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INVESTIGATION OF ORGANIC PRODUCTS FROM THE THERMAL TREATMENT OF  
GREEN RIVER OIL SHALE WITH METHANOL AND WATER

By

S-L. Chong and J. F. McKay  
Western Research Institute\*, Laramie, Wyoming 82071

INTRODUCTION

Recovery of organic material from Green River oil shale has been extensively studied. Conventional retorting methods including Fischer Assay (1), aboveground retorts (2, 3) and in situ retorts (4), recover only about 65% or less of the organic material (kerogen plus bitumen); however, this is accomplished at the expense of large amounts of char remaining on the spent shale. Different retorting methods have been applied to increase oil yields, such as hydrogenation (5) and atmospheric steam pyrolysis (6). One highly efficient method is supercritical fluid extraction which has been developed in the last two decades. Water (7), carbon monoxide and water (8), methanol and water (9) and toluene (10) have been used as supercritical extraction solvents to extract shale oil from Green River oil shale with much higher yields than obtainable by no-solvent heating techniques. The methanol-water mixture investigated in this laboratory was found to be highly efficient in recovering organics from Green River oil shale (9). At 400°C and 31.2 MPa (4525 psig), 90% of organic materials in the shale were produced as liquid oil and only 2% as gases. This high yield is very impressive and leads us to further investigate the composition of the products. The total liquid oils obtained at temperatures of 300 to 425°C were fractionated into various compound types and compared. The degree of pyrolysis at different temperatures was determined by the distribution of *n*-alkanes and *n*-carboxylic acids. The function of methanol in the treatment of Green River oil shale is also discussed.

EXPERIMENTAL PROCEDURE

Materials

The oil shale sample used was a 271.2 L/T (65 gal/ton) Green River oil shale from the Mahogany Zone of the Piceance Creek Basin near Rifle, Colorado and contained about 37.3% organic material. The oil shale was ground and screened to -150  $\mu$ m (-100 mesh) before treatment.

Silica gel (CC-7 Special) was purchased from Mallinckrodt Co. Silver nitrate on silica gel was prepared by mixing 20 g silver nitrate (Reagent Grade) (dissolved in 100 mL water) and 100 g silica gel. The mixture was dried at 100-120°C for 7 hours, placed in a desiccator and stored in the dark.

*n*-Pentane and methylene chloride were Burdick-Jackson, distilled in glass. Diethyl ether was Reagent Grade.

Extract Preparation

Oil shale samples were heated independently at temperatures of 300, 350, 375, 400 and 425°C for 1 hour at a charged argon pressure of 3.5 MPa (500 psig) in a 1-liter reaction vessel constructed of Inconel-600. The heating rate for this reaction vessel was about 2°C/min. Forty grams of shale and 120 mL each of methanol and water were used in each run. The experimental procedure was the same as used by Cummins and Robinson (8). The reacted shale and oil was Soxhlet extracted with the benzene-methanol azeotrope and the methanol-water solution also containing some oil was extracted with diethyl ether followed by methylene chloride. After extractions, the solvent was stripped from each extract using a rotary-film evaporator. The combined extracts (total liquid oil) were then separated into different compound types.

Separation Procedure

The separation scheme shown in Figure 1 is similar to that used previously (11) except that a separation of olefins using silver nitrate-silica gel was added. Twenty grams of 20% silver nitrate on silica gel was packed in a column (45 cm x 1.5 cm OD) for each 0.2 g alkanes plus

\* Formerly Laramie Energy Technology Center.

olefins, and the column was wrapped with aluminum foil to prevent photodecomposition of the silver nitrate. Alkanes were eluted with 100 mL n-pentane and olefins were eluted with 100 mL of 50/50 n-pentane/diethyl ether. Alkanes were further separated by 5A molecular sieves into n-alkanes and branched-plus-cyclic alkanes (12).

Carboxylic acid methyl esters were prepared in the following way. The acids extracted from the anion resin were first refluxed with the  $\text{BF}_3\text{-CH}_3\text{OH}$  complex in benzene for 4 hours and then water was added to react with the excess  $\text{BF}_3$ . The esterified acids obtained were then charged to a fresh IRA-904 anion resin column and the carboxylic acid methyl esters were eluted from the column with cyclohexane.

### Gas Chromatography

Both n-alkanes and carboxylic acid methyl esters were analyzed using a Hewlett-Packard 5830A gas chromatograph equipped with a 25 m x 0.2 mm ID SP2100 fused silica capillary column and a flame ionization detector. The gas chromatograph (GC) oven was programmed from 100 to 275°C at 3°C/min and maintained at 275°C for 50 min. Response factors were determined for standard  $\text{C}_{15}\text{-C}_{32}$  n-alkanes and  $\text{C}_{14}\text{-C}_{32}$  n-carboxylic acid methyl esters. The weight percent of each component was calculated by multiplying the peak area with its GC response factor.

## RESULTS AND DISCUSSION

### Extract Composition

The recoveries of liquid organic material from the treatment of Green River oil shale with a methanol-water mixture at various supercritical conditions were calculated as weight percent of total organic material in the shale (37.3% is 100%) and are given in Table I. Also, the elemental analyses and the molecular weights of the extracts are presented. Incidentally, the ash contents of all extracts were found to be less than 1%. The experimental results show that the recoveries of liquid organics increase with the increasing temperature from 300 to 400°C; however, at 425°C the recovery decreased apparently due to decomposition of liquid organics to gases. This is believed to be true because a significant pressure increase was observed on the pressure gauge after the experiment. The atomic H/C ratio of the liquid oil decreased from 1.66 to 1.52 as temperature increased from 300 to 425°C. The higher atomic H/C ratio at 300 and 350°C suggests that at these temperatures, aliphatic components are more easily generated than aromatic components. Above 350°C, the atomic H/C ratio decreased toward that (1.54) of Green River oil shale kerogen. At 425°C, a slight loss of hydrogen occurs as evidenced by the lower atomic H/C ratio (1.52). These results suggest that the improved recovery at the increased temperatures come mostly from recovery of more aromatic components. As with most other retort methods, as the temperature increases, oxygen and sulfur decrease and nitrogen increases.

TABLE I

WEIGHT PERCENT OF ORGANIC MATERIAL RECOVERED, ELEMENTAL ANALYSES AND MOLECULAR WEIGHTS OF EXTRACTS

Sample	% of Organic Material Recovered	Operating pressure MPa	Wt % of Extract					Atomic H/C Ratio	Molecular Weight
			C	H	N	S	O		
Extract									
300°C	13.6	18.5	78.4	10.8	1.3	1.1	6.6	1.66	
350°C	26.6	24.7	79.8	11.0	1.6	-	5.8	1.65	515
375°C	52.3	27.6	79.0	10.6	1.9	1.0	5.4	1.60	572
400°C	89.5	31.2	80.4	10.5	2.6	0.5	3.7	1.57	452
425°C	83.3	35.8	82.9	10.5	2.5	0.1	3.7	1.52	
Kerogen <sup>a</sup>			80.5	10.3	2.4	1.0	5.8	1.54	

a. Smith, J. W., U. S. BuMines Rept. of Inv. 5725, 16 pp (1961).

### Degree of Pyrolysis

The distribution of n-alkanes and n-carboxylic acids has been found to be sensitive to thermal conditions (13, 14). The odd-even predominance (OEP) of n-alkanes and the even-odd predominance (EOP) of n-carboxylic acids, as calculated by the method described by Scanlan and Smith (13), generally decrease with increased temperature.

For an immature oil shale, the OEP of extractable n-alkanes is very high; however, OEP decreases to about 1 as the maturity of the oil shale increases (15). In the treatment of Green

River oil shale with methanol and water, the OEP of n-alkanes was studied and found to decrease with the increased temperature. A plot of OEP of n-C<sub>31</sub>H<sub>64</sub> against temperature is shown in Figure 2. The OEP of n-alkanes for the benzene-extracted bitumen and Fischer Assay oil of the shale are also shown in Figure 2 for comparison. The OEP for a Fischer Assay oil (obtained by heating Green River oil shale at an effective temperature of 475°C and representing only 65% of organics in the raw shale) was found to be 2.2. At 400°C with a maximum oil yield (89.5%), the OEP of n-C<sub>31</sub>H<sub>64</sub> produced from methanol-water treatment was found to be 2.4, which is slightly higher than that from Fischer Assay. These results show that pyrolysis in the methanol-water treatment at 400°C is definitely not more severe than the pyrolysis in the Fischer Assay method. Therefore, the high oil yield must be caused by a combination of pyrolysis and supercritical solvent extraction effect.

The EOP distribution of n-carboxylic acids was studied by analyzing the carboxylic acid methyl esters. The normalized weight percent of n-carboxylic acid methyl esters was obtained from their weight percents calculated from GC. Figure 3 shows the EOP of n-C<sub>31</sub>H<sub>63</sub>COOH as a function of temperature, the EOP also decreased with increased temperature. In general, the EOP values of n-carboxylic acids are a few units higher than the OEP values of the corresponding n-alkanes. The decrease in the OEP of n-alkanes and the EOP of n-carboxylic acids with the increased temperatures in the methanol-water treatment suggest that the OEP and EOP values can be used as good thermal indicators for the supercritical fluid extraction process.

The amounts of olefins obtained at different temperatures were also measured and are presented in Table II. The results show that the amount of olefins stays fairly constant from 300 to 425°C, contrary to the general increase of olefins with the increased temperature of heating during Fischer Assay or retorting (about 10% at 475°C). If this trend is maintained, then it suggests that the presence of methanol and water suppressed the formation of olefins.

TABLE II  
THE AMOUNT OF OLEFINS AT DIFFERENT TEMPERATURES

Temperature, °C	Olefins, Wt % of Extract
300	3.1
350	3.2
375	2.3
400	2.6
425	3.0

#### Function of Methanol

The experimental conditions in this work were above the critical temperature and pressure of methanol. (The critical temperature and pressure of methanol are 240°C and 7.96 MPa (1154 psig), respectively.) Undoubtedly, methanol acts as a "super" solvent in the methanol-water treatment of Green River oil shale due to the high near-liquid density of the supercritical gases. In addition, methanol seems to be incorporated into the products because the infrared spectra of the extract at all temperatures contained a significant carbonyl absorption at 1730 cm<sup>-1</sup>. (Extract from the water-only-run does not have this intense IR absorption.) The infrared spectrum of the extract obtained at 400°C is shown in Figure 4. After compound-type separations, this absorption peak appeared in both the hydrocarbon and base fractions, as shown in Figure 5. Absorption at 1730 cm<sup>-1</sup> is generally due to some type of carboxyl group. However, the hydrocarbon fraction is not expected to contain polar groups such as carboxylic acids because the anion resin in the separation scheme should retain all of the carboxylic acids. Therefore, it must be due to a less polar carboxyl group, for example, carboxylic acid methyl esters.

A labelled <sup>13</sup>CH<sub>3</sub>OH-CH<sub>3</sub>OH(1.3/98.7)/H<sub>2</sub>O experiment with Green River oil shale at 400°C was performed to further prove that esterification had occurred in the treatment. The extracts obtained from the unlabelled and the labelled experiments were analyzed by <sup>13</sup>C NMR, and the NMR spectra are shown in Figure 6. The peak at 51.4 ppm (due to <sup>13</sup>CH<sub>3</sub>O group of methyl esters) in Figure 6B is much higher than that in Figure 6A showing the incorporation of <sup>13</sup>CH<sub>3</sub>OH into esters, in agreement with the infrared data. Thus, this data shows that the reaction of methanol with carboxylic acids (16) and carboxylic acid salts (17) in Green River oil shale is possible and the products are methyl esters (18).

The maximum increased weight percent (X) for the oil yield due to the incorporation of methanol can be calculated from the following equation:

$$X = \frac{MW_i}{MW_{A+S}} \times P_{A+S} \times 100$$

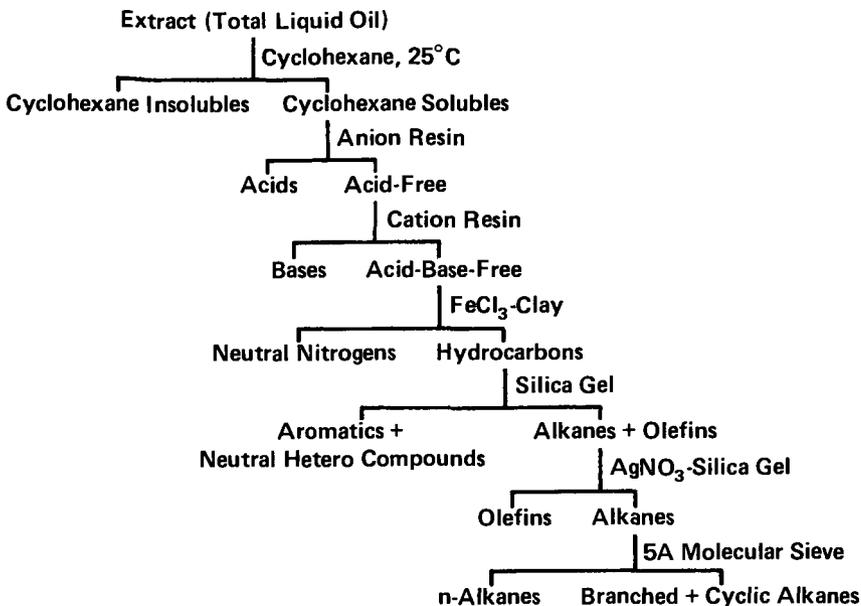


Figure 1. The separation scheme for the extracts from the methanol-water treatment of Green River oil shale.

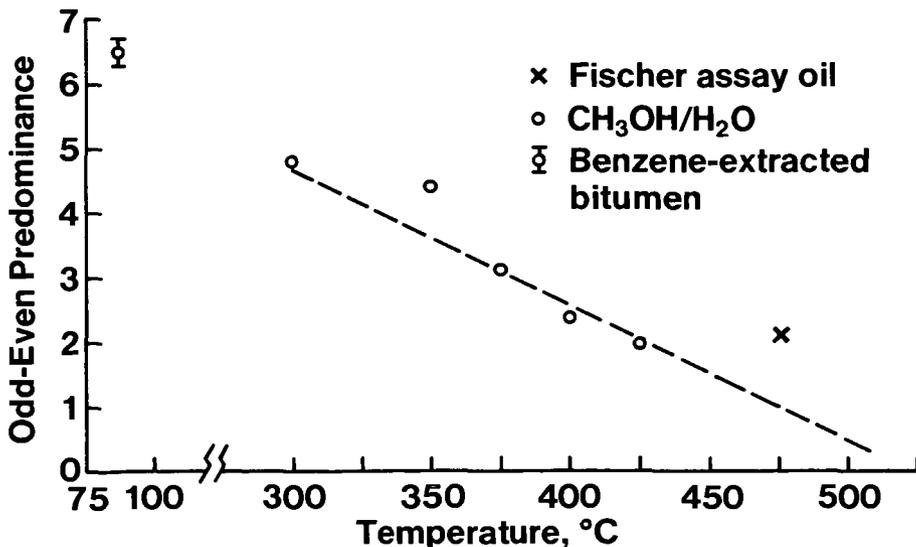


Figure 2. Changes of odd-even predominance of  $n\text{-C}_{31}\text{H}_{64}$  with temperature in the methanol-water treatment.

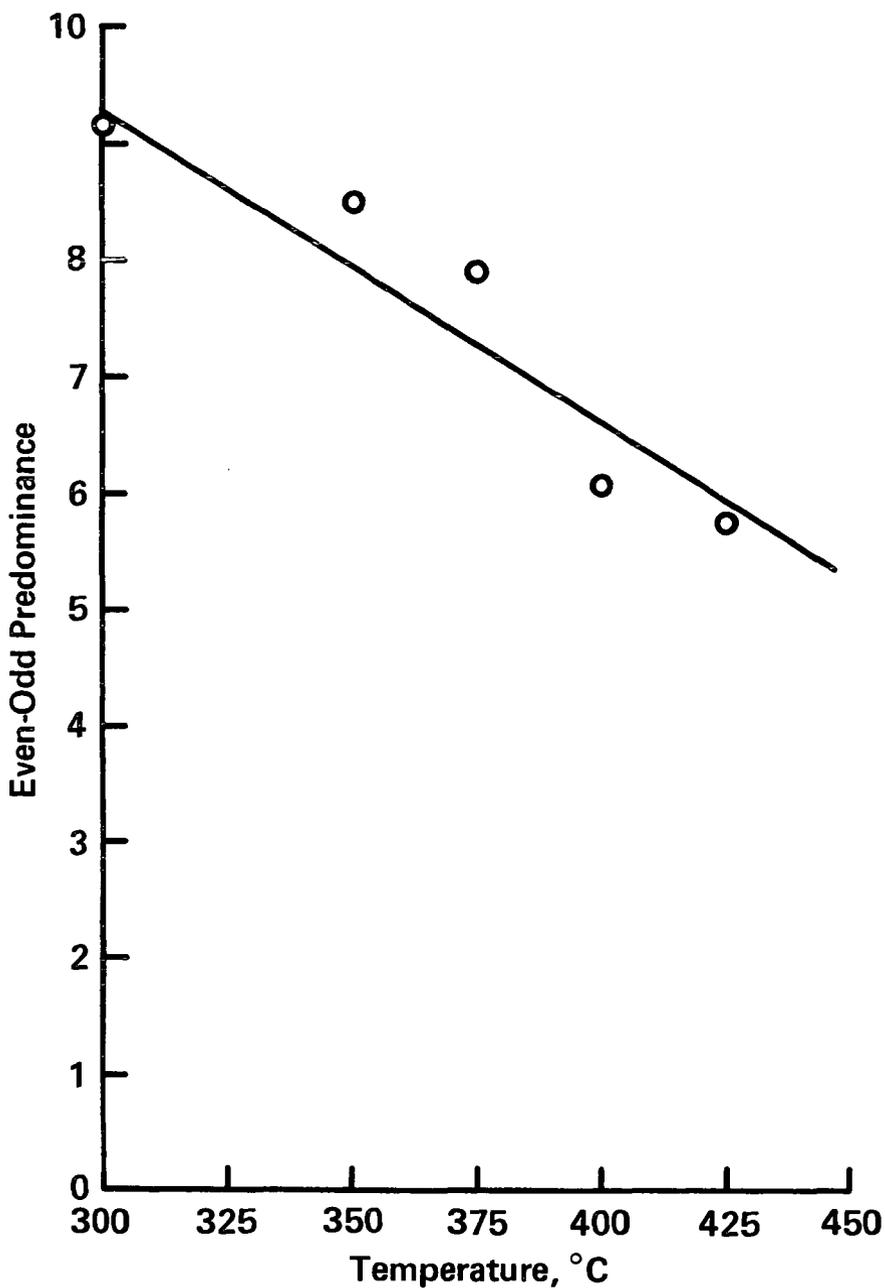


Figure 3. Changes of even-odd predominance of  $n\text{-C}_{31}\text{H}_{63}\text{COOH}$  with temperature in the methanol-water treatment.

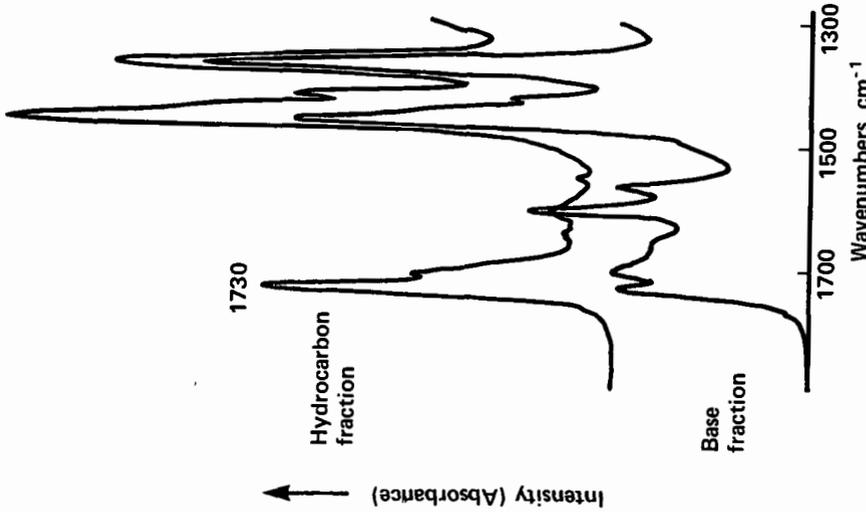


Figure 5. Partial infrared spectra of hydrocarbon fraction and base fraction from the methanol-water treatment of Green River oil shale at 400°C (in  $\text{CH}_2\text{Cl}_2$ ).

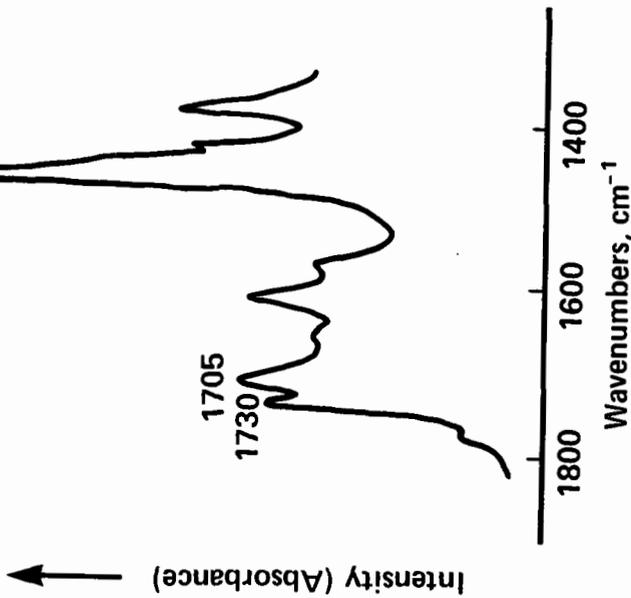


Figure 4. Partial infrared spectrum of extract from the methanol-water treatment of Green River oil shale at 400°C (in  $\text{CH}_2\text{Cl}_2$ ).

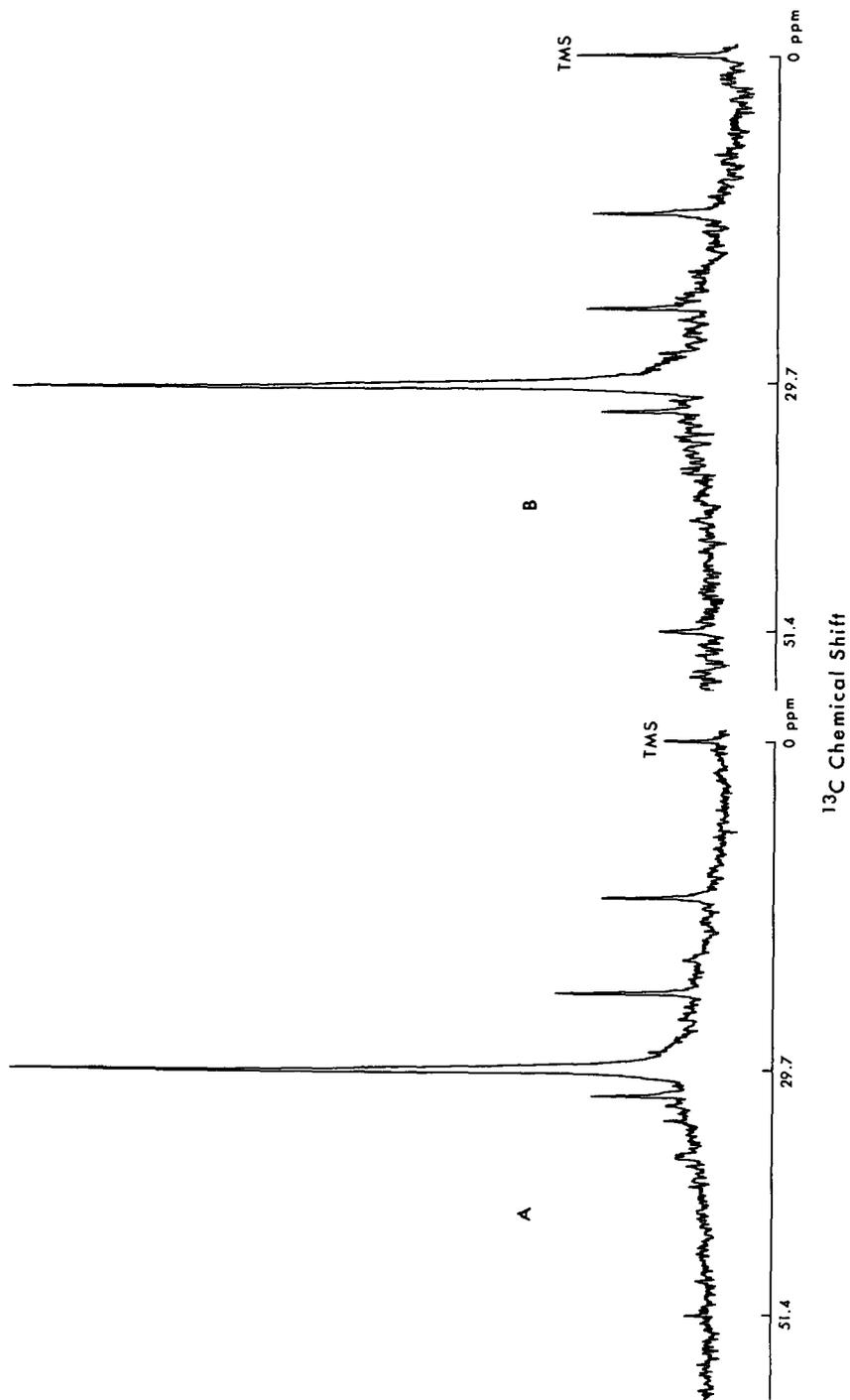


Figure 6.  $^{13}\text{C}$  NMR spectrum of extract from  $^{13}\text{CH}_3\text{OH}-\text{H}_2\text{O}$  experiment at  $400^\circ\text{C}$ .

where  $MW_i$  is the increased molecular weight for carboxylic acids and carboxylic acid salts due to incorporation of methanol,  $MW_{A+S}$  is the average molecular weight of carboxylic acids and carboxylic acid salts and  $P_{A+S}$  is the weight percent of carboxylic acids and carboxylic acid salts in the organic materials of the shale. Almost all of carboxylic acids found in the shale sample are monocarboxylic acids (16) so that a replacement of H by  $CH_3$  only increases molecular weight by 14. If carboxylic acid salts are involved in the reaction, the replacement of a cation by  $CH_3$  will only decrease the molecular weight because the cations found are sodium, calcium, aluminum, copper, etc. (17).  $MW_{A+S}$  is about 500 and  $P_{A+S}$  was found to be 20% (16). Based on these numbers, X is calculated to be 0.56%. This calculation shows that the incorporation of methanol is not enough to account for the increased oil yield found in the methanol-water treatment.

#### CONCLUSIONS

At 300 and 350°C, a methanol-water mixture generated more aliphatic organic materials from Green River oil shale than at higher temperatures. As the temperature of the treatment increased from 350 to 425°C, the atomic H/C ratio of the extract decreased towards that of Green River oil shale kerogen, suggesting that more aromatic components are generated at higher temperatures. In addition, the odd-even predominance of n-alkanes and the even-odd predominance of n-carboxylic acids were shown to be good thermal indicators for the supercritical fluid extraction process. The higher oil yield in the methanol-water treatment of Green River oil shale is apparently contributed to both by pyrolysis and by the supercritical solvent effect. There is evidence of methanol incorporation into the liquid oils in the methanol-water treatment, but not near enough to account for the higher oil yield.

#### ACKNOWLEDGMENT

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#### LITERATURE CITED

- (1) Annual Book of ASTM Standards, D3904-80.
- (2) Henderson, T. A., *Quart. Colo. School Mines*, **69** (3), 45 (1974).
- (3) Harak, A. E., Dockter, L. A. and Cohns, H. W., U. S. Bureau of Mines, Rept. Inv. 7995, 31 pp. (1974).
- (4) Sohns, H. W. and Carpenter, H. C., *Chem. Eng. Prog.*, **62** (8), 75 (1966).
- (5) LaRue, D. M. and Wise, R. L., LERC/Tech. Progress Report 77/2, 30 pp. (1977).
- (6) Campbell, J. H. and Taylor, J. R., Lawrence Livermore Laboratory, Univ. California, UCID 17770, 20 pp. (1978).
- (7) McCollum, J. D. and Quick, L. M., U. S. Patent 4,151,068, April 24, 1979.
- (8) Cummins, J. J. and Robinson, W. E., U. S. Dept. of Energy, Rept. Inv. LERC/RI-78/1, 19 pp. (1978).
- (9) McKay, J. F., Chong, S-L. and Gardner, G. W., ACS Geochemistry Div. Abstract, Abstract No. 25, New York, August 23-28, 1983.
- (10) Compton, L. E., Preprints, ACS, Div. Fuel Chem., **28** (4), 205, Washington, D. C., August 28-September 2, 1983.
- (11) Chong, S-L., Cummins, J. J. and Robinson, W. E., Preprints, ACS, Div. Fuel Chem., **21** (6), 26, August 29-September 3, 1976.
- (12) O'Connor, J. G., Burow, F. H. and Norris, M. S., *Anal. Chem.*, **34** (1), 82 (1962).
- (13) Scanlan, R. S. and Smith, J. E., *Geochim. Cosmochim. Acta*, **34**, 611 (1970).
- (14) Kvenvolden, K. A., *J. Amer. Oil Chem. Soc.*, **44**, 628 (1967).
- (15) Martin, R. L., Winters, J. C. and Williams, J. A., *Nature*, **199**, 110 (1963).
- (16) Chong, S-L., Chapter in "Chemical and Geochemical Aspects of Fossil Energy Extraction", T. F. Yen, F. K. Kawashara and R. Hertzberg, eds., Ann Arbor Science, 143 (1983).
- (17) Chong, S-L. and McKay, J. F., to be published in Fuel.
- (18) Chong, S-L. and McKay, J. F., ACS Geochemistry Div. Abstract, Abstract No. 36, Washington, D. C., August 28-September 2, 1983.