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UTILIZATION OF PRODUCTS OBTAINED FROM COPYROLYSIS OF OIL SHALE AND PLASTIC

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The main objective of the present study was to investigate pyrolysis of oil shale with polyethylene, in terms of yields and properties of the products obtained. A detailed characterization of gas, oil and char from copyrolysis is presented. Although no synergetic effect on the product yield was observed during the copyrolysis, the addition of polyethylene (PE) to oil shale improved fuel properties of shale oil leading to a decrease in the oxygen content of shale oil. As the ratio of polyethylene increased in the blends, the amount of aliphatic compounds in tars increased while that of polar compounds decreased. In addition, the presence of PE in the blend improved the composition of pyrolysis gas leading to an increase in combustible gases. The production of activated carbon from char obtained from oil shale/polyethylene (1/1) was also carried out. Although the surface area of activated carbon was smaller than that of obtained from lignocellulosic materials, it had a notable adsorption capacity for Cr(VI) (55.25 mg/g).

Introduction

The amount of waste plastics discarded each year is constantly increasing and is causing serious environmental problems. Therefore, polymer recycling has become a necessity. Due to the increased environmental awareness and depletion of natural oil deposits, the converting of waste plastics into liquid hydrocarbons is being considered a promising recyling method. For liquefaction of waste plastics, pyrolysis may provide a suitable means of recycling, of great interest both economically and enviromentally. Pyrolysis of polymers has been extensively studied for different purposes. Two types of polymers have been widely investigated: polyethylene and polypropylene (PP), because they represent 60–65% of all plastic wastes.

Another approach in utilization of plastic recycling is coprocessing. There has been considerable interest in the efficient conversion of plastic

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wastes mixed with coal into fuel or other valuable products. High conversion efficiencies have been obtained by coprocessing the coal with waste plastics [1–5]. The argument for this synergistic effect is that plastics posses a high hydrogen content, and may, therefore, serve as an inexpensive hydrogen source. On the other hand, copyrolysis of waste plastics with oil shale may be a feasible process since a mixture of solid fuel and polymers is more processable than the polymers themselves [6].

Any kind of polymer, irrespective of its composition, physical form (granules, films, bottles, etc.), color, melting point, etc., can be processed by this method without any significant feed preparation.

Oil shales represent for many countries a valuable potential source of liquid hydrocarbon and energy [7]. The deposits of oil shales are widely distributed throughout the world. In all over the world, the energy capacity of oil shale is 2.5 times than that of coal and 30 times that of petroleum [8]. It is promising resources for long-range alternatives to oil. Pyrolysis of various oil shales throughout the world has been extensively studied to determine the temperature at which the production rate is maximum, characterize the products evolved, investigate the reaction mechanism and find the effect of kerogen type on the characteristic of product [7, 9–13]. Oil shale is processed through pyrolysis (retorting process) to yield shale oil in China, Estonia and Russia as well as to generate the electric power by combustion [14].

Although coprocessing of coal with plastics has been extensively studied, there has been little study on coprocessing of plastics with oil shale. The kinetic study of thermal degradation of the mixture of oil shale and PP (3:1) showed that polypropylene acts as a catalyst in degradation of oil shale, accelerates decomposition of the organic matter in oil shale [8]. Similarly, in another thermogravimetric study carried out with the mixture of oil shale and polystyrene (PS), it was found that the PS accelerates decomposition of organic matter in oil shale [15]. An increase was observed in the total conversion values of the blends with the increase in the mass ratio of PS to oil shale in blends. Ballice et al. investigated the effect of polymer type on temperature-programmed copyrolysis of Turkish oil shales with atactic polypropylene (APP) and low-density polyethylene (LDPE) [16, 17]. Conversion into volatile hydrocarbons was found higher with an increasing APP ratio in the oil shale-APP blends while C_{16+} hydrocarbons and the amount of coke were lower in the presence of APP [16]. In contrast, conversion into volatile hydrocarbons was lower and the amount of coke was higher in the presence of LDPE [17]. On the other hand, in copyrolysis of Estonian shales with low-density polyethylene, the yields of copyrolysis products (gas, oil, solid residue) practically coincide with those calculated [18]. In another copyrolysis study, it was found that the oil from the combined pyrolysis of tyre/oil shale contained less sulfur and more light fractions than shale oil [6]. Most recently, Aboulkas et al investigated the pyrolysis of Moroccan oil shale/plastic mixtures by thermogravimetric analysis [19]. In all mixtures containing Moroccan oil shale and high-density polyethylene (HDPE), LDPE and PP, co-components have shown a behaviour differing from that of the pure materials. The experimental results indicated a significant synergistic effect leading to an increase in thermal stability during copyrolysis. They suggested that the reaction of hydrogen transfer from a polyolefinic chain to oil shale-derived radicals may probably stabilize the primary products from oil shale thermal degradation.

In this paper, we report the effect of polymer on the yield and composition of oils derived from oil shale. Providing a solution to the waste plastic problem was also aimed. The polymer selected for this purpose in this study is LDPE, as it is one of the main polymers in municipal waste plastics. In addition, the potential use of the char obtained from copyrolysis as an adsorbent was also investigated.

Materials and methods

Materials

The investigations were performed on oil shale sample taken from Göynük oil shale deposit (type I kerogen). Göynük oil shale deposit is the biggest (2.5 billion tonnes) and the most explored deposit in Turkey [16]. Oil shale sample was crushed to 1 mm particle size. Some properties of Göynük oil shale are given in Table 1. The model plastic used in this study was LDPE (as 3.2-mm extruded pellets, MW: 68500, % crystals: 26.3, d: 0.918–0.922 g cm^{-3}), which was supplied by ALPET-Izmir. To prepare the blends, LDPE, as pellet form, was physically mixed with oil shale in amounts ranging from 25 to 75 wt.% (as referred 1/3, 1/1, 3/1).

Table 1. **Properties of Göynük oil shale**

Proximate analysis, wt.%, air-dry basis	
Moisture	11.1
Ash	13.5
Volatile matter	64.91
Fischer assay analysis, wt.%	
Shale oil	22.8
Gas	25.6
Water	6.0
Residue	45.6

Copyrolysis

The copyrolysis experiments were performed in a fixed-bed design and stainless steel reactor (L: 210 mm; Ø: 60 mm) under atmospheric pressure using a semi-batch operation. In a typical copyrolysis experiment, a quantity of 100 (±0.5) g of blend was loaded and then the reactor temperature was increased at a heating rate of 5 °C min^{-1} up to 600 °C and held at this temperature for 1 h. The nitrogen gas (25 mL min^{-1}) swept the volatile products from the reactor into the traps. Liquid products were condensed in the first two traps by cooling with ice bath. Non-condensable volatiles (gases) were collected in Tedlar plastic bags. After the reaction, the aqueous phase in the condensate was separated from the organic phase (tar) by centrifugation. In each experiment, char, tar and aqueous fraction yields were determined by weight, and the gas fraction yield was calculated by weight difference.

TG analysis

Thermogravimetric analysis of Göynük oil shale and LDPE was performed in a thermogravimetric analyzer (Perkin Elmer Diamond TG/DTA) under N_2 atmosphere. The sample amount (particle size <100 µm) was about 10 mg for each TG run. The flow rate of purge gas (pure N_2, 99.99%) was kept at 200 mL min^{-1}. The sample was heated from the ambient temperature up to 800 °C with heating rate of 10 °C min^{-1}.

Gas analyses

Pyrolysis gases collected in Tedlar bags were analyzed by gas chromatography using a HP model 5890 series II with a thermal conductivity detector. A stainless steel packed column(6.0 m × 1/8 in. Propac Q, 2.0 m × 1/8 in. 5A molecular sieve, serially connected to each other) was used. The separation of CO_2, C_1, C_2, C_3, C_4, C_5 and C_6 hydrocarbons was achieved by the Propac Q column and the separation of O_2, N_2 and CO was carried out with the MS 5A column.

Oil analysis

Elemental analysis (C, H, S and N) of tars was determined with an elemental analyzer (Carlo Erba 1106). The asphaltenes of the tars were precipitated by addition of *n*-hexane. Soluble (in *n*-hexane) tar portions were fractioned by column chromatography into aliphatic, aromatic and polar fractions using hexane, toluene and methanol, respectively [20].

Demineralization and activation of pyrolysis char

The char obtained from the copyrolysis of 1/1 mixture was demineralized to decrease its inorganic content. It was boiled in HCl solution (15 wt.%) at 100 °C for 1 h. After HCl treatment, the char was washed with distillated water until no chlorine ions could be detected and then was dried at 100 °C for 24 h. Activation process was carried out in the pyrolysis reactor by carbon dioxide. In activation process, non-demineralized and demineralized chars were heated up to 900 °C under a flowing nitrogen atmosphere (25 mL min^{-1}). When 900 °C was reached, the inert atmosphere was rapidly substituted by flowing carbon dioxide (350 mL min^{-1}). The tested activation times were 2, 4, 6 and 8 h. At the end of desired the activation time, the reactor was cooled to room temperature under nitrogen atmosphere. The resulting carbons (activated carbon) from activation process were weighted to calculate the burn off value.

Characterization of char and activated carbons

The BET (Brunauer-Emmett-Teller) surface area measurements were obtained from nitrogen adsorption isotherms at 77 K using a Micrometrics FlowSorb II-2300 surface area analyzer. An automatic equipment (TriStar 3000) was used to obtain the nitrogen adsorption isotherms. The micropore volumes and the external area were calculated by the *t*-plot approach. The quantitative determination of the acidic surface functional groups was done according to Boehm’s method [21].

Aqueous adsorption characteristics

The ability of the chars and activated carbon to remove phenol and Cr(VI) from aqueous solutions was determined under batch-mode conditions. The pH of each Cr(VI) solution was adjusted to optimum value of 2. No pH adjustment was done for phenol solutions. Test solutions (100 mL) of various concentrations (50–250 mg L^{-1} for phenol and 20–80 mg L^{-1} for Cr(VI)) were added to the adsorbent (0.1 g) in flasks and suspensions were shaken for an equilibrium time determined with preliminary studies (4 and 2 hours for phenol, and Cr(VI) respectively). The speed of orbital shaker was chosen as 150 rpm The Cr(VI) solutions were prepared by dissolving potassium dichromate in distilled water. The filtrates were analyzed for residual phenol concentration using the UV-visible spectrophotometer (UV-160A, Shimadzu) at 269 nm. For residual Cr(VI) concentration, the filtrates were analysed by reaction with 1,5-diphenylcarbazide followed by absorbance measurement at 540 nm using the UV-visible spectrophotometer.

Results and discussion

Results of thermogravimetry

Thermogravimetric analysis of the Göynük oil shale revealed that major thermal decomposition occurred around 300–520 °C as shown in Fig. 1. From pyrolytic differential thermogravimetric (DTG) curves, initial weight loss corresponds to moisture removal, followed by a second degradation event around 300–520 °C, where the evolution of light volatile compounds occurs from degradation of kerogen. This is consistent with other published findings [19, 22]. At 520 °C the yield of residue was about 45% under these test conditions. For LDPE, the decomposition takes place in the range 380–500 °C with a value of T_{max} at around 470 °C, and the amount of residue is negligible. As can be seen in Fig. 1, a comparison between the pyrolysis behaviour of oil shale and the LDPE can also be made. PE has a narrow degradation temperature interval, it is interesting to observe that it entirely overlaps the maximum evolution of volatile matter from oil shale. TG-DTG results showed that organic matter in oil shale and polymer was completely decomposed at the temperature below 600 °C.

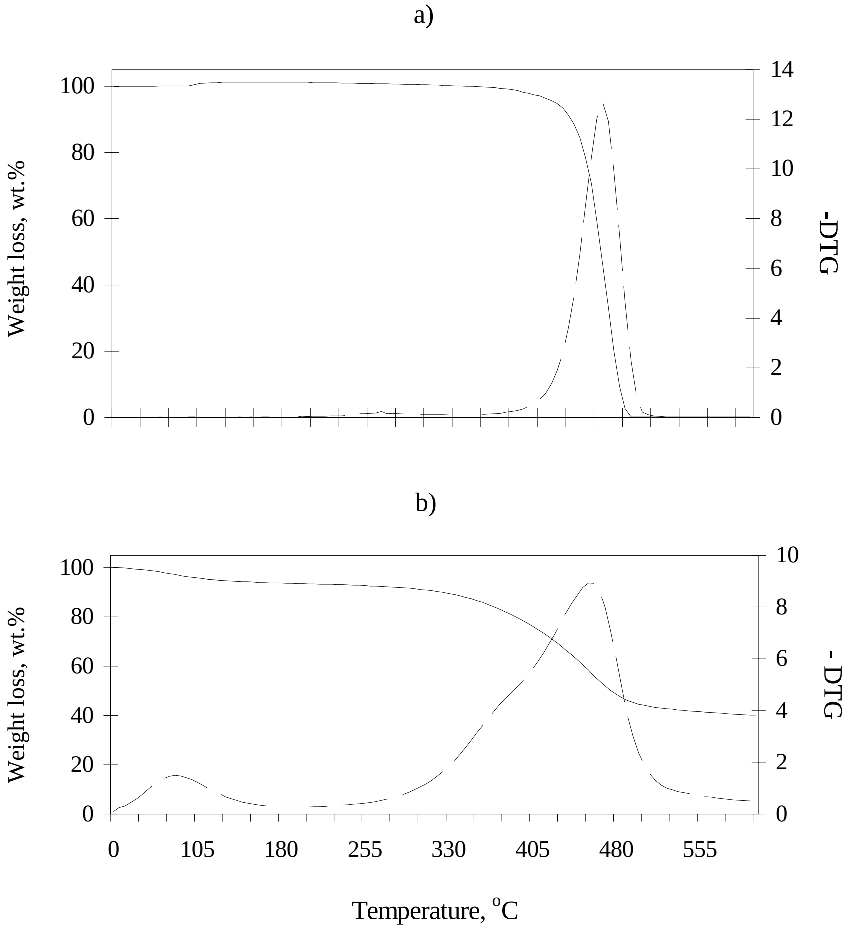

Fig. 1. TG and DTG curves of (a) Polyethylene (b) Göynük oil shale.

Copyrolysis

Based on the results obtained by TG-DTG, copyrolysis experiments were carried out at 550 °C. The product distributions from the pyrolysis of LDPE, oil shale (OS) and LDPE/oil shale blends are given in Table 2. The experimental yields of the pyrolysis of the blends are close to the theoretical ones. Only, yields of aqueous phase obtained from blends were slightly different from the theoretical ones. This will be discussed later in the text.

Table 2. **Product distributions from copyrolysis of oil shale with LDPE**

Feed (LDPE:OS)	1 : 0	3 : 1	1: 1	1: 3	0 : 1
Reaction products, wt.%					
Gas[*]	20.8	16.0	27.8	26.1	31. 7
Liquid					
Tar	79.0[**]	71.3	53.3	37.0	23.7
Aqueous	–	4.3	2.0	8.8	6.5
Char	0.2	8.4	16.9	28.1	38.1

[*] Calculated from mass balance.

[**] Waxy product at the room temperature

Pyrolysis liquids

Although LDPE-derived condensed product was in the form of wax, the product collected in traps contained the aqueous and organic phases (wax + tarry compounds) in the case of pyrolysis of oil shale and blends. Aqueous fractions consisted mainly of water (92–94%). It is well known that the water originates from a dehydration reaction of organic compounds in oil shale in addition to physically bonded and free water in it.

Table 3 shows the chemical and physical properties of tars from pyrolysis of oil shale and blends. The properties of wax obtained from pyrolysis of LDPE alone are also given in the same table. The heating values in this study were obtained from calculation by Dulong's formula [23].

$$\text{HHV (MJ/kg)} = [338.2 \times \%\text{C} + 1442.8 \times (\%\text{H} - \%\text{O}/8)] \times 0.001$$

Table 3. **Properties of pyrolysis tars, wt.%**

	PE wax	LDPE:OS			
		3:1	1:1	1:3	0:1
GCV[a], MJ/kg	48.38	45.36	44.33	43.50	32.73
Water, %	–	nil	0.32	0.85	17.11
Flash Point, °C		<30	<30	<30	<30
C	84.86	80.90	80.30	80.79	67.35
H	13.85	13.14	12.67	11.95	9.36
N	–	0.31	0.40	0.57	1.52
S	–	0.22	0.50	0.79	2.08
O[b]	1.29	5.43	6.13	5.90	19.69

[a] gross calorific value

[b] by difference

Although no synergic effect on the pyrolysis yields was observed, the addition of LDPE to oil shale had positive effect on fuel properties of shale oil. As seen from Table 3, the addition of LDPE led to a dramatic decrease in the oxygen content of shale oil. The result is reasonable, because water content of tars obtained from blends was very low. Water content of tars lower than theoretical ones shows that the tars obtained from blends were not miscible with water. The fact that the yields of aqueous phase obtained from blends were higher than the theoretical ones supports this idea. Because of the high carbon content, the calorific value of tars obtained from blends is higher than that of obtained from oil shale. Although the carbon content of the tars obtained from blends was considerable higher than that of oil shale, the ratio of LPDE in blend had no considerable effect on the carbon content of tars.

Tars are complex mixtures consisting of organic compounds from wide variety of chemical groups. To characterize the tar, the tars were separated into four fractions; asphaltenes, aliphatics, aromatics and polars. The compositions of pyrolytic oils are given in Table 4. The wax obtained from pyrolysis of LDPE alone is also given in the same table.

Table 4. **Composition of pyrolysis tars, wt.%**

	PE wax	LDPE:OS		
		1 : 1	1 : 3	0 : 1
Asphaltene	0.65	3.07	3.19	13.9
Aliphatic	72.30	66.32	56.58	24.93
Aromatic	26.68	17.84	25.14	11.66
Polar	1.02	15.84	18.28	63.41

The tar derived from oil shale consisted largely of polar compounds. As the ratio of polyethylene increases in the blends, the amount of aliphatic content in tars, which is important in the application of the tar as a fuel, increased while polars decreased. This is an expected result as degradation of polyethylene produces a significant amount of aliphatic compounds.

In addition, low sulphur content and high calorific value of copyrolysis oils reflect the potential of these oils for the use as fuels besides being used as chemical feed stocks.

Pyrolysis gases

The compositions of gases obtained from pyrolysis of PE, oil shale and oil shale/polyethylene (1/1) mixture are given in Table 5. The fact that the amount of CO_2 from copyrolysis was lower than the theoretical ones may show that the addition of PE inhibited the decarboxylation of oil shale in pyrolysis. Similarly, the lower amount of hydrogen from copyrolysis may be due to the consumption of hydrogen by hydrogenation reactions which led to a decrease in polar and asphaltenic compounds (Table 4). It is known that because of the high hydrogen content, polyolefinic plastics are excellent hydrogen sources. The total amount of hydrogen sulphide (H_2S) was also determined. The amounts of H_2S were 1.85 and 3.88 wt.% in the gaseous products for pyrolysis of oil shale and oil shale/polyethylene mixture, respectively. H_2S may evolve only from degradation of organic sulphur compounds in oil shale kerogen. Because of hydrogenation reactions, the amount of hydrogen sulphide from the mixture was higher than that from oil shale.

Table 5. **Composition of the gaseous products from pyrolysis, mol %**

Products	OS	PE:OS	PE
H_2	26.18	22.23	34.89
C_1	17.18	19.07	12.99
C_2	7.42	11.03	16.21
C_2^-	5.38	12.86	9.43
C_3	3.42	10.18	23.22
C_4	3.27	8.85	1.95
C_5	–	7.35	0.49
CO	6.07	3.73	–
CO_2	31.08	4.70	–

Moreover, gross calorific values of pyrolysis gases from the mixture and oil shale were high – about 58.9 and 25.7 MJ Nm^{-3}, respectively. These heating values represent the mean heating values of the gas mixture, and they have been calculated from the concentration of each individual gas and its corresponding heating value. Since the gaseous product from copyrolysis contains much combustible gases, it can provide some part of the energy requirements of the pyrolysis plant.

Activation of pyrolysis char

One of the aims of this study was to produce activated carbon from the solid residue of copyrolysis. Because of high ash content in oil shale, the obtained chars contain much ash. Ash content of chars did not change with the ratio of PE in blends. Ash content of all chars was around 31–35 wt.%. By demineralization, ash content could be decreased at the ratio of around 40%.

To obtain the activated carbon, demineralized and non-demineralized chars obtained from oil shale/polyethylene (1/1) were activated with CO_2. In the activation of non-demineralized char, char was completely burned in an activation time of 2 h. This result is due to high content of inorganic matter of non-demineralized char since char reactivity is related to the content of inorganic compounds of the carbonaceous materials [24]. Several other researchers have also mentioned that some inorganic compounds showed catalytic effect on gasification [25–27]. In the case of demineralized char, the carbon burn-off exhibited a linear increase with increasing activation time. Figure 2 shows the influence of activation time on the degree of burn-off in CO_2 achieved for demineralized char. The effect of activation time on the BET surface areas, micro porosity and pore size of activated chars are presented in Table 6. The BET surface area and micropore volume of activated char were considerably increased by increasing the activation time up to 12 h, but further increase in activation time led to a decrease in both surface area and microporosity. The surface areas of activated carbons are smaller than those of lignocellulosic materials obtained more traditionally and of commercial activated carbon [28–31]. The reason may be due to high ash content of activated chars.

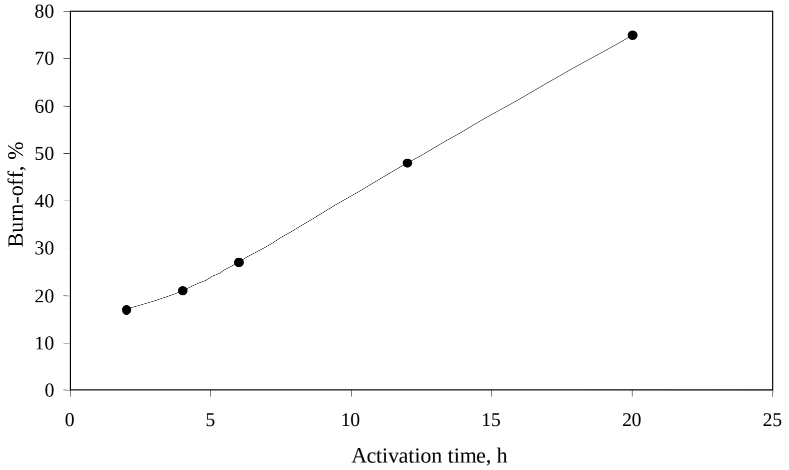

Fig. 2. Carbon burn-off in CO_2 for char obtained from pyrolysis of oil shale/PE 1:1 mixture.

Table 6. **Characteristics of activated carbons from demineralized chars varying with the activation time**

Activation time, h	BET surface area, $m^2\ g^{-1}$	External surface area, $m^2\ g^{-1}$	Micropore volume, $cm^3\ g^{-1}$	Average pore size, nm
–	39	65.33	0.024	35.1
4	83	54.09	0.113	44.7
6	107	82.29	0.140	41.9
12	129	120.43	0.148	43.2
20	61	137.83	0.021	35.8

SEM images of demineralized raw char and activated demineralized char (for 12 h) are shown in Fig. 3. It can be seen from the micrographs that the activated carbon prepared from copyrolysis char has cavities on its external surface.

The adsorptive properties of activated carbon are determined not only by its porous structure but also by its chemical composition. In this study, the amount of surface oxygen groups on the chars having acidic and basic properties has been determined by Boehm titration method. The concentrations of acidic and basic surface oxygen groups of chars and activated char (for 12 h) are shown in Table 7. The results presented in Table 7 revealed that the predominant functions at the surface of the demineralized char and activated char are acidic. Concentration of surface groups in activated char is higher than that in raw chars.

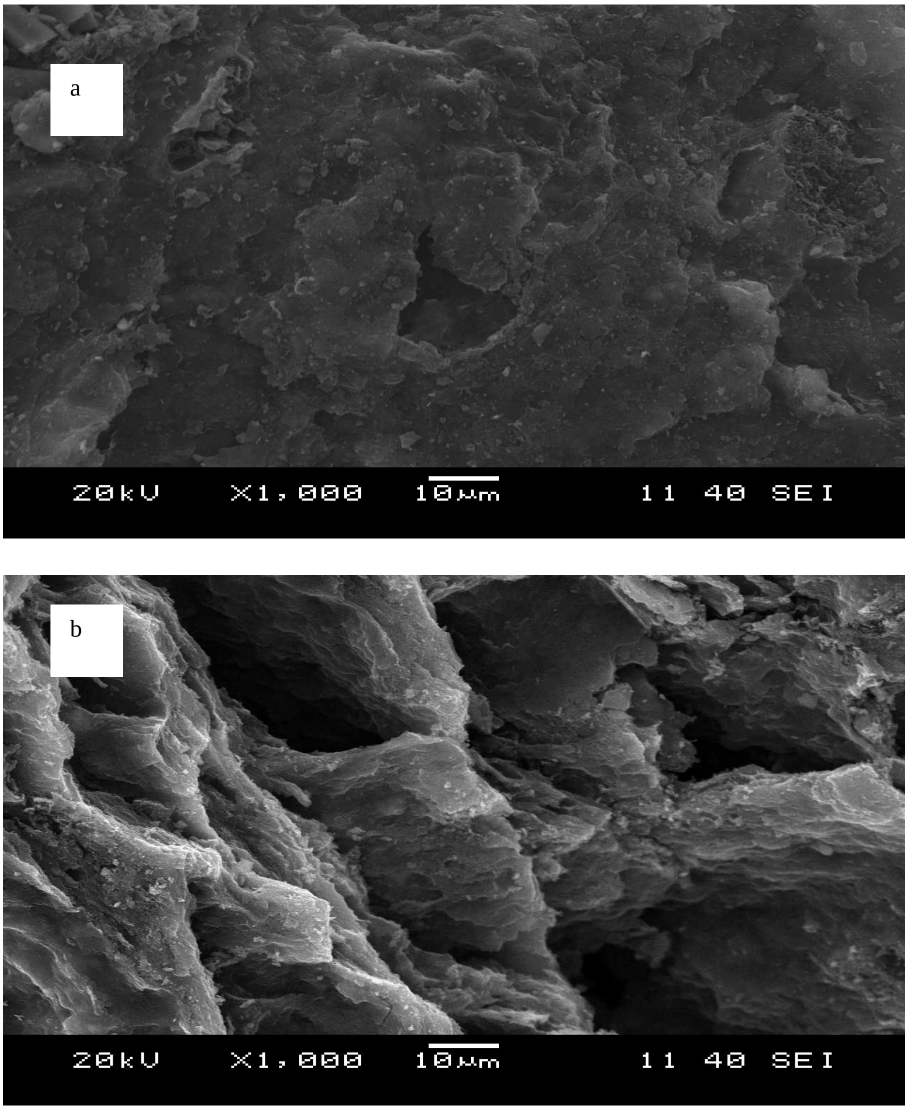

Fig. 3. SEM images of raw char (a) and activated char for 12 h (b).

Table 7. **Total amounts of surface acidic and basic sites of chars**

	Non-demineralized char	Demineralized char	Activated char
Total acidic sites, mmol H^+/g carbon	1.68	2.30	2.80
Total basic sites, mmol OH^-/g carbon	1.88	0.40	1.80

Adsorption results

Aqueous adsorption tests were conducted on char and demineralized char obtained with oil shale/PE (1/1) mixture and selected activated carbon obtained from activation for 6 hours with the aim of assessing potential applications in the water-treatment industry. Two target species were chosen as representative of toxic organic (phenol) and inorganic, Cr(VI), contaminants.

In the case of Cr(VI), the adsorption capacity of chars and activated carbon decreased significantly with increasing pH. Similar behavior has also been reported by other researchers [32, 33]. 2.0 was the optimal pH for the Cr(VI) uptake for adsorbents. The variation of adsorption of chromium ions can be explained by taking into account the surface charge of the carbon and the existing forms of chromium species at different pH values. Under acidic conditions, the surface of the activated carbons becomes highly protonated and favors the uptake of Cr(VI) in the anionic form [32].

The equilibrium adsorption measurement of Cr(VI) has been carried out at pH 2.0. The isotherm data for all tested adsorbents fit the Langmuir model well. The Langmuir model is used for homogeneous surfaces and demonstrates monolayer coverage of the adsorbate at the outer surface of the adsorbent. Table 8 shows the Langmuir parameter obtained by fitting the Cr(VI) adsorption on chars and activated carbon. Activated carbon showed the highest adsorption capacity. The result of the Boehm titration indicated that the total amounts of oxygen acidic groups on demineralized char (DC) and activated carbon (AC) were almost the same, but they exhibited different adsorption capacities. The reason for the different performance of DC and AC may mainly be due to the surface area; surface area of AC is larger. On the other hand, char exhibited slight higher adsorption capacity than DC. The reason may be high ash content of char, which attributes more active groups of mineral species. As conclusion, it can be mentioned that both characteristics of carbon surface and mineral content had an effect on the Cr(VI) uptake. Similarly, the study related to Cu(II) adsorption on the char from oil shale showed that adsorption capability of the char resulted from the presence of ionic species in the particle surface [34].

Table 8. **Parameter of the Langmuir adsorption model of Cr(VI)**

	Q_m, mg g^{-1}	K_L,L mg^{-1}	R^2
Char	38.17	0.597	0.99
Demineralized char	31.75	0.885	0.99
Activated carbon	55.25	15.877	0.93

Comparison may be made of Cr(VI) adsorption capacity found for adsorbents used in this study with more traditionally used lignocellulosic materials and low cost sorbents. Cr(VI) adsorption capacities of activated carbons or sorbents used in literature were: 7.44 mg/g for activated alumina and 12.87 mg/g for a commercial activated char coal [33], 42.1 mg/g for activated carbon from fabric cloth [35], 92.0 mg/g for activated carbo-aluminosilicate material obtained from oil shale [36] and 120 mg/g for hydrotalcite [37].

In the phenol adsorption, char and DC showed much lower adsorption capacity than AC. The experimental data obtained from the adsorption experiments did not fit for both the Freundlich and Langmuir isotherms. In contrast to Cr(VI), phenol adsorption depends only on the BET surface area and pore structure of adsorbent. Hence, AC was the only sorbent that showed considerable adsorption capacity of phenol (80.65 mg/g). The adsorption isotherm data was fitted to the Langmuir equation. But it has relatively low phenol adsorption capacity compared to most of adsorbents reported in literature. In literature, reported adsorption capasities of phenol are 216.2 mg/g for commercial activated carbon and 84.6 mg/g for synthetic zeolite [38], 158.2 mg/g and 75.48 mg/g for activated carbon from bituminous coal [39], 257 and 216 mg/g for activated carbons obtained from plum kernels [40], 107-200 mg/g from activated carbon obtained from lignin [41], 92.54 mg/g for activated carbon obtained from oreganum stalk [42], 44.9-112 mg/g for crosslinked starch polymers [43].

Conclusions

In this study, pyrolysis of oil shale/polyethylene (PE) mixtures was investigated. TGA analysis of oil shale and PE showed that interval of PE degradation overlapped the maximum evolution of volatile matter from oil shale and both they completely decomposed at the temperature below 600 °C. Copyrolysis experiments were carried out at 550 °C under nitrogen atmosphere.

In copyrolysis of oil shale with PE, no synergic effect on the pyrolysis yields was observed at all ratios of PE addition. However, the presence of LDPE in blends improved the quality of the tar obtained. The hydrocarbon content was elevated and the oxygen content reduced significantly. Although the tar derived from the oil shale consisted largely of polar compounds, since the ratio of polyethylene increased in the blends, the content of aliphatic compounds in tars increased while that of polars decreased. Besides tar quality, composition of pyrolysis gas also was effected by PE addition. PE inhibited decarboxylation of oil shale during pyrolysis leading to a decrease in CO_2 amount in the gaseous product. High amount of H_2S from the blend showed that PE also acted as hydrogen source and caused the hydrogenation of kerogen in oil shale.

All chars were not suitable for the use as a solid fuel because of their high ash content. By demineralization, ash content could be decreased at the ratio of around 40%. On the other hand, the activated carbon having a surface area of 129 $m^2\ g^{-1}$ was produced from the demineralized char by activation using

CO_2 while commercial activated carbon has a surface area more than 500 m^2 g^{-1}. The experiments related to aqueous adsorption characteristics of activated carbon showed that the prepared activated carbon could be used as an adsorbent for the removal of Cr(VI) from aqueous solutions.

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