CO-PYROLYSIS OF TURKISH SOMA LIGNITE AND ŞIRNAK ASPHALTITE.
ANALYSIS OF CO-PYROLYSIS PRODUCTS BY CAPILLARY GAS CHROMATOGRAPHY TOTAL STREAM SAMPLING TECHNIQUE

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Temperature-programmed co-pyrolysis of Turkish Soma lignites and Şırnak asphaltite was investigated with the aim to determine the volatile product distribution and product evolution rate of co-processing. A series co-pyrolysis operation was performed using three total carbon ratios of lignite to ashpaltite. A fixed-bed reactor was used to pyrolyse small samples of mixtures under an inert gas (argon) flow. A special sampling technique was used for collecting organic products eluted from the reactor 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 Soma lignites and Şırnak asphaltite 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.

Introduction

Generally asphaltic materials are formed by petroleum migration and solidification in cracks during tectonic movements [1, 2]. During and after the migration, petroleum undergoes a series of complex chemical and physical changes and loses its light components in gaseous form.

Mineral Research and Exploration Institute has determined over 60 million tons of asphaltite reserves in different areas in Turkey. Avgamasya-Mardin (14 million tons) is the largest asphaltite deposit located in south-

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eastern Anatolia. There occur also other sources of asphaltite – Silopi-Mardin and Şırnak-Siirt [1–3]. Different veins of asphaltic materials have different physical and chemical characteristics depending on the location of asphaltic material, geological formation and metamorphosis degree. As for the thermal formation, Turkish asphaltite is mostly classified between as-phaltite and asphaltic pyrobitumen. The asphaltite reserves are reported to contain 1–5.3 wt.% water, 33–45 wt.% ash, 4.1–6.4 wt.% sulfur, 24–40 wt.% volatile matter, 47–59 wt.% fixed carbon, and 3.2–5.6 wt.% hydrogen. Their average solubility in CS_2 is 4.9–30 wt.%. The spread of analytical data of the parameters indicates that the asphaltites similar to Turkish coal show chang-ing characteristics [1–4].

Bituminous coal and lignite are the most abundant naturally occurring fossil fuels in Turkey. It has been estimated that the reserves of coal amount to 1.5 billion tons and those of lignite to 8.4 billion tons [1, 3].

It has been suggested that the addition of asphaltite to coal during lique-faction may result in an enhanced conversion of coal and production of oil compared to the yields obtained when coal alone is processed. The argument for this synergistic effect is different origin of coal and asphaltite, and the effects due to alteration of the original oil during asphaltite formation are proved by the content and analysis of n-paraffins and 1-olefins. A smooth distribution of n-alkanes and 1-olefins and the predominance of C_5–C_{15} series in the pyrolysis product both indicate the effect of their different origin. The analysis of products collected at different time intervals during asphaltite pyrolysis indicated also a change in the C-number distribution of n-paraffins and 1-olefins. The n-paraffin formation rate is higher than that of 1-olefins at each temperature and ratio. n-Paraffins formed consist mainly of low-molecular-weight hydrocarbons such as C_1–C_4. The C_5–C_9 and C_{10}–C_{15} frac-tions formed from asphaltite were found to be larger than those formed from coal [3].

The pyrolysis products of asphaltite formed during initial stages of pyro-lysis are expected to be a relatively poor solvent for the lignite structures. We may also expect that the mineral matter of asphaltite plays the role of a catalyst during the thermal conversion process. However, the data of pyroly-sis oil from Turkish asphaltite are similar to those of oil from Turkish coal, in spite of the fact that the mineral matter of the asphaltite formation differs from that of lignite, which has low ash content (of about 20 %) [1, 3].

In this study, the temperature-programmed co-pyrolysis of lignite (LIG) and asphaltite (ASP) was investigated by a new, highly efficient sampling technique developed by Schulz et al. [4] and described in detail in our previ-ous paper in OIL SHALE [5].

The objective of this study was to determine the temperatures at which the product evolution rate is maximum, and to classify n-paraffins and 1-olefins in the co-pyrolysis product by carbon number at each desired tem-perature. The recovery of total organic carbon of the co-pyrolysis sample mixture as aliphatic hydrocarbons was determined and compared with the

recovery in the pyrolysis of separate LIG and ASP samples. The effect of ASP ratios on the co-processing of LIG and ASP was determined by calculating the difference between the experimental and the hypothetical mean value of conversion of total organic carbon to volatile products.

Experimental

Samples

The investigations were performed with **lignite** samples taken from the deposit near Soma of the Manisa Province and **asphaltite** samples taken from the deposit in the Şırnak Province. The results of proximate and ultimate analysis of Soma lignite are given in [5], those of Şırnak asphaltite are as follows (data from [3]), wt.%:

Ultimate analysis (dry basis): C^d_t 40.2; C^d_o 39.0; C^d_M 1.2; H^d 3.2; N^d 0.5; S^d_t 4.8

Proximate analysis (as received): moisture W^r 1.4; ash A^r 38.4; volatile matter V^r 35.1; fixed carbon 25.1

The samples were crushed and ground in a jaw mill until the desired particle size was obtained, sieved to obtain a <0.1-mm fraction and dried at 105 °C under the N_2 atmosphere.

The samples of LIG–ASP mixtures were prepared to get three total carbon weight ratios:

LIG–ASP	LIG, g	ASP, g
1 : 3	0.12	0.36
1 : 1	0.19	0.29
3 : 1	0.20	0.27

Co-Pyrolysis Procedure

The experiment protocol and product analysis technique are described in [5–11].

Results and Discussion

The chromatograms of the products of LIG and ASP pyrolysis [3] and their co-pyrolysis products (LIG–ASP total carbon weight ratio 1 : 1) are shown in Figs 1–3. The major constituents of the organic compounds obtained at maximum evolution temperatures during the temperature-programmed pyrolysis are given in Table 1. The effects of temperature and time on the rate of total product evolution are shown in Fig. 4. The temperature at which the product evolution is greatest was found to be ~ 435 °C for each co-pyrolysis operation.
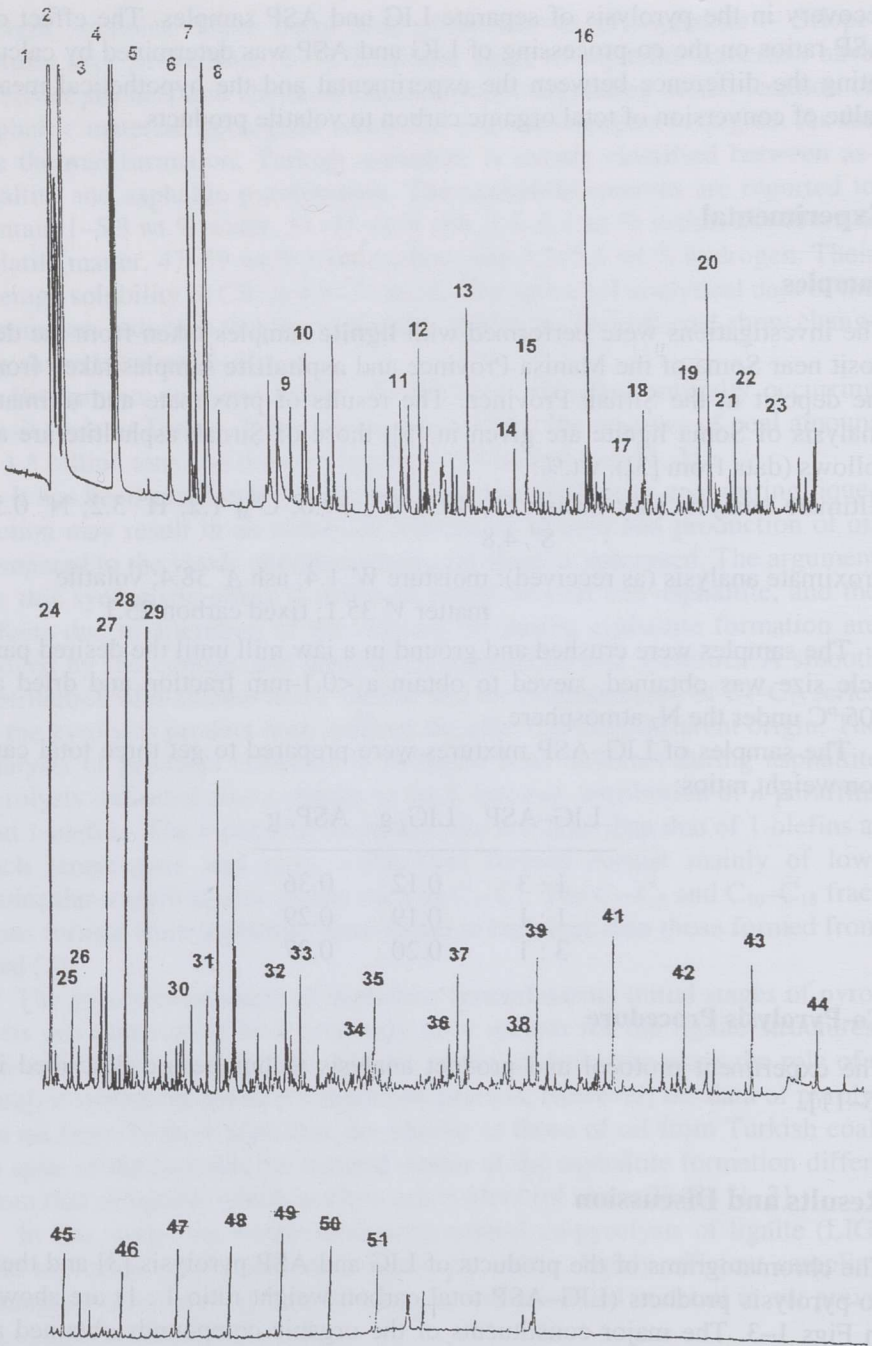
Fig. 1. Gas chromatogram of organic products at maximum evolution temperatures during temperature-programmed pyrolysis of LIG; numbers *1–51* indicate the major organic compounds (see Table 1) [3]
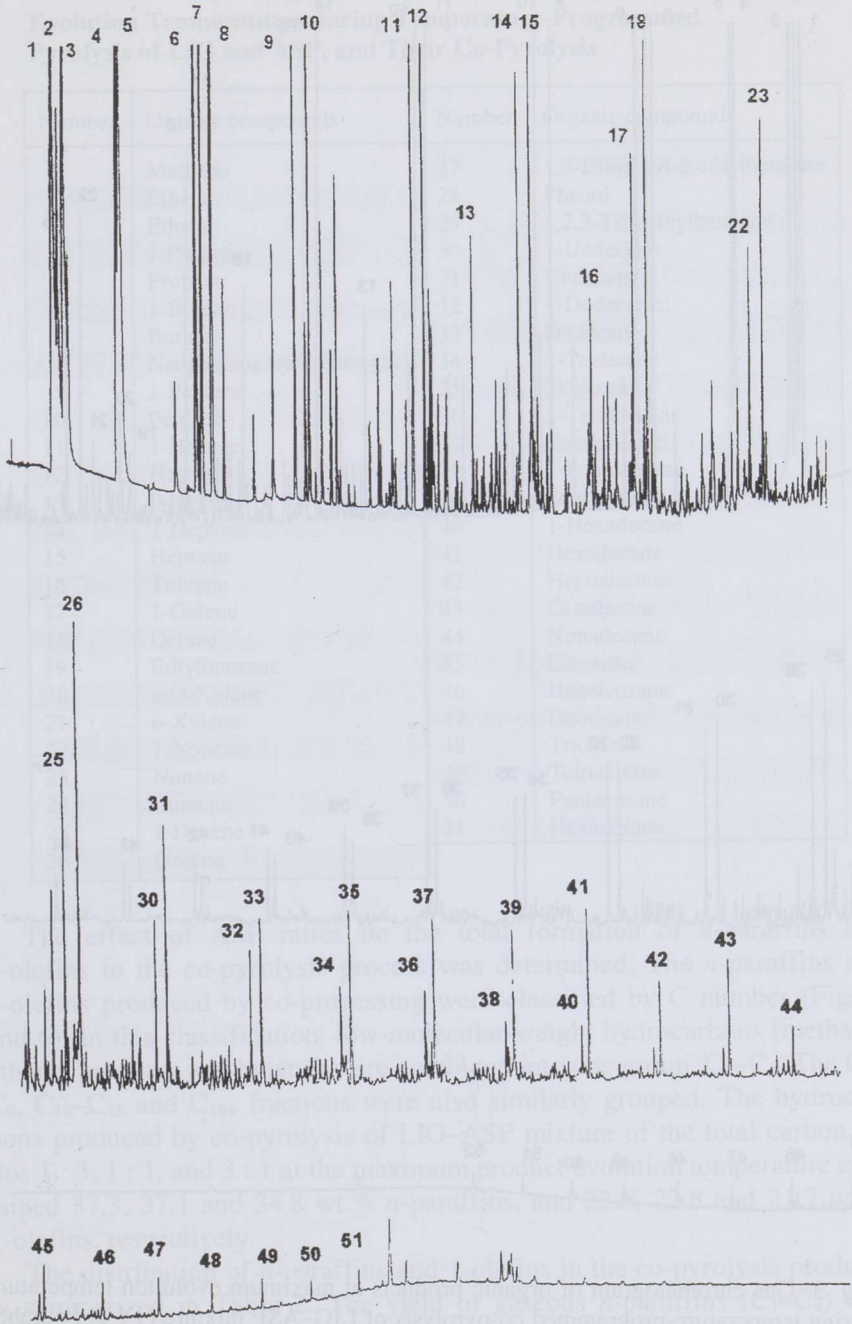
Fig. 2. Gas chromatogram of organic products at maximum evolution temperatures during temperature-programmed pyrolysis of ASP; numbers *1–51* indicate the major organic compounds (see Table 1) [3]
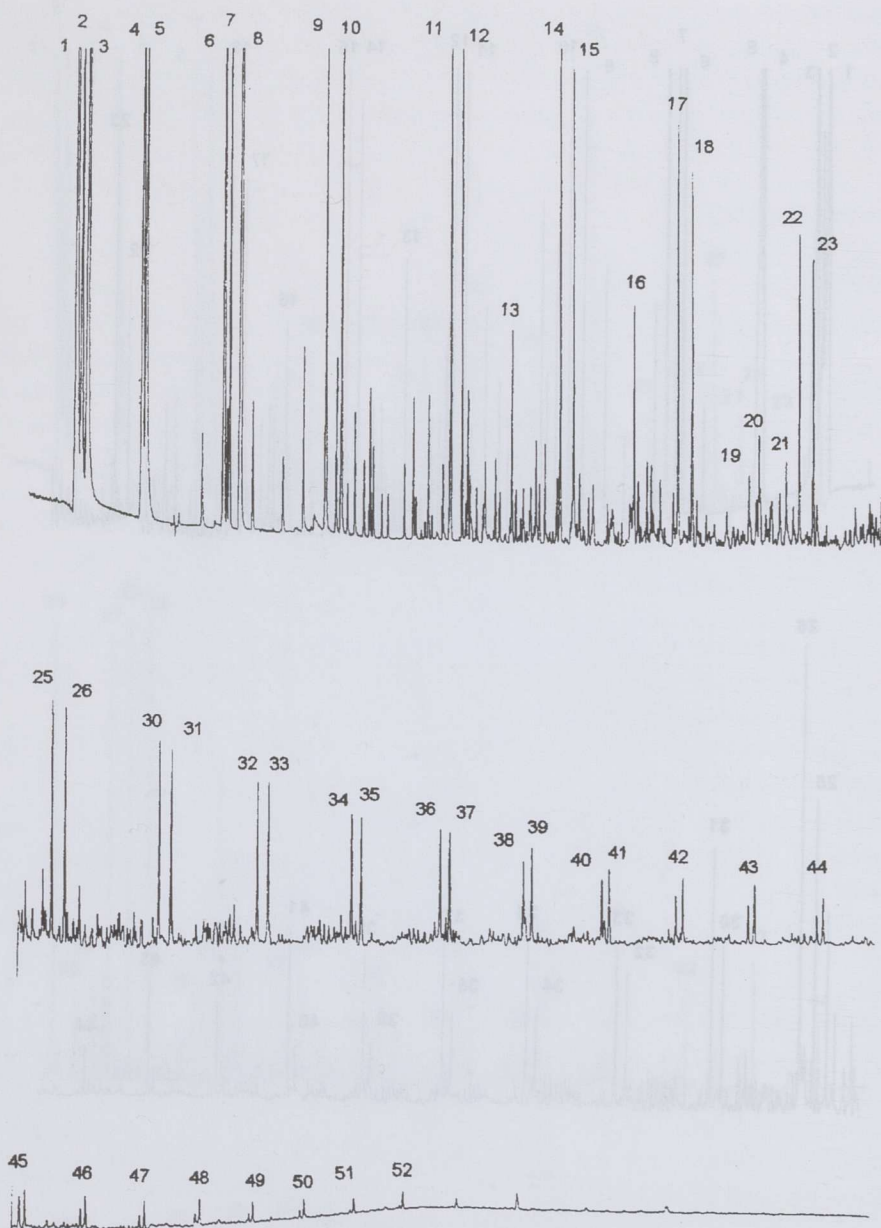
Fig. 3. Gas chromatogram of organic products at maximum evolution temperatures during temperature-programmed co-pyrolysis of LIG–ASP mixture (1 : 1) ; numbers *1–51* indicate the major organic compounds (see Table 1) [3]

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

Number	Organic compounds	Number	Organic compounds
1	Methane	27	1,3-Dimethyl-2-ethylbenzene
2	Ethene	28	Phenol
3	Ethane	29	1,2,3-Trimethylbenzene
4	1-Propene	30	1-Undecene
5	Propane	31	Undecane
6	1-Butene	32	1-Dodecene
7	Butane	33	Dodecane
8	Neopentane (reference gas)	34	1-Tridecene
9	1-Pentene	35	Tridecane
10	Pentane	36	1-Tetradecane
11	1-Hexene	37	Tetradecane
12	Hexane	38	1-Pentadecene
13	Benzene	39	Pentadecane
14	1-Heptene	40	1-Hexadecene
15	Heptane	41	Hexadecane
16	Toluene	42	Heptadecane
17	1-Octene	43	Octadecane
18	Octane	44	Nonadecane
19	Ethylbenzene	45	Eicosane
20	*m/p*-Xylene	46	Heneicosane
21	*o*-Xylene	47	Docosane
22	1-Nonene	48	Tricosane
23	Nonane	49	Tetracosane
24	Cumene	50	Pentacosane
25	1-Decene	51	Hexacosane
26	Decane		

The effect of ASP ratios on the total formation of *n*-paraffins and 1-olefins in the co-pyrolysis process was determined. The *n*-paraffins and 1-olefins produced by co-processing were classified by C number (Figs 5 and 6). In 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 similarly grouped. The hydrocarbons produced by co-pyrolysis of LIG–ASP mixture of the total carbon ratios 1 : 3, 1 : 1, and 3 : 1 at the maximum product evolution temperature contained 37.3, 37.1 and 34.8 wt.% *n*-paraffins, and 22.6, 22.8 and 21.7 wt.% 1-olefins, respectively.

The distribution of *n*-paraffins and 1-olefins in the co-pyrolysis products is summarized in Table 2. The yield of gaseous *n*-paraffins ($C_1–C_4$) was higher in the case of co-pyrolysis compared to LIG separate processing. The *n*-paraffin formation rate is higher than that of 1-olefins at each temperature and ratio. *n*-Paraffins consist mainly of low-molecular-weight volatile hydrocarbons such as $C_1–C_{15}$, the higher the ASP ratio the more $C_{1–15}$ *n*-paraffins are formed.
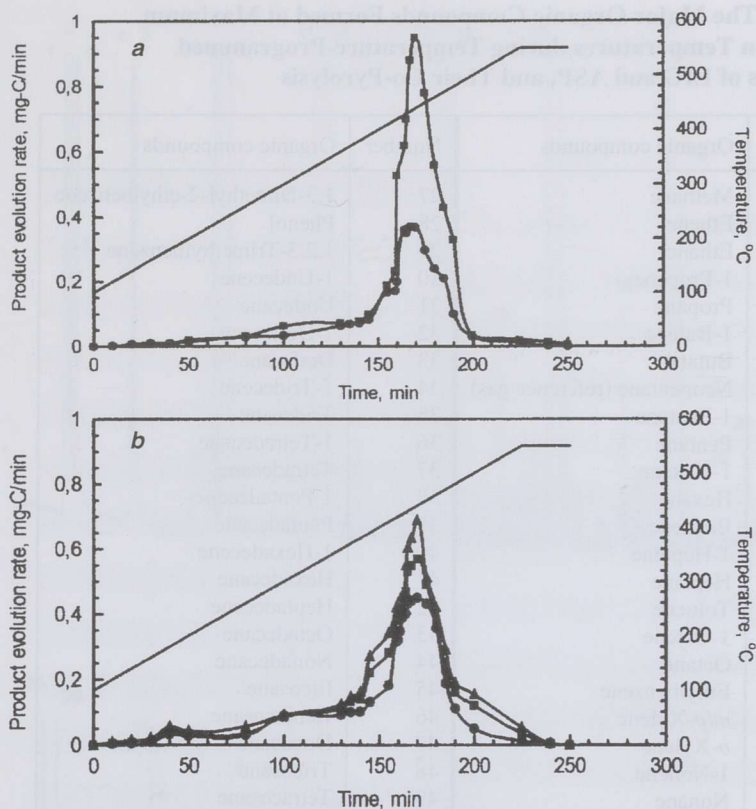
Fig. 4. Total product evolution rate of LIG and ASP (*a*) [3], and their mixture (*b*): LIG–ASP ratio 3 : 1 (●), 1 : 1 (■) and 1 : 3 (▲) as a function of temperature (straight line) and time

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

Components	LIG	ASP	LIG–ASP mixture		
			1 : 3	1 : 1	3 : 1
n - P a r a f f i n s					
C_1–C_4	57.0	47.8	59.2	61.9	60.3
C_5–C_9	8.3	26.2	23.1	16.7	7.5
C_{10}–C_{15}	9.2	16.9	11.8	10.7	6.9
C_{16+}	25.5	9.2	5.9	10.5	25.3
Σ*n*-paraffins	32.4	30.1	37.3	37.1	34.8
1 - O l e f i n s					
C_2–C_4	57.8	42.1	46.4	46.0	40.0
C_5–C_9	15.6	33.1	31.0	29.2	27.1
C_{10}–C_{15}	14.7	18.0	14.2	14.2	14.2
C_{16+}	11.9	6.8	8.4	10.6	18.7
Σ1-olefins	10.2	16.6	22.6	22.8	21.7

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

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

Indices	LIG	ASP	LIG–ASP mixture		
			1 : 3	1 : 1	3 : 1
Conversion to volatile hydrocarbons	8.2	17.0	15.7	13.7	13.0
Hypothetical mean of conversion	8.2	17.0	14.1	11.9	11.1
Difference	0.0	0.0	+1.6	+1.8	+1.9
Standard deviation σ	0.2	0.1	0.3	0.2	0.4
Conversion to coke	44.0	15.1	30.5	34.7	39.6

The experimental conversion levels were determined by numerical integration of each curve shown in Fig. 4 and the hypothetical ones were calculated by considering both individual conversion values and the LIG–ASP weight ratios in the co-pyrolysis samples. The results of the hypothetical and experimental conversion to volatile organic compounds (*n*-paraffins, 1-olefins, *iso*-parafins, branched olefins and some aromatic compounds) are given in Table 3. As one can see, the differences were found slightly positive for all ratios, and a slight synergistic effect of co-processing was determined. The earth alkali metal cations such as calcium and magnesium can act as pyrolysis promoter for coal conversion, but in the co-pyrolysis reactions the inhibition effect of the silicate minerals originally present in asphaltite seems to be greater than the catalytic effect of carbonates.

The effect of the mineral matrix of Turkish coal and oil shales on conversion of the organic matrix to organic products was also investigated by Karabakan *et al.* [12]. It was found that pyrolysis reactions were catalysed by alkaline earth metal cations of carbonates and inhibited by silicates. The interaction reaction of alkaline earth metal cations with –COOH and –OH functional groups possibly result in the formation of the alkaline M^{2+}–O surface groups. These groups have been proposed to be active sites on the coal and oil shale surface and, therefore, the alkaline earth metal cations may have some catalytic effect in the pyrolysis reactions of the organic structure [12–14].
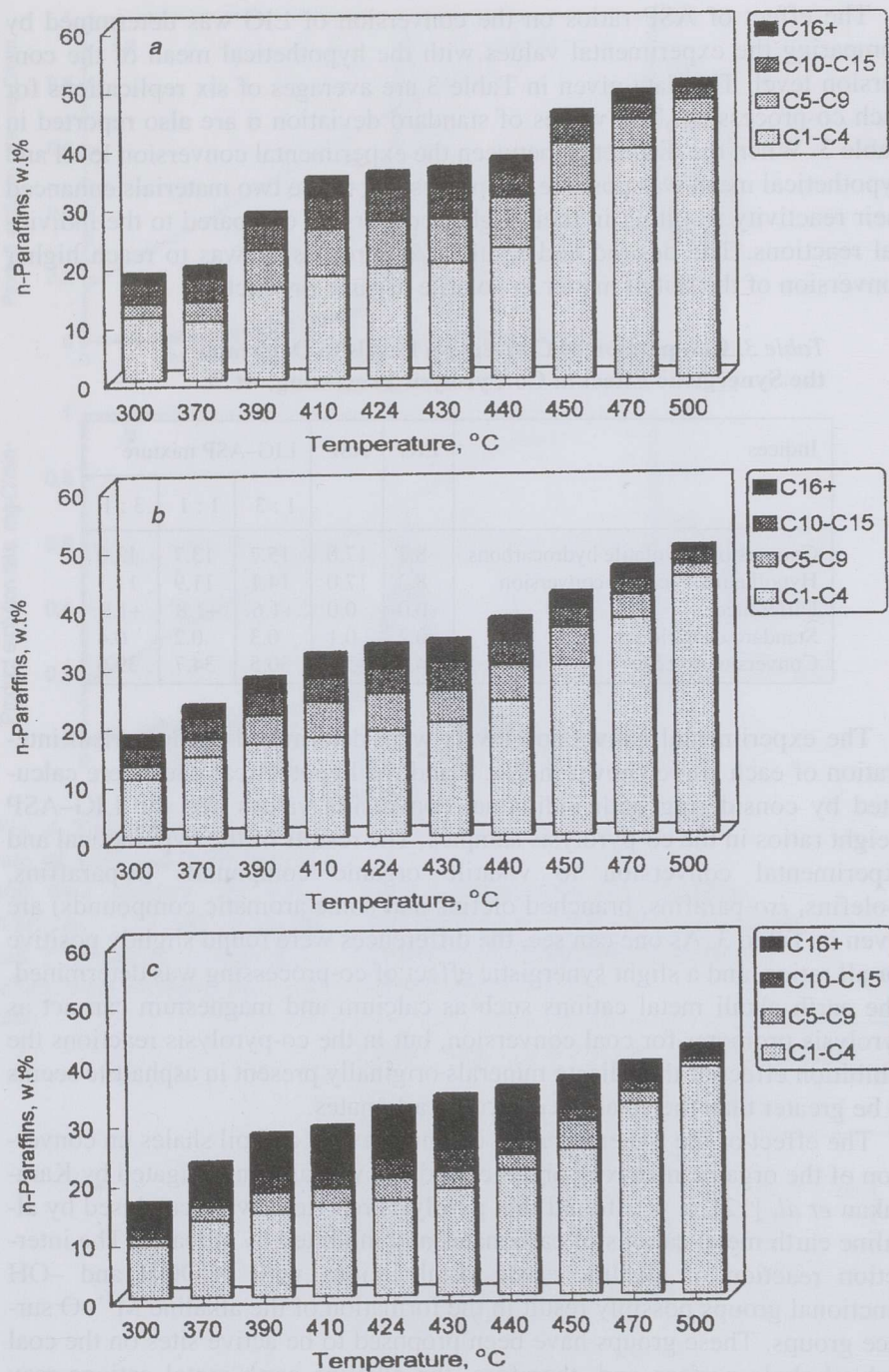
Fig. 5. Distribution of *n*-paraffins in co-pyrolysis product formed at maximum product evolution temperature by C number for mixtures of different total carbon ratios: 1 : 3 (*a*), 1 : 1 (*b*) and 3 : 1 (*c*)
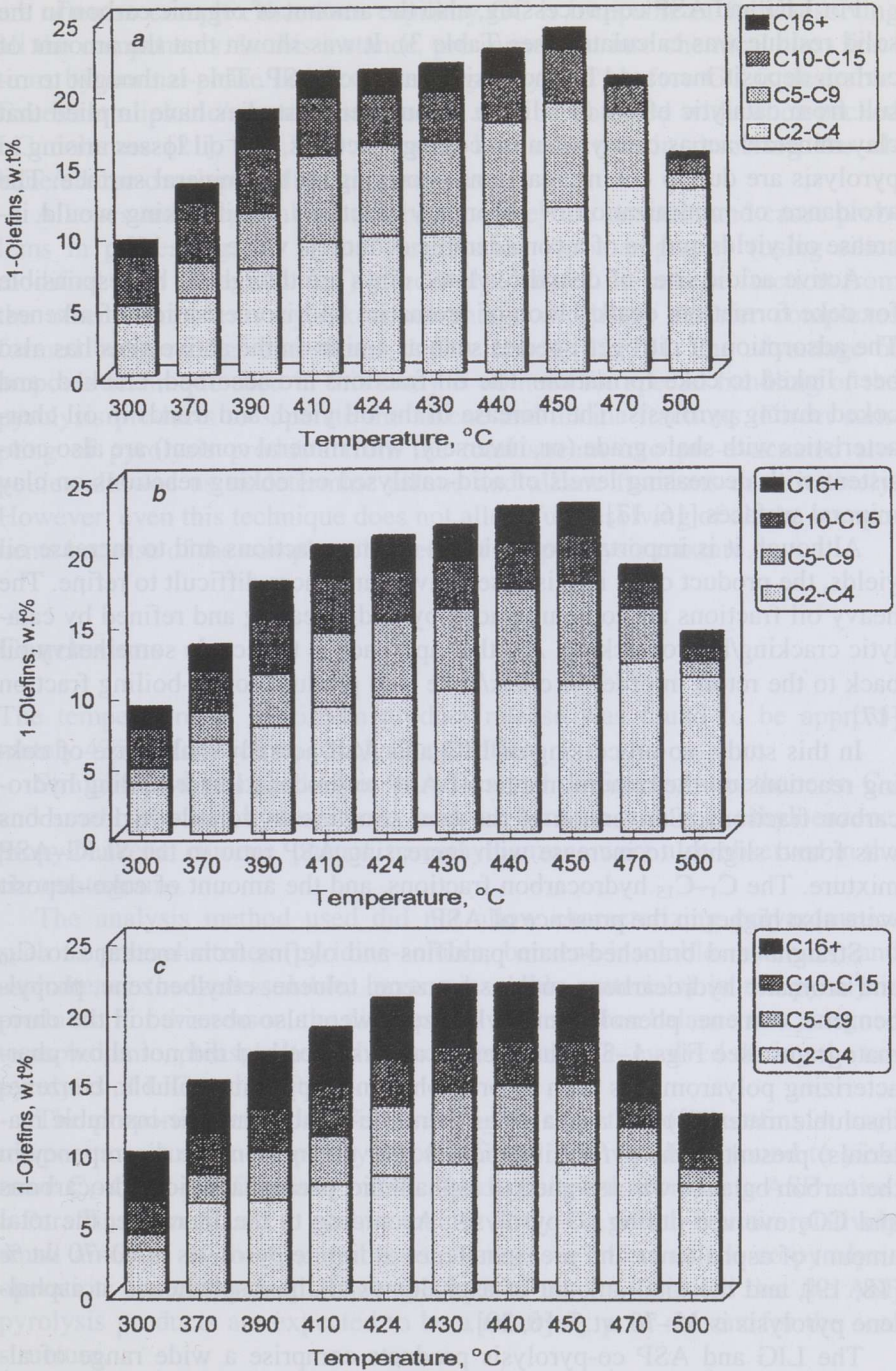
Fig. 6. Distribution of 1-olefins in co-pyrolysis product formed at maximum product evolution temperature by C number for mixtures of different total carbon ratios: 1 : 3 (*a*), 1 : 1 (*b*) and 3 : 1 (*c*)

For LIG and ASP co-processing, also the amount of organic carbon in the solid residue was calculated (see Table 3). It was shown that the amount of carbon deposit increased by increasing ratios of ASP. This is thought to result from catalytic effect of silicate. A number of studies have implied that clay minerals act as catalysts in oil coking reactions, and oil losses arising in pyrolysis are due to coking reactions occurring on the mineral surface. The avoidance or minimization of secondary reactions at oil coking would increase oil yields and be of a considerable economic value [15, 16].

Active acidic sites of dehydroxylated clays are thought to be responsible for coke formation, dealkylation of aromatics and isomerisation of alkenes. The adsorption of nitrogen species such as amine on the active sites has also been linked to coke formation. The oil fractions are adsorbed, cracked, and coked during pyrolysis. The increase in the oil yield, and trends in oil characteristics with shale grade (or, inversely, with mineral content) are also consistent with decreasing levels of acid-catalysed oil coking reactions on clay mineral surfaces [16, 17].

Although it is important to avoid oil-coking reactions and to increase oil yields, the product oil is in this case heavier and more difficult to refine. The heavy oil fractions are to be upgraded by hydrotreating and refined by catalytic cracking/hydrocracking. Another approach is to recycle some heavy oil back to the retort in order to crack/coke it to produce lower-boiling fraction [17].

In this study, co-processing of LIG and ASP actually makes use of coking reactions on the mineral matter of ASP to produce lower-boiling hydrocarbon fractions. Conversion of the coal structure to volatile hydrocarbons was found slightly to increase with increasing ASP ratio in the SLIG–ASP mixture. The C_1–C_{15} hydrocarbon fractions, and the amount of coke deposit were also higher in the presence of ASP.

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 chromatograms (see Figs 1–3). The present analysis method 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 asphaltenic, preasphaltenic hydrocarbons and CO_2 evolved during co-pyrolysis. According to the literature, the total amount of asphaltenes and preasphaltenes at lignite pyrolysis is 40–70 wt.% [18, 19], and the total amount of asphaltenes and preasphaltenes at asphaltene pyrolysis is 45–70 wt.% [6, 20].

The LIG and ASP co-pyrolysis products comprise a wide range of alkanes, alkenes, aromatics and polar components. The excellent resolving power of capillary gas chromatography (GC) makes it the method of choice for such complex analyses, and mass spectroscopic detection provides a means of positively 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, pre-separation 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 pre-evacuated ampoules allowed us to determine alkene and alkane fractions quantitatively. However, even this technique does not allow full resolving 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 435 °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, ethylbenzene, propylbenzene, cumene, phenol, trimethylbenzene were also observed in the chromatograms.

The analysis method used did not allow characterizing polyaromatics such as preasphaltenes (pyridine-soluble, benzene-insoluble materials) and asphaltenes (benzene-soluble, hexane-insoluble materials) in the pyrolysis products. For this reason, the discrepancy in the carbon balance was assigned to asphaltenic, preasphaltenic hydrocarbons and CO_2 evolved during the co-pyrolysis of LIG and ASP.

The proportion of n-paraffins was higher than that of 1-olefins at each temperature studied. Co-pyrolysis of LIG and ASP has been found to yield more C_1–C_{15} n-paraffins and more coke deposit with increasing ASP ratios. n-Paraffins were found to consist mainly of C_1–C_{15} and to contain relatively small amounts of the C_{16+} fractions. Synergistic effect of the co-pyrolysis operation was determined. The experimental results indicated that the ASP pyrolysis products are expected to be a relatively poor solvent for the coal structure.

Acknowledgements

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