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Co-Pyrolysis of Göynük Oil Shale with Polypropylene and Structural Characterizatıon of Pyrolysis Liquid

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Abstract: This study is based on the purpose of obtaining high yields of liquid product by subjecting the oil shale sample taken from one of our country's important oil shale deposits and polypropylene (PP) mixtures to co-pyrolysis process. In this study, the oil shale sample and the polypropylene were firstly subjected to pyrolysis process, and then the mixture obtained by mixing of these at certain ratios was subjected to pyrolysis process. Pyrolysis experiments were performed at three different mixture ratios of 33%, 50% and 67% PP in the mixture, and in the temperature range of 600 – 800 °C. The gas, liquid, and solid product yields obtained as a result of the experiments were calculated, and the effect of PP which was added to oil shale and the changed pyrolysis temperature on the yield of liquid product was examined. As a result of the experiments, the highest liquid product yield was achieved in the mixture ratio containing 67% PP at 800 °C. Various catalysts were added to the medium in which the highest liquid product yield was achieved, and the effect of catalysts on the liquid product yield obtained from pyrolysis was examined. The structure of the obtained liquid products was investigated by various spectroscopic methods such as GC-MS and FTIR, and the effects of experimental conditions on the structure of the liquid product were analyzed. Consequently, a noticeable synergistic effect was observed in the yield of the liquid product which was obtained as a result of the co-pyrolysis of PP and oil shale, and this effect further increased with the catalyst added to the medium. The results in this study also showed that co-pyrolysis of oil shale with PP could be an environmentally friendly method for the conversion of hazardous waste into valuable chemicals and fuels.

Keywords: Co-pyrolysis, oil shale, polypropylene, characterization.

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INTRODUCTION

The increasing energy and petroleum need has pushed researchers towards studies related to sustainable energy technologies. On the other hand, a rapid decrease in energy resources such as petrol and natural gas has made making use of asphaltite, oil shales, and especially coal as the potential energy and chemical raw material resources of the future a current issue again. Oil shales take the second place in terms of reserve compared to other resources such as petrol, coal and natural gas [1].

Oil shale is defined as a sedimentary rock which contains an organic substance called kerogen, a fine-grained, lamellar structure [2]. Kerogen has a high hydrogen/carbon ratio that provides superior potential use as a liquid fuel source than coal or heavy oil. Oil shale is usually used as a fuel, solvent, and chemical resource after a thermal conversion process [3, 4].

Oil shale is the second largest fossil fuel after lignite in Turkey and has a significant value in the country's economy [5]. Göynük and Seyitömer oil shales have the largest share in the distribution of oil shale deposits according to reserve status. Since the kerogen in the oil shale structure is rich in hydrogen, the ratio of giving a distillable liquid and gas yield is greater than coal when it is subjected to heat treatment. However, it is not possible to make use of these resources by burning them as in the coal. Because during burning, some portion of the rapid decay products occurring in the organic structure at temperatures reaching up to 450 °C are released with combustion gases without finding an opportunity to burn. Therefore, making use of it by burning is not approved in terms of environmental pollution. Based on this aspect, pyrolysis method can be used in making use of oil shales which are the most important fossil resources that can be considered after coal. Pyrolysis process can be defined as the conversion process of oil shales into liquid and gas products by subjecting to thermal degradation in an inert medium.

In the studies carried out in recent years, it has been determined that the liquid and gas product yield obtained by subjecting coals through mixing with polymers to processes such as co-pyrolysis, extraction, and gasification is higher than the products obtained by singly subjecting both coal and polymers to these processes, and the distribution of products has far more superior characteristics in the co-pyrolysis process in terms of quality [6-8]. During the co-pyrolysis of coal with polymers, radicals formed at high temperatures are saturated with hydrogen, released from the polymers, increasing the liquid yield [9]. Thus, it was revealed that a synergistic effect appeared during the co-pyrolysis of polymers with coal, and the polymers served as a hydrogen source [10, 11].

In the co-pyrolysis process, plastic wastes are the main polymer sources to be processed with coal. All over the world, plastics are the indispensable material of the future which are used as an alternative material instead of materials such as glass, metal, rubber, wood, inorganic substances, or together with these materials. The fact that it is economic and easily applicable is rapidly increasing the plastic consumption compared to other materials. The increasing use of plastics leads to an increase in plastic wastes, as well; and this situation emerges as a major environmental problem that needs to be solved. Plastic wastes are disposed by waste burial and waste incineration or utilized by using various recycling techniques. Pyrolysis, one of the methods of recycling plastics, is the most advantageous method from many aspects. Plastic wastes are converted into energy and chemical raw materials by pyrolysis.

Plastics are named in several ways depending on the type of the polymer used in production. Some types of plastic which are commonly used can be listed as polyethylene (PE), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET), polyamide (PA), polyester, polyvinyl chloride (PVC), and polyurethane. When the plastic demands of 2010 in the world and Turkey are analyzed, it is seen that PE and PP have the largest share [12, 13].

In this study, the effect of co-pyrolysis of Göynük oil shale with polypropylene waste was investigated with the aim of understanding its effect of liquid formation and fuel or raw material characteristics. In the experiments, the oil shale and polypropylene mixtures were subjected to pyrolysis process at different temperatures, and the gas, liquid and solid (residual coke) yields obtained at each temperature were determined. The effect of experimental conditions and catalysts on yields was investigated by using different catalysts such as bentonite, zeolite, and red mud under optimum conditions specified. This study is significant in terms of use co-pyrolysis of oil shale and PP with catalyst to obtain the liquid products with high heating value. An attempt to investigate the structure of the obtained liquid products was made by various spectroscopic methods such as GC-MS and FTIR.

MATERIALS AND METHODS

Oil shale sample was obtained from Bolu-Göynük located in Turkey. Pretreatments of samples were carried out before the experiments. The samples were ground to obtain the desired particle size of 1-2 mm and were subsequently dried at 105°C for 24 h. Polypropylene (PP) was provided from the Özuğur-Akçim Plastic Company (Izmir, Turkey). Elemental analysis and higher heating value (HHV) of the oil shale and PP were performed with an elemental analyzer (LECO 932 CHNS elemental analyzer) and bomb calorimeter (Parr 6200 calorimeter). The characteristics of the samples are given in Table 1.

Table 1. Main characteristics of the oil shale and PP.

	Elemental Composition, wt%, daf				Calorific value (MJ/kg)
	C	H	N	O	
Oil shale	57.50	3.50	0.70	38.30	5.90
PP	75.90	5.40	-	18.70	39.50

Characterization of products

GC–MS analysis for liquid samples (tar) were performed using an AGILENT 6890 Model gas chromatograph coupled to a HP 5973 mass selective quadrupole detector using a 50 m ×0.32 mm × 0.52 mm capillary column. Chromatographic peaks were identified by means of NIST mass spectral data library and from their retention times using standard compound when available. The percentages of the peaks were calculated from the TIC (total ion chromatogram) peak area. FTIR spectra of the liquid samples as KBr disks of the samples were recorded by a MATTSON 1000 Model FTIR spectrometer.

Pyrolysis procedure

All pyrolysis experiments were performed in a fixed bed pyrolysis system shown schematically in Figure 1 [7]. Oil shale and PP were firstly pyrolyzed, then oil shale and PP mixtures in weight percent of 33% (wt), 50%(wt) and of 67% (wt) of polymer were co-pyrolyzed at temperatures between 600°C and 800°C. Oil shale and PP were mixed together in weight percent of 33 wt% (6.66 g of oil shale and 3.33 g of PP), 50 wt % (5 g of oil shale and 5 g of PP), and 67 wt % (3.33 g of oil shale and 6.66 g of PP) of PP. In order to evaluate the effect of catalyst on product yield, different amounts of catalysts were added to 67 wt% oil shale / PP mixture and these mixtures are pyrolyzed.

The catalysts used are red mud, zeolite, and bentonite. The red mud is supplied by Seydisehir Aluminum Company, Turkey. It is filtered and then dried at 110 °C. Linde type A-zeolite is supplied by CWK Chemiewerk Köstritz Company, Germany. Zeolite is activated by heating for 2 h at 200°C and then drying for 2 h at 500 °C. Bentonite from the Kütahya region, Turkey, is used in the experiments. Bentonite is activated by heating for 6 h at 97°C in a H_2SO_4 solution (40 wt%). The specific surface area of red mud, zeolite, and bentonite are 16 m^2g^{-1}, 300 m^2g^{-1}, and 134 m^2g^{-1}, respectively.

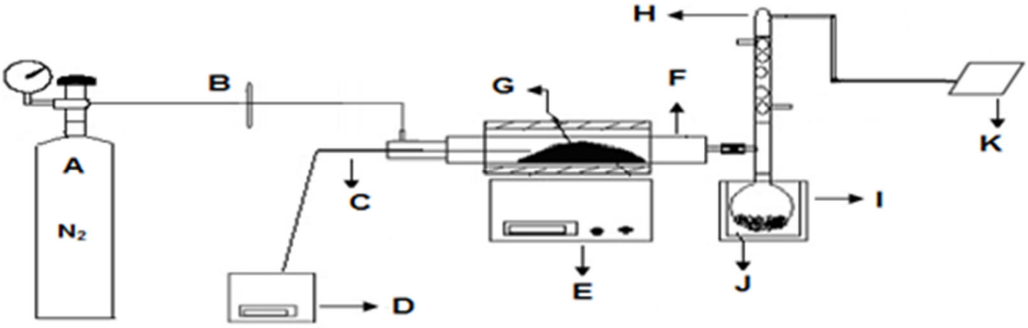

Figure 1. The schematic diagram of the experimental set-up for the co-pyrolysis. (A) nitrogen bottle, (B) float flowmeter, (C) thermocouple, (D) the temperature controller, (E) tube furnace, (F) reactor, (G) sample, (H) condenser, (I) cooling unit, (J) liquid collecting vessel, (K) gas collecting vessel.

In a typical run, the sample was placed in a stainless steel reactor. The reactor was heated by an electrical furnace in which the temperature was measured by a thermocouple inside the reactor. The air of the reactor was removed with nitrogen flow of 30 mL min^{-1} and reactor was heated to a desired temperature with a heating rate of 10 °C min^{-1}. The outlet of the reactor is connected to a round-bottomed flask with a reflux condenser where condensation of the pyrolyzate occurred. The reaction products are classified into three groups: gas, liquid hydrocarbons (tar) and residual coke. The yield of tar collected in the round-bottomed flask, and the yield of residual coke as the char remaining inside the reactor after the experiment were calculated. The gas products collected by a receiver vessel connected to the end of the reflux condenser.

RESULTS and DISCUSSION

Product yields

It is known that temperature has a significant effect on the yield of pyrolysis products [14-16]. The changes in product yields with temperature (600 °C, 700 °C and 800 °C) during the co-pyrolysis of PP and oil shale are given in Figure 2.

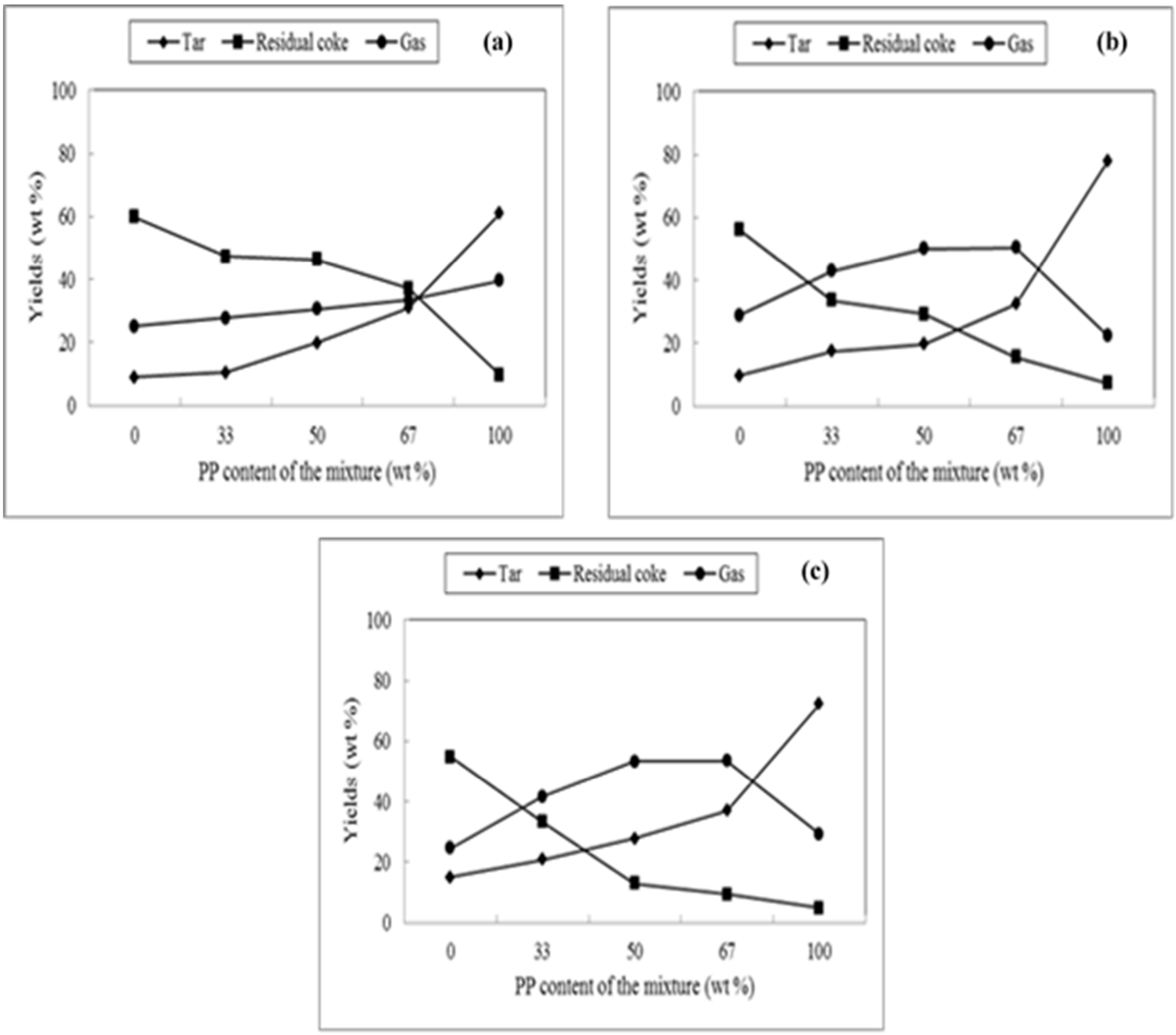

Figure 2. Effect of weight percentage of PP in the mixtures on product yields at a temperature of: (a) 600°C, (b) 700°C, and (c) 800°C.

As seen in the figure, the highest liquid yield was found to be 36.5% at the mixture ratio of 67% and at 800°C. The use of sweeping gas in the pyrolysis processes provides an inert atmosphere and helps to prevent secondary cracking reactions by removing the hydrocarbon vapors formed in during pyrolysis, and leads to an increase in the yield of the liquid product [17]. In pyrolysis processes performed at different mixture ratios and temperatures, a decrease was observed in the yield of the solid product although an increase was observed in the yields of liquid and gas products. This situation can be explained by the fact that the bonds in the structure of samples are easily broken along with the effect of increasing temperature, and this affects the pyrolysis yield positively.

According to the co-pyrolysis results, higher ratios of liquid and gas product yields were obtained when compared to the values of oil shale yields. It is considered that an increase was observed in the liquid yield by bringing free radicals that formed during pyrolysis into steady state and by reducing the crosslinks in the structure of the polymer and oil shale. The crosslinks in the both of sample mixtures structures can be broken by effect of the increasing temperature. However, the amount of hydrogen in the oil shale structure is not sufficient to stabilize the radicals. Therefore, hydrogen should be directly provided to pyrolysis medium or the oil shale should be co-pyrolyzed with the compounds containing abundant hydrogen in their structure [18, 19]. The main reason for choosing PP as the second component in the co-pyrolysis process is the fact that it is an environmental waste and contains sufficient hydrogen to saturate the free radicals formed during the pyrolysis of the oil shale.

Conversion values (%) obtained by the addition of increasing PP ratios in the oil shale during the co-pyrolysis process and the changing with temperature are given in Figure 3. As it is seen in the figure, the conversion values also increase with increasing PP content of the mixture and temperature. This is because, as it was explained previously, the bonds in the oil shale structure are broken with increasing the temperature. These radicals are stabilized by the hydrogen provided from polypropylene. As a consequence, the liquid product yield was increased, and the gas product yield was also increased by the disintegration of the products into smaller molecular products with the temperature increase.

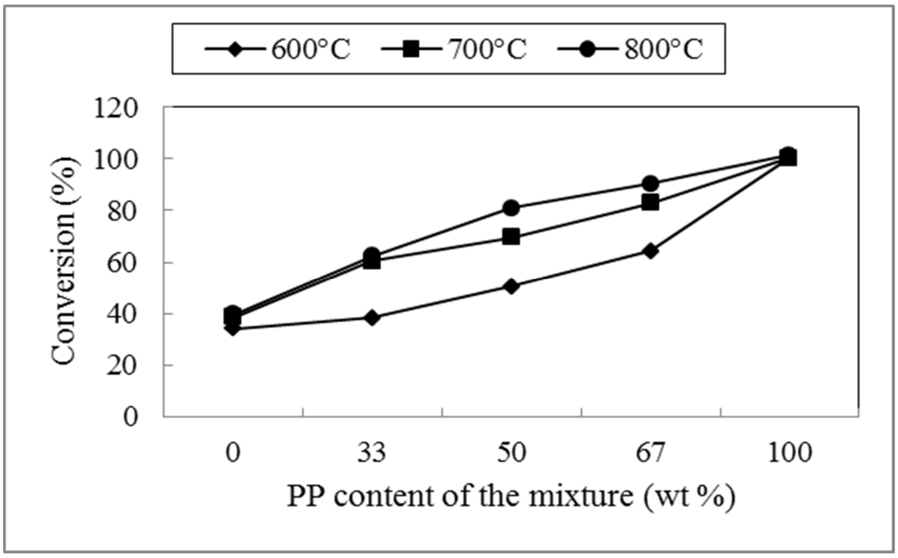

Figure 3. The effect of the percentage conversion of the PP content in the mixture**.**

Catalyst effect

It is known that various catalysts have an effect on the rate of some complex reactions in the pyrolysis process. In this study, the effects of three different catalysts selected on the co-pyrolysis of oil shale-PP mixture were examined. The red mud obtained during the production of aluminum; bentonite which is abundant in our country and zeolite which is applied in various heterogeneous reactions were selected as the catalysts. The co-pyrolysis experiments with catalyst were carried out at the mixture ratio of 67% at 800°C in which the liquid product yield was the highest. The red mud, bentonite, and zeolite were separately added to mixtures at the ratios of 0.5%, 2%, and 4% by mass to further improve the liquid product yield. The change of the liquid, gas, and solid product yields with catalytic pyrolysis is shown in Figure 4.

Any significant changes have been found when red mud is used as a catalyst (Figure 4). The surface area of red mud is smaller compared to other catalysts and therefore it does not interact sufficiently with the products during pyrolysis process. Although zeolite catalyst caused a decrease in the gas product yield, it did not cause a considerable change in the liquid product’s yield. The solid product yield also increased. This is because more aromatic hydrocarbons are formed in zeolite which has greater pore opening, and the amount of residual coke increases because aromatic compounds are inclined to coke formation with hydrogen transfer and cyclization reactions [20]. It is seen that the highest liquid product yield was obtained in the pyrolysis experiments with 4% bentonite was used as a catalyst. The reason of increasing of liquid products is the catalytic effect of metal oxides in the structure of bentonite and the large pore structure of bentonite.

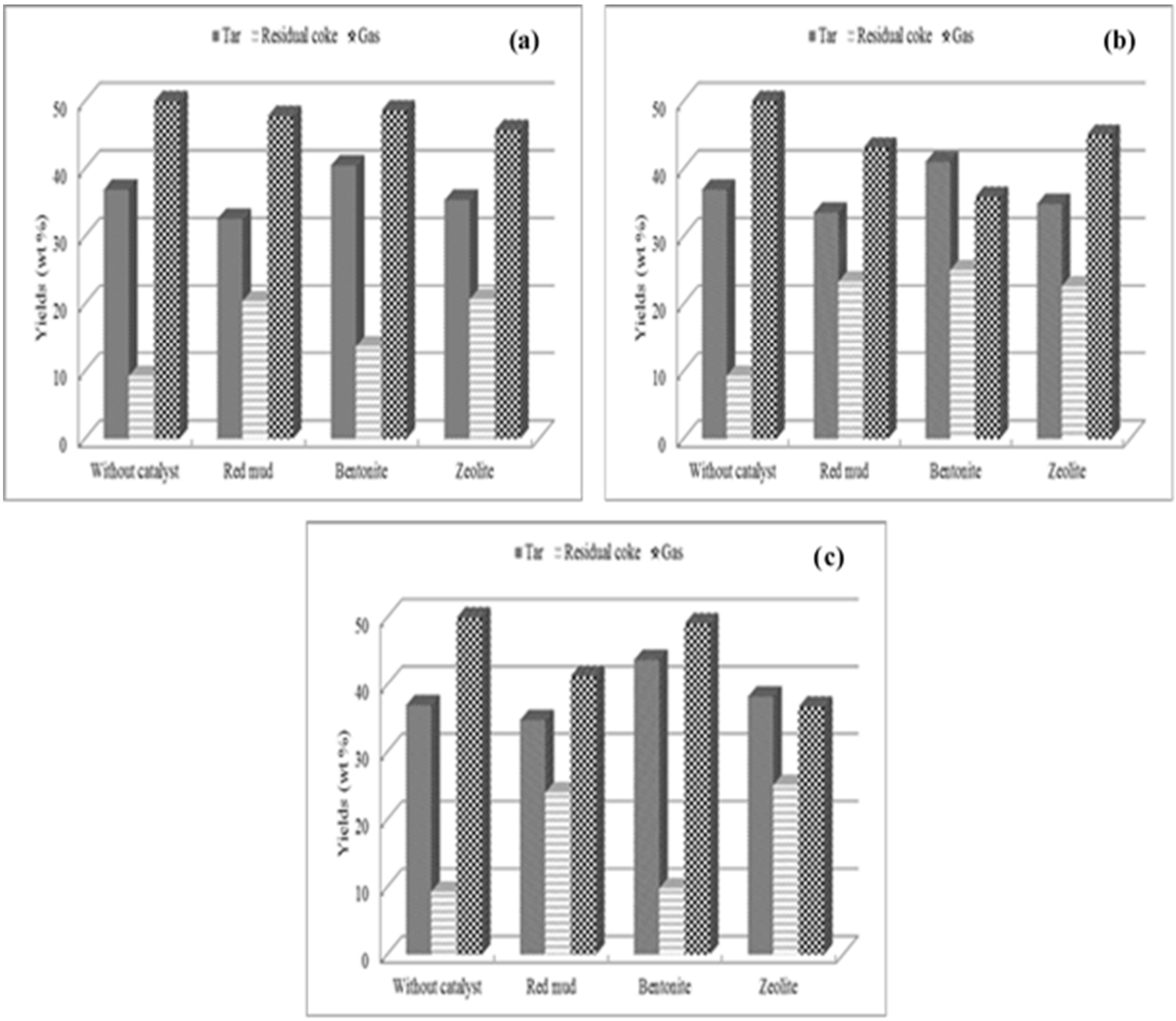

Figure 4. Effect of weight percentage of different catalyst on the yields at a temperature of 800°C and 67 wt% PP in the mixture a) 0.5 wt %, catalyst, b) 2 wt %, catalyst, c) 4 wt %, catalyst.

Characterization of pyrolysis liquid

The liquid products which were obtained from the separate pyrolysis of oil shale and PP at 800°C, the pyrolysis of 67% mixture at the same temperature, and the pyrolysis made with the addition of 4% bentonite under these conditions were given in Table 2. The substances detected in the GC-MS analysis are given as % peak area in the total chromatogram. GC-MS chromatograms of these products are shown in Figure S1-S4. During the pyrolysis process, the organic structure lost their H atoms and alkane radicals were directly converted into alkene radicals. In the pyrolysis process performed at 800°C and at the mixture ratio of 67%, alkene content is decreased when compared to the pyrolysis of oil shale and PP. This can be explained by the fact that the bonds are easily broken with increasing temperature, and consequently, free H radicals' concentration in the medium reacts with alkenes and converted to alkanes [21]. The phenol and phenol derivatives which are formed in significant amounts in the oil shale pyrolysis are not formed in the pyrolysis of oil shale and PP mixtures. The formation of phenol and its derivatives lead to a decrease in liquid and gaseous products. This is an undesired event in the pyrolysis process [22]. When polypropylene is added to oil shale, phenolic structures converted to cyclohexene structure as a result of the ring hydrogenation. This conversion is due to the hydrogen content in the PP structure. PP plays a role as the hydrogen donor for the oil shale under the experimental conditions studied. Although the addition of bentonite catalyst to co-pyrolysis medium under optimum conditions leads to an increase in the amount of alkane in the liquid product content, and it leads to a decrease in the amount of alkene.

Figure 5 shows the FTIR spectrum for the liquid products obtained from the pyrolysis processes. In the spectrum of PP, the peaks observed between 2850-2956 cm^{-1} indicate the presence of aliphatic hydrocarbon compounds in the structure. In the spectrum of oil shale, the peaks observed around 3000 cm^{-1} and at 732 cm^{-1} indicate the presence of aromatic hydrocarbon groups. When GC-MS results are considered, especially the presence of the excessive amounts of phenol and benzene derivatives in the structure of oil shale supports this situation. In the spectrum obtained from the co-pyrolysis of oil shale and PP mixture, it was observed that the aromatic groups were decreased but the aliphatic groups were increased. This also means that polypropylene served as the hydrogenation medium in the co-pyrolysis process [23]. The C-H stretching observed in the range of 2950–2850 cm^{-1} and 1460-1370 cm^{-1} in the spectrum indicates that this liquid has more aliphatic structures. When GC-MS results are considered, it is seen that liquid products of the mixture are rich in alkane and alkene compounds. In the spectrum obtained with the catalyst, the peak range of 2925-2957 cm^{-1} indicates the aliphatic C-H stretching and the functional groups including $–CH_3$, $-CH_2$ and –CH. The catalysts caused an increase the amount of aromatic hydrocarbon by saturating the functional groups with hydrogen. The increase of the peak at 1265 cm^{-1} and the increased peak group at 2950 cm^{-1} indicate increasing aliphatic hydrocarbon compounds.

HHV is one of the important parameters in determining the energy content of a fuel. The elemental analysis results showed that PP was better materials for producing fuels because of its high carbon and hydrogen contents and low oxygen content (Table 1). Therefore, the addition of PP in the pyrolysis oil shale is expected to improve the calorific value of the liquid product. In present study, obtained liquid products from different mixture ratio at 800°C had HHV of 40.1 MJ/kg for the mixture ratio of 33%, 40.8 MJ/kg for the mixture ratio of 50% and 41.3 MJ/kg for the mixture ratio of 67%. HHV values of liquid products showed their potential as an alternative of conventional diesel. As shown in these results, the addition of PP in oil shale pyrolysis obviously contributed to the increase in HHV value of the liquid products.

Table 2. GC-MS analysis results of the tars (% of total chromatogram).

			67 wt % Oil shale / PP	
Compound name	**PP 800°C**	**Oil shale 800°C**	**800°C**	**4 wt % bentonite 800°C**
ethylbenzene	-	0.22	-	-
1,3dimethyl benzene	-	1.06	1.05	1.85
1,2,3trimethyl benzene	-	0.80	-	0.40
1,2,3 trimethyl cyclohexane	4.20	0.81	-	3.72
2,4 diethyl-1-methyl cyclohexane	-	2.24	-	1.74
1,2 dimethyl-3-methyl cyclohexane	19.82	9.17	3.69	-
1,1,3,5 tetramethyl cyclohexane	4.02	30.75	5.47	1.69
1,2,4,5 tetramethyl cyclohexane	4.28	-	4.35	1.47
1,2,4 trimethyl cyclohexane	2.53	-	1.43	3.98
1 ethyl-2-propyl cyclohexane	3.87	-	4.84	1.76
4,8-nonane dimethyl-1,7-nonadien	-	-	-	1.23
n-decane	-	0.32	-	-
4-methyl-2-decene	0.48	-	0.58	-
dodecane	-	1.29	-	-
tetradecane	-	0.67	-	-
n-dodecene	-	-	-	0.63
7-methyl-6-tridecene	3.38	-	0.73	-
pentadecane	-	0.34	-	-
hexadecane	-	0.43	-	-
heptadecane	-	0.26	-	-
nonadecane	-	-	0.32	-
1,1,2-trimethyl cyclodecane	-	1.07	-	-
4 methyl decane	0.50	-	-	0.70
octadecane	0.71	0.23	0.51	-
1 methyl-3-propyl cyclo octane	7.26	-	2.64	7.42

Table 2 (Continued)

3 methyl-2-pentene	0.66	-	1.16	1.37
1,2,4,4-tetramethyl cyclopentene	-	-	0.18	-
3,3 dimethyl-1-hexene	0.33	-	0.12	-
3,3,5 trimethyl-1-hexene	-	-	0.47	1.39
2-methyl--3-heptene	3.80	-	6.41	1.89
2,4dimethyl--1-heptene	7.09	-	11.40	10.70
eicosane	-	2.13	0.18	1.51
heneicosane	-	0.34	-	-
docosane	0.23	0.38	-	-
tetracosane	-	0.29	-	-
pentacosane	0.12	0.43	-	-
hexacosane	-	0.34	-	-
heptacosane	-	0.52	-	0.35
octacosane	-	0.38	-	-
nonacosane	-	0.55	-	-
Triallysilane	12.44	9.09	14.36	9.52
Indene	-	-	0.29	-
biphenyl	-	-	0.36	-
phenol	-	5.17	-	-
4 methyl phenol	-	4.18	-	-
2,4dimethyl phenol	-	0.96	-	-
3 ethyl phenol	-	0.83	-	-
naphthalene	0.29	0.26	1.63	1.50
2 methyl naphthalene	-	0.48	0.64	1.26
2,3 dimethly thiophene	-	0.53	-	-
octadecanamide	-	3.18	-	-
benzoic acid	-	-	0.63	1.47

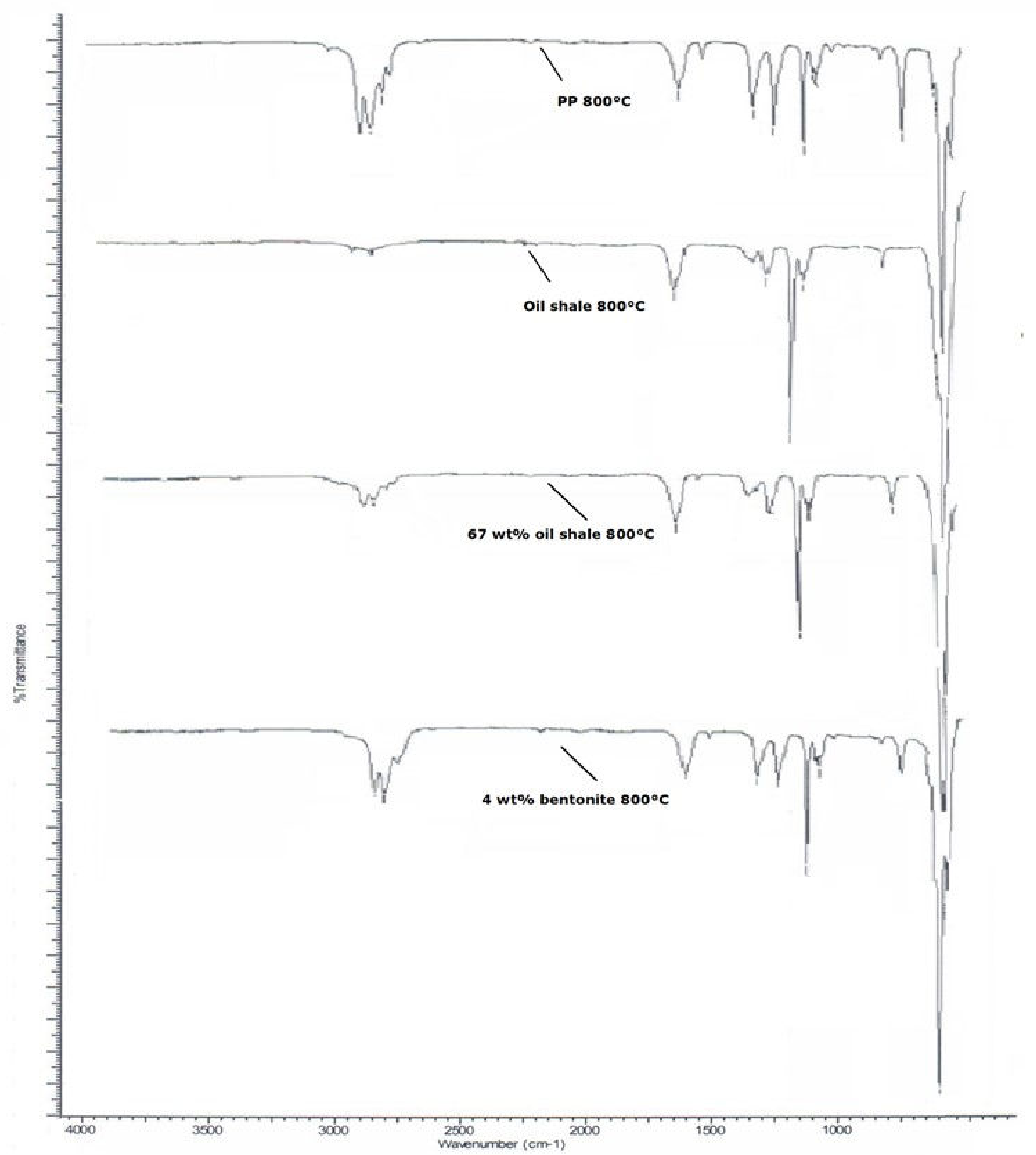

Figure 5. FTIR spectra of the tars.

CONCLUSIONS

The aim of the study is co-pyrolysis of a Turkish oil shale with PP. The conversion of oil shale and PP mixture into liquid product and other valuable chemicals using pyrolysis process is getting significant attention both as waste management and alternative energy technology.

- As a result of the experiments, precious liquid products could be obtained and the use of polypropylene as a raw material to achieve liquid products.

- In the co-pyrolysis processes, the liquid products were obtained at higher yields than the pyrolysis of the oil shale alone. During the co-pyrolysis process, PP acted as a hydrogen source, and saturated the free radicals formed as a result of breaking the crosslinks and made positive contributions to the liquid product yield by creating a positive synergistic effect.

- In the co-pyrolysis process, although the alkene structures in the liquid product decreased, the alkane structures gradually increased. This situation indicated that the hydrogen which is released in the presence of PP caused to convert alkanes into alkenes.

- The catalysts such as bentonite, zeolite, and red mud were added to the medium to further increase the liquid product yield at the mixture ratio of 67% and this mixture is pyrolyzed at temperature of 800 °C. Bentonite caused to increase the liquid product yield better than the other catalysts.

- GC-MS spectra showed that the obtained liquid products were similar to fossil-based liquid fuels, and also different types of chemicals were obtained.

- FTIR spectra showed that the aliphatic groups are predominant in all liquid products. This situation is supported in all spectra with the stretching and bending vibrations of C-H bond.

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Türkçe Öz ve Anahtar Kelimeler

Göynük Bitümlü Şistinin Polipiren ile Birlikte Pirolizi ve Piroliz Sıvısının Yapısal Karakterizasyonu

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Öz: Bu çalışma, ülkemizin önemli bitümlü şist yataklarının birinden alınan bitümlü şist numunesi ile polipropilen (PP) karışımlarının birlikte piroliz işlemine tabi tutularak yüksek verimde sıvı ürün elde edilmesi amacına dayanmaktadır. Çalışmada öncelikle bitümlü şist numunesi ve polipropilen ayrı ayrı, daha sonra da bunların belli oranlarda karıştırılmasıyla elde edilen karışım piroliz işlemine tabi tutulmuştur. Piroliz deneyleri karışım içerisinde %33, %50 ve %67 PP olacak şekilde üç farklı karışım oranında ve 600 – 800 °C sıcaklık aralığında gerçekleştirilmiştir. Deneyler sonucunda elde edilen gaz, sıvı ve katı ürün verimleri hesaplanarak bitümlü şiste eklenen PP'nin ve değişen piroliz sıcaklığının sıvı ürün verimi üzerine etkisi incelenmiştir. Deneyler sonucunda 800 °C'de ve %67 PP içeren karışım oranında en yüksek sıvı ürün verime ulaşılmıştır. En yüksek sıvı veriminin elde edildiği şartlarda ortama çeşitli katalizörler ilave edilmiş ve katalizörlerin pirolizden elde edilen sıvı ürün verimine etkisi incelenmiştir. Deneyler sonucunda elde edilen sıvı ürünlerin yapısı GC-MS ve FTIR gibi çeşitli spektroskopik yöntemler ile aydınlatılmış ve deney koşullarının sıvı ürün yapısı üzerindeki etkileri incelenmiştir. Sonuç olarak PP ve bitümlü şistin birlikte pirolizi sonucu elde edilen sıvı ürün veriminde fark edilir sinerjik etki gözlenmiş ve bu etki, ortama eklenen katalizör ile daha da artmıştır. Çalışmadan elde edilen sonuçlar PP ve bitümlü şistin birlikte piroliz işleminin tehlikeli atıkların değerli kimyasallar ve yakıtlara dönüşümü için çevre dostu bir yöntem olabileceğini göstermiştir.

Anahtar Kelimeler: Birlikte piroliz, bitümlü şist, polipropilen, karakterizasyon.

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