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Comparison of petroleum generation kinetics by isothermal hydrous and nonisothermal open-system pyrolysis

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Abstract

This study compares kinetic parameters determined by open-system pyrolysis and hydrous pyrolysis using aliquots of source rocks containing different kerogen types. Kinetic parameters derived from these two pyrolysis methods not only differ in the conditions employed and products generated, but also in the derivation of the kinetic parameters (i.e., isothermal linear regression and non-isothermal nonlinear regression). Results of this comparative study show that there is no correlation between kinetic parameters derived from hydrous pyrolysis and open-system pyrolysis. Hydrous-pyrolysis kinetic parameters determine narrow oil windows that occur over a wide range of temperatures and depths depending in part on the organic-sulfur content of the original kerogen. Conversely, open-system kinetic parameters determine broad oil windows that show no significant differences with kerogen types or their organic-sulfur contents. Comparisons of the kinetic parameters in a hypothetical thermal-burial history (2.5 °C/my) show open-system kinetic parameters significantly underestimate the extent and timing of oil generation for Type-IIS kerogen and significantly overestimate the extent and timing of petroleum formation for Type-I kerogen compared to hydrous pyrolysis kinetic parameters. These hypothetical differences determined by the kinetic parameters are supported by natural thermal-burial histories for the Naokelekan source rock (Type-IIS kerogen) in the Zagros basin of Iraq and for the Green River Formation (Type-I kerogen) in the Uinta basin of Utah. Differences in extent and timing of oil generation determined by open-system pyrolysis and hydrous pyrolysis can be attributed to the former not adequately simulating natural oil generation conditions, products, and mechanisms.
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1. Introduction

Determining the timing and extent of oil generation of a source rock are important considerations in evaluating the potential oil reserves within a petroleum system (Magoon and Dow, 1994). These determinations are based on the thermal-burial history of a petroleum system and the oil-generation kinetics of its source rock. The thermal-burial history of a petroleum system is based on its stratigraphy, lithologies, thermal conductivity, surface temperatures, and heat flow, which are integrated to determine the durations and temperatures a source rock experiences as it is buried through geologic time. This thermal-burial history is calibrated with available down-hole well temperatures or thermal stress indicators like vitrinite reflectance. Oil-generation kinetics are determined experimentally and applied to the thermal-burial history to determine timing and extent of oil generation of an identified source rock within a petroleum system.

Applying the oil-generation kinetic parameters to the thermal-burial history is typically accomplished with the use of the Arrhenius expression;

$$f(\varepsilon) = [A_0 \exp\{-E_a/(RK)\}]t \qquad (1)$$

This expression equates a function of the extent of oil generation $[f(\epsilon)]$ to heating time (**t**) and absolute temperature (**K**) through the ideal-gas constant (R), a frequency factor (A_0), and an activation energy (E_a). The time and temperature values are determined from the thermal-burial history, and the kinetic parameters, E_a and A_0, are experimentally determined for the organic

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matter within a source rock. Two experimental methods for determining these kinetic parameters are isothermal hydrous pyrolysis (Lewan, 1985) and nonisothermal open-system pyrolysis (Burnham and Braun, 1999; Ungerer and Pelet, 1987). These two methods differ in their experimental conditions, reaction products, and kinetic-parameter derivations.

The utility of the kinetic parameters determined by these two methods has been controversial as demonstrated in the discussions by Burnham (1998) and Lewan (1998a). With the exception of the study by Ruble et al. (2001) on oil generation from the Green River Fm. in the Uinta basin, no studies comparing the kinetics of these two methods using aliquots of the same source-rock samples have been conducted. Objectives of this study are to conduct such a comparative study on six well-characterized source rocks, discuss geological implications, and evaluate the cause of observed differences. The six source-rock samples used in this comparative study are described in Table 1. All of the samples contain immature oil-prone kerogen classified on the basis of elemental analyses as Type-IIS, -II, or -I. The samples are rich in organic matter with total organic carbon (TOC) values in excess of 12 wt.%. Their thermal immaturity is indicated by the high kerogen atomic H/C ratios (>1.1), low Rock-Eval production indices (PI $\leqslant 0.06$), and low vitrinite reflectance values ($\%R_0 \leqslant 0.52$). In addition to these samples representing a wide range of world-class oil-prone source rocks, they were also chosen because they have been the subject of previously published geochemical and kinetic studies as referenced in Table 1.

2. Methods and results

2.1. *Isothermal hydrous pyrolysis*

2.1.1. *Procedure*

Hydrous pyrolysis is a closed-system method of thermally decomposing organic matter in the presence of liquid water (Lewan et al., 1979). Typically, 200–500 g of gravel-sized (0.5–2 cm) immature source rock are loaded into a one-liter stainless-steel reactor with enough distilled water to insure that the rock is submerged in liquid H_2O at subcritical experimental temperatures (<374 °C). If the rock is an oil-prone source rock and the appropriate experimental time and temperature conditions are employed, generated expelled oil will accumulate on the water surface within the reactor. This expelled oil is physically, chemically, and isotopically similar to natural crude oils. All of the samples in Table 1 generate expelled oil through a bitumen intermediate, which is generated from the partial thermal

Table 1
Description of source rock samples used in comparative study

Sample no.: Abbreviation:	MR-83 *M*	P-64 *P*	AS-33 *A*	WD-5 *W*	931026-3 *N*	930923-8 *G*
Formation	Monterey	Phosphoria	Alum	Woodford	New Albany	Green River
Member		*Retort Sh.*			*Clegg Ck.*	*Parachute Ck.*
Kerogen						
Type	IIS	IIS	II	II	II	I
H/C[a]	1.25	1.20	1.11	1.17	1.11	1.51
S_{org}/C[a]	0.064	0.045	0.036	0.023	0.010	0.002
$\%R_0$[b]	0.32	0.17	0.52	0.44	0.42	0.44
Whole Rock						
TOC (wt.%)[c]	13.44	23.60	13.20	12.70	14.34	15.23
HI[d]	436	570	350	560	604	961
OI[d]	24	14	9	2	17	27
PI[d]	0.06	0.04	0.01	0.03	0.03	0.01
T_{max} (°C)	397	418	424	427	425	438
References[e]	a, b, c	a, b, d	a, b, e	a, b, d	a, f	g

[a] Atomic ratios based on elemental analyses.

[b] Mean random vitrinite reflectance.

[c] Total organic carbon.

[d] Rock-Eval analysis with HI = mgS2/gTOC, OI = mgS3/gTOC, and PI = S1/[S1 + S2].

[e] References: a = Lewan (1998b), b = Hunt et al. (1991), c = Lewan (1989), d = Lewan (1985), e = Lewan and Buchardt (1989), f = Lewan et al. (1995), and g = Ruble (1996) and Ruble et al. (2001).

decomposition of the original kerogen (Lewan, 1985; Ruble, 1996) at temperatures of 240–330 °C for 72 h. Specifics on the experimental protocol, collection procedure, reaction mechanisms, and character of the expelled oils are given in Lewan (1993, 1997). The temperatures are monitored within a standard error less than ±0.5 °C with calibrated J-type thermocouples (National Bureau of Standards). Temperatures are recorded to 0.1 °C every 30 s from initial warm up to at least the first 10 h of the cool down. As shown in Fig. 1, the experiment duration is taken from the time the reactor first comes within 0.5 °C of the intended experimental temperature to the time the reactor drops below 0.5 °C of the experimental temperature after turning off the electric heater. Warm-up times are typically between 1.1 and 1.5 h in duration depending on the intended experimental temperatures and rock and water masses used in the experiments. Cool-down times are typically 18–24 h in duration and are sometimes accelerated by carefully removing the reactors from their insulated heaters once the cool-down temperatures are less than 150 °C. The times are recorded within a standard error of ±0.5 min.

2.1.2. *Initial studies*

Kinetic parameters are determined on the expelled oil generated from hydrous-pyrolysis experiments in the classic isothermal approach. Initial kinetic studies (Lewan, 1985) on the samples from the Phosphoria Fm. (P-64) and Woodford Shale (WD-5) assumed that the extent of expelled oil generation was a first-order function, with $f(\epsilon)$ in Eq. (1) being expressed as

$$f(\varepsilon) = \mathrm{Ln}\{1/[1-X]\}, \tag{2}$$

where X is the fraction of expelled oil generated at a specified temperature and is also referred to as the transformation ratio. Determining this fraction of reaction requires knowing the maximum yield of expelled oil capable of being generated from a source rock. Maximum yields were determined by conducting a temperature-series of experiments on aliquots of a sample at temperatures between 280 and 365 °C for 72 h. As shown in Fig. 2, the maximum yields for Type-II and -IIS kerogen consistently occur between 345 and 365 °C for 72-h experiments. Type-I kerogen from the Green River Fm. is more resilient to thermal decomposition and requires additional experiments within this temperature range for longer durations to determine the maximum yield. The maximum expelled-oil yield for the Type-I kerogen used in this study was observed at 360 °C after 96 h (Ruble et al., 2001).

Using these determined maximum yields, and assuming a first-order function [Eq. (2)], rate constants (k_T) for each experimental temperature were calculated for the Woodford, Phosphoria, Alum, and Monterey source

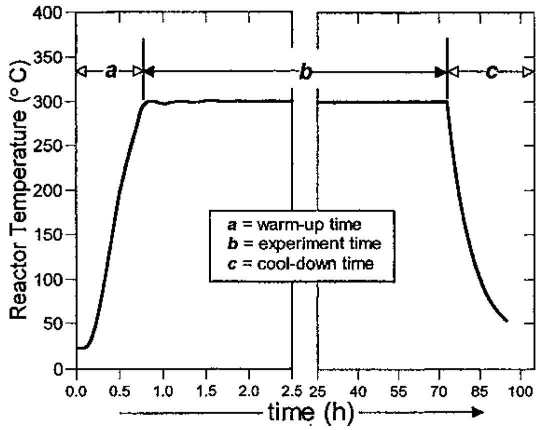

Fig. 1. Typical temperature profile through the course of an experiment including initial warm-up duration, experiment duration at intended temperature, and final cool-down duration.

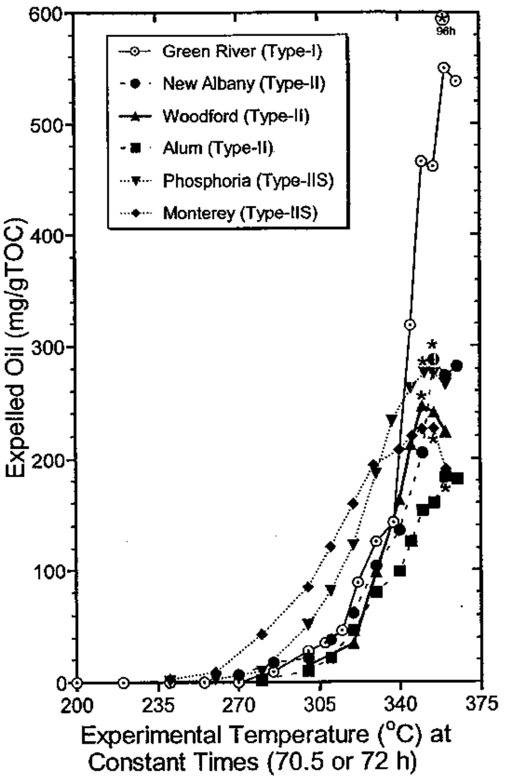

Fig. 2. Expelled oil generated by hydrous pyrolysis from aliquots of different source rocks at various temperatures at fixed times. The fixed times are 70.5 h for the Woodford and Phosphoria samples and 72 h for the other samples. Maximum yield for the Green River sample occurred at 360 °C for 96 h as indicated by $*$.

rocks. The resulting rate constants are determined by the expression

$$k_T = (\text{Ln}\{1/[1 - X_T]\})/t, \tag{3}$$

where **t** is 72 h for these experiments and X_T is the fraction of reaction that occurred at temperature T. Combining the Arrhenius expression [Eq. (1)] with the first-order function [Eq. (3)] gives the expression

$$k_T = (\text{Ln}\{1/[1 - X_T]\})/t = A_0\exp\{-E_a/(R\mathbf{K})\}. \tag{4}$$

The kinetic parameters E_a and A_0 can be derived by plotting the natural logarithm of the determined rate constants versus the reciprocal of their temperature (1/**K**). Linear relationships that result from this type of plot define E_a from the slope and A_0 from the intercept. Fig. 3 shows that good linear relationships occur in the plots for the Woodford, Phosphoria, Monterey, and Alum source rocks. In addition to being derived from explicit linear Arrhenius relationships, these kinetic parameters have been shown to make reasonable determinations of the timing and extent of oil generation under various thermal-burial histories of different petroleum systems (Hunt et al., 1991).

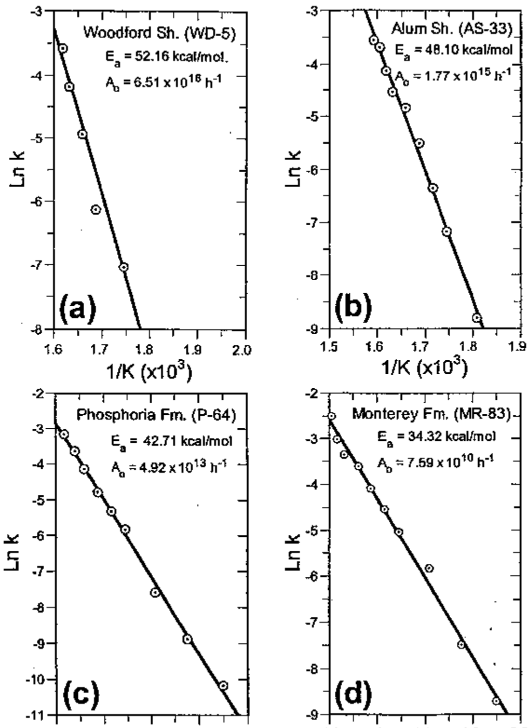

Fig. 3. Arrhenius plots derived from hydrous pyrolysis temperature-series assuming first-order rates: (a) Woodford sample WD-5, (b) Alum sample AS-33, (c) Phosphoria sample P-64, and (d) Monterey sample MR-83.

One concern with this approach is testing the validity of the assumption that the determined rate constants obey a first-order function. Although most published kinetic studies on oil shale retorting have shown oil generation to be expressed by a first-order reaction (e.g., Hubbard and Robinson, 1950), the validity of the first-order assumption remains questionable. One of the disadvantages of determining kinetic parameters by hydrous pyrolysis is the large amount of sample required to do a complete set of experiments. As an example, experiments conducted on the sample from the Phosphoria Fm. used 400-g aliquots for each of the 12 isothermal experiments (Fig. 2). A total sample weight of more than 5 kg is therefore required when considering losses during crushing of the sample. The early experiments on the samples shown in Fig. 2 were not originally designed for kinetic studies, and as a result, insufficient sample remained to conduct subsequent isothermal experiments at varying times to evaluate the assumption of a first-order rate constant. The only exception was the sample of Woodford Shale (WD-5). Sufficient sample was available after the temperature-series experiments (Fig. 2) to allow one time series of experiments to be completed at one temperature. A temperature of 330 °C was used for six different times ranging from 22.5 to 238.5 h. As shown in Fig. 4a, the linear relationship indicates that the assumption of a first-order rate constant for the generation of expelled oil is valid.

Another test of the first-order assumption for the expelled oil generated by hydrous pyrolysis was conducted with a sample of Woodford Shale (WD-4) from a bed immediately above sample WD-5 at the same outcrop. This supplemental sample has essentially the same type of organic matter and quartz-rich lithology as sample WD-5, and only differs in having a lower TOC

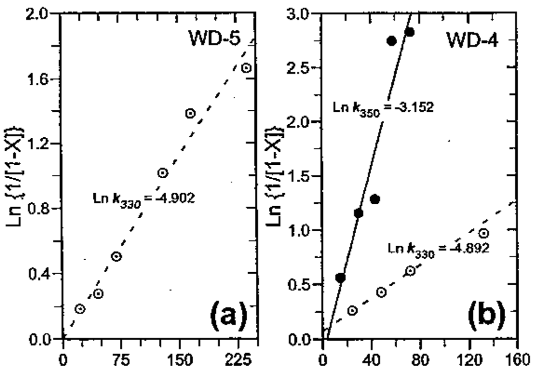

Fig. 4. First-order rate plots for (a) Woodford sample WD-5 at 330 °C and (b) Woodford sample WD-4 at 330 and 350 °C.

content of 4.3 wt.% (Lewan, 1987). Two time-series experiments were conducted at 330° and 350 °C for 24–132 and 14–72 h, respectively. As shown in Fig. 4b, both time series are described by first-order functions. Plotting these rate constants and the one determined for sample WD-5 (Fig. 3a) on the Arrhenius plot for the temperature-series (Fig. 5) shows there is good overall agreement among the experiments and the original assumption of a first-order function is valid.

2.1.3. Subsequent studies

As with most experimental techniques, preparations and procedures become more refined with time and experience. The subsequent experiments on the New Albany (931026-3) and Green River (930923-8) samples were undertaken with the primary goal of obtaining kinetic parameters. Therefore, more than 10 kg of each of these samples were collected to insure sufficient aliquots for both temperature-series experiments to determine maximum yields and time-series experiments at three or more temperatures to determine reaction order functions.

Temperature-series experiments with the sample of New Albany Shale (931026-3) indicate the maximum expelled-oil yield is 287.7 mg/gTOC at 355 °C (Fig. 2). This determined maximum is used to calculate the fractional extent of expelled-oil generation (X) for all the time-series experiments (Table 2). These X values are recalculated as first-order functions [Eq. (2)] and plotted against their experimental times to determine whether a first-order function adequately describes the rate constants. As shown in Fig. 6, the data from Table 2 are adequately described by a first-order function. The rate constants, zero-time intercepts, and correlation coefficients for the three temperatures are given in Table 3. The linear relationships have statistically significant correlation coefficients, and the slopes equate to first-order reaction rates. The small and positive intercepts decrease with decreasing experimental temperatures. This trend can be explained by the fact that experimental times represent the duration from the time the experiment reaches within 0.5 °C of the intended temperature to the time the experiment falls 0.5 °C below the intended temperature after the heater is turned off. Therefore, trace amounts of expelled oil may be generated during the warm-up and cool-down times (Fig. 1). This additional expelled oil would account for the positive intercepts and their decrease with decreasing intended experiment temperatures. Plotting the rate constants in Table 3 versus the reciprocal of their experimental absolute

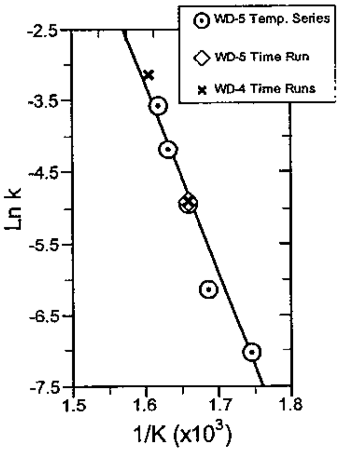

Fig. 5. Arrhenius plot of the rate constants determined from the hydrous pyrolysis temperature series on sample WD-5 assuming a first-order rate (Fig. 3a) and rate constants determined from hydrous pyrolysis time series on Woodford samples WD-4 and WD-5 (Fig. 4).

Table 2

Expelled oil generated from the New Albany Shale (931026-3) in hydrous-pyrolysis temperature- and time-series experiments

Temp. (°C)	Time (h)	Expelled oil (mg/gTOC)	Fraction (X)	f(ε) (Ln{1/[1−X]})
310.1	71.99	38.14	0.133	0.142
310.1	144.12	50.74	0.176	0.194
310.1	288.10	90.14	0.313	0.376
310.1	576.00	104.37	0.363	0.451
330.0	36.00	63.76	0.222	0.251
330.1	72.16	103.68	0.360	0.447
330.1	144.13	142.39	0.495	0.683
330.1	288.09	191.63	0.666	1.097
350.2	12.13	89.65	0.312	0.373
350.1	24.08	167.31	0.581	0.871
350.5	72.13	205.25	0.713	1.249
350.2	96.07	250.32	0.870	2.040

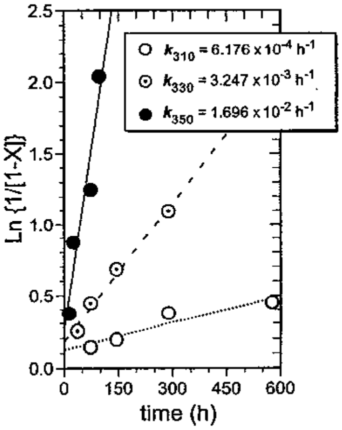

Fig. 6. First-order rate plot from hydrous-pyrolysis time series on New Albany sample (931026–3) at 310, 330, and 350 °C.

Table 3
First-order rate constants and intercepts determined for the New Albany sample by hydrous pyrolysis at 310, 330, and 350 °C

	Temperature (°C)		
	310	330	350
Rate constant (k ; h^{-1})	6.176×10^{-4}	3.247×10^{-3}	1.696×10^{-2}
0-time Intercept (Ln{1/[1−*X*]})	0.1239	0.1806	0.2669
Correlation coef. (*r*)	0.9410	0.9940	0.9562

temperature (*K*) gives a linear Arrhenius relationship as shown in Fig. 7. This relationship [Eq. (4)] gives an activation energy of 59.63 kcal/mol and a frequency factor of 1.365×10^{19} h^{-1}. These values are slightly larger than those originally published by Lewan (1998b; $E_a = 59.20$ kcal/mol and $A_0 = 0.833 \times 10^{19}$ h^{-1}) because the earlier derived rate constants did not take into account the positive intercepts resulting from warm-up and cool-down times.

Kinetic parameters for the sample from the Green River Fm. (930923-8) were derived by hydrous pyrolysis in a procedure similar to that described above for the New Albany Shale. Experimental data for the temperature-series and time-series experiments are tabulated in Ruble (1996). An apparent maximum expelled-oil yield of 549.3 mg/gTOC was observed in the temperature-series experiments at 360 °C for 72 h (Fig. 2), but the actual maximum expelled-oil yield of 593.7 mg/gTOC was observed in the time-series experiments at 360 °C for 96 h. Time-series experiments were conducted at five temperatures (i.e., 315, 330, 337.5, 345, and 360 °C). The fractional extent of expelled oil generation was calculated as a first-order function [Eq. (2)] and plotted against the experimental times. As shown in Fig. 8, the data for all five time-series temperatures can be described by first-order rate constants. The complete regression analysis and correlation coefficients are given by Ruble et al. (2001, Table 8). Plotting these five rate constants versus the reciprocal of their experimental absolute temperatures (K) gives a linear Arrhenius relationship as shown in Fig. 9. This relationship [Eq. (4)] gives an activation energy (E_a) of 66.63 kcal/mol and a frequency factor (A_0) of 3.2002×10^{21} h^{-1}. These values are slightly lower than those published by Ruble et al.

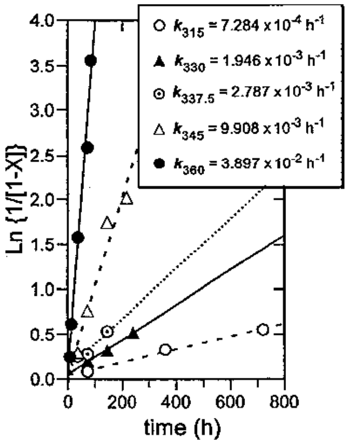

Fig. 8. First-order rate plot from hydrous-pyrolysis time series on Green River sample 930923-8 at 315, 330, 337.5, 345, and 360 °C.

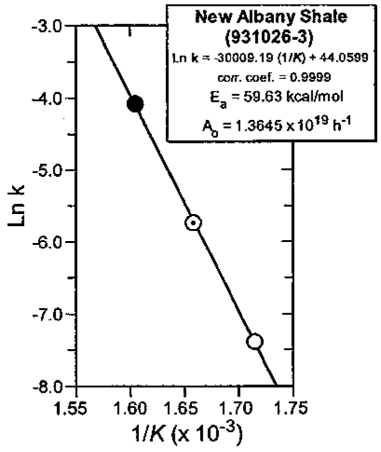

Fig. 7. Arrhenius plot of the rate constants determined from the hydrous pyrolysis time series on New Albany sample 931026-3 (Fig. 6).

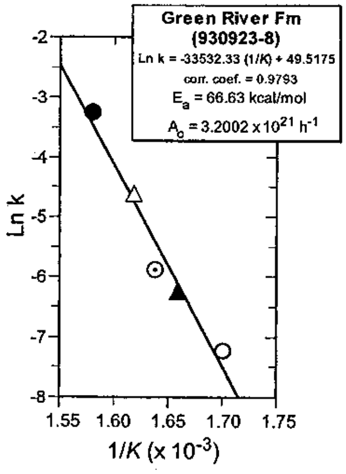

Fig. 9. Arrhenius plot of the rate constants determined from the hydrous pyrolysis time series on Green River sample 930923-8 (Fig. 8).

(2001; $E_a = 68.71$ kcal/mol and $A_0 = 1.883 \times 10^{22}$ h^{-1}) for the Green River Fm. because their derivation involved a composite of rate constants determined for the sample of mahogany shale (930923-8) and the sample from the black shale facies (930922-1). To facilitate a better comparison, this study focused on the more complete experimental data set of the former sample.

2.1.4. Parameter relationships

The maximum expelled-oil yields and kinetic parameters determined by hydrous pyrolysis in this study are given in Table 4. The maximum yields vary from 594 mg/gTOC for the Type-I kerogen in the sample of Green River Fm. (Ruble et al., 2001) to 183 mg/gTOC for the radiation-damaged Type-II kerogen in the high-uranium bearing Alum Shale sample (Lewan and Buchardt, 1989). The kinetic parameters vary from 34.32 to 66.63 kcal/mol for the activation energy (E_a) and from 7.59×10^{10} to 3.20×10^{21} h^{-1} for the frequency factor (A_0). Fig. 10 shows that the activation energies (E_a) have an excellent positive correlation with the logarithm of their frequency factors (A_0). This relationship is referred to as the compensation effect (Connors, 1990, pp. 368–371), and the slope of the relationship equates to an isokinetic temperature (β), which is 392.5 °C for expelled-oil generation. At this temperature, the rate of expelled-oil generation is the same for all the source rocks and variations in activation energies are compensated for by their different frequency factors. Rates of expelled-oil generation become increasingly controlled by frequency factors as temperatures increase above this temperature, and by activation energies as temperatures decrease below this temperature. Although the statistical significance of the compensation effect has been debated (e.g., Krug et al., 1976; Galwey, 1977), the relationship does indicate that a common overall mechanism is responsible for the generation of expelled oil in the hydrous-pyrolysis experiments. Variations in the rates above and below this isokinetic (i.e., compensation) temperature are considered a result of various catalysts, inhibitors, or initiators influencing the rate of a common overall mechanism. Lewan (1998b) has shown that increasing the concentration of sulfur-radical initiators enhances the rate of free-radical reactions, and this enhancement can explain the excellent negative correlation between activation energies for expelled-oil generation and the kerogen organic sulfur to carbon mole fraction (Fig. 11).

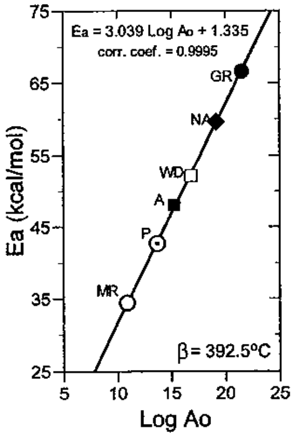

Fig. 10. Compensation-effect plot of activation energies and logarithm of their frequency factors. β is the isokinetic temperature (392.5 °C) at which the rate constants for all the source rocks are equal.

The significance of Fig. 11 is that it allows an indirect means of determining hydrous pyrolysis kinetic parameters when only a limited amount of immature source rock is available. The activation energy can be estimated from this relationship by determining the organic-sulfur mole fraction (Sorg/[Sorg+C]) of the kerogen in the immature sample. Using this activation energy, the frequency factor can then be determined from the compensation expression given in Fig. 10. This indirect approach has been used by Lillis et al. (1998) to determine petroleum-formation kinetic parameters for several Alaskan source rocks of the North Slope where sample availability was limited.

2.1.5. Geological implications

The geological significance of the determined kinetic parameters in Table 4 can be evaluated by extrapolating

Table 4

Summary of kinetic parameters derived for expelled-oil generation by hydrous pyrolysis in isothermal experiments

Formation name	Sample number	Kerogen type	Maximum oil yield (mg/gTOC)	Activation energy, E_a (kcal/mol)	Frequency factor, A_0 (h^{-1})
Monterey	MR-83	Type II-S	226.5	34.32	7.59E+10
Phosphoria	P-64	Type II-S	276.3	42.71	4.92E+13
Alum	AS-33	Type II	183.2	48.10	1.77E+15
Woodford	WD-5	Type II	246.2	52.16	6.51E+16
New Albany	931026–3	Type II	287.7	59.63	1.36E+19
Green River	930923–8	Type I	593.7	66.63	3.20E+21

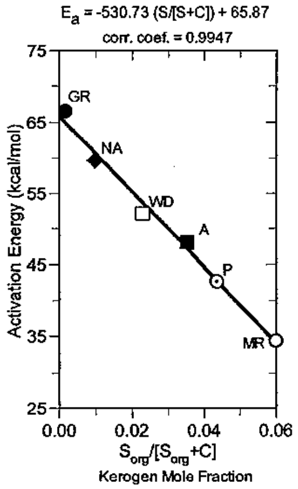

Fig. 11. Relationship between organic-sulfur mole fraction (i.e., $mS_{org}/[mS_{org}+mC]$) in immature kerogen and activation energy derived from hydrous pyrolysis.

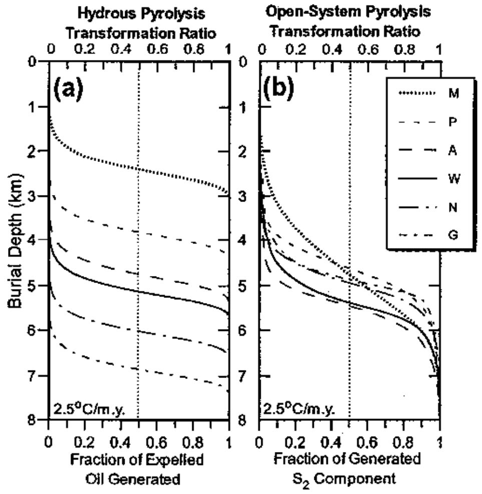

Fig. 12. Generation (transformation) curves for Monterey (M), Phosphoria (P), Alum (A), Woodford (W), New Albany (N), and Green River (G) samples in a hypothetical average thermal-burial history as determined by kinetic parameters derived from (a) hydrous pyrolysis and (b) open-system pyrolysis. The hypothetical average thermal-burial history is defined here by a thermal gradient of 25 °C/km, burial rate of 100m/my, heating rate of 2.5 °C/my, surface temperature of 15 °C, and a 80 Ma source rock.

their determined rates to lower temperatures and longer times in a hypothetical thermal-burial history. Geological heating rates in sedimentary basins may range from 1 to 10 °C/my (Gretener and Curtis, 1982), but hypothetical evaluations typically use heating rates between 0.5 and 5 °C/my (e.g., Schenk et al., 1997, p. 248; Gretener and Curtis, 1982). This study defines a hypothetical average basin as having an 80 Ma source rock that is buried at a rate of 100 m/my through a thermal gradient of 25 °C/km and a constant surface temperature of 15 °C. Although the specifics defined are arbitrary, they result in a heating rate of 2.5 °C/my, which is within the generally prescribed limits for evaluating the geological significance of petroleum-formation kinetic parameters (0.5–5 °C/my). Fig. 12a shows the curves for expelled-oil generation determined for the 80-Ma source rock using each of the hydrous-pyrolysis kinetic parameters given in Table 4 for this hypothetical thermal-burial history. In this thermal-burial history, the Monterey kinetic parameters with the lowest activation energy and frequency factor determine expelled-oil generation at the shallowest depths between 1.2 and 2.6 km ($X=0.01$–0.99). Conversely, the Green River kinetic parameters with the highest activation energy and frequency factor determine expelled-oil generation at the deepest depths between 4.9 and 6.3 km ($X=0.01$–0.99). The other kinetic parameters determine expelled-oil generation at intermediate depths that deepen with corresponding increases in their activation energies and frequency factors. These results indicate that variations in the hydrous-pyrolysis kinetic parameters are geologically significant, with the extent of expelled-oil generation varying as much as 4.5 km in this hypothetical average thermal-burial history. Despite the differences in depth for the start and end of expelled-oil generation ($X=0.01$–0.99), all these kinetic parameters consistently determine an expelled-oil generation window between 1.5 and 1.7 km thick.

2.2. Nonisothermal open-system pyrolysis

2.2.1. Procedure

The two commercial nonisothermal open-system pyrolysis instruments used in this study are Rock-Eval (Espitalié et al., 1977) and the SR Analyzer (Jarvie et al., 1996). Humble Geochemical Services conducted nonisothermal kinetic analyses with both instruments under the direction of Daniel Jarvie. The SR Analyzer with five heating rates (1, 5, 15, 30, and 50 °C/min) was used to determine the nonisothermal kinetics on the Monterey, Phosphoria, Alum, and Woodford samples. The Rock-Eval 5 instrument with three heating rates (1, 5, and 30 °C/min) run in duplicate was used to determine the nonisothermal kinetics on the New Albany and Green River samples. Powdered aliquots of the six source-rock samples are pre-extracted with an azeotropic mixture of dichloromethane and methanol. Both instruments initially heat 10–20 mg of the extracted powder for 5 min at 250 °C to remove existing volatile organic components (S_1 components) that may have not been removed by the pre-extraction step. The devolatilized powder is then heated to 650 °C at three or more different heating rates between 1 and 50 °C/min. The alloy oven and electronics maintain a uniform temperature in the sample crucible with a standard error of ±1 °C. The organic components generated (i.e., S_2 components) during this nonisothermal heating are vaporized as a result of the low near-atmospheric pressures in the oven and are swept by a He carrier gas into a flame ionization detector (FID). The FID electronic response is calibrated to a hydrocarbon standard from which a quantitative yield is determined for the S_2 component.

Assuming the yield curves generated at the different heating rates (Fig. 13a) are a composite of parallel, first-order reactions with a common frequency factor, a discrete distribution of activation energies with a single frequency factor that best describes the yield curves can be computed by an iterative series of nonlinear regression calculations. This computation assigns a portion (x_i) of the overall yield to each prescribed activation-energy increment (E_{ai}). Typically, 1-kcal/mol increments are prescribed between 40 and 70 kcal/mol, and the frequency factor is unconstrained (Fig. 13b). The curve-fitting computations were made with the Kinetics2000 program. Specifics on this curve-fitting procedure and its development are given in Burnham and Braun (1999) and Schenk et al. (1997). As shown in Fig. 13a, the calculated S_2-generation rates for the different heating rates are in good agreement with the observed yield curves. However, the overall quantity of S_2 generated (area under yield curves) decreases significantly with decreasing heating rate. Evans and Campbell (1979) have reported a similar observation in open-system retorting of oil shale, and attribute the decrease to an increase in char formation with decreasing heating rate.

2.2.2. *Derived parameters*

The resulting discrete activation energies, portion of reaction, and overall frequency factor are given in Table 5 (e.g., Fig. 13b). The activation energy at the maximum portion (x_i) of the overall yield varies from 51 kcal/mol for the Green River sample to 57 kcal/mol for the Monterey sample. The breadth of the distributions shows considerable variation with 75% of the overall yield being described by 8 kcal/mol increments for the Monterey sample and only 1 kcal/mol increment for the Green River sample. Phosphoria, Woodford, and New Albany samples have more than 75% of their overall yield described by 4 kcal/mol increments. More than 85% of the overall yield is described by activation energies between 49 and 59 kcal/mol. The weighted mean activation energies also have a narrow range between 51.1 and 55.1 kcal/mol (Table 5). The single frequency factors assigned to each of these activation-energy distributions range from 4.3×10^{16} h^{-1} for the Green River sample to 2.7×10^{18} h^{-1} for the Monterey sample (Table 5). The observed variations in kinetic parameters derived from open-system pyrolysis show no correlation with organic sulfur content of the kerogen or with other rock and kerogen properties.

2.2.3. *Geological implications*

Fig. 12b shows the curves for S_2 generation for an 80-Ma source rock using each of the open-system kinetic parameters given in Table 5 for this hypothetical average thermal-burial history. At a transformation ratio of 0.50, the yield curves for all six samples occur within a narrow 0.83 km interval. The Monterey sample initially generates the earliest of the samples, but at transformation ratios greater than 0.50, its rate of generation slows relative to the Phosphoria, New Albany,

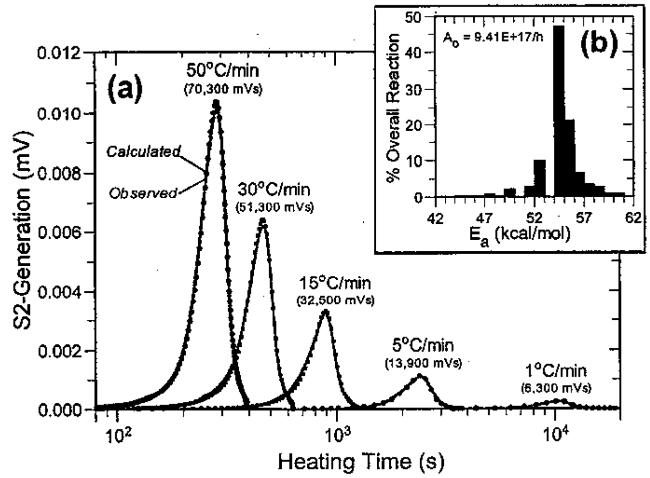

Fig. 13. (a) Observed and calculated S_2-generation versus time for Woodford sample (WD-5) at five different heating rates. The area under each heating-rate curve is given in parentheses (mVs). (b) Activation-energy distribution and single frequency factor determined by nonlinear regression analysis for calculated S_2-generation curves at five heating rates.

Table 5
Nonisothermal open-system pyrolysis kinetic parameters[a]

Sample no.	MR-83	P-64	AS-33	WD-5	931026–3	930923–8
A_o (1/h)	2.69E+18	8.00E+16	1.422E+18	9.41E+17	1.32E+17	4.32E+16
E_{ai} (kcal/mol)	x_i	x_i	x_i	x_i	x_i	x_i
41.0	0.0000	0.0007	0.0000	0.0000	0.0000	0.0000
42.0	0.0000	0.0013	0.0000	0.0002	0.0004	0.0000
43.0	0.0024	0.0027	0.0000	0.0017	0.0008	0.0000
44.0	0.0055	0.0037	0.0000	0.0000	0.0029	0.0018
45.0	0.0090	0.0025	0.0000	0.0024	0.0006	0.0044
46.0	0.0136	0.0074	0.0005	0.0023	0.0059	0.0000
47.0	0.0179	0.0028	0.0000	0.0021	0.0028	0.0284
48.0	0.0337	0.0242	0.0021	0.0079	0.0000	0.0421
49.0	0.0392	**0.1169**	0.0026	0.0026	0.0000	0.0000
50.0	**0.0558**	**0.2311**	0.0147	0.0217	0.0850	0.0000
51.0	**0.0722**	**0.3101**	0.0000	0.0000	**0.0837**	**0.8198**
52.0	**0.0834**	**0.1209**	0.0000	0.0287	**0.4877**	0.0000
53.0	**0.1000**	0.0966	0.0000	0.0988	**0.1715**	0.0702
54.0	**0.0994**	0.0311	0.0000	0.0000	**0.0891**	0.0021
55.0	**0.1130**	0.0093	**0.4490**	**0.4716**	0.0219	0.0041
56.0	**0.0895**	0.0064	**0.1761**	**0.2121**	0.0322	0.0000
57.0	**0.1270**	0.0138	**0.2244**	**0.0656**	0.0086	0.0000
58.0	**0.0519**	0.0000	0.0154	**0.0349**	0.0000	0.0271
59.0	0.0531	0.0000	0.0732	0.0288	0.0000	0.0000
60.0	0.0034	0.0185	0.0027	0.0099	0.0000	0.0000
61.0	0.0230	0.0000	0.0270	0.0087	0.0000	0.0000
62.0	0.0000	0.0000	0.0000	0.0000	0.0069	0.0000
63.0	0.0000	0.0000	0.0123	0.0000	0.0000	0.0000
64.0	0.0070	0.0000	0.0000	0.0000	0.0000	0.0000
Mean[b] E_a	53.9	53.9	51.1	56.1	55.1	52.3

[a] Bold printed values account for 75% or more of the overall yield, and underlined values denote activation energies representing the greatest portion of the overall yield.

[b] Mean kcal/mol weighted on the basis of portion of overall yield.

and Green River samples. The Alum and Woodford samples consistently have the slowest generation rates throughout the thermal-burial history. These results indicate that variations in the open-system pyrolysis kinetic parameters are not geologically significant, with the extent of S_2 generation varying by only 0.83 km in this hypothetical average thermal-burial history. In addition, all these kinetic parameters determine a broad S_2 generation window ($X = 0.01$–0.99) from a 4.3 km interval for the Green River sample to a 6.1 km interval for the Monterey sample. These broad generation windows and the narrow differences among the depths determined for S_2 generation are typical for determinations based on kinetic parameters derived from nonisothermal open-system pyrolysis. Fig. 14 shows the same characteristic S_2-generation curves for the hypothetical average thermal-burial history with published kinetic parameters derived from open-system pyrolysis on other source-rock samples.

The differences between the kinetic parameters derived from isothermal hydrous and nonisothermal open-system pyrolysis are most apparent by superimposing their generation curves for the hypothetical average thermal-burial history as shown in Fig. 15. Despite the broader oil window determined for the open-system pyrolysis kinetics, their determinations of transformation ratios between 0.25 and 0.75 are similar to those determined for the hydrous pyrolysis kinetics of the Alum and Woodford samples. These two samples contain Type-II kerogen with organic sulfur contents typical of marine source rocks (i.e., atomic $S_{org}/C = 0.02$ to 0.04). The geologically significant differences occur for the marine Type-IIS kerogen with high organic-sulfur contents (atomic $S_{org}/C > 0.04$; Phosphoria and Monterey samples) and for the marine Type-II and lacustrine Type-I kerogen with low organic-sulfur contents (atomic $S_{org}/C < 0.02$; New Albany and Green River samples). According to the generation curves for the hypothetical average thermal-burial history in Fig. 15, kinetic parameters derived by open-system pyrolysis underestimate transformation ratios for source rocks bearing Type-IIS kerogen and overestimate

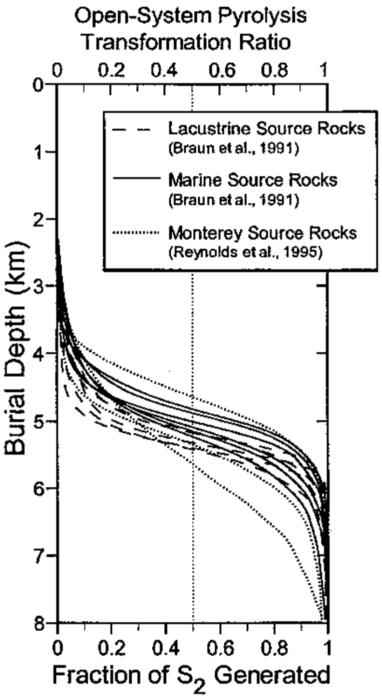

Fig. 14. Generation (transformation) curves in the hypothetical average thermal-burial history using published non-isothermal open-system kinetic parameters for lacustrine (Braun et al., 1991), marine (Braun et al., 1991), and Monterey (Reynolds et al., 1995) source rocks. The hypothetical average thermal-burial history is the same as that used in Fig. 12 with a thermal gradient of 25 °C/km, burial rate of 100m/my, heating rate of 2.5 °C/my, surface temperature of 15 °C, and a 80 Ma source rock.

transformation ratios for source rocks bearing Type-I or low-sulfur Type-II kerogen relative to the transformation ratios determined from kinetic parameters derived by hydrous pyrolysis.

2.3. Natural thermal-burial histories

The question that emerges from this comparison is which kinetic parameters best represent natural oil generation? Is there very little variation in the extent of oil generation from different kerogen types as indicated by kinetic parameters derived from open-system pyrolysis, or is there significant variation in extent of oil generation from high- and low-sulfur kerogen as indicated by kinetic parameters derived from hydrous pyrolysis? Resolving this issue requires applying kinetic parameters derived from both methods to natural thermal-burial histories involving source rocks with high- and low-sulfur kerogen. Although uncertainties in natural thermal-burial histories can result in equivocal evaluations, the high certainty of the thermal-burial histories from the Zagros and Uinta basins used in this study provide definitive assessments of the kinetic parameters.

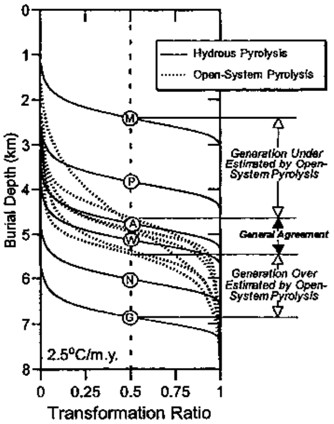

Fig. 15. Generation curves determined in hypothetical average thermal-burial history by open-system pyrolysis (Fig. 12b) superimposed on those determined by hydrous pyrolysis (Fig. 12a; M = Monterey, P = Phosphoria, A = Alum, W = Woodford, N = New Albany, and G = Green River). The hypothetical average thermal-burial history is the same as that used in Fig. 12 with a thermal gradient of 25 °C/km, burial rate of 100m/my, heating rate of 2.5 °C/my, surface temperature of 15 °C, and an 80 Ma source rock.

2.3.1. Kirkuk 109, Zagros Basin, Iraq

The Kirkuk 109 well is at the southeast end of the Kirkuk field in the Zagros basin of northern Iraq. Oils in this field and the basin have high-sulfur contents and are sourced primarily from organic-rich marlstones and limestones in the Naokelekan and Sargelu formations (Late and Middle Jurassic age, respectively; Alsharhan and Nairn, 1997, pp. 705–710). The thermal-burial history of the Kirkuk 109 well is given in Table 6. Erosional events, thermal gradients, and surface temperatures are based on the modeling efforts of Pitman et al. (2000) and Steinshouer et al. (2001). No samples of these source rocks were available to pyrolyze for direct determination of kinetic parameters or to determine organic sulfur contents of kerogen for indirect determination of kinetic parameters (Fig. 11). As suggested by Hunt et al. (1991), an alternative method, using the sulfur content of the oils, was employed with the sulfur/API-gravity relationship proposed by Orr (2001). Fig. 16 shows that the sulfur versus API gravity plot of Iraqi oils indicate that Type-IIS kerogen is the prevalent source, which is consistent with the carbonate character of the Naokelekan and Sargelu formations. The scatter in this plot makes it difficult to determine whether the Type-IIS kerogen is similar to the moderate high-sulfur Type-IIS of the Phosphoria sample (P-64) or the extreme high-sulfur Type-IIS of the Monterey sample (MR-83). As a conservative estimate in this comparative

Table 6
Burial histories used to compare generation predictions based on kinetic parameters derived from isothermal hydrous pyrolysis and nonisothermal open-system pyrolysis[a]

Events	Naokelekan Fm. Zagros Basin, Iraq Kirkuk 109 Well		Green River Fm. Uinta Basin, Utah Brotherson 1-11-B4	
	Time unit (Ma)	Thickness (m)	Time unit (Ma)	Thickness (m)
1	0.0–5.2	−1917	0.0–10.0	−1796.0
2	5.2–10.2	2163.0	10.0–20.0	0.0
3	10.2–16.2	389.0	20.0–37.0	3473.5
4	16.2–25.2	109.0	37.0–43.0	762.5
5	25.2–36.0	243.0	43.0–45.0	30.5
6	36.0–49.0	192.0	45.0–53.0	854.0
7	49.0–66.5	231.0	53.0–54.0	30.5
8	66.5–68.0	−18.6	54.0–58.3	854.0
9	68.0–84.0	217.0	**58.3–66.0**	**854.0**
10	84.0–92.0	79.0		
11	92.0–96.0	211.0		
12	96.0–108.0	415.0		
13	108.0–131.0	309.0		
14	131.0–151.0	49.0		
15	**151.0–157.0**	**305.0**		
Therm. gradient (°C/km)	22.5		25.0	
Surface temp. (°C)	25.0		10.0	

[a] Values for modeled source-rock interval are in bold print.

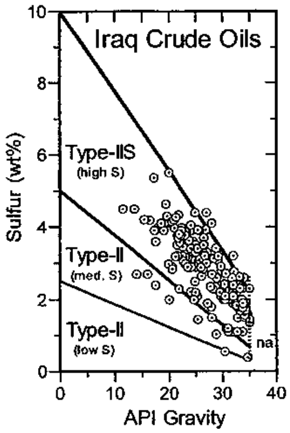

Fig. 16. Plot of sulfur versus API gravity of Iraq crude oils (Al-Gailani et al., 1998) and classification of source kerogen by Orr (2001).

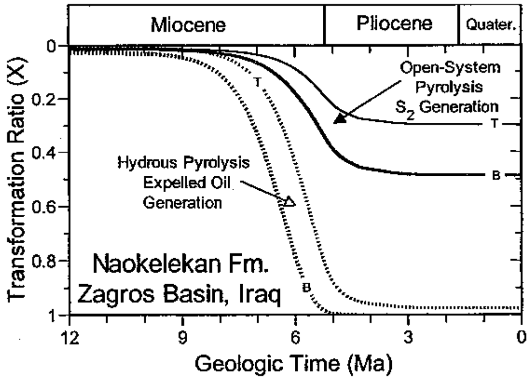

Fig. 17. Generation curves determined for the thermal-burial history of the Naokelekan source rock (T = top and B = base) in the Kirkuk 109 well using kinetic parameters derived from hydrous pyrolysis (dashed lines) and open-system pyrolysis (solid lines).

study, the kinetic parameters for the moderate high-sulfur Type-IIS of the Phosphoria sample were applied to the thermal-burial history.

Determined generation curves through geologic time are shown in Fig. 17 for the Kirkuk 109 thermal-burial history. Kinetic parameters derived from hydrous pyrolysis show that generation of an expelled oil commenced ($X = 0.01$) at approximately 10 Ma and is currently (i.e., $t = 0$ Ma) at the end of expelled-oil generation with a transformation ratio of 0.98. Kinetic parameters derived from open-system pyrolysis also show that S_2 generation commences ($X = 0.01$) at approximately 10 Ma, but is currently (i.e., $t = 0$ Ma) still in the process of S_2 generation with a transformation ratio of only 0.30. Rock-Eval analyses purchased from Petroleum Geological Analysis Ltd (2000) show that immature source rock samples from the Naokelekan and Sargalu formations of northern Iraq have hydrogen indices (HI) ranging between 619 and 790 mg/g TOC for rocks with TOC values greater than 3 wt.%.

Rock-Eval analyses of a core sample from the top of the Naokelekan Fm. in the Kirkuk 109 well had a TOC of 3.0 wt.% and an HI of 69 mg/g TOC. These results indicate that the Naokelekan is obviously at the end of oil generation, which is in good agreement with the determination made with the kinetic parameters derived from hydrous pyrolysis. The determined curve based on kinetic parameters derived from open-system pyrolysis significantly underestimates the observed extent of oil generation. Adverse consequences could result from this underestimation of oil generation because some exploration strategies in this basin have been based on the concept that oil accumulations are a result of vertical oil migration up faults from underlying mature source rock (Christian, pers. commun.).

2.3.2. *Brotherson 1-11-B4, Uinta Basin, UT*

The Brotherson 1-11-B4 (Shell) well is one of the deeper penetrations in the Altamont/Bluebell trend of the Uinta basin, Utah. The highly paraffinic and low-sulfur oils from this area have been sourced by organic-rich lacustrine marlstones in the basal Green River Formation (Ruble et al., 2001). Oil reservoirs also occur within the basal Green River Formation, and their overpressuring is attributed to active oil generation from the associated source rocks (Bredehoeft et al., 1994; McPherson, 1996). Oils within this section show compositional variations with depth (Lucas and Drexler, 1975; Montgomery and Morgan, 1998), which are attributed to differences in the thermal maturities at which the oils were generated (Ruble et al., 2001). The thermal-burial history of this well is given in Table 6 for the basal Green River Fm. (i.e., lower black shale facies). Eroded section, thermal gradients, and surface temperatures are based on modeling efforts of Ruble et al. (2001) and Sweeny et al. (1987). The Green River sample used in this study (930923–8) to derive kinetic parameters is from an outcrop updip from this well and is considered to be representative of the subsurface source rocks.

Determined generation curves through geologic time are shown in Fig. 18 for the thermal-burial history of the lower basal Green River Fm. in the Brotherson 1-11-B4 well. Kinetic parameters derived from hydrous pyrolysis show that generation of expelled oil commenced ($X=0.01$) at approximately 25 Ma and that the entire modeled section is currently (i.e., $t=0$ Ma) generating expelled oil with transformation ratios (X) from 0.08 to 0.96. Kinetic parameters derived from open-system pyrolysis show that S_2 generation commences ($X=0.01$) at approximately 40 Ma, and the entire modeled section completed S_2 generation ($X=0.98$) by 18 Ma. As discussed by Ruble et al. (2001), oil generation determined by kinetic parameters derived from hydrous pyrolysis concur with the interpretations that overpressuring results from active oil generation and that compositional variations in oils with reservoir depth are related to thermal maturity within the section. Conversely, kinetic parameters derived from open-system pyrolysis do not agree with these observations that oil generation (i.e., S_2 generation) has been essentially complete for the entire basal Green River Fm. for the last 18 my. Past modeling studies based on kinetic parameters from open-system pyrolysis have had to drastically adjust thermal-burial histories and rock properties without geological support to obtain marginal agreement with observed overpressuring (e.g., Bredehoeft et al., 1994; McPherson, 1996).

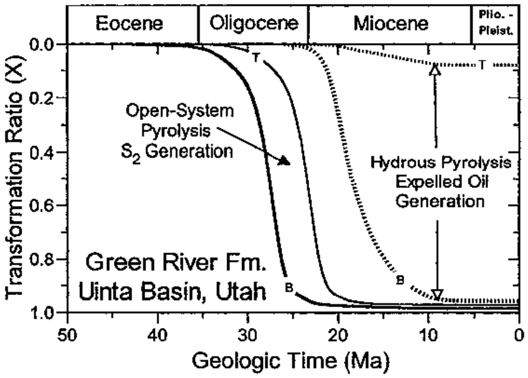

Fig. 18. Generation curves determined for the thermal-burial history of the Basal Green River source rock (T = top and B = base) in the Brotherson 1-11-B4 (Shell) well using kinetic parameters derived from hydrous pyrolysis (dashed lines) and open-system pyrolysis (solid lines).

3. Discussion

The experimental data and natural thermal-burial histories presented in this study indicate that kinetic parameters derived from open-system pyrolysis underestimate oil generation for marine source rocks with Type-IIS kerogen and overestimate oil generation for lacustrine source rocks with Type-I kerogen. In trying to understand these differences, it is important to consider differences between these two approaches with respect to pyrolysis conditions, generated products, and reaction mechanisms.

3.1. *Pyrolysis conditions*

The pyrolysis conditions employed by hydrous and open-system pyrolysis are significantly different with respect to temperature, pressure and time as shown in Fig. 19. Compared with the conditions under which natural oil generation occurs, the conditions of open-system pyrolysis are the most deviant, with low near-atmospheric pressures and high temperatures. Crude oil

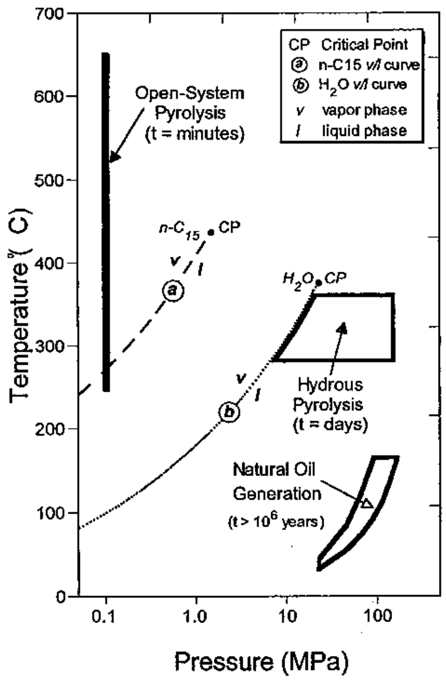

Fig. 19. Temperature-pressure plot showing conditions employed by open-system pyrolysis, hydrous pyrolysis, and natural oil generation relative to the vapor-liquid (**v/l**) phase curves and critical points (**CP**) for *n*-pentadecane (**a**) and water (**b**).

and water occur as vapor under these conditions (Fig. 19), which would only exist locally in the subsurface where igneous intrusions contact source rock at shallow depths. Liquid H_2O is ubiquitous in subsurface voids, vugs, pores, inclusions, and fractures, with the exception of local occurrences of crude oil or natural gas. Hydrous-pyrolysis conditions simulate this natural condition by having sufficient water in the reactor to ensure the source rock samples are submerged in liquid H_2O throughout the experiments (Lewan, 1993). The liquid H_2O surrounding the submerged gravel-sized source rock only serves to maintain liquid H_2O in the rock pores and dissolved H_2O in the impregnating bitumen of the rock (Lewan, 1985, 1997). No significant reactions take place in the liquid H_2O surrounding the gravel-sized source rock. As discussed by Lewan (1997), the dissolved H_2O in the bitumen is critical in experimental and natural oil generation as a source of hydrogen and in the development of expelled (immiscible) oil.

This expelled oil is generated at significantly lower temperatures (300–360 °C) than S_2 generation by open-system pyrolysis (420–500 °C). The temperature gap between hydrous pyrolysis and natural oil generation (i.e., 150–200 °C) is inescapable because of the kinetic controls on oil generation. As an example, reducing the isothermal temperature to 250 °C to attain a transformation ratio of 0.99 would require conducting an experiment for 51 years based on the kinetic parameters for the Woodford Shale sample. The advantage of using higher temperatures in open-system pyrolysis is that experimental times are typically within tens of minutes, as opposed to the tens of hours or days for hydrous pyrolysis. However, rate constants determined by open-system pyrolysis must be extrapolated with the Arrhenius expression over a wider temperature range to subsurface temperatures (~75 to 150 °C) than those determined by hydrous pyrolysis. The major assumption in these extrapolations is that the same reactions and mechanisms that are rate controlling at the higher experimental temperatures remain rate controlling at the lower natural subsurface temperatures.

Open-system pyrolysis has been considered to be more like natural oil generation in that generated products are free to leave the source rock as it continues to thermally mature. However, heating rates employed by open-system pyrolysis are 12 orders of magnitude faster (i.e., 25 °C/min) than those experienced by subsiding source rocks in natural thermal-burial histories (i.e., 5×10^{-12}°C/min). It has also been observed that oil yields from open-system pyrolysis diminish as the heating rates decrease (Evans and Campbell, 1979) because char formation by cross-linking reactions become more prevalent than oil formation by thermal-cracking reactions. Lewan (1998a, Fig. 3) showed that extrapolation of this trend to geological heating rates (1–10 °C/my) resulted in essentially little to no oil generation. This indicates that cross-linking reactions would be the dominant pathway if the same reaction pathways of open-system pyrolysis operated in the subsurface. Therefore, if oil yields generated by open-system pyrolysis cannot be extrapolated to geological heating rates, it is questionable whether kinetic parameters for S_2 generation can be extrapolation to geological heating rates.

3.2. Generated products

Differences in pyrolysis conditions between the two methods also directly affects the products they generate. Expelled oils generated in hydrous pyrolysis are the result of the thermal decomposition of bitumen, which is the intermediate thermal product derived from the breaking of weak noncovalent bonds in the kerogen (Lewan, 1997). This intermediate bitumen product has long been recognized in oil-shale retorting and natural maturation (Engler, 1913; McKee and Lyder, 1921; Franks and Goodier, 1922; Louis and Tissot, 1967; Tissot and Welte, 1984, p. 585; Miknis et al., 1987). The volume increase accompanying the generation of this polar-enriched intermediate causes the bitumen to impregnate the existing pores of the source rock (Lewan, 1987). This continuous bitumen network is saturated with dissolved H_2O, which is supplied by the water surrounding the submerged rock. With increasing thermal stress, covalent bonds within the bitumen break and a hydrocarbon-enriched oil is generated. The immiscibility of the generated oil with the water-saturated bitumen and the accompanying volume increase results in the expulsion of the generated oil from the rock. This expulsion mechanism is in agreement with the concept that oil expulsion is a consequence of its generation as originally proposed by Momper (1978). Therefore, the kinetic parameters derived from hydrous pyrolysis are determined on a distinct expelled-oil phase generated from the thermal decomposition of bitumen. Although some molecular transformations occur in the generated expelled oil with increasing extent of reaction, its overall composition with respect to the proportionality of saturates, aromatic and polar components remains essentially constant (Lewan, 1998a; Ruble, 1996).

Open-system pyrolysis does not make the distinction between bitumen generation and immiscible oil generation. As a result, the S_2 product is a composite of polar-enriched bitumen, hydrocarbon-enriched oil, and minor amounts of generated gas (Behar et al., 1997). Lewan (1994) has shown that the sum of extracted bitumen, expelled oil, and generated gas from hydrous pyrolysis at maximum yields is essentially the same as the sum of S_1 and S_2 products from open-system pyrolysis of the original unheated rock. This finding agrees with the observation that ~60 wt.% of the S_2 product from open-system pyrolysis is composed of polars (i.e., NSOs; Behar et al., 1997). Inclusion of this large proportion of bitumen and to a lesser extent the generated gas in the S_2 product, explains the broad oil window determined by open-system pyrolysis and the need for a distribution of activation energies. In addition, bitumen generation is not a significant rate-controlling step, and its overwhelming mass (i.e., ~60 wt.%) in the S_2 product may also account for the narrow range of variability in S_2 generation determined for different kerogen types by the kinetic parameters derived from open-system pyrolysis (Fig. 12b).

3.3. Reaction mechanisms

Although earlier investigators had hopes that nonisothermal derivation of kinetic parameters would help expedite chemical-kinetic studies (Freeman and Carroll, 1958; Coats and Redfern, 1964, Jüntgen, 1964; Ozawa, 1965; Friedman, 1965), it became obvious with experience that this approach was only appropriate for interpolation of data in engineering applications (Golikeri and Luss, 1972; Zsako, 1973; Wendlandt, 1974; Tang and Chaudhri, 1980; Rajeshwar and Dubow, 1982). Based on work by Antony and Howard (1976), Campbell et al. (1980) can be credited with laying the groundwork for the use of a distribution of activation energies and one frequency factor to describe the kinetics of oil shale retorting. Campbell et al. (1980) clearly state that this approach is intended for engineering calculations and should not be over interpreted in terms of the fundamental chemistry of a system. Reviews by Schneider (1993) and Brown (1997) reiterate this advisory by concluding that kinetic parameters derived from nonisothermal data cannot be used to determine reaction mechanisms or predict reactions beyond their experimental conditions. Contrary to the later advisory, kinetic parameters derived from nonisothermal open-system pyrolysis data have been extended to determine oil generation at lower temperatures and longer times. However, in accordance with the former advisory, no attempts have been made to attribute specific bond cleavages or reaction mechanisms to the individual activation energies in the distributions used to describe S_2 generation.

As originally presented by Arrhenius (1889), kinetic parameters determined with isothermal data can be used to interpret reaction mechanisms. Activation energies for oil generation derived from isothermal hydrous-pyrolysis experiments are indicative of covalent bond cleavages in organic molecules. Their correlation with organic sulfur content of immature kerogen (Fig. 11) is explained by early-formation of sulfur-radical initiators (Lewan, 1998b). Experiments with model compounds showed that rates of thermal cracking were increased significantly with moderate increases in sulfur-radical generators. The greater the amount of sulfide linkages in an immature kerogen, the greater the amount of initiating free radicals at lower thermal stresses, and the faster the rate of oil generation. As shown in this study (Tables 1 and 5) and a study by Reynolds et al. (1995), kinetic parameters derived from open-system pyrolysis do not show early oil generation (Fig. 14) or correlate with organic-sulfur contents of immature kerogen. Lewan (1998b) suggests that in open-system pyrolysis the early-formed radical initiators are removed too quickly to allow them to fully initiate reactions with the organic matter in the heated rock.

Another mechanistic concern is that bond selectivity by radical initiators can be significantly reduced at the higher temperatures used in open-system pyrolysis, and minimize the importance of selective cleavage of weaker-bonds that are rate controlling at lower temperatures. As an example, the relative susceptibility for chlorine radicals to preferentially abstract hydrogen from tertiary positions than stronger primary positions on a hydrocarbon at 100 °C (1:7.0) decreases by almost a factor of 3 at 600 °C (i.e., 1:2.6; March, 1985, p. 614). Therefore, the rate of product generation at the higher temperatures of open-system pyrolysis may not be controlled by the selective cleavage of weaker bonds, but rather by indiscriminate cleavage of different bond types with various bond strengths. This indiscriminate cleavage of various bond types at higher temperatures would explain the broad distribution of activation energies and the minimal differences in overall rates of oil generation from the different kerogen types as determined by kinetic parameters derived from open-system pyrolysis.

Although pyrolysis conditions, products, and mechanisms can explain the observed differences in kinetic parameters between open-system pyrolysis and hydrous pyrolysis, it remains to be determined why generation of expelled oil in hydrous pyrolysis can be described by a single activation energy and frequency factor. The large number of hydrocarbons envisioned in crude oil nurtures the idea that such a mixture of hydrocarbons must be the result of a complex process. Actually, 46 and 60% of the intensely studied Ponca City oil consists of only 169 and 295 individual compounds, respectively (Tissot and Welte, 1984, p. 377; Hunt, 1996, p. 38). This does represent a large number of hydrocarbons, but the cleaved covalent bonds responsible for the release of these individual hydrocarbons need not be significantly different. Radical sites most conducive to initiate thermal cracking are likely to be confined to aliphatic moieties because aromatic hydrogen is far more resistant to abstraction. Hydrogen in a tertiary position of a carbon is the most susceptible to abstraction with dissociation energies lower than hydrogen in a secondary position, which has lower dissociation energies than hydrogen in a primary position. Carbon-carbon bonds involving a carbon bound to easily abstracted hydrogen have correspondingly low bond dissociation energies, and are the most susceptible to thermal cracking or cross linking. If abstraction of secondary hydrogen was important in oil generation, aliphatic moieties would be totally reduced to methane, and ethane, which is not the case. Therefore, the carbon-carbon bonds most likely to control the cracking of aliphatic moieties in bitumen are those associated with easily abstractable hydrogen like tertiary hydrogen, secondary hydrogen bound to carbon in the β-position of an alkyl substituent on an arene, and allylic hydrogen (Benson, 1965).

This bond-strength hierarchy is demonstrated by the carbon–carbon bond energies for various C_{19} aliphatic moieties modeled by Claxton et al. (1993). A summary of their results in Table 7 shows that the carbon–carbon bonds associated with a tertiary-hydrogen or β-positioned alkyl carbon of an arene are the weaker bond types. These two bond types have comparably low bond energies that are within a 3.5-kcal/mol range. This narrow range suggests that a single overall activation energy and frequency factor as derived from hydrous pyrolysis is theoretically reasonable. Therefore, the cracking of aliphatic moieties in bitumen to generate oil may be limited to a few carbon–carbon bond types with comparably low bond strengths, as indicated by the single activation energy and frequency factor derived from hydrous pyrolysis. More rigorous studies are obviously needed to further quantify these reaction mechanisms, but the main thesis here is that oil generation may not be as complex as commonly perceived.

4. Conclusions

Kinetic parameters derived from open-system pyrolysis do not determine geologically significant differences between source rocks bearing different kerogen types. Modeled S_2-generation curves calculated by these kinetic parameters for six source rocks bearing different oil-prone kerogen types (i.e., Type-I,-II, and -IIS) give broad oil windows extending over a 4.4-km interval in a hypothetical average thermal-burial history (i.e., 2.5 °C/my). In addition, the determined 0.50 transformation ratio for the six source rocks is within a 0.83-km thick

Table 7
Modeled mean bond energies (kcal/mol) for aliphatic chains with 19 carbon atoms (Claxton et al., 1993)[a]

Molecule name	Primary (–CH_3)	Secondary (–CH_2–)	Tertiary (=CH–)	β-Akyl-aro[b] (–C–Ar)	α-Akyl-aro[b] (–Ar)
n-Nonadecane	94.8 (0.0)	88.7 (0.3)	–	–	–
Di-*n*-nonylsulfide	94.7 (0.0)	88.8 (0.8)	–	–	–
Di-*n*-nonylether	95.0 (0.0)	88.9 (0.8)	–	–	–
Pristane	87.3 (0.1)	86.9 (0.5)	81.4 (0.8)	–	–
n-Pentadecylcyclohexane	95.5 (0.0)	88.5 (0.3)	82.2 (0.0)	–	–
n-Octadeclbenzene	94.2 (0.0)	88.5 (0.3)	–	81.1 (0.0)	96.2 (0.0)
2-*n*-Octadecylpyridine	95.5 (0.0)	88.7 (0.4)	–	84.6 (0.0)	99.8 (0.0)
2-*n*-Octadecylthiophene	95.2 (0.0)	89.0 (0.3)	–	82.7 (0.0)	111.2 (0.0)
2-*n*-Octadecylpyrrole	95.1 (0.0)	88.7 (0.2)	–	84.2 (0.0)	117.8 (0.0)
2-*n*-Octadecylpyrrole	95.6 (0.0)	88.5 (0.6)	–	81.9 (0.0)	118.0 (0.0)
Total Mean (±)	93.8 (3.0)	88.6 (0.6)	**81.5 (0.8)**	**82.9 (1.5)**	108.6 (10.1)

[a] Standard deviations given in parentheses.

[b] Ar and aro = aromatic ring.

interval. These broad and uniform determinations for S_2 generation indicate that kerogen types, especially their organic-sulfur content, do not have an important role in oil generation. Conversely, kinetic parameters derived from hydrous pyrolysis do determine geologically significant differences between source rocks bearing different kerogen types. Expelled-oil generation curves calculated by these kinetic parameters for the same six source rocks gave narrower oil windows extending over only a 1.5- to 1.7-km interval in a hypothetical average thermal-burial history (i.e., 2.5 °C/my). In addition, the determined 0.50 transformation ratio for the six source rocks varied with their organic-sulfur content of the original kerogen over a 4.5-km thick interval.

Relative to determinations based on kinetic parameters derived by hydrous pyrolysis, kinetic parameters derived by open-system pyrolysis underestimate transformation ratios for source rocks bearing Type-IIS kerogen, and overestimate transformation ratios for source rocks bearing Type-I kerogen. Two well-constrained natural thermal-burial histories confirm these finding. In the Kirkuk 109 well of the Zagros basin in Iraq, geochemical data are in agreement with kinetic parameters derived by hydrous pyrolysis that the Type-IIS kerogen in the Naokelekan source rock had nearly completed oil generation with a transformation ratio of 0.97. Conversely, kinetic parameters derived by open-system pyrolysis determined that this source rock was only starting oil generation with a transformation ratio of 0.30. In the Brotherson 1-11-B4 well of the Uinta basin in Utah, reservoir oils through the Green River Formation (Type-I kerogen) show increased maturity with depth and over pressuring as a result of current oil generation. These observations are in agreement with the current varying extent of oil generation from a transformation ratio of 0.07 near the top of the section to 0.97 at the base as determined by hydrous pyrolysis kinetic parameters. Conversely, open-system kinetic parameters determine that this entire source rock section completed oil generation 20 Ma with transformation ratios greater than 0.99.

The inability of kinetic parameters derived from open-system pyrolysis to determine early oil generation from Type-IIS kerogen and late oil generation from Type-I kerogen are attributed to non-isothermal heating at high-temperatures and low-pressures. These conditions result in the inclusion of bitumen polar components in the open-system product, which are readily released from the breakdown of weak non-covalent bonds within the kerogen. This polar component constitutes ~60 wt.% of the S_2 product, and its inclusion in deriving kinetic parameters results in broad activation-energy distributions that do not differentiate significant rate differences among the kerogen types. Homogenization of oil generation rates for the different kerogen types by open-system pyrolysis may also be the related to the removal of free-radical initiators before they initiate reactions within the bitumen or to indiscriminate cleavage of various bond types at the high temperatures employed.

The intuitive concept that the multitude of hydrocarbons in oil indicates they were generated by a complex process may be overstated. The Arrhenius relationships derived from isothermal hydrous-pyrolysis experiments indicate that generation of expelled oil can be described by a single overall activation energy and frequency factor. This observation suggests that specific weak carbon–carbon bonds with similar bond dissociation energies are responsible for oil generation. Variations in the rates at which these specific bonds are cleaved are dependent in part by the concentration of sulfur-radical initiators. Therefore, the multitude of hydrocarbons in oil may be caused by the selectivity of free-radical initiators for specific weak bonds within the bitumen of a source rock, rather than the cleavage of a multitude of bond types involving a complex process.

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