

CLASSIFICATION OF ALIPHATIC HYDROCARBONS FORMED AT TEMPERATURE-PROGRAMMED CO-PYROLYSIS OF TURKISH OIL SHALES OF KEROGEN TYPES I AND II

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Temperature-programmed co-pyrolysis of Göynük and Beypazari oil shales was investigated with the aim to determine volatile product distribution and product evolution rate of co-processing. A series co-pyrolysis operation was performed using three total carbon ratios. A fixed-bed reactor was used to pyrolyse small samples of oil shale mixtures under an inert gas (argon) flow. A special sampling technique was used for collecting organic products formed at different temperature and time intervals. The co-pyrolysis products were analyzed by capillary gas chromatography and the total product evolution rate was investigated as a function of temperature and time. n-Paraffins and 1-olefins in aliphatic fraction of pyrolysis products were classified by their carbon number. In addition, the recovery of total organic carbon as an organic volatile product was determined. The effect of co-processing was determined comparing the results with the data of their separate pyrolysis. The effect of oil shale kerogen type on co-pyrolysis operation was also investigated. Conversion into volatile hydrocarbons was found to lower with increasing Beypazari oil shale share in the mixture while the amounts of C₁-C₁₅ hydrocarbons and coke to increase in the presence of this oil shale.

Introduction

Synthetic gaseous or liquid fuels can be obtained by converting a carbonaceous material into another form. Oil shales are the second (after lignites) largest solid fuel reserve in Turkey, totaling approximately 5 billion tonnes. The largest deposits are Göynük-Bolu (2.5 billion tonnes), and Beypazari-Ankara (1 billion tonnes) [1-4]. Suitability for opencast mining, availability of water at the site, and favorable geographic location all together make the Göynük oil shale a potential source of synthetic fuels [5].

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A small fraction of oil shale organic material referred to as bitumen is soluble in organic solvents, while the major fraction is a waxy substance of high molecular weight commonly referred to as kerogen. This insoluble fraction is the basic component of oil shales and cannot be extracted by ordinary solvents simply, but after appropriate treatment it is suitable for use as feedstock [1, 2].

A commonly accepted model of kerogen structure is that of a polymeric material composed of non-repeating polynuclear aromatic units with peripheral and bridging functional groups. Alkyl and alkyl/aryl chain substituents and carboxylic groups are the principal functional groups [6]. Alginite is the predominant organic matter in kerogen type I. This kerogen originates mainly from marine or lacustrine organic material and has therefore a high H/C ratio accounting for high hydrocarbon yield. Type II kerogen contains the components of terrestrial as well as of marine material [4–7], its H/C ratio is lower and O/C ratio slightly higher compared to type I. Type III kerogen is mainly terrestrial in origin with higher O/C and lower H/C ratios than those of other types, reflecting increasing proportions of polycyclic aromatics and oxygen-containing aromatic groups.

Inorganic constituents of oil shales affect the reactions of organic matter both physically and chemically. The interaction between kerogen and inorganic matrix during reactions is not well understood [8]. Minerals are known to be of importance in oil shale processing [9, 10] and mineral characteristics of oil shale can have a great influence on oil yield and quality. When comparing the *n*-alkane distribution in shale oil produced from kerogen type I and II oil shales, the selectivity of C₁₀–C₂₀ *n*-paraffins in shale oil from kerogen type II is much greater [1, 2, 4, 5]. In other words, kerogen type I oil shales give more high-molecular pyrolysis products and coke.

The purpose of this study was to determine the effects of kerogen types of oil shale on their co-pyrolysis operation. For that purpose, Göynük oil shale (GOS, kerogen type I) and Beypazari oil shale (BOS, kerogen type II) were used. Their mineral characteristics are different and the alkaline earth metal cations present in BOS and its high mineral content may have some catalytic effect on pyrolysis reactions of initial GOS. Although it is important to avoid oil cracking on mineral surface and increase oil yield, further upgrading of heavy oil fractions is expensive. As kerogen type I oil shales produce more high-molecular products than kerogen type II ones, their co-processing could be a good way to produce more lower-boiling fractions.

In this study, the recovery of total organic carbon of the co-pyrolysis mixture was determined as aliphatic hydrocarbons and compared with the recovery in GOS and BOS separate processing. The effect of GOS : BOS ratios on co-processing was determined by calculating the difference between the experimental and the hypothetical mean values of conversion of total organic carbon into volatile products. The temperatures at which the product evolution rate is maximum was determined, and *n*-paraffins and

1-olefins in the co-pyrolysis products obtained at each given temperature were classified by carbon number.

Experimental

Samples

The investigations were performed with oil shale samples obtained from Göynük-Bolu (GOS, evolution path type I) and Beypazari-Ankara (BOS, type II) deposits [4]. The results of their elemental analysis and Fisher assay are given in our previous paper (Table 1 [11]).

Oil shale samples were crushed and ground in a jaw mill, then sieved to obtain the <0.1-mm fraction and dried at 105 °C under N₂ atmosphere.

The samples for co-pyrolysis were prepared to get three total carbon ratios:

Ratio	GOS, g	BOS, g
1 : 3	0.08	0.62
1 : 1	0.13	0.46
3 : 1	0.17	0.30

Table 1. Elemental Analysis and Fisher Assay of Göynük (GOS) and Beypazari (BOS) Oil Shales, wt.% [11]

Indices	GOS	BOS
Ultimate analysis		
Moisture (as received)	3.8	0.6
C (total, dry basis)	47.2	12.9
C (organic, dry basis)	46.3	7.7
C (inorganic, dry basis)	0.9	5.2
CO ₂	3.3	19.0
H (dry basis)	5.8	1.3
N (dry basis)	1.3	0.3
S (dry basis)	2.2	1.5
Fisher assay		
Shale oil	31.8	6.4
Gas	9.6	1.1
Decomposition water	3.6	0.7
Residue	51.2	91.2
Composition of gaseous product		
H ₂	1.5	2.7
CO	10.0	5.4
CO ₂	39.1	52.7
CH ₄	15.3	4.0
C ₂ -C ₇	34.1	35.2
Elemental analysis of shale oil		
C	76.1	79.6
H	11.3	11.4
N	1.1	1.3
S	1.5	1.3
Elemental analysis of residue		
C	37.9	8.5
H	1.7	0.3
N	1.5	0.03
S	0.8	0.3

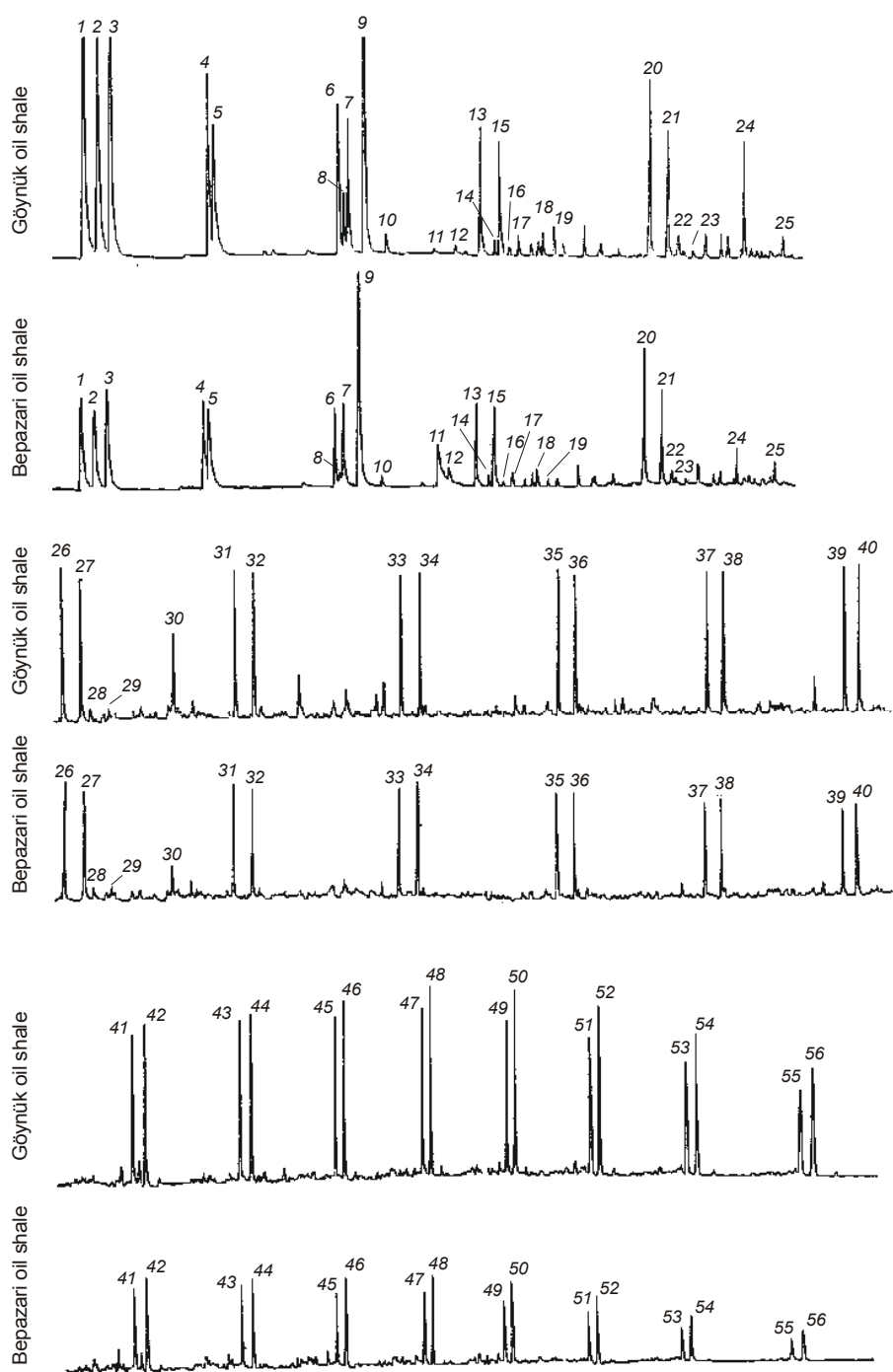


Fig. 1. Gas chromatograms of organic products formed at maximum evolution temperatures during pyrolysis of GOS and BOS: 1 – methane; 2 – ethene; 3 – ethane; 4 – propene; 5 – propane; 6 – 1-butene; 7 – 1,3-butadiene; 8 – butane; 9 – neopentane (reference gas) + *trans*-2-butene; 10 – *cis*-butene; 11 – 3-methyl-2-butene; 12 – 2-methylbutene (isopentane); 13 – 1-pentene; 14 – 2-methyl-1-butene; 15 – pentane; 16 – *trans*-2-pentene; 17 – *cis*-2-pentene; 18 – 2-methyl-2-butene; 19 – 2,2-dimethylbutane; 20 – 1-hexene; 21 – hexane; 22 – *trans*-2-hexene; 23 – *cis*-2-hexene; 24 – benzene; 25 – cyclohexane; 26 – 1-heptene; 27 – heptane; 28 – *trans*-2-heptene; 29 – *cis*-2-heptene; 30 – toluene; 31 – 1-octene; 32 – octane; 33 – 1-nonene; 34 – nonane; 35 – 1-decene; 36 – decane; 37 – 1-undecene; 38 – undecane; 39 – 1-dodecene; 40 – dodecane; 41 – 1-tridecene; 42 – tridecane; 43 – 1-tetradecene; 44 – tetradecane; 45 – 1-pentadecene; 46 – pentadecane; 47 – 1-hexadecene; 48 – hexadecane; 49 – 1-heptadecene; 50 – heptadecane; 51 – 1-octadecene; 52 – octadecane; 53 – 1-nonadecene; 54 – nonadecane; 55 – 1-eicosene; 56 – eicosane

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Table 2. The Major Organic Compounds Obtained at Maximum Evolution Temperatures during Temperature-Programmed Co-Pyrolysis of Göynük and Beypazari Oil Shales

Number	Organic compounds	Number	Organic compounds
1	Methane	31	Tetradecene
2	1-Ethene	32	Tetradecane
3	Ethane	33	Pentadecene
4	1-Propene	34	Pentadecane
5	Propane	35	Hexadecene
6	Isobutane	36	Hexadecane
7	1-Butene	37	Heptadecene
8	Butane	38	Heptadecane
9	Neopentane (Reference gas)	39	Octadecene
10	<i>cis</i> -butene	40	Octadecane
11	1-Pentene	41	Nonadecene
12	Pentane	42	Nonadecane
13	1-Hexene	43	Eicosene
14	Hexane	44	Eicosane
15	Benzene	45	Heneicosene
16	1-Heptene	46	Heneicosane
17	Heptane	47	Docosene
18	Toluene	48	Docosane
19	1-Octene	49	Tricosene
20	Octane	50	Tricosane
21	1-Nonene	51	Tetracosene
22	Nonane	52	Tetracosane
23	1-Decene	53	Pentacosene
24	Decane	54	Pentacosane
25	1-Undecene	55	Hexacosene
26	Undecane	56	Hexacosane
27	1-Dodecene	57	Heptacosane
28	Dodecane	58	Octacosane
29	1-Tridecene	59	Nonacosane
30	Tridecane	60	Triacotane

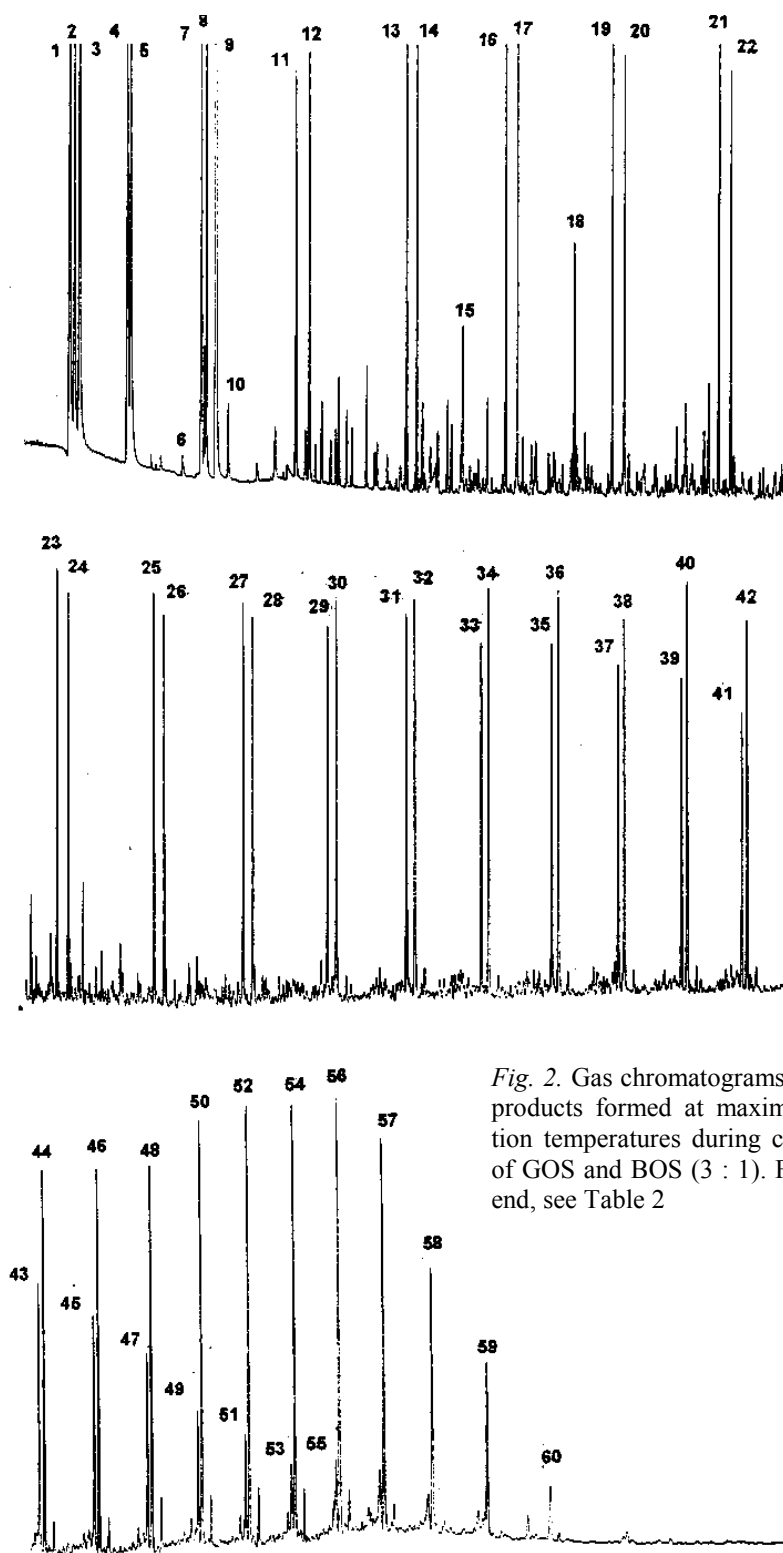


Fig. 2. Gas chromatograms of organic products formed at maximum evolution temperatures during co-pyrolysis of GOS and BOS (3 : 1). For the legend, see Table 2

Co-Pyrolysis Procedure

The experiment protocol and analysis technique are given in [11, 12].

Air was displaced from the apparatus with an inert gas (argon) stream before heating. Co-pyrolysis was carried out at $2\text{ }^{\circ}\text{C min}^{-1}$ under a 90 mL min^{-1} flow of argon. Co-pyrolysis products were swept out of the reactor and mixed with a reference gas (20 mL min^{-1} , 0.507 vol.% neopentane in N_2) before passing to a special sampling system. Samples were taken in evacuated glass ampoules at time intervals during the operation and later analyzed by capillary gas chromatography with a special designed sample introduction system. After completion of each co-pyrolysis run, the amount of coke remaining in the reactor was determined by its combustion in the flow of depleted air (120 mL min^{-1} , 20 vol.% O_2) at heating rate $2\text{ }^{\circ}\text{C min}^{-1}$.

Results and Discussion

Chromatograms of GOS and BOS separate [1, 2] and co-pyrolysis products are shown in Figs 1 and 2. The effects of temperature and time on the rate of total product evolution are shown in Fig. 3. The temperature at which product evolution is the greatest is $\sim 430\text{ }^{\circ}\text{C}$ for each co-pyrolysis operation. The major constituents of organic part formed during co-pyrolysis of GOS and BOS (3 : 1) at maximum evolution temperatures are given in Table 2.

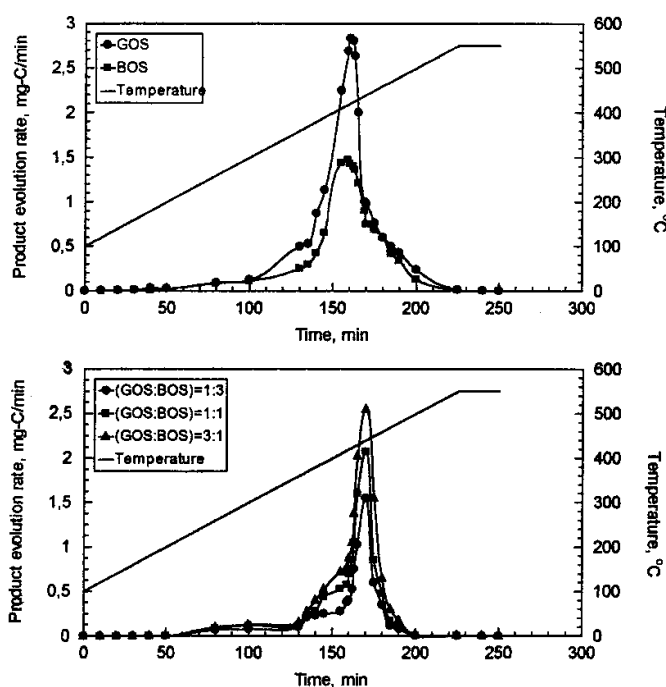
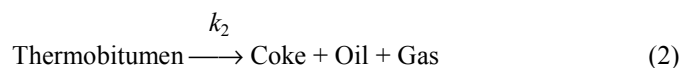


Fig. 3. Total product evolution rate at GOS, BOS and GOS : BOS mixture pyrolysis as a function of temperature and time

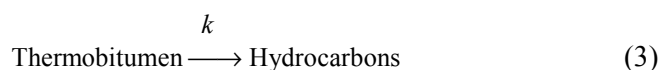
Thermal breakdown reactions of kerogen belong to three broad reaction classes. These are [6]:

- decarboxylation (involving principally decomposition of $-\text{COOH}$ groups),
- major breakdown of kerogen to form oil and gas with hydrocarbons as the main products, and
- carbonization of the aromatic char.

Previous investigations have led to the conclusion that pyrolysis of oil shale kerogen could be expressed as



At temperatures below 482 °C [13, 14], formation of intermediate thermbitumen is a considerably more rapid step compared to its further decomposition. The first step can be omitted from the present investigation because the temperature range of 265 to 400 °C was used. Exclusion of kerogen from consideration assumes the validity of Allred's suggestion [14]. Therefore, it is accepted that all of the kerogen has been converted to thermbitumen, gas and carbonaceous residue, and later no carbonaceous matter was formed [14]. Hence, the pyrolysis reaction can simply be considered as follows:



Thermbitumen has a high boiling point and remains inside the oil shale particle for a significant period. It becomes a subject to two competing processes: heavy oil formation and intra-particle (liquid phase) coking. Heavy oil formed is further subjected to thermal cracking in the vapour phase surrounding the particles. Carbonization of aromatic char occurs between about 500 and 1200 °C with evolution of hydrogen contributing only little to the total mass loss.

The present research on hydrocarbon distribution was performed in the temperature range of 280–500 °C. This temperature covers hydrocarbon generation from oil shale. Pyrolysis products include straight- and branched-chain paraffins and olefins from methane to C_{30} , and besides some aromatic hydrocarbons also polyaromatic compounds are present. The analysis method used did not allow characterizing polyaromatics such as preasphaltenes (pyridine-soluble benzene-insoluble materials) and asphaltenes (benzene-soluble hexane-insoluble materials) present in the pyrolysis products. For this reason, the discrepancy in the carbon balance was assigned to asphaltenes, preasphaltenes, and CO_2 evolved during co-pyrolysis of GOS and BOS.

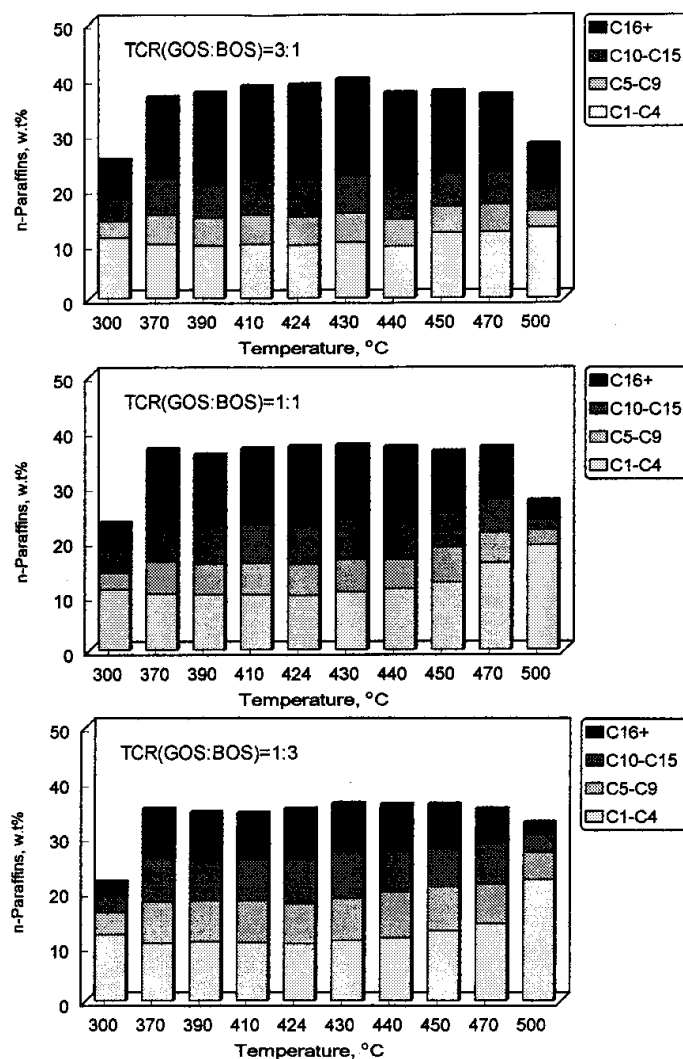


Fig. 4. Distribution of *n*-paraffins in co-pyrolysis products by carbon number for GOS : BOS mixtures of different total carbon ratios

The effect of BOS share on formation and distribution of *n*-paraffins and 1-olefins in the co-pyrolysis of Göynük and Beypazari oil shales was determined (Figs 4 and 5). The *n*-paraffins produced by co-processing were classified by C-number. Low-molecular-weight hydrocarbons (methane, ethane, propane, and butane) were combined into one group (C₁-C₄). The C₅-C₉, C₁₀-C₁₅ and C₁₆+ fractions were also similarly grouped. The hydrocarbons produced by co-pyrolysis at the maximum product evolution temperature contained 38.0, 40.5, and 41.8 wt.% of *n*-paraffins for total carbon ratios of GOS : BOS 1 : 3, 1 : 1, and 3 : 1, respectively. The corresponding percentage of 1-olefins was 21.0, 23.4, and 25.0 wt.%, respectively.

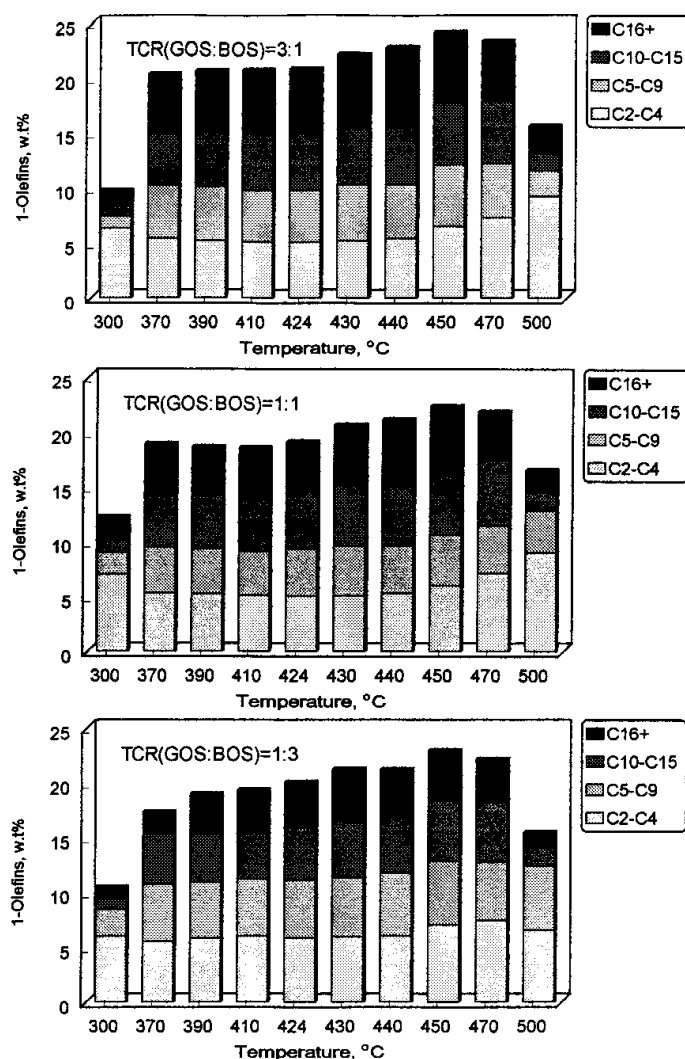


Fig. 5. Distribution of 1-olefins in co-pyrolysis products by carbon number for GOS : BOS mixtures of different total carbon ratios

Distribution of *n*-paraffins and 1-olefins in the co-pyrolysis products is summarized in Table 3. Co-pyrolysis yielded more gaseous (C_1 – C_4) paraffins than separate processing of GOS. The formation rate of *n*-paraffins was higher than that of 1-olefins at each temperature and ratio. *n*-Paraffins consist mainly of low-molecular volatile hydrocarbons such as C_1 – C_{15} . Their amount increases with increasing the share of BOS in the co-pyrolysis mixture.

The data of the experimental and hypothetical conversion to volatile organic compounds such as alkanes, alkenes and dienes are given in Table 4 (the experimental conversion values were determined by numerical integra-

tion of each curve shown in Fig. 3; and the hypothetical ones were calculated by considering both individual conversion values and the weight ratios of GOS : BOS in the co-pyrolysis samples). One can see that the differences were found negative for each mixture and synergistic effect of co-processing was not determined.

Table 3. Distribution of *n*-Paraffins and 1-Olefins in Co-Pyrolysis Product Formed at Its Maximum Evolution Temperature, wt.%

Indices	GOS [2]	BOS [1]	GOS : BOS		
			1 : 3	1 : 1	3 : 1
<i>n</i> - P a r a f f i n s					
C ₁ -C ₄	25.00	34.00	37.00	35.00	32.90
C ₅ -C ₉	21.00	23.00	19.00	16.07	14.00
C ₁₀ -C ₁₅	19.00	23.00	24.73	23.76	21.40
C ₁₆₊	35.00	20.00	19.27	27.34	31.70
Σ <i>n</i> -Paraffins	40.00	35.00	38.00	40.50	41.80
1 - O l e f i n s					
C ₁ -C ₄	27.00	28.00	28.40	26.47	25.20
C ₅ -C ₉	20.00	22.00	20.30	23.30	24.80
C ₁₀ -C ₁₅	23.00	28.00	29.40	28.10	24.80
C ₁₆₊	30.00	22.00	21.90	22.13	25.20
Σ1-Olefins	30.00	22.00	21.00	23.48	25.00

Table 4. Comparison of Conversion Levels to Determine the Synergistic Effect in Co-Pyrolysis Processing, %

Indices	GOS [2]	BOS [1]	GOS : BOS		
			1 : 3	1 : 1	3 : 1
Conversion to volatile hydrocarbons	47.0	32.6	27.2	33.2	37.5
Hypothetical mean of conversion	47.0	32.6	38.9	41.8	43.7
Difference	0.0	0.0	-11.7	-8.6	-6.2
Standard deviation σ	0.1	0.2	0.4	0.6	0.5
Conversion to coke	34.0	19.6	32.0	34.5	35.1

The effect of BOS share was evaluated comparing experimental conversion values (averages of four replications for each co-processing) and hypothetical means of conversion value. When the difference between experimental co-processing value and hypothetical mean is positive, then co-processing of two materials enhances their reactivity and produces higher conversion than obtained in individual reactions. The desired end result is to obtain higher conversion to volatile organic products during co-processing.

The type of kerogen showed a marked effect on the total conversion of GOS in co-processing with BOS. When considering the experimental conversion values for GOS : BOS (see Table 4), the conversion of GOS was found to be lower at all proportions of BOS. It can be explained by catalytic effect of minerals present in BOS. Earth alkali metal cations such as calcium and magnesium can promote oil shale conversion but inhibiting effect of silicate minerals originally present in shales seems to be greater than catalytic effect of carbonates. According to our earlier data, the mineral content of BOS and, consequently, its weight loss due to carbonate decomposition were observed to be much higher than that of GOS [4].

Judging by values of co-processing conversion of total organic carbon to coke (see Table 4), the higher the BOS content, the more coke is formed. It was also explained by inhibition effect of silicate minerals originally present in shales. A number of studies have implicated the clay minerals in the oil losses that arise from coking [15, 16]. Increase in recoveries of oil, and trends in oil characteristics, are consistent with decreasing levels of acid-catalyzed oil coking reactions on clay mineral surfaces. Active acidic sites associated with dehydroxylated clays are thought to be responsible for coke formation [16].

The effect of the mineral matrix of Turkish oil shales on the conversion of kerogen into organic materials in pyrolysis reactions was also investigated by Karabakan with co-authors [17]. They used Göynük and Green River oil shales in their studies and it was found that pyrolysis reactions were catalyzed by alkaline earth metal cations in carbonates and inhibited by silicates.

Conclusions

- The maximum product release temperature at co-pyrolysis of GOS and BOS mixture was found to be approximately 430 °C.
- Straight- and branched-chain paraffins and olefins from methane to compounds C₃₀ and some aromatic hydrocarbons were determined in co-pyrolysis products. The portion of *n*-paraffins exceeded that of 1-olefins at each temperature.
- The kerogen type was found to have a great effect on hydrocarbon distribution. Co-processing of GOS and BOS actually makes use of coking reactions on minerals present in BOS to produce lower-boiling hydrocarbon fractions. However, GOS (kerogen type I) gives more high-molecular-weight pyrolysis products than BOS (kerogen type II). Co-pyrolysis of GOS with BOS yielded more C₁₋₁₅ *n*-paraffins and coke than separate processing of GOS.
- Conversion into volatile hydrocarbons was found to lower with increasing the share of BOS in the mixture, while the amount of C₁-C₁₅ hydrocarbons and coke increase in the presence of BOS.

- The *n*-paraffins were found to consist mainly of C₁–C₁₅ and a relatively small amount of C₁₆₊ fractions. It was explained by catalytic effect of mineral content of BOS.
- Synergistic effect was not determined in the co-pyrolysis operation.

Acknowledgements

L. Ballice thanks the Department of Gas, Coal and Petroleum of the Engler-Bunte Institute, University of Karlsruhe, and Deutscher Akademischer Austauschdienst (DAAD)-German Academic Exchange Service for financial support.

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Presented by A. Kogerman

Received October 31, 2001