Intermediate pyrolysis of scrap tires in a fixed bed reactor and activation of the pyrolysis char using CO_2: Characteristics of pyrolysis products and activated char

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Abstract

Four carbonized chars were obtained from the intermediate pyrolysis of waste tires in a fixed bed reactor at different reaction temperatures (between 500 and 800 °C) in a N_2 atmosphere. Gas, liquid and char were product fractions. The liquid was again distilled to give a light oil (pryolysis oil) and distillation residue. The chars obtained were again activated using carbon dioxide at 950 °C with different activation time*. The solids (carbonized char and activated char) and liquid (or pyrolysis oil) generated in each experiment were characterized by various analytic techniques. To describe the behavior of sulfur during thermal degradation, elemental analysis of liquids and carbonized chars were performed. Pyrolysis oils were also investigated by gas chromatography/mass spectrometer (GC/MS) to determine their compositions qualitatively and quantitatively. Carbonized chars and activated chars produced were characterized using gas (nitrogen) phase adsorption. Results revealed that pyrolysis temperature and activation time significantly affected the pore structure and BET surface area of activated chars.* The maximum surface area of activated char produced in the experiment was about 440 m^2/g.

Keyword: *Intermediate pyrolysis, Scrap tire, Carbon dioxide, Activated char*

1. Introduction

As a result of the great increase in the use of automobiles, the production of scrap tires has also increased. Over 5 million tons of scrap tires are disposed annually worldwide [1]. Due to their durability, the disposal and reprocessing of scrap tires are difficult, and they are also immune to biological degradation. Landfill of scrap tires needs lots of site, and fire problem also exist. Important application of scrap tires is their use as a fuel. However, high emissions of hazardous gas during their combustion need expensive gas filtering systems. As a method of scrap tire treatment, pyrolysis offers an alternative route for high potential energy recovery, while being environmentally friendly.

Oil fraction, one of pyrolysis products, can be used as an alternative fuel and chemical feedstock in industrial processes. Pyrolytic char could be upgraded to activated char through activation process. The resultant activated chars can be used as pollutant adsorbents in both gas phase and liquid phase separation processes [2].

In this work, a fraction of scrap tires were pyrolyzed in a fixed bed reactor. The main goal of this study was to investigate the influence of reaction temperature on the characteristics of pyrolysis products and the influence of reaction temperature and activation time on the characteristics of activated char.

2. Materials and Methods

Material. Scrap tires of 1-2 mm in size was used to as the feed material of the intermediate pyrolysis. The elemental compositions of a scrap tire sample were 82.3 wt.% carbon, 7.1 wt.% oxygen, 0.5 wt.% nitrogen and 2.5 wt.% sulfur, respectively.

Pyrolysis plant and procedure. Fig.1 shows the intermediate pyrolysis plant.

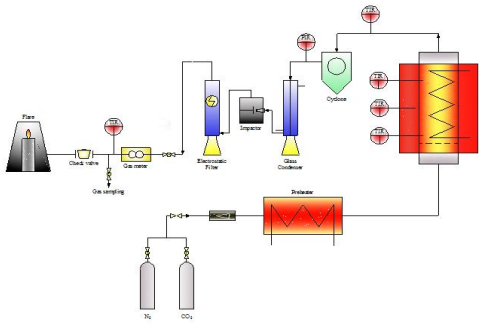

Fig. 1 Intermediate pyrolysis plant

The pyrolysis plant consisted mainly of a fixed bed reactor, cyclone and quenching system. The fixed bed reactor, which was indirectly heated by electricity, was made of a 316 SS with a height of 410 mm and an inner diameter of 83 mm. The cyclone designed to capture the particle size bigger than 10 μm. The quenching system consisted of one steel condenser which was water-cooled at 10 °C and one impactor separator which can capture larger molecular weight in pyrolysis vapor. The latter part of the quenching system was electrostatic precipitator that can capture an aerosol phase in the pyrolysis vapor. Non-condensable gas passed through into bent line and burned using a Bunsen burner.

Nitrogen or carbon dioxide gas passed into the fixed bed reator through a pre-heater to keep the reaction temperature constant.

Pyrolysis conditions. In each experiment, 50 g of scrap tires was put into the reactor. Subsequently the reactor was heated at a heating rate of 10 °C/min until the desire temperature (500, 600, 700 and 800 °C) reached, and then held for 2 hr. In the intermediate pyrolysis, the flow rate of nitrogen gas was fixed at 5 NL/min.

Activation conditions. The resultant carbonized chars from the intermediate pyrolysis were continuouly heated at a heating rate of 10 °C/min up to 950 °C at the flow of 5 NL/min of carbon dioxide. The activation time was varied between 1 and 3 h.

Analysis of products. After pyrolysis, the liquid and solid fractions were recovered. The liquid fraction was distillated to analyze its components with GC/MS. The distillation of liquid was carried on a laboratory scale apparatus under reduced pressure (210 °C, 13.3 Kpa). After the distillation of liquid, a light fraction, which was analyzed by GC-MS, and a viscous fraction were obtained. In this study, the light fraction and the viscous fraction were designated as pyrolysis oil and distillation residue,respectively. This distillation condition corresponded to the boiling point of 9H-fluorene (boiling point = 295 °C at atmospheric pressure). The applied capillary column for GC-MS was a HP-5MS, and helium was used as the carrier gas. After each activation process, mass loss was calculated by burn-off. Activated chars obtained from activation of carbonized char were characterized from nitrogen adsorption isotherms at 77 K using BEL, Belsorp-mini II. The each value of surface area, pore size distributions, mesopore and micropore volume was obtained noted data using Brunauer-Emmet-Teller (BET) equipment.

3. Results and Discussion

Pyrolysis product. In each experiment, the liquid and char yields were determined by weighing them after each experiment. The gas yield was calculated by difference. The effect of reaction temperature on the yields of pyrolysis products was presented in Table 1.

Table 1. Yields of pyrolysis products with the reaction temperature.

Reaction temperature (°C)	Yield (wt.%)		
	Liquid	Char	Gas
500	40.7 ± 2.47	36.7 ± 0.08	22.6 ± 1.01
600	34.7 ± 1.58	36.6 ± 0.15	28.7 ± 1.08
700	33.5 ± 1.25	37.0 ± 0.22	29.5 ± 1.21
800	33.1 ± 2.20	36.8 ± 0.08	30.1 ± 2.69

Elemental compositions of liquid and solid were detected by elemental analysis. The result is presented in Table 2.

Table 2. Elemental analysis of liquid and solid fractions.

Element composition (wt.%)		Reaction temperature (°C)			
		500	600	700	800
Liquid	C	84.0 ± 0.00	78.6 ± 0.00	83.9 ± 0.00	84.6 ± 0.00
	H	10.0 ± 0.00	8.2 ± 0.00	8.4 ± 0.00	8.7 ± 0.00
	N	1.8 ± 0.00	3.7 ± 0.00	2.2 ± 0.00	2.0 ± 0.00
	S	4.2 ± 0.00	9.5 ± 0.00	5.5 ± 0.00	4.7 ± 0.00
Solid [a]	C	94.3 ± 0.13	94.0 ± 0.09	97.4 ± 0.09	97.1 ± 0.02
	H	0.6 ± 0.10	0.4 ± 0.01	0.4 ± 0.01	0.4 ± 0.04
	N	0.5 ± 0.03	0.5 ± 0.07	0.2 ± 0.01	0.2 ± 0.03
	S	4.6 ± 0.00	5.1 ± 0.00	2.0 ± 0.00	2.3 ± 0.00

[a] Ash free

GC-MS analysis revealed that the pyrolysis oils consisted mainly of aromatic hydrocarbons such as styrene, xylenes, 2-methylnaphtalene and 1,2,3-trimethylindene. Other major components in the oils were limonene which could be used as an important commercial chemical. In the GC-MS analysis, it was also found that a decrease in the yield of aliphatic compounds with increasing reaction temperature, accompanied by an increase in the contents of aromatic compounds. This result was due to the fact that the monomer recyclization occured through Diels-Alder reaction mechanism at higher reaction temperatures. The limonene yield was also raised due to the depolymerization of natural rubber by β-scission of double bonds. [3].

Activated char. Activation was carried out to develop the porosity of carbonized char. As can be seen in Table 2, the pyrolysis temperature and activation time significantly affected the pore structure and BET surface area of activated chars. The maximum BET surface area of activated char produced was about 440 m^2/g.

Table 3. Textural parameters of activated char.

	Pyrolysis temperature (°C)	Activation temperature (°C)	Activation time (hr)	Burn-off (%)	S_{BET} (m^2/g)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)	V_{micro} (cm^3/g)
P_500	500	-	-	Control	73.5	0.0022	0.1829	0.0110
AC_500_1	500	950	1	21.5	202.8	0.0461	0.7680	0.0442
AC_500_2	500	950	2	33.0	313.0	0.0876	0.6113	0.2609
AC_500_3	500	950	3	44.8	437.1	0.1224	1.0719	0.1399
P_600	600	-	-	Control	77.6	0.0047	0.1806	0.0092
AC_600_1	600	950	1	21.6	240.3	0.0613	0.5506	0.1055
AC_600_2	600	950	2	32.7	332.9	0.0988	0.4630	0.0654
AC_600_3	600	950	3	43.2	420.1	0.1245	0.6568	0.1730
P_700	700	-	-	Control	71.6	N.D [a]	0.3505	0.0167
AC_700_1	700	950	1	17.5	182.4	0.0403	0.4962	0.1522
AC_700_2	700	950	2	32.9	335.7	0.1068	0.2910	0.0099
AC_700_3	700	950	3	42.2	389.1	0.1288	0.3168	0.0048
P_800	800	-	-	Control	70.9	N.D	0.3645	0.0776
AC_800_1	800	950	1	18.5	198.4	0.0555	0.2269	0.0038
AC_800_2	800	950	2	31.8	274.5	0.0719	0.6036	0.1115
AC_800_3	800	950	3	42.7	349.1	0.0902	0.7091	0.2716

[a] Not detected

4. Conclusions

In this study, a fraction of scrap tires were pyrolyzed in a fixed bed reactor at various temperatures. The yield of gas increased with increasing reaction temperature; whereas the liquid yield decreased. A distillation of liquid was conducted to give rise to two fractions, pyrolysis oil and distillation residue.The chemical compositions of the pyrolysis oil were complex, and it was mainly composed of aromatic and aliphatic compounds. The contents of aromatic hydrocarbons increased with increasing reaction temperature. The maximum surface area of activated char produced in the experiment was high with a value of about 440 m^2/g. The activated char appeared to be used as an adsorbent of liquid pollutants such as phenol and dyes.

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