

Assessing Natural Oil Expulsion from Source Rocks by Laboratory Pyrolysis

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Abstract

The amount of oil a pod of active source rock is capable of expelling is an important parameter in determining the ultimate oil potential of a petroleum system. Laboratory pyrolysis methods available for determining this parameter can be grouped into three categories: (1) *hydrous pyrolysis*, (2) *closed anhydrous pyrolysis*, and (3) *open anhydrous pyrolysis*. The processes responsible for expulsion of oil in nature are best simulated by hydrous pyrolysis. The presence of water in both nature and hydrous pyrolysis ensures the occurrence of a water-saturated bitumen within a source rock. This dissolved water reduces cleavage of bitumen molecules by terminating free radicals with water-derived hydrogen and allows the cleavages that do occur to form an immiscible oil. The importance of water is best demonstrated by its absence in closed anhydrous pyrolysis, which generates a bitumen that ultimately decomposes into an insoluble pyrobitumen rather than an expelled oil. As a result, this method is not useful in evaluating oil expulsion. Conversely, a vaporized oil may be generated in open anhydrous pyrolysis, but the amount of oil generated is dependent on experimental conditions, and the processes responsible for this evolved oil are not operative in nature.

INTRODUCTION

Determining the amount of oil that may be expelled from a pod of active source rock is an important consideration in assessing and ranking the hydrocarbon potential of a petroleum system. Once a source rock has been identified and its mature and overmature volume determined, reliable expulsion efficiencies may be used to determine the ultimate petroleum charge. Although economic accumulations from this charge will be determined by secondary migration and trapping, the ultimate charge is critical in evaluating the efficiencies of these processes within a petroleum system. Determining this ultimate petroleum charge is not only essential in ranking frontier systems but also necessary in assessing when drilling budgets should shift from exploration to exploitation strategies in extensively drilled systems. The success of these applications depends on accurately determining the amount of oil that may be expelled from a pod of active source rock for a given petroleum system. Laboratory pyrolysis methods offer a feasible approach in understanding primary oil migration and determining expulsion efficiencies of source rocks, but the type of pyrolysis method used is an important consideration in extrapolating experimental results to a petroleum system. The objective of this paper is to examine the

utility of various pyrolysis methods in determining the amount of oil expelled from a source rock. The pyrolysis methods are discussed under three general headings: (1) hydrous pyrolysis, (2) closed anhydrous pyrolysis, and (3) open anhydrous pyrolysis.

HYDROUS PYROLYSIS

Hydrous pyrolysis involves heating a rock or kerogen sample in liquid water at subcritical temperatures in a closed reactor (Lewan et al., 1979; Lewan, 1985). If the proper time and temperature conditions are employed, a generated oil is expelled from the sample and accumulates on the water surface within the reactor. This generated and expelled oil is compositionally similar to natural crude oils and is typically a free-flowing liquid oil (Winters et al., 1983). Although the amounts of expelled oil generated in hydrous pyrolysis may be exaggerated, the processes responsible for the expulsion of oil are conceivably the same as those in nature (Lewan, 1991). Petroleum formation as determined by hydrous pyrolysis consists of two overall reactions: (1) partial decomposition of kerogen to bitumen and (2) partial decomposition of bitumen to oil (Lewan, 1985). This reaction series has long been recognized in oil shale

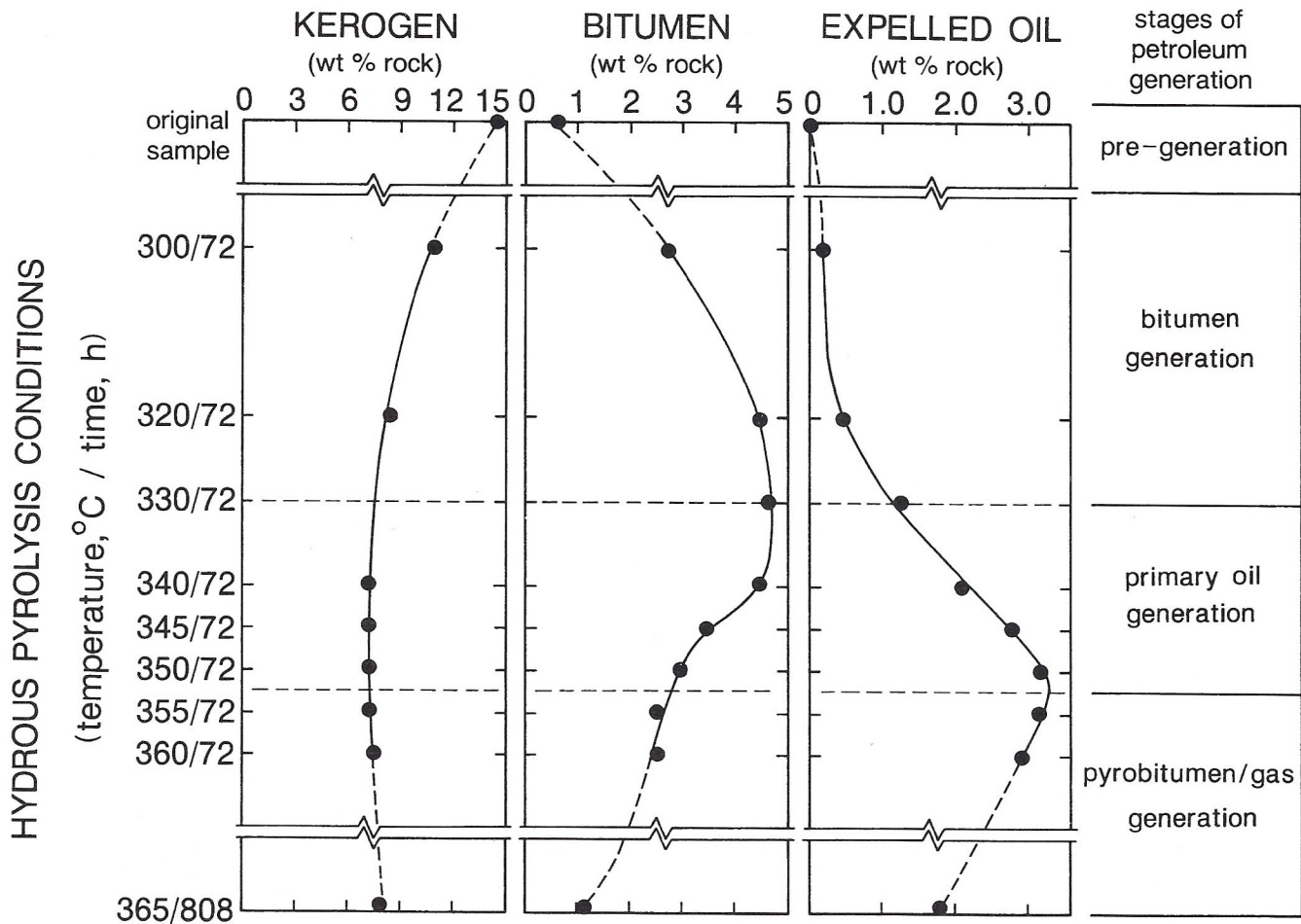


Figure 11.1. Amounts of kerogen, bitumen, and expelled oil collected after conducting isothermal hydrous pyrolysis experiments on aliquots of a Woodford Shale sample (WD-5) at temperatures ranging from 300° to 360°C for 72 hr, and at 365°C for 808 hr. Each experiment consists of heating 500 g of a separate aliquot of the original sample with 260 g of distilled water in a 1-L reactor at the temperature and time specified along the vertical axis. The bitumen generation stage represents the partial decomposition of kerogen to bitumen through the cleavage of weak noncovalent bonds. The primary oil generation stage represents the partial decomposition of bitumen to an immiscible expelled oil through cleavage of covalent bonds. The pyrobitumen/gas generation stage represents the decomposition of expelled oil and bitumen to insoluble organic matter (pyrobitumen) and gas.

retorting (Hershkowitz et al., 1983) and has also been suggested in natural petroleum formation (Louis and Tissot, 1967). Figure 11.1 illustrates these two overall reactions with a series of isothermal hydrous pyrolysis experiments conducted on aliquots of a sample of Woodford Shale (WD-5) at temperatures from 300° to 365°C.

The original rock used in this experimental maturation sequence contains insoluble oil-prone kerogen (type II), which constitutes more than 95 wt. % of the total organic matter (Figure 11.1). As thermal stress is applied in the experiments, part of the kerogen decomposes to a bitumen, which can be extracted from the rock with organic solvents (e.g., benzene and dichloromethane). This extracted bitumen is a tarry substance that consists mainly of high molecular weight components. Low activation energies ranging from 10 to 20 kcal/mol for this overall reaction (Connan, 1974; Barth et al., 1989) indicate that kerogen decomposition to bitumen involves

cleavage of weak noncovalent bonds. Bonds of this type are not well defined, but they may include hydrogen bonds or electron donor-acceptor complexes as suggested in structural models for coals (Larsen and Mohammadi, 1990; Kirchko and Gagarin, 1990). Petrographic studies of rocks subjected to hydrous pyrolysis and natural maturation show that continuous organic networks may be established by expansion of bitumen into the rock matrix during kerogen decomposition to bitumen (Lewan, 1987). This bitumen network impregnates the micropores and bedding plane partings as a result of a net volume increase in the organic matter within a confining mineral matrix. Petrophysical (Meissner, 1978) and petrographic data (Lewan, 1987) suggest that the development of a continuous bitumen network is essential for oil migration within and oil expulsion from effective source rocks. As denoted in Figure 11.1, this stage in which kerogen partially decomposes is referred to as *bitumen generation*.

As thermal stress increases, the subsequent overall reaction commences with the partial decomposition of bitumen to oil. Kerogen content does not change during this overall reaction, but the bitumen content decreases in proportion to the amount of expelled oil generated (Figure 11.1). This overall reaction does involve cleavage of covalent bonds with activation energies ranging from 34 to 67 kcal/mol (Lewan, 1985, 1989; Huizinga et al., 1988). In addition to the distinctly different activation energies between bitumen and oil generation, the concept of bitumen and oil being two different organic phases from two different overall reactions is also supported by their distinct compositional differences and their occurrence in hydrous pyrolysis experiments with only isolated kerogen (Lewan, 1991, 1993). An important prerequisite for differentiation of these two organic phases is the presence of dissolved water in the bitumen network. Although the solubility of hydrocarbons in water is low, the solubility of water in hydrocarbons is two orders of magnitude greater (Griswold and Kasch, 1942; Guerrant, 1964; Brady et al., 1982). As a result, sufficient quantities of water may be dissolved within the bitumen to participate in the partial decomposition of bitumen to oil. Water surrounding a bitumen-impregnated rock sample during hydrous pyrolysis is therefore only important in maintaining a bitumen network that is fully saturated with dissolved water (Lewan, 1991).

A generalized reaction pathway for thermal maturation of bitumen under hydrous pyrolysis conditions is proposed in Figure 11.2. The hypothetical bitumen molecule at the beginning of the reaction pathway is considered to be only one of many different molecular motifs that are produced from the breaking of noncovalent bonds during the thermal decomposition of kerogen (Figure 11.2a). These high molecular weight molecules make up the soluble bitumen phase, which under hydrous pyrolysis conditions is saturated with dissolved water derived from the original pores, parting planes, and fractures in a rock. As thermal maturation increases, encounters with extraneous free radicals from the decomposing kerogen or other bitumen molecules generate free radical sites on the bitumen molecule. At this point in the reaction pathway, Lewan (1991) suggests that hydrogen derived from dissolved water in the bitumen frequently terminates these free radical sites (Figure 11.2b, open circles), which prevents the cleavage of covalent carbon-carbon bonds in the β -position from the terminated free radical site (i.e., β -scission). Those free radical sites that are not terminated subsequently initiate β -scission in the bitumen molecule (Figure 11.2c). The cleaved free radical fragments may at this time be terminated by water-derived hydrogen or continue to undergo β -scission until termination occurs. Highly aliphatic fragments generated by β -scissions are hydrophobic in character and separate from the water-saturated bitumen as an immiscible oil phase (Figure 11.2c, dotted area).

The lower density of the immiscible oil relative to the water-saturated bitumen generates a buoyancy force, but the presence of an opposing capillary force within a source rock requires an additional force for oil expulsion.

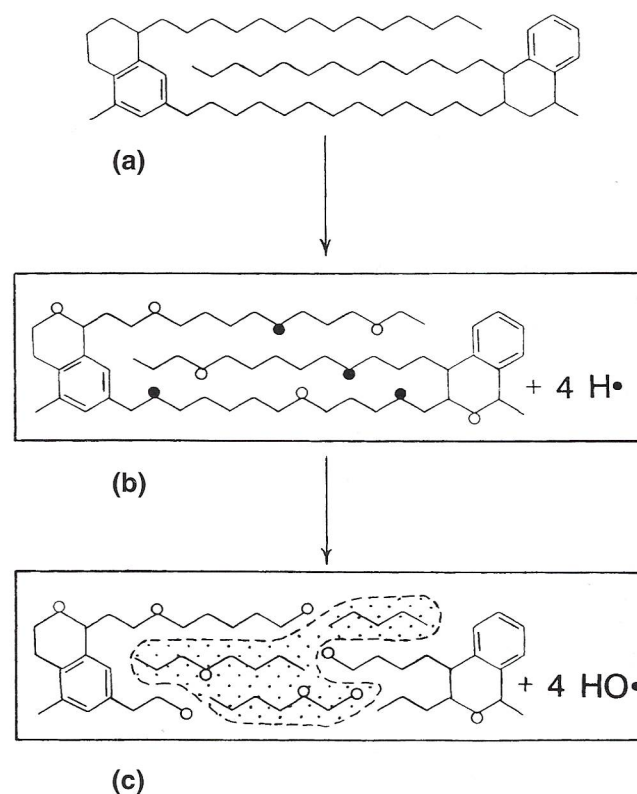


Figure 11.2. Generalized reaction pathway proposed for thermal maturation of bitumen in a closed system under hydrous pyrolysis conditions. (a) Hypothetical bitumen molecule generated from the partial decomposition of kerogen by the breaking of weak noncovalent bonds. (b) Bitumen molecule in water-saturated bitumen phase (denoted by enclosing rectangle) after encountering free radicals generated from other bitumen molecules and decomposing kerogen. Some of the free radical sites imposed on the bitumen molecule are terminated by water-derived hydrogen (open circles) from dissolved water in the bitumen. (c) The remaining unterminated free radical sites (solid circles) initiate cleavage of covalent bonds in the bitumen molecule by β -scission. The cleaved free radical fragments are subsequently terminated by water-derived hydrogen from dissolved water in the bitumen. The hydrophobic character of the cleaved products results in their separation from the water-saturated bitumen as an immiscible oil phase (dotted area).

This additional force is most likely an internal pressure resulting from a net volume increase of the organic components within the confining inorganic matrix of a source rock. Evidence of this volume increase associated with oil generation during hydrous pyrolysis is the development of an echelon parting separations in the rock that are parallel to the bedding fabric and filled with oil (Lewan, 1987). This oil is included with the expelled oil by rinsing the rock sample with an organic solvent at room temperature after the water is decanted at the end of an experiment (Lewan, 1987).

At least three causes of this volume increase can be envisaged. The first involves the chemical volume increase that accompanies thermal cracking, as observed

in petroleum refining (Egloff and Davis, 1954; Nelson, 1958). The second involves the physical volume increases resulting from thermal expansion of the generated oil (Lewan, 1987). The third involves a physicochemical volume increase due to the uptake of more dissolved water in the bitumen as it becomes more hydrophilic with increasing maturity (Lewan, 1991). The individual importance of each of these causes remains to be evaluated quantitatively, but their cumulative effect is the generation of an internal pressure as the water-saturated bitumen network partially decomposes to an immiscible oil. As denoted in Figure 11.1, this stage of petroleum generation is called *primary oil generation*.

The processes and mechanisms responsible for generation and expulsion of oil in hydrous pyrolysis experiments are conceivably the same as those in nature. However, the degree to which they are operative in nature remains to be determined. Overburden and confining pressures may have some influence on these processes and mechanisms (Takeda et al., 1990), but as a first approximation, the higher temperatures used in hydrous pyrolysis are likely to have the greatest influence. The effect of this higher temperature is most obvious in the decrease in solubility of water in bitumen with decreasing temperatures (Lewan, 1991). A reduction in the amount of water dissolved in the bitumen may cause a corresponding reduction in the amount of immiscible oil generated. In addition, the internal pressure resulting from the physical volume increase associated with oil generation is expected to be reduced at the lower temperatures in nature due to a reduction in thermal expansion of the generated oil. Therefore, the same processes and mechanisms may be operative in both hydrous pyrolysis and nature, but the amount of oil generated and expelled by hydrous pyrolysis is exaggerated relative to nature. An implication of this qualitative assessment is that thermally immature rocks that do not generate and expel oil in hydrous pyrolysis experiments will definitely not be effective source rocks in nature.

CLOSED ANHYDROUS PYROLYSIS

Anhydrous pyrolysis is defined here as experiments in which samples are pyrolyzed in the absence of liquid water. Anhydrous pyrolysis experiments reported in the literature can be described as either closed or open. These two types are distinguished on the basis of whether the generated products are maintained in the same thermal regime as the pyrolyzed samples. Pyrolyzing samples in a sealed reactor that is uniformly heated at a given temperature constitutes closed pyrolysis. The previously described hydrous pyrolysis experiments are also conducted in a closed system, and similar experiments without liquid water in a sealed reactor are referred to as *closed anhydrous pyrolysis*. Comet et al. (1986) reported pyrolysate yields from kerogens at 330°C after 72 hr to be 16–41% lower in closed anhydrous pyrolysis than in hydrous pyrolysis. Similarly, Tannenbaum et al. (1986) reported pyrolysate yields from kerogen–mineral mixtures at 300°C after 10 and 100 hr to be 9% and 44%

lower, respectively, in closed anhydrous pyrolysis than in hydrous pyrolysis.

Pyrolysate yield in both of these comparative studies is defined as the total solvent-soluble organic matter within the sample and reactor, with no distinction made between expelled oil and bitumen in their hydrous pyrolysis yields. To better assess the amount of oil expelled in closed anhydrous pyrolysis relative to hydrous pyrolysis, a series of 72-hr experiments at 300°, 330°, and 350°C were conducted on aliquots of an immature sample of Woodford Shale (WD-26) under anhydrous and hydrous conditions. All of these experiments were conducted in 1-L stainless steel-316 reactors with 400 g of crushed rock ranging in size from 0.5 to 2.0 cm. Hydrous pyrolysis experiments at the three temperatures were conducted with 320 g of deionized water and an initial helium pressure of 241 kPa. The comparable closed anhydrous pyrolysis experiments were conducted in the same type of reactor with the same amount of rock, but without water and with an initially evacuated gas space.

Pyrolysate yields from these comparative experiments in Table 11.1 (experiments 1–6) show the most obvious difference to be the total lack of expelled oil in the closed anhydrous experiments. Surfaces of the rock chips removed from the anhydrous experiments are devoid of oil droplets and oily films. At 300°C for 72 hr (experiments 1 and 2), only a small amount of expelled oil is generated in the hydrous experiment and the amount of oil plus bitumen is essentially the same under hydrous and anhydrous conditions. Partial decomposition of kerogen to bitumen predominates at this time-temperature condition (Figure 11.1), and the presence of water appears to have no significant effect on this overall reaction. However, significant differences are evident at the higher temperature experiments (330°C/72 hr, experiments 3 and 4, and 350°C/72 hr, experiments 5 and 6), which represent conditions under which bitumen partially decomposes to an expelled oil (Figure 11.1). The large decrease in bitumen and lack of an expelled oil through the anhydrous experimental sequence indicates that the decomposition of bitumen ultimately forms an insoluble pyrobitumen and gas under closed anhydrous conditions. Conversely, bitumen decomposes to an expellable oil under hydrous conditions. Lewan (1991) suggests this difference between closed anhydrous and hydrous reaction pathways is the result of water-derived hydrogen being available for free radical terminations and the immiscibility of generated oil in a water-saturated bitumen under hydrous conditions. The lack of dissolved water in bitumen under closed anhydrous conditions results in cross-linking polymerization and aromatization through free radical recombinations and disproportionations, respectively.

Table 11.1 shows the final pressures at the experimental temperatures to be significantly lower in the closed anhydrous experiments than in the hydrous experiments. The higher pressures in the hydrous experiments are a result of water vapor, generated gases, and helium, and the lower pressure in the closed anhydrous experiments are only a result of the generated gases.

Table 11.1. Experimental Conditions and Pyrolysate Yields from Hydrous and Anhydrous Pyrolysis Experiments on Aliquots of Woodford Shale Sample WD-26^a

Experiment Reference Number	Experimental Temperatures (°C)	Final Pressure at Experimental Temperature (MPa)	Experimental Conditions	Expelled Oil (wt. % rock)	Bitumen Extract (wt. % rock)	Oil Plus Bitumen (wt. % rock)
1	300.1	2.17	Anhydrous	0.00	8.66	8.66
2	300.4	9.76	Hydrous	0.65	8.35	9.00
3	330.0	4.24	Anhydrous	0.00	6.62	6.62
4	329.7	15.89	Hydrous	2.79	8.19	10.98
5	350.6	5.69	Anhydrous	0.00	3.30	3.30
6	350.3	21.13	Hydrous	4.15	5.71	9.86

^aDuration of all experiments was 72 hr. Details on experiments and collection procedures are given by Lewan (1993).

Monthioux et al. (1985) have concluded on the basis of a comparative experimental study on coals that pyrolysate yields from closed anhydrous pyrolysis at high confining gas pressures are similar to those obtained from hydrous pyrolysis. Pyrolysate yields from aliquots of the Woodford Shale (sample WD-26) in Table 11.2 for closed anhydrous pyrolysis with high confining pressures of helium (experiment 7) and generated gases (experiment 8) at 350°C for 72 hr do not support their conclusion. The high helium pressure (experiment 7) was attained in the one anhydrous experiment by loading the reactor at room temperature with 7.72 MPa of helium. The final pressure of 23.48 MPa at 350°C in this experiment consists of mostly helium and lesser amounts of generated gas. The high generated gas pressure was attained in the other anhydrous experiment (experiment 8) by mechanically pressing an excess of rock sample into a reactor to reduce the available gas space. The final pressure of 21.76 MPa at 350°C in this experiment consists only of generated gases. No expelled oil was generated in either of these experiments (experiments 7 and 8). Similar to the lower pressure anhydrous experiment (experiment 5), the amount of bitumen generated was significantly lower than that in hydrous pyrolysis. This discrepancy with Monthioux et al. (1985) is attributed by Lewan (1991b) to be their use of coals that are not capable of generating oil.

A generalized reaction pathway for thermal maturation of bitumen in a closed system under low- and high-pressure anhydrous conditions is proposed in Figure 11.3 for comparison with the hydrous pyrolysis pathway proposed in Figure 11.2. The bitumen generated by the breaking of weak noncovalent bonds in the kerogen is not apparently influenced by the presence of water, and therefore the hypothetical bitumen molecule at the beginning of the reaction pathway is considered the same under anhydrous- and hydrous conditions (Figures 11.3a and 11.2a, respectively). As thermal maturation increases, encounters with extraneous free radicals from the decomposing kerogen or other bitumen molecules generate free radical sites on the bitumen molecule. These free radical sites under anhydrous conditions are infrequently terminated by hydrogen atoms due to the lack of dissolved water in the bitumen (Figure 11.3b). Consequently, more free radical sites and subsequent β -

scissions occur in closed anhydrous pyrolysis (Figures 11.3b and c) than in hydrous pyrolysis (Figures 11.2b and c). The resulting free radical fragments under anhydrous conditions are also deprived of terminations by water-derived hydrogen and alternatively resort to terminations by recombination with other free radical sites on the bitumen molecule or neighboring free radical fragments (Figure 11.3d). These carbon-carbon bond terminations form a highly cross-linked bitumen molecule, which develops into an insoluble pyrobitumen. The inability of this method to generate an expelled oil renders it useless in assessing oil expulsion.

OPEN ANHYDROUS PYROLYSIS

Open anhydrous pyrolysis involves moving pyrolysate products out of the thermal regime in which they are generated. This movement of products is typically accomplished with a carrier gas that sweeps the volatile products into an external detector or with a cooling gradient that concentrates the condensable volatile products in an external cold trap. Neither of these transport methods are operative in subsiding sedimentary basins, but their adaptation to subjecting small amounts of sample to high-temperature heating ramps (300°–550°C) over short durations (15–60 min) makes them useful in providing a rapid screening method for assessing relative hydrocarbon potential of a rock. Rock-Eval is one of the most commonly used open anhydrous pyrolysis methods and employs a carrier gas and a flame ionization detector (Espitalié et al., 1977). Table 11.3 compares samples of Woodford Shale and Phosphoria Retort Shale with their hydrous pyrolysis yields at maximum oil generation. The total pyrolysate yield for both methods is similar, but the Rock-Eval makes no distinction among bitumen, oil, and gas. As a result, the generated hydrocarbon yields from Rock-Eval are greater than the expelled oil yields from hydrous pyrolysis by a factor greater than two.

The other open anhydrous pyrolysis method distinguishes gas and oil pyrolysate products by using a cold trap to collect the condensable volatile products. There are many variations on the conditions under which this method is done, but they can be collectively referred to

Table 11.2. Experimental Conditions and Pyrolysate Yields from Hydrous Pyrolysis and Closed Anhydrous Pyrolysis With and Without High Confining Pressures^a

Experiment Reference Number	Final Pressure at 350°C (MPa)	Major Source of Pressure ^b	Experimental Conditions	Expelled Oil (wt. % rock)	Bitumen Extract (wt. % rock)	Oil Plus Bitumen (wt. % rock)
6	21.13	H ₂ O, He, gen. gases	Hydrous	4.15	5.71	9.86
5	5.69	Gen. gases	Anhydrous	0.00	3.30	3.30
7	23.48	He, gen. gases	Anhydrous	0.00	2.99	2.99
8	21.76	Gen. gases	Anhydrous	0.00	2.27	2.27

^aAll experiments were conducted at 350°C for 72 hr. Experimental details on procedures are given by Lewan (1993).

^bGen. gases = gases generated during the experiment; He = helium initially added to the gas space at the beginning of the experiment; H₂O = water vapor from water added at the beginning of experiments.

as *modified Fischer assays*. In its simplest form, a rock sample is heated from room temperature to 500°C at a specified heating rate and then held at 500°C for a specified duration referred to as a *soak period* (Smith, 1962). The volatile pyrolysate products are usually self-purged through an external cold trap where condensable liquid products are collected. Although this method provides what is referred to as a modified Fischer assay oil yield, this yield is dependent on the heating rate, soak period, temperature, and physical state of the rock (Stanfield and Frost, 1949; Heistand, 1976; Wildeman, 1977).

Oil yields from aliquots of the same rock sample subjected to a Fischer assay and hydrous pyrolysis are currently not available for comparison. However, pyrolysate yields from aliquots of the same rock sample subjected to a modified Fischer assay and Rock-Eval pyrolysis are available for comparison, as shown in Figure 11.4 (solid dots). The pyrolysate yields from the Toarcian oil shales done by the modified Fischer assay and Rock-Eval pyrolysis are essentially the same despite the inclusion of pyrolysate gases in the latter. The modified Fischer assay used to generate these data are presumed to have involved heating samples from room temperature to 500°C at a heating rate of 12°C/min with a soak period of 20 min and a cold trap temperature of 0°–100°C (Stanfield and Frost, 1949).

Figure 11.3. Generalized reaction pathway proposed for thermal maturation of bitumen in a closed system under anhydrous pyrolysis conditions. (a) Hypothetical bitumen molecule generated from the partial decomposition of kerogen by the breaking of weak noncovalent bonds. (b) Free radical sites (solid circles) are generated on the bitumen molecule through encounters with extraneous free radicals generated from other bitumen molecules and decomposing kerogen. (c) Lack of water-derived hydrogen for free radical terminations results in frequent covalent bond cleavage by β -scission. The resulting free radical fragments remain miscible due to the lack of a water-saturated bitumen, and an oil phase does not occur. (d) Termination of the free radical fragments (open circles) occurs by recombination, which results in carbon-carbon bond cross-linking and the development of an insoluble pyrobitumen.

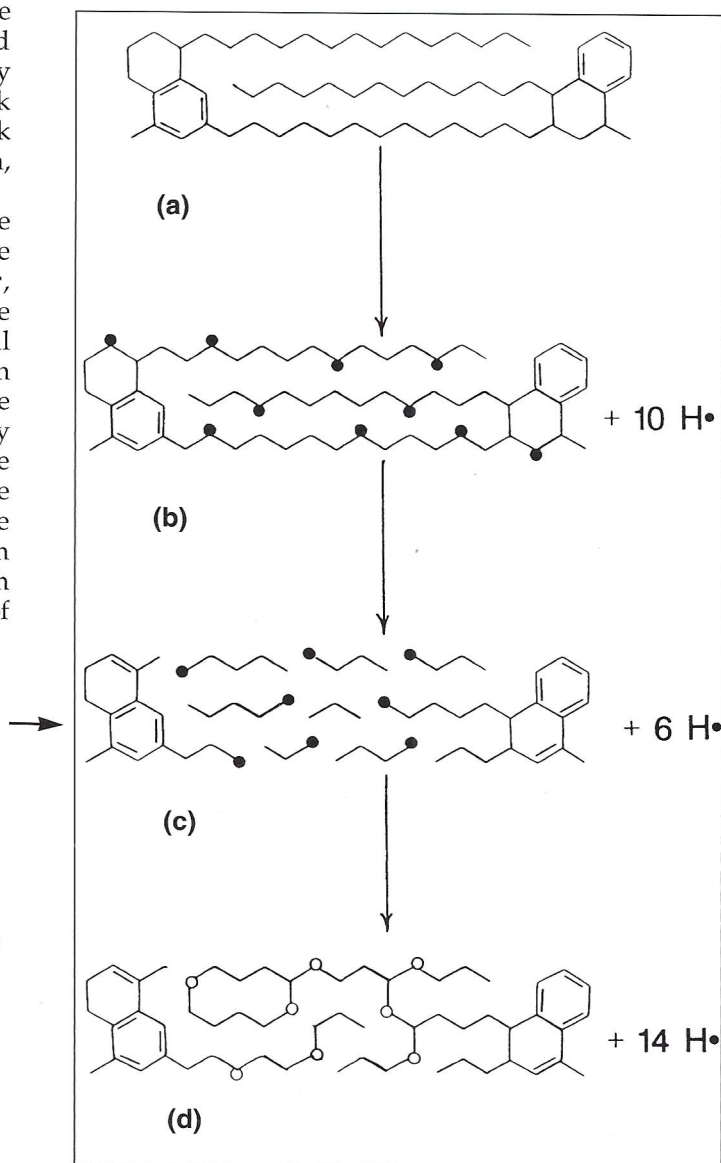


Table 11.3. Comparison of Rock-Eval Pyrolysis and Hydrous Pyrolysis Yields (wt. % of rock) from the Same Samples of Woodford Shale (WD-5) and Phosphoria Retort Shale (P-64)^a

Pyrolysis Method	Type of Pyrolysate	Woodford Shale	Phosphoria Retort Shale
Rock-Eval II (Cycle 1) on original sample	Volatile hydrocarbons (S ₁)	0.25	0.50
	Generated hydrocarbons (S ₂)	7.11	13.45
	Total pyrolysate (S ₁ + S ₂)	7.36	13.95
Hydrous pyrolysis at maximum oil generation	Bitumen extract	2.56	6.52
	Expelled oil	3.14	6.52
	Hydrocarbon gas	0.63	0.94
	Total pyrolysate	6.33	13.98

^aFrom Lewan (1985).

Different conditions for a modified Fischer assay were used by Burnham (1991) on a variety of petroleum source rocks, which were also subjected to Rock-Eval pyrolysis. The modified Fischer assay in this study involved heating compressed rock samples from 100°C up to 450–500°C at a heating rate of either 2°C/min or 0.033°C/min (2°C/hr) with the collection tube at room temperature. As shown in Figure 11.4, the oil yields from this modified Fischer assay (open triangles) are significantly lower than their corresponding hydrocarbon yields from Rock-Eval pyrolysis (solid triangles) compared to the relationship for the Toarcian oil shales. This difference between the relationships is a function of differences in heating rates, with slower heating rates giving lower oil yields by modified Fischer assays. This effect of heating rate on oil yields from modified Fischer assays has been reported previously (Campbell et al., 1978; Burnham and Singleton, 1983) and is evident in Figure 11.4 by the consistently lower oil yields from aliquots of the same samples at the slower heating rate of 0.033°C/min.

A generalized reaction pathway for thermal maturation of bitumen under open anhydrous conditions is proposed in Figure 11.5. Similar to closed anhydrous and hydrous pyrolysis, bitumen generation from the breaking of weak noncovalent bonds in the kerogen can be observed in open anhydrous pyrolysis when conducted isothermally at lower temperatures (Hubbard and Robinson, 1950). The generation of free radical sites on the hypothetical bitumen molecule (Figure 11.5b) with increasing thermal maturation leads to the same frequency of β -scissions and subsequent free radical fragments in open anhydrous pyrolysis (Figure 11.5c) as in closed anhydrous pyrolysis (Figure 11.3c). The critical difference between the open and closed anhydrous system depends on the rate at which the free radical fragments are vaporized in and removed from the pyrolysis chamber.

Pyrolysis conditions that promote rapid vaporization and removal of pyrolysate products with rapid heating and flow rates result in essentially all of the bitumen decomposing into a volatile product (Figure 11.5d). Scarcity of hydrogen atoms or donors and lack of contact between free radical fragments in the vapor state causes

terminations by disproportionation to dominate under these conditions. Terminations of this type produce pyrolysate products enriched in alkenes, which are rarely found in natural crude oils. Examples of this extreme condition include Rock-Eval pyrolysis (Table 11.3), which uses rapid heating rates (25°C/min) with a carrier gas, and the modified Fischer assay, which typically uses a rapid heating rate (12°C/min).

Conversely, pyrolysis conditions that promote slow vaporization and removal of pyrolysate products from the pyrolysis chamber result in more bitumen decomposing into pyrobitumen (Figure 11.5e) rather than vaporized oil (Figure 11.5d). The ultimate extreme results in all of the bitumen converting to a pyrobitumen by recombination of free radical fragments to form carbon-carbon bond cross-linking, as described for the reaction pathways of closed anhydrous pyrolysis (Figure 11.3d). It has been well documented that the proportionality between generation of vaporized oil (Figure 11.5d) and generation of pyrobitumen (Figure 11.5e) in open anhydrous pyrolysis is dependent on heating rates (Campbell et al., 1978), which control the rate at which free radical fragments in a vapor state are removed from a rock. As heating rates decrease below about 12°C/min, pyrobitumen yields increase at the expense of decreasing vaporized oil yields. Accompanying the increase in pyrobitumen formation is an increase in hydrogen generation (Figure 11.5e), which may be active in free radical terminations and may reduce the frequency of disproportionations in the vaporized oil (Figure 11.5d). Therefore, as the vaporized oil yield decreases with decreasing heating rates, its alkene content decreases because of the increased availability of hydrogen generated by pyrobitumen formation. Alkene contents of vaporized oils from open anhydrous pyrolysis have been shown to decrease as heating rates decrease and oil yields decrease (Evans and Campbell, 1979).

Although the conditions under which open anhydrous pyrolysis is conducted can be manipulated to give vaporized oil yields and compositions comparable to those from hydrous pyrolysis, the unnatural processes involved in obtaining these vaporized oils makes their use in determining amounts of oil expelled in nature highly speculative and tenuous. Specifically, removal of

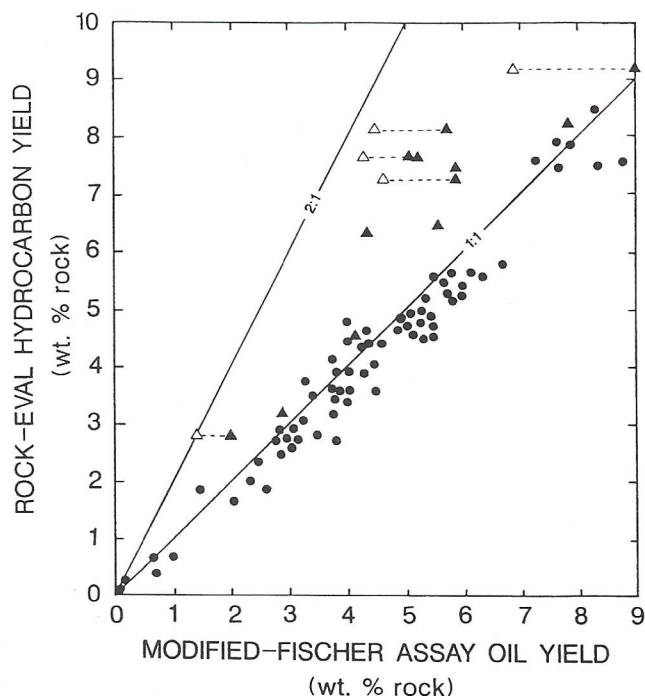
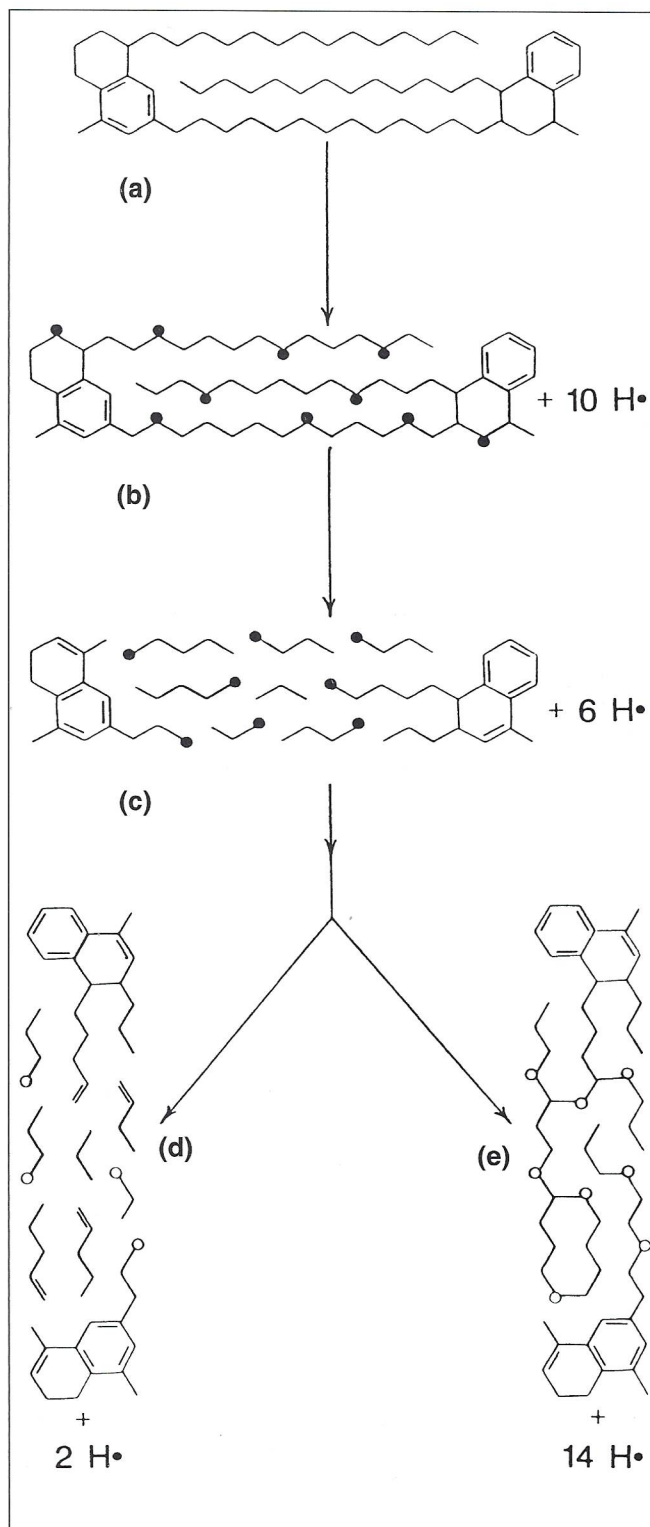


Figure 11.4. Plot of Rock-Eval pyrolysis hydrocarbon yields versus modified Fischer assay oil yields determined on the same samples of Toarcian oil shales from the Paris basin, presumably using a 12°C/min heating rate in the modified Fischer assay (solid circles) (Madec and Espitalié, 1984), and a variety of petroleum source rocks using 2°C/min (solid triangles) and 0.033°C/min (open triangles) heating rates in a modified Fischer assay (Burnham, 1991). Dashed lines connect samples that were subjected to the modified Fischer Assay at both heating rates. The 1:1 and 2:1 lines are included as reference lines.

Figure 11.5. Generalized reaction pathways proposed for thermal maturation of bitumen in an open system under anhydrous pyrolysis conditions. (a) Hypothetical bitumen molecule generated from the partial decomposition of kerogen by the breaking of weak noncovalent bonds. (b) Free radical sites (solid circles) are generated on the bitumen molecule through encounters with extraneous free radicals generated from other bitumen molecules and decomposing kerogen. (c) Lack of water-derived hydrogen for free radical terminations results in covalent bond cleavage by β -scission. The subsequent pathways followed by the resulting free radical fragments depends on the conditions under which the open anhydrous pyrolysis is conducted. (d) If the pyrolysis conditions promote rapid vaporization and removal of the free radical fragments from the thermally maturing bitumen, then essentially all of the bitumen will decompose into a volatile product. The volatilized free radical fragments are terminated by disproportionation resulting in alkenes or by available hydrogen donors (open circles) resulting in alkanes. (e) If the pyrolysis conditions promote slow vaporization and removal of the free radical fragments from the thermally maturing bitumen, then more of the bitumen will decompose into nonvolatile pyrobitumen as a result of free radical terminations by recombination.



generated oil in a vapor state from a source rock is critical to determining evolved oil yields from open anhydrous pyrolysis (Stout et al., 1976; Campbell et al., 1978). This required vaporization of generated oil is not operative under the pressure-temperature conditions of subsiding sedimentary rocks, which are also water saturated.

The unlikelihood of oil yields from open anhydrous pyrolysis being applicable to nature is also evident by the decrease in oil yields with decreasing heating rates. A linear extrapolation of this experimental relationship (Evans and Campbell, 1979) (Figure 11.2) to heating rates typical for subsiding sedimentary basins (1°–10°C/m.y.) indicates that only pyrobitumen formation will occur (Figure 11.5e) by this process. It is therefore not feasible to use open anhydrous pyrolysis directly to determine the amount of oil expelled from a source rock in nature. However, indirect determinations may be feasible on the basis of well-established correlations between expelled oil yields from hydrous pyrolysis and vaporized oil yields from open anhydrous pyrolysis.

CONCLUSIONS

Hydrous pyrolysis is the most useful laboratory method for understanding expulsion of oil in nature. The liquid water used in this method ensures the presence of a water-saturated bitumen within a heated source rock. This dissolved water within a bitumen network reduces the frequency of carbon-carbon bond cross-linking in the bitumen and allows the occurrence of an immiscible oil to form from the partial decomposition of the bitumen. In addition to the buoyancy force generated by the density difference between immiscible oil and water-saturated bitumen, a net volume increase associated with the partial decomposition of bitumen to oil generates an internal pressure within the confining mineral matrix of a rock. As a result, the immiscible oil is expelled from the rock as it is being generated.

These processes are also considered operative in nature, but they may be exaggerated to some degree under hydrous pyrolysis conditions due to its use of higher temperatures. The possibility of some degree of exaggeration suggests that rocks incapable of expelling a generated oil under hydrous pyrolysis conditions are definitely not effective source rocks for oil expulsion in nature. Although hydrous pyrolysis gives the most realistic expulsion efficiencies for petroleum source rocks, additional research to determine the degree to which it exaggerates nature is needed.

Closed anhydrous pyrolysis is the least useful laboratory method for understanding primary migration or expulsion of oil because an expelled oil is not generated. The lack of dissolved water in the bitumen prevents frequent terminations of free radical sites on bitumen molecules with water-derived hydrogen. Consequently, frequent carbon-carbon bond cleavages occur and terminations of the resulting free radical fragments are accomplished by recombination to form carbon-carbon cross-linking bonds due to the lack of water-derived hydrogen. No internal pressure nor immiscible oil is generated by

this process, and only a pyrobitumen is formed. Excluding the gases generated, the recoverable pyrolysate yield from hydrous pyrolysis at maximum expelled oil generation is three times greater than that from closed anhydrous pyrolysis with or without a confining pressure. The total lack of an expelled oil by this method renders it useless in determining expulsion efficiencies for source rocks.

Similarly, open anhydrous pyrolysis is not a useful method in determining expulsion efficiencies of source rocks unless it is calibrated against expelled oil yields generated by hydrous pyrolysis. Although open anhydrous pyrolysis is capable of generating a vaporized oil, the amount of oil varies considerably with experimental conditions (e.g., heating rate), and the processes responsible for its vaporized oil (e.g., vaporization) are not operative in natural systems.

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