

## STEPWISE OXIDATION OF BIOLEACHED OIL SHALE

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The study of organic matter present in the Green River shale formation (Eocene Age) is of considerable geochemical interest as evidenced by the reports in the past dealing with isolation and identification of the hydrocarbon fraction contained in both the solvent soluble organic portion (the bitumens) and the generally insoluble organic portion (the kerogen) of the shale. Depending on the location of the shale sample collected for analysis, the amount of organic matter is estimated to be around 15%; however, due to the extensiveness of the oil shale formation, the potential use of the entrapped organic matter, as a possible source of liquid fuel, (ca. 1.5 trillion barrels of known reserves) (1) has provided the incentive for industry to develop the most efficient process of extracting this reserve.

Destructive pyrolysis (or retorting), is the process where major industrial investigative efforts are presently centered around. The basic retorting techniques themselves are not new; they were known at least 50 years ago (2). The only industrially feasible adaptation of these basic techniques to the present problem of shale oil recovery is the in situ retorting process. The in situ technique obviates the high costs of mining, crushing, transporting, and ultimately of disposing the spent shale. To date various in situ schemes, such as injection of hot gas or steam, electrical discharge, and underground nuclear explosion, have been considered in order to provide the necessary source of heat to start the retorting process and to overcome the low permeability of the formation. Estimates of the recovery efficiency is around 50% of the organic matter with 25% burnt for the retorting process and another 25% as unrecoverable carbon-rich residue (coke).

As an alternative way of releasing the organic material, primarily the kerogen portion since the bitumens are easily extracted with solvent from the mineral matrix, we have investigated the feasibility of mild oxidative degradation. The use of oxidation as a tool for structural elucidation is well documented in the literature (3), a variety of oxidants have been used and the starting material is usually a kerogen concentrate with a major portion of the mineral matrix removed by concentrated hydrofluoric acid treatment. In the present study, the shale sample has been pretreated with dilute acid (ca. 0.1 N) for the removal of soluble mineral (dolomite and calcite) only. This can also be accomplished by leaching the shale sample with the acid medium produced by sulfur oxidizing bacteria as has been demonstrated in this laboratory (4). The shale sample, which has undergone this bioleaching process, is about 70-75% in mineral constituent, composed largely of quartz and feldspar. Starting with this 'bioleached' shale, the release of the entrapped kerogen will be carried out in mild oxidative steps using potassium permanganate solution and ozone separately. Mild stepwise oxidation is intended to prevent further fragmentation of released organic matter since it is more reactive than the still entrapped kerogenic material. Permanganate solution and ozone (5) are known to oxidize saturated hydrocarbons, however the mode of oxidation is not likely to be the same.

The basic skeletal structure of kerogen has been postulated to compose of largely cross linked aliphatic chains (3); it would be of interest to compare the effect of these two oxidants on the kerogen entrapped in a resistant mineral matrix. Results of the permanganate oxidation are presented in the rest of the report; ozone oxidation is presently in progress.

#### EXPERIMENTAL

The shale sample was collected from the Mahogany ledge of the Green River formation and was crushed to pass a 150 mesh screen. From the elemental analysis the shale was estimated to contain around 13% organic matter by weight and the solvent extractable material, the bitumens, was found to be around 2%. Direct bioleaching of the raw shale with the acid medium of the sulfur oxidizer was not done and instead it was pretreated by dilute hydrochloric acid; resulting in a similar weight loss of 40% as compared with directly bioleached shale. The dilute acid treated shale was Soxhlet extracted with a (4:1) benzene:methanol mixture for 84 hours to remove the soluble material. The hydrocarbon fraction from the soluble material was analyzed by gas chromatography (Hewlett-Packard Model 5750) on a 9 ft x 1/8 in stainless steel column, packed with 3% SE-30 on Chromosorb Q. The branched and cycloalkane components are essentially identical with early report (6).

Stepwise permanganate oxidation of 10 grams of the shale treated above was carried out in a fashion similar to Djuricic et al. (3). For each step 25 ml of a solution with 0.08 M  $\text{KMnO}_4$  and 0.2 M KOH was warmed with the shale to a temperature of  $75^\circ\text{C}$ . Upon completion of the oxidation the solid residue (oxidized shale and  $\text{MnO}_2$ ) was separated from the aqueous layer by centrifugation and a fresh portion of  $\text{KMnO}_4$  solution was added to continue the oxidation. The oxidation was terminated after the 28th step. The shale at this point still contains entrapped organic matter since carbon analysis showed a carbon content of 0.83% in the solid residue.

The aqueous layer from each step of the oxidation was combined and acidification with hydrochloric acid yielded a precipitate (fraction I), the precipitate turned into a lustrous dark brown material upon drying. An amount of 1.24 grams of the precipitate was isolated which corresponds to about 7.45% of the untreated raw shale. This fraction was analyzed further. The organic material that remained in the aqueous layer was isolated by first evaporating the solution to dryness with a rotary evaporator and then the residue was extracted thoroughly with diethyl ether. Evaporation of the diethyl ether left behind 0.39 grams of extract (fraction II). Together the two fractions constituted 9.78% of the raw shale.

A portion of the oxidation product (fraction I) was dissolved in pyridine- $d_5$  and subjected to NMR analysis (Varian Model TC-60) in order to characterize its overall structure (Fig. 1).  $\text{BF}_3$  esterification in methanol and subsequent heptane extraction yielded 293 mg (per gram of the material) of heptane-soluble esters. Gas chromatography, under conditions mentioned above, of the heptane soluble esters is shown in Fig. 2. The identification of the unbranched aliphatic esters (both mono-, and di-basic) was done by use of known methyl ester standards. The branched and cyclic carboxylic esters were inferred from the change of peak heights by urea clathration method which removed the unbranched esters to a considerable amount.

## RESULTS AND DISCUSSION

The products of the oxidation reaction are potassium salts of carboxylic acids. Intermediate products of consecutive oxidation were not obtained. The compounds were identified using various techniques; a comparison of the gas chromatograms with a collection of standard samples confirmed the presence of saturated unbranched aliphatic monocarboxylic acids ( $C_{11}$ - $C_{31}$ ), saturated straight-chained aliphatic dicarboxylic acids ( $C_{12}$ - $C_{18}$ ), and branched aliphatic (or naphthenic) carboxylic acid (ca.  $C_{12}$ - $C_{26}$ ). NMR spectra of the oxidation products in pyridine- $d_5$  solvent revealed the absence of aromatic protons. Since it has been shown that alkyl-substituted aromatic compounds are converted to aromatic carboxylic acids, one can thus conclude that Green River kerogen contains little aromatic sites which is in agreement with the results of Djuricic et al. (3). There is, however, no apparent dominance of the unbranched aliphatic dibasic acids as was observed by Djuricic and co-worker. A likely cause for this may be due to incomplete oxidation of the kerogen 'nucleus,' since the presence of mineral (e.g., quartz, feldspar and clay) that is resistant to mild chemical conditions would hinder the oxidation of the kerogen bound to it. This is consistent with the drastic increase polyfunctional aliphatic acids (especially dicarboxylics) as oxidation of kerogen concentrate progresses (Burlingame et al.) (7).

The results of the present investigation indicates that oxidative release of the entrapped organic material in an aqueous medium is possible without the necessity of disaggregating or dissolution of the resistant mineral. Under the mild oxidative conditions used a significant amount of the organic matter is released as soluble acids (ca. 9.78% of the total raw shale). If an efficient method can be devised to quickly remove the acids released, so that further oxidative degradation is prevented, a stronger oxidizing medium could be used.

Pyrolysis of Green River shale at high temperature ( $\sim 500^\circ\text{C}$ ) tend to yield some aromatic hydrocarbons (8), possibly due to rearrangement of aliphatic hydrocarbons. Oxidation in an aqueous medium can proceed at much lower temperature ( $\sim 75^\circ\text{C}$ ) while the product is mainly aliphatic in nature. Apparently all the available organic material present can be released by oxidation and there is no coke formation as in pyrolysis.

Permanganate is not a suitable oxidant for large scale oxidation even though it is a very effective oxidant for analytical purposes. Once the permanganate is reduced to  $\text{MnO}_2$  there is no simple and economical method of oxidizing it back to  $\text{MnO}_4^-$ , besides one must be wary of the possible environmental effects of excessive usage of a metal such as manganese. Ozone has been considered as an alternative oxidant, it can be easily generated from oxygen and excess ozone can be easily destroyed (by a catalyst) before releasing to the atmosphere as oxygen. Robinson et al. (9) have partially oxidized the Green River shale with ozone; Bitz and Nagy (10) have used ozone on coal and kerogenic materials. Results of the ozonolysis of Green River shale will be reported at a later date.

## ACKNOWLEDGEMENT

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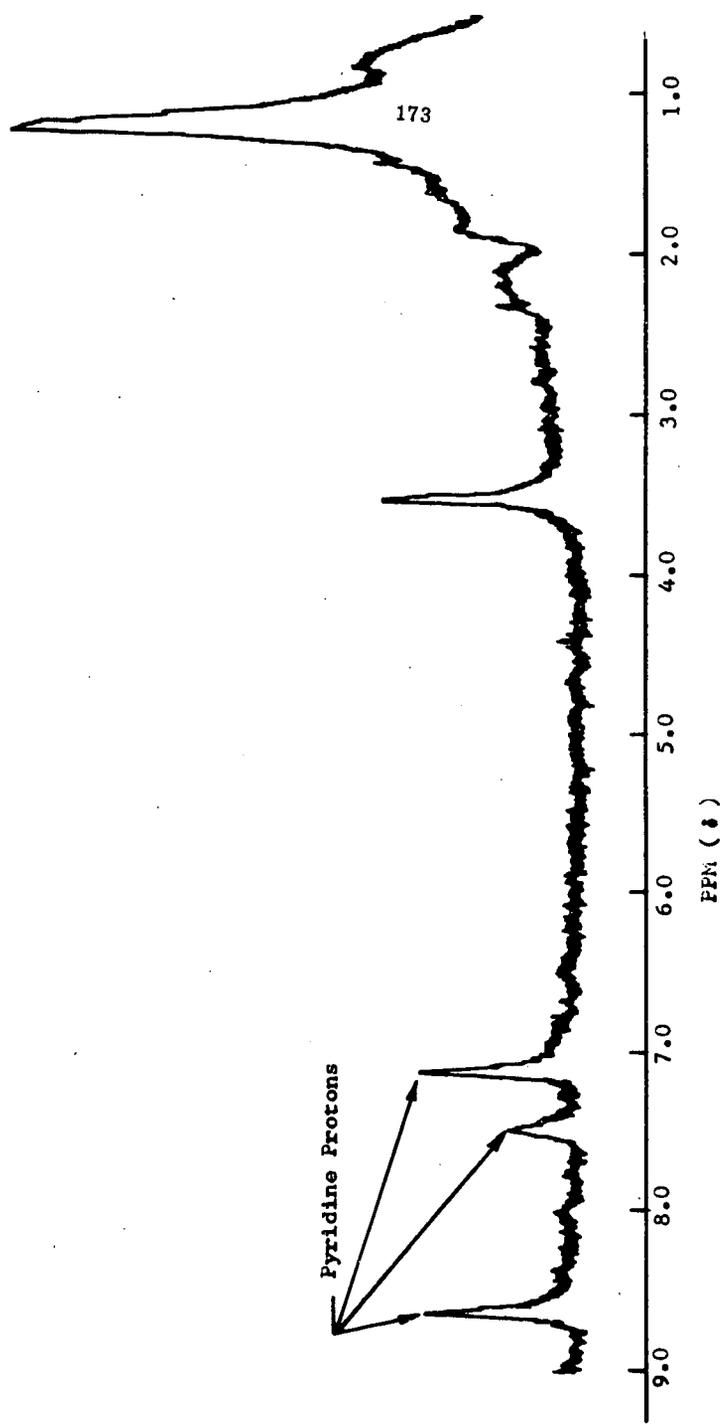


Fig. 1. NMR Spectrum of Fraction I dissolved in (99.9%) Pyridine-D<sub>5</sub>.

N - unbranched aliphatic carboxylic methyl esters.  
 D - unbranched aliphatic dicarboxylic methyl esters.  
 B - branched or cyclic acid methyl esters.  
 The numbers refer to the number of carbon atoms (not including the methoxyl carbon).

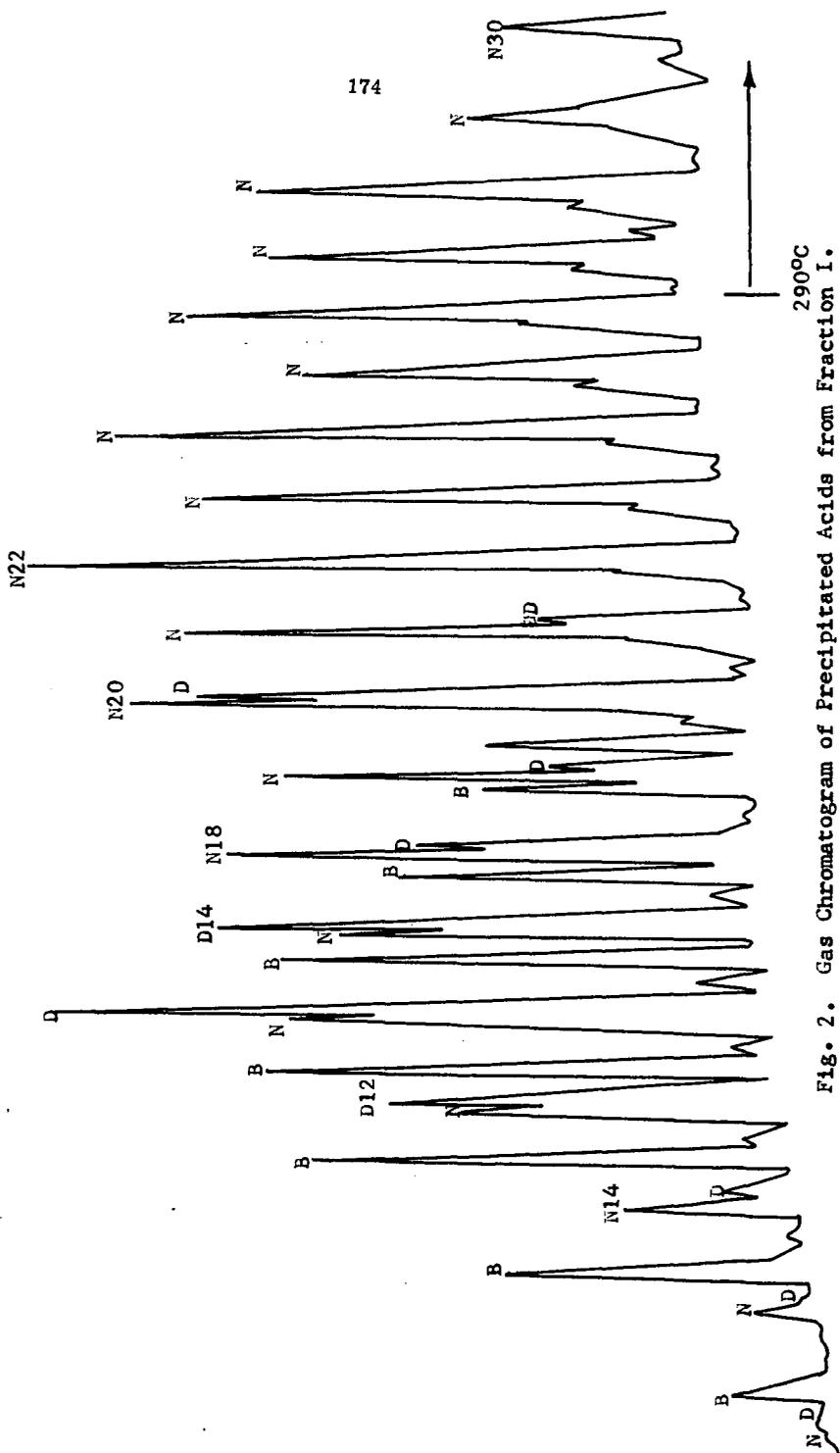


Fig. 2. Gas Chromatogram of Precipitated Acids from Fraction I.