Evaluation of Petroleum Generation by Hydrous Pyrolysis Experimentation [and Discussion]

M. D. Lewan, B. Spiro, H. Illich, R. Raiswell, A. S. Mackenzie, B. Durand, D. A. C. Manning, P. A. Comet, R. A. Berner and J. W. De Leeuw

Phil. Trans. R. Soc. Lond. A 1985 **315**, 123-134
doi: 10.1098/rsta.1985.0033

Phil. Trans. R. Soc. Lond. A **315**, 123–134 (1985)

Printed in Great Britain

Evaluation of petroleum generation by hydrous pyrolysis experimentation

By M. D. Lewan

Amoco Production Company Research Center, P.O. 3385, *Tulsa, Oklahoma* 74102, *U.S.A.*

Generation and expulsion of oil from organic sedimentary rocks have been achieved in the laboratory by a technique known as hydrous pyrolysis. This technique maintains a liquid water phase in contact with organic sedimentary rocks during their heating at subcritical water temperatures (less than 374 °C). The expelled oil accumulates on the water surface and contains no measurable olefinic hydrocarbons. Hydrous pyrolysis provides a means of acquiring information relating to stages, kinetics and indices of petroleum generation that would be difficult to obtain from a study of only the natural system.

Introduction

Studies on thermal maturation in the natural system provide useful information on the changes in the bitumen and kerogen of organic rocks, but not on corresponding changes in their expelled crude oil. At the present time it is not feasible in the natural system to acquire samples of crude oils that have been expelled from the same rock unit at different levels of thermal maturity. This gap between the retained and expelled organic phases may be bridged in part by hydrous pyrolysis. Hydrous pyrolysis is a laboratory technique that closely simulates petroleum generation in the natural system (Lewan *et al.* 1979; Lewan 1983; Winters *et al.* 1983). The technique involves maintaining a liquid water phase in contact with organic sedimentary rocks during their heating at subcritical water temperatures (less than 374 °C). Pyrolysate expelled from an organic sedimentary rock accumulates on the water surface and may be quantitatively collected at the end of the experiment. The pyrolysate expelled by this technique is more closely analogous to crude oil expelled in the natural system than that afforded by pyrolysis techniques that employ carrier gases, cryogenic traps, or solvent extraction methods. Although higher temperatures (260–365 °C) must be employed in hydrous pyrolysis to compensate for the longer time (1–100 Ma) experienced in the natural system, the pyrolysates are similar to natural crude oils (Lewan *et al.* 1979; Hoering 1984). The object of this study is to evaluate the different stages, kinetics and indices of petroleum generation by hydrous pyrolysis of Woodford Shale (Devonian–Mississippian) and Phosphoria Retort Shale (Permian). Organic matter in both of these rock units consists primarily of immature amorphous type II kerogen.

Materials and methods

The sample of Phosphoria Retort Shale is from a 12 cm thick interval in the Retort Shale Member of the Phosphoria Formation at Retort Mountain, Montana (section 23, T.9S, R.9W, Beaverhead Co.). As reported by Lewan (1983), the sample of Woodford Shale is from a 7 cm thick interval in an exposure on the southern flank of the Arbuckle Anticline, Oklahoma (section 25, T.2S, R.1E, Carter Co.). Weathered portions of the outcrops were avoided by using the field criteria proposed by Lewan (1980) for collecting unweathered samples. Table 1 lists the results of whole rock analyses performed on the samples collected from the two rock units.

Table 1. Whole rock analyses on the original samples used in the hydrous pyrolysis experiments

type of analysis	Woodford Shale	Phosphoria Retort Shale
laboratory classification (Lewan 1978)	quartzose claystone	argillaceous claystone
mineralogy		
major minerals (greater than 10% by mass)	quartz, illite	quartz, kaolinite, illite
minor minerals (less than 10% by mass)	pyrite, kaolinite	pyrite
organic carbon content (percentage by mass)	12.7	23.6
Rock Eval analysis		
S_2/organic C	0.56	0.57
$S_1/(S_1+S_2)$	0.034	0.036
elemental mole fractions		
$Al/(Si+Al)$	0.09	0.19
organic C/(Al + organic C)	0.90	0.91
$(Na+K)/(Ca+Mg+Na+K)$	0.69	0.70
$S_{tot}/(Fe_{tot}+S_{tot})$	0.75	0.84

The samples were matured to different stages of petroleum generation by heating separate aliquots isothermally for 72 h at temperatures ranging from 240 to 360 °C. To achieve advanced stages of petroleum generation at subcritical water temperatures, aliquots were isothermally heated at 360 or 365 °C for periods in excess of 72 h. The starting material in these experiments was unextracted crushed rock ranging in size from 0.5 to 2.0 cm. One-litre reactors were filled with 500 g of crushed rock and 260 ml of deionized (A.S.T.M.† type III) water in the Woodford Shale experiments and 400 g of crushed rock and 290 ml of deionized (A.S.T.M. type III) water in the Phosphoria Retort Shale experiments. The remaining volume was purged and filled with 240 kPa of helium.

The three organic phases collected from the reactor after hydrous pyrolysis include expelled oil, bitumen and kerogen. Expelled oil occurs in the reactor as a floating liquid pyrolysate layer on the water surface and as a sorbed liquid pyrolysate film on the rock chips. The floating liquid pyrolysate is collected with a Pasteur pipette and transferred to a tared glass vial. Water in the reactor is decanted into a separatory funnel where the minor quantity of floating liquid pyrolysate is concentrated and collected. Benzene is used to rinse off and collect the sorbed liquid pyrolysate film on the rock chips, reactor walls, collection pipette and separatory funnel. The resulting solution is filtered through a 0.45 μm Fluoropore filter and the sorbed liquid pyrolysate is concentrated by rotary vacuum evaporation of the benzene. There are no significant compositional differences between the floating and sorbed liquid pyrolysate and collectively they are referred to as expelled oil. The floating liquid pyrolysate usually comprises more than 75% by mass of the total expelled oil.

† A.S.T.M. is an abbreviation for American Society of Testing and Materials.

The rock chips are removed from the reactor and dried in a vacuum oven at 50 °C for 24 h. Bitumen is extracted from pulverized rock chips in a Soxhlet apparatus for 72 h with a mixture of benzene and methanol (60 : 40 by mass). The refluxed solvent is filtered through a 0.45 µm Fluoropore filter and the bitumen is concentrated by rotary vacuum evaporation. Kerogen is isolated from pulverized rock chips by a series of acid treatments, which include an 18% (by mass) solution of HCl for 2 h, a 52% (by mass) solution of HF for 18 h and a hot (100 °C) concentrated solution of HCl for 1 h. This is followed by a density separation with a 2.1 g cm^{-3} solution of zinc bromide. The floating residue is collected and termed kerogen after it has been extracted in a Soxhlet apparatus for 72 h with a mixture of benzene and methanol (60 : 40 by mass).

RESULTS AND DISCUSSION

Stages of petroleum generation

Results of the experiments in figures 1 and 2 show that pyrolysate generation may be divided into four distinct stages; (i) pre-oil generation, (ii) incipient oil generation, (ii) primary oil generation, and (iv) post-oil generation. Pre-oil generation is characterized by the lack of expelled oil and no significant change in the amount of kerogen or bitumen. Thermal decomposition of kerogen during incipient oil generation results in the generation of bitumen and minor amounts of expelled oil. The amount of kerogen shows only a slight decrease through primary oil generation, while thermal decomposition of bitumen results in the primary generation of expelled oil. Thermal decomposition of expelled oil denotes the start of post-oil generation. Bitumen and expelled oil during this last stage generate gas and pyrobitumen. The insoluble character of the latter makes it difficult to isolate from the kerogen and therefore a slight apparent increase in the amount of kerogen is observed in the post-oil generation stage.

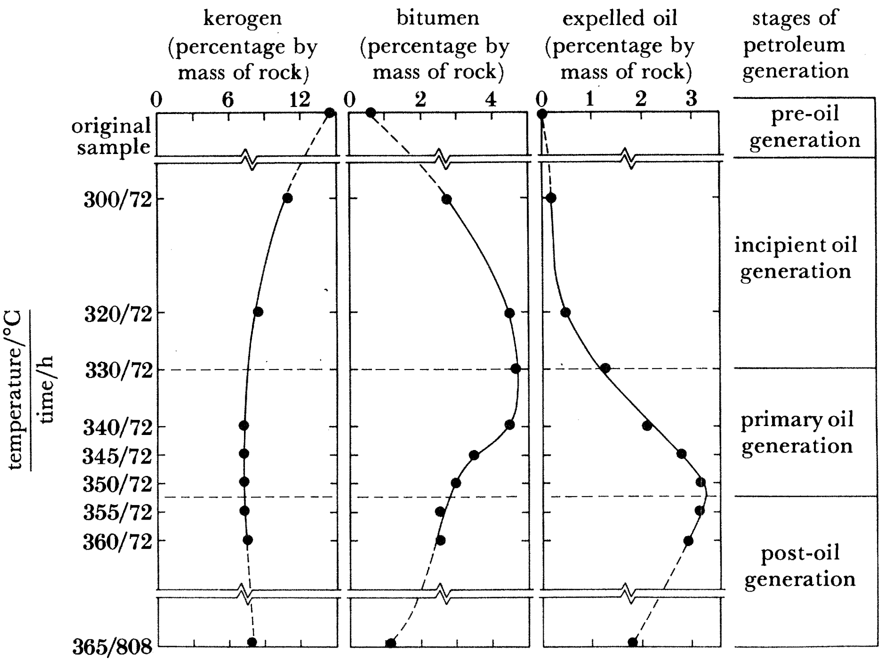

FIGURE 1. The amounts of kerogen, bitumen and expelled oil from aliquots of Woodford Shale pyrolysed at different temperatures and times.

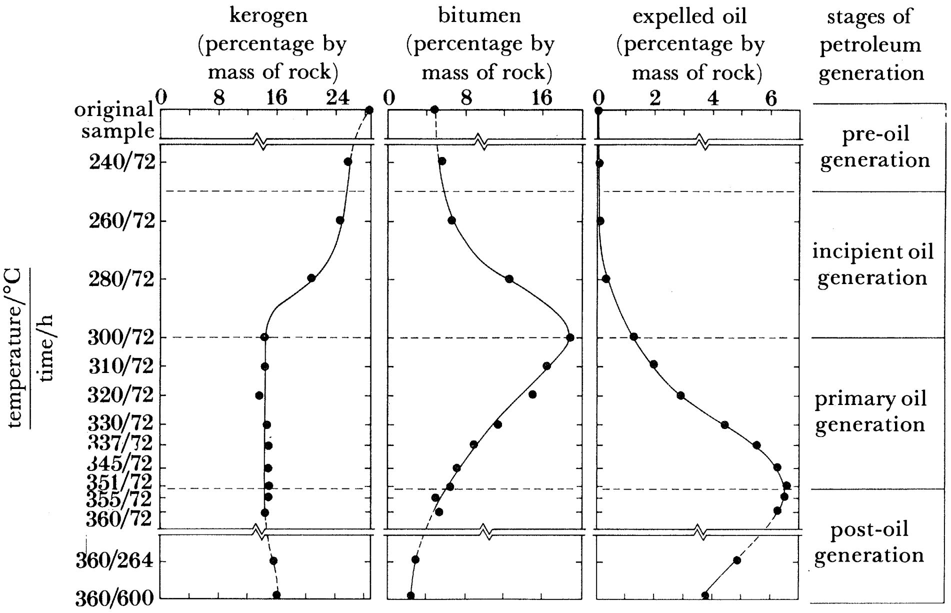

Figure 2. The amounts of kerogen, bitumen and expelled oil from aliquots of Phosphoria Retort Shale pyrolysed at different temperatures and times.

Figures 1 and 2 show that maximum bitumen generation does not coincide with maximum oil generation as is sometimes assumed in the natural system. Maximum bitumen generation is defined in the figures by a broad peak for the Woodford Shale and a relatively sharp peak for the Phosphoria Retort Shale. The different temperatures at which these maxima occur indicates that primary oil generation starts at a lower thermal stress in the Phosphoria Retort Shale than in the Woodford Shale. This difference cannot be explained by differences in the initial maturity levels of the two samples and suggests that the kinetics for oil generation may not be the same for all amorphous type II kerogens.

Kinetics of petroleum generation

Petroleum generation undoubtedly involves a multitude of elementary reactions. Formulation of these reactions into a comprehensive kinetic model is preferable but not possible at this time. Hydrous pyrolysis offers an alternative by providing kinetic data on the overall reaction involving the generation of expelled oil. This overall reaction collectively encompasses oil generation within a rock and oil expulsion from it. The definition and monitoring of reactants is not feasible in this collective approach, and therefore, the kinetic modelling is based on the fraction of maximum expelled oil generated (denoted as X) at a given time and temperature. Figure 3 shows the Arrhenius plots that result when a first-order reaction rate (i.e. $\mathrm{d}X/\mathrm{d}t = k - kX$) is assumed for the generation of expelled oil. Regardless of the internal complexity of this overall reaction, the Arrhenius plots show good linear relations that encourage their extrapolation to lower temperature régimes within the natural system.

The calculated kinetic parameters in figure 3 show the Woodford Shale to have a larger activation energy (E_A) and pre-exponential factor (A_0) than the Phosphoria Retort Shale. The

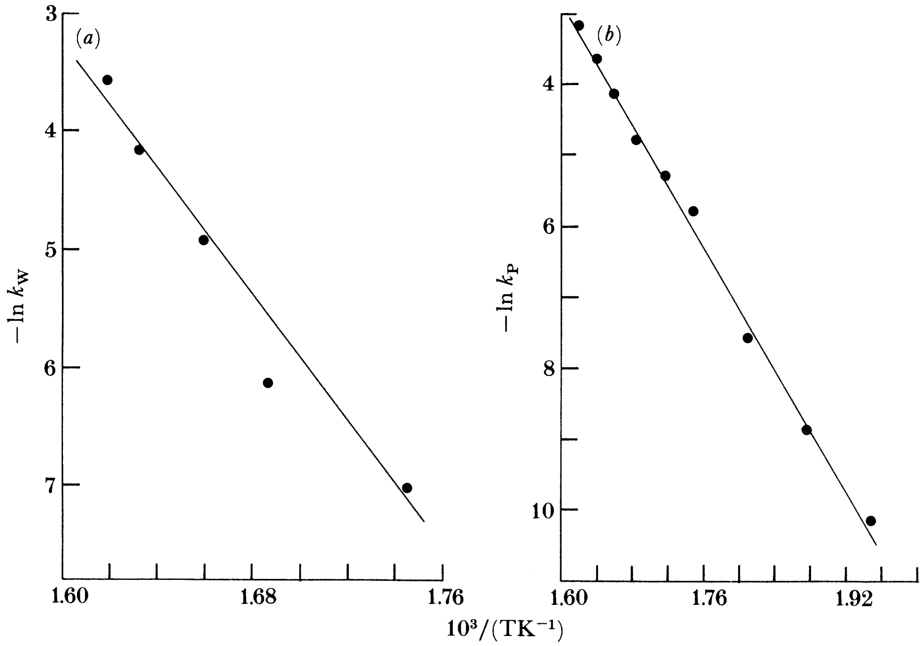

FIGURE 3. Arrhenius plots for the expelled oil generated from (*a*) Woodford Shale; $\ln k_W = -26247.4\,(\mathrm{T}^{-1}) + 38.72$, $E_A = 218.25\ \mathrm{kJ\ mol^{-1}}$, $A_0 = 6.51 \times 10^{16}\ \mathrm{h^{-1}}$, and (*b*) Phosphoria Retort Shale; $\ln k_P = -21490.6\,(\mathrm{T}^{-1}) + 31.53$, $E_A = 178.69\ \mathrm{kJ\ mol^{-1}}$, $A_0 = 4.92 \times 10^{13}\ \mathrm{h^{-1}}$. Rate constants were calculated from the expelled oil data presented in figures 1 and 2.

significance of these differences in the natural system may be evaluated by extrapolating the kinetic parameters into two models for subsiding basins. The first model considers rapid subsidence ($304.8\ \mathrm{m\ Ma^{-1}}$) of a Miocene source bed (15 Ma B.P.) in a basin with a high thermal gradient ($47.4\ ^\circ\mathrm{C\ km^{-1}}$). These conditions are analogous to those in some of the Neogene pull-apart basins in Southern California. Cumulative integration of the Arrhenius equation (i.e. $\ln k = \ln A_0 - E_A/RT$) with the integral of the first-order rate expression over the subsidence history of this basin at 0.2 Ma increments results in the expelled oil generation curves in figure 4*a*. These two curves indicate that type II kerogens governed by kinetic parameters similar to those of the kerogen in the Woodford Shale generate expelled oil at deeper depths and after longer durations than those similar to the type II kerogen in the Phosphoria Retort Shale. Although the 670 m depth and 2.2 Ma time differences are not likely to be significant in evaluating deep basins (greater than 3 km), they may prove to be critical in evaluating the petroleum potential of some shallow basins (less than 3 km).

The second basin model considers slow subsidence ($12.2\ \mathrm{m\ Ma^{-1}}$ from 520 to 240 Ma B.P. and $1.2\ \mathrm{m\ Ma^{-1}}$ from 240 Ma B.P. to present) of a Cambrian source bed (520 Ma B.P.) in a basin with a low thermal gradient ($32.8\ ^\circ\mathrm{C\ km^{-1}}$). These conditions are analogous to some of the Paleozoic cratonic basins in the mid-continent area of North America. Cumulative integration of the Arrhenius equation with the integral of the first-order rate expression over the subsidence history of this basin at 4 Ma increments results in the expelled oil generation curves in figure 4*b*. These two curves extend over a wider depth range and have a greater separation than the pull-apart basin model. The 985 m difference between the two curves accentuates the significance of employing the proper kinetic parameters in evaluating the petroleum potential of shallow basins (less than 3 km).

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

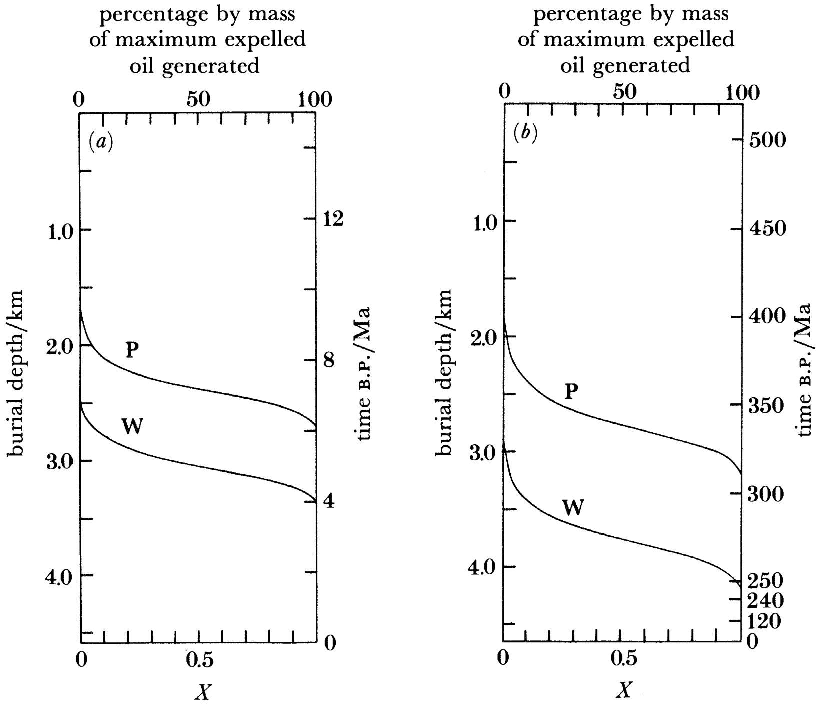

FIGURE 4. Expelled oil generation curve for amorphous type II kerogens with kinetic parameters similar to those derived from the Woodford Shale (W) and the Phosphoria Retort Shale (P), in two types of subsiding basins; (*a*) rapidly subsiding basin with a high thermal gradient analogous to Neogene pull-apart basins and (*b*) slowly subsiding basin with a low thermal gradient analogous to Paleozoic cratonic basins. *X* denotes the decimal fraction of maximum expelled oil generated.

One conspicuous difference between these two similar kerogen types that may explain their different kinetics for oil generation is their organic sulphur content. As shown in table 2, the kerogen in the Phosphoria Retort Shale has almost twice the organic sulphur content as the kerogen in the Woodford Shale. Organic sulphur contents of type II kerogens are most probably related to early diagenetic reactions between aqueous hydrogen sulphide species (such as H_2S or HS^-) and proto-kerogen.

The aqueous hydrogen sulphide is derived from the dissimilatory bacterial reduction of dissolved sulphate. If the amount of hydrogen sulphide produced in the interstitial water exceeds the amount of iron available in the sediment, the excess hydrogen sulphide is likely to react with the organic constituents involved in the development of kerogen. It is conceivable that within a kerogen its carbon–sulphur bonds may cleave more readily to generate liquid hydrocarbons than its carbon–carbon bonds. This hypothesis contends that the greater the amount of organic sulphide incorporated into the matrix of developing type II kerogens, the lower the thermal stress necessary for their generation of oil. A continuum between and beyond the kinetic parameters for the type II kerogens in the Phosphoria Retort Shale and Woodford Shale may be envisaged with corresponding variations in organic sulphur contents.

Table 2. Analysis on kerogens isolated from original samples used in the hydrous pyrolysis experiments

type of analysis visual analysis	Woodford Shale: amorphous	Phosphoria Retort Shale: amorphous
	elemental analysis	
normalized percentage by mass		
carbon	78.2	74.5
hydrogen	7.7	7.5
oxygen	7.0	6.2
nitrogen	2.1	2.8
sulphur[a]	5.0	9.0
	mole fractions	
$H/(C+H)$	0.542	0.547
$O/(C+O)$	0.063	0.059
$N/(C+N)$	0.023	0.031
$S/(C+S)$	0.023	0.043
	isotopic analysis[b]	
$\delta^{13}C$	−29.6	−29.3
	F.t.i.r. analysis[c]	
aliphatic ratio	0.87	0.82
carbonyl ratio	0.19	0.18

[a] This value represents organic sulphur in the kerogen and does not include inorganic sulphide in the form of iron sulphide that may be associated with the kerogen.

[b] $\delta^{13}C = \left(\frac{R_{spl}-R_{std}}{R_{std}}\right)\times 10^3$, where $R_{spl} = {}^{13}C:{}^{12}C$ of sample and $R_{std} = {}^{13}C:{}^{12}C$ of *Belemnitella americana* standard from the Pee Dee Formation, South Carolina.

[c] Fourier transform infrared; the aliphatic ratio is the area of the 2930 cm^{-1} peak divided by the sum of the areas of the 1630 and 2930 cm^{-1} peaks; the carbonyl ratio is the area of the 1710 cm^{-1} peak divided by the sum of the areas of the 1630 and 1710 cm^{-1} peaks.

Indices of petroleum generation

Organic maturation studies in the natural system rely on indices within organic sedimentary rocks to determine the stage of petroleum generation they have experienced. Elemental analyses and reflectances measurements on kerogens are the most commonly employed indices. The atomic H:C ratio of a kerogen is calculated from elemental analyses of C, H, O and N and may be used as an index of petroleum generation. Figure 5 shows that kerogens from the pyrolysed aliquots of Woodford Shale and Phosphoria Retort Shale have essentially the same relation between their atomic H:C ratios and percentage of expelled oil. This common relation suggests that the atomic H:C ratio may be used as an index for stages of petroleum generation, irrespective of the differences in the magnitude of thermal stress required for oil generation from type II kerogens.

Therefore, the atomic H:C ratio by itself may be a good index for the different stages of petroleum generation, but may not always be a good index for the magnitude of thermal stress experienced by a kerogen unless its kinetics for oil generation are known. As an example, an atomic H:C ratio of 0.65 indicates that 80% by mass of the maximum amount of expelled oil has been generated by the type II kerogens in both the Woodford Shale and the Phosphoria Retort Shale (figure 5). Figure 4 shows that the magnitude of thermal stress to attain this stage of petroleum generation is considerably higher for the Woodford Shale than for the Phosphoria Retort Shale.

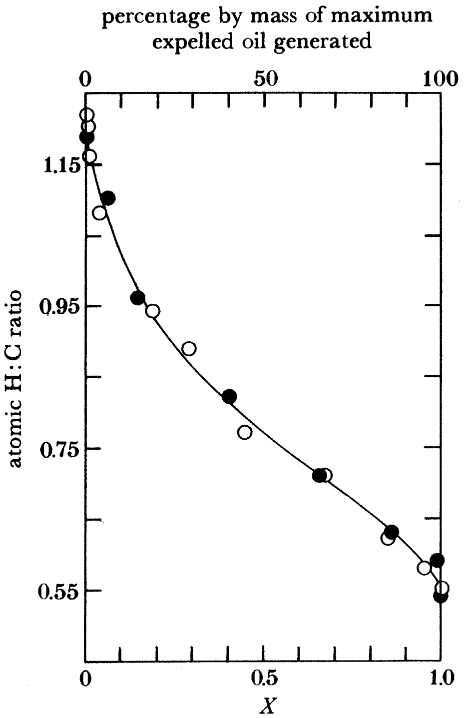

FIGURE 5. Congruent relation between the atomic H:C ratio of kerogen and the percentage by mass of maximum expelled oil generated for the Woodford Shale (●) and the Phosphoria Retort Shale (○). Carbon and hydrocarbon contents were determined on the Carlo Erba elemental analyser Model 1106 with acetanilide as a standard. X denotes the decimal fraction of maximum expelled oil generated. $H:C = 1.08x^3+2.06x^2-1.615x+1.184$; correction coefficient = 0.996.

In contrast to the elemental analyses, reflectance measurements on structured type III kerogens appear to be a good index for the magnitude of thermal stress experienced by the kerogens, but may not always be a good index of their stage of petroleum generation. Figure 6 shows that the reflectance measurements on minor amounts of structured type III kerogens that accompany the amorphous type II kerogens in the Woodford Shale and Phosphoria Retort Shale have essentially the same relation with the magnitude of thermal stress induced by hydrous pyrolysis. This common relation suggests that reflectance measurements on structured type III kerogens may be used as an index for magnitude of thermal stress, irrespective of differences in the kinetics for oil generation from accompanying amorphous type II kerogens. An important aspect that emerges from these results is that indices for the stages of petroleum generation may not always be universally equated to indices of thermal stress and vice versa.

Hydrous pyrolysis experiments also reveal that the rate of change in reflectance for structured type III kerogens dispersed in sedimentary rocks is not the same for those concentrated in coal seams. Figure 6 shows the change in reflectance on structured type III kerogens in two humic coals that have been subjected to a series of hydrous pyrolysis experiments. Changes in the reflectance of these humic coals are initially rapid up to approximately 1.1% R_0 between 300 and 310 °C and increase more slowly thereafter. Conversely, changes in the reflectance of the dispersed type III kerogens are initially slow up to approximately 0.7% R_0 at 340 °C and increase more rapidly thereafter. These differences are geologically significant and offer an explanation for the enigma of low activation energies for coalification (35 kJ mol^{-1} from Huck & Karweil 1955; 32–45 kJ mol^{-1} from Scaroni *et al.* 1981) and higher activation energies for oil generation (209 kJ mol^{-1} from Tissot & Espitalié 1975; 178 and 218 kJ mol^{-1} from this study), which is often equated with coal rank.

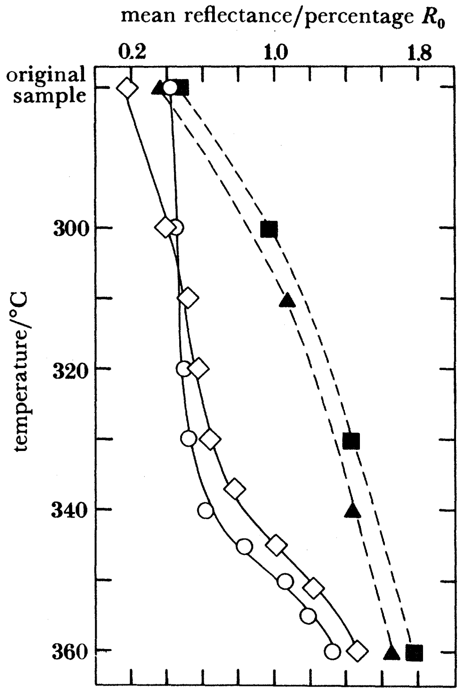

Figure 6. Relation between thermal stress induced by hydrous pyrolysis and mean reflectance measurements on structured type III kerogens dispersed in sedimentary rocks (Phosphoria Retort Shale, ◇, and Woodford Shale, ○) and concentrated in autochthonous humic coals (Wilcox Fairfield Lignite, ▲, and Blackhawk Hiawatha Coal, ■). (Time = 72 h.)

Although vascular plant debris is the probable precursor for structured type III kerogens in both reflectance trends, the depositional history before lithification may be the discriminating factor. Concentrated type III kerogen in coals is usually autochthonous and likely to be involved with reducing reactions (such as gelification) early in its depositional history. Conversely, dispersed type III kerogen in sediments is usually allochthonous and likely to be involved with a high degree of degradation and oxidation during the transport period of its depositional history. A more refractory type III kerogen with a higher lignin than cellulose component may be envisaged in the latter case.

Conclusions

Hydrous pyrolysis experimentation on organic sedimentary rocks provides useful information relating to the stages, kinetics and indices of petroleum generation. Stages of petroleum generation for amorphous type II kerogen include pre-oil generation, incipient oil generation, primary oil generation and post-oil generation. The three basic reactions that define these stages are thermal decomposition of kerogen to bitumen, bitumen to oil and oil to gas and pyrobitumen. This sequence of reactions indicates that maximum bitumen generation should not be equated to maximum oil generation in studying the natural system.

Oil generation involves a multitude of elementary reactions and determining the kinetics for each of these reactions is not currently possible. As a first approximation of the kinetics for the generation of expelled oil, these elementary reactions may be considered collectively in terms of an overall reaction. Kinetic parameters determined on the overall reaction indicate that the timing for generation of expelled oil is not the same for all amorphous type II kerogens. Differences in their kinetics can be geologically significant, and appear in part to be related to the amount of organic sulphur incorporated into a kerogen matrix. Conceptually, amorphous type II kerogens with a high organic sulphur content may be expected to generate expelled oil at a lower thermal stress than those with a low organic sulphur content.

Hydrous pyrolysis experiments indicate that the atomic H:C ratio of amorphous type II kerogen is a reliable index for the stages of petroleum generation, but may not always be a reliable index for the amount of thermal stress experienced by a kerogen. Conversely, reflectance measurements on structured type II kerogen may not always be a reliable index for the stages of petroleum generation, but is a reliable index for the amount of thermal stress experienced by a kerogen. Proper evaluation of thermal stress from reflectance measurements requires making the distinction between structured type III kerogens that are dispersed as allochthonous debris in sediments and those that are concentrated as autochthonous remains in humic coals.

The author thanks the Amoco Production Company for its support of this research and permission to publish it. J. C. Winters, J. A. Williams and H. D. Winland are gratefully acknowledged for their encouragement and helpful suggestions. J. H. McDonald and J. D. Redding provided valuable assistance in the laboratory.

REFERENCES

Hoering, T. C. 1984 *Org. Geochem.* **5**, 267–278.
Huck, G. & Karweil, J. 1955 *Brennst.-Chem.* **36**, 1–11.
Lewan, M. D. 1978 *Geology* **6**, 745–748.
Lewan, M. D. 1980 *Geochemistry of vanadium and nickel in organic matter of sedimentary rocks.* Dissertation, University of Cincinnati.
Lewan, M. D. 1983 *Geochim. cosmochim. Acta* **47**, 1471–1479.
Lewan, M. D., Winters, J. C. & McDonald, J. H. 1979 *Science* **203**, 897–899.
Scaroni, A. W., Walker, P. L., Jr & Essenhigh, R. H. 1981 *Fuel* **60**, 71–76.
Tissot, B. & Espitalié, J. 1975 *Revue Inst. fr. Petrole* **30**, 743–777.
Winters, J. C., Williams, J. A. & Lewan, M. D. 1983 In *Advances in organic geochemistry* 1981 (ed. M. Bjoröy *et al.*), pp. 524–533. Chichester: Wiley.

Discussion

A. S. MACKENZIE (*BP Geochemistry Branch, Sunbury-on-Thames*). Dr Lewan has presented many new conclusions about petroleum formation based entirely on laboratory pyrolysis experiments. Does he have any field studies to support his claims?

M. D. LEWAN. There is some field evidence to support these conclusions. For example, published literature on the Monterey Formation suggests that it generates oil at a lower temperature than many other source rocks. Also the reflectance measurements on vitrinite in the Monterey Formation are not good indicators of petroleum generation. Additional studies on the relation between the reflectance of coal and dispersed vitrinite are in progress. There is some indication from published works that such a difference may exist.

B. DURAND (*Institut Français du Pétrole, Rueil Malmaison, France*). Did Dr Lewan examine the influence of variations in the concentration of organic matter on the products of pyrolysis and does the kerogen in his experiments change in the same way as it does in source rocks? Does the vitrinite in the Phosphoria Retort Shale really have the same chemical composition as that in the coals? If so, why does it behave differently?

M. D. Lewan. It is difficult to perform quantitative analyses on the products of hydrous pyrolysis unless the organic carbon content exceeds 3% by mass. No significant variations have been found at this or larger concentrations.

The experiments on the Phosphoria and Woodford shales show trends on the Van Krevelen diagram similar to those observed in natural samples. Kerogens with higher oxygen contents than those in these two shales deviate slightly from the natural trends and this deviation may be an artefact of the heating rate.

I suspect the kerogen compositions are slightly different, but this has not yet been verified.

D. A. C. Manning (*Department of Geology, The University, Newcastle-upon-Tyne*). The experiments presented here generally have a duration of 72 h with only a few longer runs of 808 h. For the shorter experiments, it is perhaps unlikely that the mineralogical components of the rock will have reached an equilibrium assemblage and metastable phases or structures may be present. In view of the possible involvement of mineral phases in organic reactions, have experiments of varying duration been performed and has any consequent variation in the organic run products been observed?

M. D. Lewan. On the basis of a number of tests the mineralogical changes in these two samples are minimal and the amount of petroleum generated is within approximately a 10% error.

R. A. Berner (*Department of Geology and Geophysics, Yale University, U.S.A.*). If sulphur-rich kerogens produce petroleum at lower temperatures than sulphur-free kerogens, is oil formation favoured in rocks that contain little iron such as carbonates where early diagenesis produces sulphur-rich kerogen?

M. D. Lewan. I have not done any experiments on carbonate source rocks that contain type II kerogen. However, the Phosphoria shale used in these experiments is associated with considerable quantities of chert and carbonate.

P. A. Comet (*Organic Geochemistry Unit, The University, Newcastle-upon-Tyne*). Has any systematic comparison of hydrous and anhydrous pyrolysis been made? Our results indicate tht hydrous and anhydrous pyrolysis give similar results, i.e. both pyrolysis techniques yield the same range of biological marker pyrolytic artefacts and no alkenes.

M. D. Lewan. Anhydrous pyrolysis tends to leave more charred residue and less liquid oil than in hydrous pyrolysis.

P. A. Comet. Our experience at Newcastle has indicated that the same artefacts are present in both cases, and that there is little difference between the two types of experiment. In both cases alkenes are absent.

M. D. Lewan. We have found that anhydrous pyrolysis generates an oil with greater amounts of aromatic and polar components than hydrous pyrolysis.

J. W. de Leeuw (*Technical University, Delft, The Netherlands*). The term 'pyrolysis' does not accurately describe your experiments, which are thermal simulation experiments performed in closed systems.

Alkane–alkene doublets are always produced by heating, but when the system is closed the unsaturated forms are not stable. Some are transformed to the saturated forms and others react with the organic matrix. When flash pyrolysis or thermal degradation is done in an open vessel both alkanes and alkenes are produced.

M. D. Lewan. Alkenes are also produced as a result of higher temperatures and low pressures.

B. Spiro (*British Geological Survey, London*). Did Dr Lewan compare the composition of the bitumen with the pyrolysate, much of which may be original bitumen? In some hydrous pyrolysis experiments, the biomarkers in the pyrolysate show a lower maturity than those in the corresponding bitumen. Therefore, although the products are comparable to naturally generated oils, the process is different and is similar to distillation. The material in the pores is driven out by heating and the pyrolysate is simply a mixture of this newly formed pyrolysate material and the original bitumen. This mechanism may also account for Dr Comet's results.

M. D. Lewan. I have not studied the biomarker changes in the bitumen relative to the expelled pyrolysate.

H. Illich (*Sun Oil Company, Dallas, Texas, U.S.A.*). Has Dr Lewan examined whether there is a correlation between sulphur content and early oil generation in carbonate rocks, to test the suggestion made by a number of speakers?

M. D. Lewan. Unfortunately there is little information about the organic sulphur content of kerogens and so such a study is hard to do. The method used in this study is based on total iron and sulphur determinations. X-ray diffraction is used to verify that the iron sulphide is present as pyrite. The organic sulphur content can then be calculated on the assumption that the organic iron content is negligible. This assumption was verified by surface analysis with the use of X.p.s.

R. Raiswell (*Department of Earth Sciences, Leeds University*). Both euxinic and normal marine sediments lose large quantities of hydrogen sulphide. It is therefore unlikely that the only control on whether sulphur combines with organic material is the availability of iron.

M. D. Lewan. The residence time of the hydrogen sulphide in the sediment may also be important and it will be affected by bioturbation. However in most sulphur-rich source rocks bioturbation is uncommon.

Editorial note

Dr Lewan's paper describes hydrous pyrolysis experiments resulting in the generation of pyrolysates, the composition of which bear some similarities to those of natural crude oils. The valuable results and inferences drawn from them refer to the generation of these pyrolysates and not directly to the generation of natural petroleums.