Distribution of Short Chain n-Fatty Acids in Retort Water from Green River Oil Shale

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ABSTRACT AND SUMMARY

n-Fatty acids in the range of C_2 to C_{10} were found in retort water from a simulated in situ retorting process of Green River oil shale. The distribution of these fatty acids shows no preference between molecules of odd and even numbers of carbon atoms. A comparison with retort water from an aboveground retorting process suggests that differences in the distribution of these acids depend largely on the technique and operating conditions employed in the retorting process.

INTRODUCTION

Numerous organic-rich rocks, termed oil shale, represent an important potential source of energy. Recovery of shale oil from oil shale is based on a thermal decomposition of the shale's solid organic substance. The term "retorting," as applied to oil shale, signifies the process of adding heat to the shale to decompose its organic material into products. There are two basic categories of retorting: in situ and aboveground. In the in situ process, thermal decomposition takes place underground. The Laramie 10-ton simulated in situ retort (LISR) presently in operation provides an opportunity to study in situ technique. In the aboveground or TOSCO II process, retorting is performed in a rotating drum in which crushed oil shale is heated by direct contact with heated ceramic balls.

Retort water, along with shale oil, is a product of the retorting process. The amount of retort water formed may equal the 20-100 barrels of shale oil yielded or may even be produced in volumes in excess of the oil yield (1, 2). Inasmuch as retort water is laden with considerable quantities of soluble organic and inorganic materials, it presents serious disposal and purification problems (1-6).

Organic acids in Green River oil shale retort water from the TOSCO II process have been reported by Cook (7). Recently, Wen et al. (3), in their study of benzene-soluble organics by GC-MS method, showed that a series of fatty acid methyl esters was present in esterified samples of retort water from Green River oil shale. However, esterification of the sample for gas chromatographic analysis is usually limited to the determination of the high carbon numbered fatty acids. The technique of using a column packed with SP-1200 has been claimed suitable for short chain fatty acid analysis (8). The present work is an attempt to investigate the distribution of short chain fatty acids and their role in the oil shale retort water.

EXPERIMENTAL PROCEDURES

Retort waters were formed from the Laramie 10-ton simulated in situ retorting process of Green River oil shale. A homogeneous representative sample of retort water was obtained by filtration through a submicron filter unit for the removal of oily particulate prior to sampling. To avoid effects from biodegradation, all samples were kept under refrigeration. A quantity of 200 ml of retort water was measured and adjusted to pH 10.0 from the original pH 8.6 by 0.5N NaOH. Upon com-

pletion of 24 hr of liquid-liquid extraction with benzene to remove nonacidic materials, the aqueous retort water phase was acidified with 1 N HCl to pH 1.2, and then, reextracted with ethyl ether. The ether extract was adjusted to the desired concentration by evaporating the ether solvent with a purified nitrogen stream for the gas chromatographic analysis. A Hewlett-Packard HP 5750 gas chromatograph equipped with a flame ionization detector was employed. The column was 1/8 in. x 6 ft stainless steel and packed with 10% SP-1200/1% H_3PO_4 on Chromosorb W.

The total volatile acids in the filtered retort water were determined by chromatographic separation utilizing a column of silicic acid and eluting with an appropriate solvent of chloroform-butanol mixture (9-11). The eluted sample was titrated with NaOH (0.02N) to the phenolphthanlein end point by purging nitrogen gas to prevent contact with atmospheric CO_2 during titration.

RESULTS AND DISCUSSION

The gas chromatogram of fatty acids isolated from retort water of the ether fraction was achieved by comparison of the chromatographic retention time of each peak with those of standard components and also by co-injection of known standards with samples. The relative quantities of fatty acids presented in Table I show acetic acid to be dominant. An infrared spectrum was taken to further identify those fatty acids predominant in the ether fraction. As shown in Figure 1, a strong carbon absorption peak at 1720 cm-1 is observed clearly indicating the presence of carboxylic acids. The quantity of total volatile acids as determined through a silicic acid column was calculated to be ca. 2304 mg per liter of filtered retort water. The vast number of organic compounds, particularly dicarboxylic acids, coexisting with the volatile acids in the retort water may cause some errors in this determination (9).

Analysis of volatile organic acids in the Green River oil shale retort water from the TOSCO II process has been previously reported (7). Figure 2 shows the relative distribution of short chain n-fatty acids found in retort waters from the TOSCO II process and the LISR process of Green River oil shale. A striking difference exists in those distribution patterns (Fig. 2) as compared with that of the extract of the raw Green River oil shale (12, 13).

TABLE I

Short Chain n-Fatty Acids in Oil Shale Retort Water

Acid	Relative quantity[a] % (wt)
Acetic	100
Propionic	50.4
Butyric	30.8
Valeric	36.2
Caproic	38.9
Heptanoic	37.2
Caprylic	34.5
Nonanoic	23.0
Capric	1.2

[a]Relative to the area of acetic acid from gas chromatogram.

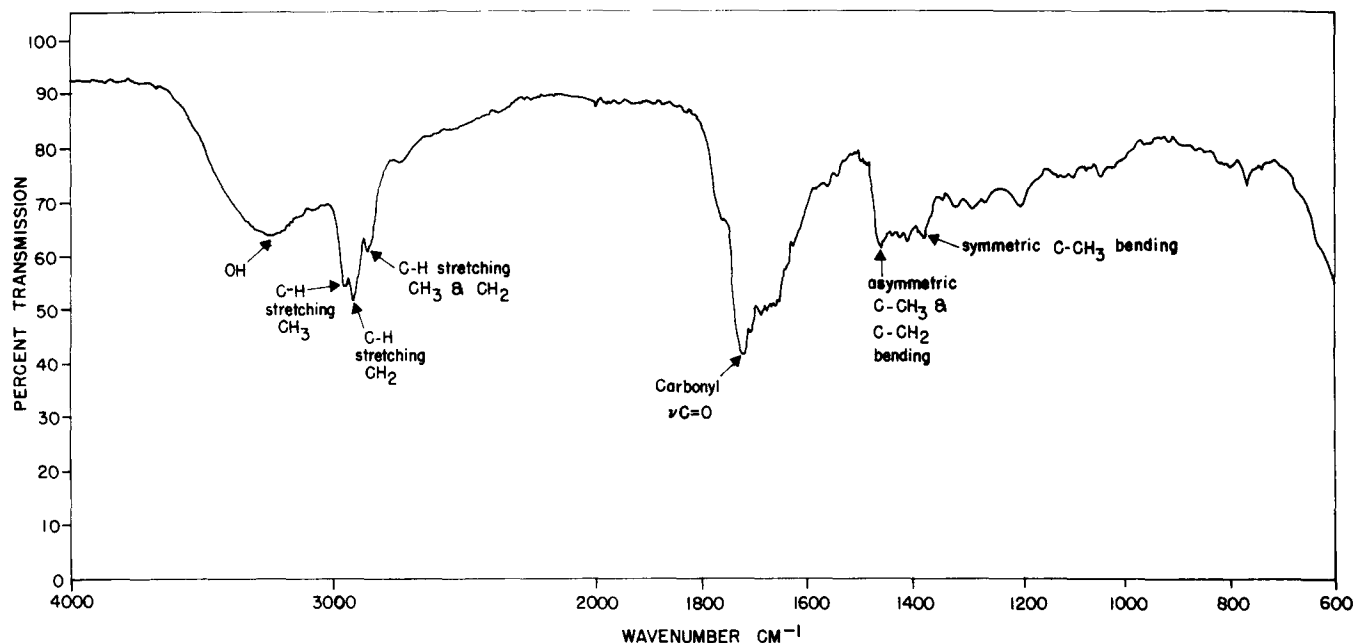[1]To whom all inquiries are to be addressed.

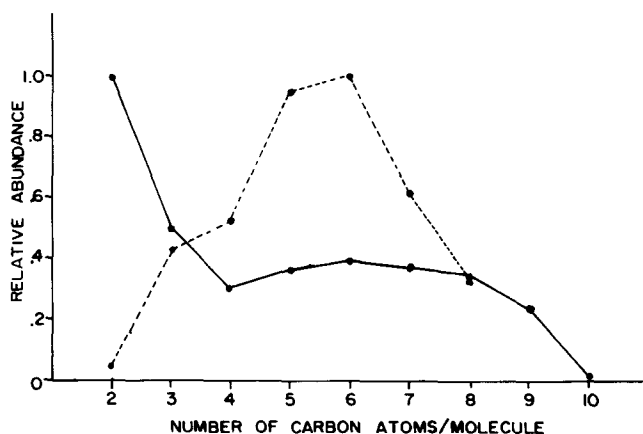FIG. 1. Infrared spectrum of fatty acid fraction from retort water.

FIG. 2. Relative distribution of short chain n-fatty acids found in retort waters from TOSCO II (---) and Laramie 10-ton simulated in situ retorting (———) processes.

Namely, there is no preference for the abundance of the even numbered carboxylic acids, which is a geochemical indicator of the shale sample. This difference indicated that the presence of short chain n-fatty acids in the retort water can be attributed to the combustion of oil shale. Generally, the product water from combustion-type in situ processes is produced in quantities greater than those from aboveground combustion retorting processes (2). In the TOSCO II process, crushed oil shale is heated by preheated ceramic balls in combination with oil shale (14). In contrast, large blocks of oil shale are heated by direct gas-solid phase internal combustion in the LISR process (15, 16). The main difference between the two retorting processes was the heating history of the retort waters produced. Changes in bond-breaking patterns of kerogen by cracking due to different operating temperatures and the presence or absence of an oxidative atmosphere during retorting may have been responsible for the variation in the distribution of short chain n-fatty acids. In the case of the analytical results for retort water of the TOSCO II process published by Cook (7), the acetic acid is especially low (Fig. 2). Actually, the value could be higher; the low value reported by Cook (7) may be due to the instrumental method that he used.

The high temperature retorting of oil shale tends to yield a myriad of hydrocarbons and hydrocarbon derivatives. As a result of the high content of inorganic ions present in the retorting water, water-soluble salts of organic acids are formed. Although this work only discusses short chain n-fatty acids, it is not surprising that long chain fatty acids could come partially from the original oil shale sediment while the short chain fatty acids could come directly from the combustion of oil shale during the retorting processes. The amount and distribution of these short chain fatty acids in retort water could be used as a criterion or parameter for establishing the most feasible operating conditions for the oil shale retorting process, thus providing a more economical method for recovery of valuable materials from the oil shale retort water.

Wastewater disposal and treatment also gain importance, since pollutants in retort water may be able to contaminate clean surface water by diffusion through the soil environment. The retrieval of the organic portion from wastewater will be of value, especially since the organic portion can be put to production use. Although the volatile acid content for most oil shale retort waters only amounts to 2,000 ppm, the daily disposal of a million gallons of wastewater would yield a sufficient quantity of fatty acids to defray the cost of pollutant recovery, provided that some knowledge about the distribution and source of these fatty acids is acquired.

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