

COMPARISON OF HYDROCARBONS FORMED AT PYROLYSIS OF TURKISH TYPE I KEROGEN (GÖYNÜK) AND TYPE II KEROGEN (BEYPAZARI)

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Kerogen samples isolated from the Göynük and Beypazari oil shales were pyrolyzed to study the effect of kerogen type on the rate of product evolution and composition of the pyrolysis products. Kerogens were isolated by successive treatment with HCl, HNO₃ and HF. A series of temperature-programmed pyrolysis operation was performed on kerogens of Göynük Type I (GKT I) and Beypazari Type II (BKT II) oil shales. The operation of the experimental apparatus was investigated by establishing carbon balance. The degree of recovery of total organic carbon of the samples as organic compounds and solid residue was determined. The results show that the type of kerogen affected the conversion of organic matter into volatile hydrocarbons and transformation of carbon into the residue. BKT II yielded more aliphatic hydrocarbons, the ratios of n-paraffins to 1-olefins being higher and coking loss less, on a carbon unit basis. Yields of volatile hydrocarbons differ by kerogen type. It has been observed that mainly linear aliphatic hydrocarbons form at pyrolysis of GKT I, particularly in the range of C₁ to C₁₅, in contrast those to produced from BKT II. The share of branched hydrocarbons, dienes, aromatics, asphaltenes and preasphaltenes was higher in the pyrolysis products of BKT II.

Introduction

Pyrolysis refers to the decomposition of organic matter by heat in the absence of the air. When coal or oil shale is pyrolyzed, hydrogen-rich volatile matter and carbon-rich solid residue are formed. Pyrolysis of oil shale means its destructive distillation. Pyrolysis is one of the methods commonly used to produce liquid fuels from coal, and it is principal method used to convert oil shale to liquid fuels. Moreover, as gasification and

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liquefaction are carried out at elevated temperatures, pyrolysis may be considered to be the first stage of any conversion process [1].

The process by which a solid kerogen is thermally cracked by pyrolysis techniques and transformed to hydrocarbons and solid char may be divided into four stages.

- (1) thermal breakdown of kerogen to form liquid, gaseous and solid products (char);
- (2) migration and interaction of liquid and gaseous hydrocarbons within the rock matrix;
- (3) expulsion of the products from the rock and further reactions on the rock surface and reactor walls;
- (4) condensation of the products and final reactions of unstable products [2].

Pyrolysis chemistry is a complex phenomenon, and the mechanism of decomposition during pyrolysis is not completely understood. There are two major mechanisms considered. (1) Cleavage of organic matrix *via* free-radical mechanism that favors the evolution of straight-chain aliphatics and C₂ hydrocarbons, and (2) cracking of hydrocarbon products *via* a carbonium ion mechanism that favors the formation of isoparaffins, internal olefins, and C₃ gases [2].

There are, of course, other reaction pathways of some significance such as cyclization and dehydrogenation, whose course is strongly dependent on the type of oil shale kerogen and whose relative importance requires further investigation. The yield and composition of final products is affected by the type of oil shale kerogen and kerogen mineral matrix. One way to understand the interaction between kerogen and mineral matter is to compare the pyrolysis products obtained at treatment of partially and completely demineralized samples of original oil shale, or to compare the pyrolysis products formed from oil shales of different kerogen type. The yield of hydrocarbon is affected by kerogen type, and the type I kerogens richer in kerogen show a lesser decrease in pyrolysis yield than type II and III kerogens [2].

Göynük and Beypazarı oil shales were classified using IR analysis technique, and the results are previously reported [3]. Types of these kerogens have been determined to be evolution path type I for Göynük oil shale and type II for Beypazarı oil shale [3]. The temperature-programmed pyrolysis of Göynük and Beypazarı oil shales has also been investigated [4, 5]. The work reported here is a continuation of that study and focuses on the comparison of the pyrolysis products from different types of kerogen without rock matrix.

The aim of this work was to study the effect of type of oil shale kerogen on the composition of pyrolysis products and on pyrolysis reactions at temperatures up to 550 °C in an inert gas atmosphere. The rates of product evolution and product composition were determined by using a new sampling technique for collecting pyrolysis products eluted from the reactor at different temperatures and times. The effect of kerogen type on the yield

and composition of the product was determined by establishing carbon balance around the reactor. The recovery of carbon as volatile hydrocarbons and the amount of solid residue left at the end of each pyrolysis run was determined.

Experimental

Samples

Oil shale samples were obtained from the Göynük oil shale deposit located near the town of Bolu in northwest of Turkey and Beypazarı oil shale deposit located near the town of Ankara in the middle of Turkey. For pyrolysis experiments, the samples were crushed and thereafter ground in a jaw mill until the desired particle size was obtained. The samples were sieved to obtain the size fraction <0.2 mm and subjected to successive demineralization process. The results of elemental analysis of raw and demineralized oil shale samples from Göynük (GKT-I) and Beypazarı (BKT-II) are given in Table 1.

Demineralization

Oil shale samples were demineralized with HCl, HNO₃ and HF using a standard method [3, 6]. To 1 g oil shale sample, 10 mL 12 N HCl and 10 mL distilled water were added. The slurry was stirred for 48 h under nitrogen atmosphere, thereafter filtered and washed with 3 L distilled hot water

(60–70 °C) until the filtrate became neutral. The solid residue was dried at 50 °C, for 24 h under vacuum. Next, 10 mL HNO₃ (20 wt.%) and 10 mL distilled water were added to 1 g pre-treated oil shale sample. The slurry was stirred for 2 h at room temperature, thereafter filtered and washed with 3 L distilled hot water (60–70 °C). The material was dried at 50 °C, for 24 h under vacuum. Finally, 25 mL of HF (48 wt.%) was added to the residue, and this mixture was stirred for 48 h. After filtering, the demineralised oil shale (kerogen) was washed with 3 L distilled hot water (60–70 °C) and dried at 50 °C, for 24 h under vacuum.

Table 1. Elemental Analysis of Göynük and Beypazarı Oil Shales and Kerogens

Sample	C _{organic} , %	H, %	Ash, %	H/C
GOS-R*	46.3	5.8	16.0	1.5
BOS-R*	7.7	1.0	61.0	1.6
GKT I	63.8	8.0	0.1	1.5
BKT II	62.5	8.1	0.7	1.6

* Without demineralization (raw oil shale).

Pyrolysis Experiments

Temperature-programmed pyrolysis of GKT I and BKT II samples was performed in an electrically heated fixed-bed reactor consisting of a stainless steel reactor shell (400 mm long, 15 mm i.d) and a Duran-glass reactor tube (10 mm i.d.). The samples were mixed with 5 mL quartz sand (particle size

0.1–0.25 mm) and transferred to the reactor tube. The amounts of samples used in experimental studies were 0.37 g GKT I and 0.24 g BKT II.

A thermocouple was inserted into the middle of the sample bed, and the reactor tube was placed into the stainless steel reactor shell. Three thermocouples were fitted to the outside of the reactor shell. The reactor shell was placed in a temperature-programmable furnace heated by a three-zone electric heater. The middle zone of the heater was connected to a programmer and controller, and the other two heaters were controlled manually. The same experimental equipment had been previously used for pyrolysis and co-pyrolysis studies [3–5, 7, 8].

The equipment was flushed with a stream of nitrogen before heating. The pyrolysis was carried out at 2 K min^{-1} under a 90 ml min^{-1} flow of nitrogen. Pyrolysis products were swept out of the reactor and mixed with a reference gas (10 mL min^{-1} , 0.507 vol.% neopentane in N_2) before passing to a special sampling system. The fractions were collected in pre-evacuated glass ampoules at different times. The ampoules were sealed by a gas burner and analyzed later by capillary gas chromatography using a sample introduction system of a special design. Schulz with coworkers developed this sampling technique to analyze a gas-vapor multicomponent mixture [9]. This technique offers a number of advantages: simplification of sampling as compared with conventional procedures of fractionation for product recovery; safe handling and storage of samples; decoupling of sampling from analysis; and sampling in small time intervals, which allows non-stationary systems to be studied [9].

Pyrolysis products were identified using gas chromatograph GC-HP 5890. The operating conditions for GC-HP 5890 are as follows:

Column	100 m × 0.25 mm fused silica
Stationary phase	100-% Polydimethylsiloxane (HP-1)
Film thickness	0.5 μm
Carrier gas	Hydrogen
Detector	Flame ionization detector (FID)
Detector temperature	350 °C
Injector temperature	290 °C
Temperature program	Start –80 °C, isothermal 1.0 min
	20 °C min^{-1} to –10 °C, isothermal 2.5 min
	15 °C min^{-1} to 40 °C, isothermal 1.0 min
	7 °C min^{-1} to 300 °C, isothermal 30.0 min

After the completion of each run of pyrolysis, the amounts of carbon in the solid residue remaining in the reactor were determined by their combustion in the flow of depleted air (100 mL min^{-1} , 10 vol.% O_2) at heating rate 20 °C min^{-1} . The concentrations of CO_2 , CO and O_2 in the reactor effluent were measured by a continuous gas analyzer.

Results and Discussion

Petroleum geochemists have long been interested in obtaining mineral-free and chemically unaltered kerogen concentrates. Despite attempts with a number of chemical reagents, no general method has been developed which enables complete separation of the unchanged kerogen from a complex sedimentary mixture. The conventional hydrochloric/hydrofluoric acid treatment is effective for removing most of carbonate, oxide, and monosulfide minerals from sedimentary rocks and leaves kerogen and pyrite largely unaffected [10, 11].

Effective removal of pyrite is usually the main problem [6]. Quantitative removal of pyrite is not possible without alteration of the composition of organic matter. The magnitude of the change in the organic matter depends on the chemical nature of the kerogen as well as on the reaction conditions. The extent of oxidation of oil shales and coals by nitric acid varies, but introduction of carboxyl groups is a major cause of the increase in oxygen content [6]. The major part of the products formed at strong oxidation of kerogen is usually carboxylic acids with perhaps smaller amounts of hydrocarbons, terpenes, pyrole resins, tannin, pigments etc. [6], but the effect can be minimized by using diluted acid at moderate temperatures for as short time as possible [6].

In our previous study, an enriched in kerogen sample of Göynük oil shale (GOS-R) was prepared by treating with HCl, HNO₃ and HF acid [3]. In contrast to the method previously used in demineralization [3], pyrite was removed by applying HNO₃ acid at moderate temperatures. In this study, IR spectra of the samples were recorded between 4000 and 400 cm⁻¹. IR study of oil shale after demineralization showed no change in the aliphatic CH stretching frequency, and bands at 1330 and 1540 cm⁻¹ corresponding to R-NO₂ groups. Oxidation of aliphatic CH bond groups would not be expected, and so any oxidation that might occur would have a little impact on the substantial CH groups present, but more evident if there is an evidence of newly formed carbonyl groups in 1700–1750 cm⁻¹ where kerogen oxidation is often apparent and which represent absorption bands with high extinction coefficient. It has also been checked and no evidence found for any newly formed carbonyl groups in that range, and IR spectroscopic measurement showed no remarkable change in organic structure.

Series of pyrolysis operations were performed with kerogens of the Göynük (GKT I) and Beypazari (BKT II) oil shales. Chromatograms of the pyrolysis products of GKT I and BKT II are shown in Figs 1 and 2.

In all cases the chromatograms are dominated by the homologous series of normal alkanes, starting at C₁ and terminating at about C₂₉. The above figures show that each peak of a normal alkane is accompanied by the corresponding peak of linear alkene, as it is normally the case for shale oil produced by pyrolysis. The major organic compounds obtained at maximum evolution temperatures during temperature-programmed pyrolysis of GKT I

and BKT II are listed in Table 2. The effect of temperature and time on the rate of total product evolution at pyrolysis of GKT I and BKT II is shown in Fig. 3. The temperature at which the evolution of the products is greatest is 440 °C for each pyrolysis run.

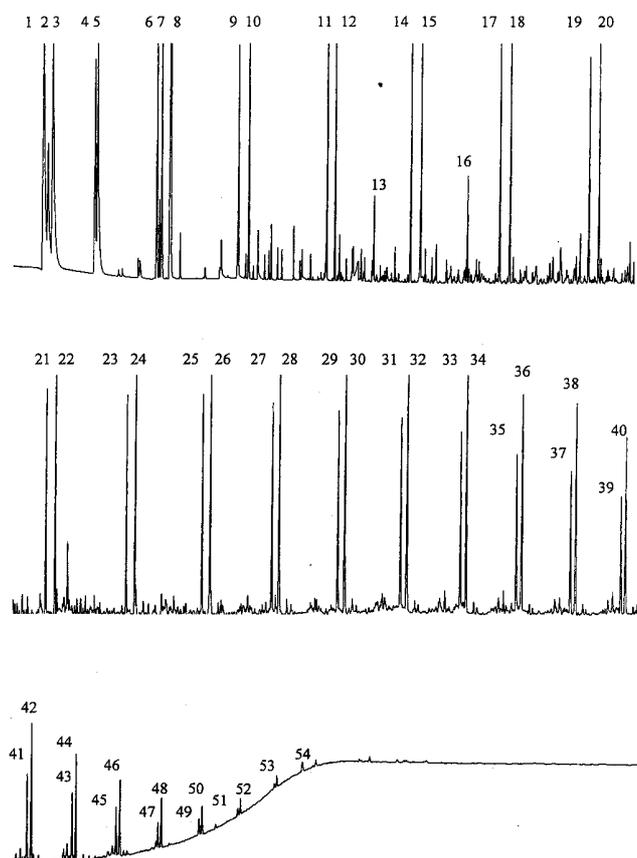


Fig. 1. Gas chromatograms of organic products at maximum evolution temperatures during temperature-programmed pyrolysis of GKT I; numbers 1–54 indicate the major constituents of organic compounds (see Table 2)

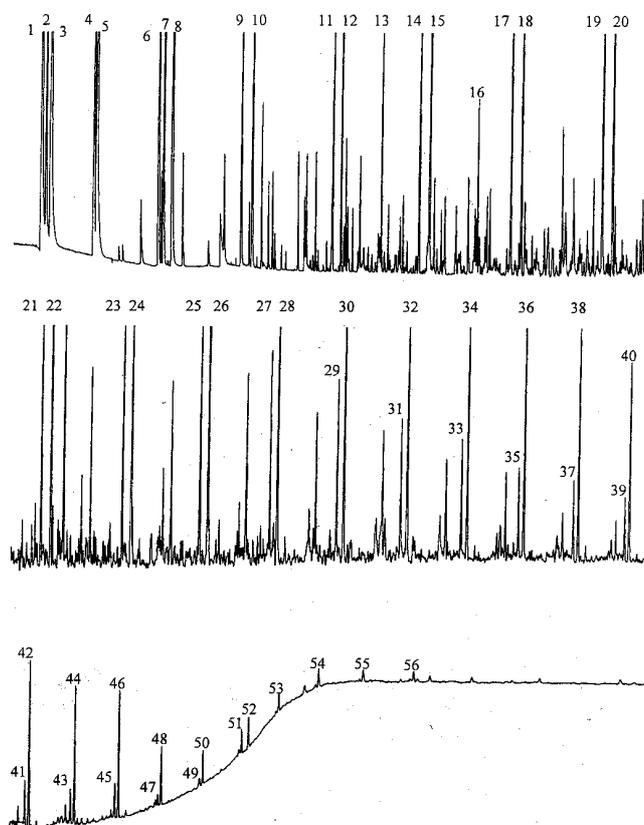


Fig. 2. Gas chromatograms of organic products at maximum evolution temperatures during temperature-programmed pyrolysis of BKT II; numbers 1–56 indicate the major constituents of organic compounds (see Table 2)

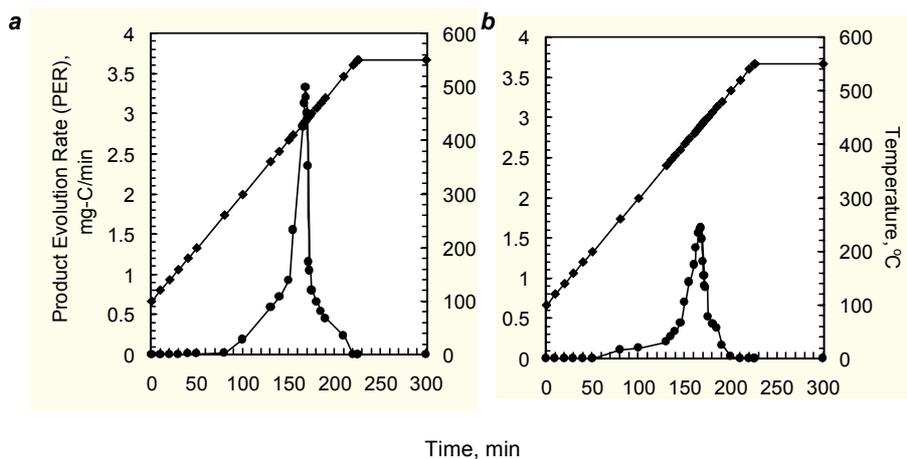


Fig. 3. Total product evolution rates of GKT I (a), BKT II (b) as a function of temperature and time: ● – PER ◆ – temperature

Table 2. Major Constituents of Organic Compounds at Maximum Evolution Temperatures during Temperature-Programmed Pyrolysis of GKT I and BKT II

Number	Organic compounds	Number	Organic compounds
1	Methane	29	1-Tetradecene
2	Ethene	30	<i>n</i> -Tetradecane
3	Ethane	31	1-Pentadecene
4	Propene	32	<i>n</i> -Pentadecane
5	<i>n</i> -Propane	33	1-Hexadecene
6	1-Butene	34	<i>n</i> -Hexadecane
7	<i>n</i> -Butane	35	1-Heptadecene
8	Neopentane (Reference gas)	36	<i>n</i> -Heptadecane
9	1-Pentene	37	1-Octadecene
10	<i>n</i> -Pentane	38	<i>n</i> -Octadecane
11	1-Hexene	39	1-Nonadecene
12	<i>n</i> -Hexane	40	<i>n</i> -Nonadecane
13	Benzene	41	1-Eicosene
14	1-Heptene	42	<i>n</i> -Eicosane
15	<i>n</i> -Heptane	43	1-Heneicosene
16	Toluene	44	<i>n</i> -Heneicosane
17	1-Octene	45	1-Docosene
18	<i>n</i> -Octane	46	<i>n</i> -Docosane
19	1-Nonene	47	1-Tricosene
20	<i>n</i> -Nonane	48	<i>n</i> -Tricosane
21	1-Decene	49	1-Tetracosene
22	<i>n</i> -Decane	50	<i>n</i> -Tetracosane
23	1-Undecene	51	1-Pentacosene
24	<i>n</i> -Undecane	52	<i>n</i> -Pentacosane
25	1-Dodecene	53	<i>n</i> -Hexacosane
26	<i>n</i> -Dodecane	54	<i>n</i> -Heptacosane
27	1-Tridecene	55	<i>n</i> -Octacosane
28	<i>n</i> -Tridecane	56	<i>n</i> -Nonacosane

The *n*-paraffins produced from GKT I and BKT II were classified by carbon number (Fig. 4*a,b*). In this classification, low-molecular weight hydrocarbons (methane, ethane, propane and butane) were combined into one group, C₁–C₄. The fractions C₅–C₉, C₁₀–C₁₅, and C₁₆₊ were also similarly grouped. The hydrocarbons produced by pyrolysis of GKT I and BKT II at the temperature of maximum product evolution contained 39.8 and 42.5 wt.% of *n*-paraffins, respectively.

1-Olefins produced from GKT I and BKT II were classified by carbon number, and the results are given in Fig. 4*c,d*. In this classification, low-molecular-weight hydrocarbons (ethene, propene and butene) were combined into one group, C₂–C₄. The fractions C₅–C₉, C₁₀–C₁₅, and C₁₆₊ were also similarly grouped. The hydrocarbons produced at pyrolysis of GKT I and BKT II contained 24.8 and 19.6 wt.% 1-olefins, respectively, at the temperature of maximum product evolution. The results of distribution of *n*-paraffins and 1-olefins in the pyrolysis products are summarized in Table 3.

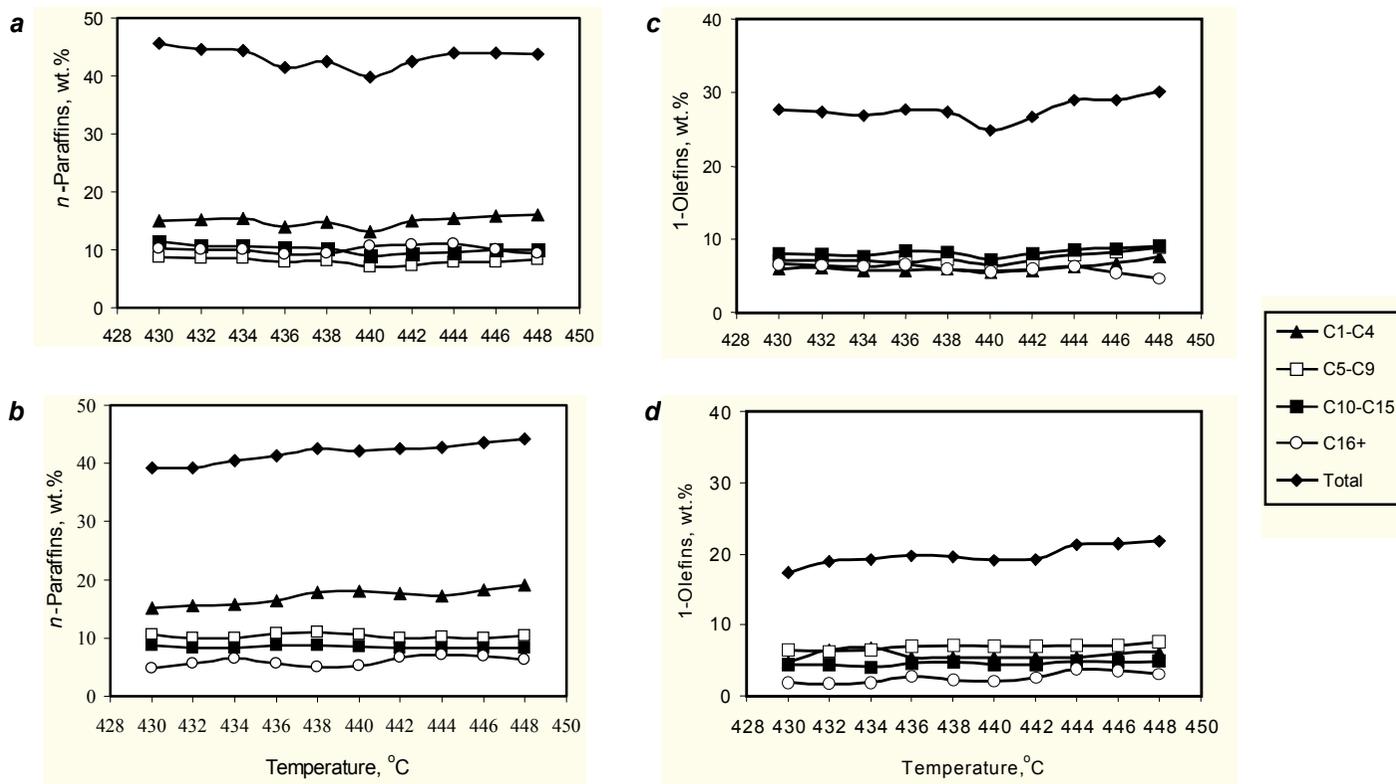
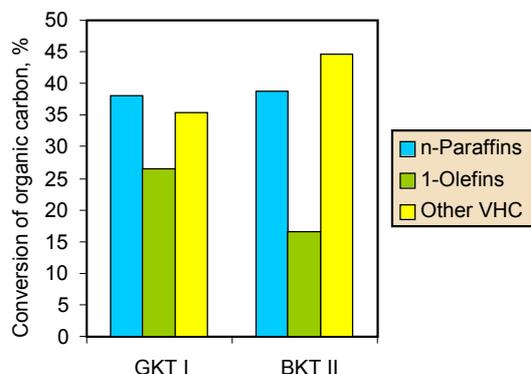


Fig. 4. Distribution of *n*-paraffins (a, b) and 1-olefins (b, c) in pyrolysis products by carbon number for GKT I (a, c) and BKT II (b, d)

Table 3. Distribution (wt.%) of *n*-Paraffins and 1-Olefins in Pyrolysis Products, of GKT I and BKT II at Maximum Temperature of Product Evolution

	GKT I	BKT II	GKT I	BKT II
<i>n</i> -Paraffins			1-Olefins	
On the basis of VHC				
C ₁ -C ₄	13.2	17.9	5.4	5.4
C ₅ -C ₉	7.0	10.9	6.5	7.2
C ₁₀ -C ₁₅	9.0	8.8	7.3	4.8
C ₁₆ ⁺	10.6	4.9	5.6	2.2
Total	39.8	42.5	24.8	19.6
On the basis of total <i>n</i> -paraffins On the basis of total 1-olefins				
C ₁ -C ₄	33.2	42.1	21.8	27.7
C ₅ -C ₉	17.6	25.6	26.2	36.7
C ₁₀ -C ₁₅	22.6	20.7	29.4	24.9
C ₁₆ ⁺	26.6	11.6	22.6	10.7
Total	100.0	100.0	100.0	100.0

Conversion of carbon present in GKT I and BKT II to *n*-paraffins and 1-olefins is illustrated in Fig. 5. The total recovery of *n*-paraffins and 1-olefins at pyrolysis of GKT I was higher compared with BKT II. It can be explained by the difference between the kerogen types of two oil shales. Kerogen type I oil shales originate mainly from marine or lacustrine organic material and they yield more paraffinic hydrocarbons than type II kerogens being of terrestrial as well as of marine organic material origin [3, 12].



*Fig. 5. Conversion of carbon in GKT I and BKT II to *n*-paraffins and 1-olefins*

The formation of the selected liquid components was monitored in order to gain some insight into the pathways of pyrolysis reactions. The most obvious difference between the GKT I and BKT II is in the ratio of straight-chain *n*-paraffins to 1-olefins. To express these changes in more quantitative terms, the integrated areas of 24 straight-chain paraffins were summarized and divided by the sum of 24 straight-chain olefins for the temperature range at which the product evolution rate is highest.

The ratio of *n*-paraffins to 1-olefins was found to be higher at pyrolysis of GKT I. The results are shown in Fig. 6. During kerogen pyrolysis, cracking reactions have been shown to proceed *via* a free-radical mechanism to form shorter linear paraffins and 1-olefins. Such linear molecules may also undergo cyclization and dehydrogenation reactions and ultimately form coke in the presence of silicate mineral.

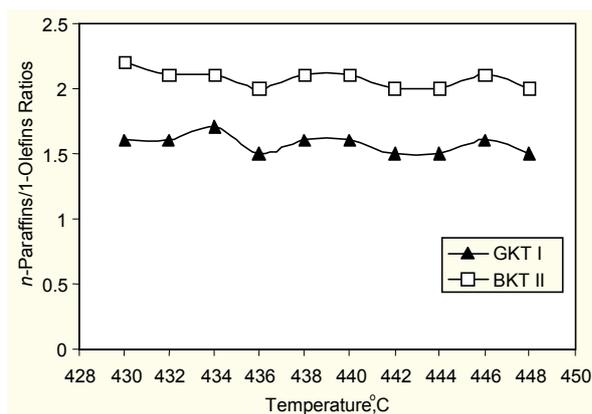


Fig. 6. Ratio of *n*-paraffins to 1-olefins for GKT I and BKT II

It is difficult to understand if linear olefins are more prone to secondary reactions than paraffins, and so removal of silicate should aid their passage from the reactor resulting in an increase in the ratio of *n*-paraffins to 1-olefins. The present situation can be explained in this way: with removal of silicates, larger molecules escape the reactor without undergoing cracking reactions to form 1-olefins and thus, the ratio of *n*-paraffins to 1-olefins increases. The decreased content of 1-olefins may also be due to re-polymerization reactions leading to a decrease in the yield of 1-olefins and increase in evolution of asphaltenes at slow heating rates. Olukcu *et al.* have studied liquefaction of Beypazarı oil shale [13]. They have reported that kerogen type of oil shale had an effect on the re-polymerization reactions, and conventional pyrolysis yielded less 1-olefins but more asphaltenes [13].

The formation of the selected aromatic compounds such as benzene and toluene was also monitored in order to investigate the pathways of coking reactions. To express these changes in more quantitative terms, the integrated areas of benzene and toluene were summarized and divided by integrated areas of aliphatic hydrocarbons for the temperature range at which the product evolution rate was highest. It is generally speculated that the tendency to form aromatics is directly responsible for the high rate of coking. This is because a more rapid rate of formation of aromatic compounds would result in a higher concentration of these components which in the pyrolysis reactor undergo coking reactions.

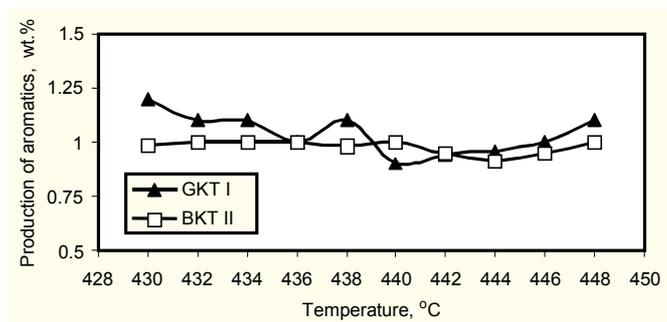


Fig. 7. Share of aromatics in volatile hydrocarbons at pyrolysis of GKT I and BKT II

However, this opinion was not supported by the experimental data as the share of aromatics in volatile hydrocarbons did not change at pyrolysis of both GKT I and BKT II within a certain temperature range (Fig. 7).

Such a result can be explained by the mineral-kerogen interaction. If pyrolysis is carried out with raw oil shale or in the presence of mineral matter, the concentration of aromatic hydrocarbons will be responsible for the high rate of coking. The effect of kerogen type on the loss of oil yield due to coking reactions in the absence of mineral matter can be assumed to be of less importance.

Conversion level of organic carbon to VHC, polyaromatics (asphaltenes, preasphaltenes) and carbon in solid residue is illustrated in Fig. 8.

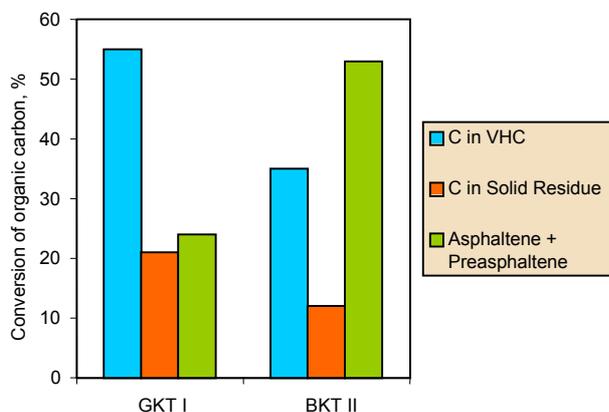


Fig. 8. Conversion levels of organic carbon to VHC, polyaromatics (asphaltenes + preasphaltenes) and carbon in solid residue at pyrolysis of GKT I and BKT II

The discrepancy in the carbon balance (Fig. 9) was assigned to asphaltenic, and preasphaltenic hydrocarbons. The analysis method used did not allow detecting polyaromatics such as the fraction of preasphaltenes (pyridine-soluble and benzene-insoluble materials) and asphaltenes (benzene-soluble and hexane-insoluble materials) in the pyrolysis products. It was found that the discrepancy was higher in the case of BKT II and

speculated that kerogen of type II yields more polycyclic aromatic compounds.

It is generally known that aromatics are more prone to undergo coking reactions than aliphatics [2]. When the pyrolysis reaction runs, the coke aggregates and accumulates on the solid surface of the shale. Although the yield of polyaromatics of BKT II is much higher than that of GKT I, carbon content of solid residue of pyrolysis of GKT I and BKT II was determined to be 21 and 12 wt.%, respectively. Active acidic sites associated with clays seem to be responsible for accumulation and removal of the minerals from oil shales so increasing the recovery of total hydrocarbon yield and decreasing deposition of carbon in solid residue. The type of kerogen did not show any effect aiding the deposition of carbon in the solid residue of pyrolysis reactions. Several researchers have observed a significant loss in oil yield during retorting in the presence of clay minerals. Hutton *et al.* studied retorting of oil shale from the Rundle and Stuart deposits (both Queensland) and noticed that oil vapors were more cracked when Rundle oil shale was retorted [14].

The reaction pathway for pyrolysis of GKT I and BKT II – dealkylation of aromatic structures, dehydrogenation of aliphatic fractions and cyclization was investigated by considering both the gas yields and cyclohexanes: benzene ratio (Figs 9 and 10). Pyrolysis of BKT II yields slightly more gaseous components. The differences can be interpreted as an increase in dealkylation reactions relative to dehydrogenation and cyclization during pyrolysis of BKT II. The observation considering dealkylation of aromatic structures is also supported by the high yield of polyaromatic hydrocarbons such as asphaltenes and pre-asphaltenes at pyrolysis of BKT II. There are, of course, other reactions such as dehydrogenation and cyclization occurring during pyrolysis, but the dealkylation of aromatic structures seems to be more effective in the case of BKT II.

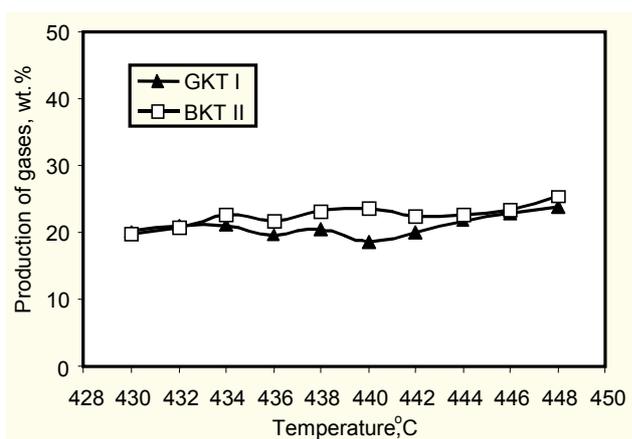


Fig. 9. Share of gaseous hydrocarbons (*n*-paraffins + 1-olefins) in pyrolysis products of GKT I and BKT II

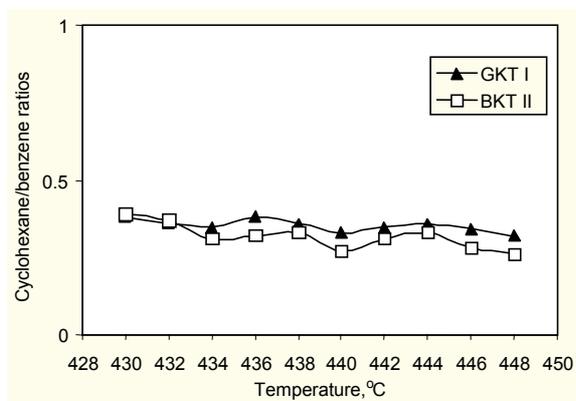


Fig. 10. Ratio of cyclohexane to benzene in pyrolysis products of GKT I and BKT II

The reactions occurring during pyrolysis are of complicated nature and not able to be interpreted by free-radical mechanism only. Comparison of pyrolysis routes of these two shales indicates that the type of kerogen plays the most significant role in formation of the products. At pyrolysis of BKT II more aromatic and gaseous hydrocarbons were formed. The differences in product yields are too great to be explained by some certain reaction mechanism such as dealkylation, cyclization and dehydrogenation of volatile components or addition. Although it has been reported that single aromatic structures form by either cyclization and dehydrogenation of aliphatic liquids or addition and subsequent dehydrogenation of gaseous components [15], the type of kerogen determines reaction pathway.

Conclusion

The effect of kerogen type on product yield and composition was studied. Pyrolysis of kerogen of different type yielded hydrocarbon products of different ratio of *n*-paraffins to olefins and different yields of aromatics. Kerogen type seems to determine the carbon content of the solid residue, the ratio of *n*-paraffins to 1-olefins and the yield of aromatics. Reactions occurring during pyrolysis – dealkylation, cyclization, dehydrogenation of volatile components, etc. – seem not to proceed according to free-radical mechanism only.

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