DOE/PC/91053-T5 0-2
3

SRI International

SEP 16 1993

RECEIVED
NOV 26 1993
OSTI

SRI Report No. 2847-21 - Quarterly Report No. 7
14 July 1993

FUNDAMENTAL STUDIES OF COAL LIQUEFACTION

David S. Ross
Chemistry Laboratory

Covering the Period April 1 to July 1, 1993

Prepared for:

U. S. Department of Energy
Pittsburgh Energy Technology Center
P.O. Box 10940, MS 921-165
Pittsburgh, PA 15236

Contract No. DE-AC22-91PC91053

Approved:

David M. Golden
Vice President
Physical Sciences Division

MASTER

do

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

INTRODUCTION AND BACKGROUND

In our last report we discussed observations in our cell concerning the behavior or Illinois No. 6 coal in tetralin to 460°C. We noted that there were possibly two distinct types of particles comprising the organic phase, reacting respectively at 420°-430°C, and at 450°-460°C. Alternatively we could interpret the data as describing a range of reactivity bounded by those temperatures. As evidenced by the contraction of the particles, the reactions were rapid. The particles lost half of their substance within 1 min, and we suggested that the rates were too fast to be accommodated by the commonly held scheme for coal liquefaction involving thermolytic scission of weak, bibenzyl-like bonds.

Our analyses were aided by our use of Adobe Photoshop, which allows us to store digitized versions of our recorded images. The images can then be manipulated at will to provide quantitative data on morphological changes. We noted in our last report that printer limitations prevented us from presenting images with the desirable quality, and we are at present attempting to find access to equipment which will provide satisfactory figures. Accordingly our progress will be described here without any photographs, and we expect to present a more complete account of our work in our next report.

The work reported here includes studies of Illinois No. 6 coal with water as the medium, and a control run with argon as medium. One of us (DR) is an invited speaker at the 4th International Symposium on Hydrothermal Reaction, to be held in Nancy, France over 31 August to 3 September, 1993, and the paper prepared for that meeting is presented in the Appendix.

CURRENT RESULTS

Our temperature ramping was like that used last time, 25°C/min to 250°C, and then 10°C/min to 450°C. The results from the earlier work and the data presented here can therefore be directly compared.

The work with water was conducted with the pressure relief valve set at 200 bar. Thus as shown in Figure 1, the density of the aqueous medium is that of the liquid phase up to the critical point of 374°C, and thereafter it is dictated by the system pressure. The dielectric constant of the medium is also shown in the figure. The study under argon as the medium was conducted at around 5 bar.

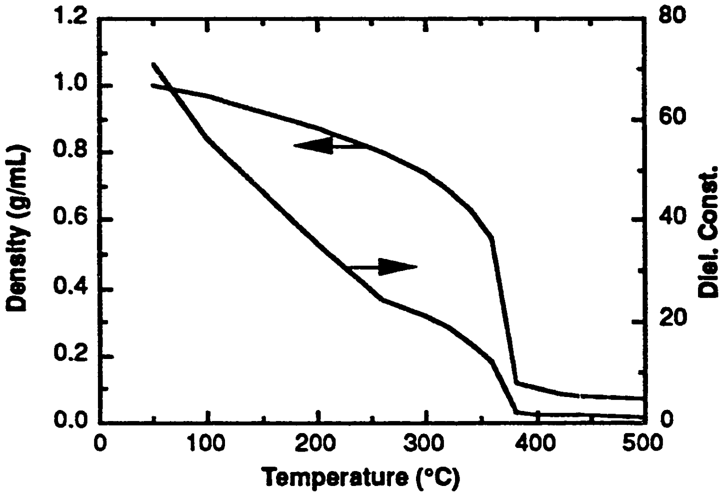


Figure 1. Density and dielectric constant of water at autogeneous pressures to 374°C, and at 200 bar at higher temperatures.

The changes in particle size from the present work along with data from our last report in tetralin are shown in Figure 2. It is clear from the figure that very different behavior is observed for the three cases. First, the activity for the water and argon runs begins at just above 300°C, or about 100° below that for tetralin. Second, the effects with argon and water media are strikingly in the opposite directions; under argon the coal initially swells and then shrinks, while in water it initially shrinks and then appears to swell.

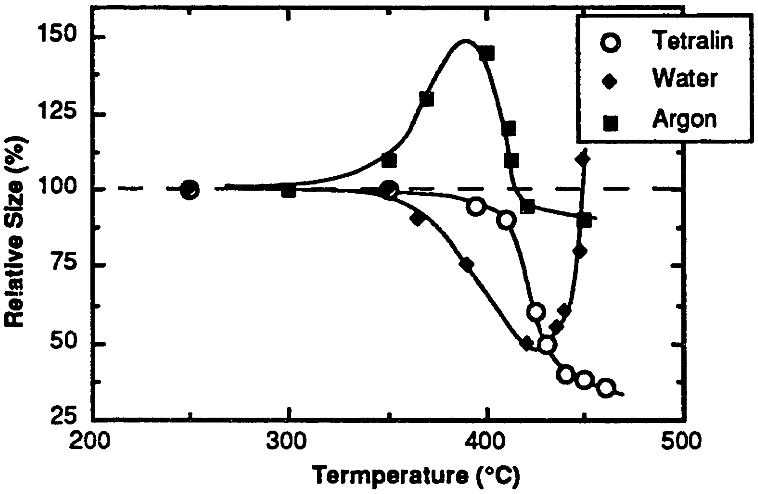


Figure 2. Changes in particle size with temperature for argon, water and tetralin media.

In the argon case the swelling maximum falls near that seen for the thermal dependence of the fluidity of Illinois No. 6 coal (Solomon, et al., 1992), shown in Figure 3. Our images of the process show the initially irregular particles swelling to almost spherical shapes, and then at near 400°C collapsing and returning at around 450°C to shapes *remarkably similar to the starting shapes*. This behavior was unexpected, since the common view of thermal behavior of bituminous coals asserts that they become highly liquid at the peak of their fluidity range, and then become increasingly nonfluid as crosslinking in the melt increases in rate with increasing temperature. Since the softening is viewed as taking throughout the bulk, there is no expectation that the final particles have the same shape as the starting particles.

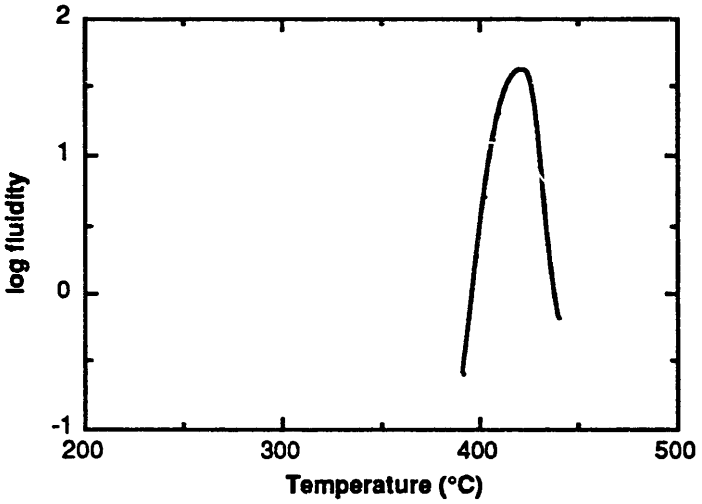


Figure 3. Fluidity of Illinois No. 6 coal with temperature as reported by Solomon, et al.

Our current data suggest a different scenario. We submit that the fluid (gases/liquid) and solid (crosslinked) phases are created essentially simultaneously with heating. (See the discussion of the model for this process discussed in the Appendix.) The gases then expand the liquid phase in a balloon-like fashion over the rigid understructure maintained by the solid. The balloon skin thins and then fails at some point, collapsing around the frame.

The findings for water were similarly unexpected. The images show particles shrinking to about half their initial size up to 435°C, and then appearing to swell to well above their initial size at higher temperatures. The particles grow above 435°C to "blob-like" shapes, that is with rounded boundaries and clearly fluid rather than solid.

We interpret the changes in these images in the following way. The shrinking is ascribed to the water-prompted generation of hydrocarbons (see Appendix), and their dissolution in the medium. It is significant that in this range water is a good solvent for organic compounds; water and naphthalene are fully miscible in all proportions for example. Thus significant fractions of the tar components dissolve in the water, a feature of the process that must be important to the kinetics of the process.

Next, recognizing that we are observing events taking place on the surface of the lower diamond of the cell, we presume that the apparent growth of the particles at the higher temperatures is in fact simply a spreading of the liquid on the surface. The sequence is suggested in Figure 4. We thus see the process as one of continuing conversion of the organic phase to liquids and gases, with little formation of char. At some point, however, as the density of the water declines with increasing temperature, crosslinking activity must begin to compete with the conversion process, and larger char fractions are formed.

Figure 4. Presumed sequence of morphology in the conversion of a coal particle in water, sitting on the diamond window surface, from ambient to 465°C.

FUTURE WORK

We expect to be able to provide satisfactory photos of the processes described here in our next report. We are at present conducting experiments in *n*-undecane ($C_{11}H_{24}$) as the medium. It has a critical temperature about the same as that of water, and should be unreactive with the coal over the short period of our experiments. These runs will serve as additional controls.

REFERENCES

Solomon, P. R., Best, P., Yu, Z., and Charpenay, S., 1992. Energy and Fuels, 143-154.

APPENDIX

PAPER PRESENTED AT THE 4TH INTERNATIONAL SYMPOSIUM ON HYDROTHERMAL REACTIONS*

HYDROTHERMAL MEDIA, OIL SHALE, AND COAL

D. S. Ross, I. Jayaweera, and S. Hoogwater
SRI International
Menlo Park, CA 94025

ABSTRACT: We propose a model for the generation of petroleum hydrocarbons during hydrous pyrolysis which involves disproportion (internal oxidation and reduction) of kerogen at active sites in the mineral matrix. The model views naturally occurring mineral buffers of oxygen fugacity in hydrothermal systems as sites where the redox can occur, and predicts that CO_2 should accompany alkane generation. The process is very highly favored thermochemically, and is supported by recent experimental results described in the literature.

1. INTRODUCTION

Hydrous pyrolysis is viewed by many as a useful tool for the study of accelerated petroleum hydrocarbon generation in source rocks (Lewan et al., 1981, Hoering, 1984), although there are several questions about the process. Some workers have questioned the claim that it mimics natural systems (Monthioux et al., 1985; Comet et al., 1986). Landais and coworkers have suggested that the key factors are confinement and pressure, and that the need for water is as yet unclear (1992).

The process employs liquid water as a medium at 290°-360°C (critical temperature = 374°C), and its role remains an alluring puzzle. A particularly intriguing observation was recorded by Hoering, who found in work with preextracted Messel shale that 60% of an alkene added to the water/rock mixture was recovered as the corresponding alkane (1984). Thus the mixture provides a surprising reduction potential, the source of which is the focus of the discussion here.

---

* Held in Nancy, France, 31 August - 3 Sept., 1993.

2. DISCUSSION

A. The Medium and Radical Reactions.

A number of workers have suggested that water acts to cap thermally generated organic free radicals (Monthioux et al., 1985; Hoering, 1984; Comet et al., 1986).

$$H_2O + R\cdot \longrightarrow HO\cdot + R\text{-}H \qquad (1)$$

This reaction is unlikely to be significant, however, as is reflected in Table 1, which assesses the probable route of reaction of organic free radicals in water at 330°C. The rate constants have been estimated by the techniques of Benson (1968). The table shows that the least competitive process is scission of a C-H bond β to the radical site. And while reaction with water is somewhat faster, it is still much too slow to compete with β C-C scission to yield an olefin and another radical. The significance of even that process can be questioned, however, since it should be so rapid that at 330°C most of the alkyl content of the sample should "unzip" to ethylene and other simple olefins. But since that process is not observed, it would appear that routes involving alkyl radicals may not be significant to the generation of products during hydrous pyrolysis.

Table 1. Estimated reaction rates for a secondary carbon radical at 330°C

			k/s^{-1}
$-\dot{C}H-CH_2-CH_2-$	->	$-CH{=}CH-CH_2+\dot{H}$	1.0
$-\dot{C}H-CH_2-CH_2-$	->	$-CH{=}CH_2+\dot{C}H_2-$	2.0×10^4
$-\dot{C}H-CH_2-CH_2-+H_2O$	->	$-CH_2-CH_2-CH_2-+\dot{H}O$	60.0^a

---

a. For water at 37 M.

B. Alkane Generation via Disproportionation.

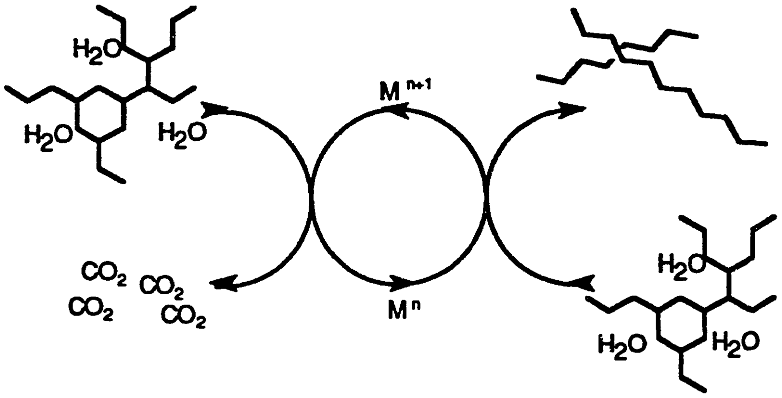
Accordingly we suggest a model for alkane generation that involves action at the mineral-organic interface in the source rock. The model employs disproportionation (internal oxidation-reduction) of the kerogen carbon, prompted at mineral sites that engage in mineral buffering of oxygen fugacity in hydrothermal systems. These sites are commonly iron-bearing silicate assemblages, although many other elements with multiple oxidation states including other transition metals and sulfur can serve the same function (Barnes, 1987). While reactions at buffer sites are usually seen as directly involving molecular O_2, they are viewed here as regions facilitating electron transfer, and bringing about oxidation and reduction of the organic phase. For the $Fe_2SiO_4/Fe_3O_4/SiO_2$ (FMQ) system, for example, magnetite can in principle oxidize a portion of the kerogen to CO_2, going to fayalite.

$$3\,Fe_3O_4 + 4.5\,SiO_2 + -CH_2- \longrightarrow 4.5\,Fe_2SiO_4 + CO_2 + H_2O \qquad (2)$$

The fayalite in turn can act to reduce another portion of the kerogen, regenerating magnetite.

$$1.5\ Fe_2SiO_4 + \text{-}CH_2\text{-}CH_2\text{-} + H_2O \text{ --> } 2\ \text{-}CH_3 + 1.5\ SiO_2 + Fe_3O_4 \qquad (3)$$

The overall disproportionation of the carbon phase and concomitant oxidation state cycling of the metal ion can be represented as a chain process as in (4), consuming kerogen and ultimately yielding petroleum hydrocarbons and CO_2.



(4)

To assess the likelihood of such chemistry we have calculated the equilibrium constant from standard thermodynamic data (Stull, et al., 1969) for the hydrothermolytic process in eq (5) over a range of temperatures. Propane is used as the feed for simplicity, although any hydrocarbon or hydrocarbon fragment could be used in the calculation. The net process is the hydrogenolysis of C-C bonds in three of the starting propanes, while one of the carbons in the fourth is converted to CO_2. For comparison we include pyrolytic routes of hydrocarbon degradation at anhydrous conditions in eqs 6 and 7. The formation of benzene in 7 simulates the production of graphitic char.

$$4\ C_3H_8 + 2\ H_2O \text{ --> } 3\ CH_4 + 4\ C_2H_6 + CO_2 \qquad (5)$$

$$C_3H_8 \text{ --> } C_3H_6 + H_2 \qquad (6)$$

$$2\ C_3H_8 \text{ --> } C_6H_6 + 5\ H_2 \qquad (7)$$

The results in Figure 1 show that while the dry processes are unfavored at temperatures below about 450°C, hydrothermolysis is very heavily favored to temperatures well above those used in hydrous pyrolysis.

A thermochemical argument does not mean a route for reaction necessarily exists, of course, and it must be emphasized that eqs 2 and 3 are conjecture at this point. However some recently reported experimental data provide support for the model. Lewan reports high yields of expelled oil combined with significant CO_2 production for hydrous conditions in studies with Woodford Shale (1992). In contrast no expelled oil developed in parallel anhydrous experiments, and the CO_2 levels for this case were only about 10% of the quantities seen in the hydrous runs. The author was careful to point out that since the mineral phase was virtually free of carbonates, the CO_2 source must be oxidation of the kerogen carbon.

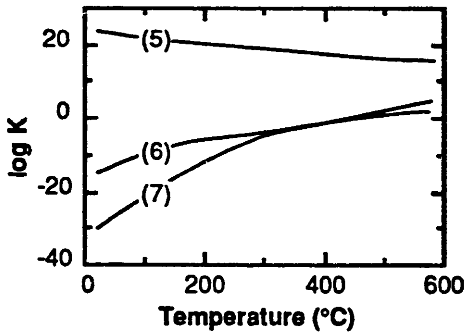


Figure 1. Equilibrium constants for eqs 3, 4, and 5 as a function of temperature

Results from our work with Wyodak coal in hydrothermal media also support the model (Ross, et al., 1990). We found that expelled tars were developed only in hydrous experiments; they were not observed in the absence of water nor when water was replaced by an inert fluid. The tars, moreover, underwent continued upgrading in extended experiments.

Finally there is evidence that disproportionation for some carbonaceous materials may take place in hydrothermal media even in the absence of a bulk mineral phase. In water at low, gas-like densities glucose is converted to a char and some quantities of CO_2, methane, and other light gases (Amin, 1975). However when the water density is increased to liquid-like levels, the char for the most part is replaced by an oil, and the gas quantities are increased by a factor of 3.

ACKNOWLEDGMENT

We acknowledge support of the US Dept. of Energy for a portion of the work reported here.

REFERENCES

Amin, S. I. (1975). "Reforming and Decomposition of Organics in Water, " thesis prepared for M. Modell, MIT.

Barnes, H. L. (1987). Buffers for pH and Redox Control of Hydrothermal Systems in *Hydrothermal Experimental Techniques,* G. C. Ulmer and H. L. Barnes, eds. John Wiley and Sons, Inc., New York.

Benson, S. W. (1968). *Thermochemical Kinetics.* John Wiley and Sons, Inc., New York.

Comet, P. A., McEvoy, J., Giger, W., and Douglas, A. G. (1986). Hydrous and anhydrous pyrolysis of DSDP Leg 75 kerogens--a comparative study using a biological marker approach. *Organic Geochemistry,* 9, 171-182.

Hoering, T. C. (1984). Thermal reactions of kerogen with added water, heavy water and pure organic substances, *Org. Geochem.* 5, 267-278.

Landais, P., Michels, R., Elie, M, Gerard, L., and Mansuy, L., 1992. Evaluation of factors influencing the thermal maturation of organic matter during confined pyrolysis experiments, *American Chemical Society Division of Fuel Chemistry Preprints*, 37 (4), 1588-1594.

Lewan, M. D., Winters, J. C., and Williams, J. A. (1981). A laboratory study of petroleum generation by hydrous pyrolysis, *Adv. in Organic Geochemistry 1979*, M. Bjorøy et al., eds., John Wiley and Sons, Ltd., Chichester, p. 524-533

Lewan, M. D. (1992). Water as a source of hydrogen and oxygen in petroleum formation by hydros pyrolysis. *American Chemical Society Division of Fuel Chemistry Preprints*, 37 (4), 1643-1649.

Monthioux, M., Lanais, P., and Monin, J-C. (1985). Comparison between natural and artificial maturation series of humic coals from the Mahakam delta, Indonesia. *Organic Geochemistry*, 8, 275-292.

Stull, D. R., Westrum, Jr., D. F., and Sinke, G. C.(1969). *The Chemical Thermodynamics of Organic Compounds*. John Wiley and Sons, Inc., New York.

END

DATE
FILMED

2/2/94