

WATER AS A SOURCE OF HYDROGEN AND OXYGEN IN PETROLEUM FORMATION BY HYDROUS PYROLYSIS

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The importance of water in laboratory experiments designed to understand natural processes is well documented in the studies of granite melts (Goranson, 1932; Tuttle and Bowen, 1958), metamorphic reactions (Winkler, 1974, p. 15; Rumble et al., 1982; Ferry, 1983), coal formation (Berl and Schmidt, 1932; and Schuhmacher et al., 1960), and clay mineral diagenesis (Whitney, 1990). Prior to 1979, organic geochemists did not fully appreciate the ubiquity of water in sedimentary basins and its role in petroleum formation. A notable exception is the work by Jurg and Eisma (1964). Noting difference in the thermal decomposition of behenic acid in the presence and absence of liquid water, these investigators suggested that water played an important role in petroleum formation. Although a subsequent study in 1969 by Brooks and Smith employed water in laboratory simulations of petroleum generation from coals, laboratory experiments over the next decade did not consider the role of water in petroleum formation (e.g., Tissot et al., 1974; Larter et al., 1977, Harwood, 1977). Lewan and others (1979) reported that heating organic-rich rocks submerged in liquid water resulted in the generation and expulsion of a free-flowing oil that accumulated on the water surface above the submerged rock. Physically, chemically, and isotopically this expelled oil pyrolyzate was similar to natural crude oils. This experimental approach was referred to as hydrous pyrolysis. Although hydrous pyrolysis has since been shown to provide useful information on primary migration, stages and kinetics of petroleum generation, and thermal maturity indices (Lewan, 1983, 1985, 1987; Winters et al., 1983; Lewan et al., 1986), the actual role of water in petroleum formation has not been determined.

In order to better understand the role of water in petroleum formation, a series of pyrolysis experiments were conducted on aliquots of a sample of Woodford Shale under hydrous and anhydrous conditions. The experiments involved isothermally heating 400 g of thermally immature, gravel-sized (0.5-2.0 cm) rock in one-liter stainless steel-316 reactors at 300°, 330° and 350°C for 72 hours. Hydrous experiments included 320 g of deionized water and 241 kPa of helium in the headspace. No water was added to the anhydrous experiments and the head space was evacuated at the start of the experiment. The experiments were conducted at these three temperatures for 72 hours because previous experiments with Woodford Shale showed that the two overall reactions responsible for petroleum formation occur in part over these conditions. The first overall reaction occurs at temperatures below 330°C for 72-hour experiments, and involves the cleavage of

weak noncovalent bonds in the kerogen to form a soluble, high-molecular-weight tarry bitumen (kerogen to bitumen). This bitumen impregnates the ground mass of the rock to form a continuous organic network. The second overall reaction occurs at temperatures from 330°C to 350°C for 72-hour experiments, and involves the cleavage of covalent bonds in the bitumen to form an immiscible oil that is expelled from the organic network in the rock (bitumen to oil).

Pyrolyzate yields from these comparative experiments are given in Table 1 in terms of generated gas, expelled oil, bitumen extract, and total pyrolyzate (i.e., gas + oil + bitumen). The most obvious difference is the total lack of expelled oil in the anhydrous experiments, with no signs of oil droplets or an oily film on the surfaces of the rock chips. At 300°C for 72 hours, only a small amount of expelled oil is generated in the hydrous experiment and the amount of total pyrolyzate generated is essentially the same in the hydrous and anhydrous experiments. Partial decomposition of kerogen to bitumen predominates at this time-temperature condition and the presence of water appears to have no significant effect on this overall reaction. However, distinct differences in the amounts of total pyrolyzate are evident in the 330°C and 350°C experiments (Table 1), which represent conditions for the partial decomposition of bitumen to oil. Amounts of total pyrolyzate and bitumen decrease significantly under anhydrous conditions, but the amount of bitumen decreases to a lesser extent and the amount of total pyrolyzate increases under hydrous conditions. These results indicate that bitumen degrades to an insoluble pyrobitumen under anhydrous conditions, while it decomposes to an expellable immiscible oil under hydrous conditions.

Another difference between the hydrous and anhydrous experiments is the significantly higher amounts of CO₂ generated by the former. Table 2 shows the total amount of aqueous and gaseous CO₂ to be one order of magnitude higher under hydrous conditions than under anhydrous conditions at 350°C for 72 hours. Mass balance calculations for the loss of oxygen from kerogen at 350°C for 72 hours indicate that under hydrous conditions the kerogen oxygen accounts for only 64 percent of the oxygen in the generated CO₂. The lack of carbonate minerals in the original rock implicates H₂O as the source of the excess oxygen in the generation of CO₂ under hydrous conditions. Several reactions, including gas-shift reactions, have been considered to explain this excess oxygen, and the most feasible reaction appears to be oxidation of carbonyl groups in the kerogen or bitumen by H₂O. A working hypothesis envisages formation of carboxylic intermediates that are decarboxylated with increasing thermal stress to generate CO₂.

Regardless of the specific mechanism responsible for H₂O to act as a source of the excess oxygen generated as CO₂, the remaining hydrogen from the reacted H₂O would be available for terminating free radical sites. This source of hydrogen is supported by a hydrous pyrolysis experiment that was conducted on the Woodford Shale at 330°C for 72 hours with D₂O instead of water. Deuterium-NMR analyses of the pyrolyzate products from this experiment showed that the expelled immiscible

oil as well as the bitumen and kerogen retained in the rock contained significant quantities of deuterium. Quantification of the deuterium content of the isolated kerogen was not performed, but the NMR spectrum was typical for powdered solids containing deuterium. Quantification of the deuterium content of the oil and bitumen was determined from the NMR analyses with an internal standard of deuterated dichloromethane. Assuming hydrogen contents of 13 wt. % for undeuterated oil and 10 wt. % for undeuterated bitumen, deuterium substitution for hydrogen is approximately 40% for the expelled oil and 33% for the extracted bitumen in the D_2O experiment. This high degree of deuterium substitution is interpreted to be the result of free radical sites being terminated by deuterium atoms derived from the oxidation of carbonyl groups by D_2O .

The ability of hydrous pyrolysis to generate an expelled oil while anhydrous pyrolysis generates a pyrobitumen may be explained by differences in the availability of hydrogen and type of free-radical terminations that occur during bitumen decomposition. Figure 1 diagrammatically presents a working hypothesis for hydrous and anhydrous reaction pathways involving a hypothetical bitumen molecule (Figure 1a) subjected to a barrage of extraneous free radicals thermally generated from other bitumen molecules or the kerogen (Figure 1b). Under hydrous conditions, the free radical sites formed on the bitumen molecule by encounters with incoming free-radicals are frequently terminated with water derived hydrogen (Figure 1c) before β -scission in the molecule occurs. Free-radical fragments that do occur by the infrequent β -scissions are also frequently terminated by water-derived hydrogen (Figure 1d). As a result, a liquid oil is generated. H_2O in this reaction pathway occurs as a dissolved species in the bitumen that impregnates the rock. Although the solubility of hydrocarbons in water is low, the solubility of water in hydrocarbons is two orders of magnitude higher. This solubility is sufficient to supply H_2O for the proposed reactions within the bitumen impregnated rock (Lewan, 1992). Dissolved water in the bitumen network of the rock is maintained at a fully saturated level by the water surrounding the rock in the reactor. Lewan (1992) proposes that this H_2O -saturated bitumen is also responsible for the development of an oil that is immiscible in the bitumen network of the rock. Under anhydrous conditions, the lack of water-derived hydrogen for terminating free-radical sites that occur on the bitumen molecule results in frequent β -scissions (Figure 1e). The numerous free-radical fragments that consequently occur are also deprived of terminations by water-derived hydrogen, and resort to termination by recombination with other free radical sites on the bitumen molecule or on neighboring molecular fragments (1f). In a closed pyrolysis system, these carbon-carbon bond terminations result in the formation of pyrobitumen through the development of a highly cross-linked structure that aromatizes through disproportionation.

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Table 1. Comparison of pyrolyzate yields from hydrous and anhydrous pyrolysis of crushed aliquots (0.5-2.0 cm) of an immature sample of Woodford Shale (WD-26). All of the experiments were conducted with 400g of rock in one-liter stainless steel-316 reactors.

Experimental Conditions (temp./time)	Generated Gas (wt. % of rock)	Expelled Oil (wt. % of rock)	Bitumen Extract (wt. % of rock)	Total Pyrolyzate ¹ (wt. % of rock)
300°C/72 hr				
Hydrous ²	0.43	0.65	8.35	9.43
Anhydrous ³	0.78	0.00	8.66	9.44
Δ%	-81.4	+100.0	-3.7	-0.1
330°C/72 hr				
Hydrous ²	1.05	2.79	8.19	12.03
Anhydrous ³	1.74	0.00	6.62	8.36
Δ%	-65.7	+100.0	+19.2	+30.5
350°C/72 hr				
Hydrous ²	1.68	4.15	5.71	11.54
Anhydrous ³	2.40	0.00	3.30	5.70
Δ%	-42.9	+100.0	+42.2	+50.6

$$\Delta\% = [(\text{Hydrous}-\text{Anhydrous})/\text{Hydrous}] \times 100$$

¹Total pyrolyzate = generated gas + expelled oil + bitumen extract.

²Crushed rock with 320g of deionized (ASTM type I) water under an initial He pressure of 241 kPa.

³Crushed rock initially in an evacuated reactor.

Table 2. Millimoles of headspace gas (g) and dissolved aqueous gas (aq) generated from 400 grams of Woodford Shale sample WD-26. Total gas quantities do not include species dissolved in expelled oil or bitumen.

EXPERIMENT CONDITIONS	300°C/72 h		330°C/72 h		350°C/72 h	
	Hydrous	Anhydrous	Hydrous	Anhydrous	Hydrous	Anhydrous
CO ₂ (g)	20.07	14.39	31.17	20.88	44.01	21.56
CO ₂ (aq)*	15.06	—	49.12	—	196.14	—
TOTAL CO ₂	35.13	14.39	80.29	20.88	240.15	21.56

$$*CO_2(aq) = H_2CO_3 + HCO_3^- + CO_3^{2-} = K_H PCO_2 \{1 + (k_1/H^+) + (k_1k_2/(H^+)^2)\}$$

where PCO_2 = partial pressure of CO_2 gas (atm), $K_H = 10^{-1.47}$ mol/Latm (Butler, 1982), H^+ = hydrogen ion concentration (mol/l), k_1 = first disassociation constant ($10^{-6.352}$), and k_2 = second disassociation constant ($10^{-10.329}$).

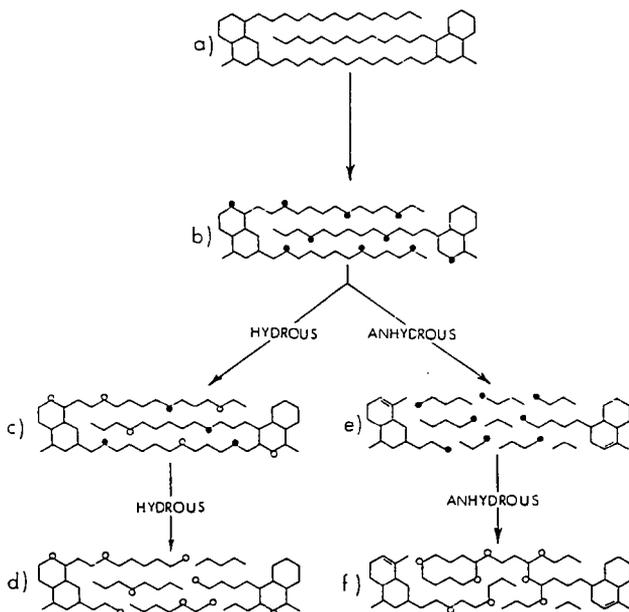


Figure 1. Reaction pathways suggested for thermal maturation of bitumen under hydrous and anhydrous closed-system pyrolysis. Solid circles denote free radicals formed by the loss of hydrogen atoms. Open circles denote terminated free radicals. a) Hypothetical molecule representing aliphatic component of bitumen. b) Molecule with free radical sites, after being subjected to a barrage of extraneous free radicals. c) Termination of free radical sites with water-derived hydrogen atoms before β -scission of chains and disproportionation of cyclics occurs. d) Termination of free-radical fragments with water-derived hydrogen atoms from dissolved water in bitumen. e) Free-radical fragments resulting from frequent β -scissions, which are infrequently terminated by hydrogen atoms due to the lack of dissolved water. f) Termination of free-radical fragments by recombination to form carbon-carbon bond cross linking in the absence of hydrogen atoms from dissolved water.