

CLASSIFICATION OF VOLATILE PRODUCTS EVOLVED AT FAST CO-PYROLYSIS OF GÖYNÜK OIL SHALE WITH LOW DENSITY POLYETHYLENE

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Fast co-pyrolysis of Göynük oil shale (GOS) with low density polyethylene (LDPE) was investigated. The aim of the research was to determine the distribution of volatile products and conversion of blends at different temperatures and time intervals. Pyrolysis of oil shale, LDPE and co-pyrolysis of oil shale-LDPE blend of the total carbon ratio of 1:1 were performed by using the fast pyrolysis method in an isothermal pyrolysis reactor. Volatile organic products eluted from the reactor were collected at different temperatures and time intervals by using a special sampling technique. Fast pyrolysis products were analyzed by capillary gas chromatography. In the aliphatic fraction of pyrolysis products, n-paraffins and 1-olefins were classified by their carbon number. The effect of co-pyrolysis on conversion of total organic carbon into volatile products was identified by determination of the experimental and the hypothetical mean values. Possible synergetic effect was investigated by comparing the results on fast pyrolysis of GOS and LDPE. The effect of co-processing of GOS with LDPE was determined by calculating the difference between experimental and hypothetical mean value of conversion of total organic carbon into volatile products. The experimental conversion of the blend to volatile hydrocarbons was found to be lower than hypothetical mean value of conversion at co-pyrolysis, and thus, no synergetic effect was observed.

Introduction

One of the most important concerns of the world is the energy production. Many aspects have to be considered to meet future demands and current needs on energy. These aspects cover exploration of new reserves, new

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techniques for efficient utilization of resources and searching the evaluation possibilities of alternative resources.

The oil and natural gas reserves in Turkey are in minor scale, and solid fossil fuels account for primary energy sources. From 1990 to 2001, the energy consumption of Turkey was recorded to increase from 53 to 77 Mtoe (million tonnes of oil equivalent). Oil shales are the second largest fossil fuel potential of Turkey. Oil shale deposits in Turkey are widely distributed in middle and western Anatolia. Oil shales in Turkey are of Paleocene-Eocene and Middle-Upper Miocene age [1–3]. The main oil shale deposits in Turkey are Beypazarı (Ankara), Seyitömer (Kütahya), Himmetoğlu (Bolu) and Hatildağ (Bolu) with total reserves (geological and possible) of 327, 122, 65 and 467 million tonnes, respectively. The amount of explored reserves in Turkey is nearly 2.22 billion tonnes [4, 5].

Oil shale covers a mixture of tightly bound organic (bitumen and kerogen) and inorganic (quartz, clay, carbonates, pyrite and trace elements) matrix. Insoluble organic fraction of oil shale is called kerogen. Bitumen and/or prebitumen can exist in relatively low amounts. Type of kerogen can change from deposit to deposit because of variations in the amounts of organic carbon, hydrogen and oxygen.

The organic material in both tar sand and oil shale is characterized by H/C mole ratio about 1.5, which is close to that of crude oil and about twice of coal. For this reason processing of oil shale and tar sands to produce liquid fuels is considerably simpler than obtaining liquid fuel from coal [6].

Search for reducing undesired environmental effects of plastic wastes has give rise to the idea of performing co-pyrolysis of plastic wastes with oil shale. There is a considerable interest in the efficient conversion of plastic waste mixed with oil shale into clean hydrocarbon fuel or other valuable products.

The disposal of municipal and industrial waste is now recognized to be a major environmental problem throughout the world. Municipal waste consists largely of paper and woody materials to the extent of 59–63%. Another and even more troublesome component of waste streams is plastics, as they are biodegradable at present. Of the organic waste stream, remaining after removal of glass, metals, etc., plastics are about 9–12% by weight. In addition to the plastics present in municipal waste streams, many wastes collected from manufacturing or service industries may contain much more plastics [7]. Thermal decomposition of polymers to produce petrochemical feedstock is often considered for addition polymers such as polyethylene, polypropylene, polystyrene and polyvinylchloride. These processes may accept mixed and contaminated waste streams without or with minimal cleaning, and products are useful as monomers and liquid or gaseous fuels [8]. Co-pyrolysis of heavy shale oil with polyethylene waste in an autoclave at various temperatures and times has been studied, and it was found that co-pyrolysis improves the quality of oil and gives possibility to convert the wastes into liquid fuels [9].

Considering the facts stated above, this study concerns co-pyrolysis of Göynük oil shale with LDPE by using the fast pyrolysis method. The aim of the study was to determine the volatile product distribution profile with temperature and residence time and to investigate the existence of synergetic effect of co-pyrolysis operation.

Experimental

Samples

LDPE samples from Petkim Petrochemical Company in İzmir were ground in an air-cooled jaw mill until the desired particle size was obtained. The sample was sieved to obtain a < 0.2 mm fraction.

The investigations were performed with oil shale sample obtained from the Göynük oil shale deposit located near the town of Bolu in north-west of Turkey. For the operations, oil shale was crushed and ground in a jaw mill until the desired particle size was obtained. The sample was sieved to obtain a < 0.1 mm fraction and dried at 105 °C under the nitrogen atmosphere. The results of ultimate analysis of Göynük oil shale are as follows; (ultimate analysis – dry basis, wt.%) C_t – 47.2; C_o – 46.3; C_M – 0.9; H – 5.8; N – 1.3, S – 2.2 (o – organic, M – mineral, t – total) [10]. Characteristics of plastic sample used in the experiments are as follows: density – 0.93 g cm⁻³; melt flow index – 0.30 g 10 min; softening point – 98 °C; melting point – 105 °C.

The amounts of oil shale and LDPE in co-pyrolysis samples were taken to give the total carbon ratio GOS:LDPE = 1:1. The amounts of GOS, LDPE and GOS:LDPE blend used in fast pyrolysis were as follows: GOS – 2 g; LDPE – 2 g; LDPE:GOS (g:g) – 1.41:0.77.

Fast pyrolysis

Fast pyrolysis was carried out in an isothermal pyrolysis reactor (120 cm long, 5 cm i.d.) constructed of stainless steel 316. The schematic diagram of the experimental equipment is given in Fig. 1. There is a sample introducing unit at the top of the reactor where GOS, LDPE or GOS:LDPE blend were placed. There are three zones in the equipment: the bottom and middle zones of the reactor and the special sampling system. These zones of the reactor were heated electrically by resistances wrapped around certain parts of the reactor. The bottom zone heater was connected to a programmer and controller, whereas the other two were controlled manually. Three chromenickel thermocouples were fitted to the mentioned zones to measure temperatures. The bottom of the reactor, which represents the pyrolysis region, was heated up to the desired pyrolysis temperature (450, 500, 550, 600 and 650 °C) and controlled by a digital temperature controller. The middle zone of the reactor was heated up to 300 °C for preheating the samples. The special sampling apparatus was heated to 200 °C, and thus, the condensation of high molecular weight hydrocarbons was prevented. A two-sequence

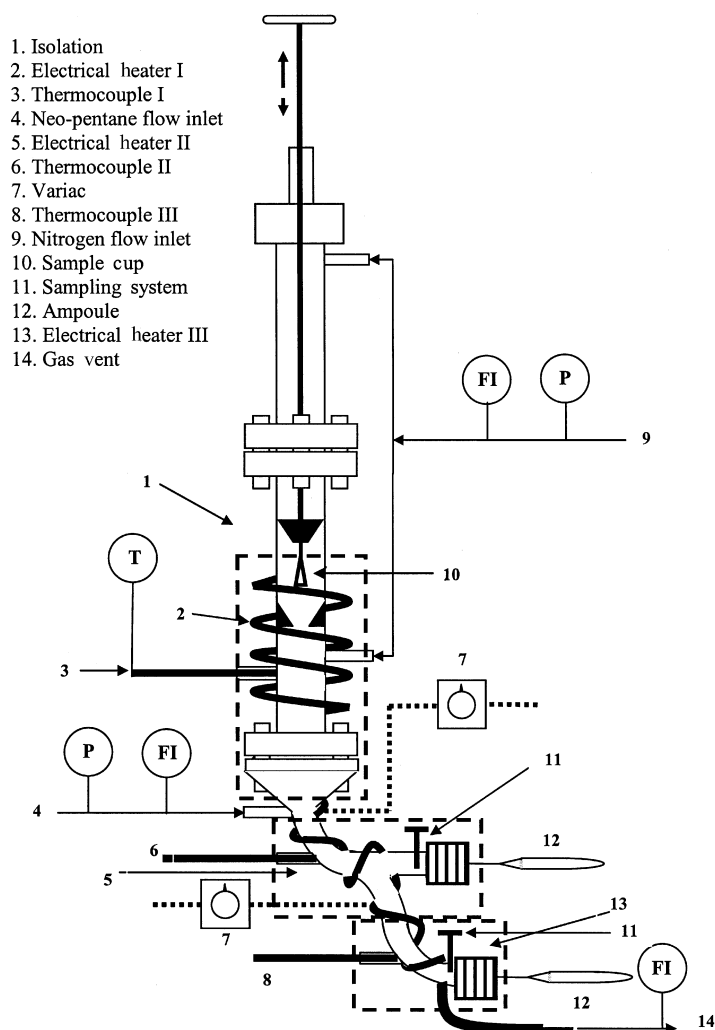


Fig.1. Schematic diagram of the fast pyrolysis reactor.

sampling system was used to collect the samples at the same time, sampling and reproducibility of the data were checked in this way.

Fast pyrolysis operation was carried out under 80 ml min^{-1} flow of nitrogen. After reaching required temperatures for each reactor zone, piston of the reactor was pushed downward and the samples were conveyed to the pyrolysis region. Pyrolysis products were swept from the pyrolysis region by the carrier gas and mixed with the reference gas (20 mL min^{-1} 0.507 vol.% neopentane in nitrogen) which was supplied from the bottom part of the reactor before passing through the special sampling system. The time required to complete pyrolysis was selected to be 10 min to enable to compare the degree of conversion of samples as a function of temperature. The products were taken into pre-evacuated glass ampoules at the initial time $t = 0$, and at 1,

2, 4, 7 and 10 minute intervals for each temperature run. When the samples were brought into the pre-heated pyrolysis zone, decomposition of organic structure begun and quick sampling of the pyrolysis product was required to determine the first decomposition product. The data assigned to the initial time ($t = 0$) represent the evaluation of data after sampling of the pyrolysis product evolved in the first few seconds. The ampoules were sealed by a gas burner and analyzed later by capillary gas chromatography equipped with a specially designed sample introducing system. The residual solid remaining in the sample cup was weighed as spent shale at the end of each pyrolysis run.

Product analysis

High-resolution separation of C_1 - C_{25} hydrocarbons was succeeded by using a temperature-programmed capillary gas chromatograph (between -80 to 275 °C). A methyl silicone coated fused capillary column (50 m long, 0.2 mm i.d., 0.5 μ m film thickness) was temperature programmed from -80 °C (hold for 1.0 min.), at a rate of 20 °C min^{-1} to -10 °C (hold for 2.5 min.), at a rate of 15 °C min^{-1} to 40 °C (hold for 2.5 min.), at a rate of 15 °C min^{-1} to 40 °C (hold for 1.0 min.) and at a rate of 7 °C min^{-1} to 300 °C. Hydrogen carrier gas and a flame ionization detector (FID) were applied. Injection port and detector temperature were set at 290 °C and 350 °C, respectively.

Results and discussion

Figure 2 depicts the chromatogram of a fast co-pyrolysis product (GOS with LDPE, total carbon ratio 1:1, at 600 °C). The major constituents of this product are listed in Table 1. As for fast pyrolysis of each sample (GOS, LDPE and GOS:LDPE blend), aliphatic fraction of recovered hydrocarbons (on the basis of organic carbon) and total hydrocarbon recovery (on total mass basis) and the percentage of solid residue are given in Table 2. At fast pyrolysis of each sample, both the aliphatic fraction of recovered hydrocarbons and total hydrocarbon recovery increased with increasing temperature. Also, aliphatic fraction of recovered hydrocarbons was found to be less than total hydrocarbon recovery at all pyrolysis temperatures. This denotes that the products of fast pyrolysis of samples at all pyrolysis temperatures mainly consist of polyaromatic and/or high molecular weight hydrocarbons. The increase in aliphatic hydrocarbon recovery with increasing temperature indicates that molecular weight of hydrocarbons shows a decreasing trend with increasing temperature. Moreover, conversion of solid residue decreased with increasing temperature. Thermal decomposition of kerogen in oil shale occurs in two main reaction steps. In the first step, kerogen undergoes thermal breakdown into bitumen. In the second step, decomposition of bitumen into gas and oil formation of heavy fraction by secondary reactions take place [6]. In the co-pyrolysis process, decomposition products of LDPE and bitumen react at this temperature and form a more heavier fraction in the

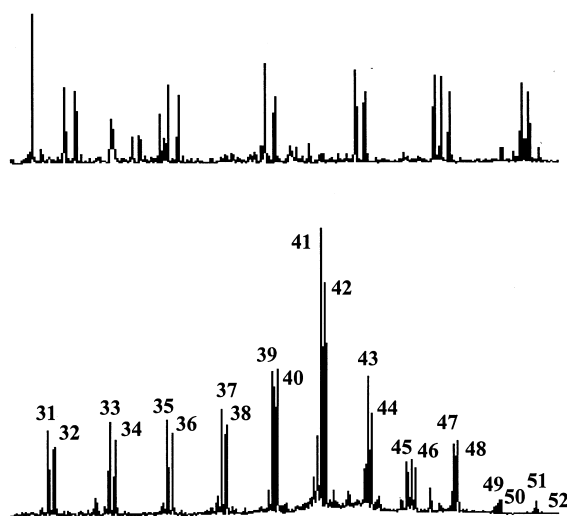


Fig. 2. Fast pyrolysis products of GOS:LDPE (1:1) at 600 °C.

Table 1. The major constituents of fast pyrolysis products of GOS with LDPE

Peak No.	Organic compounds	Peak No.	Organic compounds
1	Methane	27	1-Dodecene
2	Ethene	28	Dodecane
3	Ethane	29	1-Tridecene
4	1-Propene	30	Tridecane
5	Propane	31	1-Tetradecene
6	1-Butene	32	Tetradecane
7	Butane	33	1-Pentadecene
8	Neopentane (ref. gas)	34	Pentadecane
9	<i>cis</i> -2-Butene	35	1-Hexadecene
10	1-Pentene	36	Hexadecane
11	Pentane	37	1-Heptadecene
12	<i>cis</i> -2- Pentene	38	Heptadecane
13	1-Hexene	39	1-Octadecene
14	Hexane	40	Octadecane
15	<i>cis</i> -2- Hexene	41	1-Nonadecene
16	Benzene	42	Nonadecane
17	1-Heptene	43	1-Eicosene
18	Heptane	44	Eicosane
19	Toluene	45	1-Heneicosene
20	1-Octene	46	Heneicosane
21	Octane	47	1-Docosene
22	Xylene	48	Docosane
23	1-Nonene	49	1-Tricosene
24	Nonane	50	Tricosane
25	1-Decene	51	1-Tetracosene
26	Decane	52	Tetracosane

Table 2. Aliphatic hydrocarbon recovery (AHCR) and total hydrocarbon recovery (THCR) at fast pyrolysis of samples

Temperature, °C	AHCR*, wt. %			THCR**, wt. %			Solid residue**, wt. %		
	GOS	LDPE	GOS:LDPE	GOS	LDPE	GOS:LDPE	GOS	LDPE	GOS:LDPE
450	16.9	5.9	5.0	52.5	31.2	19.0	47.5	68.8	81.0
500	16.9	14.4	15.8	51.9	75.5	59.6	48.0	24.5	40.4
550	21.3	16.1	18.5	62.2	73.0	69.9	37.8	27.0	30.1
600	24.9	16.3	19.9	60.4	88.0	75.3	39.7	12.0	24.7
650	27.0	19.8	20.3	59.5	84.0	72.9	40.5	16.0	27.1

* – organic carbon basis

** – total mass basis

first step of kerogen decomposition. Heavy fraction can also decompose to give low molecular weight hydrocarbons and more coke residue.

Comparison of conversion values of fast pyrolysis of GOS and LDPE showed that LDPE yields less aliphatics than GOS, whereas the total hydrocarbon recovery at fast pyrolysis of LDPE was higher than that of GOS at each pyrolysis temperature. The ratios of aliphatic hydrocarbon recovery to total hydrocarbon recovery (selectivity) were found to be 0.32, 0.33, 0.34, 0.41 and 0.45 for GOS, 0.18, 0.19, 0.22, 0.19 and 0.24 for LDPE and 0.26, 0.27, 0.26, 0.26 and 0.28 for GOS:LDPE blend at 450, 500, 550, 600 and 650 °C, respectively (Fig. 3).

Aliphatic fractions of the recovered hydrocarbons were analyzed by capillary gas chromatography technique and classified according to carbon number as follows: gases C₁-C₄ or C₂-C₄ and liquids C₅-C₉, C₁₀-C₁₅ and C₁₆₊. The proportion of *n*-paraffins and 1-olefins (selectivities) in C₁-C₄ (C₂-C₄),

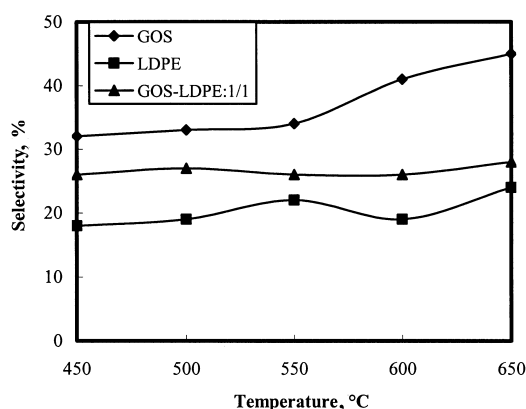


Fig. 3. The ratios of aliphatic hydrocarbon recovery to total hydrocarbon recovery (selectivity) for GOS, LDPE and GOS-LDPE blend at various temperatures.

C_5 - C_9 , C_{10} - C_{15} and C_{16+} were determined at each pyrolysis temperature and at each pre-determined retention time. By multiplying these selectivities with the product evolution rates at each retention time, product evolution rates of these groups were obtained at each time. At each temperature, graphical integration of the product evolution rates of these groups gives the cumulative fractions of these groups at the end of 10 minutes. Variations of n -paraffins and 1-olefins with time at fast pyrolysis of each sample at 550 °C are given in Figures 4 and 5. Cumulative selectivities of n -paraffins and

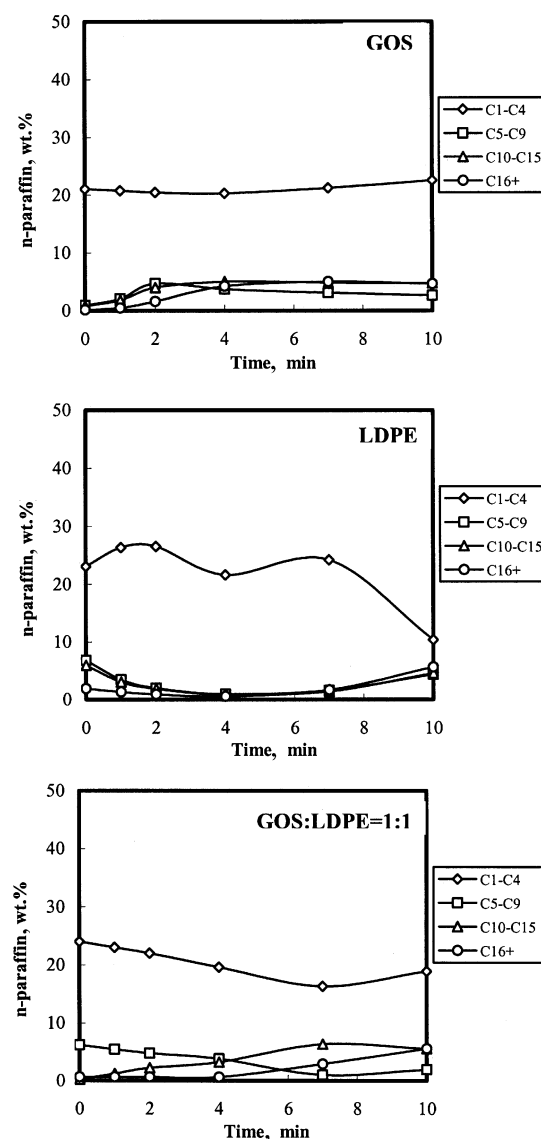


Fig. 4. Distribution of n -paraffins in fast pyrolysis product at 550 °C and at different sampling times.

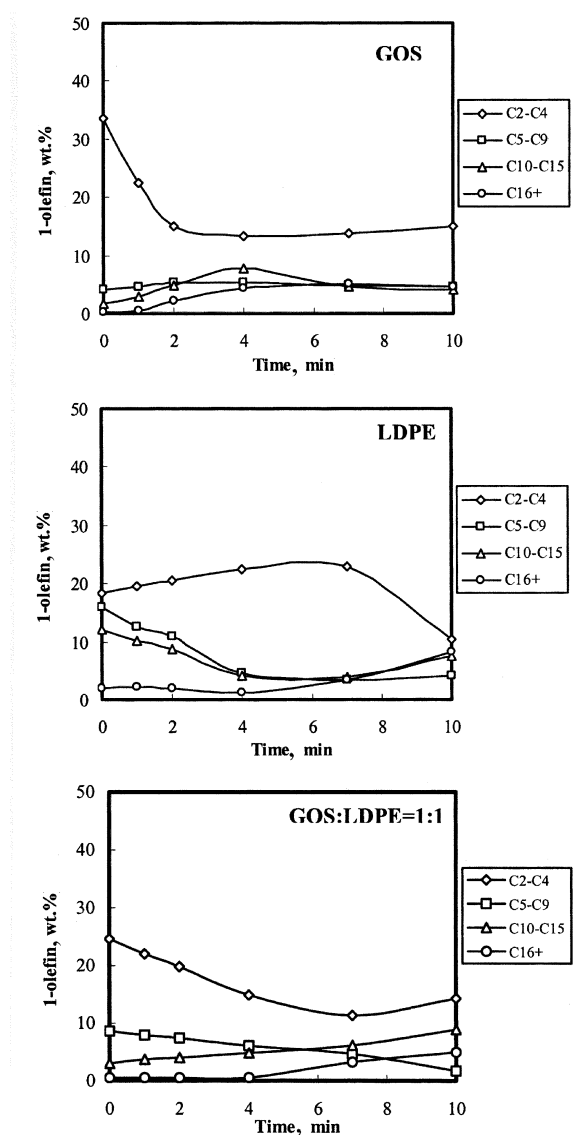


Fig. 5. Distribution of 1-olefins in fast pyrolysis product at 550 °C and at different sampling times.

1-olefins formed during fast pyrolysis of GOS, LDPE and GOS:LDPE blend are given in Figures 6 and 7. Graphs of cumulative *n*-paraffin and 1-olefin selectivities at each pyrolysis temperature show that the share of gas fractions increases with increasing pyrolysis temperature. Also, it can be clearly seen that gaseous *n*-paraffins and 1-olefins constitute the highest portion of the pyrolysis products. An temperature increase causes just slight changes in the product groups C₅-C₉, C₁₀-C₁₅, C₁₆₊. The major effect of temperature reflects as a change in the yield of gaseous products – as temperature

increases, the amount of gaseous products increases which results in an increase in aliphatic hydrocarbon recovery. Also, temperature-programmed pyrolysis of these samples showed that selectivity of *n*-paraffins is higher than that of 1-olefins at each pyrolysis temperature [10].

It was indicated that the temperature range of 430–440 °C is of critical importance for decomposition of GOS during temperature-programmed pyrolysis and thermogravimetric studies [6]. In the case of temperature-programmed pyrolysis of GOS, total organic carbon conversion is relatively high compared to fast pyrolysis. The reason of this is that the products

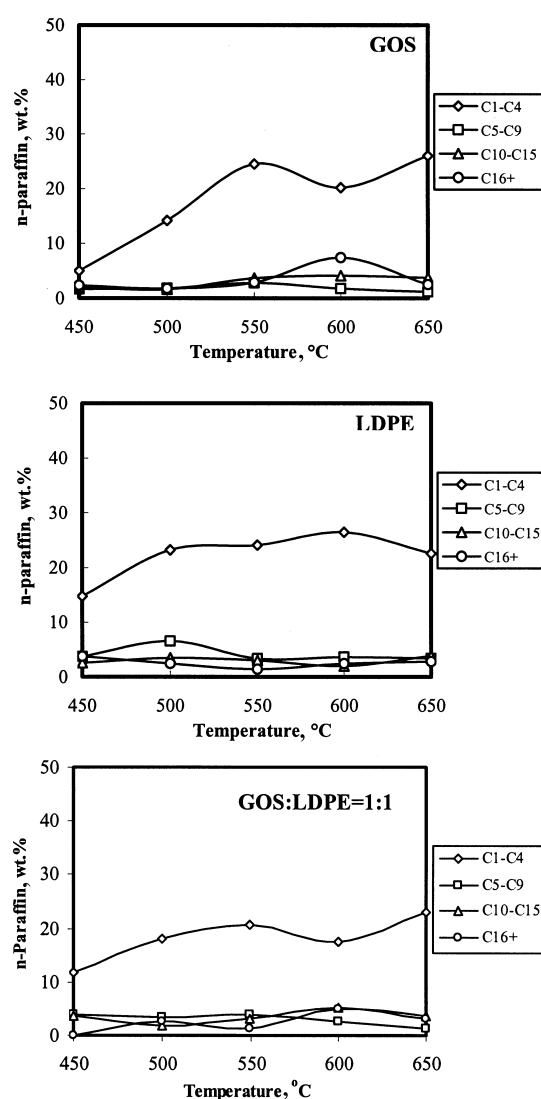


Fig. 6. Cumulative *n*-paraffin selectivity at fast pyrolysis at different temperatures.

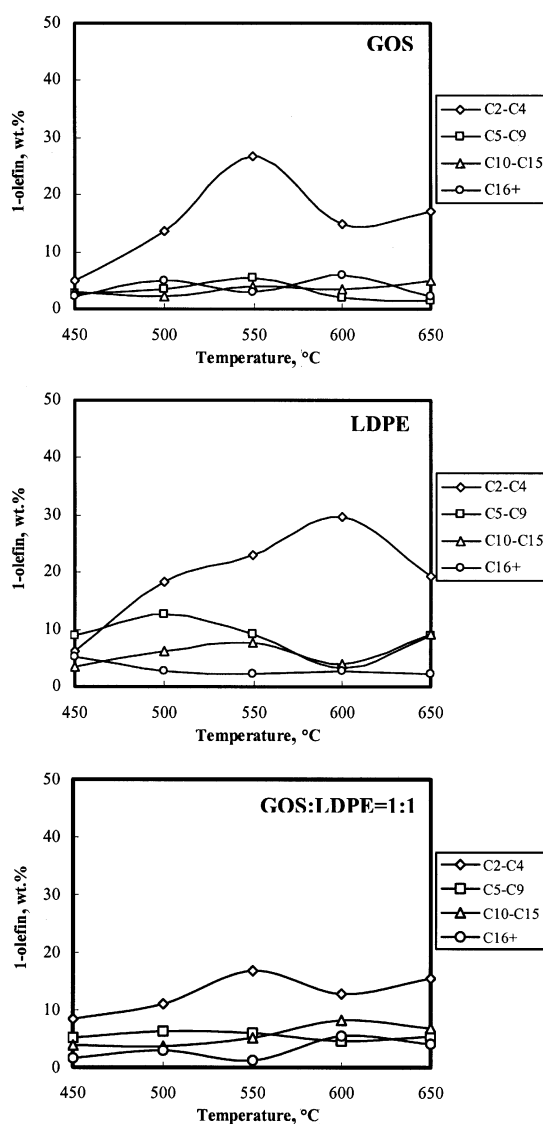


Fig. 7. Cumulative 1-olefin selectivity at fast pyrolysis at different temperatures.

formed during temperature-programmed pyrolysis were continuously swept out from the pyrolysis medium. Also, the retention time at temperature programmed pyrolysis was longer compared to fast pyrolysis; high molecular weight hydrocarbons produced by the decomposition of kerogen could decompose further to lower molecular weight hydrocarbons.

The effect of LDPE on the conversion of GOS was evaluated by comparing the experimental and the hypothetical mean of conversion values (Table 3). When the difference between the experimental co-processed value and hypothetical mean was positive, co-processing of the two materials

Table 3. Comparison of some values to determine the synergetic effect at fast co-pyrolysis processing for GOS:LDPE

Temperature, °C	Conversion to volatile HC, %	Hypothetical mean of conversion, %	Difference, %
450	5.0	11.40	-6.40
500	15.8	15.65	+0.11
550	18.5	18.73	-0.24
600	19.9	20.63	-0.72
650	20.3	23.38	-3.02

enhanced their reactivity and produced higher conversion than obtained in individual reactions. The desired end result was to obtain higher conversion to volatile organic products during co-processing. Although total hydrocarbon recovery yields obtained in fast co-pyrolysis operations carried out at 500 °C were slightly higher than the hypothetic yields, this situation should not be taken into account in synergic point of view. This might be originated from the catalytic effect of the mineral structure of GOS as indicated in literature. In the case of co-pyrolysis of GOS:LDPE, no synergetic effect was observed for fast pyrolysis method. In a similar work, conversion values determined for temperature-programmed co-pyrolysis of GOS with LDPE were higher than those of fast pyrolysis of GOS with LDPE at all temperatures [10].

Conclusions

The ratios of aliphatic hydrocarbon recovery to total hydrocarbon recovery were found to be 0.32, 0.33, 0.34, 0.41 and 0.45 for GOS, 0.18, 0.19, 0.22, 0.19 and 0.24 for LDPE and 0.26, 0.27, 0.26, 0.26 and 0.28 for GOS:LDPE blend at 450, 500, 550, 600 and 650 °C, respectively. Cumulative *n*-paraffin and 1-olefin selectivity graphs at each pyrolysis temperature show that the share of gas fractions increases with increasing pyrolysis temperature. Additionally, it can be seen that gaseous *n*-paraffins and 1-olefins constitute the highest portion of the pyrolysis products. The major effect of temperature reflects as a change in the yield of gaseous products: as temperature increases, the amounts of gaseous products increase which results as an increase in aliphatic hydrocarbon recovery.

Compared with the previous study [12], conversion values determined for temperature-programmed co-pyrolysis of GOS with LDPE were higher than those of fast pyrolysis of GOS with LDPE at all temperatures. In the case of co-pyrolysis of GOS:LDPE, no synergetic effect was observed for fast pyrolysis operation.

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