

Simple kinetic models of petroleum formation. Part II: oil–gas cracking

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Kinetic schemes describing oil–gas cracking are a required component of models which predict the masses, compositions and phases of petroleum expelled from source rocks; an additional application is in predicting the temperature zone over which reservoir oil deposits will be degraded to gas. This simple first-order kinetic model, calibrated on closed-system laboratory pyrolysis of 16 different source rock samples, describes the bulk conversion of oil (C_{6+} molecular range) to gas (C_{1-5} molecular range). Cracking rates vary markedly between samples, depending on the saturate to aromatic ratio of the generated oil. The initial hydrogen index (HI^0) of the sample, taken as an indirect measure of the saturate to aromatic ratio of the oil it generates, correlates strongly with optimized rate constants for oil cracking in individual samples. Thus cracking rates are predictable using a simple, routinely performed geochemical screening measurement. Source rocks with high HI^0 tend to generate saturate-rich oils with a high mean activation energy and a tight distribution of bond energies, which crack relatively slowly over a high but relatively narrow temperature range. Source rocks with low HI^0 generate aromatic-rich oils with a low mean activation energy and a broad distribution of bond energies, which crack relatively rapidly over a lower, but relatively wide, temperature range. This is an important contributing factor in the observed gas-proneness of 'type III' source rocks with low HI^0 . The projected cracking window (defined limits at 10–90% of initial oil degraded; reference heating rate 2°C Ma^{-1}) varies from 155 to 205°C in very high quality source rocks ($HI^0 > 600 \text{ mg g}^{-1}$) to 115–205°C in very poor quality source rocks ($HI^0 50 \text{ mg g}^{-1}$). An order of magnitude increase (decrease) in heating rate elevates (depresses) these temperature windows by ca. 15°C. The extrapolations to the geological subsurface are subject to a confidence limit no better than 7°C.

Extrapolation to the reservoir environment requires caution because kerogen, an important potential catalyst and hydrogen donor allowing 100% cracking efficiency in the source rock, is absent. Furthermore, fractionation during expulsion causes saturate enrichment of expelled, ultimately reservoir oils. Thus in-reservoir cracking should be at least as slow as cracking in good quality source rocks, and coke or pyrobitumen formation is needed to conserve the hydrogen balance. A case history based on deep petroleum pools of the UK Central North Sea confirms these projections, demonstrating no positive evidence of significant in-reservoir cracking at temperatures as high as 174°C, and perhaps even 195°C. Previous studies have overestimated the importance of in-reservoir cracking. Future studies aiming to predict petroleum composition in traps should concentrate on understanding the charge composition expelled from the kitchen.

Keywords: kinetic models; oil–gas cracking; petroleum formation

This paper is the second in a trilogy describing a simple methodology for modelling potential charges delivered by petroleum source rocks heated in the geological subsurface. Three main processes control the masses and compositions of petroleum charges (see Figure 1,

Pepper and Corvi, this issue). As we will discuss them, the processes are arranged in sequential order, which also turns out to be the order of decreasing understanding and consensus among petroleum geochemists: Part I of this series (Pepper and Corvi, this issue) dealt only with the first process, describing a kinetic model for the *generation* of petroleum (oil and gas) from sedimentary organic matter. This second paper will document our current understanding of the quantitation of oil cracking. Part III (Pepper and Corvi, in press) describes the

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open-system modelling of these processes, when coupled with a previously described model of petroleum expulsion (Pepper, 1989; 1991).

These modules form the basis of a model of petroleum generation and expulsion used within BP Exploration for the last five years, superseding earlier models described by Cooles *et al.* (1986), Quigley *et al.* (1987), Quigley and Mackenzie (1988) and Mackenzie and Quigley (1988).

There remain relatively few published kinetic schemes for oil cracking of use in geochemical modelling. The petroleum industry still tends to rely on empirically derived concepts ('oil deadline' or 'phase-out') based on compilations of oil and gas pool occurrence; such compilations often confuse the issue because they potentially attribute the effects of charge compositional variation to in-reservoir cracking processes.

Determining rates of oil to gas cracking in the geological subsurface poses the most difficult of kinetic calibration problems facing the geochemist. Because the petroleum source rock and reservoir are open systems, it is never possible to calibrate directly theoretical predictions versus observation. Thus cautious use must be made of laboratory experiments in determining rate constants for the process. In this important respect, calibration of the oil to gas cracking process differs from calibration of oil and gas generation from kerogen. Kerogen breakdown may be monitored by measuring differences between initial and residual potentials, which allows manipulation of field data to provide input data for the calibration (Ungerer, 1984; Cooles *et al.*, 1986; Quigley *et al.*, 1987; Mackenzie and Quigley, 1988; Part I).

Previous work

A literature review (Tables 1 and 2) reveals a large and varied body of experimental data on the thermal cracking of oils. However, relatively few data are of immediate application in petroleum geochemistry. This is because these studies are strongly biased towards heavy oil and bitumen cracking, which is of economic importance in the exploitation of this enormous oil resource (Table 1a; McNab *et al.*, 1952; Henderson and Weber, 1965; Rogers *et al.*, 1974; Braun and Rothman, 1975; Connan *et al.*, 1975; Hayashitani *et al.*, 1978; Audibert and Monin, 1985; Fassihi *et al.*, 1985; Phillips *et al.*, 1985; Abu-Khamsin *et al.*, 1987; Lin *et al.*, 1987; Monin and Audibert, 1987).

Table 1b contains the results of investigations of oil in the 10–25° API gravity range (McNab *et al.*, 1952; Henderson and Weber, 1965; Phillips *et al.*, 1985; Lin *et al.*, 1987), but most data relevant to understanding 'conventional' oil cracking have come from purpose-designed petroleum geochemical experiments (Table 2). These have involved studies of cracking both outside (Table 2a: Ungerer *et al.*, 1988; Behar *et al.*, 1988; Burnham and Braun, 1990; Burnham and Sweeney, 1991) and within (Table 2b; Quigley *et al.*, 1987; see also Quigley and Mackenzie, 1988 and Mackenzie and Quigley, 1988) the source rock medium.

Others have studied relatively simple compounds or compound mixtures, which provide an opportunity to

Table 1 Various published oil cracking kinetic parameters. Single activation energy model used in all instances

Reactant	Product	A (s ⁻¹)	E _{mean} (kJ mol ⁻¹)	Reference
Part a: asphalt, heavy oil and bitumen cracking				
Asphaltene	Coke	1.160 × 10 ¹³	174.3	1A
Asphalt	Heavy oil	6.37 × 10 ¹⁸	239.0	1A
Heavy oil	Asphalt	5.61 × 10 ¹⁶	215.8	1A
Heavy oil	Distillate	5.22 × 10 ¹³	180.9	1A
Distillate	Heavy oil	2.04 × 10 ¹³	180.9	1A
Asphaltene	Coke	1.16 × 10 ¹³	174.4	1B
Asphalt	Heavy oil	4.99 × 10 ¹⁹	250.3	1B
Asphaltene	Gas	1.41 × 10 ¹⁶	194.6	1B
Heavy oil	Asphalt	1.91 × 10 ¹⁷	222.1	1B
Heavy oil	Middle oil	4.04 × 10 ¹⁴	192.1	1B
Bitumen		1.00 × 10 ¹⁷	224.4	2
Bitumen		1.36 × 10 ¹⁵	205.0	3
Bitumen		5.00 × 10 ¹⁴	188.5	4
Bitumen	Heavy oil	1.00 × 10 ¹⁸	239.7	5
Heavy oil	Gas	7.20 × 10 ¹³	200.3	5
Oil 'K'	Heavy oil	2.10 × 10 ⁸	119.7	5
Heavy oil 'K'	Gas	1.60 × 10 ⁹	131.9	5
Bitumen	Oil		178.0	6
Part b: 'conventional oil' cracking parameters				
Middle oil	Light oil	3.79 × 10 ¹⁸	230.0	1
9.4 API oil		2.60 × 10 ¹³	182.5	7
12.4 API oil		4.20 × 10 ¹⁴	198.9	7
15.2 API oil		3.00 × 10 ¹⁶	226.1	7
15.5 API oil		4.80 × 10 ¹⁵	205.0	7
16.8 API oil		6.80 × 10 ¹⁷	244.1	7
24.5 API oil		1.00 × 10 ¹⁹	198.9	7
26.5 API oil		1.70 × 10 ¹²	169.6	2
McMurray oil			205.0	3
C ₂₁ alkane			198.0	8
Oil			209.2	9

Key to references: (1) Phillips *et al.*, 1985 (A = model A; B = model B); (2) Lin *et al.*, 1987; (3) McNab *et al.*, 1952; (4) Hayashitani *et al.*, 1978; (5) Fassihi *et al.*, 1985; (6) Braun and Rothman, 1975; (7) Henderson and Weber, 1965; (8) Shimoyama and Johns, 1971; (9) Tissot and Welte, 1984 (based on McNab *et al.*, 1952 and Johns and Shimoyama, 1972)

examine with greater clarity the reaction mechanisms involved (Voge and Good, 1949; Fabuss *et al.*, 1962; Doue and Guiochon, 1968; Shimoyama and Johns, 1971; Ford, 1986; Mango, 1990a; 1990b; 1990c).

When the kinetic parameters *A* (frequency factor) versus *E* (activation energy) from Tables 1 and 2 are cross-plotted (Figure 2), we see that heavy oil/bitumen cracking and 'geochemical' pyrolysis conform to separate *A* versus *E* trends. Wood (1988) and Part I showed that petroleum-forming and related reactions tend to follow a common *A* versus *E* trend, therefore different cracking mechanisms may be operative in the two experimental data sets. We conclude that data from heavy oil and bitumen cracking are of little direct value in understanding the thermal degradation of conventional oils under geological conditions. Thus, despite the potential usefulness of cracking models in understanding expulsion from petroleum source rocks (e.g. Barker, 1988) and the composition of petroleum fluids reseroured at great depth (e.g. Hunt, 1975; Waples, 1987; Zolotov *et al.*, 1987), the volume of relevant published information on oil cracking is fairly small, prompting a recent call for further work in the area (Andresen *et al.*, 1991).

Our experimental approach is similar to that used in a previous kinetic calibration (Quigley *et al.*, 1987; Quigley and Mackenzie, 1988; Mackenzie and Quigley, 1988). The differences are (1) we use substantially

more experimental data (16 sealed capsule pyrolysis data sets) and (2) we seek to elucidate systematic variations in cracking behaviour, rather than to establish simple global rules of thumb. Our ultimate goal was a simple, deterministic approach to predicting variations in oil cracking rates in the geological subsurface.

Basic kinetic scheme of oil cracking

Before proceeding, we stress that our primary objective is to understand the process of oil to gas cracking in the source rock. This highlights an important departure from other experimental techniques where oil to gas conversion is studied in the context of natural or artificial in-reservoir cracking; implications will be discussed later in the paper.

The kinetic scheme we have adopted for oil degradation is directly analogous to that for kerogen degradation (Part I). Oil cracking can be modelled as a first-order chemical reaction, in which the rate of degradation dc/dt is proportional to the concentration c_o of oil

$$dc_o/dt = -k_o C_o \quad (1)$$

The rate constant k is described by the Arrhenius equation

$$k_o = A_o \exp(-E_o/RT) \quad (2)$$

where A is the frequency factor (in s^{-1}), E is the activation energy (in $J mol^{-1}$), R ($8.31441 J mol^{-1} K^{-1}$) is the universal gas constant and T is absolute temperature (K). For a given chemical reaction, A may be conceptually considered to be proportional to the vibrational frequency of the reactant molecules, whereas E is proportional to the bond energy. Incidentally, we recognize that the results of detailed studies by e.g. Rosen (1941), Greensfelder *et al.* (1949) and Fabuss *et al.* (1964) show our assumption of first-order kinetics for oil cracking to be a convenient simplifica-

tion. However, there remains little practical alternative to an assumption of first-order behaviour, as reaction mechanisms involved in cracking of even simple compounds such as ethane and propane are highly complex (Albright *et al.*, 1983). Furthermore, it is important to keep in mind that complex models with large numbers of free variables are of little practical value in the modelling of the petroleum potential of sedimentary basins — an environment of relatively poor knowledge compared with the petroleum refinery or petroleum geochemical laboratory!

Oils are complex mixtures of molecules, some with as few as six carbon atoms, some with 40 or more, belonging to various compound classes: alkanes, aromatics, heteroaromatic compounds, etc. (Bestougeff, 1967; Hunt, 1979; Tissot and Welte, 1984). In principle, knowledge of the specific A and E parameters for each (bond-breaking) oil cracking reaction is required for precise calculation of the extent of oil degradation at a given level of thermal stress. Given our difficulty in describing the mechanisms by which individual oil components crack (above), it is unrealistic to expect that our model should require all these A 's and E 's as input. So, as with the generation of petroleum from kerogen, we simply assume that oil will crack to gas via a manageable series of parallel reactions, which in gross terms reflect the many types of physical and chemical bonds being broken.

Some petroleum geochemical cracking models (Tissot and Welte, 1984; IFP-Beicip MATOIL; Burnham and Sweeney, 1991) have treated oil as a single component degrading according to the kinetic laws of Equations (1) and (2). The discussion above highlighted a fundamental objection to the use of such single activation energy models and the validity of the resulting kinetic parameters (Tables 1 and 2). Early advances in multicomponent modelling were made by McNab *et al.* (1952) and Henderson and Weber (1965), who divided oil into two pseudo-components. Hayashitani *et al.* (1978) followed with three to five component models. As with modelling of kerogen

Table 2 'Geochemical' oil cracking kinetic parameters

Reactant	Product	A (s^{-1})	E_{mean} ($kJ mol^{-1}$)	s_E ($kJ mol^{-1}$)	Reference
Part a: extra-source cracking					
'Type I' oil	Gas + coke	3.00×10^{11}	226.1	*	1
'Type II' oil	Gas + coke	3.00×10^{14}	238.6	*	1
'Type III' oil	Gas + coke	5.50×10^{14}	257.6	*	1
Boscan C_{14+}	†	1.11×10^{14}	239.9	*	2
Boscan C_{6-13}	†	1.11×10^{14}	255.8	*	2
Boscan C_{2-5}	CH_4 + coke	1.11×10^{14}	278.3	*	2
Pertamina C_{14+}	†	6.51×10^{13}	243.3	*	2
Pertamina C_{6-13}	†	6.51×10^{13}	251.6	*	2
Pertamina C_{2-5}	CH_4 + coke	6.51×10^{13}	274.2	*	2
Oil	Gas + coke	1.00×10^{12}	225.9	*	3
Part b: intra-source cracking					
Low mol. wt. oil	Gas	1.00×10^{13}	228	15	4
High mol. wt. oil	Gas	1.00×10^{13}	230	5	4

* Single activation energy model

† Products are coke, C_{6-13} oil, C_{2-5} and CH_4 gases in proportions determined by stoichiometric balance

Key to references: (1) IFP-Beicip MATOIL program; (2) Ungerer *et al.*, 1988; Behar *et al.*, 1988; Forbes *et al.*, 1991; (3) Burnham and Sweeney, 1991; (4) Quigley *et al.*, 1987; Quigley and Mackenzie, 1988; Mackenzie and Quigley, 1988

degradation, more recent increases in computing power and accessibility have allowed increasingly detailed multicomponent cracking models (Fassihi *et al.*, 1985; Phillips *et al.*, 1985; Abu Khamsin *et al.*, 1987; Lin *et al.*, Ungerer *et al.*, 1988; Behar *et al.*, 1988; Forbes *et al.*, 1991). These models effectively describe the interactions between multiple oil compound classes; relative proportions of products are determined by stoichiometric balance. The last three references apply multicomponent models in a petroleum geochemical context.

In such multicomponent models governed by parallel reactions, Equation (1) can be replaced by a system of equations

$$dC_{oi} / dt = -k_{oi} C_{oi} \quad (3)$$

where the subscript *i* denotes the *i*th component within the oil's activation energy distribution. As in all current geochemical kinetic models, the frequency factor *A* is assumed to be the same for all activation energies *E_i*, so that

$$k_{oi} = A_o \exp(-E_{oi} / RT) \quad (4)$$

Oil cracking should therefore be governed by an activation energy distribution, and single activation energy models have effectively been superseded. Remaining differences between published 'petroleum geochemical' oil cracking models concern the allowed distribution of components. The current IFP cracking model (Ungerer *et al.*, 1988; Behar *et al.*, 1988; Forbes *et al.*, 1991) considers degradation of three classes (*C*₁₄₊, *C*₆₋₁₃ and *C*₂₋₅), each with a characteristic *A* and (single) *E* parameter (Table 2); six kinetic parameters are required in total. Ultimate products are methane and coke. Strictly speaking, the *C*₂₋₅ component is classified as gas, so that oil is effectively divided into only two compound classes, described by a total of four kinetic parameters.

Quigley *et al.* (1987), Quigley and Mackenzie (1988) and Mackenzie and Quigley (1988) adopted the method of Pitt (1962) and Anthony and Howard (1976), assuming that the range of activation energies is continuous and can therefore be approximated by a normal or Gaussian distribution. This is reasonable as compound groups considered in multicomponent models can alternatively be viewed as part of a continuum. A Gaussian distribution also offers a computational simplification as it can be described using only two parameters: an *E*_{mean} and a standard deviation *σ_E* about this mean. Obviously, a weakness in any Gaussian model arises if the true activation energy distribution is markedly non-Gaussian in form. Given our current state of knowledge the potential importance of such deviations is hard to quantify.

Our preferred model (below) continues to assume a Gaussian energy distribution, so that calculation of the gas quantities generated by cracking of oil requires knowledge of only three parameters: *A*, *E*_{mean} and *σ_E*, to describe a full parallel suite of oil cracking reactions. For the full mathematical formalism describing the Gaussian energy spectrum, refer to Quigley *et al.* (1987), Quigley and Mackenzie (1988) or Mackenzie and Quigley (1988).

Experimental

Origin of data

The oil and gas content of a naturally matured source rock is determined by the relative rates of generation, cracking and expulsion: the effects of cracking cannot be studied in isolation. Thus we are unable to study oil to gas cracking using data from source rocks matured under natural conditions. Instead, we are forced to study oil cracking in the laboratory and to extrapolate our results to the geological environment.

The dangers of such extrapolations were spelled out in Part I: extrapolation introduces uncertainty in our ability to predict. To minimize such uncertainty we must study the cracking process under the mildest practicable laboratory thermal regime. It is generally agreed that confined and/or hydrous pyrolysis offers a close simulation of natural thermal degradation: reactants and products remain intimately associated; the time involved is relatively long (hours or days), though still geologically insignificant; temperatures involved are lower than bulk flow pyrolysis (300–400°C), though still much higher than in nature; and products resemble natural oils much more closely than do the products of anhydrous bulk flow pyrolysis, which produces substantial amounts of unsaturated hydrocarbons (alkenes) not found in natural oils (Lewan *et al.*, 1979; Monthieux *et al.*, 1986; Bjørøy *et al.*, 1988).

Experimental method

BP's proprietary sealed capsule pyrolysis experimental technique and resulting data were discussed previously in Quigley *et al.* (1987), Quigley and Mackenzie (1988) and Mackenzie and Quigley (1988). The method involves heating of separate aliquots of immature source rock in sealed platinum capsules at 370°C for durations of 1, 2, 4, 8, 16, 32 and 64 hours. Both the concentration and composition of the residual kerogen is monitored using pyrolysis and pyrolysis-GC. At the end of each experiment, the effluent is discharged directly into a gas chromatograph, allowing measurement of its composition (gas to oil ratio, *n*-alkane distribution, etc.).

The 16 data sets used here are a combination of previous sealed capsule pyrolysis studies in addition to experiments commissioned as part of this and subsequent studies (Table 3).

Calculations

Using mass balance techniques, these data were manipulated (using computer spreadsheets) to derive the quantity *ε*, the cumulative mass fraction of oil which has been converted to gas, at any given level of thermal stress. Briefly, the masses of oil and gas generated from kerogen during each experiment are monitored by the difference between the starting and residual kerogen concentrations as described in Part I; the additional quantity of gas derived from oil is then calculated by the difference between the measured mass of oil in the capsule. The result is a set of up to eight experimental *ε* versus time pairs for each source rock.

Optimization procedure for kinetic parameters

Background

We have shown above that the rates of geochemical processes are described using the Arrhenius law [Equation (2)] adapted to a spectrum of activation energies [using the system of equations shown in Equation (4)]. To fully describe the assumed Gaussian activation energy population it is necessary to know both E_{mean} and σ_E , the mean and standard deviation of the assumed normal distribution, in addition to a common frequency factor A .

If a series of data is available for at least two different thermal regimes (e.g. heating rates), optimization procedures can be used to derive a unique solution for A , E_{mean} and σ_E . Constrained by finite resources, we decided that investigation of a large number of different samples (16, each subjected to seven separate heating experiments of duration up to 64 hours) was more important than optimization of a full set of kinetic parameters, requiring a repeat of every experiment under at least one alternative thermal regime.

Provided A can be set to some reasonable value, it is still possible to derive values for E_{mean} and σ_E from time series data gathered at a single temperature. For example, Quigley *et al.* (1987), Quigley and Mackenzie (1988) and Mackenzie and Quigley (1988) chose $A = 10^{13} \text{ s}^{-1}$, whereas Burnham and Sweeney (1991) chose $A = 10^{12} \text{ s}^{-1}$ (Table 2).

We judged that reasonable values for A could be estimated from previous experimental work where A had been derived as a free parameter (Table 2a; Figure 2). Further guidance is provided by the knowledge that parameters A and E co-vary for many geochemical reactions (Wood, 1988; Figure 12 of Part I); oil cracking appears to be no exception (Figure 1). $A = 10^{14} \text{ s}^{-1}$, similar to values obtained by Ungerer *et al.* (1988) and Behar *et al.* (1988), should be appropriate to our experimental results, as previous results gave E_{mean} and σ_E in the ranges 228–230 kJ mol^{-1} and 5–15 kJ mol^{-1} , respectively (Table 2b; Figure 1; Quigley *et al.*, 1987). Having fixed A we proceeded to optimize E_{mean} and σ_E using the proprietary non-linear regression package MINEX, described in Part I.

Results and interpretation

Results from the 16 experiments are summarized in Table 3 (plots of the individual experimental data will be shown later during comparison with predicted trends). An immediate observation is the large variation in cracking rates and resulting kinetic parameters characterizing individual samples in Table 3. Because the objective of our study was to derive a predictive rather than purely empirical description, we set out to investigate potential predictor variables. Later in the paper we investigate the sensitivity of optimized E_{mean} and σ_E to changes in assumed A , and the implications for projection to the subsurface.

Does organofacies control cracking rates?

In Part I, kerogens were grouped into five global organofacies, each characterized by a unique set of kinetic parameters describing the breakdown of oil-

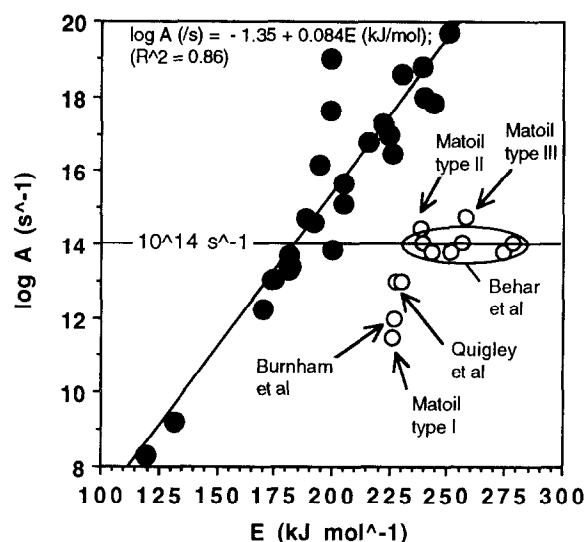


Figure 1 Optimized A versus E from previously published oil cracking experiments (Tables 1 and 2). Data for cracking of heavy oils, tars and bitumens plot on a separate A versus E trend to parameters from 'geochemical' cracking experiments

and gas-generative components. Our initial approach was also to look for a further generic link between the organofacies of the host kerogen (Table 3) and the kinetic parameters governing oil cracking. However, E_{mean} and σ_E follow no such predictable relationship with parent source organofacies A–F; within any given organofacies the variation in parameters is greater than that between organofacies. This suggests that oil cracking is not governed by the same bond-breaking processes which govern fragmentation of the host kerogen.

Importance of oil composition

That the origin of an oil molecule does not appear to influence its rate of degradation is not surprising; for example, *n*-octadecane and toluene molecules generated by the Kimmeridge Clay and Brown Limestone would be identical, except perhaps in isotopic signature. However, it would be reasonable to expect the overall composition of the generated oil (e.g. the ratio of *n*-octadecane to toluene in this example) to control the bulk rate of oil cracking. Although oils are complex molecular mixtures, the compound types present are found to be actually very similar, irrespective of provenance; differences in chemical and physical properties between oils result largely from differing proportions of the same molecular families (Bestougeff, 1967).

On visual inspection of product distributions in the various experiments, we found a remarkable variation in the bulk composition of the pyrolysis effluent. Two extremes of cracking profile are illustrated in Figure 2: a vitrinitic coal (Westfield opencast mine, Scotland) produces a highly aromatic oil (e.g. Senftle *et al.*, 1986), in contrast with waxy, saturate-rich oil generated by a lacustrine mudstone (Pematang Brown Shale, Central Sumatra, Indonesia). Of key importance in our oil cracking model, this product distribution appears related to the rates of cracking. Initially, Westfield oil cracks rapidly before cracking rates decrease with time, as higher activation energy species need to be

Table 3 Organofacies classification, HI⁰ data, optimized and predicted kinetic parameters for the 16 samples studied

Source rock	Organofacies	HI ⁰ (mg _{HC} g _C ⁻¹)	Optimised*		Predicted†		Figure reference
			E _{mean} (kJ mol ⁻¹)	σ _E (kJ mol ⁻¹)	E _{mean} (kJ mol ⁻¹)	σ _E (kJ mol ⁻¹)	
Brown Limestone	A	< 711 > ± 189	245.5	7.0	245.0	8.1	5a
St. Medard	A	310	241.6	12.0	242.3	11.2	5b
Garlin	A	44	237.0 [‡]	20.0 [‡]	235.9	18.4	5c
KCF	B	833	245.0 [§]	11.0 [§]	245.5	7.5	5d
PAL	B	277	243.0	9.0	241.9	11.6	5e
LC2 995	B	178	238.7	15.0	240.5	13.3	5f
LC2 1005	B	161	239.6	12.0	240.2	13.6	5g
AWD	C	596	244.2	10.0	244.4	8.8	5h
Pematang 45.2	C	529	246.0	5.0	244.0	9.2	5i
Pematang 52.7	C	504	245.0	8.0	243.9	9.4	5j
Maui	D/E	< 485 > ± 40	241.0 [‡]	15.0 [‡]	243.7	9.5	5k
Tuna	D/E	341	244.0	10.0	242.6	10.8	5l
Tarakan	D/E	226	243.0	11.0	241.3	12.4	5m
COST	D/E	167	239.0	10.0	240.3	13.5	5n
Haltenbanken	F	105	236.0	15.0	238.8	15.2	5o
Westfield	F	100	241.0	18.0	238.6	15.4	5p
Typical	A	617			244.5	8.6	11a
	B	592			244.4	8.8	11b
	C	600			244.4	8.7	11c
	D/E	333			242.5	10.9	11d
	F	158			240.1	13.7	11e
Nominal		50			236.3	18.0	7,8
		100			238.6	15.4	7,9
		200			240.9	12.8	9
		300			242.2	11.3	7,9
		600			244.4	8.7	7,9
		1176			246.6	6.2	7,8,12,13

* With A = 10¹⁴ s⁻¹

† Predicted using Equations (5) and (6)

‡ Statistical 'outlier'

§ Indicates statistical 'influential point'

< > Mean and standard deviation from offset data

degraded. In contrast, Pematang oil cracks more slowly and at a more uniform rate, implying a less diverse range of bond energies. (As a rule of thumb, decreasing E_{mean} causes data trends to swing clockwise on these plots; decreasing σ_E causes the trends to become more linear). These observations are consistent with other

laboratory experimental results showing paraffinic oils to be more stable than naphthenic and aromatic oils (Kartsev, 1964; Henderson and Weber, 1965; Andreev *et al.*, 1968; Connan *et al.*, 1975; Bjørøy *et al.*, 1988; Ungerer *et al.*, 1988). For example, Connan *et al.* (1975) observed an increase in the saturate to aromatic

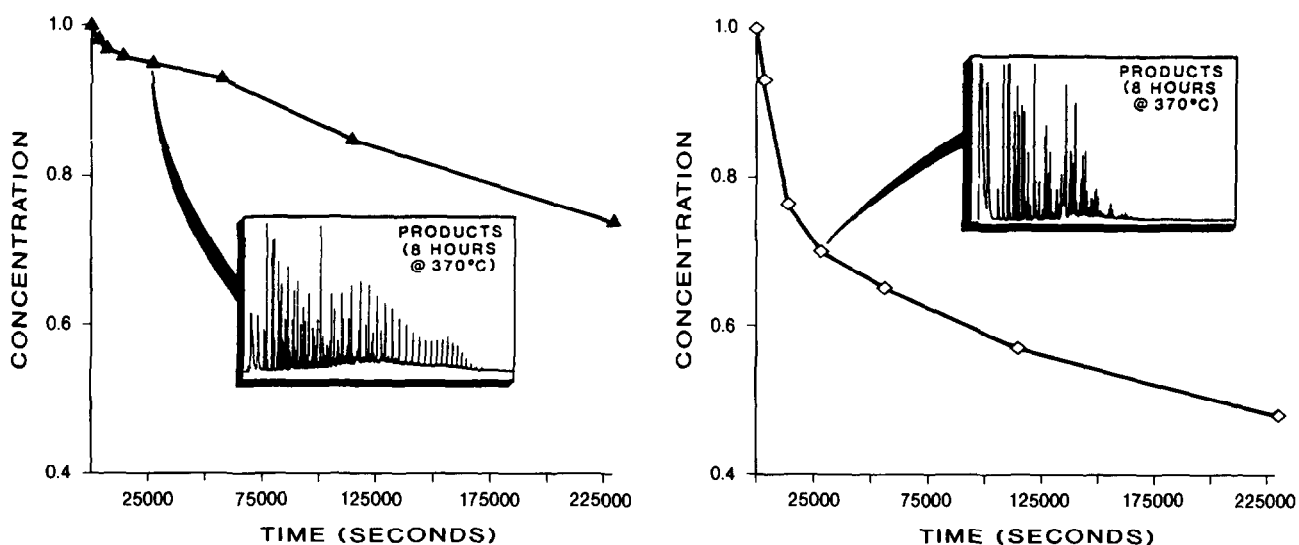


Figure 2 Oil cracking rates are related to product distributions in hydrogen-rich and hydrogen-poor kerogen pyrolysates. The figure compares and contrasts two extremes in oil cracking behaviour. (a) Indonesian Palaeogene lacustrine freshwater algal kerogen (Pematang Brown Shale, Central Sumatra, Indonesia) generates an oil rich in saturated hydrocarbons (inset) which cracks slowly to gas under 370°C isothermal sealed capsule pyrolysis conditions. The quasi-linear cracking curve is a feature of reactions governed by a narrow range in activation energies. (b) Namurian coal sample (Westfield Vitrinite, Scotland) generates an oil rich in aromatic hydrocarbons (inset) which cracks rapidly to gas under 370°C isothermal sealed capsule pyrolysis conditions. The arcuate cracking curve is a feature of reactions governed by a broad range in activation energies

ratio from 0.28 to 1.0 after heating an Aquitaine Basin oil for 12 months at 300°C.

Predictive model

Basis of model

Following these initial observations, we investigated the possibility that a simple bulk geochemical parameter might allow a global description of variation in oil cracking rates — in particular, a parameter reflecting the saturate to aromatic generation potential of a source rock.

A correlation with initial hydrogen index (HI^0) is investigated in Figure 3. As saturated hydrocarbons are more hydrogen-rich than aromatic hydrocarbons (Smith *et al.*, 1987a; 1987b), the saturate to aromatic ratio of a generated oil will determine its H:C ratio. Furthermore, the bulk H:C ratio of the generated oil should reflect that of its host kerogen; ^{13}C -NMR provides the experimental evidence linking the saturate to aromatic ratio, aliphatic to aromatic carbon bond ratio and elemental H:C and HI of the kerogen (e.g. Miknis *et al.*, 1982; Behar and Vandenbroucke, 1986; Newman *et al.*, 1988; Table 4). Elemental analysis of kerogen composition is a relatively unpopular and expensive analytical technique; however, the correlation between the H:C ratio and the pyrolysis-derived HI of the organic carbon is well established (Espitalié *et al.*, 1977). The HI is routinely measured during screening of potential source rocks and therefore represents a useful predictor variable against which the kinetic parameters might be correlated.

Calibration of model

Figure 4 plots the two optimized kinetic parameters against HI^0 for the 16 source rock samples. E_{mean} decreases, and the spread in activation energies σ_E

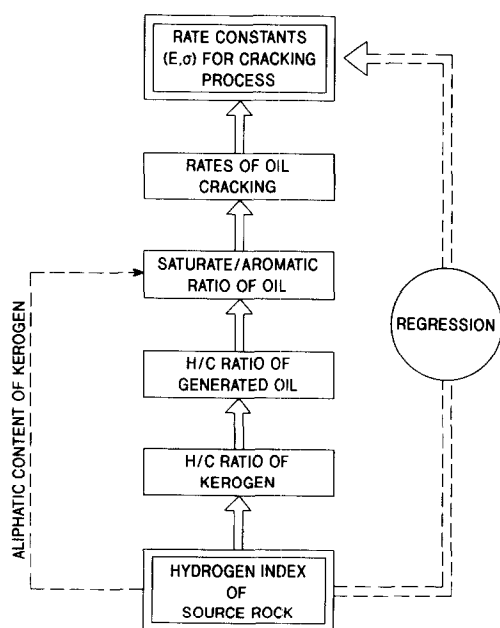


Figure 3 Rationale behind use of HI^0 of parent SOM as a predictor variable for intra-source oil cracking kinetic parameters

Table 4 Relationship between HI^0 and saturate to aromatic ratio of kerogen. Data supplied by Dr R. L. Patience, based on ^{13}C -NMR data

'IFP' type	HI^0 or H:C ratio	Fractional aliphatic C (mainly CH_2)	Fractional aromatic carbon
I	High	> 0.8	< 0.2
II	Moderate	0.6–0.75	0.25–0.4
III	Low	0.4–0.5	> 0.5

decreases, as HI^0 (kerogen and oil S:A ratio) increases. So saturate-rich oils generated by hydrogen-rich kerogens such as the Pematang with $HI^0 = 504 \text{ mg}_{\text{HC}} \text{ gC}^{-1}$ (Figure 2a) will have high E_{mean} (Figure 4a) with a relatively narrow distribution of bond energies (Figure 4b); aromatic-rich oils generated by hydrogen-poor sedimentary organic matter (SOM) such as the Westfield with $HI^0 = 100 \text{ mg}_{\text{HC}} \text{ gC}^{-1}$ (Figure 2b) will have a much broader spread of activation energies (Figure 4b) distributed around a relatively low E_{mean} (Figure 4a). HI^0 constitutes a viable predictor variable for these two kinetic parameters.

Curve fitting

Our next step was to perform regression analysis on the two data sets. We used the statistical software RS EXPLORE/DISCOVER, considering different regression options and the resulting fits to data. We experimented with fitting of polynomials of increasing complexity, investigating the sensitivity of the results to the inclusion or exclusion of critical data points. The trends are obviously non-linear; the ultimate compromise between minimizing the residuals and introducing increasingly complex polynomial terms was found to be a cubic polynomial fit. Progressive rejection of the identified outlier Maui followed by the influential points Garlin and KCF in the regression resulted in better fits, as shown by smaller residuals. However, we rejected such 'statistically preferable' polynomial fits because: (1) rejection of these data caused some fitted curves to deviate significantly from the relationship being sought on theoretical grounds (above); and (2) rejection of the Maui data — whose HI^0 is estimated from a formation average — as an outlier is no more justifiable than rejection of the Brown Limestone data whose HI^0 is similarly estimated.

Finally, sensitivity analysis showed that differences in rate constants predicted by complex cubic polynomial expressions and more simple logarithmic functions were trivial; we decided to use the latter (Figure 4). Final results of regression of E_{mean} (kJ mol^{-1}) versus HI^0 ($\text{mg}_{\text{HC}} \text{ gC}^{-1}$) were

$$E_{mean} = 223.6 + 7.5 \log(HI^0) \quad (5)$$

and of σ_E (kJ mol^{-1}) versus HI^0 ($\text{mg}_{\text{HC}} \text{ gC}^{-1}$) were

$$\sigma_E = 32.5 - 8.55 \log(HI^0) \quad (6)$$

Figure 5 shows how (broken) curves predicted from HI^0 , using Equations (5) and (6) to derive E_{mean} and σ_E , compare with the raw data and the original curves created during optimization of E_{mean} and σ_E for the 16

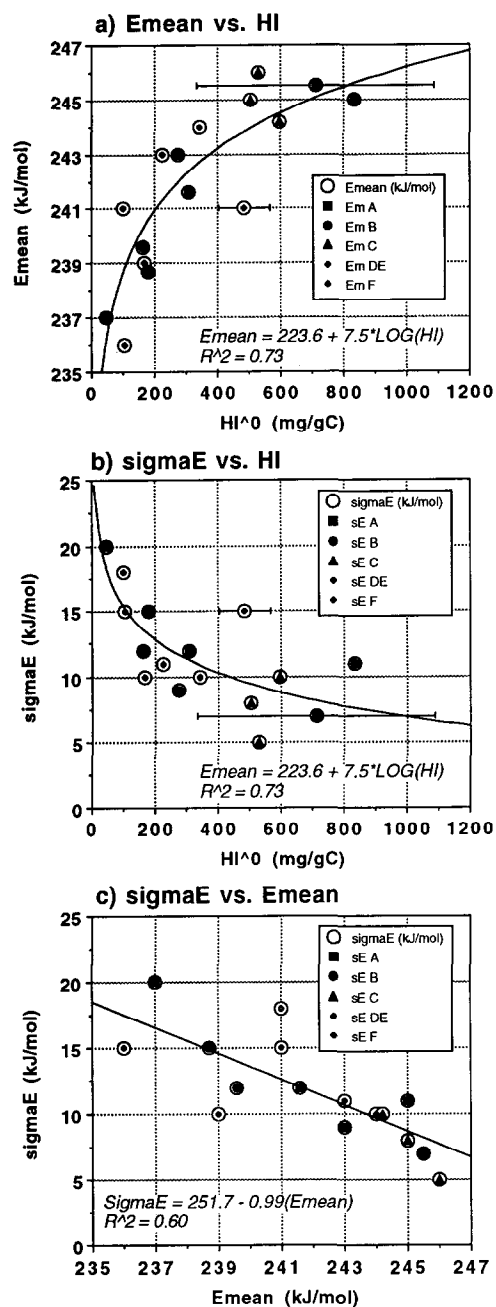


Figure 4 Correlation of Arrhenius kinetic parameters governing intra-source oil cracking with HI^0 of parent SOM. (a) Mean activation energy increases with increasing HI^0 (hydrogen-rich rocks generate more thermally stable, saturate-rich oils). (b) s_E , the standard deviation of the assumed normal distribution, increases with decreasing HI^0 (hydrogen-poor rocks generate oils with wider ranges of bond energies; saturate-rich oils are tighter in their bond energy distribution). In two cases (data plotted with error bars) HI^0 data was not available for the exact sample subjected to sealed capsule pyrolysis and was estimated from average formation data

source rocks. Except for the outlier (Maui coal) the comparison is favourable, as far as we can determine given within the limits of measurement error.

Intra-source cracking at geological heating rates

Potential errors in extrapolation

Before describing the application of the model in the geological subsurface (i.e. naturally matured source

rocks), it is important to be fully aware of the potential errors propagated due to the assumption, rather than the derivation, of a value $A = 10^{14} \text{ s}^{-1}$ in the study. Confident extrapolation of laboratory-derived parameters to the geological subsurfaces (see Snowdon, 1979, for discussion) requires that this assumption is not a potentially major source of error.

We tested this by re-optimizing E_{mean} given various reasonable alternative values for A (i.e. varying it by \pm an order of magnitude between 10^{13} and 10^{15} s^{-1}) and extrapolating the results to subsurface conditions. Table 5 and Figure 6 summarize the results for the Garlin source rock. Optimized E_{mean} shifts by about 12 kJ mol^{-1} to compensate for an order of magnitude change in assumed A . To examine the typical potential error, we chose 2°C Ma^{-1} as the subsurface reference. This is close to the slowest rates of continuous heating observed in nature (e.g. old passive margins or intra-continental rift-sag basins). The result (Figure 6) is a propagated error of $\pm 15\%$ in ϵ at the reaction midpoint ($\epsilon = 0.5$). Expressed as a temperature error, the cracking profile shifts by $\pm 7^\circ\text{C}$ at the same reaction midpoint.

SOM quality controls cracking temperatures

Figure 7 summarizes the effect of SOM quality (HI^0) on the predicted extent of cracking, for a nominal heating rate of 2°C Ma^{-1} . Theoretical curves are displayed for $HI^0 = 50, 100, 300, 600$ and $1176 \text{ mg}_{\text{HC}} \text{ gC}^{-1}$. In rocks with low HI^0 , rates of cracking become significant at relatively low temperatures, but the cracking process extends over a very broad (ca. 100°C) temperature window, reflecting the wide range of bond energies available for cleavage. In rocks with high HI^0 , cracking rates are not significant until a higher and narrower (ca. 50°C) temperature window is reached.

As discussed in Part I, a problem arises when assigning a threshold event to a process such as petroleum generation that actually represents a continuum. Oil cracking is no different. Hence it is meaningless to discuss 'onset of cracking' or 'oil phase-out' without being clear about the arbitrary limits being assigned. As with definition of the oil and gas-generation 'windows' in Part I, we circumvent this problem by proposing a strict definition for the oil cracking window (OCW): more than 10% (= oil cracking threshold or OCT) but less than 90% (= oil floor) of oil converted to gas.

Although frequently used in the petroleum industry, vague terms such as 'oil phase-out' are potentially misleading or confusing because it is often unclear as to whether composition or phase is being referred to. The

Table 5 Tests show the sensitivity of E_{mean} to uncertainty in pre-exponential constant A (with σ_E set to 20 kJ mol^{-1}). Increasing (decreasing) the assumed value of A by an order of magnitude increases (decreases) the optimal value of E_{mean} by ca. 12 kJ mol^{-1} . The effect on temperature prediction at geological conditions is ca. 7°C (Figure 6)

$A_{\text{assumed}} (\text{s}^{-1})$	$E_{\text{optimized}} (\text{kJ mol}^{-1})$
10^{13}	225.0
10^{14}	237.0
10^{15}	249.0

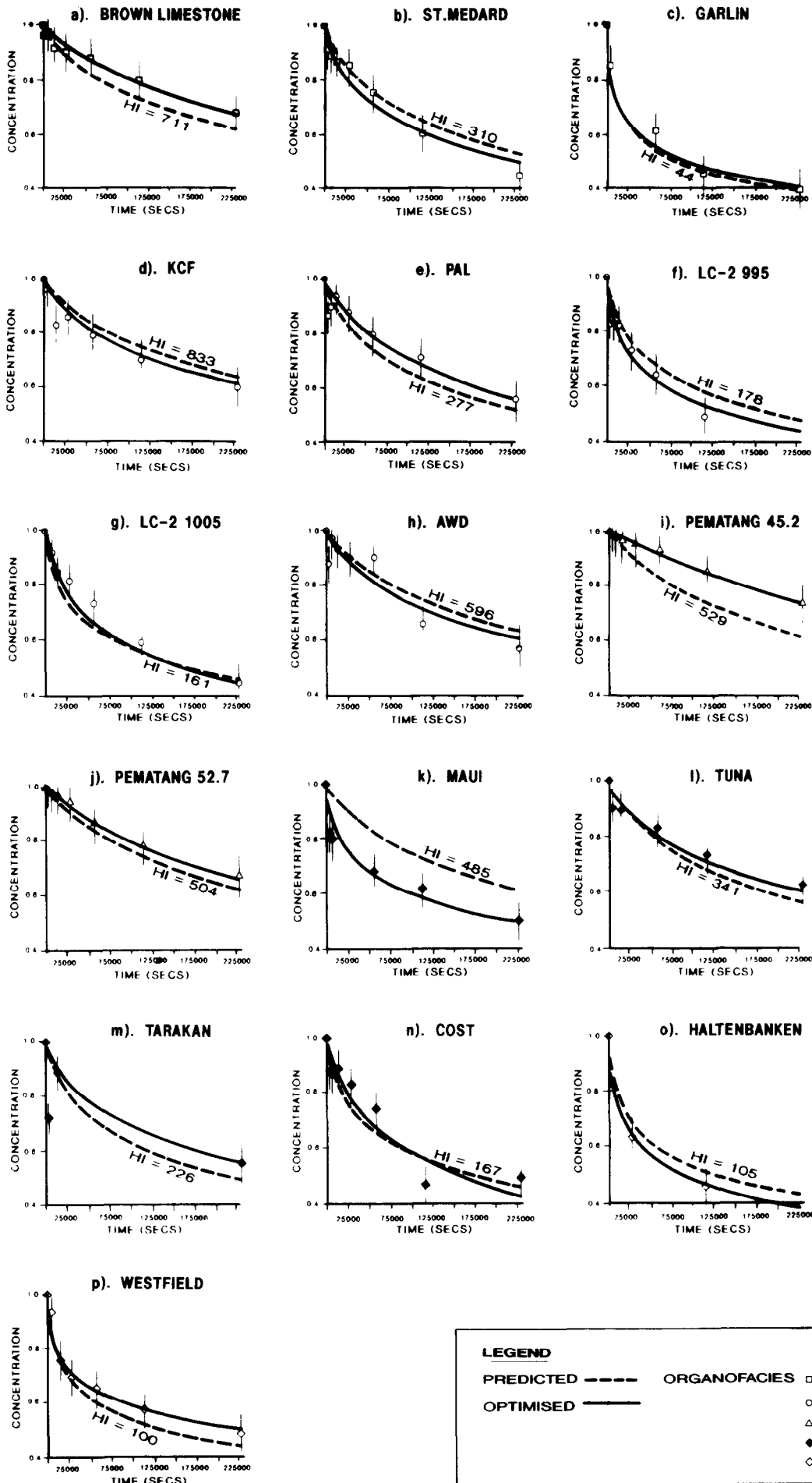


Figure 5 Matching of predictions (based on HI^0 of the sample) with ϵ versus time data for 16 source rocks (a-p; Table 3) subjected to sealed capsule pyrolysis at 370°C for time periods between 1 and 64 hours. Also shown for comparison are the original optimized curves. Error bars were derived arbitrarily by considering the effect of a compound 20% error in G and g data used to calculate ϵ

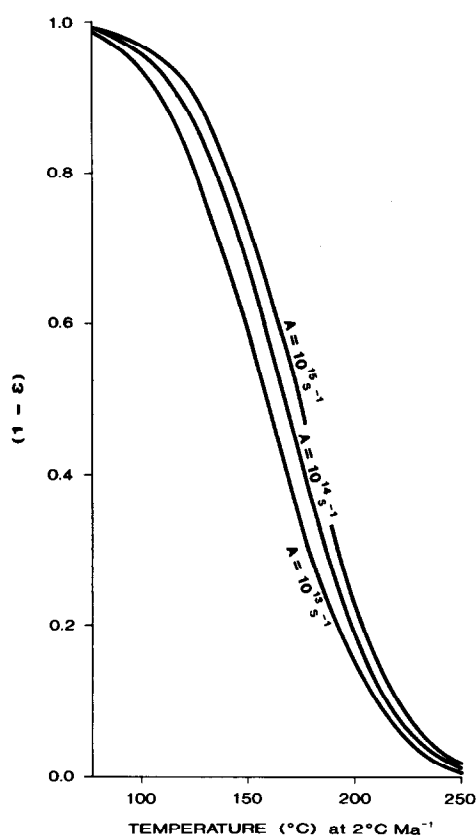


Figure 6 Effect of variation in assumed pre-exponential constant A in extrapolation of the resulting optimized E_{mean} and σ_E to geological heating rates. An order of magnitude change in the assumed initial value of A (i.e. from 10^{14} to 10^{13} or 10^{15} s^{-1}) results in $\pm 7^\circ\text{C}$ uncertainty in extrapolated cracking window temperature in the geological subsurface

depth of appearance of gas caps and the disappearance of oil legs in the subsurface is strongly governed by the pressure-temperature regime, as well as by the petroleum composition, i.e. the gas to oil ratio (England *et al.*, 1987). Indeed, some reservoired petroleum phases variously termed 'volatile oils', 'dense phases', 'supercritical fluids' or 'gas condensates' by reservoir and petroleum engineers (Dake, 1978), actually contain fairly evenly balanced mass proportions ($G = 0.5 \pm 0.2$) of oil and gas (e.g. over-pressured Cretaceous chalk reservoirs and deep Jurassic sandstone reservoirs of the North Sea Basin). As condensate is nothing more than (usually low molecular weight) oil taken into solution by a gas phase, the placing of an oil phase out at some particular condensate to gas ratio is completely arbitrary.

The purpose of using the above 10-90% limits as guidelines, however, is that we can now discuss meaningfully any differences in cracking temperatures in the geological domain of heating rates (Figure 8).

Cracking threshold temperature

Above ca. $600 \text{ mg}_{\text{HC}} \text{ g}_{\text{C}}^{-1}$, changes in HI^0 have a minimal impact on the cracking threshold (defined as above), which can be considered effectively constant at ca. 150°C . The further HI^0 drops below ca. $600 \text{ mg}_{\text{HC}} \text{ g}_{\text{C}}^{-1}$, the more sensitive the generated oil becomes to cracking. Within the range $\text{HI}^0 < 300 \text{ mg}_{\text{HC}} \text{ g}_{\text{C}}^{-1}$, the cracking threshold becomes

extremely sensitive to HI^0 variation, dropping rapidly from ca. 145 to 115°C , overlapping significantly with the oil generation window (Part I, Figure 16). This, in our view, is one of the two main reasons for the observed gas-proneness of 'type III' kerogen rocks: the lower the HI^0 , the more prone is the source rock to destruction of oil as it is being generated. (In Part III, the second factor will be explained).

Oil floor

For all values of HI^0 the oil floor (defined as above) can be considered effectively constant at ca. 205 - 215°C . However, and especially in samples with low HI^0 , some small refractory population of oil is predicted to be stable in the temperature region up to 250°C . Thus completely dry gases (i.e. with no associated condensate) of thermal cracking origin will be a relatively rare occurrence in nature. This can be verified both in source rocks and in petroleum fluids: extract or thermal volatilate (= oil) yields from source rocks which have reached temperatures in excess of 200°C show that some small oil concentration persists at these thermal stress levels (e.g. Cooles *et al.*, 1986); even highly mature coal-derived gases (e.g. Palaeozoic southern North Sea Basin) usually produce condensate at a ratio of a few bbl mmscf^{-1} .

Effect of time: heating rate

Quigley *et al.* (1987), Quigley and Mackenzie (1988) and Mackenzie and Quigley (1988) promoted the use of 'oil half-life curves' in displaying results of their kinetic

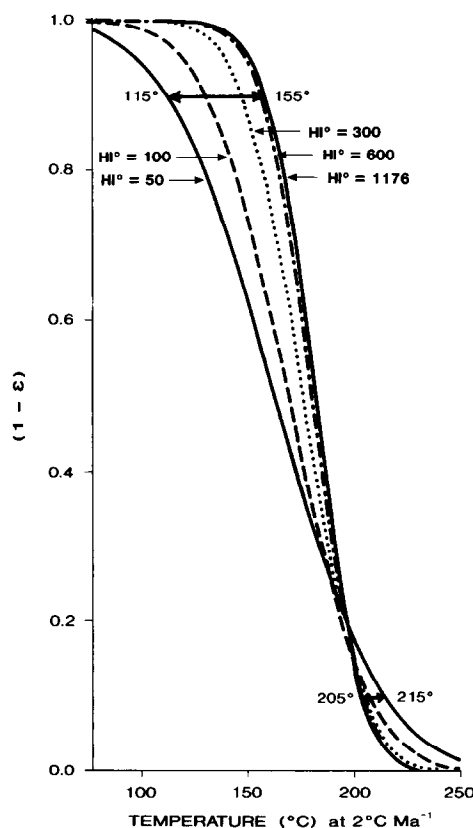


Figure 7 Modelled curves showing fraction of oil remaining $(1-\epsilon)$ versus temperature for a heating rate of 2°C Ma^{-1} : effect of variation in HI^0 of parent source rock

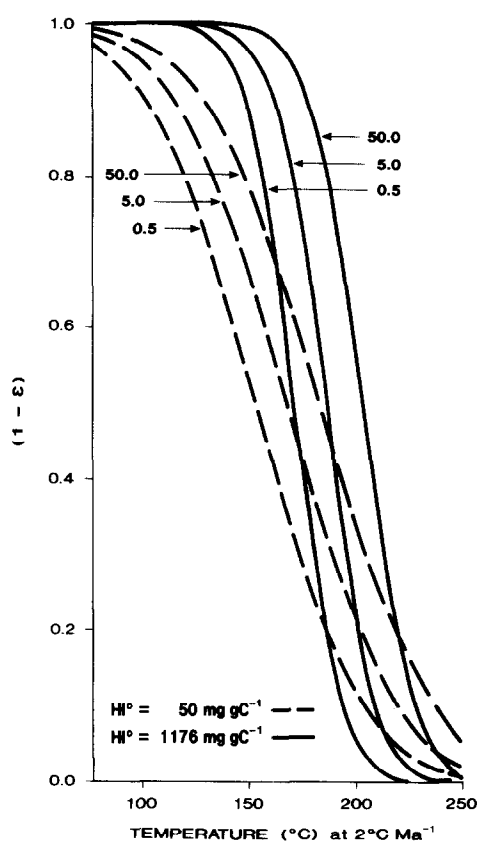


Figure 8 Modelled curves showing effect of heating rate (values in $^{\circ}\text{C Ma}^{-1}$) on fraction of oil remaining ($1-\varepsilon$) versus temperature for effective end-member HI^0 values ($50-1000 \text{ mg}_{\text{HC}} \text{ gC}^{-1}$). An order of magnitude shift in heating rate causes the cracking window to shift by ca. 15°C

predictions. Although highly illustrative, the concept of oil half-life has a relatively restricted geological application as significant periods of isothermal maturation are rare in sedimentary successions, which are dynamic: we observe them in the course of either warming up

(through subsidence and deposition) or cooling down (through uplift and erosion). Thus we prefer to present results of our predictions for a series of heating rates, as for kerogen degradation (Part I).

Figure 8 shows the effect of order of magnitude changes in heating rate for source rocks representing the extremes likely to be encountered in nature ($50 < \text{HI}^0 < 1176 \text{ mg}_{\text{HC}} \text{ gC}^{-1}$). The range of heating rates considered ($0.5-50^{\circ}\text{C Ma}^{-1}$) encompasses the extremes likely to be experienced in sedimentary basins unaffected by igneous intrusions. An order of magnitude increase (decrease) in heating rate elevates (depresses) the reaction mid-point temperature by ca. 15°C . This is typical for other geochemical reactions with similar kinetic parameters (A of the order 10^{14} s^{-1} and E_{mean} of the order $235-245 \text{ kJ mol}^{-1}$), including kerogen degradation [Part I, Equation (16)].

Note that this magnitude of shift — requiring extreme variation in heating rate — is no greater than the shift induced by variation in source rock quality: the temperature for $\varepsilon = 50\%$ shifts by ca. 15°C over the range $50 < \text{HI}^0 < 1176 \text{ mg}_{\text{HC}} \text{ gC}^{-1}$. Thus, in many basins — particularly those with low quality source rocks (i.e. 'type III' kerogens such as humic coals) — it will be more important to know kerogen quality (HI^0) than heating rate.

'Dynamic' half- and quarter-life nomograms

Because half-life curves *sensu stricto* are of limited use in basin evaluation, we introduce the concepts of 'dynamic half- and quarter-life', which represents the non-isothermal thermal stress levels necessary to degrade an oil to one-half and one-quarter of its original mass, respectively. Nomograms in Figure 9 show combinations of maximum temperature, heating rate and HI^0 which are required to reduce a mass of oil to one-half ($\varepsilon = 0.5$) and one-quarter ($\varepsilon = 0.75$), respectively. These charts emphasize that the geological conditions required for significant thermal degradation of oil in source rocks are extreme.

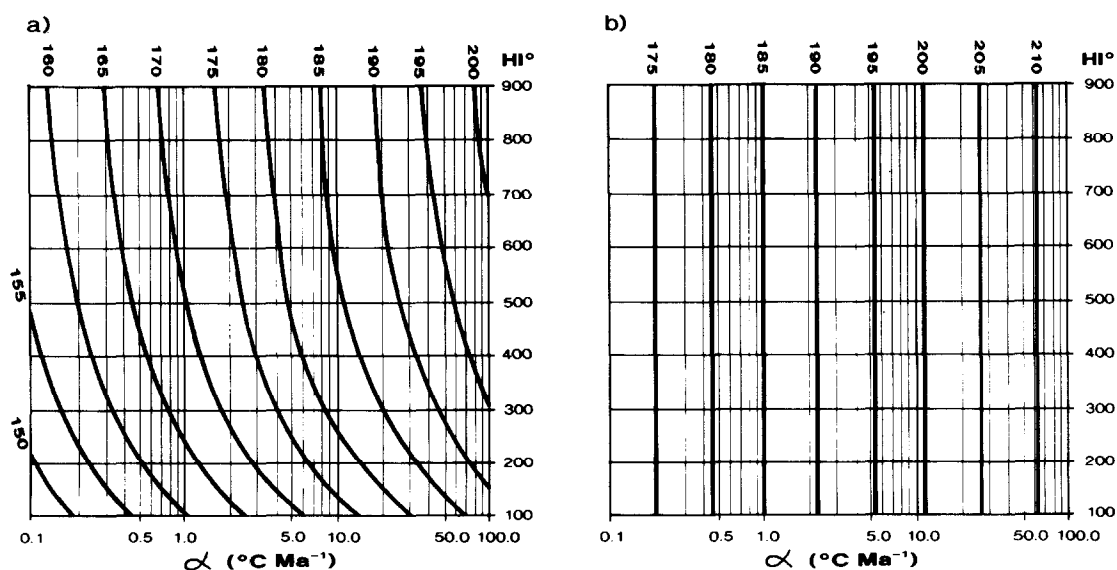


Figure 9 Modelled nomograms showing various HI^0 and heating rate conditions required for degradation of various portions of oil in the source rock environment. (1) 50% degradation ($\varepsilon = 0.50$); and (b) 75% degradation ($\varepsilon = 0.75$)

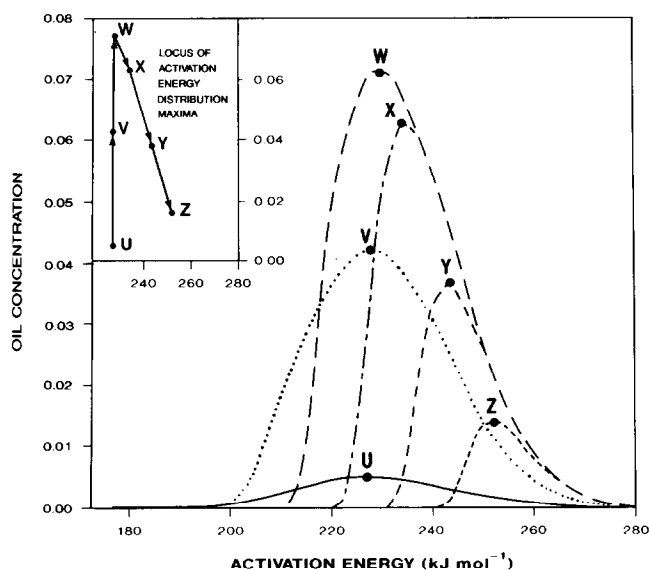


Figure 10 Evolving activation energy distribution, shown at regular increments of temperature, of oil in a closed system where it is generated and subsequently cracked to gas. In the model, oil is 'born' with the same activation energy distributed at all stages of oil-generative kerogen breakdown. Initially, during early oil generation, rates of oil cracking are insignificant with the result that the concentration of oil accelerates (T_{U-V}). By T_w , the situation is finely balanced: the oil generation rate is slowing and cracking rates are becoming perceptible, as shown by the very slight increase in E_{mode} between T_{V-W} . Cracking rates accelerate rapidly and oil generation rates diminish dramatically (as the residual kerogen shrinks in concentration) from T_{W-X-Y} . Note the accompanying increase in E_{mode} as cracking reactions preferentially consume the lowest activation energy members of the oil spectrum; this process also results in the skewing of the residual profiles at T_{W-X-Y} . By T_z , cracking rates too are slowing as the residual oil shrinks in concentration (further stages of cracking not shown)

Modelling a closed source rock system

Workings of the model: the link with generation

So far we have discussed cracking in isolation, as a process decoupled from generation. Furthermore, as we have not yet introduced an expulsion module (Part III), we limit our presentations here to show the impact of assuming a closed system. We stress that this is geologically highly unrealistic (although until relatively recently, this was the limit of capability of some commercially available kinetic modelling packages!). Figures 10 and 11, presented and described below, illustrate a number of important points.

Our kinetic parameters for oil generation (Part I) and destruction (Table 3) imply that under geological conditions, and particularly for low quality organofacies D/E/F source rocks, they will proceed concurrently. So, in a closed system, the net rate of oil formation is governed by a modified form of Equation (3)

$$dc_{oi} / dt = S_{oi} - k_{oi}c_{oi} \quad (7)$$

where, at any given time, S_{oi} is the rate of formation of oil of energy i within the assumed distribution of energies (due to degradation of oil-generative kerogen; Part I); k_{oi} is the rate constant for degradation of oil of energy i [and is itself described by the Arrhenius

equation; see Equation (2)]; and c_{oi} is the existing concentration of oil of energy i .

Although an equation of similar form was presented by Quigley and Mackenzie (1988), their kinetic data implied relatively little overlap. Consequently, in their general model of petroleum formation, Mackenzie and Quigley (1988) simplified the situation to one in which the generation and cracking of oil were treated as processes occurring in series. Although this may be a close approximation in the case of many high quality source rocks, we are convinced by our larger kinetic database of the need for a linked model of generation and cracking.

To satisfy chemical kinetic principles, any model of oil to gas cracking must account for a number of experimental observations: (1) as cracking proceeds, low activation energy species react first, leaving the residual material enriched in more stable products; and

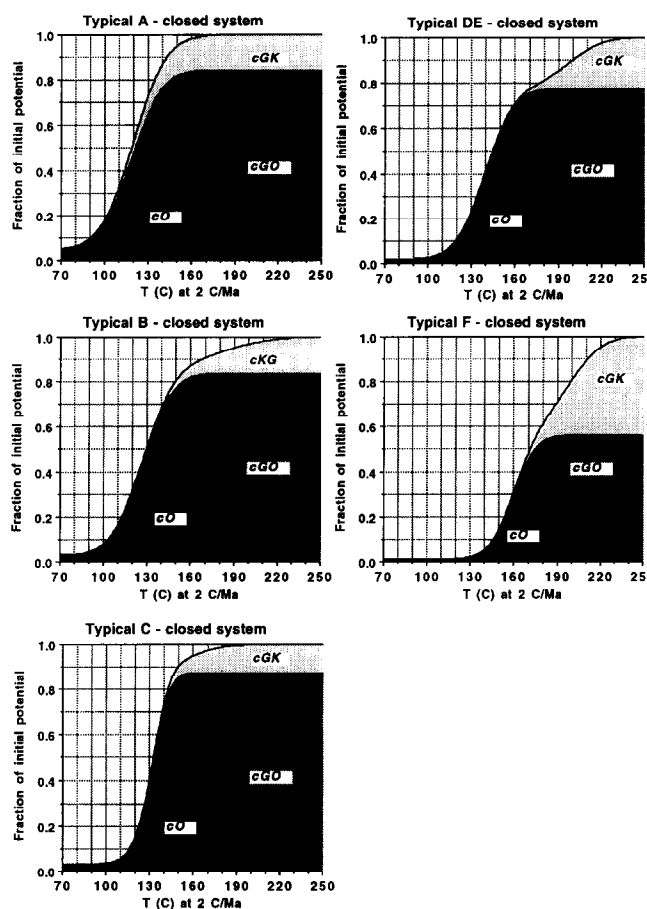


Figure 11 (a-e) Model closed systems for typical source rocks belonging to organofacies A, B, C, DE and F, respectively. Each graph shows the evolution of products under a common thermal stress regime (increasing temperature at a linear heating rate of 2°C Ma^{-1}). The net increase or decrease in the oil concentration curve (c_o) depends on relative rates of two competing reactions [c.f. Figure 13 and Equation (7)]: breakdown of oil-generative kerogen versus destruction of the produced oil. Breakdown of oil results in a complementary increase in cracking derived gas (c_{GO}). Gas generation direct from the gas-generating kerogen portion (c_{GK}) increases independently and in parallel with these processes. See text for fuller discussion. These graphs are intended for comparison with Figure 18a-e of Part I, which deliberately neglect the effects of cracking and consider only the cumulative effects of generation

(2) the average activation energy increases, and reaction rate decreases, as the reaction progresses — a result of the first process. *Figure 10* describes how these conditions are satisfied by our model which assumes Gaussian activation energy distributions for both the degrading oil-prone kerogen and oil it generates.

'Typical' source rocks as closed systems

Part I (*Figure 18*) showed model generation profiles for typical members of their five source rock organofacies. Having shown in principle how generation and cracking can be linked (Equation 7; *Figure 10*) we now describe the consequences of linking oil generation and oil cracking in the natural system, for the same five typical organofacies members (*Figure 11*).

The general form of each of the closed source rock systems is similar. Primary yields of oil and gas are derived by degradation of oil- and gas-generative kerogen. Gas generated from kerogen c_{GK} merely accumulates and is distinguished from gas generated from cracking of oil c_{GO} . At low levels of thermal stress, oil is generated faster than it can be destroyed by cracking, and c_o rises in concentration. At some point, cracking rates become dominant, causing c_o to decrease again. The oil concentration curve defines the well known form of the 'Philippi' curve which can be seen when carbon-normalized extract or S1 yields are plotted with respect to temperature. The quantities c_o and c_{Go} are complementary, as all carbon in generated oil is assumed to be eventually converted to gas; no 'coke' or 'pyrobitumen' formation is required in the model.

Important differences between *Figure 11a–e* are governed by

1. The kinetics of kerogen degradation. The organofacies determines the temperature at which the oil curve initially increases in concentration. The higher the temperature at which this occurs, the greater will be the overlap in the temperature zones of oil generation and destruction; organofacies A has the smallest, and F the largest, overlap.
2. Cracking commences at lower temperatures in source rocks with HI^0 progressively lower than ca. $500 \text{ mg}_{\text{HC}} \text{ g}_{\text{C}}^{-1}$. The cracking threshold in typical high quality organofacies A, B and C source rocks ($HI^0 \geq 500 \text{ mg}_{\text{HC}} \text{ g}_{\text{C}}^{-1}$) will be around 150°C , which results in a relatively small overlap in the generation and destruction processes. For typical organofacies D/E (HI^0 ca. $300 \text{ mg}_{\text{HC}} \text{ g}_{\text{C}}^{-1}$) and F (HI^0 ca. $150 \text{ mg}_{\text{HC}} \text{ g}_{\text{C}}^{-1}$) source rocks, the cracking threshold will be systematically lower, resulting in progressively further overlap.

Combinations of the two factors determine the maximum concentration of oil attained, and the temperature at which it is attained. Organofacies A has the most favourable combination; organofacies F source rocks typically have the worst combination of high generation temperature and low cracking temperature, which results in a low oil maximum attained at high temperature. The latter observation is an important one as some workers (e.g. Huc *et al.*, 1986) have, we believe wrongly, interpreted the low oil

concentrations present in some mature coal series as evidence of efficient expulsion.

A further general observation is that all five source rocks potentially create more gas from cracking of oil (c_{GK}), even in the case of the 'type III' examples D/E and F. We find these observations consistent with the concept that expulsion efficiency is the dominant process in determining the overall oil versus gas-proneness of source rocks (Pepper, 1989; 1991; Part III).

Application to in-reservoir cracking?

The preceding sections of this paper have concerned themselves with the cracking process as it occurs in maturing source rocks. Thus the kinetic constants for oil cracking — a hydrogen-consuming process — have only been derived for the source rock environment. Application of the results to the reservoir environment requires caution for two reasons: (1) fractionation effects during migration (especially expulsion) cause significant compositional differences between residual and expelled oils; and (2) there is a change in the hydrogen budget of the environment.

Expulsion effects

Significant bulk compositional changes accompany expulsion of oil from the source rock (Vandenbroucke, 1972; Vandenbroucke *et al.*, 1983; Leythaeuser *et al.*, 1983; 1984a; 1984b; 1988a; 1988b; Mackenzie *et al.*, 1983; 1987; Leythaeuser and Schaefer, 1984). These fractionation effects strongly favour the release of saturates in preference to the aromatic hydrocarbons and NSO compounds. If migrating, ultimately reservoir oil is enriched in (thermally resilient) saturates, our model implies that its thermal stability may no longer be predicted from a knowledge of the quality of its source rock. Reservoir oils are thus likely to be more thermally resilient than the residual oils retained in their source rocks, by an amount controlled by the degree of fractionation which has occurred. Currently, we are unable to determine the magnitude of the difference; for the present we can only speculate that reservoir oils should be at least as resilient as the oils generated by high quality source rocks, which allows a maximum estimate of ϵ to be made using a curve based on $HI^0 = 1176 \text{ mg}_{\text{HC}} \text{ g}_{\text{C}}^{-1}$ — the theoretical maximum HI^0 assuming $W = 0.85 \text{ kg}_{\text{C}} \text{ kg}_{\text{HC}}^{-1}$ (*Figure 12a* and *12b*).

Hydrogen budget and coke formation

In the source rock medium, kerogen can be invoked as a potential catalyst or donor of hydrogen — derived from condensation/aromatization reactions in the residual kerogen (Brooks and Smith, 1969; Magril, 1973; Evans *et al.*, 1984; Herschkowitz *et al.*, 1983; Smith *et al.*, 1987a; 1987b; Serio *et al.*, 1987). In some reservoirs, catalytic properties have also been ascribed to carbonaceous residues (Raaben *et al.*, 1975). Thus our model has assumed ready availability of hydrogen (i.e. availability of hydrogen is unlikely to be rate-limiting) and that coke formation is not a requirement (cracking of oil to gas may be 100% efficient).

Once intimate association with the potential

hydrogen donor kerogen ends (i.e. following expulsion), oil enters a region of limited hydrogen budget. Interactions with water have been suggested (Hoering, 1984), but it is most likely that some sort of stoichiometric balance will be required, resulting in the formation of a hydrogen-poor residue ('coke' or 'pyrobitumen') in addition to gas, from cracked oil (Appleby *et al.*, 1962; Barker, 1979; 1990; Ungerer *et al.*, 1988; Burnham and Sweeney, 1991). We do not currently know whether the rates of cracking we predict using our kinetic parameters will change in the absence of kerogen; if they do not, then the volumetric impact of coke formation will be to simply multiply the gas yield at any stage of oil degradation by the appropriate stoichiometric factor x



where C_o , C_{GO} and C_{CO} are the carbon quantities in oil, oil-derived gas and oil-derived coke, respectively. Ungerer *et al.* (1988) proposed stoichiometric factors ranging from around 0.3–0.6 and depending on oil type; Burnham and Sweeney (1991) suggest 0.5; Connan *et al.* (1975) found 'solid bitumen' yields increasing to 40% after heating an Aquitaine Basin oil for up to 12 months at 300°C.

Figure 12a shows the impact of hydrogen balance on the amount of gas produced by in-reservoir cracking: this emphasizes the simple point that, although e.g. half of the oil may be degraded at a certain temperature, only half of this mass will be converted to gas; to attain an equal gas to oil ratio through in-reservoir cracking (Figure 12b), two-thirds of the initial oil must be degraded.

Mineral catalysis

The potential influence of mineral catalysis depends on the reaction mechanism by which oil is supposed to crack under geological pressure–temperature–time conditions. The mechanisms of thermal and catalytic cracking are different (Greensfelder *et al.*, 1949). Pure thermal cracking is thought to proceed via a free radical mechanism (Kossiakoff and Rice, 1943); evidence of free radical formation is provided by electron spin resonance data on naturally matured samples (Pusey, 1973). Catalytic cracking proceeds via a carbonium ion mechanism (Greensfelder *et al.*, 1949; Thomas, 1949), requiring the presence of an acid catalyst. Only if the latter mechanism is operative in the subsurface will mineral catalysis play an important part in cracking.

Catalysts require intimate association with reactants to be effective, and it is the exception rather than the norm for oil to be in direct contact with mineral surfaces in rocks, as most reservoirs (and probably all source rocks; Pepper, 1991) remain water-wet on emplacement of a petroleum phase. Perhaps this is why some experimental results involving cracking of oil in the presence of a clastic mineral matrix have observed catalytic effects (Phillips *et al.*, 1985; Abu-Khamsin *et al.*, 1987), whereas others have not (McNab *et al.*, 1952; Henderson and Weber, 1965; Hayashitani *et al.*, 1978).

We are unaware of any field data in support of a more rapid in-reservoir cracking rate in clastic versus carbonate reservoirs. In the absence of conclusive

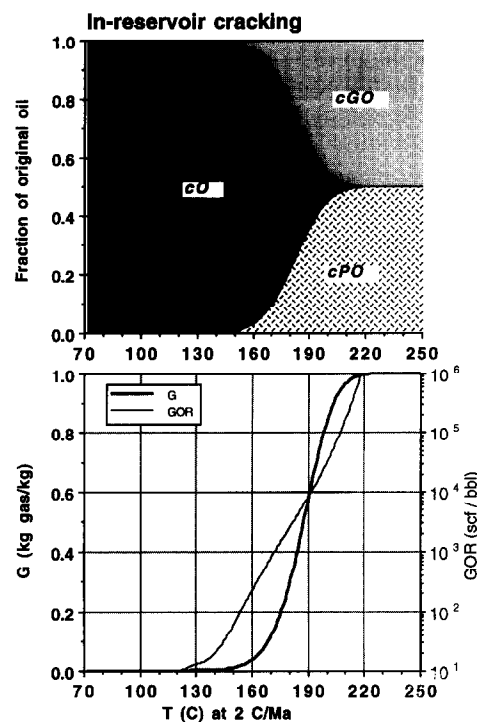


Figure 12 Speculative curves for cracking of oil in reservoir systems, at reference heating rate $2^{\circ}\text{C Ma}^{-1}$. (a) Formation of pyrobitumen is required to satisfy hydrogen budget in the reservoir environment; here carbon is assumed to partition between gas and pyrobitumen in equal proportions. (b) Effect of cracking on reservoir gas: oil proportions (net of pyrobitumen yield), expressed in mass units (mass fraction gas) and oilfield GOR units (volumes at STP, calculated for gas and oil of density 0.8 and 850 kg m^{-3} , respectively), for an oil deposit with zero initial GOR

experimental or field data we will neglect the contribution of mineral catalysis in any further discussion of oil cracking.

Testing the results

Direct testing

To be truly universal, our kinetic parameters (Table 3) should enable predictions to be made outside the range of data used to derive them in the first instance. However, because petroleum source rocks and reservoirs are not closed systems, we find it extremely difficult to envisage a rigorous test of our laboratory derived kinetic predictions in the subsurface. In this respect, the calibration of oil–gas cracking rates differs from oil and gas generation from kerogen, where rates of conversion of oil- and gas-prone kerogen can be derived from field data sets by the difference between the concentration of starting kerogen and the residual quantities at any stage (e.g. Cooles *et al.*, 1986).

One potential line of investigation involves the use of petroleum-bearing fluid inclusions. Perhaps a situation might occur where fluid inclusion data were available from a series of cement phases which trapped migrating or reservoir oil at an early stage of thermal maturity of the source rock. These fluid inclusions would then represent microscopic closed systems, protected from potential gas-flushing during the later stages of thermal maturity of the source rock. If these inclusion-bearing reservoir cements were then buried to a range of depths

and temperatures, including those at which oil–gas cracking might be taking place, analysis of the gas to oil ratio of the inclusions, if performed with sufficient accuracy, might provide an independent field calibrant.

Indirect methods

We are currently forced to make the most of indirect or negative observations in natural systems to validate our model. This approach is frustrated by the ‘openness’ of most petroleum reservoir systems: are examples of evolution in GOR or oil gravity with reservoir depth coincidentally related to reservoir temperature, while actually being controlled by increasing thermal stress in the respective kitchens?

Similarly, global plots of API and GOR versus depth show only broad trends with low correlation coefficients, and only serve to emphasize the point that reservoir fluid composition has little to do with thermal stress levels incurred in the reservoir. For example, Hunt’s (1979) compilation shows an API gravity increase from $28 \pm 15^\circ$ at 0.76 ± 0.15 km to $35 \pm 15^\circ$ at 3.50 ± 0.15 km, at a very low gradient of 3° API km^{-1} . Referring to a study of 58 petroleum pools in Alabama by Claypool and Mancini (1989; their Table 2), it seems unreasonable to ascribe a broad trend of increasing GOR between reservoir temperatures of ca. 90–140°C (10 000–16 000 ft) to the effects of oil to gas cracking when much lower GORs (as low as 1052 scf bbl^{-1} ; mass fraction gas G ca. 0.2) are present in deeper reservoirs at 160–163°C. Excellent field data sets of this sort require very careful interpretation before drawing conclusions about in-reservoir cracking (see below for more details).

Comparison with other studies

Although comparison of our results with other (laboratory-based) studies does not in itself help in determining the accuracy of prediction at geological heating rates, it is comforting to find agreement between independent lines of laboratory investigation. Unfortunately, almost all previous investigations of which we are aware (Tables 1 and 2) are concerned with the cracking of oil outside the source rock environment. The exception is Quigley *et al.* (1987), summarized also in Quigley and Mackenzie (1988) and Mackenzie and Quigley (1988), whose limited experimental data suggested that most oil cracking should occur within the temperature window 150–190°C. This is narrower than our range of predictions for source rocks of differing HI^0 (Figures 7–10), based on a larger set of intra-source cracking data.

Mackenzie and Quigley (1988) suggested 180°C as an approximate upper temperature bound for preservation of oil accumulations. Their supporting negative evidence, and that of others (Landes, 1967; Baybakov, 1969; Rogers *et al.*, 1972; Pusey, 1973), was that major oil accumulations do not exist at temperatures $>180^\circ\text{C}$. Before using such evidence, it is important to be very clear about what is being monitored: phase state or composition? This observation may be true for ‘black oil’ (implying an undersaturated subsurface liquid, i.e. whose GOR is lower than the bubble-point GOR). However, significant concentrations of oil *sensu stricto* (i.e. C_{6+} molecular weight range) may persist at

high temperatures in a form which will depend on the pressure regime.

In low pressure systems, uncracked oil will persist in an oil leg beneath an expanding gas cap, provided that reservoir volume is not exceeded (Barker, 1990). Indeed, a failure to appreciate situations where oil has been completely displaced via this mechanism may lead to the erroneous conclusion that a gas condensate accumulation has formed through complete cracking of oil. Under high pressure ‘black oil’ may evolve over geological time into ‘volatile oil’, ‘dense phase’, ‘supercritical fluid’ or ‘rich gas condensate’ phase associations, as the C_{6+} material becomes incorporated into a phase state whose GOR evolves continuously without segregation. The oil/condensate yield of such deposits usually has great commercial value, and thus C_{6+} yield, rather than phase, prediction is a more useful aim in geochemical modelling.

Note that in both situations the C_{6+} does not suddenly disappear — it merely changes phase state! Subsurface phase and volume, though important to petroleum reservoir engineers, only tend to confuse true patterns of compositional change in the subsurface. We overcome such problems by monitoring changes in pool composition on a gas to petroleum mass fraction basis, as we show in the following North Sea case history.

Our projections are optimistic with respect to preservation of low GORs in hot reservoirs. This partly results from the inclusion of pyrobitumen in the reservoir cracking scheme [Equation (8); Figure 12a], which Quigley *et al.* (1987), Quigley and Mackenzie (1988) and Mackenzie and Quigley (1988) did not assume. Figure 12b shows the effect on reservoir fluid composition (net of pyrobitumen). A low GOR oil deposit ($G = 0.1$; $\text{GOR} = 500$ scf bbl^{-1}) is theoretically possible at ca. 170°C, where it will probably exist as a single ‘black oil’ phase. At 185°C it will still be half oil by mass ($G = 0.5$; $\text{GOR} = 6000$ scf bbl^{-1}) and may exist as a two-phase or supercritical reservoir fluid, depending on the pressure regime. A temperature of 205°C is required to reduce it to 5% oil ($G = 0.95$; $\text{GOR} = 100\,000$ scf bbl^{-1}), where it will almost certainly exist as a single reservoir phase (i.e. gas condensate with a lean yield 10 bbl mmsc^{-1}).

Even accounting for hydrogen balance, these projections will be valid only if the oil degradation rates we observed in the source rock were not catalysed by kerogen. Otherwise, Figure 12 may still be overestimating the extent of cracking in reservoir systems. Such projections would be considered speculative were it not for their agreement with two independent lines of laboratory investigation.

Extrapolation of the most recent set of IFP extra-source cracking kinetics (Ungerer *et al.*, 1988) to a geological heating rate of $1.5^\circ\text{C Ma}^{-1}$ (i.e. very close to our reference heating rate) predicts that very little cracking (a few per cent) should take place at temperatures as high as 170°C (Boscan, a relatively aromatic, sulphur-rich oil) and even 185°C (Pematang, a saturate-rich, waxy oil; c.f. our Figure 2a).

Detailed laboratory studies of single compounds (Fabuss *et al.*, 1962; Doue and Guiochon, 1968; Shimoyama and Johns, 1971; Ford, 1986; Mango, 1990a; 1990b; 1990c) also yield useful insights into the

subsurface behaviour of whole petroleum deposits. For example, Mango (1990a; 1990b; 1990c) studied the thermal decomposition of cycloalkanes relative to open chain alkanes in the laboratory and noticed that thermal cracking resulted in elevated certain ratios of cyclic versus acyclic alkanes. Comparing the same ratios in a series of more than 2000 North American oils and condensates, Mango (1990c) found evidence of major ($\epsilon > 80\%$) thermal degradation in only one gas condensate deposit at great depth (6000 m; formation temperature not given). Kinetic parameters derived from these and other experiments imply that many (saturated) hydrocarbons have half-lives of the order 10–1000 Ma at 150°C (e.g. Ungerer, 1990); this is consistent with Figure 9a where 50% degradation at 150°C requires a rather special combination of ultra-low heating rate and organic matter quality (HI^0) in the source rock. In fact if, as suggested above, a reservoir oil is best represented as a pseudo-source rock with high HI^0 , then there is no geologically reasonable heating rate that permits 50% cracking at even 160°C (Figure 9a).

Mango (1990c) goes further, suggesting that thermal decomposition of oil to gas is an unimportant, statistically insignificant process within petroliferous regions of the earth, except to speculate that the presence of 'carbonaceous residues' in reservoirs might catalyse the decomposition of otherwise stable hydrocarbons (note the possible role of organic matter implied here and the potential for hydrogen donation which is a prerequisite of our cracking kinetic model). Other workers have stressed the importance of thermochemical reduction of hydrocarbons in reservoirs associated with sulphate mineral deposits (Orr, 1974; Sassen and Moore, 1988; Claypool and Mancini, 1989; but note our earlier warning about the interpretation of field data sets). Takach *et al.* (1987) and Barker and Takach (1992) have also demonstrated the importance of reservoir mineralogy in determining the ultimate destruction of methane, which is governed by the thermodynamics of mineral–fluid interactions at very high pressure and temperature.

Aside from these possible exceptions, there seems to be a high level of agreement that in-reservoir cracking should occur only at extremely severe levels of thermal stress, i.e. those which are, even today, rarely reached by the drill bit. In the final and following part of this paper, we test this concept by studying the composition of petroleum in deep reservoirs of the UK Central North Sea Basin.

In-reservoir cracking: case study

Quads 22, 23, 29 and 30 of the Central Graben, North Sea present an ideal test bed for our kinetic model (provided that our in-source kinetic parameters are applicable outside the source rock environment). Here, numerous oil and gas condensate pools or pool complexes are reservoirised in tilted fault blocks bearing Triassic and Middle Jurassic sandstones, overlain by the main source rock in the area, the Upper Jurassic Kimmeridge Clay Formation. The crestal portions of these fault blocks are currently at a range of temperatures from 120 to 174°C (Figure 13a). These crestal temperatures are accurately known as they are

measured during flow testing of the reservoirs. The temperatures of the unpenetrated deeper portions of the fault blocks are less well known as they are predicted from one-dimensional model-derived thermal profiles calibrated at nearby well locations to an accuracy probably within 10°C. The deepest portions of all the fault blocks are at temperatures well in excess of 200°C.

Reservoirs rarely constitute a closed system within which cracking can be studied. However, in the case of the Central Graben where these isolated, tilted reservoir 'slabs' are highly overpressured, each tilted fault block conforms approximately to a closed petroleum system within which we can attempt an approximate petroleum mass balance. Furthermore, at such high reservoir pressures and temperatures almost all fluid compositions will exist as a supercritical phase. This means that if losses occur from the system, then the residual fluids will not change composition in the same way that in a two-phase accumulation, leakage of the gas cap or spillage of the oil leg might alter substantially the overall composition of the petroleum.

In this crude natural laboratory we may investigate the compositions of (i.e. gas to oil proportions in) the reservoirised petroleums, their correlation with present day reservoir temperature, and whether this is consistent with our kinetic model of oil–gas cracking in reservoirs (e.g. Figure 12a and 12b). The gas to oil ratios of the pools have been converted from oilfield volume ratios (gas to oil ratios in scf bbl⁻¹) to mass fractions of gas ($kg_{GAS} kg^{-1}$) for comparison with kinetic model predictions expressed in mass terms.

Figure 13a shows the mass fractions of gas in the various pools plotted against reservoir temperature. In pools currently experiencing temperatures of up to 174°C, there is no correlation between composition and reservoir temperature. This observation can be confirmed at the molecular level. Figure 14 compares the C_{12–36} *n*-alkane envelopes of three oils (*sensu stricto*) from the area, spanning a reservoir temperature interval from 150 to 195°C. There is no perceptible change in distribution of the higher *n*-alkanes, confirming that cracking of these species is not occurring at significant rates (c.f. Ungerer, 1990). Species which may have been affected by in-reservoir cracking include the high molecular weight cyclic and aromatic hydrocarbons (hopanes and steranes); however, cracking of such volumetrically minor oil components is unlikely to perceptibly alter the gas to oil ratio of a petroleum deposit.

Also on Figure 13a, our kinetic model-derived curve predicts that at the range of reservoir temperatures encountered and at the appropriate heating rate of ca. 5°C Ma⁻¹, oil to gas cracking will be in its early stages, with perhaps a maximum gas fraction of 0.1 $kg_{GAS} kg^{-1}$ attributable to cracking at 174°C. Both data and model suggest that some factor other than reservoir temperature is dominant in controlling the wide range of compositions observed in these reservoirs.

Figure 13b shows the mass proportions of gas in the various pools, now plotted against midpoint temperature of the source rock within each tilted fault block, representing crudely the 'average' kitchen temperature. A clear compositional trend is now observed: pool

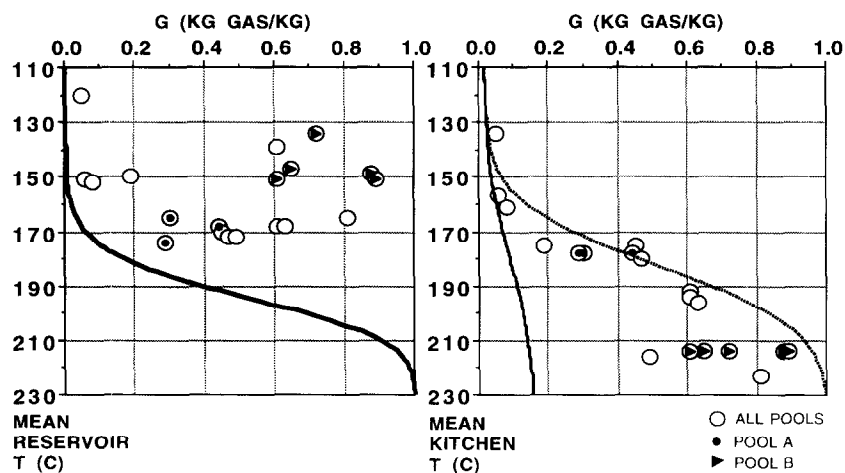


Figure 13 (a) Petroleum pool compositions (mass fraction gas) in deep Central North Sea Basin, plotted against reservoir temperature. No correlation is apparent at reservoir temperatures up to 174°C. Pool complexes A and B are represented by several compositions tested in different segments. Our model curve is consistent, showing that significant cracking (i.e. $G > 0.1$) would not be expected in these reservoirs at this heating rate ($5^{\circ}\text{C Ma}^{-1}$). (b) Same petroleum pool compositions, now plotted against midpoint temperature of the source kitchen. The strong correlation demonstrates the importance of kitchen processes, rather than reservoir processes, in determining the composition, and hence phase, of petroleum in deep, hot reservoirs. Curves show two model projections, assuming a grossly simplified picture: a typical organofacies B (Part I, Table 6) source rock exposed to the mid-point kitchen temperature at a heating rate of $5^{\circ}\text{C Ma}^{-1}$. The two curves show the possible envelope of predicted cumulative charge compositions, depending on expulsion behaviour: solid curve assumes completely efficient expulsion (open system; c.f. Part I, Figure 16g); broken curve assumes completely inefficient expulsion (closed system, Figure 11b, this paper). Observed compositions are intermediate and are consistent with a finite expulsion efficiency. This demonstrates the need for quantitative modelling of expulsion in prediction of charge composition, which we will illustrate in Part III

composition depends strongly on kitchen temperature.

We conclude with the statement that these observations are consistent with our experiences elsewhere in modelling petroleum systems: oil to gas cracking in deep, hot reservoirs is a frequently cited but greatly overestimated risk. Reservoirs are almost always in communication with deeper, hotter source kitchens, and it is these that largely determine the composition, and phase, of entrapped petroleum fluids.

Conclusions

Laboratory experiments yield rate constants for oil to gas cracking which may be extrapolated to the geological subsurface with a probable temperature confidence no better than 7°C .

Kinetics of the cracking process, and hence kinetic

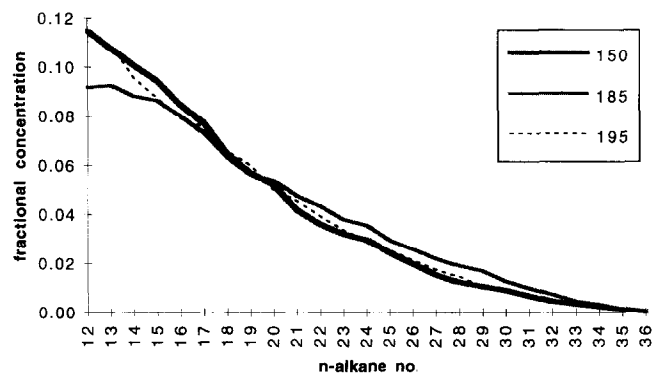


Figure 14 C_{12-36} n -alkane profiles for three oils (C_{6+} range petroleum) from the Central North Sea Basin. There is no significant change in the shape of the n -alkane envelope over the reservoir temperature interval 150–185–195°C

modelling parameters, are highly dependent on oil composition, primarily the saturate to aromatic ratio of the generated oil.

The HI^0 of the source rock, reflecting indirectly the saturate to aromatic ratio of the generated oil, can be correlated with the rate constants for oil cracking, thus allowing prediction of cracking rates based on knowledge of a simple routinely performed geochemical measurement.

We have established temperature thresholds for onset of cracking (defined here as $\epsilon_{0.1}$ or 90% oil remaining). For source rocks with $\text{HI}^0 < 300 \text{ mg}_{\text{HC}} \text{ g}_{\text{C}}^{-1}$ the cracking threshold varies significantly: from less than 115 to 145°C . When HI^0 exceeds ca. $600 \text{ mg}_{\text{HC}} \text{ g}_{\text{C}}^{-1}$ the threshold can be considered effectively constant: $\epsilon_{0.1} = 155^{\circ}\text{C}$.

For the oil deadline (defined here as $\epsilon_{0.9}$ or 10% oil remaining), or oil floor, can be considered effectively constant for source rocks with $\text{HI}^0 > 300 \text{ mg}_{\text{HC}} \text{ g}_{\text{C}}^{-1}$, at ca. 205°C . However, especially in low HI^0 samples, some small refractory population of the generated oil will persist at temperatures up to 250°C .

These predictions are derived for a heating rate $2^{\circ}\text{C Ma}^{-1}$. An order of magnitude increase (decrease) in heating rate elevates (depresses) the temperatures of the reaction midpoint (at which 50% cracking has occurred; $\epsilon_{0.5}$) by approximately 15°C .

Application of the results of this study to the reservoir environment requires caution for two reasons. Firstly, there are marked fractionation effects during expulsion which result in significant enrichment in saturates of the expelled, ultimately reservoir oil relative to the residual oil. Secondly, the reservoir environment, unlike the source rock, is a region of limited hydrogen budget.

Currently we have no way of quantifying potential errors due to the application of our rate parameters to in-reservoir cracking. However, we speculate that oil cracking will proceed at least as slowly in the reservoir as in the best quality source rocks, and will require the formation of coke or pyrobitumen to conserve hydrogen balance.

Whichever, it is likely that our kinetic parameters will overestimate gas to oil ratios due to in-reservoir cracking. This is confirmed by field data which show little evidence of in-reservoir cracking at temperatures at least high as 174°C and possibly as high as 195°C.

Previous studies have largely overestimated the importance of in-reservoir cracking. Future studies aiming to predict entrapped petroleum composition and phase should concentrate on understanding the charge composition expelled from the kitchen.

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