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PYROLYSIS OF THREE TURKISH OIL SHALES AND ANALYSIS OF SHALE OILS USING FT-IR AND NMR SPECTROSCOPY

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Pyrolysis of Turkish oil shales from Beypazari, Seyitömer and Himmetoğlu deposits has been studied and oil yields determined. Two different experimental set-ups – a lab-scale and a Corexport 7000 model standard pyrolysis units were used. For comparison pyrolysis experiments with Fischer apparatus were carried out. In all experiments, particles of the size between 0.7 and 2.83 mm were used. FT-IR, as well as ^{1}H and ^{13}C NMR spectra of oils were obtained. Elemental analysis of raw shales, spent shales and shale oils was made.

Introduction

High-quality oil yield is vitally important in economics of synthetic liquid fuel production from fossil fuels such as oil shales. Oil shale that can be considered a fuel between coal and crude oil with respect to its properties has a fine and laminated structure [1, 2].

Oil shale organic matter is referred to by two terms – bitumen, the soluble component, and kerogen, the insoluble one. Bitumen is a minor component in most oil shales. Kerogen is a complex heterogeneous mixture of organic matter, and shale oil produced by pyrolysis is formed by many different reactions involving this matter.

To evaluate the potential of an oil shale formation as oil resource, two important factors must be considered: 1) the amount of organic matter in the formation, and 2) its amount convertible into oil. The first factor relates to the total quality of organic matter in the sediment, while the second one relates to the quality of organic matter type.

Oil shale pyrolysis as well as kinetic parameters of kerogen decomposition have been studied by a great number of researchers employing various

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oil shales [3–21]. Most of these studies have been carried out in lab-scale apparatuses using different types of processes, for example TGA, fixed-bed, fluidized-bed, etc. Pyrolysis experiments have been conducted in the temperature range 480–550 °C [3–22]. All of these studies have shown that shale oil yields depend on oil shale type. Oil yields obtained were compared with standard reference method data (Fischer assay). Shale oil yields up to 110 % of Fischer assay have been recorded in lab-scale pyrolysis units [18, 23, 24].

Shale oil composition may be examined employing various methods. In early studies, amounts of aliphatics and aromatics in shale oil have been determined using column chromatography, but nowadays Fourier-transform infra-red (FT-IR) spectroscopy and nuclear magnetic resonance (NMR) methods are mostly used [25–28]. FT-IR spectroscopy provides rough measuring of various organic and inorganic functional groups, aliphatic and aromatic carbon and hydrogen [26]. It is possible to employ this technique to examine chemical changes occurring during pyrolysis. Additionally, NMR has been used to determine carbon and hydrogen in shale oil [29, 30].

This paper reports an experimental study using lab-scale pyrolysis apparatus and two different standard pyrolysis apparatuses to determine shale oil yields of three Turkish oil shales (Beypazari, Seyitömer and Himmetoğlu) of Paleocene-Eocene and Middle Upper Miocene age [31] widely distributed in the middle and western Anatolia.

Experimental

Shales Used

Samples of oil shales studied in this work (Table 1) were ground and sieved to give three particle sizes: 1.2, 2.1 and 2.8 mm.

Table 1. **Proximate and Elemental Analysis of Three Turkish Raw Oil Shales, wt% (dry basis)**

Indices	Beypazari	Seyitömer	Himmetoğlu
VM	23.15	30.52	41.88
FC	6.03	1.78	30.73
Ash	70.82	67.70	27.39
C	12.81	19.43	53.70
H	1.05	2.32	6.13
N	0.48	0.79	1.73
S	1.77	2.51	3.93
O (by difference)	13.07	7.25	7.12
Moisture	5.00	10.25	8.42
Higher heating value, kJ kg^{-1}	2,971	5,481	11,297
Density, kg m^{-3}	2,235	2,185	2,165

Pyrolysis Procedure

Lab-Scale Experiments

Pyrex glass column of the apparatus (Fig. 1) in which pyrolysis was carried out was placed in a vertical furnace. Column inside diameter and height were 40 mm and 1200 mm, respectively. A 4.5-kW heater was used. Samples of about 100 g were placed on the sieve in the column and pyrolysed in the pure nitrogen atmosphere. During experiments, nitrogen flow rate was fixed at 50 L h^{-1}.

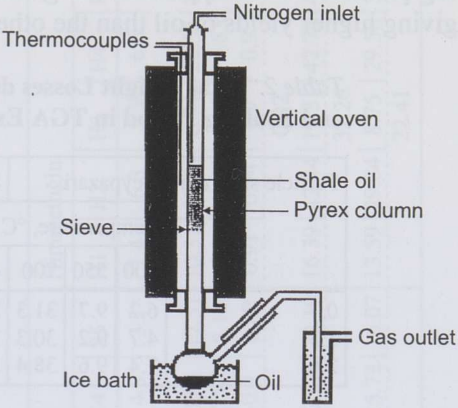

Fig. 1. Lab-scale pyrolysis apparatus

Standard Experiments

A Corexport 7000 model standard pyrolysis apparatus for raw petroleum analysis and a Fischer assay apparatus were used. In the Corexport 7000 model experiments were carried out in a closed chamber containing ten stainless steel vessels. Samples of about 100 g were put into these vessels and the vessels placed over an oil collection cover. Collected oil and water were measured with a graded cover. This method is similar to Fischer assay. The Fischer assay experiments were carried out using standard apparatus (ISO R-647). Standard experiments were repeated at least three times.

Analysis

Elemental analysis of raw shales, shale oils and spent shales were performed using a C, H, N and S elemental analyzer Leco 610. FT-IR (Mattson 1000, spectra analyzed using software Enhanced FIRST) and NMR (Bruker GmbH DPX-400) spectrometers were used to determine functional groups, carbon and hydrogen.

Results and Discussion

Determination of Oil Yields

In our previous work [22], experimental results obtained using TGA were given; variations of the decomposition percentage with time and the effect of temperature were shown there in detail. It was found that the increase in the amount of decomposed oil shale with increasing temperature was greater between 400 and 550 °C than between 550 and 700 °C. This observation consolidates the well-known fact that a temperature of ~550 °C is the optimum for oil shale pyrolysis [32].

As seen from Table 2, where total weight losses during heating and soaking period in TGA apparatus are given, Himmetoğlu oil shale was better in giving higher yields of oil than the other two.

Table 2. **Total Weight Losses during Heating and Soaking Period in TGA Experiments [22], %**

Particle size, mm	Beypazari			Seyitömer			Himmetoğlu		
	Temperature, °C								
	400	550	700	400	550	700	400	550	700
0.7	6.2	9.7	31.3	37.0	35.1	47.2	55.6	60.2	64.6
1.3	4.7	9.2	30.3	32.2	41.0	45.8	57.0	64.1	67.7
2.6	7.4	9.6	38.4	34.0	42.0	50.1	56.5	68.4	75.3

Lab-scale experiment setup is shown in Fig. 1; the results of lab-scale pyrolysis at 550 °C are given in Table 3. Each value in this table is the average of at least three experiments. The values of weight losses and oil yields were quite similar for every different particle size of a given oil shale. Both TGA [22] and lab-scale experiments showed that for all oil shales examined the extent of pyrolysis was practically independent of the particle size. Even though the values of average weight loss measured for Beypazari and Himmetoğlu oil shales are similar, this value for Seyitömer oil shale is smaller (compare data in Tables 2 and 3). This difference may be attributed to its heterogeneous structure, as well as to the necessity of using very small amounts of shale in TGA experiments. Actually, the results obtained during lab-scale tests may be accepted as characteristic data, because in this case larger amounts of oil shales were used.

Evolution of hydrocarbons was observed with increasing temperature with respect to their volatilities. At the end of experiments, unpyrolyzed hydrocarbons remained in the spent shale bounded to the kerogen matrix structure. One may suppose that some gas, oil and also coke remain in the spent shale. These values differ for different types of oil shale. In this study, Beypazari shale oil was obtained as a liquid of moderate viscosity at the room temperature, whereas Himmetoğlu and Seyitömer oils were very viscous and tarry-looking.

The results of experiments carried out using standard devices are given in Tables 4 and 5. Examination of the data given in Tables 2–5 shows that all the values of weight losses and oil yields are rather similar. The results of oil and spent shale elemental analysis are given in Table 6. Oils contain about 1 % sulfur and this value is too high. When these shale oils are used as a fuel, sulfur should be removed. Higher heating values for Beypazari, Seyitömer and Himmetoğlu shale oils (Gallenkamp Bomb Calorimeter) are 22,925, 40,650 and 31,740 kJ kg^{-1}, respectively (Table 6). Oil densities are approximately 0.9 g cm^{-3} (see Table 4).

Table 3. **Weight Losses and Shale Oil Yields Determined in Lab-Scale Apparatus at 550 °C**

Indices	Beypazari				Seyitömer				Himmetoğlu			
	Particle size, mm											
	1.22	2.05	2.83	Mixed	1.22	2.05	2.83	Mixed	1.22	2.05	2.83	Mixed
Weight losses, %	12.1	11.8	11.7	12.5	21.1	22.5	22.7	21.3	64.0	61.2	64.8	62.5
Average, %	12.03				21.9				63.13			
Shale oil yield, %	5.9	6.2	6.5	7.0	7.6	8.0	8.3	8.6	37.3	32.1	38.8	39.6
Average, %	6.4				8.13				36.95			

Table 4. **Results of Pyrolysis Experiments Using Corexport 7000 at 550 °C**

Indices	Beypazari					Seyitömer					Himmetoğlu				
	B1	B2	B3	B4	B5	S1	S2	S3	S4	S5	H1	H2	H3	H4	H5
Water, cm^3	0.9	1.0	0.1	1.2	1.2	3.8	4.4	0.5	4.8	3.1	1.4	6.3	5.3	6.6	5.5
Shale oil:															
By volume, cm^3	4.13	3.71	–	4.13	4.13	9.63	12.1	0.9	12.1	12.51	10.31	21.73	6.74	22.55	22.41
By weight, g	2.73	2.43	0.06	2.82	2.78	6.53	7.96	0.7	7.88	8.13	6.8	14.92	4.39	14.83	14.77
Shale oil density, g cm^{-3}	0.91	0.9	–	0.94	0.93	0.93	0.9	–	0.9	0.89	0.91	0.94	0.9	0.9	0.93
Average, g cm^{-3}	0.92					0.905					0.92				
Weight losses (shale oil + water) %	7.24	6.82	0.32	8.02	7.93	20.66	24.37	–	25.3	22.19	16.39	42.44	19.31	42.72	40.44
Average, %	6.07					23.13					32.26				
Shale oil yield, wt%	5.44	4.83	–	5.63	5.54	13.06	15.69	–	15.72	16.07	13.59	29.84	8.75	29.56	30.33
Average, wt%	5.36					15.14					22.41				

Table 5. **Fischer Assay Data, wt%**

Indices	Beypazari	Seyitömer	Himmetoğlu
Shale oil	5.1	7.1	32.5
Gas	1.6	3.3	11.4
Spent shale	92.1	86.4	50.7
Water	1.2	3.20	5.4

One may see that the data in Table 5 are quite close to the results obtained from TGA [22] and lab-scale tests. According to Table 5, half of the total amount of Himmetoğlu oil shale is transformed into liquid and gaseous products. The oil yields obtained at lab-scale pyrolysis of Beypazari, Seyitömer and Himmetoğlu oil shales were 126, 114, and 114 % of Fischer assay, respectively.

Table 6. **Elemental Analysis of Spent Shale and Shale Oil Obtained from Lab-Scale Experiments**

Indices	Beypazari		Seyitömer		Himmetoğlu	
	Spent shale	Shale oil	Spent shale	Shale oil	Spent shale	Shale oil
C	2.82	52.62	8.22	50.25	21.98	57.28
H	0.12	8.64	0.5	10.39	0.9	10.49
S	1.33	1.15	0.023	0.86	3.15	1.24
Higher heating value, kJ kg^{-1}	680	22,925	1,975	40,650	8,785	31,740

Analysis of Shale Oils

It is seen from FT-IR spectra of Beypazari, Seyitömer and Himmetoğlu shale oils (Fig. 2) that they contain much more aliphatic compounds than aromatic ones (see also Table 7).

Integrated areas were centered in the absorption bands near:

- 3400 cm^{-1} for hydroxyl, OH^{-}
- 3050 cm^{-1} for aromatic C–H
- 2956 cm^{-1} for asymmetric methyl groups
- 2900 cm^{-1} for aliphatic C–H
- 2872 cm^{-1} for symmetric methyl groups
- 1700 cm^{-1} for carbonyl C=0
- 1600 cm^{-1} for aromatic C=C
- 1450 cm^{-1} for aliphatic C–C
- 700 (or 900) cm^{-1} for CH_2

The ratio of aliphatic to aromatic compounds in three shale oils was determined to be between 6 and 10. It means that in all of them aliphatic groups dominate. The percentage of aromatic compounds in Himmetoğlu shale oil was determined to be higher than in other ones (Table 7). In addition, Seyitömer shale oil is abundant in hydroxyl group, OH^{-}, indicating the

Fig. 2. FT-IR spectra of (*a*) Beypazari, (*b*) Seyitömer, and (*c*) Himmetoğlu shale oils

presence of phenolic structure. On the other hand, Beypazari shale oil contains much carbonyl groups, for example acetyl or carboxylic. The percentage of CH_2-groups is smaller than that of methyl ones. Therefore, one may say that the complexity of oil structure is expressed mostly through the functional groups of hydrocarbon molecules.

^{1}H NMR spectra (Fig. 3) were obtained in the range of 0–8 ppm (0–3 ppm for aliphatic H and 5–8 ppm for aromatic H). Distribution of hydrogen atoms between aliphatic and aromatic region was determined by integrated spectra (Table 8). The number of hydrogen atoms in aromatic structure of all shale oils examined equals approximately one, whereas that for aliphatic hydrogen differs greatly in the case of Beypazari samples. This explains why Beypazari shale oil is lighter than the other two and is also in agreement with its being a less viscous liquid at the room temperature.

Table 7. **Functional Group Analysis, %**

Functional groups	Beypazari	Seyitömer	Himmetoğlu
Hydroxyl OH^-	7.9	16.6	11.0
Aromatic C–H	4.4	3.5	5.0
Asymmetric methyl groups	3.5	5.0	3.1
Aliphatic C–H	32.2	35.6	30.8
Symmetric methyl groups	11.8	5.0	10.8
Carbonyl C=0	5.2	3.7	3.8
Aromatic C=C	2.9	2.4	3.0
Aliphatic C–C	8.1	7.2	8.3
CH_2	1.4	1.2	1.6

^{13}C NMR spectra (Fig. 4) were taken in the range of 10–140 ppm. $CDCl_3$ was used as a solvent, the signals at 78 ppm belonging to it. Aliphatic C (13–40 ppm) and aromatic C (114–140 ppm) were measured. Carbon percentages in Beypazari and Himmetoğlu oils are very close. Seyitömer shale oil has the highest value of aliphatic C (Table 9). It can be explained by deeper decomposition of its aromatic structure under thermal treatment. One may clearly see that all of NMR results agree with FT-IR data. The results of the present research are also in good accordance with literature data [29, 30, 33].

Table 8. **Distribution of H Atoms in Shale Oils**

Indices	Beypazari	Seyitömer	Himmetoğlu
Aliphatic H	410.87	14.979	15.679
Aromatic H	1.000	1.002	1.000
Total	411.87	15.981	16.679
Aliphatic H, %	99.76	93.73	94.00
Aromatic H, %	0.24	6.27	6.00

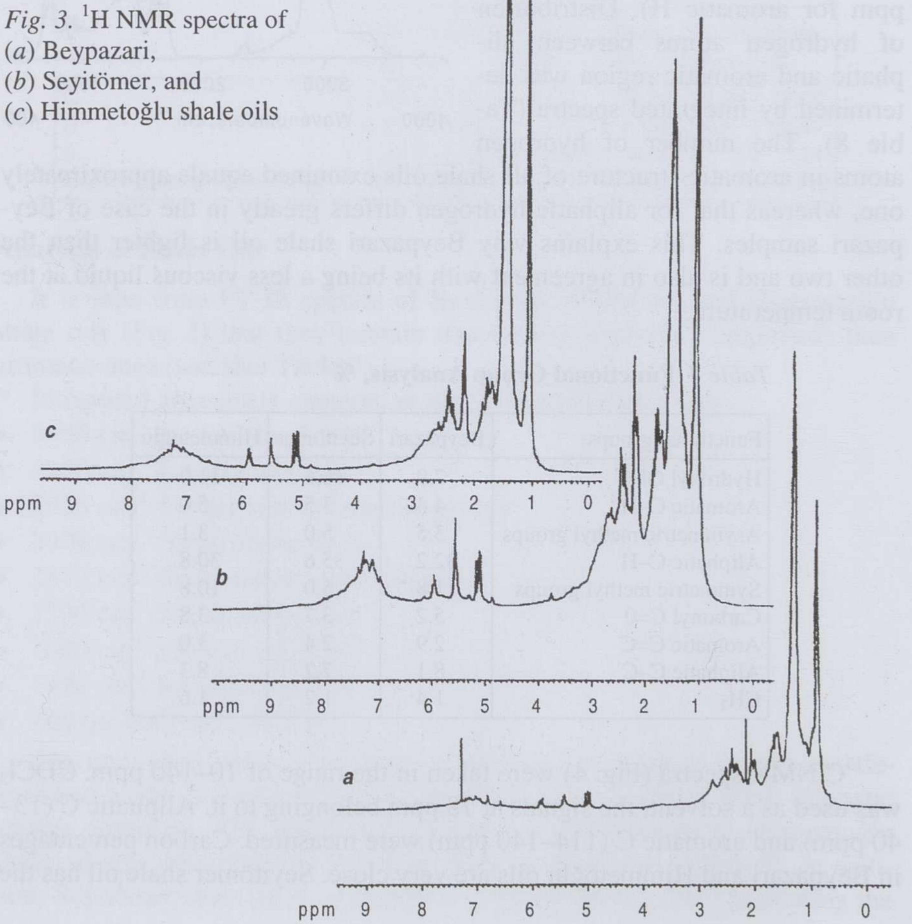

Fig. 3. ^{1}H NMR spectra of
(*a*) Beypazari,
(*b*) Seyitömer, and
(*c*) Himmetoğlu shale oils

Fig. 4. ^{13}C NMR spectra of
(*a*) Beypazari,
(*b*) Seyitömer, and
(*c*) Himmetoğlu shale oils

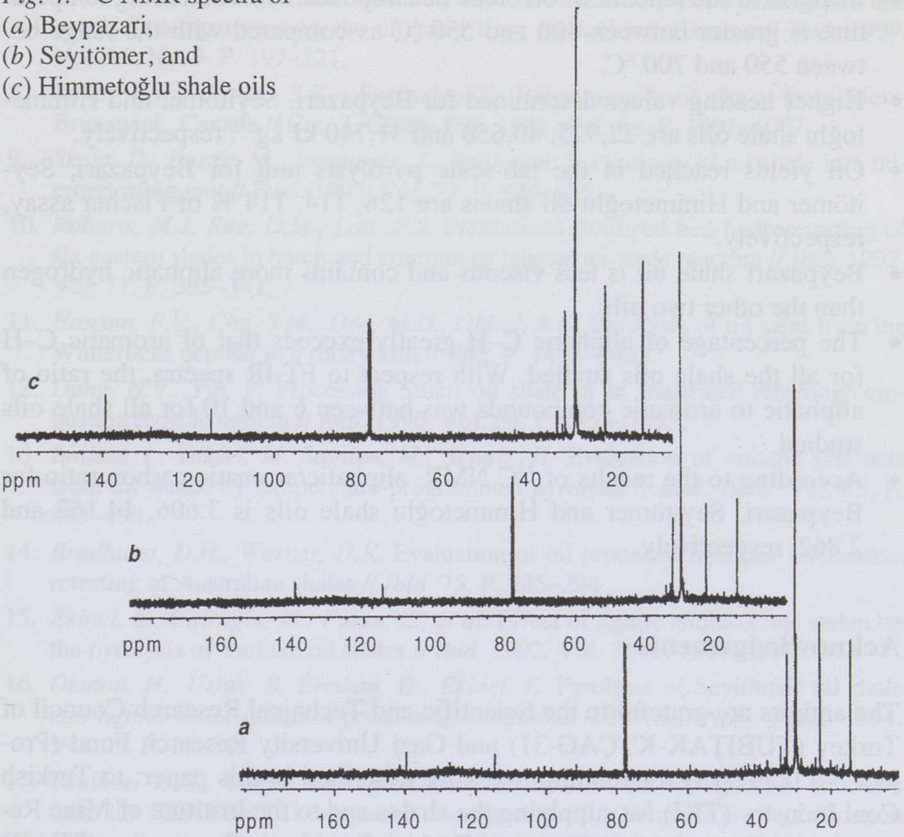

Table 9. **Distribution of C Atoms in Shale Oils**

Indices	Beypazari	Seyitömer	Himmetoğlu
Aliphatic carbon, %	78.29	93.4	74.1
Aromatic carbon, %	21.71	6.6	25.9
Aliphatic C/Aromatic C	3.606	14.162	2.862

Conclusions

Conclusions drawn from examination of three Turkish oil shales (Beypazari, Seyitömer and Himmetoğlu) with respect to shale oil yields are summarized as follows:

- TGA [22], lab-scale experiments, and two kinds of standard pyrolysis tests indicated that Himmetoğlu oil shale yields more oil than the other two.
- Extent of pyrolysis was found to be practically independent of particle size for all oil shales studied.

- Increase in the amount of oil shale decomposed with increasing temperature is greater between 400 and 550 °C as compared with the range between 550 and 700 °C.
- Higher heating values determined for Beypazari, Seyitömer and Himmetoğlu shale oils are 22,925, 40,650 and 31,740 kJ kg^{-1}, respectively.
- Oil yields reached in the lab-scale pyrolysis unit for Beypazari, Seyitömer and Himmetoğlu oil shales are 126, 114, 114 % of Fischer assay, respectively.
- Beypazari shale oil is less viscous and contains more aliphatic hydrogen than the other two oils.
- The percentage of aliphatic C–H greatly exceeds that of aromatic C–H for all the shale oils studied. With respect to FT-IR spectra, the ratio of aliphatic to aromatic compounds was between 6 and 10 for all shale oils studied.
- According to the results of ^{13}C NMR, aliphatic/aromatic carbon ratio for Beypazari, Seyitömer and Himmetoğlu shale oils is 3.606, 14.162 and 2.862, respectively.

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