

## HYDROTHERMAL MEDIA, OIL SHALE, AND COAL

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### INTRODUCTION

Hydrous pyrolysis has proved to be a useful tool for the study of accelerated petroleum generation in source rocks. The technique uses liquid water as a medium at thermolytic conditions in the 290°-360°C range (Lewan et al., 1979; 1981). Dry pyrolysis provides olefins in the pyrolysate, but with the addition of water the olefin yield is reduced and n-alkanes resembling those in petroleum emerge. Hoering (1984) extended the work using D<sub>2</sub>O, developing results discussed below. The claim that hydrous pyrolysis mimics the natural process has been questioned recently (Monthioux et al., 1985; Tannenbaum and Kaplan, 1985; Comet et al., 1986). Nonetheless there is little question that the chemistry operating at hydrolysis conditions generates alkanes and other hydrocarbons from the immature source material.

The lack of understanding of the chemistry at hydrothermal conditions is underscored by a several observations. For example highly condensed polynuclear aromatic hydrocarbons (PAHs) including pyrene, benzopyrenes, and coronene are found in hydrothermal vent petroleum (Simoneit, 1985a; 1988). These compounds are commonly observed as products of hydrocarbon pyrolysis above 550°C, and coronene itself is not generated in pyrolyses at temperatures below 650°C (Commins, 1969). However it is difficult to explain their presence in the vent zones where temperatures are considerably lower.

Another curious point is the unusually high rate of epimerization of biological markers in hydrous pyrolysis. Although cationic centers generated on highly acidic clay surfaces could be responsible (Alexander et al., 1984), the acidity of the clay sites is substantially reduced in an aqueous environment (Tannenbaum and Kaplan, 1985), and the high acidities required for epimerization at the rates observed cannot be present. The activity of acid clay sites can be questioned further because of the presence of normal alkanes, whereas acid-promoted cationic chemistry should produce highly branched alkanes. Calcium carbonate has also been suggested as significant to the isomerization (Eglinton et al., 1986), but the mechanistic aspects of that process are not apparent.

The role of water in the maturation process has not been clearly defined. It has been suggested that water transfers hydrogen to organic free radicals in the reaction mixture (Monthioux et al., 1985; Hoering, 1984; Comet et al., 1986).



However this reaction is endothermic by 25-30 kcal/mol and should not be significant at hydrous pyrolysis temperatures.

In the discussion here we seek to develop some understanding of the chemical processes in hydrous pyrolysis by first modeling the results of Hoering in D<sub>2</sub>O. Some of that work has been recently reviewed (Ross, 1992), and the results are summarized here. We then seek to extend this view to the chemistry of coal, discussing our findings in studies of Argonne samples of

Wyodak coal in hydrothermal media (Ross, et al., 1990a,b). We begin with a summary of the nature of the medium at hydrous pyrolysis conditions.

## RESULTS AND DISCUSSION

### The Nature of the Hydrothermal Medium

Under common conditions, water is a highly polar, fluid medium accommodating ionic salts and having a modest capacity for dissolving some gases and polar organic compounds. However, liquid water near its critical point (374°C/220 atm) becomes a very different medium. The shifts in the key physical properties of liquid water up to its critical temperature are presented in Figure 1, with the shaded portion representing the region where hydrous pyrolysis is commonly conducted. The figure shows that while the density of the medium stays in the liquid-like region (> 0.3 g/mL) over most of the subcritical regime, the viscosity falls early to very low, almost gas-like, values. The net result is an interesting region where the medium has a liquid-like solvent capacity combined with a very high gas-like diffusivity. The mobilities of both neutral and charged solutes are much higher than they are in normal liquids, overcoming what could be mass transfer limitations at more conventional conditions.

The dielectric constant falls to levels like that of organic solvents, dramatically affecting the solubilities of organic materials. Thus naphthalene, virtually insoluble in water at ambient conditions, it is miscible in all proportions in liquid water at temperatures as low as 300°C (Jockers and Schneider 1978). Fully homogeneous combinations of ionic salts and nonpolar organics, which might not be feasible at common conditions, can easily be established at these conditions (Alwani and Schneider, 1969).

### Hydrous Pyrolysis with D<sub>2</sub>O -- The Results of Hoering

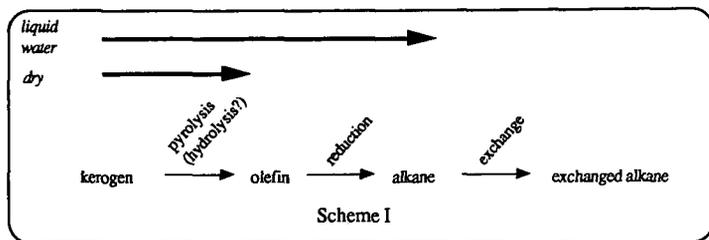
Hoering's data on the D-content in the n-alkanes from the treatment of preextracted Messel shale with D<sub>2</sub>O at 330°C/3 days (1984) have been used to model the process (Ross, 1992). The profiles for the heptadecane recovered from the treatment are shown in Figure 2. The figure also shows the results of control experiments in which heptadecane was purposely added to the treatment mixture, and for heptadecane recovered from work in which heptadecane was initially added. In the latter, 60% of the added olefin was recovered as alkane, a remarkable result reflecting a considerable reducing potential in the reaction mixture, and requiring an explanation.

The added alkane does not undergo much exchange, and the fact that the kerogen-generated alkane is very highly exchanged rules out preexisting alkane as the source. The olefin-generated alkane contains considerable deuterium, but the distribution pattern is very different from that for the kerogen-derived material.

A process reconciling these facts is shown as Scheme I. The scheme features the view that water is significant to the reduction of olefins generated pyrolytically from the kerogen. The general arrangement was confirmed in modeling work done employing an integration routine based on the Gear algorithm (Moore and Pearson, 1981) and operated on a VAX 11/750 computer. The fit, shown in Figure 3, was generated for a reaction rates alignment in which reduction  $\gg$  pyrolysis and exchange  $\approx$  2 x pyrolysis. It is emphasized that for the fit, it is necessary that reduction requires water, but produces *protio* alkane. The alkane then exchanges with the medium, presumably likely on the mineral surface.

A key question concerns the reduction step; there are no obvious reducing species introduced into the reaction. A clue to that chemistry may lie in the results of Amin, who studied the

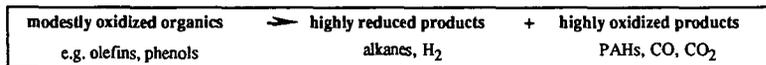
pyrolysis of glucose in water at its critical point (1975). Data from the study in Table I show that the pyrolysis yields char, an oil, and gases including CO, CO<sub>2</sub>, H<sub>2</sub>, and CH<sub>4</sub>.



Significantly, however, as the density of the medium is increased from a gas-like value to one more liquid-like, the quantity of gas and oil increase substantially with a corresponding decrease in the char yield. Factors associated with the increased density that appear to promote reduction of the starting glucose and formation of simple gases.

Hoogwater reports similar findings in the pyrolysis a series of haloorganic compounds in supercritical water at liquid densities (1991). The results for trichloroethane are shown in Figure 4. These experiments, conducted in sealed quartz tubes and therefore eliminating metal wall-promoted reactions, yielded surprisingly large quantities of CO, CO<sub>2</sub>, H<sub>2</sub>, and a collection of hydrocarbons including alkanes and benzene.

These data suggest that liquid water in the near critical region or supercritical water at liquid densities promotes gasification reactions. Such conversions are essentially the water-promoted disproportionation of carbon, i.e.



They could be the basis of alkane production in petroleum genesis. We are unaware of studies confirming such chemistry, and submit that this area is an important one for development.

### Hydrous Pyrolysis of Wyodak Coal

Our earlier accounts of this work described the effects of the treatment of Argonne samples of Wyodak coal with liquid water (hydrothermal) and with no medium (under N<sub>2</sub>/thermal) at 250°-350°C for periods of 30 min and 5 hr (Ross, et al, 1990a). Much of the data were developed using thermal gravimetric analysis (TGA) and SRI's field ionization mass spectrometer (FIMS), both operating from ambient to 500°C at 2.5°C/min. A later report included additional results from studies in which water was replaced by n-undecane, a hydrocarbon with a critical temperature (363°C, estimated by the method of Lydersen, 1955) near that of water (374°C), and expected to be chemically unreactive over at least the 30-min heating period (Ross, et al., 1990b).

A tar representing 5-7% of the starting coal was consistently deposited on the quartz insert walls solely at the hydrothermal conditions. There was no evidence of tar in the thermal and undecane runs. In all cases the coal lost oxygen, with O-losses falling in the order:

hydrothermal (5 hr) > [hydrothermal (30 min) = thermal (30 min) = thermal (5 hr)] > undecane (30 min)

Some properties of the recovered coal and the tars are presented in Table II.

Our earlier accounts discussed these data; however there are two features of specific interest here. The first is the fact that the hydrothermally-promoted tars are at the same time more volatile and of a greater molecular weight than the FIMS-volatile products from the recovered coals. They are also considerably richer in hydrogen. They are thus substantially less polar, and it is tempting to view these results as parallel to those for hydrocarbon production in the hydrous pyrolysis of petroleum source rock and due to water-promoted reduction chemistry.

The second are the volatility changes shown in Figure 5, which displays the total FIMS ion count vs evaporation temperature for samples for both 30 min and 5 hr treatments. The profile for the untreated coal is also presented for comparison. (FIMS mass analysis begins at  $m/e$  48, and so the profiles are independent of the evolution of water and carbon dioxide. They reflect solely organic volatiles.) For the 30 min treatment the undecane result is little different from that for the untreated coals. The thermally pretreated sample shows the presence of volatiles beginning to emerge at around  $100^{\circ}\text{C}$ ; however these materials must be the thermolytically volatiles generated during the pretreatment. They are deposited on the coal, and then evaporated into the instrument during the FIMS heating.

The aqueous pretreatment, however, clearly has produced new material. It is emphasized that the ordinate in the figure is logarithmic and thus the absolute quantities of product are significantly greater than for the thermal case. This new material would seem to be the portion of the tar that condensed on the coal rather than on the insert walls.

For the 5-hr treatment little of the tar remains on the coal, and the hydrothermal and thermal results are similar. It is notable from Table II that the tar has become considerably more volatile with little change in the molecular weight. We found in addition by FIMS that the arenol content of the 30 min tar was less than 30% that of the treated coals. The arenols in the 5 hr tar were reduced yet further by another factor of 3.\* Continued hydrothermal treatment appears to provide extended reduction and convert phenols to less polar material.

Remarkably, the undecane treatment has drastically reduced the volatility of the coal, essentially converting it to a char. The shaded portion of the figure reflects the loss in volatile material, those fractions becoming irreversibly reincorporated into the coal matrix.

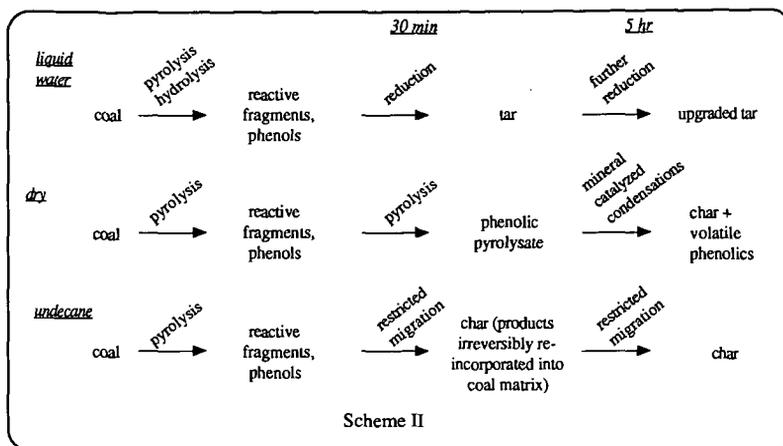
## CONCLUSIONS

The effects of water on the thermolysis of coal suggest a process similar to that in Scheme I for petroleum source rock (Scheme II). As in I, water promotes reduction of the initial pyrolytic products, and tar is the result. The scheme shows that extended hydrothermal treatment substantially increases the volatility of the tar.

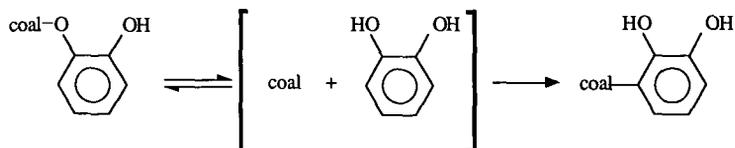
In the absence of added water there is a pyrolytic release of material, including olefins and large quantities of phenolic material. These fragments will migrate to other regions of the coal and will probably tend to concentrate at the mineral sites due to acid/base interactions. At this point the recent results of Stein et al. can apply (1989). Their work showed that at  $400^{\circ}\text{C}$  dihydroxybenzenes are very reactive and undergo acid catalyzed dehydroxylation and condensation. For coal, with distributions of clay and silica particles throughout the organic phase in sizes down perhaps to the nanometer level (Allen and VanderSande, 1984), we can expect significant degrees of such retrogressive chemistry.

For undecane the process is even more retrogressive. Neither water nor alkanes are good coal swelling media at ambient temperatures, the former because it is too polar, and the latter because

\* The arenol content is the sum of the FIMS signals for phenol, dihydroxybenzene, and their respective  $\text{C}_1$ -,  $\text{C}_2$ -, and  $\text{C}_3$ - derivatives.



it is not polar enough. However water becomes increasingly more coal-accommodating in the hydrothermal region because its dielectric constant decreases to values like those for polar organic liquids (Schneider and Jockers, 1978). Undecane in contrast likely becomes an even poorer solvent, or in effect an antisolvent. In that medium coal should thus not swell but possibly collapse, a negative solvent action discussed for polymers by Magda et al. (1988). Such a tendency for the coal would trap otherwise volatile fractions, resulting ultimately in their irreversible reincorporation into the coal matrix, and the formation of char. As a consequence, the arenols will increasingly react within the cage.



The essential component of this process is the replacement of labile, aryl ether links by stable, C-aryl bonds. That activity ultimately leads to the accumulation of structures that will tend to condense with further heating, and proceed to char. Such alkane-promoted condensation chemistry is clearly an undesirable component in conversion generally. Its regressive action, however, could be most seriously encountered in coprocessing, and additional studies in this area could prove profitable.

#### ACKNOWLEDGMENT

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**Table I**  
**PRODUCTS FROM THE PYROLYSIS OF**  
**GLUCOSE IN WATER (374°C/30 MIN)**

Pressure (atm)	Density (g/ml)	Fraction of Starting C (%)		
		Oil	Solid	Gas
152	0.07	27.8	68.9	3.4
220	0.32	60.4	8.5	9.5

**Table II**  
**Some Properties of the Recovered Coals and Tars**

	Treatment Period	Starting coal	Hydrothermal	Thermal	Undecane
$H/C$		0.90			
	30 min	-	0.82	0.83	0.81
	5 hr	-	0.72 1.13 (tar)	0.76	0.75
$O/C^a$		0.24			
	30 min	-	0.16	0.15	0.18
	5 hr	-	0.12 0.18 (tar)	0.16	-
$T_{1/2}(^{\circ}C)^b$	-	395-400	-	-	-
	30 min	-	340-350 200 (tar)	377-395	405
	5 hr	-	410 140 (tar)	425	465
$\bar{M}_w^c$	-	403-411	-	-	-
	30 min	-	410-421 393 (tar)	329-380	373
	5 hr	-	332	308 432 (tar)	201

a. Oxygen determined by direct O-analysis.

b. The temperature at which one-half of the FIMS volatiles has passed into the instrument.

c. Weight average molecular weight.

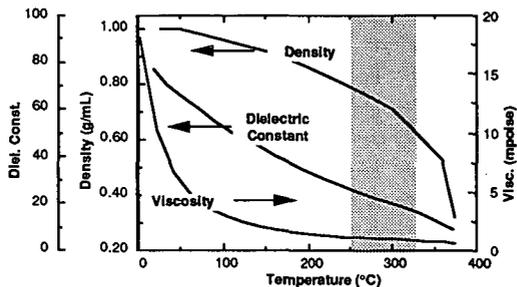


Figure 1. Some key properties of liquid water.

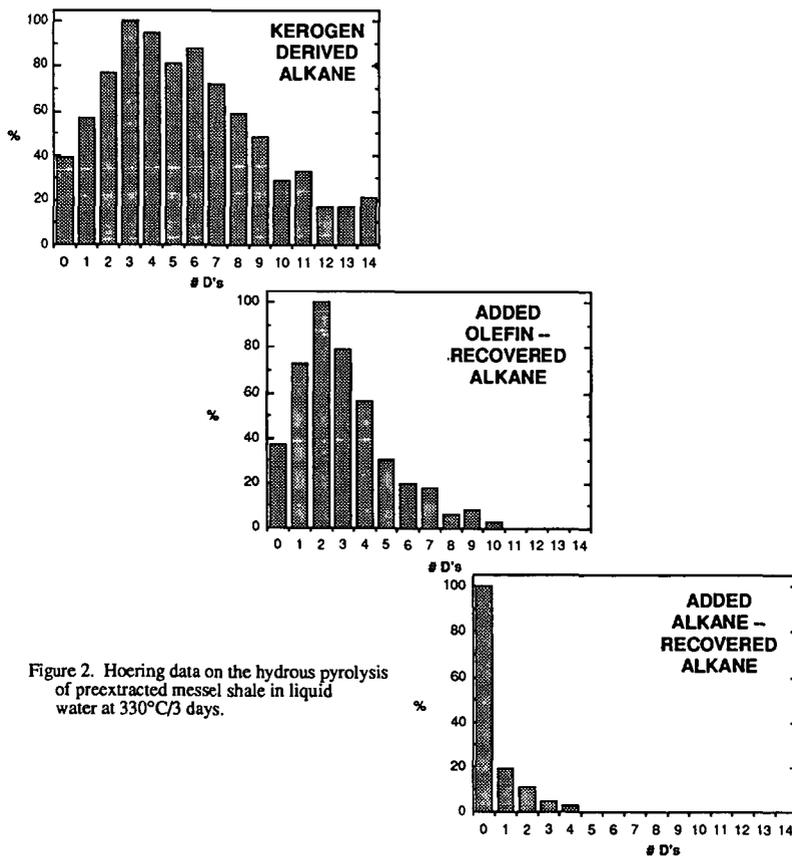


Figure 2. Hoering data on the hydrous pyrolysis of preextracted messel shale in liquid water at 330°C/3 days.

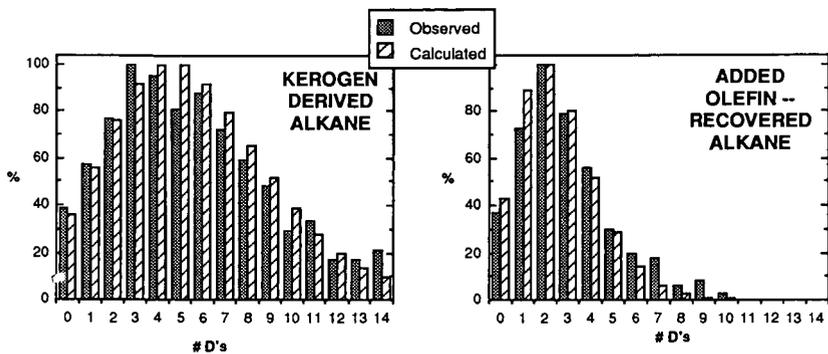


Figure 3. Hoering data and calculated profiles. The kinetic factors are reduction  $\gg$  pyrolysis and exchange  $\approx$  2 x pyrolysis.

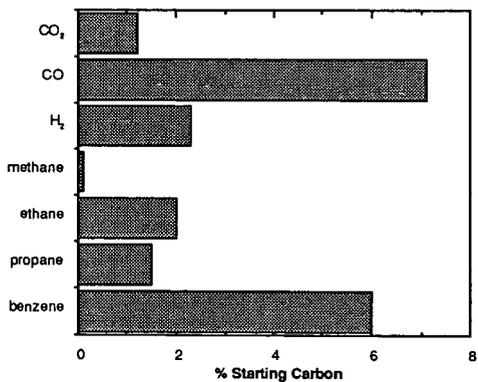


Figure 4. 1,1,2-trichloroethane conversion 428°C/ $\rho$  = 0.32mL/50 min.

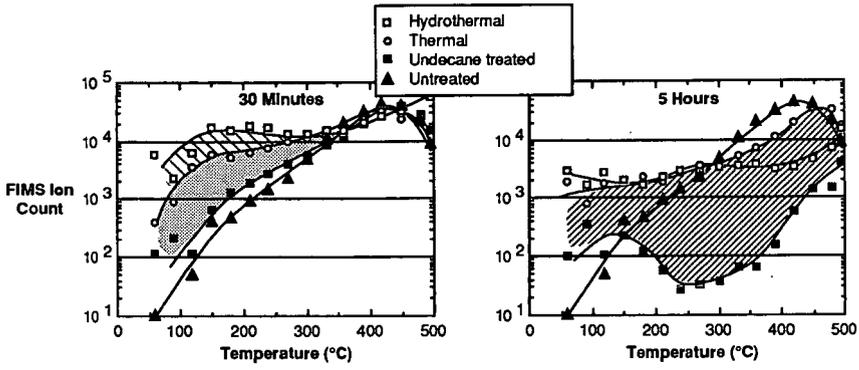


Figure 5. FIMS ion count values vs evaporation temperature for 30-min and 5-hr runs at 350°C.