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The synergistic effect of co-pyrolysis of oil shale and low density polyethylene mixtures and characterization of pyrolysis liquid

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In this study, co-pyrolysis of oil shale (Kütahya-Seyitömer, Turkey) and low density polyethylene (LDPE) is performed in a fixed bed reactor under different temperature and mixture ratios. The product yields and characters of co-pyrolysis and individual pyrolysis are compared. The aim of the study is also aimed to find out possible synergistic effects on the yields of tar. Pyrolysis experiments are carried out at various mixture ratios of oil shale/LDPE at the weight ratio of 33%, 50%, 67% and in the temperature range of 600–800 °C. The effects of temperature, LDPE amount in the mixture and catalysts on the thermal degradation of oil shale are investigated in terms of both yield and properties of tar. Tar obtained during the experiments have been characterized with GC–MS and FTIR. The synergistic effect on the formation of valuable products is also discussed. As expected the co-pyrolysis of oil shale and LDPE gave high percentage of tar yields. In addition a remarkable synergetic effect was observed in the co-pyrolysis of oil shale and LDPE and this effect was improved by adding zeolite as a catalyst to the oil shale/LDPE mixture.

1. Introduction

Energy is essential to the economic and social development of life all over the world. The energy problem is a comprehensively discussed subject, and the number of concerns about the future of energy supply is increasing. The current share of energy sources worldwide and in Turkey has been shown in Table 1 [1].

Predicted oil prices, growing concern about the environmental pollution of fossil fuels, government policies and support for the construction of renewable production facilities in many countries, has increased the use of renewable energy sources. It is difficult for most renewable technologies to compete economically with fossil fuel over the planning stage. Renewable energy systems require electricity distribution and cogeneration (combined heat and power) with large capital cost. Therefore, these systems are usually founded on a small-scale [2].

In addition to renewable energy sources, there is also an interest in alternative energy sources due to the increasing energy requirement in recent years. Research for alternative energy has been intensified [3,4].

Oil shale as a kind of alternative energy source has attracted more and more attention due to large reserves and great commercial potential [5]. Oil shale is an organic-rich fine-grained sedimentary rock containing a great quantity of kerogen (10–65 wt% of the total mass) and mineral matrix [6]. The kerogen has high a hydrogen/carbon ratio, giving it the potential to be superior to heavy oil or coal as a source of liquid fuel. Oil shale is usually used as a source of fuel, solvent, chemical and other products after a thermal conversion process [7,8].

In Turkey, oil shale is the second largest fossil fuel source following the lignite reserves. The main oil shale deposits are widely distributed in the middle and western regions of Anatolia. The total reserves of these resources are estimated to be around 3–5 billion tons but the amount of discovered reserve is about 2.22 billion tons. The calorific value of oil shale varies between 500 and 4500 kcal/kg. Therefore, a detailed study must be made on the possible use for each reserve [9]. Owing to its importance in energy utilization, effective and economic utilization of oil shale is under intensive study [7,10–15].

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Table 1
Share of energy sources.

Fuel type	Share, % world	Share, % Turkey
Oil	32.4	27.0
Coal	27.3	29.0
Gas	21.4	32.0
Nuclear	5.7	0
Hydroelectric	2.3	4.0
Geothermal, wind, solar	0.9	3.0
Biofuels and waste	10.0	5.0

Among many conversion processes, pyrolysis is an efficient energy conversion technology. Pyrolysis of oil shale leads to the productions on of gases, liquid (water and tar) and char. The conversion of oil shale in the pyrolysis process should be investigated to obtain optimal conditions which will lead to high product yields and high quality of products.

Recently, co-pyrolysis has become an attractive method for a variety of economic reasons: in-place evaluation of fossil fuels, reduction of the volume of waste and recovery of chemicals [16–20]. Research on the co-pyrolysis process is generally focused on the synergistic effect. All improvements in pyrolysis oil quality and quantity during co-pyrolysis occur through synergistic effects. This effect depends on the type of feedstock, pyrolysis duration, temperature, heating rate, removal or equilibrium of volatiles formed, and addition of catalysts [21,22]. The type of feedstock is important among these factors; thus, synergistic effects on co-pyrolysis can be changed based on feedstock.

The co-pyrolysis method can be an environmentally friendly way for the conversion of oil shale and plastic waste into valuable products. The use of plastics in our daily life has increased rapidly during the last few decades. The amount of waste plastics discarded each year is constantly increasing and is causing serious environmental problems. Many of the plastic waste are evaluated by inappropriate environmental regulations for disposal methods such as incineration or landfill. Therefore, plastic recycling has become a necessity. Due to the increased environmental awareness and depletion of natural oil deposits, the conversion of waste plastics into liquid hydrocarbons has been considered a promising recycling method. Conversion of plastic waste to energy and chemical raw materials is provided by pyrolysis. However, it has been suggested that the addition of plastic into the coal during pyrolysis process may result in an increased coal conversion and liquid yield when compared to that obtained when coal alone is pyrolyzed [23–25].

Plastic waste materials could act as an inexpensive hydrogen source aiding the dissolution of coal during the thermal co-processing with mining materials with less hydrogen content such as oil shale, coal or biomass [26,27]. Product yield and its composition in co-pyrolysis of coals with plastic materials depend on the type of plastic. Having a high hydrogen-to-carbon ratios and convenient molecular chain structure, waste commodity plastics such as low and high density polyethylene, polyethylene terephthalate (PET), polystyrene (PS), and polyvinyl chloride (PVC) are suitable for liquid production [28]. Among these, low and high density polyethylene is such a polymer, used for various purposes. The use of polyethylene composes massive waste which cannot be recycled completely. Furthermore, the recycling process consumes huge amounts of energy and also produces low quality polymer.

Co-pyrolysis of plastic waste materials with oil shale has been studied by a few authors in recent years and these studies indicated a synergistic effect for co-pyrolysis of oil shale and plastic waste mixtures in the form of enhanced liquid yields.

Aboulkas et al. investigated the pyrolysis of Moroccan oil shale and plastic mixtures by thermogravimetric analysis [29]. In all mixtures containing Moroccan oil shale and high-density polyethylene (HDPE), low density polyethylene (LDPE) and polypropylene (PP), the maximum degradation temperatures of each component were higher than those of the individual components. The experimental results indicated a significant synergistic effect leading to an increase in thermal stability during co-pyrolysis. On the other hand, in co-pyrolysis of Tarfaya oil shale with plastics, experiments were performed in an autoclave reactor and the effects of the heating rate and pyrolysis temperature on product yields were investigated [30]. The results indicated that co-pyrolysis process leads to the higher oil yields comparing to individual pyrolysis of oil shale. Recently, in another co-pyrolysis study made by the same group, it was investigated a detailed characterization of the oil obtained by co-pyrolysis of Tarfaya oil shale and high density polyethylene (HDPE) and by pyrolysis of oil shale and HDPE individually [31]. The addition of HDPE to oil shale improved fuel properties of shale oil leading to a decrease in the oxygen content of shale oil. Ballice et al. investigated temperature-programmed co-pyrolysis of Turkish oil shales with at low density polyethylene (LDPE) and studied to determine the volatile product distribution and product evolution rate of coprocessing of oil shale with LDPE [32]. Conversion into volatile hydrocarbons was found lower with increasing LDPE ratio in oil shale-LDPE mixture while $C16+$ hydrocarbons and the amount of coke deposit were higher in the presence of LDPE.

The objective of the present study is to determine the synergetic effect in co-pyrolysis of oil shale and low density polyethylene (LDPE) with the aim of increasing the pyrolysis liquid yield. For this reason, the influence of pyrolysis temperature, mixture ratio of LDPE/oil shale on the product yields and distribution were investigated. In addition, the effect of catalysts on the products was investigated in order to determine the optimum pyrolysis parameters which given maximum liquid yield. In this study, Kütahya-Seyitömer (Turkey) oil shale was used as fossil fuel. On the other hand, polyethylene was selected as waste plastic, one of the main polymers in municipal waste plastics.

2. Experimental

2.1. Materials

Seyitömer oil shale sample was obtained from the city of Kütahya located in the west part of central Turkey. Pretreatments of samples were carried out before the experiments. The samples were crushed and sieved to obtain <2 mm fraction and dried at 105 °C for 24 h. Low density polyethylene (LDPE) was provided from the Özuğur-Akçim Plastic Company (Izmir, Turkey). A LECO 932 CHNS elemental analyzer was used to perform the elemental analysis of the oil shale and LDPE and the results are given in Table 2.