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Influence of oily wastes on the pyrolysis of scrap tire

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ABSTRACT

The co-pyrolysis of scrap tires with oily wastes from ships (bilge water oil and oily sludge) was studied to investigate the effect of oily wastes on the pyrolysis of scrap tire. Co-pyrolysis experiments were carried out in a fixed bed reactor in the absence and the presence of catalyst at 500 °C. The catalysts used in the pyrolysis were a commercial refinery catalyst and an industrial by-product containing iron. The fuel characteristics and chemical compositions of pyrolysis products were characterized by means of chromatographic, spectroscopic and standard ASTM methods. Although, the oily wastes did not affect the product yields from the pyrolysis of scrap tire, they improved the fuel characteristics of scrap tire derived oils. The fuel characteristics of co-pyrolysis oils (except flash point and sulfur content) had similar fuel characteristic with the commercial diesel. It was also found that the amounts of metal impurities in all pyrolytic oils were smaller than 0.3 ppm, which was a significantly low amount compared with those in the original oily wastes. Gross calorific values of pyrolysis gases were found to be in the range of 20.4–26.4 MJ Nm^{-3}. It was concluded that co-pyrolysis of scrap tire with oily wastes could be an environmentally friendly way for the conversion of disposable and hazardous wastes such as scrap tires, bilge water oil and oily sludge into fuels.

1. Introduction

Evaluation of disposable and hazardous wastes such as oily wastes and scrap tire is an important event in terms of environmental and economic reasons. One of the oily wastes is bilge water oil. It contains seawater, oily fluids, lubricants, cleaning fluids and other similar wastes which cumulate in the lowest part of a ship. In addition, it includes volatile organic compounds, semi-volatile organics, inorganic salts and metals [1]. Besides bilge water oil, another waste stream in the ship is oily sludge which is produced by the constant purification of fuel and lubricating oil by centrifugation. Discharge of untreated oily wastes is prohibited. If wastes have a hydrocarbon content >15 ppm, they are kept on ship and discharged to reception facilities in harbor [2]. Because of their varied nature and composition, they are difficult wastes to treat. Gravity separation is commonly used as a first step to separate the oily phase from aqueous phase. Then a post treatment technology such as coagulation, filtration, adsorption and membrane technologies is employed in order to clean water sufficiently [3–5]. The oily phase derived from all of these treatments creates another problem. They are classified as hazardous waste and disposed via incineration, mostly in cement plants [6,7]. However, a strict criteria has to be met before they can be accepted for incineration. Since they are not regulated by burner standards, they can only be burned by mixing with conventional solid fuels. Although oily wastes represent a problem for the environment, they can be considered as an energy resource. Recycling of these wastes provides greener, cost effective alternatives to fossil fuels.

Pyrolysis is one of the alternatives to incineration; it is environment friendly way to obtain useful products which may be used as fuels or chemical feedstock. In the case of the wastes containing heavy metals (expect mercury and cadmium), metals could be safely retained in the solid char produced from pyrolysis. There are number of studies dealing with conversion of waste lubricant oils [8–11] and oil sludge from oil storage tanks [12–15] into fuels by pyrolysis. Chang et al. [12] investigated the pyrolysis of oil sludge at 873 K. They obtained the oil, with a yield of 80.68%, which its' distillation characteristics was close to diesel fuel. For the improvement of pyrolysis oil, some catalyst/additives have been tested in oil sludge pyrolysis. Shie et al. [13,14] investigated the effect of some solid wastes (fly ash, DAY-zeolite and oil sludge ash), sodium and potassium compounds on the pyrolysis of oil sludge. And they have pointed out that the addition of these solid wastes improved the qualities of liquid oils. Moliner et al. [9] investigated the effect of pyrolysis conditions on the product yields and composition in the pyrolysis of waste lube oil. Their study showed that pyrolysis at high temperatures (650–700 °C) mainly

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produced products (C_2–C_4 olefins and BTX) as petrochemical feedstock while pyrolysis at 600 °C mainly yielded liquid product and C_1–C_3 alkanes. Similarly, Lam et al. [10,11] reported that the production of light olefins and aromatic compounds enhanced by increasing the temperature whereas decreased the yield of liquid product in a microwave-induced pyrolysis of waste engine oil.

Besides oily wastes, scrap tires can be considered as energy sources. The used three main processes for scrap tire valorization are combustion, gasification and pyrolysis. Among these processes, scrap tire pyrolysis provides valuable fuels such as combustible gases, liquid and solid fuels. A number of studies have been done to investigate the pyrolysis of scrap tires. In those studies which were carried out in different reactor types such as fluidized bed [16,17], fixed bed [18,19], conical spouted bed [20], plasma [21] and tubular reactor [22], the effect of temperature and/or catalyst on the yield and quality of pyrolysis products were investigated. It was reported that liquid product produced from pyrolysis of scrap tire is a complex mixture of hydrocarbons of 5–20 carbons and contains a higher proportion of aromatics and sulfur than conventional fuel. Co-processing of scrap tire with waste petroleum hydrocarbons may be one of the effective processing method since oily wastes can provide good solvency and hydrocarbon source especially aliphatic hydrocarbons. In our previous study [23], we studied the co-pyrolysis of scrap tire with oily sludge in a glass reactor (V = 0.25 L) in the presence of catalyst (in vapor phase contact mode). And the synergic effects in co-pyrolysis at different temperatures were investigated from the point of pyrolysis yields and chemical composition of pyrolysis oil.

The main aim of this study is to investigate the effect of the oily waste addition on the fuel characteristics of products derived from pyrolysis of scrap tire. For this purpose, co-pyrolysis of scrap tires with oily wastes was carried out in a fixed-bed reactor (V = 1 L) at 500 °C in the presence and absence of catalyst. In the catalytic experiments, the catalysts were used in contact directly with the feedstock. Therefore, catalysts effected the degradation of wastes itself. The special interest was placed in the fuel characteristics of whole pyrolysis products (gases, pyrolytic oil and char). The fuel characteristics of pyrolysis products were determined by using of standard test methods named as American Society for Testing and Materials (ASTM) and the chemical compositions of pyrolysis products were characterized by gas chromatography with a flame ionization detector (GC-FID), proton nuclear magnetic resonance spectroscopy (^{1}H NMR) and refinery gas analyzer (RGA).

2. Experimental section

2.1. Materials

Scrap tire (ST) was provided by a rubber recycling enterprise named as Akin Rubber Plant, Samsun, Turkey. Scrap tire samples were taken from the sidewall rubber of scrap tires and they were ground to particle size less than 2 mm. The scrap tire included no steel thread or textile netting. The rubber composition of scrap tire was 51 wt.% natural rubber, 39 wt.% styrene butadiene rubber and 10 wt.% butadiene rubber. Oily wastes (bilge water oil and oily sludge) were supplied by one of the companies contracted by the Port Authority of Aliağa-Turkey (Batı Çim Co.). The company is responsible for the collection, handling, treatment and disposal of ship generated liquid wastes. In the plant, both two oily wastes are treated by an oil/water separator to separate the oil phase from water phase and oil phase is sent to a cement fabric for incineration. Oily wastes were centrifuged at 5000 rpm for 30 min in our laboratory to separate the water phase from oily wastes. The oil phases obtained by centrifugation were denoted as bilge water oil (BW) and oily sludge (OS). The main properties of scrap tire and oily wastes are shown in Table 1. Metal contents of oily wastes are also given in Table 2.

The catalysts used in the pyrolysis were a commercial fluid catalytic cracking catalyst (FCC) and a disposable catalyst named as Red Mud (RM) which is a by-product from Aluminum Company. The FCC is a faujasite type zeolite catalyst. It contains SiO_2 – 58.0 wt.%, Al_2O_3 – 38.0 wt.%, Re_2O_3 – 1.5 wt.%, Na_2O – 0.3 wt.% and Fe – 0.5 wt.%. It has following properties: density – 0.89 g cm^{-3}; specific surface area – 255 m^2 g^{-1}; pore volume – 0.25 cm^3 g^{-1}. Red mud was supplied by Seydişehir Aluminum Company, Turkey. It mainly contains Fe_2O_3 – 37.72 wt.%, Al_2O_3 – 17.27 wt.%, SiO_2 – 17.10 wt.%, TiO_2 – 4.81 wt.%, Na_2O – 7.13 wt.%, CaO – 4.54 wt.% and has specific surface area of 16 m^2 g^{-1}. Red mud was calcinated at 600 °C before using as catalyst in the pyrolysis process.

2.2. Pyrolysis procedure

The pyrolysis experiments were carried out in a fixed bed design and stainless steel reactor (L; 210 mm; Ø; 60 mm) under atmospheric pressure using a semi-batch operation. The schematic experimental set-up was given in our previous study [24]. Pyrolysis was performed at the temperatures of 400, 500 and 600 °C with individual BW, OS and ST and at 500 °C on binary mixture with a

Table 1
The properties of scrap tire and oily wastes.

Feed	ST	BW	OS
Proximate analysis (as received, wt.%)			
Moisture	1.5	9.6	2.3
Volatile matter	66.7	88.4	93.4
Fixed carbon	27.4	1.9	3.6
Ash	4.4	0.1	0.7
Ultimate analysis (ash free basis, wt.%)			
C	84.05	80.30	84.53
H	7.99	12.05	12.72
N	0.23	–	–
S	1.41	0.84	1.10
O[a]	6.32	6.81	1.65
HHV[b] (MJ kg^{-1})	37.7	44.8	44.1
Viscosity at 100 °C (SUS)	–	9.8	1900

[a] Calculated from difference.
[b] High heating value.

Table 2
Metal contents in bilge water oil and oily sludge.

Feed	BW	OS
Heavy metals (ppm)		
Ag	<3	<3
Al	6.3	44
B	<3	<3
Ba	<3	<3
Ca	388	1800
Cd	<3	<3
Cr	<3	<3
Cu	<3	<3
Fe	62	170
Mg	<3	29.2
Mn	<3	<3
Mo	<3	<3
Na	15	33
Ni	<3	12
P	102	215
Pb	<3	<3
Sn	12	39
Ti	<3	<3
V	35	66
Zn	<3	54.6