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INTERACTION OF KEROGEN AND MINERAL MATRIX OF GÖYNÜK OIL SHALE IN AN AIR ATMOSPHERE

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ABSTRACT

The oxidation behaviour of Göynük oil shale and its demineralization products up to 500 ° C, in an air atmosphere was investigated. The kerogen of a Turkish shale was isolated by successive HCl and HF demineralization procedures. The products obtained after each demineralization step were oxidized in an air atmosphere at different reaction temperatures. The weight-loss data was recorded and the effect of carbonates and silicates on the total yield of oxidation products was determined. The spent shale after the oxidation experiments were analysed by infrared spectroscopy. The results indicated that the oxidation reactions are catalysed by carbonates and inhibited by silicates.

INTRODUCTION

The basic principles of the oxidation mechanism of oil shales may be understood by examining the overall oxidation behaviour of the original oil shale and taking into account the interaction between kerogen and the inorganic matrix. The oxidation behaviour of the demineralization products provides useful information on the interaction between the kerogen and inorganic matrix of the oil shale. The aim of the present study was to investigate the oxidation behaviour of Göynük oil shale and its demineralization products up to 500 ° C, in an air atmosphere.

Oxidation studies of oil shales using thermal-analysis techniques have indicated that the high-temperature oxidation of kerogen is a complex two-stage phenomenon [1–3]. It has been found that the first step is completed at about 400 ° C for an Israeli shale. The oxidized product after the first stage comprised a char which contained an aromatic structure. Calcium minerals present in the inorganic matrix were found to increase the reactivity of the aromatic part of the kerogen towards the oxidation reactions [3].

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In the present study the kerogen of a Turkish shale was isolated by successive HCl and HF demineralization procedures. The products obtained after each demineralization step were oxidized in an air atmosphere at different reaction temperatures. The weight-loss data were recorded and the effect of carbonates and silicates on the total yield of the oxidation products was determined. The spent shale after the oxidation experiments was analysed using IR spectroscopy. The results indicated that the oxidation reactions are catalysed by carbonates and inhibited by silicates.

EXPERIMENTAL

The samples of oil shale used in this study were from the Göynük oil shale deposit located in Bolu, Turkey. The results of the elemental and mineral analyses of the Göynük oil shale are represented in Tables 1 and 2, respectively.

The kerogen was isolated according to a method described elsewhere [4,5]. Dried oil shale (100 g) was extracted with benzene and methanol (7 : 3, 4 ml g^{-1} shale) in order to extract the bitumens. The bitumen-free shale was

TABLE 1

Results of the elemental analysis of Göynük oil shale

Element	% (dry)
Carbon	11.20
Hydrogen	1.34
Nitrogen	0.18
Sulphur (total)	1.51
Oxygen (diff.)	3.77
Carbonate	25.40
Non-volatiles	56.60
H/C	1.44
Fischer assay	14.10

TABLE 2

Results of the mineral analysis of Göynük oil shale

Mineral	% (dry)
Bitumens	1.0
Carbonates	57.8
Silicates	23.1
Pyrite	1.1
Kerogen	17.0

stirred at room temperature with aqueous HCl solution (conc. HCl, 1 : 6, 5 ml g^{-1} bitumen free shale) until no carbon dioxide evolved. The shale was washed with water until the silver nitrate test for chloride in the washings was negative. The carbonate-free shale was wetted with concentrated HCl and stirred with concentrated HF (5 ml g^{-1} carbonate-free shale) at 60 °C for 1 h. The silicate-free shale was washed with water, the HF treatment step was repeated and the product was dried. Pyrite in the silicate-free shale was removed by $LiAlH_4$ treatment. The silicate-free shale was stirred with $LiAlH_4$/THF (5 g $LiAlH_4$ per g SF shale) solution at 60 °C for 1 h. After the reaction, $LiAlH_4$ was decomposed with propanol and first washed with dilute HCl solution and then with water and dried.

The oxidation experiments were carried out in a Pyrex tube (56 cm length, 5 cm ID) energized with a 1000 W electrical heater. The temperature was measured with an iron–constantan thermocouple and controlled by means of a Variac and an on–off control system.

The oxidation experiments were performed in an air atmosphere according to the following procedure. The original oil shale or demineralization products, of 354 μm particle size, in a pyrex boat was placed in the tube furnace and the system was heated to the experimental temperature. The zero reaction time was the time when the desired reaction temperature was attained. The experiments were continued for 0, 15, 30, 45 and 60 min. The tube furnace was cooled down to room temperature by blowing air at the end of each experiment and the weight loss in the experiment was recorded.

Original oil shale, kerogen, carbonate-free shale and mixtures of kerogen + $CaCO_3$ and kerogen + SiO_2 were used in experiments done at 300 °C, 400 °C and 500 °C. 1 g of original oil shale was used in the experiments. The amounts of kerogen and carbonate-free shale used in the oxidation experiments were the amounts present in 1 g of the original oil shale. In the experiments 0.58 g of $CaCO_3$ and 0.23 g of SiO_2 were used with 0.17 g of kerogen; these were the amounts of carbonates, silicates and kerogen present in 1 g of the original oil shale.

The total percentage of oxidation products based on dry and ash-free oil shale were calculated according to the formula

$$C_t = \{W_s(1-n) - W_r)/[W_s(1-a)(1-n)]\} \times 100$$

where C_t is the total percentage of oxidation products (% dry, ash free), W_s is the amount of sample charged initially (g), n is the water content of the sample (w/w), W_r is the residual amount of sample after oxidation (g), and a is the ash content of the sample (w/w, dry basis).

The IR spectra were recorded on a Hitachi 270-30 IR spectrometer. KBr pellets were prepared by grinding 2.5 mg, 150 μm particle size, raw shale (or demineralization product) with 200 mg KBr. Pellets, diameter 13 mm, were pressed in an evacuated die from an approximately 60 mg mixture of KBr and sample, and dried at 110 °C for 72 h under a nitrogen atmosphere to remove water.

RESULTS AND DISCUSSION

The change in the total percentage of products during the oxidation of the original oil shale and the demineralized material with time at different reaction temperatures are presented in Figs. 1–3. The results presented in Figs. 1–3 show that the total percentage of oxidation products obtained in the experiments at 300 °C, 400 °C and 500 °C obeyed the order: C_t (kerogen + $CaCO_3$) > C_t(kerogen) > C_t(kerogen + silicates). This indicates that, while carbonates promoted the oxidation processes and increased the total conversion of coal into oxidation products, silicates inhibited the combustion reactions. The total percentage of the oxidation products of the original oil shale in the experiments at 300 °C were less than those obtained for kerogen. The inhibition effect of silicates seemed to be greater than the catalytic effect of carbonates in the oxidation reactions of original oil shale. In other words, the catalytic effect of carbonates was probably overcome by silicates at 300 °C. Yürüm et al. [3] have reported that the oxidation of kerogen occurs in two stages and the first step is completed at about 400 °C for an Israeli oil shale. The first stage involved the oxidation of aliphatic material to give a char containing aromatic moieties, while the second stage of the oxidation was merely the combustion of the char produced. The present results are in accord with those of Yürüm et al. [3]. It seemed that the effects of the calcium minerals were only pronounced in the second stage of oxidation and the calcium minerals could increase the reactivity of the aromatics of organic material in the oxidation reactions only at temperatures above 400 °C.

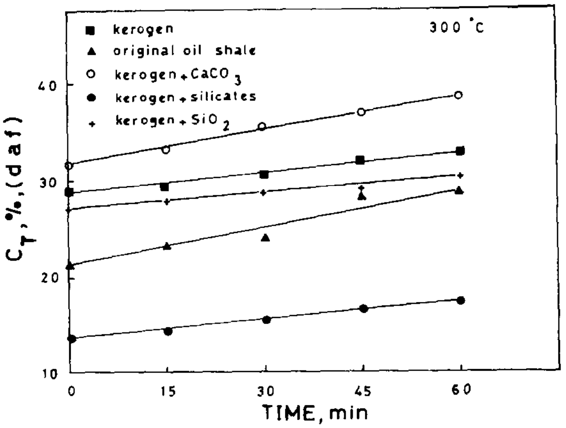

Fig. 1. Change in the total conversion with time at 300 °C.

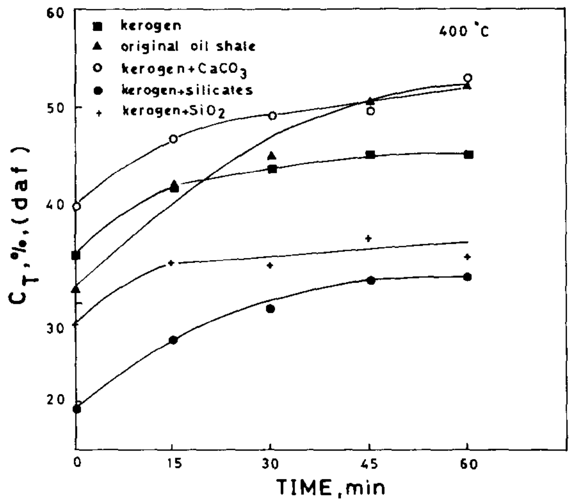

Fig. 2. Change in the total conversion with time at 400 °C.

Two kinds of kinetic behaviour have been observed in the combustion of original oil shale and demineralization products as the temperature was raised from 300 to 500 °C. The reaction order of Göynük oil shale and its demineralization products in an oxidative atmosphere at 300 °C was different from those at 400 °C and 500 °C. The change in the amount of oxidation products with time was linear at 300 °C and, therefore, zero-order kinetics could be assumed for the oxidative reactions which originated probably from the cleavage of the weaker bonds in the kerogen at 300 °C. A non-linear relation between the percentage of oxidation products and time

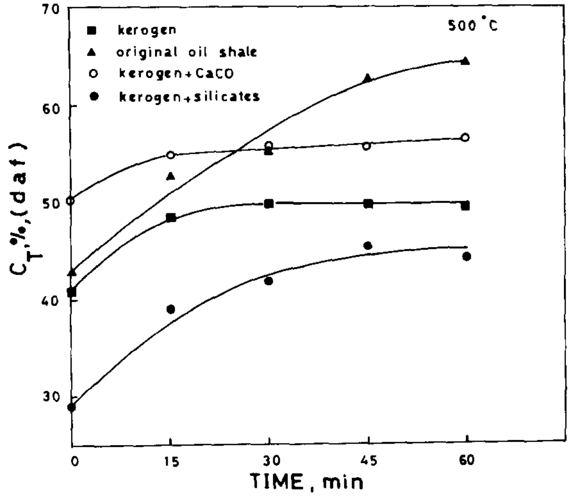

Fig. 3. Change in the total conversion with time at 500 °C.

was observed in experiments performed at 400 and 500 ° C. Thus experiments done at temperatures higher than 400 ° C probably pursued a reaction order greater than that at 300 ° C. It appeared that the catalytic activity of carbonates was greater than the inhibition of silicates at 400 ° C and the total conversion values of the original oil shale into oxidation products for extended reaction periods become very close to those obtained in experiments done with a mixture of kerogen + $CaCO_3$. A reasonably stable reaction rate and high total conversion values for extended reaction periods were obtained for the original oil shale at 500 ° C. The total percentage of the oxidation products obtained at longer times with the original shale was greater than those obtained in the experiments of kerogen + $CaCO_3$ mixture. $CaCO_3$ and SiO_2 were selected to simulate the effects of carbonates and silicates present in the mineral matrix of the oil shale, respectively. It seemed that $CaCO_3$ and SiO_2 were not as effective as the mineral structures originally present in the shale. This indicated that the structures of the carbonate and silicate minerals present in the inorganic matrix were different and probably more complex than those of the model compounds added and, therefore, dissimilar effects were seen in the production of the oxidation products.

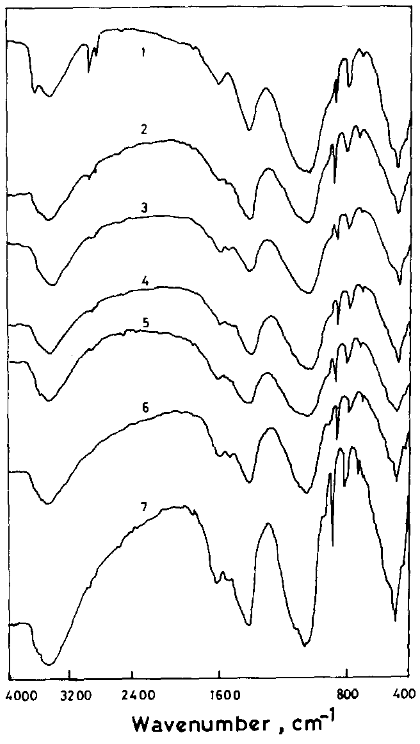

Fig. 4. IR spectra of Göynük oil shale: (1) untreated; (2) 300 ° C, 0 h; (3) 300 ° C, 1 h; (4) 400 ° C, 0 h; (5) 400 ° C, 1 h; (6) 500 ° C, 0 h; (7) 500 ° C, 1 h.

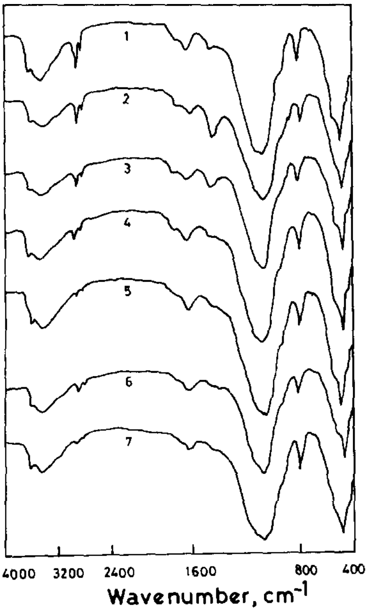

Fig. 5. IR spectra of carbonate free shale: (1) untreated; (2) 300 ° C, 0 h; (3) 300 ° C, 1 h; (4) 400 ° C, 0 h; (5) 400 ° C, 1 h; (6) 500 ° C, 0 h; (7) 500 ° C, 1 h.

The IR spectra of the residual matter after oxidation experiments are presented in Figs. 4–7. The relative intensities of the 1440 cm^{-1} and 1700 cm^{-1} bands due to aliphatic and carbonyl absorptions, with respect to absorption due to the aromatic C–C vibration at 1600 cm^{-1}, are listed in Table 3. The aliphatic absorption at zero time decreased from 2.0 to 1.6 as the temperature was raised from 300 to 500 ° C in the oxidation of the original shale. The absorption of the aliphatic material in the residual matter of the carbonate-free shale increased from 0.9 in the case of untreated carbonate-free shale to 1.8 in the residue obtained at 300 ° C and then decreased to 0.9 in the residues of experiments done at 400 and 500 ° C. This increase in the absorption of aliphatic material was somehow unusual in the case of carbonate-free shale, this might be due to the absence of carbonate minerals where the rate of oxidation of aliphatic material decreased at 300 ° C. The absorption of the aliphatic compounds in the residual material of the kerogen remained constant, as it was in the original kerogen at zero time. The same trend was observed in all the residual matter obtained in experiments of 1-h duration; however, the absorptions decreased slightly to lower values than those obtained in the previous set of experiments.

The intensity of the carbonyl absorption in the original shale increased from 0.7 to 1.0 in the residual matter obtained in experiments of zero reaction time at 300, 400 and 500 ° C. It seemed that the effect of the oxidation was more pronounced as the temperature was increased from 300 to 500 ° C, probably due to the catalytic effect of the carbonate minerals.

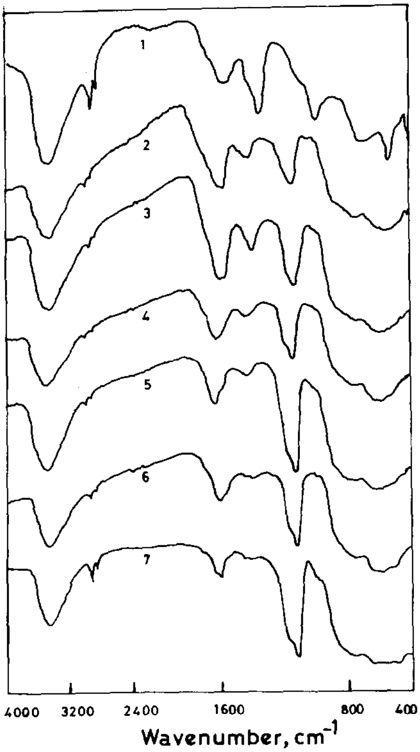

Fig. 6. IR spectra of kerogen: (1) untreated; (2) 300 ° C, 0 h; (3) 300 ° C, 1 h; (4) 400 ° C, 0 h; (5) 400 ° C, 1 h; (6) 500 ° C, 0 h; (7) 500 ° C, 1 h.

TABLE 3

The relative intensities of the 1440 cm^{-1} and 1700 cm^{-1} IR bands of the residual material

Time (h)	Band	Untreated	Temperature (° C)		
			300	400	500
Original oil shale					
0	1440/1600	2.0	2.0	1.8	1.6
0	1700/1600	0.7	0.7	0.8	1.0
1	1440/1600	2.0	1.6	1.5	1.6
1	1700/1600	0.7	0.6	0.7	1.0
Carbonate-free shale					
0	1440/1600	0.9	1.8	0.8	0.9
0	1700/1600	0.7	0.7	0.7	0.5
1	1440/1600	0.9	1.3	0.8	0.9
1	1700/1600	0.7	0.7	0.7	0.6
Kerogen					
0	1440/1600	0.6	0.7	0.6	0.5
0	1700/1600	0.5	0.6	0.5	0.5
1	1440/1600	0.6	0.7	0.5	0.5
1	1700/1600	0.5	0.5	0.3	0.3

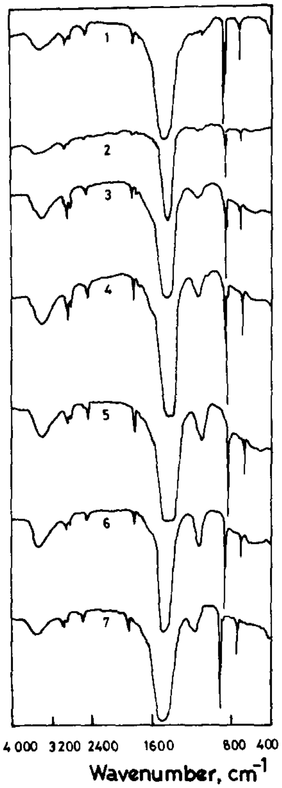

Fig. 7. IR spectra of: (1) $CaCO_3$; (2) kerogen + $CaCO_3$ at 300 ° C, 0 h; (3) kerogen + $CaCO_3$ at 300 ° C, 1 h; (4) kerogen + $CaCO_3$ at 400 ° C, 0 h; (5) kerogen + $CaCO_3$ at 400 ° C, 1 h; (6) kerogen + $CaCO_3$ at 500 ° C, 0 h; (7) kerogen + $CaCO_3$ at 500 ° C, 1 h.

Extended reaction times did not have any significant effect on the intensity of the carbonyl absorption. In the case of carbonate-free shale the intensity of the carbonyl bands remained unchanged in all the experiments in which both the temperature and the reaction time was increased. This is an indication of the positive effect of the carbonate minerals to increase the rate of the oxidation reactions. The same trend was observed in the intensity of the carbonyl absorption of the residual matter of kerogen obtained in the experiments of zero reaction time. The intensity of the carbonyl bands of the residual kerogen decreased from 0.5 to 0.3 in experiments of 1-h duration.

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