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CLASSIFICATION OF VOLATILE PRODUCTS OF TEMPERATURE-PROGRAMMED CO-PYROLYSIS OF TURKISH SOMA LIGNITE AND GÖYNÜK OIL SHALE

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Temperature-programmed co-pyrolysis of Turkish Soma lignites and Göynük oil shale was investigated with the aim to determine volatile product distribution and product evolution rate of their co-processing. A fixed-bed reactor was used to pyrolyse small samples of lignite and oil shale mixture under an inert gas (argon) flow as well as special sampling technique 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 by calculating the difference between the experimental and the hypothetical mean value of conversion of total organic carbon into volatile products. Conversion of organic carbon into volatile hydrocarbons increased while the amount of carbon in solid residue decreased with increasing oil shale ratio in the lignite-shale system.

Introduction

Successive world energy crises and large increases in the prices of oil derivatives have caused a renewed interest in different possibilities offered by valorization of carbonaceous material as an energy source and in chemical exploitation of pyrolysis products [1]. Synthetic gaseous or liquid fuels are obtained by converting a carbonaceous material into another form. The most abundant naturally occurring materials suitable for this purpose are coal, oil shale and tar sand. Worldwide deposits of oil shale are equivalent to 400 billion tons of shale oil from which 30 billion tons are recoverable under the existing technological conditions [2–4].

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Fig. 1. Geological map indicating some of the lignite and oil shale locations in Turkey

In Turkey, over 5 billion tons of oil shale reserves have been estimated by Mineral Research and Exploration Institute in seven areas, Göynük-Bolu (2.5 billion tons), and Beypazari-Ankara (1 billion tons) being the largest oil shale deposits [2–4]. Hard coal and lignite are the most abundant naturally occurring materials. Coal deposits are equivalent to 1.5 billion tons of hard coal and 8.4 billion tons of lignite [5–7]. Afşin-Elbistan (3.2 billion tons), Beypazari-Ankara (400 million tons), Mengen-Bolu (100 million tons), Tunçbilek-Kütahya (328 million tons), Seyitömer-Kütahya (200 million tons), and Soma-Manisa (130 million tons) are the largest lignite deposits (Fig. 1).

Lignite deposits are widespread all over Turkey in Neogene formations. Lower heat values of lignite vary from 1100 to 4500 Kcal/kg, some are even higher. However, their sulfur content is generally high. Soma (Manisa) and Tunçbilek (Kütahya) lignites have higher heat and lower sulfur content.

The liquefaction of coal to produce clean transportation fuels is an active area of research and the new trend in liquefaction is to co-process coal with waste materials such as waste plastic, waste oil, used tires, all of which have expensive disposal cost. Most of those waste materials are either incinerated or used for landfilling.

However, due to stringent environmental regulations, these methods of disposal are not applicable any more. It has been suggested that the addition of plastic to the coal during liquefaction may result in an enhanced coal conversion and oil production compared to the yields obtained when coal alone is processed [8, 9]. The argument for this synergistic effect is that waste materials such as plastics and rubber tires posses a high hydrogen content, and may therefore serve as an inexpensive hydrogen source aiding the dissolution of coal during liquefaction [4, 8].

Co-pyrolysis of a lignite and Australian oil shale (Rundle) has recently been reported by Sato and Saxby [10]. They found that the addition of lignite gave a slightly synergistic effect in terms of increasing the oil yield from the shale and also reduced the molecular weights of the resulting oils considerably [8, 10]. For the Turkish reserves, co-processing is an attractive option, as the lignites and oil shales lie in close proximity and, in the case of Göynük deposit, much of shale forms an overburden for the lignite [11].

In this study, the temperature-programmed co-pyrolysis of Soma lignites (LIG) with Göynük oil shale (OS) was investigated by using a new, highly efficient sampling technique for gas-vapor multicomponent mixture developed by Schulz et al. [12]. It 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.

Pyrolysis products were swept out from the reactor and mixed with a reference gas (20 mL min^{-1} of 0.507 vol.% neopentane in N_2) before passing them through the sampling system. Fractions were collected in pre-evacuated glass ampoules sealed with a gas burner, and samples were analyzed later by capillary gas chromatography using a special-design sample introducing system.

The objective of this study was to determine the temperatures at which the product evolution rate is maximum and to classify the *n*-paraffins and 1-olefins in the co-pyrolysis product by carbon number at each test temperature. The recovery of total organic carbon in the co-pyrolysis mixture sample as aliphatic hydrocarbons was determined and compared with that in the pyrolysis of separate LIG and OS samples. The effect of OS ratios on the co-processing of OS and LIG was determined by calculating the difference between the experimental and hypothetical mean value of conversion of total organic carbon into volatile products.

Experimental

Samples

For investigations lignite from the Soma-Manisa deposit and oil shale from the Göynük-Bolu deposit were taken.

Oil shale was classified using IR analysis technique, and its type of kerogen was found to be evolution path type I [13]. Data of elemental analysis and Fisher assay [2, 3, 14] are as follows (wt.%):

- Ultimate analysis: moisture $W^r{}_t$ 3.8; $C^d{}_t$ 47.2; $C^d{}_o$ 46.3; $C^d{}_M$ 0.9; CO_2 3.3; H^d 5.8; N^d 1.3; $S^d{}_t$ 2.2
- Fischer assay: shale oil 31.8; gas 9.6; decomposition water 3.6; residue 51.2
- Composition of gaseous product: H_2 1.5; CO 10.0; CO_2 39.1; CH_4 15.3; C_2–C_7 34.1

- Elemental analysis of shale oil: C 76.1; H 11.3; N 1.1; S 1.5
- Elemental analysis of residue: C 37.9; H 1.7; N 1.5; S 0.8

Lignite analysis data are as follows (wt.%):

- Ultimate analysis (dry basis): $C^d{}_t$ 60.4; $C^d{}_o$ 58.7; $C^d{}_M$ 1.7; H^d 5.6; N^d 0.9; $S^d{}_t$ 1.2
- Proximate analysis (as received): moisture W^r 13.7; ash A^r 14.6; volatile matter V^r 37.3; fixed carbon 34.4

For pyrolysis experiments, lignite and oil shale samples were crushed and ground in a jaw mill until the desired particle size was obtained. The samples were sieved to obtain a <0.1-mm fraction and dried at 105 ºC in N_2 atmosphere.

The samples of LIG-OS mixtures were prepared to get tree total carbon weight ratios:

Ratio	LIG, g	OS, g
1 : 3	0.12	0.31
1 : 1	0.18	0.23
3 : 1	0.24	0.15

Co-Pyrolysis Procedure

Co-pyrolysis tests were carried out 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. A thermocouple was inserted into the middle of the sample bed and the reactor tube was fitted into the stainless steel reactor shell. Three thermocouples were fitted to the outside of the reactor shell and connected to a temperature controller. The reactor shell was enclosed in a temperature-programmable furnace by a three-zone electric heater. The middle zone of heater was connected to a programmer and controller whereas the other two were controlled manually. The same equipment had been used for the pyrolysis of oil shale and co-pyrolysis of Turkish oil shale with low-density polyethylene [14–16].

The air was extruded from the apparatus with an inert gas (argon) stream before heating. The co-pyrolysis was carried out at 2 ºC min^{-1} under a 90 ml min^{-1} flow of argon. Co-pyrolysis products leaving the reactor were 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 into evacuated glass ampoules at certain time intervals during the operation. The ampoules were sealed on a gas burner and analyzed later by capillary gas chromatography with a special-design sample introduction system.

After the completion of each co-pyrolysis run, the amount of carbon in solid residue remaining in the reactor was determined by combustion in the flow of depleted air (120 mL min^{-1}, 20 vol.% O_2) at heating rate 2 ºC min^{-1}.

Application of Capillary GC-Total Stream Sampling Technique for Gas Vapour Multicomponent Mixture

Product streams of many processes of fuel chemistry as well as of petroleum chemistry contain multicomponent mixtures of gases and vapours with the boiling range from –200 to 400 °C. Small representative samples taken from the homogeneous gas phase of these streams were sealed into pre-warmed and pre-evacuated ampoules to be analysed by capillary gas chromatography.

A temperature-programmed capillary gas chromatography (between –80 and 250 °C) enables to separate the hydrocarbons C_1–C_{25} with high resolution. This technique offers a number of advantages: simplification of sampling compared to conventional procedure of fractionation for product recovery, safe handling and storage of the total sample, uncoupling sampling from analysis, and sampling at small intervals which allows studying instationary systems [12].

The separation of gas/vapor hydrocarbon mixture into individual components in the column was achieved in hydrogen atmosphere using a flame ionization detector.

Gas chromatography operating conditions: column 50 m × 0.2 mm fused silica; stationary phase methyl silicone (cross-linked) (OV-1); film thickness 0.5 μm; carrier gas hydrogen; flame ionization detector; 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

The pyrolysis products were also identified with gas chromatography/mass spectrometry (GC/MS) using a HP6890 system.

GC/MS operating conditions: special analysis column HP 624, 60 m × × 0.25 mm fused silica; pressure 1.415 bar; nominal initial flow 1.3 mL/min; carrier gas helium; resulting EM voltage 1411.8.

Scan parameters: low mass 30; high mass 350; threshold 50; MS Quad 150 °C; MS source 230 °C;

Temperature program: 30 °C, isothermal 8.0 min
30 °C min^{-1} to 220 °C, isothermal 25 min

Results and Discussion

Chromatograms of the products obtained at oil shale and lignite separate pyrolysis, and their co-pyrolysis (LIG-OS mixture 3 : 1) are shown in Figs 2–4. The major constituents of the organic part obtained at temperatures of maximum evolution are listed in Table 1.

Table 1. **The Major Organic Compounds Obtained at Maximum Evolution Temperatures during Temperature-Programmed Pyrolysis of LIG and OS, and Their Co-Pyrolysis**

Number	Organic compounds	Number	Organic compounds
1	Methane	35	Dodecane
2	1-Ethene	36	1-Tridecene
3	Ethane	37	Tridecane
4	1-Propene	38	Tetradecene
5	Propane	39	Tetradecane
6	Isobutane	40	Pentadecene
7	1-Butene	41	Pentadecane
8	Butane	42	Hexadecene
9	Neopentane (Reference gas)	43	Hexadecane
10	Cis-butene	44	Heptadecene
11	1-Pentene	45	Heptadecane
12	Pentane	46	Octadecene
13	1-Hexene	47	Octadecane
14	Hexane	48	Nonadecene
15	Benzene	49	Nonadecane
16	1-Heptene	50	Eicosene
17	Heptane	51	Eicosane
18	Toluene	52	Heneicosene
19	1-Octene	53	Heneicosane
20	Octane	54	Docosene
21	Ethylbenzene	55	Docosane
22	*m*/*p*-Xylene	56	Tricosene
23	*o*-Xylene	57	Tricosane
24	1-Nonene	58	Tetracosene
25	Nonane	59	Tetracosane
26	Cumene	60	Pentacosene
27	1-Decene	61	Pentacosane
28	Decane	62	Hexacosene
29	1,3 Dimethyl-2-Ethylbenzene	63	Hexacosane
30	Phenol	64	Heptacosane
31	1,2,3 Trimethylbenzene	65	Octacosane
32	1-Undecene	66	Nonacosane
33	Undecane	67	Triacontane
34	1-Dodecene		

The effect of temperature and time on the rate of the total product evolution in co-pyrolysis process is shown in Fig. 5. At each co-pyrolysis operation product evolution rate was the greatest at ~440 °C.

The effect of OS ratios on the total formation of *n*-paraffins and 1-olefins in the OS-LIG mixture co-pyrolysis was studied. The *n*-paraffins and 1-olefins produced by co-processing were classified by carbon number (Figs 6 and 7). With this classification, low-molecular-weight hydrocarbons (methane, ethane, propane, and butane) were combined into one group, C_1–C_4. The C_5–C_9, C_{10}–C_{15} and C_{16+} fractions were also grouped. The hydrocarbons produced at co-pyrolysis optimum temperature contained 40.9, 36.0, and 35.0 wt.% *n*-paraffins and 16.8, 20.1, and 22.7 wt.% 1-olefins for the total carbon ratios LIG-OS mixture 1 : 3, 1 : 1, and 3 : 1, respectively.

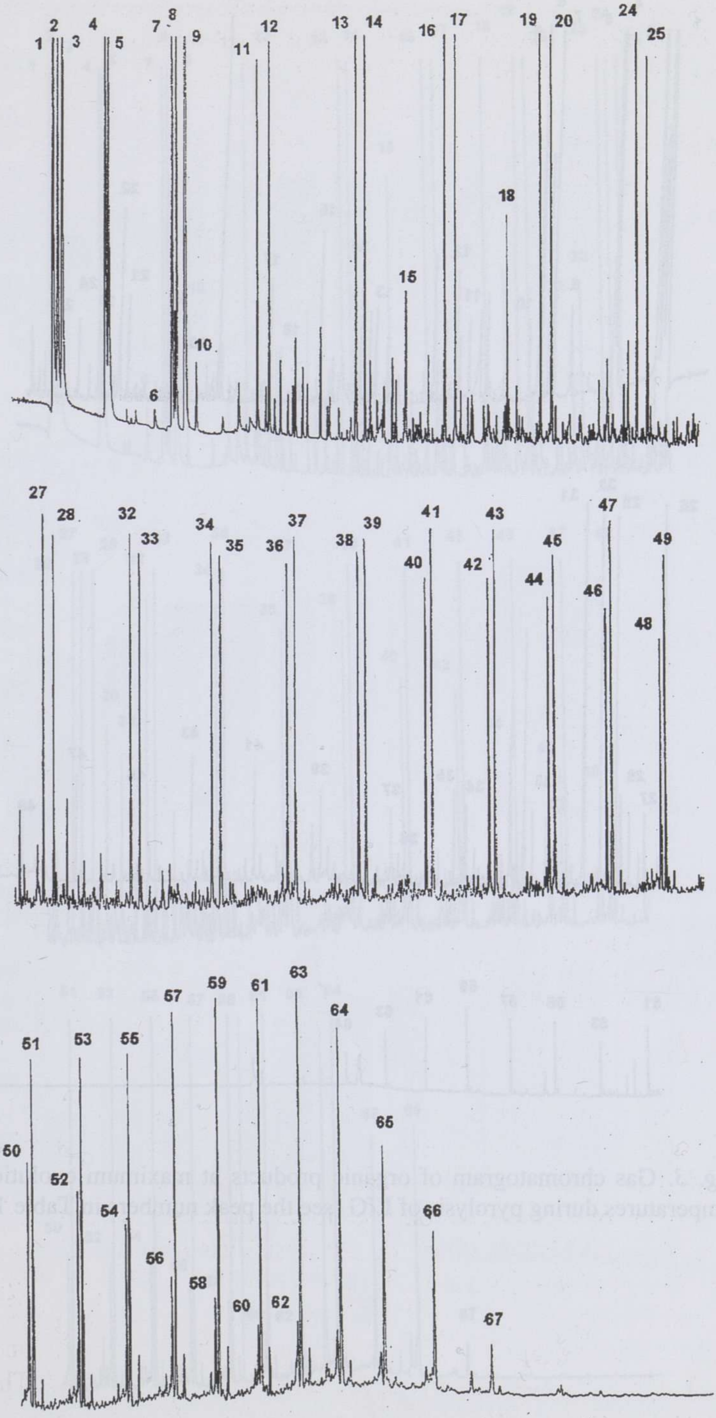

Fig. 2. Gas chromatogram of organic products at maximum evolution temperatures during pyrolysis of OS [3] (see the peak numbers in Table 1)

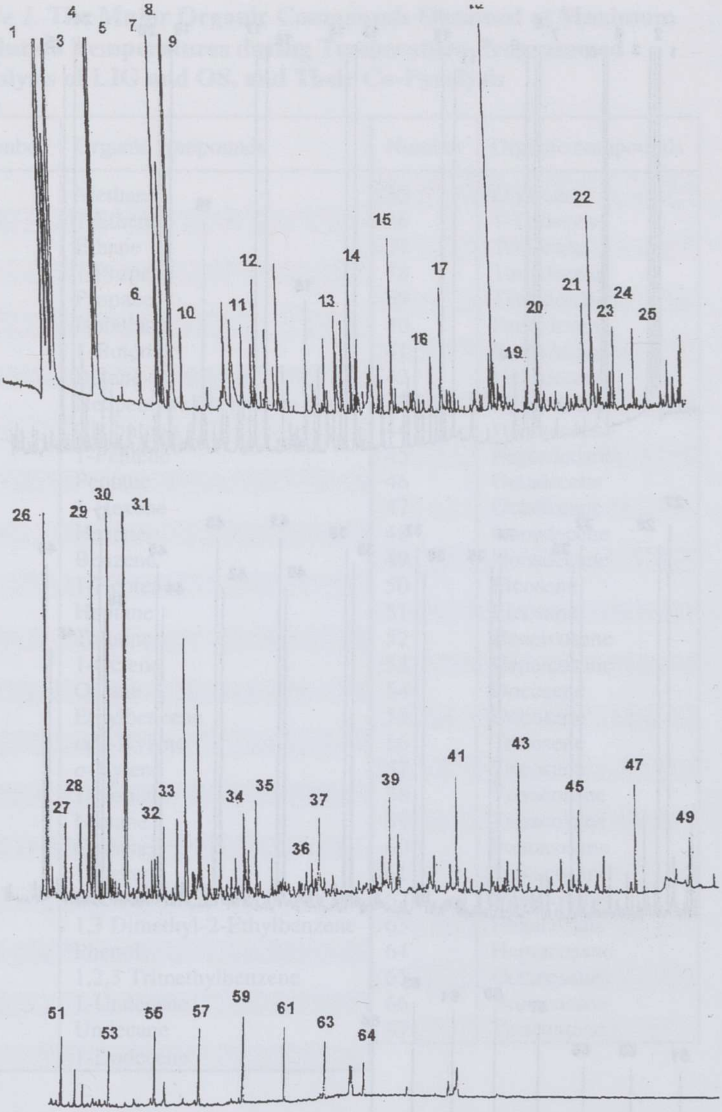

Fig. 3. Gas chromatogram of organic products at maximum evolution temperatures during pyrolysis of LIG (see the peak numbers in Table 1)

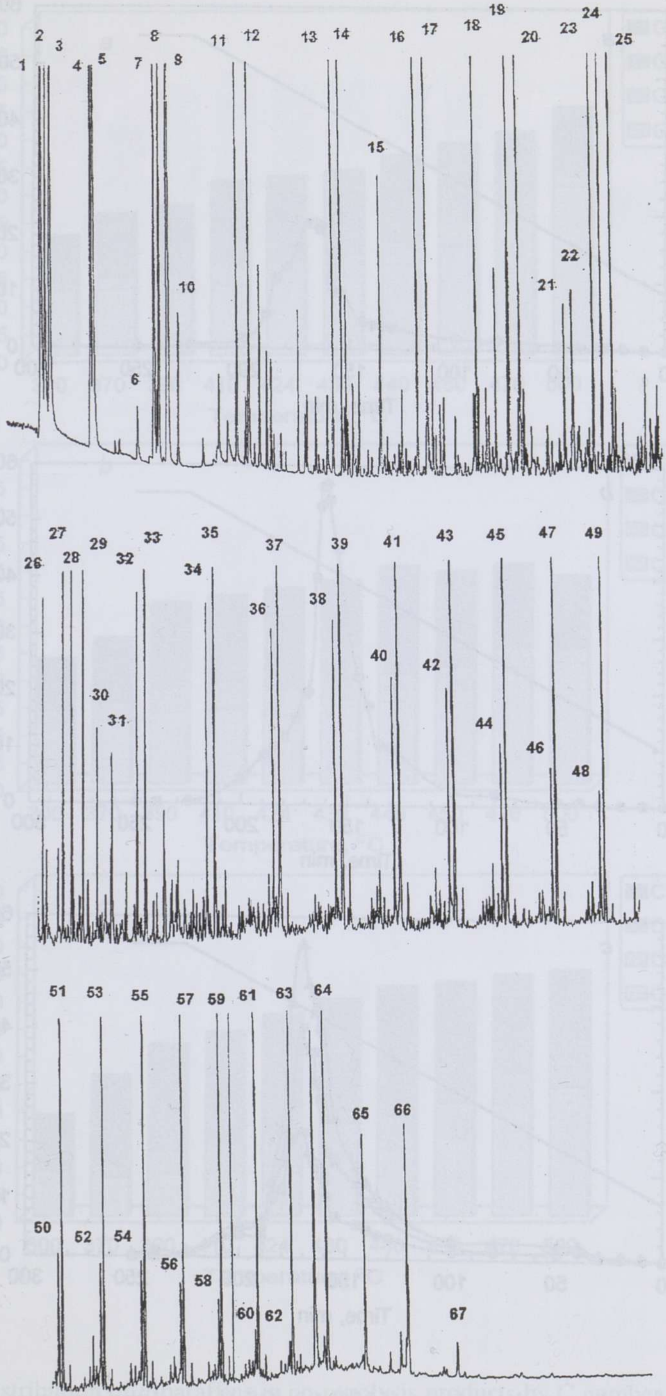

Fig. 4. Gas chromatogram of organic products at maximum evolution temperatures during co-pyrolysis of LIG-OS mixture (1 : 3) (see the peak numbers in Table 1)

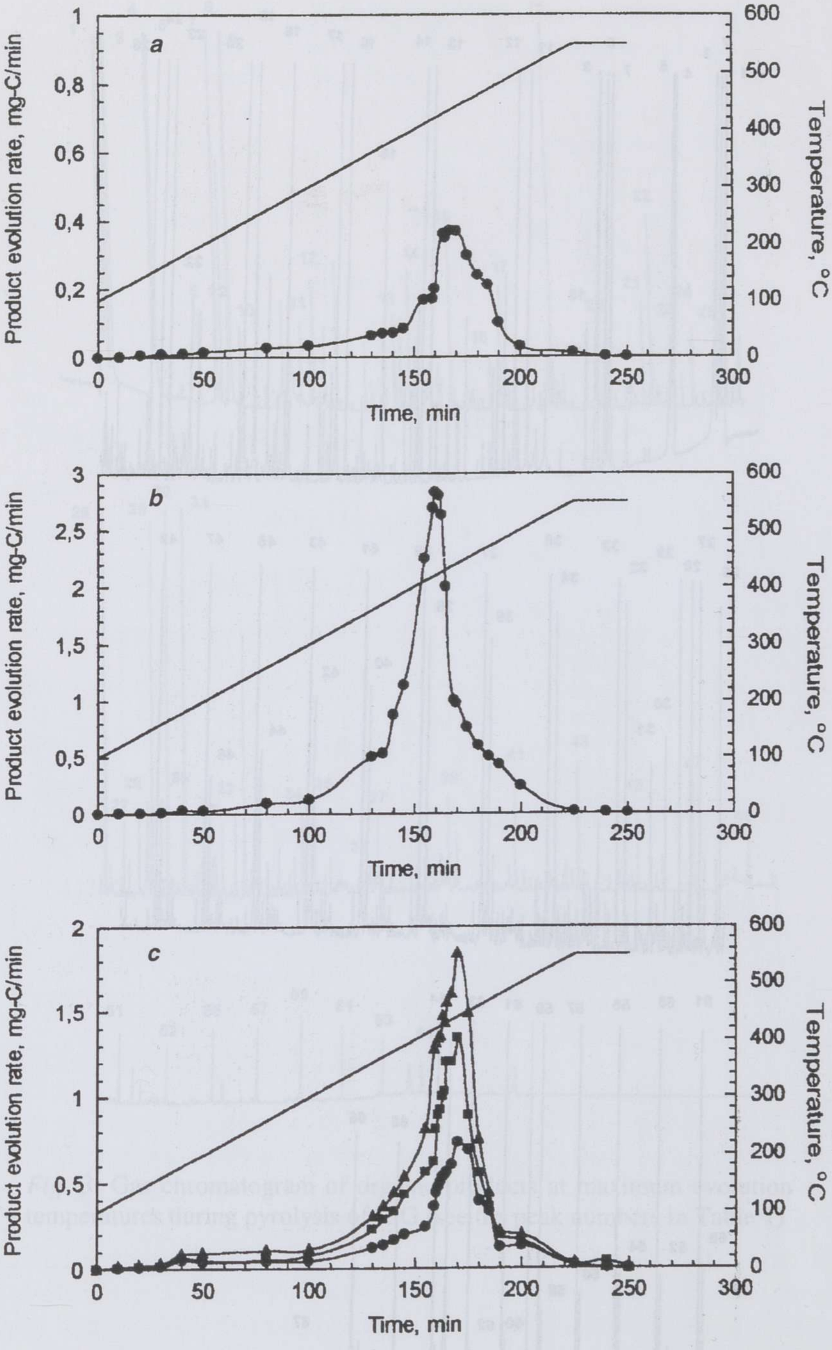

Fig. 5. Total product evolution rate of LIG (*a*), OS (*b*), and their mixture (*c*): LIG–OS ratio 3 : 1 (●), 1 : 1 (■) and 1 : 3 (▲) as a function of temperature and time; straight line – temperature

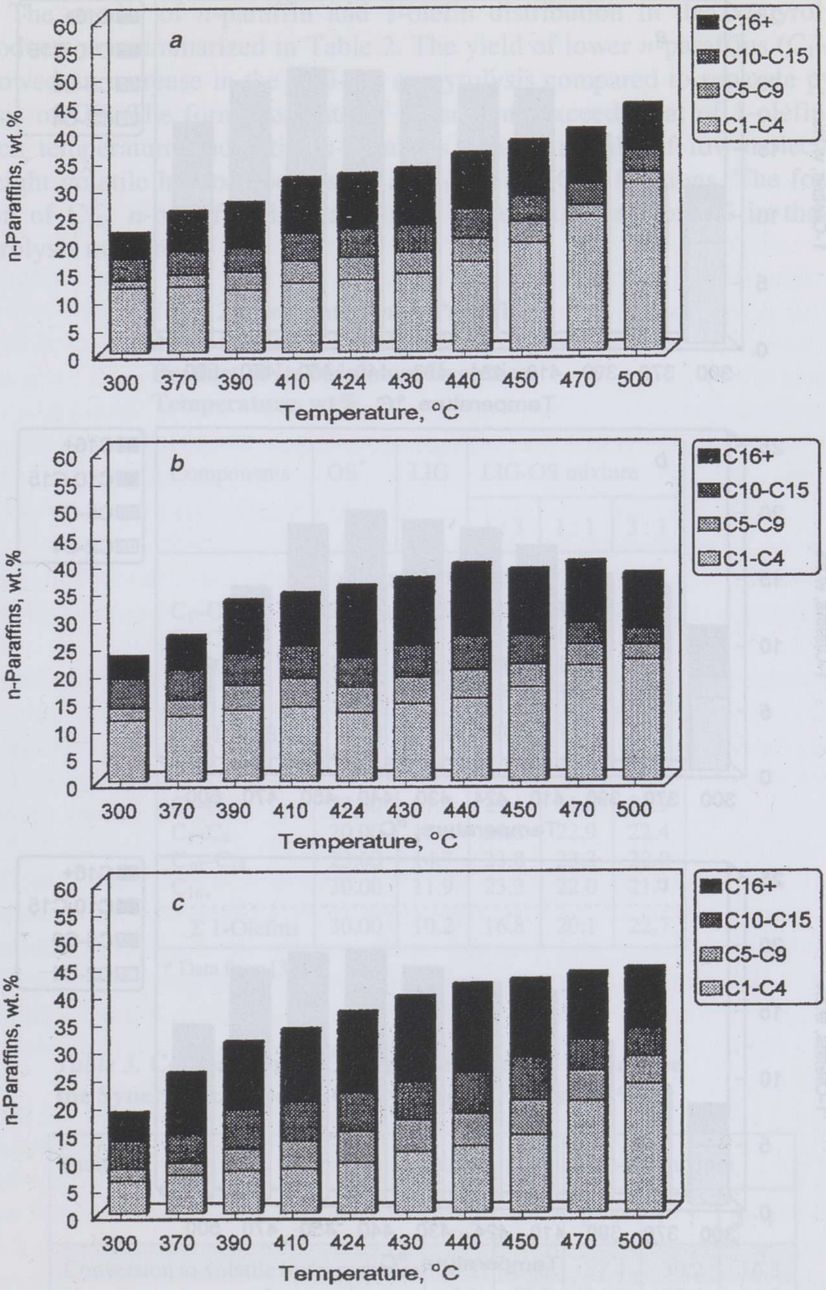

Fig. 6. Distribution of *n*-paraffins in co-pyrolysis products by C number for LIG-OS mixtures of different total carbon ratios: 3 : 1 (*a*), 1 : 1 (*b*) and 1 : 3 (*c*)

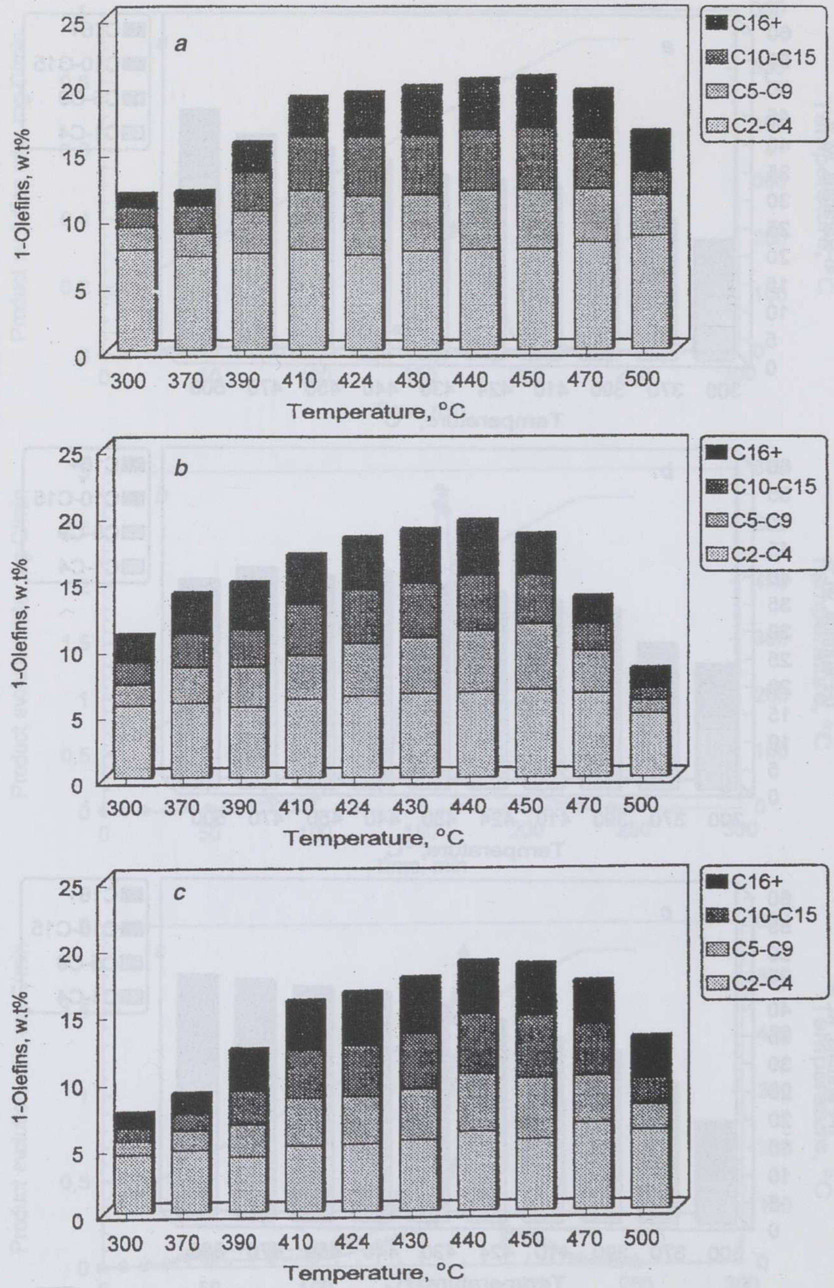

Fig. 7. Distribution of 1-olefins in co-pyrolysis products by C number for LIG-OS mixtures of different total carbon ratios: 3 : 1 (*a*), 1 : 1 (*b*) and 1 : 3 (*c*)

The results of *n*-paraffin and 1-olefin distribution in the co-pyrolysis products are summarized in Table 2. The yield of lower *n*-paraffins (C_1–C_4) showed an increase in the LIG-OS co-pyrolysis compared to separate pyrolysis of OS. The formation rate of *n*-paraffins exceeds that of 1-olefins at each temperature and ratio. *n*-Paraffins consist mainly of low-molecular-weight volatile hydrocarbons such as C_1–C_4 and C_{16+} fractions. The formation of C_{16+} *n*-paraffins increases with increasing share of OS in the co-pyrolysis mixture.

Table 2. **Distribution of *n*-Paraffins and 1-Olefins in LIG-OS Co-Pyrolysis Product at Its Maximum Evolution Temperature, wt%**

Components	OS*	LIG	LIG-OS mixture		
			1 : 3	1 : 1	3 : 1
n-Paraffins					
C_1–C_4	25.00	57.0	31.3	35.8	51.1
C_5–C_9	21.00	8.3	13.7	12.2	12.2
C_{10}–C_{15}	19.00	9.2	19.1	15.3	13.7
C_{16+}	35.00	25.5	35.9	36.7	23.0
Σ *n*-Paraffins	40.00	32.4	40.9	36.0	35.0
1-Olefins					
C_2–C_4	27.00	57.8	29.1	31.8	33.9
C_5–C_9	20.00	15.6	23.8	22.9	22.4
C_{10}–C_{15}	23.00	14.7	23.8	23.3	22.0
C_{16+}	30.00	11.9	23.3	22.0	21.7
Σ 1-Olefins	30.00	10.2	16.8	20.1	22.7

* Data from [3].

Table 3. **Comparison of Conversion Levels to Determine the Synergistic Effect in Co-Pyrolysis Processing, %**

Indices	LIG	OS*	LIG-OS mixture		
			1 : 3	1 : 1	3 : 1
Conversion to volatile hydrocarbons	8.2	47.0	37.4	30.2	16.3
Hypothetical mean of conversion	8.2	47.0	34.2	27.6	21.0
Difference	0.0	0.0	+ 3.2	+ 2.6	− 4.7
Standard deviation σ	0.2	0.1	0.3	0.2	0.3
Conversion to coke	44.0	34.0	33.2	37.7	45.8

* Data from [3].

The effect of OS ratios on the conversion of LIG was evaluated by comparing the experimental values with the hypothetical mean of the conversion level. The values of conversion level given in Table 3 are averages of five replications for each co-processing. The standard deviation σ for the experimental conversion values are also reported in Table 3. When the difference between the experimental value and hypothetical mean was positive, co-processing of the two materials enhanced their reactivity resulting in their higher conversion compared to individual reactions. The desired end result of co-processing was to reach higher conversion of initial matter to volatile organic products.

The experimental conversion levels were determined by numerical integration of each curve shown in Fig. 5. The hypothetical conversion levels were calculated by considering both individual conversion values and the weight ratios LIG : OS of the co-pyrolysis samples. The results of the hypothetical and experimental conversion to volatile organic compounds (*n*-paraffins, 1-olefins, *iso*-paraffins, branched olefins and some aromatic compounds) are given in Table 3. As one can see, the differences were found positive for higher ratios of OS in the mixture, and synergistic effect of co-processing was determined. The difference was found negative only for the ratio 3 : 1.

Pyrolysis of Turkish oil shale and lignite has been investigated by Okutan et al. [13]. The experiments of co-pyrolysis of Göynük oil shale and Yatagan lignite in weight ratios of 1 : 0; 1 : 2; 1 : 1; 2 :1, and 0: 1 have been studied and tar yields determined. They found that the ratios oil shale–lignite 1 : 1 and 2 : 1 were 25 and 32 % tar, respectively. The yields obtained at their separate pyrolysis were 21 and 24 %, respectively [13].

The effect of lignite addition on the pyrolysis of Turkish oil shale has been investigated also by Ekinci et al. [11]. They found that oils obtained were highly aliphatic and assumed that the precursor of oils pyrobitumen formed during initial stages of pyrolysis was a relatively poor solvent for the lignite structure. They reported that the oil yield was the highest for the oil shale : lignite mass ratio 3 : 1. Relatively large amounts of oil shale are required as compatibility between OS and LIG is relatively poor.

For LIG-OS co-processing, the amounts of organic carbon in the solid residue are calculated and also given in Table 3. The amount of carbon deposit decreased with increasing the ratios of OS. It can be explained by thermal decomposition characteristics of oil shales. Thermal decomposition of oil shale kerogen occurs in two broad reaction steps. The first step is the breakdown of kerogen to bitumen and decomposition of bitumen into gas and oil. Formation of heavy fraction by secondary reactions takes place in the second step [17–19]. In the co-pyrolysis process, OS pyrolysis products are reasonably effective in partly preventing retrogressive char-forming reactions of the lignite [11].

In this study, straight- and branched-chain paraffins and olefins from methane to C_{30}, and aromatic hydrocarbons such as benzene, toluene, ethylbenzene, propylbenzene, cumene, phenol, trimethylbenzene were also observed in the chromatogram. The analysis method used did not allow to detect polyaromatics such as preasphaltenes (pyridine-soluble and benzene-insoluble materials) and asphaltenes (benzene-soluble and hexane-insoluble materials) fractions in the pyrolysis products. For this reason, the discrepancy in the carbon balance was assigned to alsphaltenic, preasphaltenic hydrocarbons and CO_2 evolved during co-pyrolysis. According to the literature, the total amount of asphaltenes and preasphaltenes in pyrolysis of lignite is 40–70 wt% [13, 17], and the total amount of aromatic hydrocarbons in the pyrolysis products of OS was found to be 19 wt.% [20].

The oil shale and lignite co-pyrolysis products comprise a wide range of alkanes, alkenes, aromatics and polar components. The excellent resolving power of capillary GC makes it the method of choice for such complex analyses, and MS detection provides a means of identifying the eluted compounds. However, the samples are often so complex that even capillary GC is incapable of fully resolving all the components. In this instance, preseperation into chemical class fractions by normal-phase liquid chromatography (LC) before GC is desirable. Excellent aliphatic/aromatic separation may be obtained with silica-packed LC columns [21], but bare silica is less effective in resolving the alkane/alkene overlap of aliphatic fractions.

Alkenes are of special interest because they are unstable and cause problems in processing the lignite. Argentation chromatography, using silica modified with silver ion (Ag^+), effectively isolates the alkene fraction from the other components by taking advantage of charge transfer complexes formed between Ag^+ and alkene double bonds [22, 23].

The advantage of ampoule technique used in this study is no need for special handling of the pyrolysis products to separate the alkene and alkane fractions. Direct sampling of pyrolysis products from the total stream into evacuated ampoules allowed us to determine alkene and alkane fractions quantitatively. However, even this technique does not allow full resolution of all the components because of the complex character of the pyrolysis mixture.

Conclusions

The temperature of maximum product release was found to be approximately 440 °C for each co-pyrolysis operation. Straight- and branched-chain paraffins and olefins from methane to C_{30} and small aromatic hydrocarbons such as benzene, toluene, ethyl benzene, propylbenzene, cumene, phenol, trimethyl benzene were also observed in the chromatogram. The analysis method used did not allow to characterize polyaromatics such as preasphaltenes (pyridine-soluble and benzene-insoluble materials) and asphaltenes (benzene-soluble and hexane-insoluble materials) in the pyrolysis products. For this reason, the discrepancy in the carbon balance was assigned to alsphaltenic, preasphaltenic hydrocarbons and CO_2 evolved during the pyrolysis of lignite.

The share of *n*-paraffins exceeded that of 1-olefins at each temperature studied. Co-pyrolysis of LIG-OS mixture yielded more C_{16+} *n*-paraffins and less coke with increasing OS ratios. *n*-Paraffins were found to consist mainly of C_1–C_9, C_{16+} and to contain relatively small amounts of the C_{10}–C_{15} fractions. Synergistic effect of the components on pyrolysis was determined.

The experimental results indicated that the pyrobitumen, the precursor of oils, produced from oil shale at the initial stages of pyrolysis, is expected to be a relatively poor solvent for the coal structure.

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