Yields And Sulphur Contents Of Pyrolysis Products Of Waste Tires

Tuba (Aksoy) Bahtlı
Necmettin Erbakan University, Faculty of Engineering and Architecture, Department of Metallurgical and Materials Engineering
Konya, Turkey
taksoy@konya.edu.tr

Hakan Burak Karadağ
Necmettin Erbakan University, Faculty of Engineering and Architecture, Department of Metallurgical and Materials Engineering
Konya, Turkey
hbkaradag@konya.edu.tr

Derya Yeşim Hopa
Afyon Kocatepe University, Faculty of Engineering, Department of Chemical Engineering,
Afyonkarahisar, Turkey
dyhopa@aku.edu.tr

Şerife Yalçın Yastı
Selçuk University, Faculty of Fine Arts, Department of Ceramic
Konya, Turkey
syasti@selcuk.edu.tr

Veysel Murat Bostancı
Necmettin Erbakan University, Institute of Science, Mechanical Engineering
Konya, Turkey
vmuratb@hotmail.com

***Abstract*— Waste tires is an increasing enviromental and economical problem. Pyrolysis is a thermochemical process that can be used for recovery of the waste tire. In this study, firstly, granulated waste tires have been pyrolyzed in a fixed bed reactor under different reaction conditions of temperature, heating rate, and N_2 flow rate to find the optimum conditions that gave the highest liquid yield. The conditions that gave the maximum liquid yield were: 450°C reaction temperature, 10 °C/min heating rate and 1 liter $N_{2(g)}$/min flow rate. In this work, the sulphur contents of pyrolytic products were also compared. The results revealed that, the most important parameters affecting the sulphur amount of products were temperature and N_2 flow rate. Pyrolysis conditions for producing solid product containig the lowest amount of sulphur content were 500 °C with 15 °C/min heating rate and 0.5 liter N_2/min flow rate. For producing the liquid product with the lowest sulphur content the reaction conditions were found to be 400 °C, 15 °C/min heating rate and 1.5L/min N_2 flow rate.**

Keywords—Pyrolysis, waste tires, yield, sulphur.

I. INTRODUCTION

The main purpose of studies on waste recycling is to obtain an energy benefit with a minimum environmental impact [1, 2, 3]. One of the biggest and increasing enviromental problem in the world is end-of-life tyres as more than 3 million tonnes of waste tires are discarded in European Union annually [4].

Pyrolysis is a suitable method for the recovery of valuable products from waste tires to produce pyrolytic oil that is a mixture of hydrocarbons, and produced by the condensation of reaction gases [5, 6]. Pyrolytic liquid product can be used as a fuel directly or mixing with petroleum refined oils [4].

The waste tires are composed of valuable natural or petroleum based chemicals such as natural rubber and/or stirene-butadiene rubber [4]. Pyrolytic oil obtained from waste tire can replace valuable chemicals such as limonene, benzene, toluene and xylene [7].

Gas and solid products of waste tire pyrolysis also can be used as a fuel, solid products can be used as low grade carbon black in many production areas [8].

In the literature there are many reports about optimum parameters for producing the pyrolytic oil with the highest yield. In their work, Banar et al. studied on pyrolysis of waste tires under the conditions of 350–600 °C with the heating rates of 5 and 35 °C/min in a fixed bed reactor to produce pyrolytic oil. The maximum pyrolytic oil yield was obtained at 400 °C for both of the heating rates. Pyrolytic oil yield decreased from 38.8% to 31.1% with the increasing heating rate from 5°C/min to 35 °C/min. Pyrolytic oils showed similar fuel properties with the diesel from the point of HHV, density and viscosity. Functional analysis of pyrolytic oils also showed the pyrolytic oil is partially similar to diesel than gasoline with their significant concentrations of aliphatic and aromatic hydrocarbons. These results show that pyrolytic oil had fuel properties similar to liquid fuel [5].

C. Roy et al. studied the pyrocycling of tires was typically carried out at a temperature of 480–520°C under vacuum into the reactor. They found that the oil yield with the vacuum process was higher than the oil yield from an atmospheric pyrolysis process. Their pyrolysis oil had a higher calorific value (44 MJ:kg) than the used tire from which it was recovered (33 MJ:kg) and wood charcoal (30 MJ:kg). And also this pyrolysis oil had low ash (0.05 wt.%), sulphur (0.8–1.5 wt.%) and residual carbon (1–2 wt.%) contents. They assumed that based on fuel properties of their pyrolysis oil, tire-derived pyrolytic oils could be considered a valuable component for use with conventional fuels. Then the total pyrolytic oil could be directly used as fuel [9].

Williams et al. observed that in tire pyrolysis, as the pyrolysis temperature was increased, liquid and gas product yields increased, however, solid product yield decreased [10]. Laresgoiti et al reported that liquid product yield increased with the increase in temperature [11]. Aydın and Kılıc studied on effect of nitrogen gas flow rate on product yield and found negligible effect on product yield [12].

Sulphur is incorporated as a processing aid for vulcanization process during tire manufacture. Because of that fact, pyrolysis products of waste tire contain high amounts of sulphur in their chemical structure [13]. The amount of sulphur is limited for environmental reasons. The maximum limit for diesel fuel in Turkey is 0.1 wt. according to TS 6838 EN ISO 8754 standard [14]; but for marine diesel the maximum limit for sulphur is 2 wt% according to the ISO 8217 standard [4]. In literature there are works on sulphur amount [15] and some methods to decrease the amount of sulphur especially in liquid product [14, 16]. Among them acidic desulphurization methods with acetic acid and formic acid are sucessful methods for decrease of sulphur in pyrolytic oil to very close values to that of diesel.

The objective of this work was to investigate the effects of pyrolysis parameters on the pyrolytic oil yield, and the sulphur content of the oil.

II. EXPERIMENTAL

Granulated waste tires that have 0.85-1.6 mm particle size were supplied by Selçuk Rubber and Plastic Plant in Konya /Turkey. A fixed bed reactor was used to produce tire derived pyrolytic oils as a function of pyrolysis temperature (400 °C, 450 °C and 500 °C) and heating rate (10 °C/dk., 15 °C/dk., 20°C/dk.,). The yield of liquid product, solid product (char) and the gas product was calculated for all pyrolysis parameters. The sulphur content of waste tire, pyrolythic oils and solid products were analyzed by using carbon-sulphur analyser (MetMultilab). The sulphur amount of gas product was calculated from mass balance. TGA analysis was conducted using Shimadzu DTG-60 in N_2 atmosphere. The peak firing temperature was 550 °C and heating rate was 10 °C min^{-1}. Chemical components of the pyrolytic oil with highest yield, that was obtained at 450°C, 10 °C/min and 1L N_2/min, were determined using Agilent HP-5MS device. GC-MS conditions are given in Table 1.

TABLE I. GC-MS CONDITIONS

<table>
<tr><td colspan="2">Column oven temperature</td><td>45˚C</td></tr>
<tr><td colspan="2">Injection temperature</td><td>250˚C</td></tr>
<tr><td colspan="2">Flow control mode</td><td>Pressure</td></tr>
<tr><td colspan="2">Column flow</td><td>1.03 ml/min</td></tr>
<tr><td colspan="2">Carrier gas</td><td>Helium 99.99% purity</td></tr>
<tr><td colspan="3"><i>Column oven temperature progress</i></td></tr>
<tr><td>Rate</td><td>Temperature (˚C)</td><td>Hold time (min)</td></tr>
<tr><td></td><td>45</td><td>4</td></tr>
<tr><td>3</td><td>280</td><td>30 min total</td></tr>
</table>

III. RESULTS AND DISCUSSIONS

A. *Analysis of Feedstock*

Analyses of waste tires were determined according to ASTM standards (Ash: ASTM D 3174, Volatile Matter: ASTM D 3175) . The moisture analysis was done by using moisture analyzer (AND, MX-50), Fixed carbon was calculated by mass difference and the amount of sulphur (wt.) was determined by a C-S analyzer (MetMultilab). The results are shown in Table 2.

TABLE II. ANALYSES RESULTS OF WASTE TIRES

UNIT	***MOISTURE***	***ASH***	***VOLATILE MATTER***	***FIXED CARBON***	***SULPHUR***
%	0.24	8.66	62.63	28.47	2.6

The TG and differential thermogravimetric (DTG) curves for the waste tire are shown in Figure 1. The TG curve showed that, thermal degradation took place in a range from 250 to 500 °C. The DTG curve showed that there are three decomposition regions. The first region around 240-300 °C can be attributed to the loss of additives such as oils and stearic acid. Second region with a clear peak around 380-400 °C appeared mainly due to the degradation of natural rubber. The last region between 450-500 °C was attributed to degradation of stirene-butadiene rubber and butadiene rubber. Based on the results of TGA analysis, pyrolysis experiments were conducted at different temperatures of 400, 450 and 500 °C.

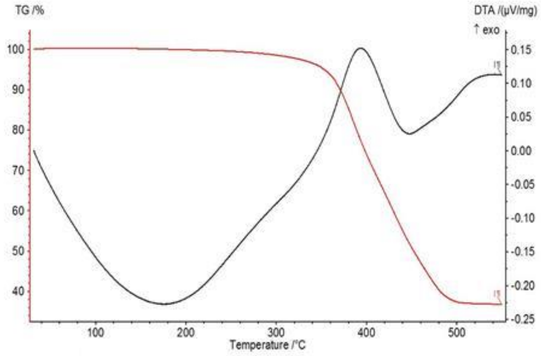
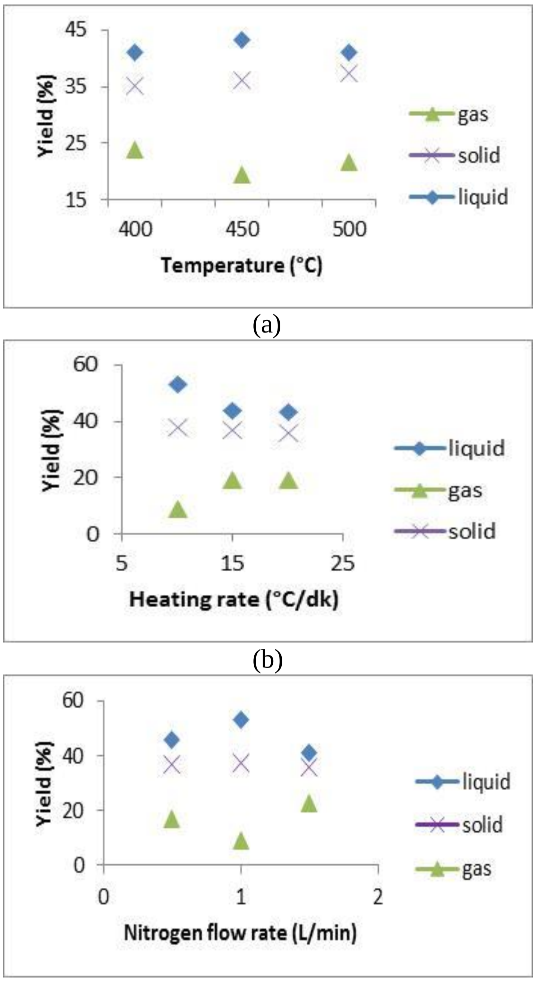


Fig. 1. The TG and differential thermogravimetric (DTG) curves for the waste tire.

B. *Pyrolysis Yield of Pyrolysis Products*

Firstly, studies were conducted to obtain the optimum pyrolysis temperature that gives the highest liquid yield. Pyrolysis of waste tires were carried out at 400,450,500 °C temperatures, at a heating rate of 20 °C/min, and under 1 L/min N_2 flow rate. The results revealed that, the optimum temperature was 450°C (Figure 2(a)). Then, pyrolysis of waste tires were carried out at 450°C with N_2 flow rate of 1 L/min; and at different heating rates such as 10, 15, 20 °C/min to obtain the optimum heating rate. Maximum liquid product yield was observed at 450 °C temperature and 10 °C/min heating rate (Figure 2(b)). In order to find the optimum N_2 flow rate, the experiments were conducted under 450 °C with a heating rate of 10 °C/min, and with 3 different N_2 flow rates: 0.5, 1 and 1.5 L/min. According to the results, 1 L/min gave the maximum oil yield of 53.33 wt.% (Figure 2(c)).

Temperature is an important parameter for pyrolysis yields of waste tires. In literature, generally pyrolytic conversion is complated at near 500 °C [6, 17,18]. Also increasing temperature above 500 °C causes only a small change in oil yield [11, 19]. In a study, pyrolytic oil yield was 38 wt.% at 500°C and 38.5 wt.% at 700 °C in a fixed bed reactor [11]. TG results also strongly confirm that the fastest and biggest decompositions occur after 450 °C and nearly be complated at about 500 °C. In this study, the oil yield decreased and gas yield increased with increasing heating rate. Probably, increasing heating rate caused rapid breaking of bonds and then a sudden formation of hydrocarbon molecules that could not be condensed and converted into liquid due to its very low molecular weight [5].



(a)

(b)

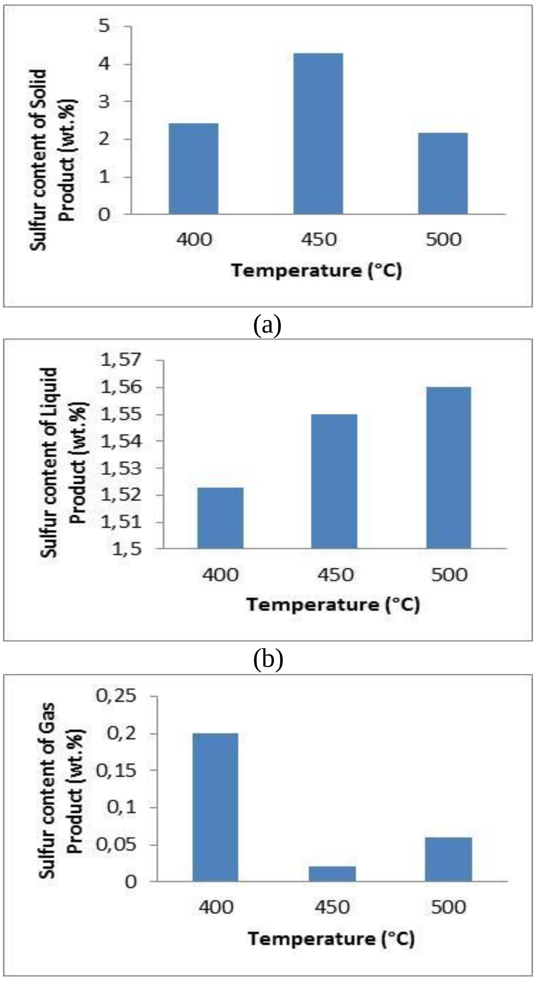
(c)

Fig. 2. Liquid, Solid and gaz yields as a function of different pyrolysis parameters (a) Temperature, (b) Heating rate, (c) N_2 flow rate.

The use of inert gas importantly gives opportunity to control the occurrence of thermal cracking, repolymerisation, recondensation and char formation reactions [20]. The flow rate of N_2 can influence the quantity of products. In our study, 1 L/min N_2 flow rate gave the maximum oil yield with decreasing the residence time of volatiles to prevent those reactions. The pyrolytic oil yield decreases as the flow rate increases.

C. Effect of Temperature, Heating Rate and (N_2) Flow Rate On Sulphur Content Of Pyrolytic products

The sulphur content of solid and liquid product obtained by pyrolysis of waste tires were carried out at 400 °C, 450 °C, 500 °C temperatures (20 °C/min heating rate and 1L/min N_2 flow rate); b) 10, 15, 20 0C/min heating rate (450 °C and 1L/min N_2 flow rate); c) 0.5, 1, 1.5 L/min N_2 flow rate (450 °C and 10 °C/min heating rate) are shown in Figures 3-5.



(a)

(b)

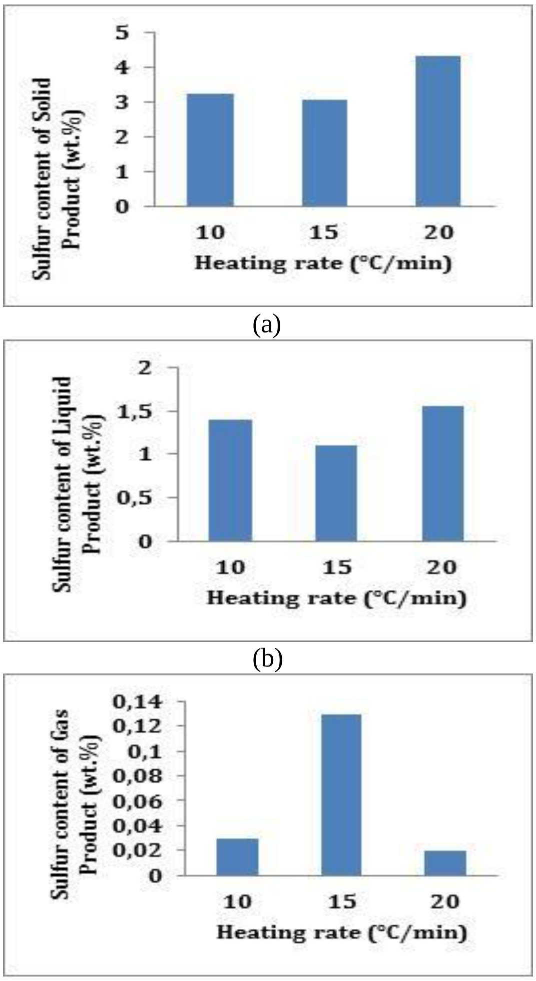
(c)

Fig. 3. The effect of temperature on sulphur content.

Most of sulphur was found in solid product which was mainly due to the great thermal stability of sulphur-containing compounds formed during the pyrolysis process [21]. However, a large amount of sulphur was transformed into liquid product and small amounts of sulphur was found in gas product. The sulphur content of liquid product increased slightly with increasing temperature. During pyrolysis of waste tires, desulphurization reactions start at low temperatures near 120 °C, at 250 °C decomposition reactions of sulphur containing compounds are nearly complated [22]. At higher temperatures above 250 °C, the formation of sulphur containing compounds like benzothiazol and H_2S occurs in liquid and gas, respectively [15]. High temperatures induce desulphurization reactions from solid and causes an increase in sulphur that is captured in liquid. According to our results, solid product with the lowest amount of sulphur is produced at the highest pyrolysis temperature, 500 °C. Oppositely, the liquid product at 500 °C has the highest amount of sulphur inside.

The gas product contains very small amounts of sulphur. The behaviour in sulphur amount of gas is in opposite direction with liquid; increase in temperature causes a decrease in sulphur. It was supposed that the interactions between sulphur-containing gases and other volatiles and solid, enhanced sulphur enrichment in liquid [21].

This situation decreases the amount of sulphur containing gases. As a result, in pyrolysis products sulphur is distributed mostly in the liquid fraction and solid in; in the gaseous phase, sulphur distribution decreases with the increasing temperature.



(a)

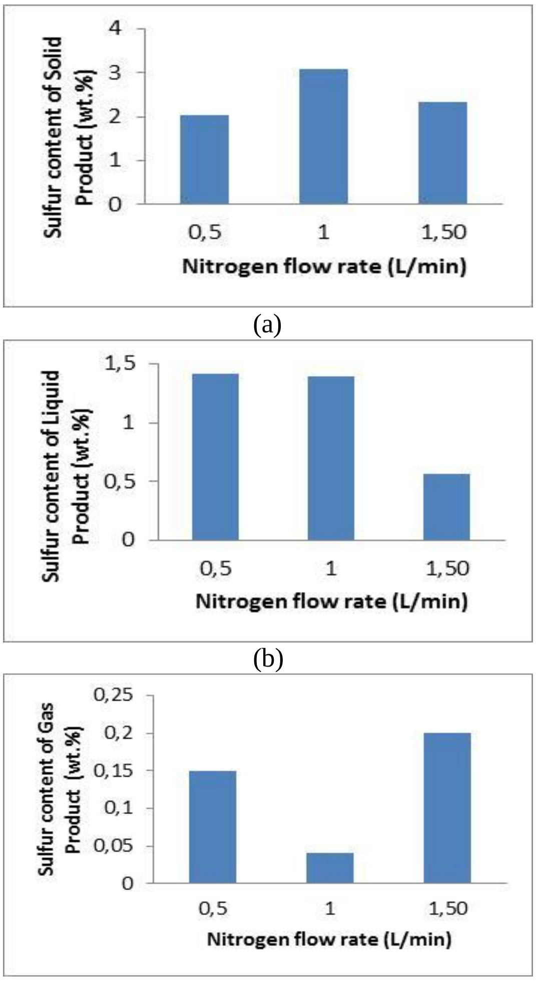
(b)

(c)

Fig. 4. The effect of heating rate on sulphur content.

In Figure 5 the effect of heating rate on sulphur content of products is shown. Although there is not an evident behaviour; there is a considerable effect at 15°C/min. At this heating rate gasification of sulphur containing compounds were maximum giving highest amount of sulphur in gas product. As expected, at 15°C/min the sulphur contents of solid (carbon black) and liquid were at the lowest levels.Increasing the N_2 flow rate, causes an increase in sulphur content of gas product while decreasing the amount of sulphur in liquid product. Increasing the flow rate of inert gas, probably causes a sudden sweeping away of sulphur containing gases from hot zone without letting them interact with other volatiles and solid.

According to the results, the most important parameters affecting sulphur amount of products were temperature and N_2 flow rate. The parameters under which minimum sulphur contents in solids obtained were 500 °C, 15 °C/min heating rate and 0.5L/min N2 flow rate. Minimum sulphur in liquid product was observed under conditions of 400 °C, 15 °C/min heating rate and 1.5L/min N_2 flow rate.



(a)

(b)

(c)

Fig. 5. The effect of N_2 flow rate on sulphur content.

D. GC-MS Analysis Results

GC-MS analysis gave information about variety of components present in pyrolytic oil. According to GC-MS analysis of waste tire pyrolytic oil, 85 selected compounds which has the peak with high degree of probability were given. The selected components of pyrolytic oil were given in Table 3. The pyrolytic oil is a mixture of C5-C15 compounds which are mostly aromatic. Limonene; benzene, naphthalene, indene, stirene, toluene and xylenes are the most commonly seen components. Benzothiazol which is the main source of sulphur in liquid product is also detected by GC-MS analysis with a peak area of 1.42% (Table 3).

TABLE III. Results of the GC-MS analysis

Rt Min	Peak Area (%)	Compound	Molecular Formula	Rt Min	Peak Area (%)	Compound	Molecular Formula
2,962	1,28	Toluene	C_7H_8	16,714	0,77	Benzene, 1,2,4,5-Tetramethyl-	$C_{10}H_{14}$
3,056	0,09	2-Methyl-Cyclohexa-1,3-Dıene	C_7H_{10}	16,967	0,48	Benzene, 4-Ethenyl-1,2-Dimethyl	$C_{10}H_{12}$
4,901	0,49	2-Pentanone, 4-Hydroxy-4-Methyl-	$C_6H_{12}O_2$	17,255	0,35	2,4-Dimethylstyrene	$C_{10}H_{12}$
5,247	0,84	Benzene, Ethyl-	C_8H_{10}	17,579	0,66	1h-Indene, 2,3-Dihydro-5-Methyl-	$C_{10}H_{12}$
5,377	0,12	2,3-Dimethyl-Cyclohexa-1,3-Diene	C_8H_{12}	18,134	3,12	2-Methylindene	$C_{10}H_{10}$
5,535	3,33	Benzene, 1,4-Dimethyl-	C_8H_{10}	18,415	2,55	1h-Indene, 3-Methyl-	$C_{10}H_{10}$
5,694	0,13	Octa-2,4,6-Triene	C_8H_{12}	18,61	0,58	Triquinacene	$C_{10}H_{10}$
6,177	0,11	Thiophene, 2,3-Dimethyl-	C_6H_8S	18,769	0,33	Naphthalene, 1,2-Dihydro-	$C_{10}H_{10}$
6,285	1,38	Styrene	C_8H_8	19,734	2,06	Naphthalene	$C_{10}H_8$
6,335	0,96	P-Xylene	C_8H_{10}	19,987	0,58	2,2-Dimethylindene	$C_{11}H_{14}$
7,539	0,3	Benzene, (1-Methylethyl)-	C_9H_{12}	20,484	0,51	1h-Indene, 2,3-Dihydro-1,6-Dimethyl-	$C_{11}H_{14}$
8,461	0,27	Benzene, 2-Propenyl-	C_9H_{10}	21,94	1,42	Benzothiazole	C_7H_5NS
8,771	0,31	Benzene, Propyl-	C_9H_{12}	23,18	1,45	1h-Indene, 1,3-Dimethyl-	$C_{11}H_{12}$
8,872	0,6	dl-Limonene	$C_{10}H_{16}$	23,454	1,71	1h-Indene, 4,7-Dimethyl-	$C_{11}H_{12}$
9,175	2,41	Benzene, 1-Ethyl-3-Methyl (M-Ethylmethylbenzene)	C_9H_{12}	23,706	1,71	1,1a,7,7a-Tetrahydro-2h-Cyclopropa[B]Naphthalene	$C_{11}H_{12}$
9,225	1,16	Benzene, 1-Ethyl-2-Methyl (O-Ethylmethylbenzene)	C_9H_{12}	23,893	0,63	1h-Indene, 1,3-Dimethyl-	$C_{11}H_{12}$
9,449	0,68	Benzene, 1,3,5-Trimethyl(S-Trimethylbenzene)	C_9H_{12}	25,025	2,68	Naphthalene, 2-Methyl-	$C_{11}H_{10}$
9,939	0,57	Benzene, 1-Ethyl-2-Methyl-		25,774	1,84	Naphthalene, 1-Methyl-	$C_{11}H_{10}$
10,112	1,16	Benzene, (1-Methylethenyl)-	C_9H_{10}	28,701	1,04	1h-Indene, 1,1,3-Trimethyl-	$C_{12}H_{14}$
10,602	2,41	Benzene, 1,2,3-Trimethyl	C_9H_{12}	29,508	0,52	Naphthalene, 2-Ethyl-	$C_{12}H_{12}$
10,689	1,22	Benzene, Ethenylmethyl-	C_9H_{10}	30,005	1,83	Naphthalene, 1,6-Dimethyl-	$C_{12}H_{12}$
10,746	0,44	Benzene, 2-Propenyl-	C_9H_{10}	30,632	2,32	Naphthalene, 1,3-Dimethyl-	$C_{12}H_{12}$
10,84	0,93	Benzene, 1-Ethenyl-3-Methyl	C_9H_{10}	30,784	1,86	Naphthalene, 1,7-Dimethyl-	$C_{12}H_{12}$
11,51	0,17	Benzene, Methyl(1-Methylethenyl)-	$C_{10}H_{12}$	31,959	1,38	Quinoline, 2,4-Dimethyl-	$C_{11}H_{11}N$
11,654	0,26	Alpha -Terpinolene	$C_{10}H_{16}$	32,081	0,85	Naphthalene, 2,3-Dimethyl-	$C_{12}H_{12}$
11,936	1,95	Benzene, 1,2,4-Trimethyl	C_9H_{12}	33,544	0,8	1,1'-Biphenyl, 3-Methyl-	$C_{13}H_{12}$
12,123	2,15	Benzene, 1-Methyl-2-Ethyl	C_9H_{12}	33,898	0,91	1,1'-Biphenyl, 4-Methyl-	$C_{13}H_{12}$
12,332	3,71	L-Limonene	$C_{10}H_{16}$	34,222	1,63	Naphthalene, 1,4,6-Trimethyl-	$C_{13}H_{14}$
12,808	0,11	Isolimonene	$C_{26}H_{32}O$	35,339	1,78	Naphthalene, 1,6,7-Trimethyl-	$C_{13}H_{14}$
12,981	1,46	Indene	C_9H_8	36,06	0,58	2,3,5-Trimethylnaphthalene	$C_{13}H_{14}$
13,11	0,23	Benzene, 2-Butenyl	$C_{10}H_{12}$	37,112	2,21	9H-Fluorene	$C_{13}H_{10}$
13,298	0,1	Benzene, 1,2-Diethyl-	$C_{10}H_{14}$	37,566	0,39	5-Methoxy-2,2-Di-Methylindan-1-One	$C_{12}H_{14}O$
13,384	0,45	Benzene, 1-Methyl-3-Propyl	$C_{10}H_{14}$	38,237	0,42	1-Methylethylidene	C_3H_6
13,528	0,22	Benzene, (1-Methylpropyl)-	$C_{10}H_{14}$	42,561	1,62	1,4,5,8-Tetramethylnaphthalene	$C_{14}H_{16}$
13,752	0,66	5-Ethyl-M-Xylene	$C_{10}H_{14}$	43,318	0,32	3h-Benz[e]İndene, 2-Methyl-	$C_{14}H_{12}$
14,105	0,23	Phenol, 3-Methyl	C_7H_8O	44,724	0,51	Phenanthrene	$C_{14}H_{10}$
14,285	0,1	(+)-Trans-Isolimonene		48,789	0,42	Phenanthrene, 2-Methyl-	$C_{15}H_{12}$
14,631	0,18	Benzene, 4-Ethyl-1,2-Dimethyl	$C_{10}H_{14}$	49,791	0,45	Phenanthrene, 2-Methyl-	$C_{15}H_{12}$
14,811	0,11	1H-Indene, 1-Methyl-	$C_{10}H_{10}$	56,047	0,34	Heptadecanenitrile	$C_{17}H_{33}N$
15,028	1,14	Benzene, (2-Methylcyclopropyl)	$C_{10}H_{12}$				
15,193	0,25	Alpha Terpinene	$C_{10}H_{16}$				
15,338	2	Benzene, 1-Methyl-4-(1-Methylethenyl)	C_9H_{10}				
15,568	0,26	Benzene, 1-Ethenyl-3,5-Dimethyl	$C_{10}H_{12}$				
15,835	0,64	Benzene, 2-Ethenyl-1,4-Dimethyl	$C_{10}H_{12}$				
16,217	0,38	Benzene, 1-Methyl-4-(1-Methylpropyl)	$C_{10}H_{14}$				
16,476	0,28	1,3-Cyclopentadiene, 1,2,3,4-Tetramethyl-5-Methylene	$C_{10}H_{16}$				

IV. CONCLUSIONS

The combination of parameters that gave the maximum oil yield (53.33 wt.%) was 450 °C pyrolysis temperature, 10 °C/min heating rate and 1L N_2/min flow rate. When sulphur amounts of pyrolytic oils obtained at different pyrolysis conditions were compared, it was observed that there was no big difference between sulphur amounts of oils. The minimum amount of sulphur in pyrolytic oil was 1.103 wt.% and maximum amount was 1.56 wt.%. The amount of sulphur in solid product was chancing between 2.04-4.303 wt. %.

The main parameters effecting sulphur content of solid were temperature and heating rate. The minimum amount of sulphur in solid was 2.04 wt.% and obtained at 450°C, 10 °C/min and 1L N_2/min.

According to the results, the most important parameters affecting sulphur amount of products were temperature and N_2 flow rate. The parameters under which minimum sulphur contents in solids obtained were 500 °C, 15 °C/min heating rate and 0.5L/min N_2 flow rate. Minimum sulphur in liquid product was observed under conditions of 400, °C, 15 °C/min heating rate and 1.5L/min N_2 flow rate.

According to GC-MS analysis results, the pyrolytic oil is a mixture of C5-C15 compounds which are mostly aromatic. Limonene, benzene, naphthalene, indene, stirene, toluene and xylenes are the most commonly seen components.

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REFERENCES

[1] Yu D.G., Colloids Surf. B: Biointerf. 59 (2007) 171. F.J. Mastral, C. Berrueco and E. Esperanza., “Pyrolysis of waste tires in an atmospheric static-bed batch reactor: Analysis of the gases obtained”, Jour. of Anal. and App. Pyro., vol.74, 245-253, Aug. 2004.

[2] Turkey Ministry of Environment , Regulations for the Conrol of Waste Tires, 2006.

[3] http://www.csb.gov.tr/turkce/?Sayfa=faaliyetdetay&Id=1317 (Last access: 26.02.2016)

[4] Acevedo B., Barriocanal C."Fuel-oils from co-pyrolysis of scrap tires with coal and a bituminous waste. Influence of oven configuration", Fuel,vol.125, 155-163, June 2014.

[5] Müfide Banar, Vildan Akyıldız, Aysun Özkan, Zerrin Çokaygil, Özlem Onay, “Characterization of pyrolytic oil obtained from pyrolysis of TDF (Tire Derived Fuel)”, Energy Conversion and Management, vol. 62, 22–30, 2012.

[6] J.Yanık and S. Ucar, “Evaluation of two different scarp tires as hydrocarbon source by pyrolysis”, Fuel , vol.84, 1884-1892, Oct. 2005.

[7] Quek A., Balasubramanian R., "Liquefaction of waste tires by pyrolysis for oil and chemicals—A review", Journal of Analytical and Applied Pyrolysis, vol.10, 1–16, 2013.

[8] K.P. Shadangi, and K. Mohanty, “Comparison of Yield and Fuel Properties of Thermal and Catalytic Mahua Seed Pyrolytic Oil”, Fuel, vol. 126, 109-115, Jun. 2014.

[9] C. Roy , A. Chaala, H. Darmstadt, “The vacuum pyrolysis of used tires End-uses for oil and carbon black products”, Journal of Analytical and Applied Pyrolysis, vol.51, 201–221, 1999.

[10] P.,T.Williams, S.Besler and D.T. Taylor, “The pyrolysis of scrap automotive tires: The influence of temperature and heating rate on product composition”, Fuel, vol. 69, 1474-1482, Dec. 1990.

[11] M.,F.,Laresgoiti and B.M.Caballero, “Characterization of the liquid products obtained in tire pyrolysis”, Journ. of Anal. and App. Pyro., vol.71, 917-934, Jun.2004.

[12] H.Aydın and C. İlkılıç, “Optimization of fuel production from waste vehicle tires by pyrolysis and resembling to diesel fuel by various desulphurization methods”, Fuel, vol.102 605-612, Dec. 2012.

[13] Choi G.G., Jung S.H., Oh S.J., Kim J.S., "Total utilization of waste tire rubber through pyrolysis to obtain oils and CO_2 activation of pyrolysis char", *Fuel Processing Technology* 123, 57-64, 2014.

[14] Seidelt S., Hagedorn M.M., Bockhorn H., "Description of tire pyrolysis by thermal degradation behaviour of main components", J. Anal. Appl. Pyrolysis, vol. 75, 11–18, 2006.

[15] Susa D., Haydary J., "Sulphur distribution in the products of waste tire pyrolysis", Chemical Papers, 67(12),1521–1526, 2013.

[16] Ahmad S. , Ahmad M.I., "Desulphurization of Oils; Produced from Pyrolysis of Scrap Tires", NUST Journal of Engineering Sciences, 6(1), 27-32, 2013.

[17] Mastral, A.M., Murillo, R.,Callen, M.S.,Garcia, T.,Snape, C.E., "Influence of process variables on oils from tire pyrolysis and hydropyrolysis in a swept fixed bed reactor", Energy Fuel, vol.14, 739–44,2000.

[18] Rodriguez, I., Laresgoiti, M.F., Cabrero, M.A., Torres, A.,Chomon, M.J., Caballero, B., "Pyrolysis of scrap tires", Fuel Processing Technology, vol. 72, 9–22, 2001.

[19] Murillo, R., Aylon, E., Navarro, M.V., Callen, M.S., Aranda, A., Mastral, A.M., "The application of thermal processes to valorise waste tire", Fuel Processing Technology, vol. 87, 143–147, 2006.

[20] Martinez J.D., Puy, N., Murillo R., Garcia T., Navarro M. V., Mastral A.M., "Waste Tire Pyrolysis-A Review", Renewable and Sustainable Energy Reviews, vol. 23, 179–213, 2013.

[21] Hu H., Fang Y., Liu H., Yu R., Luo G., Liu W., Li A., Yao H., The fate of sulphur during rapid pyrolysis of scrap tires, Chemosphere, vol. 97, 102–107, 2014.

[22] Uzun B.B., Yaman, E., " Atık Lastiklerin Katalitik Pirolizi Üzerine Bir İnceleme", ISEM Proceedings Book, Adıyaman, Turkey, 2014.