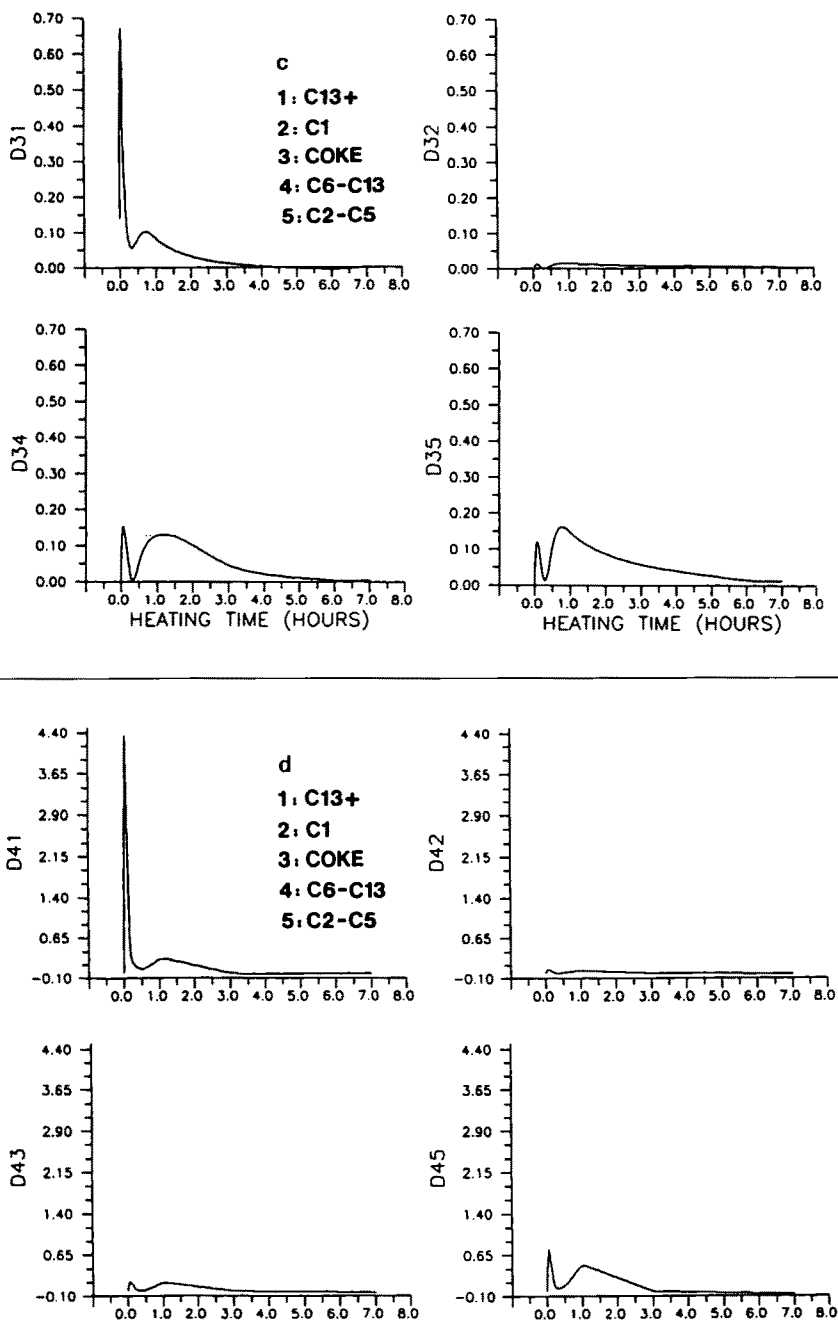


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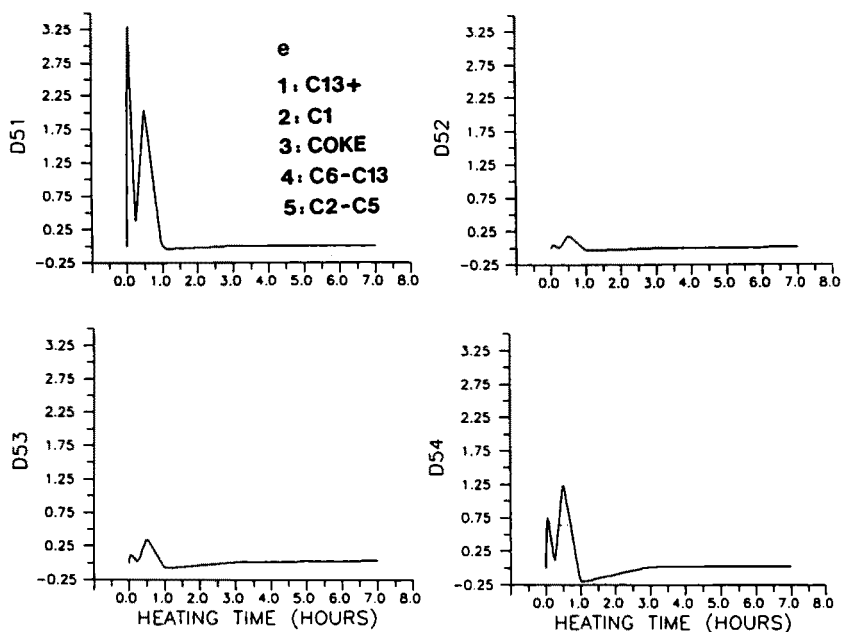


Fig. 6. Continued

show that the D_{ij} distributions vary with time for the three cases for each component of D_{ij} .

From Figs. 5 and 6, four points are apparent:

1. Despite the difference in source material, D_{ij} values determined for data sets 1 and 2 show some similar variations with increasing time. The two source materials appear to cause differences mainly in the magnitude of D_{ij} .
2. In the first hour, D_{ij} increases and decreases very sharply. After the first hour, all D_{ij} values tend toward zero. The values of most D_{ij} 's in the first hour of the reaction are apparently greater ($D_{ij} > 0$) or smaller ($D_{ij} < 0$) than the D_{ij} 's after the first hour of reaction, indicating that products are not only derived from the degradation of source material but also transformed from other products.
3. All the D_{i1} are highest (where $j = 1$ refers to the source material), indicating that products are mainly generated from the degradation of source material.
4. D_{4j} in the first hour of reaction shows an increasing trend, but a decreasing trend thereafter, indicating that the C_6-C_{13} product was gen-

erated from the degradation of C_{13+} in the first hour, and then cracking to other products caused a decrease in the amount of C_6 - C_{13} .

By comparing Figs. 5 and 7, we see that:

1. Although they have the same source material, data sets 1 and 3 show very different behaviors for D_{ij} with time. Variations of D_{ij} in data set 3 are relatively smooth, there are no sharp changes between the highest D_{ij} values and lower D_{ij} values. This behavior is in contrast to the variation of D_{ij} for data set 1.
2. Transformation between different products are relatively weak. D_{i1} tends to be higher than other D_{ij} values, so that source production dominates.

Comparison of the D_{ij} for the three data sets shows that: (1) the thermodynamic conditions (rather than source materials) have more control on oil cracking kinetics; and (2) there are also apparent differences in the magnitude of D_{ij} when the source material is different.

Model Results Using D_{ij} as a Function of Time

The above section has shown that the D_{ij} obtained from the three data sets vary with the heating time. Especially in the high-temperature and short heating time experiments (data sets 1 and 2), D_{ij} shows a strong dependence on the heating time.

Indeed Fig. 8a-e, (data set 1), Fig. 9a-e (data set 2), and Fig. 10a-e (data set 3) show the fit of predicted values and the input data sets. The figures all show that the predicted values and data sets are virtually identical, indicating that D_{ij} is indeed time-dependent. Thus, the reaction mechanisms, and therefore the kinetics in these experiments, are different with time. This result accounts for the relatively large mismatch between the predictions and input data based on other modeling with these three experimental data sets (Ungerer et al., 1988b). In turn, the applicability of the experimental reaction kinetics to geological situations needs to be rethought.

An Average Matrix

Although the D_{ij} varied with time in these three cases, it is still interesting to know whether an average D_{ij} , \bar{D}_{ij} , will provide rough predictions for the products. We obtained a least-squares estimate of \bar{D}_{ij} by averaging over time,

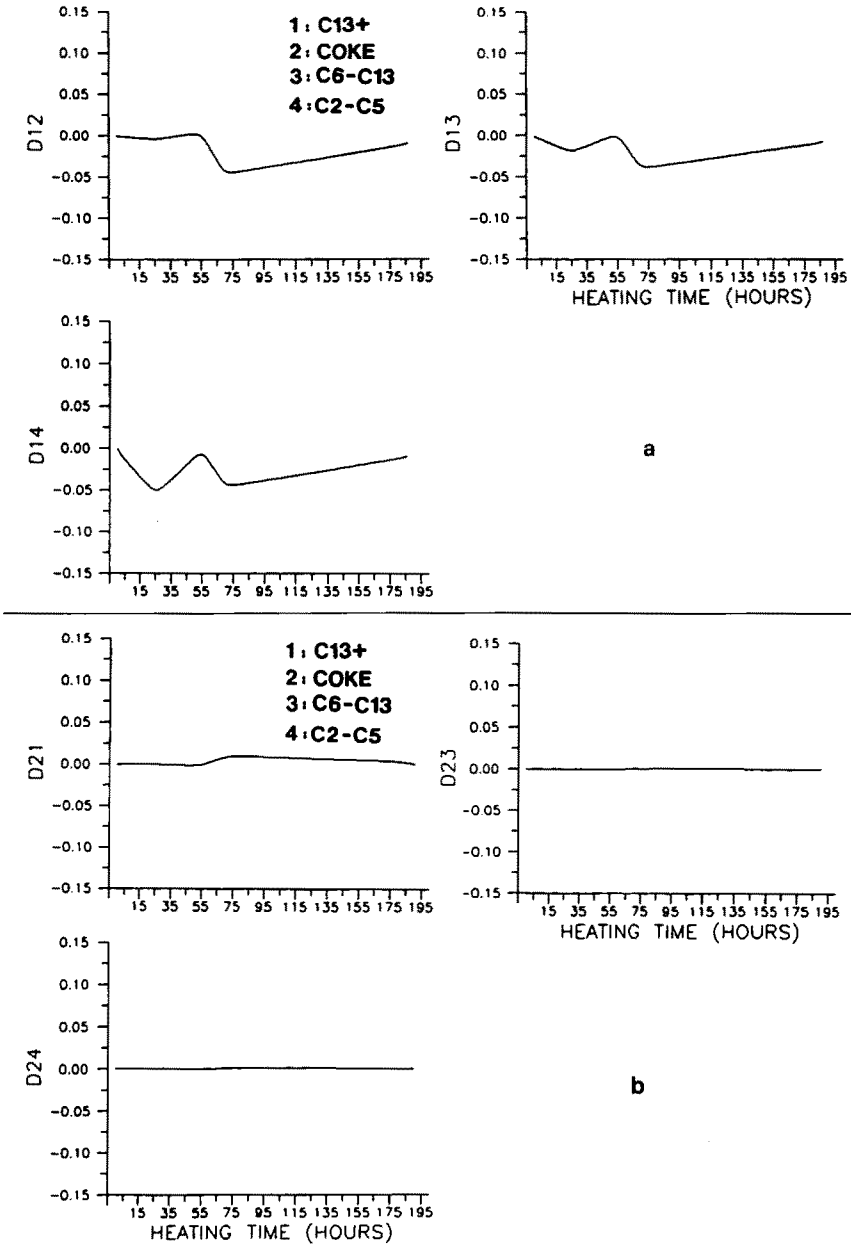


Fig. 7. The variations of the elements of the transformation matrix D_{ij} with heating time for Boscan oil at 357°C: (a) D_{1j} ; (b) D_{2j} ; (c) D_{3j} ; (d) D_{4j} .

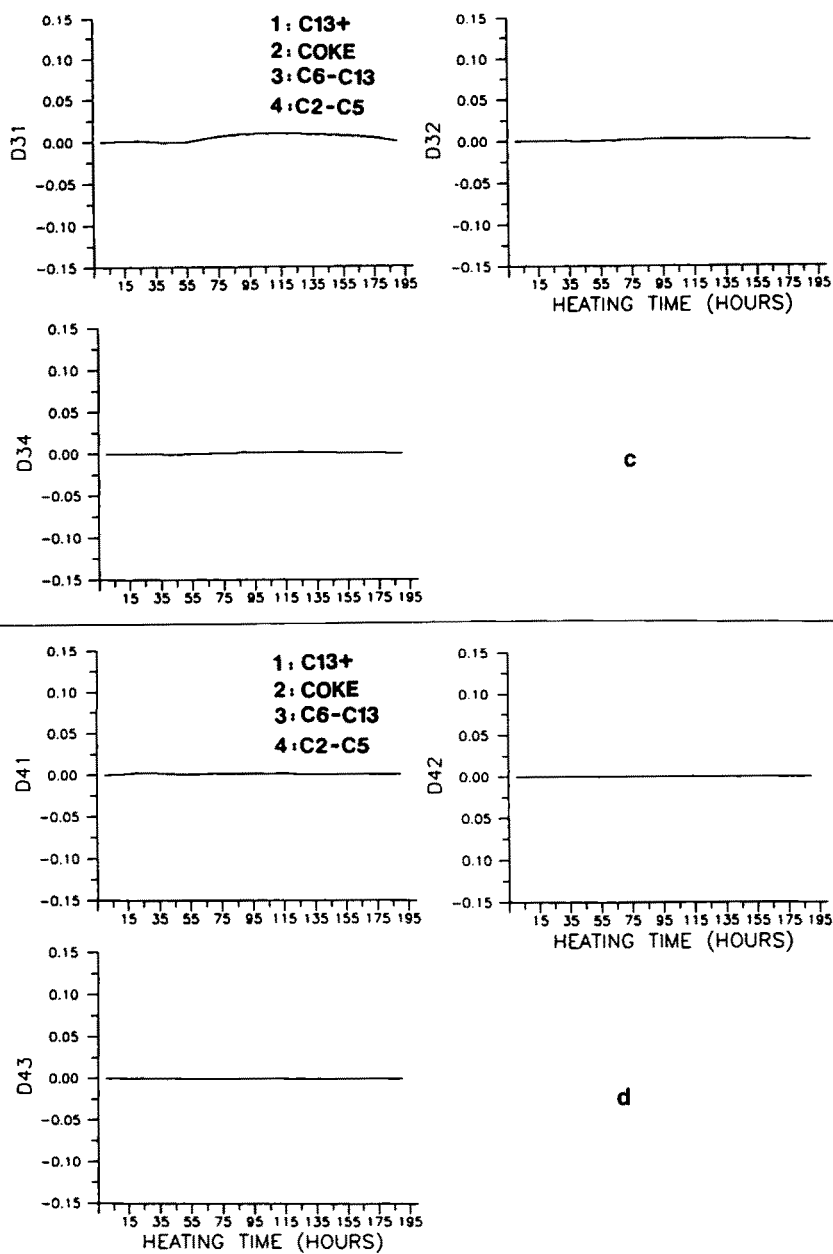


Fig. 7. Continued

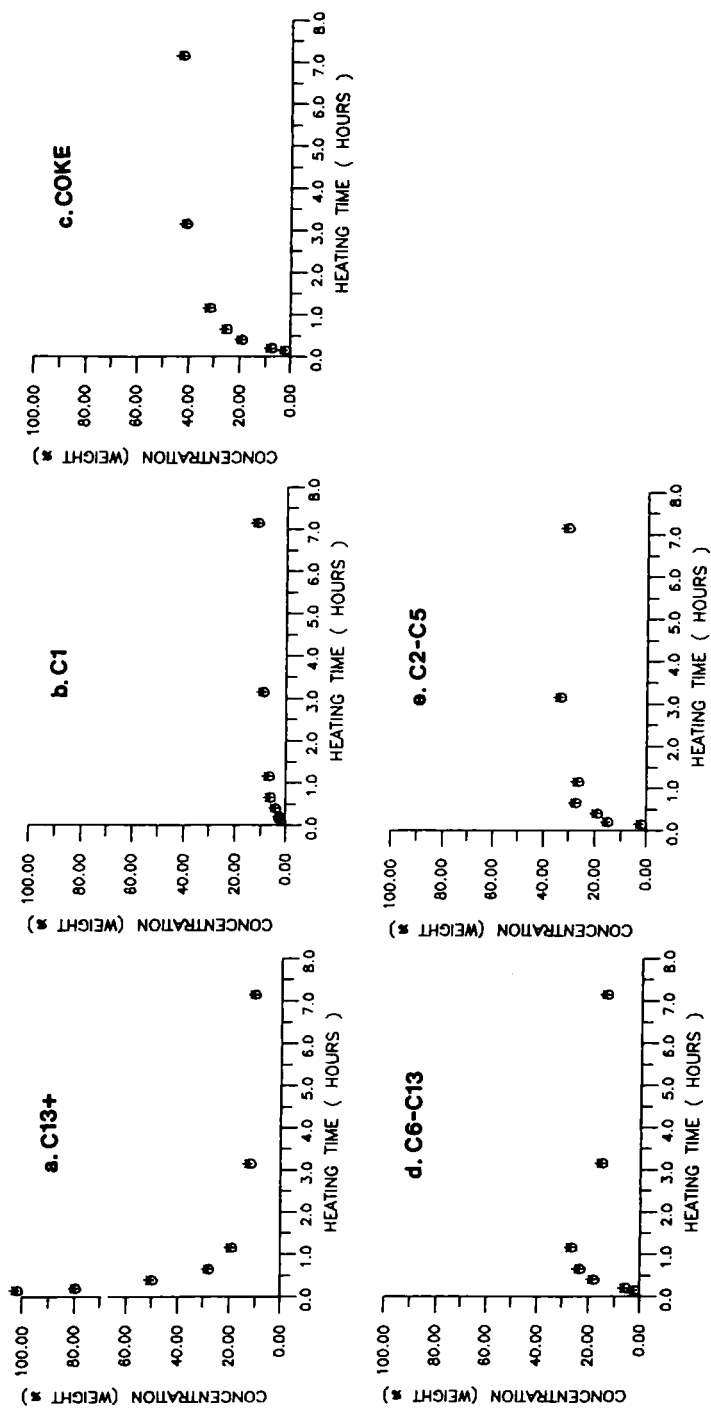


Fig. 8. Measured concentrations of the various fractions from the pyrolysis of the Boscan oil (stars) at 450°C and values computed from the inverse model (circles) plotted vs. heating time at 450°C using D_j as a function of heating time: (a) C13+; (b) C1; (c) coke; (d) C6-C13; (e) C2-C5.

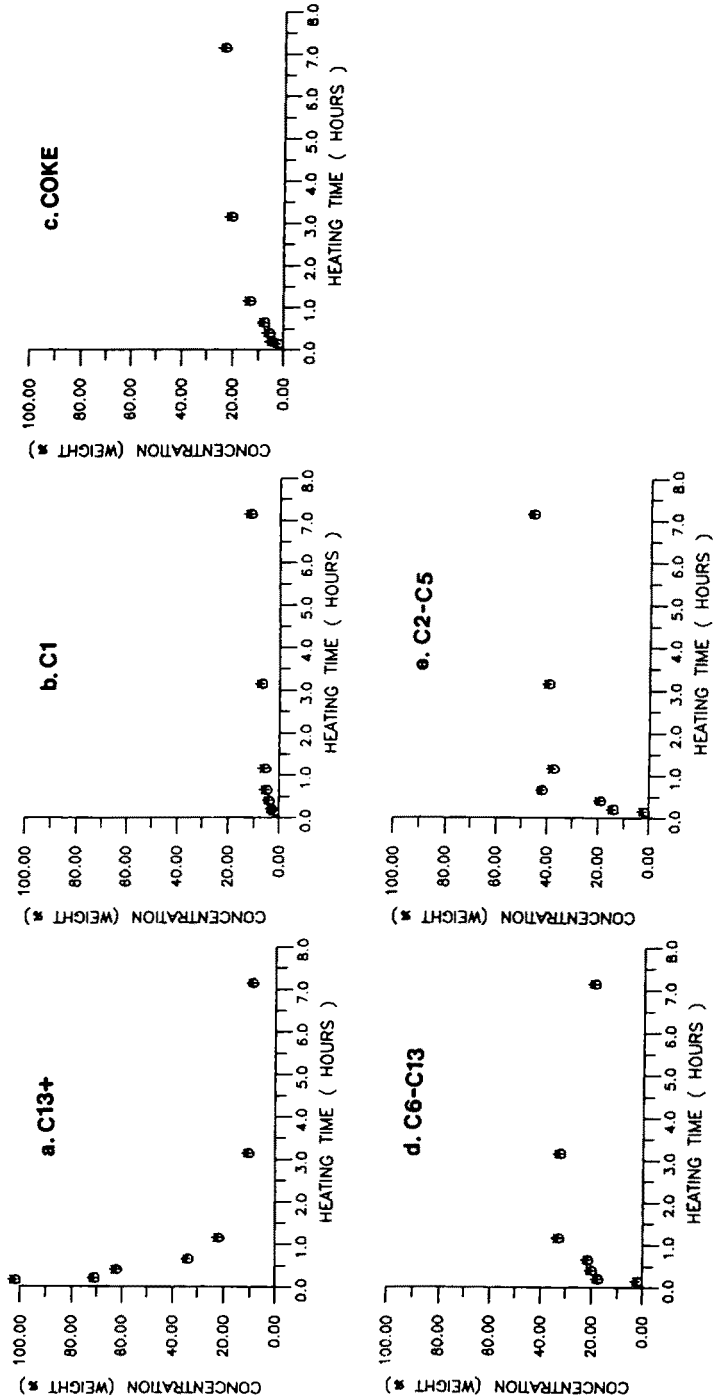


Fig. 9. Measured concentrations of the various fractions from the pyrolysis of Pematang oil (stars) at 450°C and values computed from the inverse model (circles) plotted vs. heating time using D_{ij} as a function of heating time: (a) C13+; (b) C1; (c) coke; (d) C6-C13; (e) C2-C5.

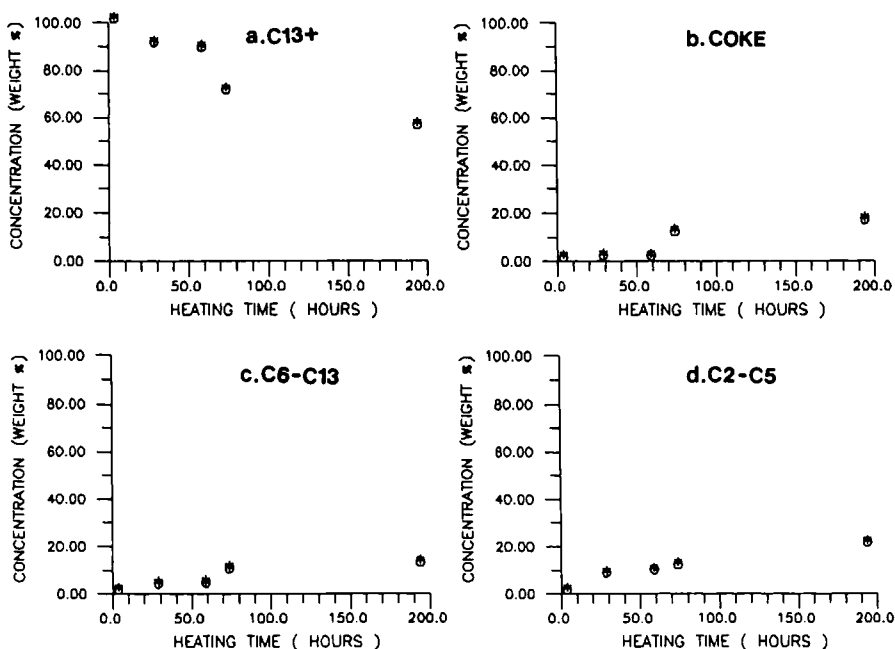


Fig. 10. Measured concentrations of the various fractions from the pyrolysis of Boscan oil (stars) plotted vs. heating time at 357°C and values computed from the inverse model (circles) using D_{ij} as a function of heating time: (a) C13+; (b) coke; (c) C6-C13; (d) C2-C5.

with

$$\bar{D}_{ij} = \sum^N \left\{ \frac{(dq_i/dt U_j)}{N} \middle/ |U_s^p U_s^p| \right\}$$

where N is the number of time points.

Figures 11a-e (data set 1), 12a-e (data set 2), and 13a-e (data set 3) compare input data and predicted values for all three data sets using the best least-squares average \bar{D}_{ij} . Because the D_{ij} for data sets 1 and 2 vary sharply with time, the fits between input data and predicted values are poor. A 30-50% mismatch arises in most of the products for these two cases, especially in the first hour of reaction, which includes the majority of the reaction information in these two cases.

For data set 3, D_{ij} varies slowly with time, so that the predicted behaviors are closer to the observations using the best least-squares estimate of D_{ij} than in the other two cases.

It appears that with longer heating time and lower temperature, the experimental results may provide reaction rate "constants" closer to constant values

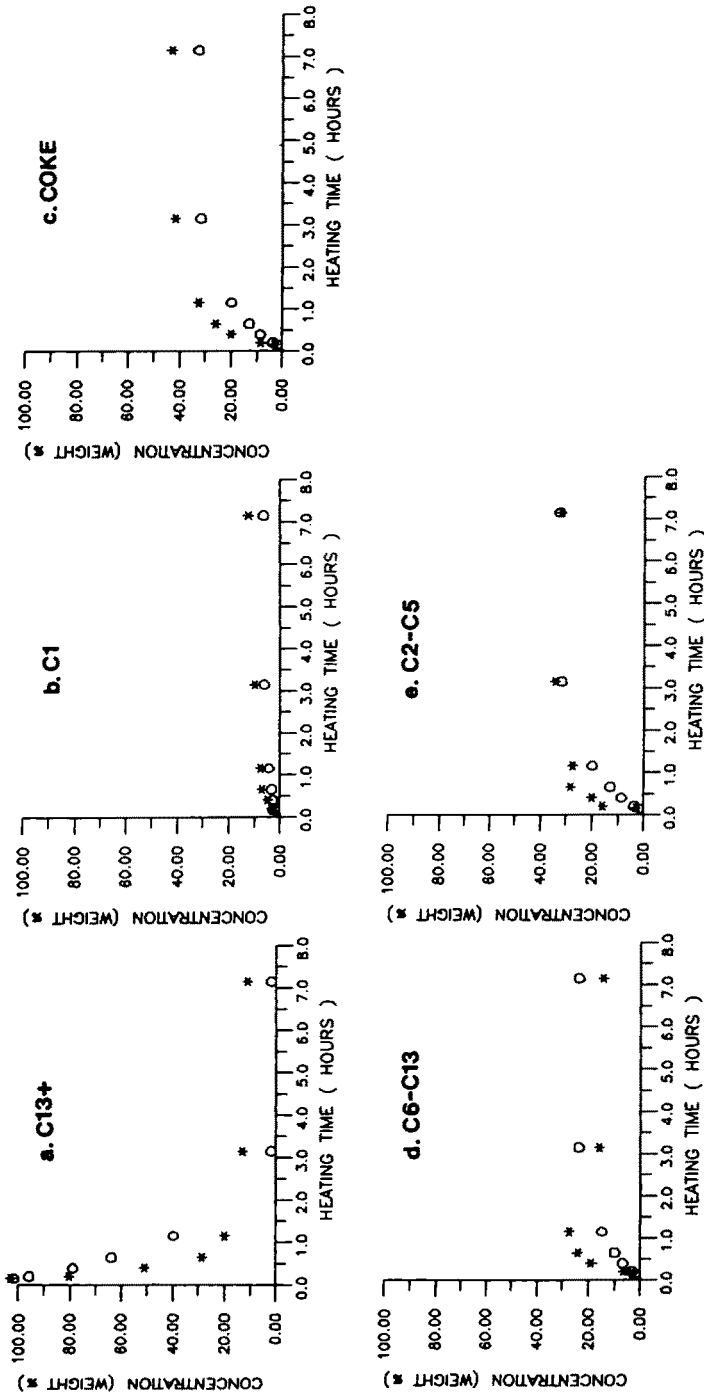


Fig. 11. Measured concentrations of the various fractions from the pyrolysis of Boscan oil (stars) at 450°C and values computed from the inverse model (circle) using an average \bar{D}_{ij} : (a) C13+; (b) C1; (c) coke; (d) C6-C13; (e) C2-C5.

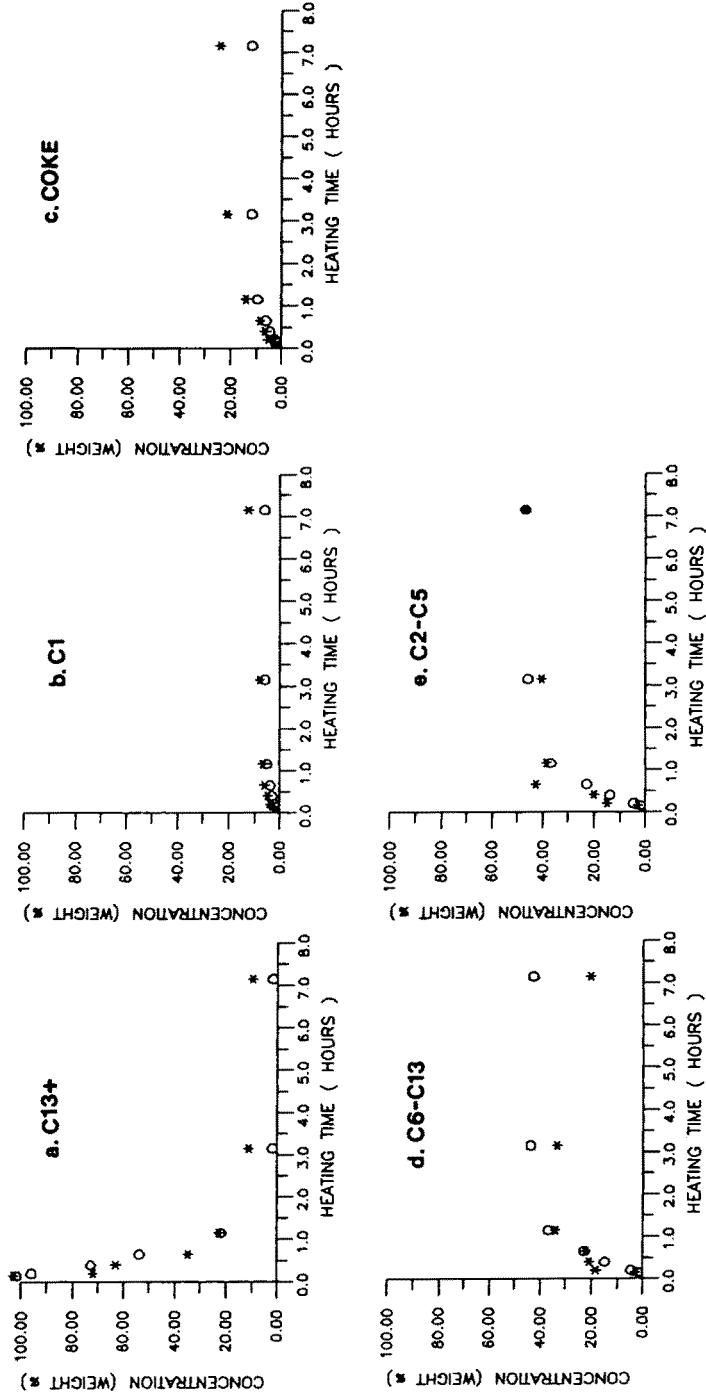


Fig. 12. Measured concentrations of the various fractions from the pyrolysis of Penatang oil (stars) at 450°C and values computed from the inverse model (circles) using an average \bar{D}_{ij} : (a) C13+; (b) C1; (c) coke; (d) C6-C13; (e) C2-C5.

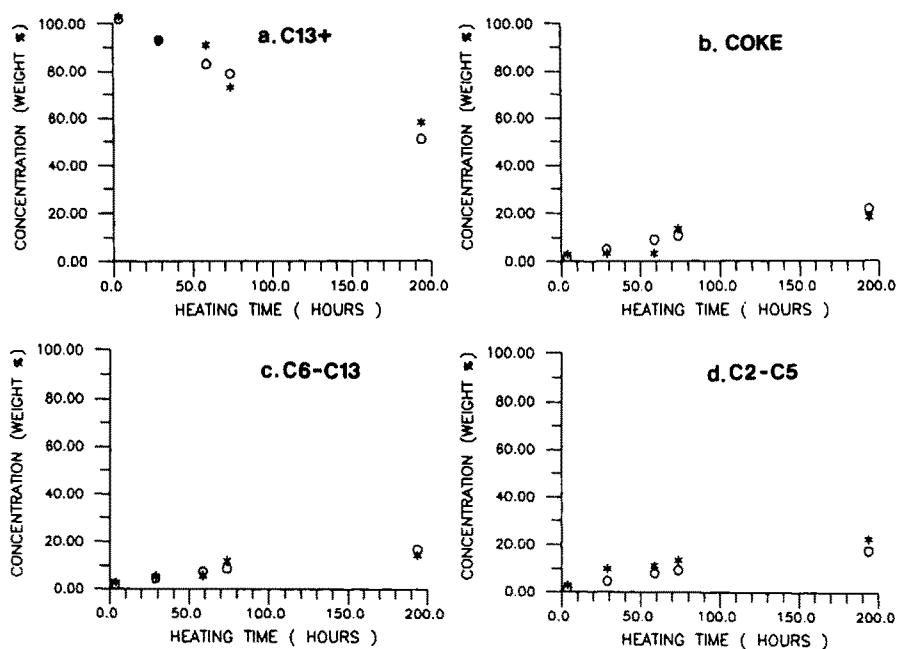


Fig. 13. Measured concentrations of the various fractions from the pyrolysis of Boscan oil (stars) at 357°C and values computed from the inverse model (circles) using an average \bar{D}_{ij} : (a) C13+; (b) coke; (c) C6-C13; (d) C2-C5.

which would be more reproducible and so useful in assessing hydrocarbon kinetic processes on a geologic timescale.

CONCLUSIONS

Based on the results obtained above, it appears that:

1. Checking of the model results, using D_{ij} 's as functions of time, shows accurate fits between predictions and experimental data. This fact indicates that the model is appropriate both in terms of the mathematical procedure and numerical implementation.
2. The D_{ij} provide quantitative information about the thermal changes of the different hydrocarbon products. The D_{ij} show a time dependence for experimental data obtained under high temperatures and short time periods.
3. D_{ij} vs. time can be used to indicate if laboratory experimental data can be applied to a prediction model. Usually, this step is very important when extrapolating the experimental results to geological timescales.

because if D_{ij} is time-dependent, as appears to be the case, then a useful hydrocarbon prediction equation of generic validity is not available.

4. The experimental data from lower temperature and longer time period experiments may be more pertinent for constructing a kinetic model for oil-cracking and thermal changes of hydrocarbon products.

From the above discussion, it seems necessary: (a) to classify different source materials according to their behaviors in the oil-cracking processes to determine whether a few sets of D_{ij} values can be obtained to construct different prediction models for different groups of source materials; (b) to have more laboratory experiments performed at low temperatures and over longer time periods, in order to determine whether it is possible to construct stable values of D_{ij} , which are independent, in a statistical sense, from the experiments, and which are therefore of generic validity.

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