

INTERNATIONAL CONFERENCE ON OIL SHALE AND SHALE OIL

May 16-19, 1988 Beijing, China

RECOVERY OF ORGANIC MATERIAL BY SUPERCRITICAL TOLUENE
FROM TURKISH GÖYNÜK OIL SHALEYUDA YURUM and ABDÜLKERİM KARABAKAN
Hacettepe University, Department of Chemistry
Beytepe, Ankara 06532, Turkey

ABSTRACT

Effect of the mineral matrix on the recovery of organic material by supercritical toluene extraction from Turkish Goynuk oil shale was investigated. Samples were prepared by successive demineralization procedures to study the interaction of different mineral groups during the supercritical interaction. Extraction experiments were done in a stainless steel autoclave of 75 ml capacity at 350 °C for 60 minutes. Effect of the toluene/kerogen ratio and reaction time on the recovery of organic material was studied. Infrared spectra of the spent material were measured to determine the structure of the organic material remaining after the supercritical treatment. The inorganic matrix of the shale was composed of calcite, silicate and pyrite minerals. Recovery of the organic material in supercritical interaction increased from 42 % to 98 % as the toluene/kerogen ratio was increased from 23.5 to 275. Dissolution of carbonates and silicates decreased the organic material recovery extensively. The yields of the carbonate-free shale are about 50 % lower than those of the original shale. Removal pyrites did not affect the recovery of the organic matter. Yield of organic material recovery increased when CaCO_3 or SiO_2 was added to kerogen and silicate free shale. These findings indicated that CaCO_3 and SiO_2 originally present in the shale increased the organic matter recovery by supercritical toluene. Increasing the toluene/kerogen ratio, yielded more polar organic material. The aliphatic content of the recovered material was not affected by an increase in the toluene/kerogen ratio.

1. INTRODUCTION

Oil shales consist of complex sapropelic organic material of high molecular weigh (kerogen) which is finely distributed in an inorganic matrix. The inorganic constituents of the oil shales affect the reactions of the organic matter both physically and chemically. The interactions between kerogen and the inorganic matrix during supercritical treatment of the oil shale with a solvent is not well understood. Oil shales contain material readily soluble in the high density solvent vapor formed under supercritical conditions. Some initially insoluble material my be solubilized by chemical changes occurring during the supercritical treatment (1,2) which may be affected by oil shale . The aim of this report is to detail, in part, the affects of

the mineral matrix on the solubilization of the kerogen of Turkish Goynuk oil shale by supercritical toluene.

2. EXPERIMENTAL

Turkish Goynuk oil shale was used in this work. The raw shale was ground and sieved to $-177\ \mu\text{m}$ (-80 mesh ASTM) and the kerogen was isolated by a method described recently (3, 4, 5).

The material remaining after demineralization was investigated by infrared spectroscopy. The X-ray diffractograms of the mineral groups remaining in the original and demineralized oil shale sample were also measured.

Supercritical extraction experiments to recover organic material from the oil shale were performed in a stainless steel high pressure Parr autoclave of 75 ml capacity. Toluene was used as the solvent in all of the experiments at a Vapor density of 0.27 g/ml. In all of the experiments 20 g of toluene and 0.4-3.0 g of shale were used. Thus, the toluene/kerogen ratio was changed from approximately 10 to 200. A weighed amount of shale (or demineralization product) and 20 g of toluene were charged into the autoclave. The autoclave was sealed and checked for leaks. Then the pressure in the autoclave was adjusted to 1 atm. with nitrogen. The experimental temperature was 350°C , which is approximately 30°C above the critical temperature of toluene. The temperature was increased at a rate of $5^{\circ}\text{C}/\text{min}$. The temperature was held constant at 350°C for minutes. At the end of an experiment the autoclave was cooled to room temperature by blowing air on it. The solution in the autoclave was separated from the spent shale by decantation. The spent shale was washed with toluene at room temperature, dried in an oven under a nitrogen atmosphere at 100°C and weighed to determine the yield of extraction. The toluene washings and the extract solution obtained in the supercritical experiment were combined and saved for spectroscopical measurements.

3. RESULTS AND DISCUSSION

Yields of Demineralization

The yields of demineralization procedures are presented below. Carbonates constitute the bulk of the shale (57.8 %). Silicates make 23.1 % of the oil shale. The pyrites are 1.1 % of the shale. Turkish oil shales generally contain about 15 % organic matter. Our figures for total organic matter is higher than this value; bitumen and kerogen of the shale used in the present work constitute 18.0 % of the whole shale. A technique suggested by Yürüm et al (3), was used to determine the organic matter content of the shale. The result obtained by this method (18.1 %) is in good agreement with those determined by demineralization experiments which indicated 1 % bitumens and

17.0 % kerogen. The H/C ratio of the oil shale is 1.4. This indicated that the shale contained higher quantities of aliphatic material.

The X-ray diffratograms and infrared spectra of shale and its demineralized products showed that the mineral matrix of Goynuk shale was mainly composed of calcite, quartz, cristobalite, tridymite and pyrite. In the following sections the probable catalytical effects of these minerals in the supercritical interaction between shale and toluene is presented.

Change of Yield of Recovery of Organic Material with Toluene/Kerogen Ratio

Fig. 1 presents the change of organic material recovery with toluene/kerogen ratio. Fig. 1 contains the results of experiments done with original shale and its demineralization products. Organic material recovered from the original shale by supercritical toluene increased from 42 % to 98 % as the toluene/kerogen ratio was increased from 23.5 to 275 (Fig. 1A). There is a linear relationship between the yield of organic material recovery and the logarithm of toluene/kerogen ratio. This relationship is also confirmed by the experiments of the demineralized products. Fig. 1B presents the change of yield of CF shale with the toluene/kerogen ratio. In experiments with a toluene/kerogen ratio of 20 the yields in the original shale and CF shale were 42 % and 20 %, respectively. When toluene/kerogen ratio was increased to 185 the yields in the original and CF shale were 90 % and 58 %, respectively. It seemed dissolution of carbonates extensively decreased the yield of organic matter. The slopes of the yield versus toluene/kerogen ratio graphs of the original and CF shale experiments are identical; but the yields of the CF shale are about 40 % lower than those of the original shale.

The yield of organic material from SF shale (Fig. 1C) and kerogen (Fig. 1D) also follows a linear relationship with the logarithm of the toluene/kerogen ratio as it was observed for the original and CF shale. The slopes of the lines are lower in this case. It appears that less organic material can be recovered from SF shale and the kerogen with the same experimental conditions used previously for the original shale and CF shale. Removal of the silicates and pyrites did not affect the recovery of the organic matter extensively, but the slopes of the recovery lines of SF shale and kerogen were lower than those of the original shale and CF shale. Thus, we speculate that the dissolution of the silicates altered the mechanism of the recovery of the organic material. Dissolution of the pyrites has no significant effect in the recovery of the organic material. The yields of the supercritical treatment of the kerogen with toluene are about 10 % lower than those of SF shale

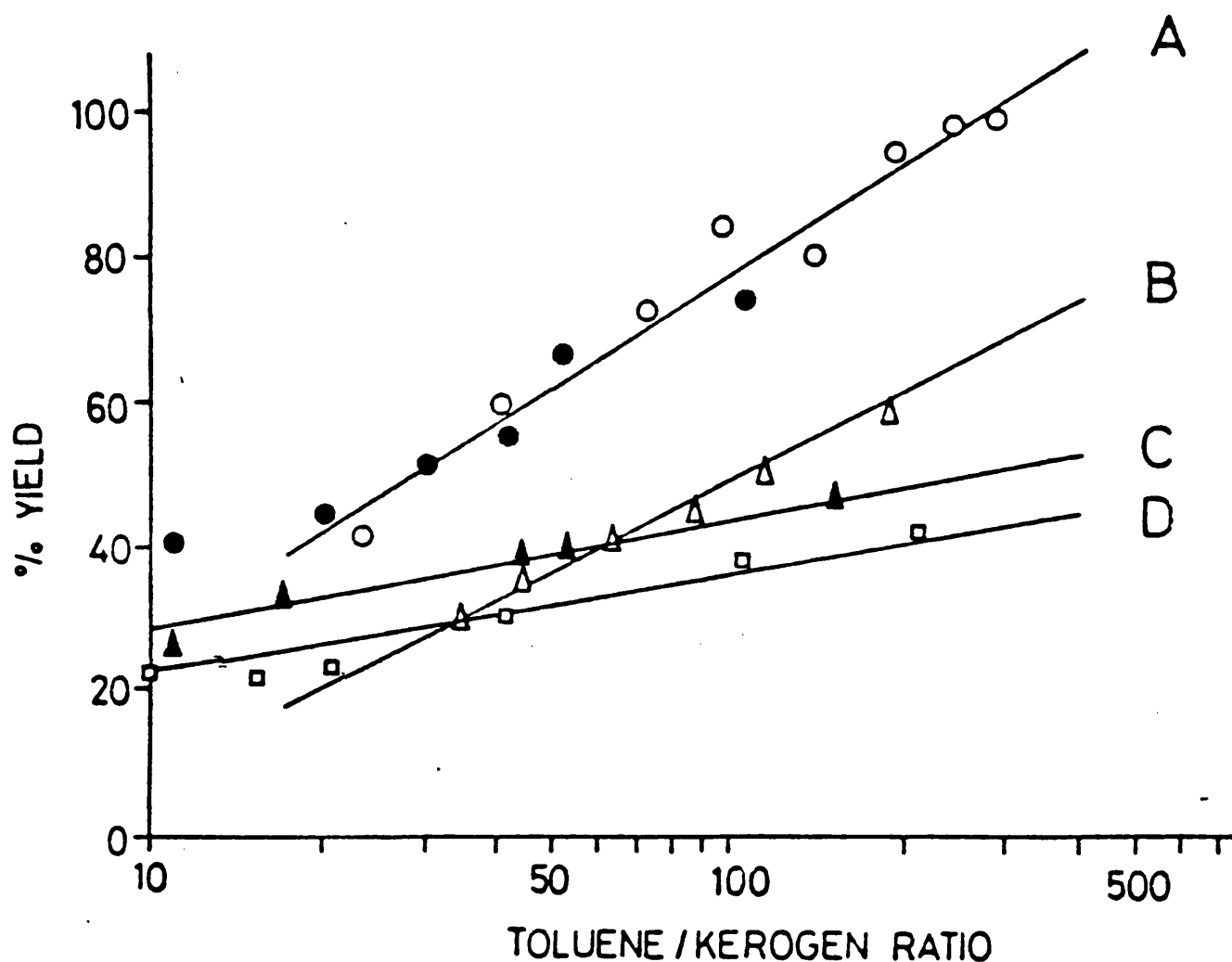


FIG. 1. Yield of organic material recovered from A) original shale, B) CF shale, C) SF shale and D) kerogen. ● 's are points obtained in kerogen and CaCO_3 experiments.

This may be due to the additional hydroxyl groups produced during the lithium aluminium hydride treatment. The production of such new hydroxyl groups was recently shown by Yurum et al. (4). These hydroxyl groups contribute to the intermolecular hydrogen bonding in the kerogen structure^s and thus the solubility of the organic material may be lowered.

REFERENCES

- (1) Yurum, Y.; Kramer, R.; Levy, M. *Thermochimica Acta*, 1986, 105, 51.
- (2) Yurum, Y.; Kramer, R.; Levy, M. *Fuel.Sci.Technol.Int.*, 1986, 4, 501.
- (3) Yurum, Y.; Kramer, R.; Levy, M. *Thermochimica Acta*, 1985, 94, 285.
- (4) Yurum, Y.; Dror, Y.; Levy, M. *Fuel Process. Technol.*, 1985, 11, 71.
- (5) Spiro, B. Ph.D. Thesis, Hebrew University of Jerusalem, Israel, 1980.