

## SIMPLIFIED KINETICS OF OIL SHALE PYROLYSIS

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### ABSTRACT

Analytical techniques have been developed that permit a distinction between the aromatic and aliphatic carbon fractions in kerogen. A new investigation of the kinetics of oil shale pyrolysis based on the aromatic-aliphatic carbon distribution in the kerogen indicates that simplified reaction mechanisms can account for the formation of products during retorting of oil shale. Some preliminary results of this study are presented and compared with previously published results.

### INTRODUCTION

In the last few years new methods have been advanced for the analysis of oil shales. Among the more promising of these new analytical methods are Fourier Transform Infrared (FTIR) spectroscopy (1) and solid state carbon-13 Nuclear Magnetic Resonance (NMR) spectroscopy (2,3). Both techniques have been employed as means for evaluation of the amount of hydrocarbon products that can be generated from kerogen during pyrolysis, i.e. the genetic potential (4). FTIR analysis measures the aliphatic hydrogen content of oil shales, whereas NMR analysis measures the aliphatic and aromatic carbon contents.

A very interesting result of such analyses is a strong correlation between the aliphatic components in raw oil shales and the ultimate oil yield from those shales. This result suggests that, under conditions similar to Fischer assay pyrolysis, there is almost complete conversion of the aliphatic components to liquid and gaseous products. An immediate implication of this result is that the aromatic carbon in raw oil shales should correlate with the carbonaceous residue in retorted shales. That interpretation is supported by NMR analysis (3). These observations provide the basis for a simplified

mechanism for the description of oil shale pyrolysis that incorporates quantitative molecular structure detail. Such detail has not been used in previous kinetic studies of oil shale.

An experimental program to investigate the kinetic behavior of oil shales under a variety of retorting conditions is currently in progress at Laramie Energy Technology Center. The NMR analysis of the shales at various stages of retorting is performed under a research contract with the Department of Chemistry at Colorado State University. The results reported in this paper are preliminary in nature.

### ANALOGY WITH COAL

The hypothesis that there is a close correspondence between the aromatic carbon content in raw oil shales and the carbonaceous residue in spent shales is apparently neoteric (1,3). Because of the similarity of such carbonaceous residue to fixed carbon in coals, it is natural to investigate the existence of an analogous relationship between the aromatic carbon content in raw coals and the coke or char content in pyrolyzed or devolatilized coals. In fact, it has long been known (5-17) that the same general relationship does exist. In 1951, Van Krevelen et al. (5) stated, "The fully condensed aromatic skeleton proves to be very thermostable; ..." Mazumdar et al. (10) have stated, "The proportion of carbon normally fixed in coke and char on carbonization at 600°C corresponds to the aromatic carbon in coal." Anthony and Howard (14) have remarked, "In the absence of external hydrogen, the aromatic clusters appear immune to internal rupture." For a final sample of opinion, Solomon and Colket (16) have observed, "The values of  $f_{NVC}$  are slightly greater than  $f_a$  suggesting that after the release of

the tar, all of the remaining  $C_{ar}$  and a fraction of the C aliphatic are the source for the char."

Thus there is a substantial body of opinion, well documented in the literature, supporting the contention that the hydrogen rich volatile products of coal pyrolysis evolve primarily from chemical reactions which deplete the aliphatic carbon content of the coal, and that the aromatic carbon content remains largely unaffected during pyrolysis to yield a carbon rich solid residue. Van Krevelen and Schuyer (6) quantified this last relation as

$$FC = 1.032 C_a,$$

where FC is the percentage of a coal remaining as fixed carbon after pyrolysis and  $C_a$  is the percentage of aromatic carbon in a coal before pyrolysis. Here the definition is employed (6) that

FC = 100 minus percentage of volatile matter.

Clearly Van Krevelen's relation is an oversimplified idealization, but it has been found to hold surprisingly well for a wide variety of coals of differing rank and pyrolysis processes (17). This simple relation ignores any secondary reactions, reactions involving added hydrogen, reactions occurring at high temperatures (above 600°C), or reactions that are limited by mass transfer effects.

#### ANALOGY WITH GEOCHEMISTRY

The generation of oil and gas from organic matter in sedimentary basins over geological time is a low temperature pyrolysis process on a vastly expanded time scale. An excellent description of the diagenesis, catagenesis, and metagenesis of organic matter as it is transformed into geochemical fossils, kerogen, and petroleum has been given by Tissot and Welte (4). As they state, "To some extent the pyrolysis leading to shale oil formation from kerogen is comparable to the burial of the source rocks at depth, that generates oil by the resulting elevation of temperature."

As an illustration of the metagenesis of kerogen, Tissot and Welte present data for samples from the Sahara that were buried at depths to 4000 m. These samples were taken from a location with a high

geothermal gradient. Infrared spectra showing evolution of the kerogen provide evidence that the residual kerogen has undergone thermal decomposition to various degrees as a function of depth. Proceeding from lesser to greater depths, the infrared spectral bands for aliphatic carbon and carbonyl progressively diminish. At the bottom extreme (where the temperatures are greatest), those bands have essentially vanished. However, the aromatic bands are virtually independent of depth; i.e. the indicated aromatic carbon content is the same for samples from all depths.

This result supports the hypothesis that the aromatic carbon in kerogen remains relatively stable during retorting of oil shale. Similar evidence is provided by Simoneit et al. (18) in regard to an organic rich shale in the eastern Atlantic that has been exposed to a steep thermal gradient imposed by basaltic intrusions. They conclude that the kerogen is more aromatic near the diabase sill, whereas kerogen from thermally unaltered sediment is more aliphatic in character. Other investigators (19,20) have suggested that such a relationship might exist; however, they lacked quantitative measurements of the organic carbon distribution in oil shales to test those conjectures.

#### THEORY

The idea to be exploited for a simplified kinetic scheme for oil shale pyrolysis is that the aromatic fraction of the carbon remains relatively stable during retorting. This means that the carbon in the residue is accountable directly from the starting material, without the requirement of a kinetic step for its formation. Coking reactions to produce additional carbon on the residue are regarded as second-order perturbations in this kinetic scheme. This also means that it is the aliphatic fraction of the carbon which undergoes thermal decomposition under conditions similar to Fischer assay pyrolysis (but including lower temperatures), and is largely responsible for the liquids produced. A schematic diagram of this reaction model is shown in Figure 1. Such a reaction scheme is in accord with Bradley's observation (20) that Green River oil shale contains kerogen that is bipartite in nature: one part readily producing oil and the other producing very little oil. Therefore, it is only necessary to account for disappearance of aliphatic

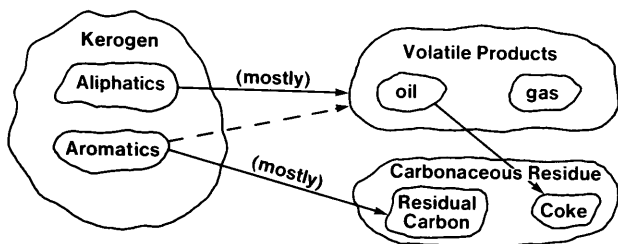
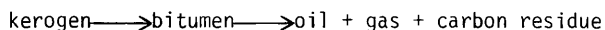


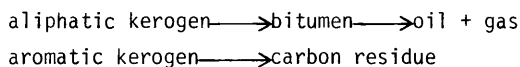
FIGURE 1 - Schematic Diagram of Reaction Model

carbon, the quantity of aromatic carbon remaining constant, in order to account for pyrolysis yields, independent of product composition. Accordingly it is the fraction of aliphatic carbon converted that is to be described as a function of time.

This kinetic model is a radical departure from the usual first-order kinetic schemes, such as:



Instead this model is further simplified to:



In parallel with standard convention (21,22), X is used to denote the mass fraction of aliphatic carbon converted to pyrolytic products. In conventional schemes, X denotes the mass fraction of the total organic carbon converted, without regard to any structural features of the oil shale kerogen. The unconverted aliphatic carbon in the kerogen is then represented by 1-X. For a first order reaction, the governing relation is of the form

$$\ln(1-X) = -kt,$$

where t denotes time and k denotes the specific rate constant at a fixed temperature (23). The Arrhenius equation can be used to represent k as a function of temperature (23).

#### RESULTS AND DISCUSSION

The retorted shale samples used in this study are from the experimental program conducted by Cummins and Robinson (22) at Laramie Energy Technology Center. The raw shale was taken from the DOE

(then Bureau of Mines) oil shale mine near Rifle, Colorado. Fischer assay of the sample indicated that it contained 272 l of oil per Mg (tonne) of shale. The organic carbon content of the shale was 30.2 weight percent. Soluble organic material in the raw shale was removed by benzene extraction. 7.5 weight percent of the organic material was removed by the extractions. About 80 weight percent of the organic material in raw shale is organic carbon, therefore each 100 g sample of extracted shale contained 28.75 g organic carbon.

The samples subjected to NMR analysis came from isothermal conversion of the extracted raw shale at 350°C (22). The heating times were 0.5, 1.0, 2.0, and 4.0 days. The NMR spectra of the partially retorted samples are shown in Figure 2. Other NMR

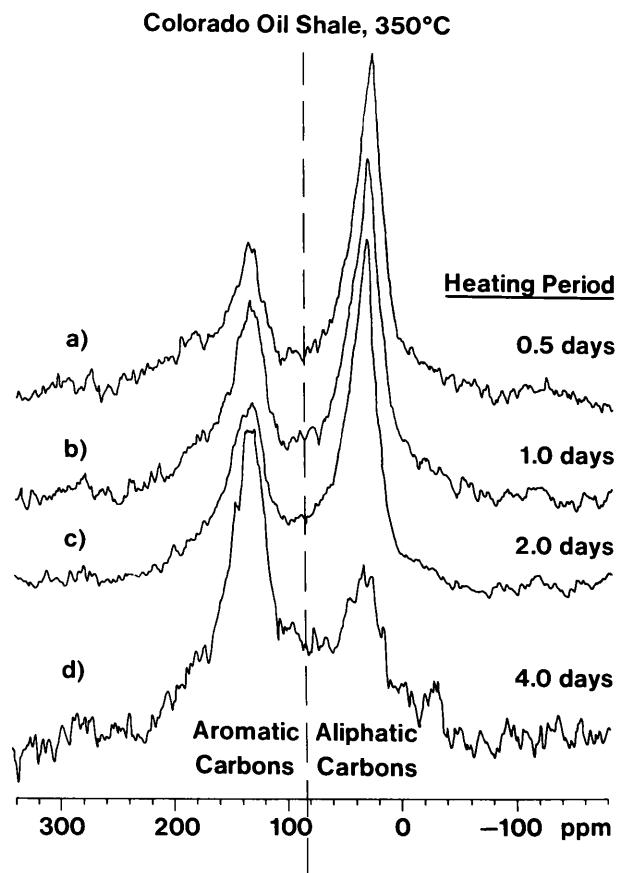


FIGURE 2 - NMR Spectra of Partially Retorted Samples spectra of oil shales heated to higher temperatures are shown in the paper by Miknis and Maciel (3).

NMR analysis (2) also was performed on the benzene extracted, solid remnant from each heating time period. Because the weight of the sample is decreased as volatile products are produced, the aromatic and aliphatic carbon fractions of each sample are relative to a different mass of carbon in the remaining shale. Values of the aromatic and aliphatic carbon fractions were determined by integration of the appropriate spectral regions as delineated by the dashed line in Figure 2.

NMR analysis of the extracted raw shale indicated the aromatic carbon fraction to be 0.26. This is in excellent agreement with the experimental result reported by Cummins and Robinson (22) that 27.9 percent of the kerogen carbon was converted to carbon residue. Each 100 g sample of extracted shale contained  $0.26 \times 28.75 = 7.48$  g of aromatic carbon. Under the hypothesis that the amount of aromatic carbon remains constant during pyrolysis of each sample, the amount of unconverted kerogen carbon,  $k_u$ , in each partially retorted sample was computed from

$$k_u = 7.48/f_a,$$

where  $f_a$  denotes the aromatic carbon fraction at any given time. The amount of unconverted aliphatic carbon then was found from  $(1-f_a)k_u$ . The values for converted and unconverted kerogen carbon based on NMR analysis are given in Table 1. The least

constant for conversion of total organic carbon. Figure 3 presents a plot of  $\ln(1-X)$  as a function of time. The aromatic carbon fractions for each heat-

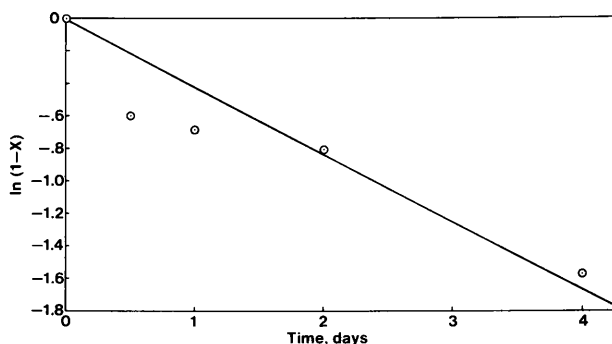


FIGURE 3 - Conversion of Aliphatic Carbon to Pyrolytic Products at 350°C

ing time period are shown in Table 2. The NMR precision of these fractions is not known. The amount of unconverted kerogen determined in the experiments of Cummins and Robinson (22) can be used as a check on the accuracy of the hypothesis that  $f_a \cdot k_u = 7.48$  at all times. Those values are given in Table 3. The fluctuation in the values of  $f_a \cdot k_u$  indicates that experimental agreement with the hypothesis is not complete; however, it is not known

TABLE 1. - Kerogen Aliphatic Carbon Converted to Pyrolytic Products

Heating Time (Days)	Kerogen Aliphatic Carbon (Heating Temperature = 350°C)			
	Converted (g)	Unconverted (g)	1 - X	$\ln(1 - X)$
0.0	0.00	21.28	1.00	0.000
0.5	9.59	11.69	0.55	-0.599
1.0	10.52	10.76	0.51	-0.682
2.0	11.76	9.52	0.45	-0.805
4.0	16.89	4.39	0.21	-1.578

squares estimate for the specific rate constant for aliphatic carbon conversion is  $k = 0.42$ . The rate constant for total organic conversion at 350°C was found to be 0.2 by Cummins and Robinson (22). The rate constant should be greater for conversion of the aliphatic portion of the carbon because it is relative to a smaller initial mass than is the rate

at present to what extent the lack of agreement is due to the oversimplified nature of the hypothesis or due to inaccuracies in the NMR values of  $f_a$  and the experimental values of  $k_u$ .

Finally a comparison of the experimental values of Cummins and Robinson (22) for organic carbon

TABLE 2. - Aromatic Carbon Fractions of Partially Retorted Shale

Heating Time (Days)	Aromatic Carbon Fraction, $f_a$
0.0	0.26
0.5	0.39
2.0	0.44
4.0	0.63

TABLE 3. - Calculated Values of Aromatic Carbon Mass,  $f_a \cdot k_u$

Heating Time (days)	Experimentally Determined $k_u$ (g)	$f_a \cdot k_u$ (g)
0.0	28.75	7.48
0.5	20.82	8.12
1.0	15.96	6.54
2.0	13.25	5.83
4.0	10.03	6.32

conversion with the values obtained by NMR analysis are presented in Table 4. Also presented are the predicted values assuming a first-order reaction model with the least squares estimate for the specific rate constant. Agreement is better for the longer time periods. Again the precision of the experimentally determined and analytically determined values is unknown.

TABLE 4. - Kerogen Organic Carbon Converted to Pyrolytic Products (Heating Temperature = 350°C)

Heating Time (Days)	Experimental Values (22) (g)	NMR Analysis (g)	Model Predictions (g)
0.0	0.0	0.0	0.0
0.5	7.9	9.6	4.0
1.0	12.8	10.5	7.3
2.0	15.5	11.8	12.1
4.0	18.7	16.9	17.3

Some advantages of the proposed kinetic model are as follows:

- 1) Volatile products and carbon residue are formed from different carbon material in kerogen, there is no need for a separate mechanism to account for carbon residue in retorted shale.
- 2) Molecular structural parameters are incorporated into the model.
- 3) In principle, the model applies to any type of oil shale, i.e. carbonaceous or siliceous or "coaly type".
- 4) The discrimination between unconverted kerogen and carbon residue via NMR analysis is incorporated into the model.
- 5) It may serve as a first step toward a general pyrolysis scheme for organic fossil fuels, including oil shales, coals, and tar sands. Pyrolysis of such fuels occurs at similar temperatures, indicating that similar bonds are being broken.

Limitations of the model in its present form are:

- 1) More data are required to substantiate the model.
- 2) Aromatic carbon types in liquid products are not explained by the model.
- 3) The model only considers the two major carbon types (aliphatic and aromatic);

other types, such as C=O, are not considered.

- 4) Secondary reactions, such as coking and cracking, are not considered in the model.

#### SUMMARY AND CONCLUSIONS

NMR analyses have been made on a limited number of partially retorted oil shale samples. The NMR spectra indicate the mass fractions of aromatic and aliphatic carbon in the unconverted kerogen remaining in the samples. The NMR data generally support the hypothesis that the aromatic carbon in kerogen remains stable during retorting, and that it is the aromatic carbon that is left after retorting as the carbonaceous residue. It is the aliphatic carbon in kerogen that undergoes thermal decomposition to form volatile products. These results suggest that coking of the liquid products is not significant under conditions similar to Fischer Assay pyrolysis (but including lower temperatures).

A simple first order kinetic model is presented to describe the conversion of aliphatic carbon during retorting at 350°C. Additional experimental data are required to extend the temperature range of the model. A research program to provide such data is currently in progress at LETC. The model presented has the advantage that it requires no separate mechanism to account for formation of carbonaceous residue.

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