

FAST PYROLYSIS AND CO-PYROLYSIS OF GÖYNÜK OIL SHALE (TURKEY) AND POLYPROPYLENE IN FREE FALLING REACTOR (FFR)

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Abstract. Fast pyrolysis of Göynük oil shale (GOS), polypropylene (PP) and the blend of GOS:PP on a 1:3 total carbon ratio basis was studied. The maximum product evolution temperature and the existence of synergistic effect were determined and the characteristics of pyrolysis products by carbon number were investigated.

Pyrolysis products were analyzed by capillary gas chromatography. The volatile fraction of pyrolysis products was classified according to carbon number.

Conversion to the volatile fraction of recovered hydrocarbons in fast co-pyrolysis of GOS:PP increased with increasing temperature. The effect of PP on the conversion of GOS was determined by calculating the difference between experimental and hypothetical mean values of conversion of total organic carbon into volatile products and a slight synergistic effect was observed at 600 °C (4.78%) and 650 °C (5.07%).

Keywords: Göynük oil shale (GOS), oil shale, pyrolysis, synergism, co-pyrolysis, fast pyrolysis, polypropylene (PP).

1. Introduction

In Turkey, energy is produced from such primary energy resources as hard coal, lignite, asphaltite, petroleum and natural gas. The share of hydroelectric energy and geothermal energy is also significant.

Being used directly, coal, petroleum and traditional fossil fuels account for most of the world's energy consumption today. These fuels are rich in carbon and hydrogen. A relatively large amount of energy is stored in them and they have a high calorific value. However, these are not the only fossil

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fuels found on our planet. As they are depleted, or their price increases, other fossil fuels can become more attractive for commercial exploitation. Coal, oil shale and tar sand are the most abundant naturally occurring materials for this purpose [1]. Considering the fact that fuel consumption in Turkey is increasing, the existing energy sources should be utilized in the best possible way. Of these sources, oil shale is the second-ranking fossil fuel in Turkey [2].

It has been estimated that the world deposits of oil shale are equivalent to 400 billion tonnes of shale oil, of which 30 billion tonnes are recoverable under existing technological conditions. In Turkey, the Mineral Research and Exploration Institute has characterized over 5 billion tonnes of oil shale reserves. The main oil shale deposits in Turkey are Beypazarı (Ankara), Seyitömer (Kütahya), Hımmetoğlu (Bolu) and Hatıdağ (Bolu), in terms of quality, amount and exploitability. These four deposits constitute around 50% of the total oil shale potential of Turkey [3–4].

One of the largest deposits is also Göynük-Bolu with 2.5 billion tonnes of oil shale. Oil shale reserves are the second most abundant solid fuel deposits after lignite in Turkey [5].

Like conventional natural energy resources, most organic waste materials such as municipal solid waste (MSW), lignocellulosic waste and plastics are also potential energy resources.

The disposal of municipal and industrial wastes is now recognized to be a major environmental problem throughout the world. Municipal waste consists mostly of paper and woody materials, forming 59–63%. Another and more troublesome component of waste stream is plastics, inasmuch as they are not presently biodegradable. Plastics constitute only 7–9% of total waste stream weight, after removal of glass, metal, etc., plastics account for about 9–12% of total waste by weight. Of the plastics discharged as waste, packaging materials make up 50–70% of the total, of this amount 89% are polyolefins (polyethylene, polypropylene, polystyrene, polyvinylchloride) [6].

Oil shale can be defined as a compact rock of sedimentary origin with ash content of more than 33% and containing organic matter that yields oil when destructively distilled, but not appreciably when extracted with ordinary solvents. Oil shales contain organic matter mostly in the form of kerogen which is defined as the fraction of organic matter in a sedimentary rock that is insoluble in common petroleum solvents. The other fraction called bitumen is soluble in organic solvents, but represents only a small amount of the organic matter in an oil shale [7].

Oil shales must have a large fraction of organic matter to be of economic interest. The organic matter content of an oil shale should be approximately 5.5 wt.%, just to meet the calorific requirements necessary to heat the rock to 500 °C in order to produce shale oil by thermal decomposition of organic matter. Below this amount of organic matter, the rock cannot be a source of energy, because it takes more energy to heat the rock than can be derived

from the produced oil shale. A lower limit of 5% organic matter is sometimes used to define a commercial deposit [8].

Kerogen is a complex substance with large molecules consisting mainly of carbon, hydrogen, nitrogen, sulphur and oxygen atoms. The average molecular weight is 3000 and approximate empirical formula is $C_{200}H_{300}SN_5O_{11}$ [9]. Oil shale consists of marlstone-type sedimentary inorganic material containing complex organic polymers, which are high molecular weight solids. Kerogen is a three-dimensional polymer, is soluble in conventional solvents, and is associated with a small amount of benzene soluble organic material, bitumen [5]. The mineral matter present in oil shales is believed to play an important role in the thermally induced catalytic alteration of kerogen during petroleum formation [10].

The pyrolysis process is exceedingly complex, and many competing processes contribute to thermal curves. In the initial stages of pyrolysis, distillation of low molecular weight species occurs, but as the temperature is raised, in addition to the increased rate of volatilization due to progressive evaporation of larger molecules, cracking of the compounds to volatile fragments may also occur [8].

There are many studies on pyrolysis that have been made by other oil shale experts around the world. For example, Ishiwatari [11] investigated the thermal decomposition behavior by use of stepwise pyrolysis-gas chromatography for four oil shales (Colorado, Condor, Maoming and Timahdit oil shales from the USA, Australia, China and Morocco, respectively) and their kerogen concentrates. It was revealed that product distribution was dependent on pyrolysis temperature for all the kerogens examined as well as for the oil shales. Isoprenoid hydrocarbons were mostly generated at 430 °C from all the samples under study, while the majority of 1-alkenes and *n*-alkenes were generated at 470 °C and/or 520 °C. In the research of Gaboriaud et al. [12], the evolution of major gases, i.e. H₂, CO, CO₂, CH₄ and C₂ and C₃ hydrocarbons, evolved during the primary step of pyrolysis of Timahdit oil shale, was studied under isothermal conditions. Kök and İşcan [13] investigated the pyrolysis and combustion behavior of three different oil shale samples from Turkey, carrying out thermal analysis (TG/DTG).

On the other hand, accumulation of the enormous amount of plastic waste generated all over the world has unfavourable impacts on the environment. In pyrolysis or thermal cracking, polymeric materials are heated to high temperatures, so their macromolecular structures are broken down into smaller molecules and a wide spectrum of hydrocarbons are formed. These pyrolytic products can be divided into a gas fraction, a liquid fraction consisting of paraffins, olefins, naphthenes and aromatics (PONA), and solid residues [14]. Pyrolysis of plastic waste could have an important role in converting this waste into economically valuable hydrocarbons, which can be used either as fuels or as feedstock in the petrochemical industry. End product yields and properties depend on the plastic waste composition. The presence of polyethylene (PE) increased the alkane content, whilst polystyrene (PS)

led to a higher aromatic content in the end product. The presence of polypropylene (PP) favored alkene formation. Therefore, both PS and PP increased the octane number of the end product. Hence, the desired end product can be obtained by an adequate blending of plastic wastes [15].

Co-processing techniques have received much attention in recent years because they should be considered as a beneficial process of recovering valuable hydrocarbons and recycling the waste materials with advantageous environmental and economic effects [16].

In this study, the co-pyrolysis of Turkish (Göynük) oil shale with plastic (PP) was studied for exploring the possibility of their utilization to obtain liquid and gas products. A special sampling technique was used for collecting organic products eluted from the reactor at different temperatures and time intervals. The pyrolysis products were analyzed by capillary gas chromatography and the total product evolution rate was investigated as a function of temperature and time. In the co-pyrolysis of GOS:PP, the existence of synergistic effect was also investigated.

This technique was developed for a gas/vapor multi-component mixture and offers a number of advantages: simplification of sampling compared to conventional procedures 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 in stationary system [17].

2. Experimental

2.1. Materials

Oil shale samples from the Göynük deposit, Turkey, were ground to the < 0.1 mm particle size and polypropylene samples from Petkim Petrochemical Company in İzmir were ground to < 0.2 mm in the presence of liquid nitrogen.

2.2. Pyrolysis

Fast pyrolysis experiments were performed with a 2.0 g sample of powdered GOS, moisture 3.8%, or polypropylene. The reactor, which has a length of 120 cm and a diameter of 5 cm, was constructed of stainless steel 316. At the top of the reactor there is a sample dropping unit in which GOS, PP and the blend of GOS:PP at a 1:3 total carbon weight ratio were placed. The solid residue was collected with the aid of a sieve placed just above the conical portion at the bottom of the reactor.

The bottom of the reactor, which could be considered as the pyrolysis region, was heated up to the desired pyrolysis temperatures. These temperatures were 450 °C, 500 °C, 550 °C, 600 °C, and 650 °C. At each set, the top zone of the reactor was heated up to 200 °C to preheat the samples. The special sampling apparatus was heated up to about 200 °C to prevent the

condensation of high molecular hydrocarbons that might be present in the product stream.

Fast pyrolysis operation was carried out under a 80 mL min^{-1} flow of N_2 . After attaining the desired pre-selected temperatures at three different zones of the reactor, the samples were dropped from the sample dropping unit to the bottom of the reactor, the pyrolysis region. The samples were taken in evacuated glass ampoules at 0, 1, 2, 3, 5, 7, 9, 15, 20 and 30 minutes. The ampoules were sealed by a gas burner and analyzed by capillary gas chromatography with a specially designed sample introducing system. The co-pyrolysis experiments were repeated twice for reproducibility.

2.3. GC analysis of prolysis products

The pyrolysis products were analyzed using an HP 6890 capillary gas chromatograph. The products were swept out of the reactor and mixed with a reference gas used as an internal standard in GC analysis (20 mL min^{-1} , 0.507 vol.% neopentane in nitrogen) before passing to the special sampling system. Hydrogen gas was used as a carrier gas and a Flame Ionization Detector (FID) was employed for analysis. The characteristic chromatograms of pyrolysis products and detailed chromatograms, which include $\text{C}_1\text{--C}_8$ fractions in detail, are shown in Figures 1 and 2.

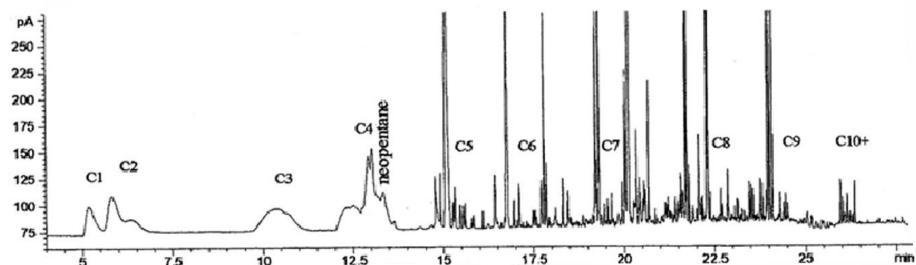


Fig. 1. Gas chromatogram of organic products from co-pyrolysis of GOS:PP.

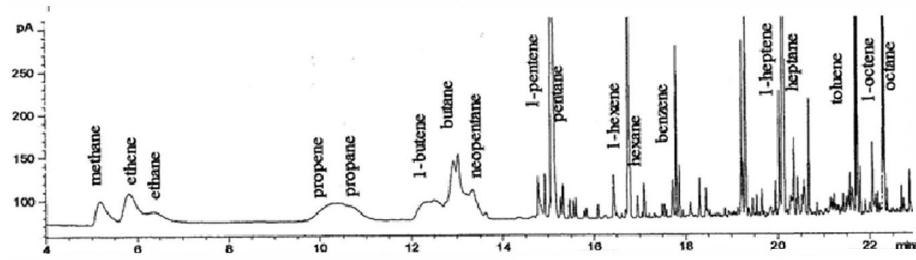


Fig. 2. Detailed chromatogram of pyrolysis of GOS:PP including $\text{C}_1\text{--C}_8$ fractions.

3. Results and discussion

As for fast pyrolysis of each sample (GOS, PP and GOS:PP blend), the aliphatic fraction of recovered hydrocarbons (on organic carbon basis) and total hydrocarbon recovery (on total mass basis) and the percentage of solid residue are given in Table 1, at the pyrolysis temperatures of 450 °C, 500 °C, 550 °C, 600 °C, and 650 °C, respectively.

Table 1. Volatile hydrocarbon recovery (VHCR) and total hydrocarbon recovery (THCR) at fast pyrolysis of samples

Temperature, °C	VHCR*, wt%			THCR**, wt%			Solid residue**, wt.%		
	GOS	PP	GOS PP (1:3)	GOS	PP	GOS PP	GOS	PP	GOS PP (1:3)
450	16.9	30.7	11.3	52.5	97.4	71.9	47.5	2.6	28.1
500	16.9	41.7	19.7	51.9	96.4	72.3	48.0	3.6	27.7
550	21.3	43.1	19.6	62.2	98.9	82.6	37.8	1.1	17.4
600	24.9	43.3	43.5	60.4	99.8	83.9	39.7	0.2	16.1
650	27.0	51.9	50.7	59.5	99.8	84.5	40.5	0.2	15.5

* – organic carbon basis

** – total mass basis

In the fast pyrolysis of GOS and PP and co-pyrolysis of GOS:PP (1:3), it was noticed that both the aliphatic fraction of recovered hydrocarbons, which can be analyzed by our analytical technique, and total hydrocarbon recovery increased with increasing temperature. It can easily be seen that the aliphatic fraction of recovered hydrocarbons was lower than total hydrocarbon recovery at all pyrolysis temperatures. This denotes that the products of fast pyrolysis at all pyrolysis temperatures consist mainly of polyaromatics and high molecular weight hydrocarbons. The increase in conversion of the aliphatic fraction of recovered hydrocarbons with increasing temperature indicates that the molecular weight of hydrocarbons shows a decreasing trend with increasing temperature.

As can clearly be seen from Figure 3, the aliphatic fraction of recovered hydrocarbons, which could be analyzed by our analytical technique, increases with increasing temperature. In other words, as the temperature increases, low molecular weight aliphatic hydrocarbon products constitute a higher portion among the total product recovery. Moreover, conversion to coke decreased with increasing temperature. This can be explained by the increasing trend of low molecular weight aliphatic hydrocarbon products. At high pyrolysis temperatures and at the same reaction times (10 minutes), primary pyrolysis products did not react to give higher molecular weight hydrocarbons, adversely, they decomposed to low molecular weight

aliphatic hydrocarbons, so, the aliphatic fraction of recovered hydrocarbons increased.

In the co-pyrolysis of GOS:PP, the experimental and hypothetical ratios of the volatile fraction of recovered hydrocarbons to total hydrocarbon recovery are compared in Figure 3 and the same results parallel to the previous ones have been obtained. At 450 °C, 500 °C and 550 °C, the experimental ratios were found to be lower than the hypothetical ones. This means that at these temperatures, total hydrocarbon recoveries were found to be high.

Although, total hydrocarbon increases, this is mainly because of the increase of C₂₅₊ fractions, which cannot be analyzed by our analytical technique. At temperatures of 600 °C and 650 °C, high molecular weight organic compounds degraded and total hydrocarbon recovery also increased. Thus, volatile fractions that could be analyzed by our analytical technique increased, resulting in higher ratios of VHC/THCR at 600 °C and 650 °C. Another reason for possible synergism is that the decomposition products of PP were reacted with the pyrolysis products of GOS in order to prevent their secondary reactions from affording high molecular weight hydrocarbons.

The cumulative distribution of volatile hydrocarbons (n-paraffin and l-olefin) graphs at each pyrolysis temperature shows that gas fractions increased with increasing pyrolysis temperature. Also, it can clearly be seen that n-paraffin and l-olefin gaseous products constitute the highest portion of the pyrolysis products.

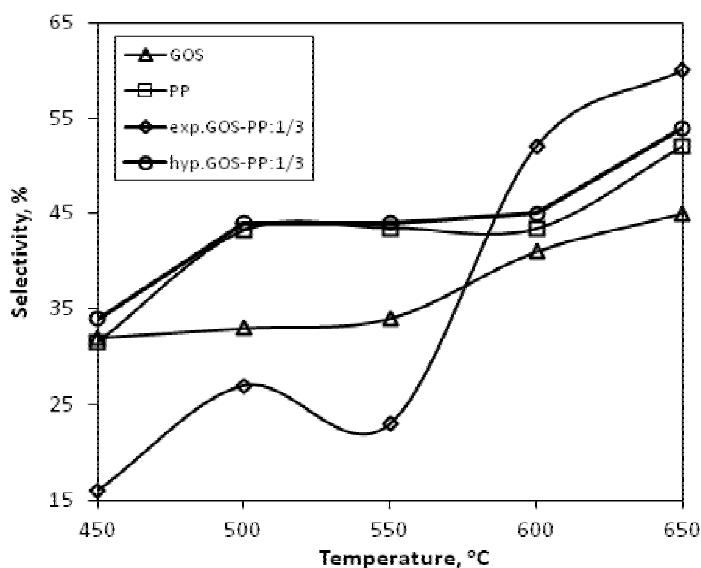


Fig. 3. The ratios of aliphatic hydrocarbon recovery to total hydrocarbon recovery (selectivity) for GOS, PP and the GOS:PP blend at various temperatures.

Increasing the temperature causes just slight changes in product groups C₅–C₉, and C₁₀₊. The major effect of temperature is reflected on the change in gaseous product yield: as the temperature increases, gaseous products increase, which results in an increase in aliphatic hydrocarbon recovery.

In the fast pyrolysis of PP, gas fractions decreased with increasing pyrolysis temperature. Also, it can clearly be seen that n-paraffin and 1-olefin liquid products constitute the highest portion of the pyrolysis products.

In the fast co-pyrolysis of GOS:PP, cumulative product distribution characteristics of fast co-pyrolysis operations show similarities with those of the fast pyrolysis of PP. It was reported earlier that PP accelerates the decomposition of the organic matter in the oil shale. The degradation of the studied materials can be considered as a first-order reaction, as was indicated by the results obtained by the isoconversion method [18].

The aliphatic fractions of the recovered hydrocarbons analyzed by our gas chromatographic technique were classified according to carbon number as gases C₁–C₄ or C₂–C₄ and liquids, C₅–C₉, and C₁₀₊. In experimental studies, aliphatic hydrocarbon selectivities for C₁–C₄ (C₂–C₄), C₅–C₉ and C₁₀₊ fractions were determined at 0 (where t = 0 indicates initial time such as t ≤ ¼ min), 1, 2, 4, 7, 10 minutes at the pyrolysis temperatures of 450 °C, 500 °C, 550 °C, 600 °C, and 650 °C.

By multiplying these selectivities with the product evolution rates at the above-mentioned times, product evolution rates of these groups were obtained at each time. At each temperature, the graphical integration of the group product evolution rates gives the cumulative fractions of these groups formed in the 10th minute. The results are shown in Figure 4. These values help to determine the exact product characteristics obtained in the 10th minute at each pyrolysis temperature. To be able to comment on the product characteristics, cumulative fractions of the groups formed in the 10th minute should be considered because by looking only at the selectivities of these groups at each time, it is almost impossible to determine a trend.

The effect of PP on the conversion of GOS was evaluated by comparing the experimental values and the hypothetical mean of the conversion value. When the difference between the experimental co-processed values and hypothetical mean was positive, then co-processing the two materials enhanced their reactivity and produced higher conversion than was obtained in the individual reactions. It has been suggested by other researchers that polyolefinic polymers such as PE and PP could provide hydrogen during thermal co-processing with oil shale, coal or biomass, and can lead to an increase of liquid production [19].

Similarly, Ballice [19, 20] and Gersten et al. [21] studied the co-pyrolysis of oil shale with polyolefinic plastics and obtained oils with higher yields and better quality in comparison to those produced from oil shale alone.

As can be seen from Table 2, considering the conversions on total hydrocarbon recovery basis, there is no synergistic effect for co-pyrolysis of GOS:PP (1:3).

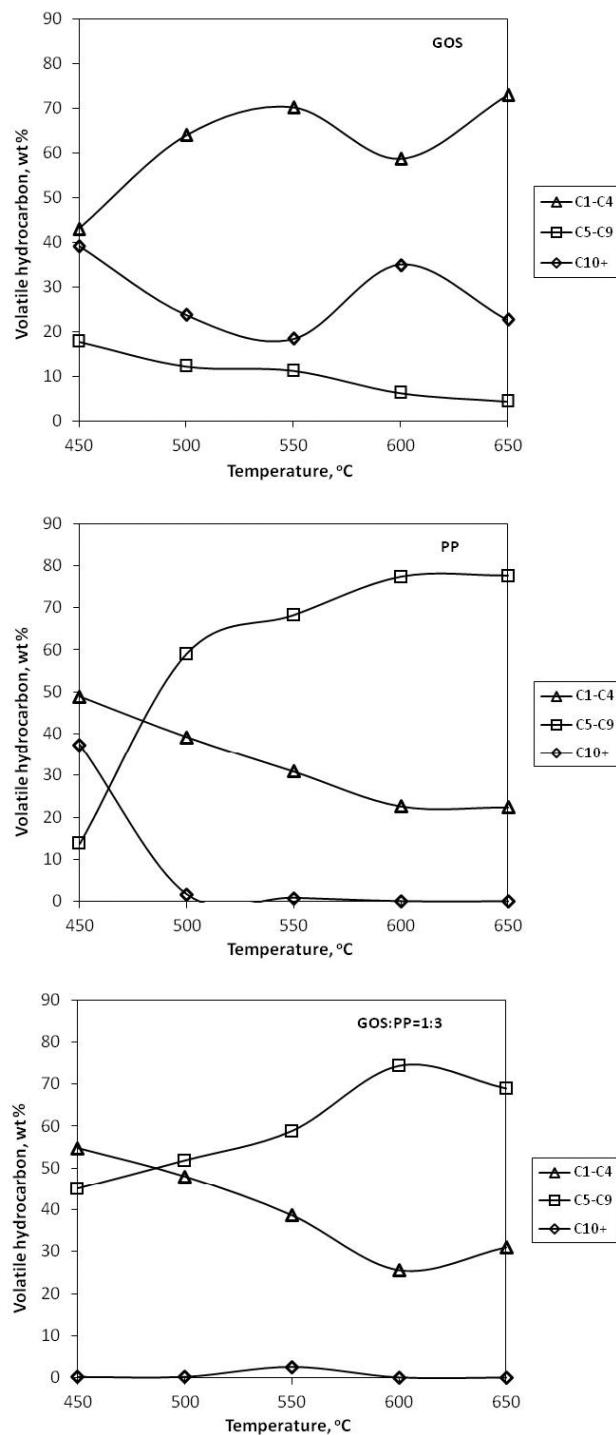


Fig. 4. Cumulative volatile hydrocarbon selectivity for fast pyrolysis at different temperatures.

Table 2. Experimental and hypothetical conversions of GOS:PP on total hydrocarbon recovery basis

Temperature, °C	Experimental conversion, %	Hypothetical conversion, %	Difference, %	Comments on synergistic effect
450	71.9	80.4	-8.5	No
500	72.3	79.5	-7.2	No
550	82.6	85.0	-2.4	No
600	83.9	84.8	-0.9	No
650	84.5	84.5	0.0	No

The results of the experimental and hypothetical conversion to volatile organic compounds such as n-paraffins, 1-olefins, iso-paraffins, branched olefins, simple aromatic compounds (such as benzene, toluene and xylene) are given in Table 3.

A slight synergistic effect was observed at 600 °C and 650 °C, when the experimental and hypothetical conversions based on the volatile fraction of recovered hydrocarbons were taken into account. The experimental results obtained by other researchers indicate a significant synergistic effect during pyrolysis of oil shale mixed with plastic [16].

Table 3. Experimental and hypothetical conversions of GOS:PP on volatile fraction of the recovered hydrocarbons basis

Temperature, °C	Experimental conversion, %	Hypothetical conversion, %	Difference, %	Comments on synergistic effect
450	11.3	27.3	-16.0	No
500	19.7	35.5	-15.8	No
550	19.7	37.7	-18.0	No
600	43.5	38.7	+4.8	Yes
650	50.7	45.7	+5.0	Yes

4. Conclusions

Fast co-pyrolysis experiments were performed with GOS and PP by using a 1:3 total carbon ratio of GOS to PP at temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C. The data obtained was evaluated in the same manner as those obtained by the fast pyrolysis of GOS and PP, separately. As in conversion to total hydrocarbon recovery and conversion to the volatile fraction of recovered hydrocarbons, the possible existence of synergistic effect was investigated in co-pyrolysis experiments.

Conversion to the volatile fraction of recovered hydrocarbons in the fast co-pyrolysis of GOS:PP increased with increasing temperatures, conversion values were higher than those of the fast pyrolysis of GOS at 500 °C, 600 °C

and 650 °C. This situation can be explained by PP, which is dominant in the co-pyrolysis product distribution. The decomposition products of PP can react with bitumen to give a less heavy fraction with branched structure and the heavy fraction can also be degraded to give low molecular weight hydrocarbons and less coke residue than that of the coke deposit for pyrolysis of GOS.

As can be seen from Table 2, considering the conversions on total hydrocarbon recovery basis there is no synergistic effect for co-pyrolysis of GOS:PP. Contrary to experimental and hypothetical conversions based on total hydrocarbon recovery, a slight synergistic effect was observed at 600 °C and 650 °C.

When the experimental and hypothetical ratios of VHC to THCR were compared, at 450 °C, 500 °C and 550 °C, the experimental ratios were found to be lower than the hypothetical ones. This means that at these temperatures, THCR were found to be high. Although, total hydrocarbon increases, this is mainly because of the increase of C₂₅₊ fractions, which cannot be analyzed by our analytical technique.

In addition, cumulative product distribution characteristics of fast co-pyrolysis operations show similarities with those of the fast pyrolysis of PP.

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