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SCIENCE

Generation of Oil-Like Pyrolyzates from Organic-Rich Shales

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Abstract. *Pyrolyzates similar to natural crude oils were generated from organic-rich shales by hydrous pyrolysis. With this type of pyrolysis it is possible to make more sophisticated correlations between crude oils and their source rocks, evaluate the hydrocarbon potential of a source rock, and elucidate the variables involved in the natural oil-generating process.*

The products generated by anhydrous pyrolysis and retorting of organic-rich shales contain significant amounts of olefins (Fig. 1). The rarity of olefins in natural crude oils (1) indicates that these pyrolysis methods do not duplicate the natural oil-generating process. In June 1977 we generated pyrolyzates that did not contain olefins from organic-rich shales (Fig. 1). In addition, the pyrolyzates had other properties that closely match those of natural crude oils. The process, called hydrous pyrolysis, involves filling half of a pressure vessel with equal volumes of water and crushed or sawed blocks of organic-rich shale. The remaining void is filled with helium at 1 to 2 atm, and the vessel is then heated to 330°C for 3 to 4 days.

The organic-rich shales used in this process are in their prehydrocarbon generation stage of diagenesis. This is evaluated before pyrolysis by elemental analyses and visual analysis of the kerogen portion of the organic matter (2-5). Oil-like pyrolyzates have been generated by this process from shales containing algal and liptinitic kerogens. Woodford Shale from Carter County, Oklahoma, which contains liptinitic kerogen and 4.3 percent (by weight) organic carbon, is used in this report as an example of hydrous pyrolysis.

A gas chromatogram of the pyrolyzate generated by hydrous pyrolysis of Woodford Shale (Fig. 2A) is similar to that of a natural crude oil (Fig. 2B) that has been geochemically correlated (6)

Table 1. Comparison of natural crude oils with pyrolyzates generated by hydrous pyrolysis.

Substance	<i>n</i> -Alkane range	CPI*	Pristane/phytane ratio	Optical rotation	$\delta^{13}\text{C}$ (PDB)†
Natural Woodford crude oils	C ₁ to C ₃₇	1.0	1.4 to 1.5	0.1 to 0.3	-29.8 to -30.0
Pyrolyzates from hydrous pyrolysis of Woodford Shale	C ₁ to C ₃₇	1.0 to 1.1	1.1 to 2.3	0.1 to 0.2	-29.4 to -30.0
Crude oils (overall range)	C ₁ to C ₃₇	0.8 to 1.2	0.4 to 8.0	-0.1 to 4.5	-21.0 to -35.0

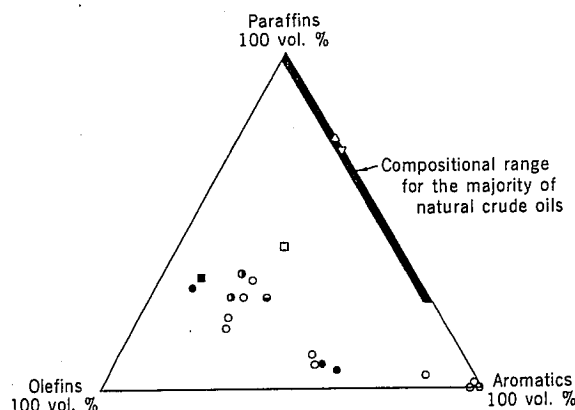
*Carbon preference index (CPI) = $1/2 [(C_{25} + C_{27} + C_{29})/(C_{24} + C_{26} + C_{28}) + (C_{25} + C_{27} + C_{29})/(C_{26} + C_{28} + C_{30})]$. †Per mil increment in ^{13}C relative to Pee Dee belemnite.

Table 2. Composition of natural crude oils and pyrolyzates generated by hydrous pyrolysis at 330°C for 96 hours. Values are percentages by weight.

Substance	Eluted fraction* (%)				Non-eluted† fraction (%)
	Saturates	Aromatics	Polars	Total	
Natural Woodford crude oils	80-89	10-16	1-4	100	0
Pyrolyzates from hydrous pyrolysis of Woodford Shale	62	28	10	62	38

*Portion eluted on an activated alumina column with *n*-heptane (saturates), dichloromethane (aromatics), and dichloromethane-methanol mixtures (polars). †Portion not eluted on an activated alumina column with dichloromethane-methanol mixtures.

Fig. 1. Ternary diagram showing the compositions of pyrolyzates generated by different pyrolysis and retorting methods with natural crude oils. (O) Class I retorting of Green River Shale (10, 17); (●) class II retorting of Green River Shale (17); (◐) class III retorting of Green River Shale (17); (◑) hydrogasification of Green River Shale (9); (□) anhydrous vacuum pyrolysis of Green River Shale (12); (■) Fischer assay of Green River Shale (17); (Δ) hydrous pyrolysis of Woodford Shale; and (∇) hydrous pyrolysis of Green River Shale.



with the Woodford Shale. Conversely, the gas chromatogram of the product generated by pyrolysis without water (Fig. 2C) is distinctly different. Additional similarities between pyrolyzates and crude oils from Woodford sources are shown in Table 1. The wide range in the pristane/phytane ratio of the pyrolyzate appears to be dependent on the duration of the experiment. Although the temper-

Table 3. Total yields of expelled pyrolyzate phases from Woodford Shale at 330°C for 72 hours. Values are percentages (by weight) of whole rock.

Expelled pyrolyzate phases*	Hydrous pyrolysis	Anhydrous + helium-pressured pyrolysis†	Anhydrous pyrolysis
Free	1.5	0.0	0.0
Sorbed	0.6	0.5	0.1
Aqueous	0.01	0.0	0.0
Gas	0.7	0.7	2.1
Total	2.8	1.2	2.2

*Free phase, pyrolyzate layer on top of water; sorbed phase, pyrolyzate film on shale chips; aqueous phase, pyrolyzate dissolved in water; and gas phase, pyrolyzate in the gaseous phase. †Helium pressure at 330°C is 140 atm.

Table 4. Hydrogen budget of hydrous and anhydrous pyrolysis. Values are moles per 100 g of Woodford Shale measured at 25°C, except where noted otherwise.

Hydrogen form	Amount (moles per 100 g × 10 ³)		
	Hydrous	Anhydrous	ΔH ₂ (hydrous - anhydrous)
H ₂ (gas)	5.67	4.82	0.85
H ₂ S (gas)	0.84	9.80	-8.96
2H ⁺ (aq)*	0.08	0.00	0.08
	× 10 ⁻³		
H ₂ S (aq)†	0.08	0.00	0.08
Total H ₂	6.59	14.62	-8.03

*Abbreviation: aq, aqueous. †Calculated from thermodynamic data.

ature used for hydrous pyrolysis may be 200° to 250°C higher than that inferred for natural petroleum generation (7, 8), the similarities between the pyrolyzate and natural crude oils suggest that hydrous pyrolysis approaches duplication of the natural process. The higher temperature used during hydrous pyrolysis increases the reaction rate, but differences between the gross properties of the pyrolyzate and the natural product are apparently minor.

Two noticeable differences are the larger noneluted fraction of the pyrolyzate and its slightly lower content of saturated compounds in the eluted fraction (Table 2). The pyrolyzates are under considerably lower pressure than natural crude oils and migrate relatively short distances. The noneluted fraction is quite polar, and in the natural system it may not be expelled from the shale or it may be chromatographically removed during migration. The higher temperatures used in hydrous pyrolysis are another possible cause of this deviation. The smaller portion of saturates in the eluted fraction of the pyrolyzate is probably a result of the higher temperature used. Studies of retorting of shales have shown that the content of saturates decreases with increasing retorting temperatures (9, 10).

Hydrous pyrolysis differs from other pyrolysis methods in the following way: during hydrous pyrolysis shale and its organic constituents are in contact with liquid water (11) at a pressure of more than 127 atm; in other pyrolysis methods shale is surrounded by a vacuum (12), nitrogen (13), or inert gas (14) at essentially 1 atm. Whether liquid water is important as a reactant or because of its confining and pressuring effect, or both, is not yet known. The presence of bulk liquid water apparently results in the best product in greatest yield (Table 3). On the other hand, some oil-like pyrolyzate was gen-

erated at 330°C from Woodford Shale, using helium to provide a reactor pressure similar to the water vapor pressure. It is not yet clear whether the helium pressure inhibits escape of pyrolysis products into the bulk vapor space, keeping them where they can react with other pyrolysis products in the rock, or alters factors other than the behavior of the organic phase, giving products different from those produced at low pressure. Harwood (15) showed that in anhydrous vacuum pyrolysis of kerogen more than 50 percent (by volume) of the evolved gas may be hydrogen. Confinement of hydrogen within the rock by external pressure could be critical to the hydrogenation of olefins in the pyrolyzate. The hydrogen budget in Table 4 shows that sufficient hydrogen is generated during both hydrous and anhydrous pyrolysis.

A practical advantage of hydrous pyrolysis is that representative liquid product forms a layer on top of the water in the pressure vessel and may be easily removed with a pipette for analysis (16). The pyrolyzate from helium-pressured pyrolysis occurs as a liquid film on the shale chips, which must be removed by quickly rinsing the chips with an organic solvent such as benzene or methylene chloride. This type of pyrolysis is less precise, is subject to loss of lower-boiling products, and does not give a good indication of the amount of pyrolyzate that may be expelled from a particular type of shale.

The pyrolyzate apparently migrates out of the shale as a separate phase, not

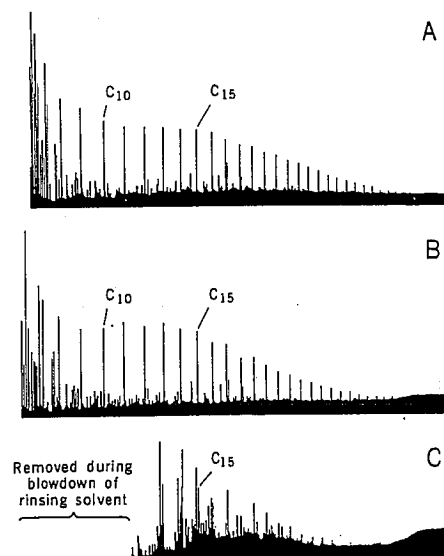


Fig. 2. Gas chromatograms of (A) pyrolyzate generated from Woodford Shale by hydrous pyrolysis at 330°C for 72 hours, (B) natural Woodford crude oil, and (C) pyrolyzate generated from Woodford Shale by anhydrous pyrolysis at 330°C for 72 hours.

miscible with water. Petrographic examination of thin sections of hydrous pyrolyzed shale shows that the liquid product fills wavy fractures that are parallel to and sharp-sided fractures that are perpendicular to the linear fabric of the shale. In some fractures the filling may be traced to the edge of a shale block, where the pyrolyzate continues as a thin film. We observed some of these textural features in shales from cores and outcrops.

Hydrous pyrolysis may prove to be a sophisticated method for correlating crude oils with their source rocks and evaluating the generating capability of a source rock. It should provide more information on the natural oil-generating processes and the dependence of the composition of crude oil on such variables as temperature, pressure, time, and water. It may also help to elucidate the primary migration mechanisms of crude oils in their source rocks.

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11. At 25°C and 1 atm the total volume of shale and liquid water is about half that of the pressure vessel. During pyrolysis (330°C) the shale is completely submerged in the expanded liquid water phase, and the remaining void space has a vapor pressure of at least 127 atm. This pressure is the result of water vapor. Higher pressures may occur, depending on the amount of gases and liquids that evolve from the shale.
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