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Pyrolysis of waste tyres with zeolite USY and ZSM-5 catalysts

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Abstract

Pyrolysis of waste tyres was carried out with a two-stage bed reactor. The waste tyres were first pyrolysed in a fixed bed reactor, and then the evolved pyrolysis gases were passed through a secondary catalytic reactor filled with two types of zeolite catalysts, which were ultrastable Y-type (USY) and ZSM-5 catalyst. The catalytic temperatures were examined to determine their influence on the yield of product from the pyrolysis–catalyst of waste tyres. The results indicated that with the increase of catalytic temperature, the gas yield increased at the expense of oil yield. The light fractions (<220 °C) distilled from the derived oils with the two catalyst were analyzed by gas chromatography/mass spectrometry (GC/MS). It showed that there was a dramatic increase in the concentration of single ring aromatic compounds in the light fractions of the derived oils after catalysis. For example, toluene reached a value in the light fraction of 11.62 wt%, benzene 1.6 wt%, *m*/*p*-xylene 12.27 wt% and *o*-xylene 4.42 wt%, with the catalysis of USY catalyst, at the pyrolysis temperature, catalysis temperature and catalyst/tyre ratio of 500, 400 °C and 0.5, where the light fraction was about 71 wt% in the derived oil. The yield of aromatic hydrocarbons in the derived oils were related to the different properties of the two catalysts such as the pore size which influenced the selectivity, and the silica/alumina (Si/Al) ratio which influenced the number of active sites on the catalyst surface.
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Keywords: Pyrolysis; USY; ZSM-5; Tyre

1. Introduction

Waste tyres give rise to a serious environmental problem. For example, Amount to 5×10^6 t/year waste tyres was produced in the world, and 2×10^6 t of which are produced in Europe, 2.5×10^6 t in North America and 0.5×10^6 t in Japan [1]. The EU, the USA and Japan together were responsible for the disposal of a total of five million tones of waste tyres per year [2]. China is the biggest consumption country of rubber, which is about 4.2×10^6 t in 2004.

There are several ways to dispose this residue such as tyre retreading, mechanical grinding, rubber reclaim, combustion, pyrolysis, etc. Recently, pyrolysis of the waste tyre is receiving renewed attention, since the process may be optimized to produce some high value products. For example, it generates the oil, char, gas and residual steel products, all of which have the potential to be reused. The gas has sufficient calorific value so that it may be used to provide process energy [3–5] and the char may be used as activated carbon or carbon black [6–8]. The oil may be combusted as a substitute fuel [9–11]. However, the high concentrations of aromatic hydrocarbons [9,12–15] limited the derived oil form tyres pyrolysis to be used as a fuel. For example, Benallal et al. [15] compared the derived oil from tyre pyrolysis with petroleum naphtha. He found that the naphtha had a higher octane number than petroleum naphtha but must be hydrofined and reformed. Therefore, the low quality and variable properties of the derived oil show some resistance to the use of the oil as recycled product. The derived oils contain concentrations of valuable chemicals such as benzene, toluene, xylenes, etc., which can be extracted from the derived oils and used as chemical feedstocks in the chemical industry. For example, benzene is surfactants, dyestuffs and pharmaceuticals, and toluene is used in the production of pesticides, dyestuffs, surfactants and solvents. *o*-Xylene is used to produce plasticizers, dyes and pigments, *m*-xylene derivatives are used in the fibre industries and *p*-xylene derivatives are used in the production of polyester fibres [16]. However, their concentrations are not sufficiently high to enable their extraction from the oil and utilization as a chemical feedstock, so catalysts are introduced to produce more single ring aromatic compounds. Williams and Brindle [10,11] have done some important research in this field by using zeolite ZSM-5 and

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zeolite Y-type catalysts with different Si/Al ratios and pore sizes to study the influences of pyrolysis temperature, catalytic temperature and catalyst/tyre ratio on the yields of products and the composition of derived oils. They obtained the oil with high concentration of certain single ring aromatic compounds such as benzene, toluene and xylenes after catalysis. They also found that, for zeolite ZSM-5, the production of benzene, toluene and xylenes were markedly increased, but to a lesser extent than the Y-zeolite catalyst.

USY was a zeolite and frequently used as a catalyst for upgrading products in chemical industry [17,18] because of its higher activity and stable characteristic. However, few studies about USY applying in tyre pyrolysis were reported. In this paper, waste tyres were pyrolysed in a fixed bed reactor and the derived gases passed directly to a second catalytic reactor containing a catalyst under a vacuum circumstance. Zeolite USY catalyst and ZSM-5 catalyst were investigated. The catalytic temperature was investigated to determine their influence on the yield of the derived oils. The composition of light fraction (<220 °C) distilled from the derived oil in relation to the two catalysts had been analyzed by GC–MS. The main purpose of this paper is to obtain much higher concentrations of certain single ring aromatics such as benzene, toluene and xylenes by using USY zeolite catalyst. And the ZSM-5 zeolite was investigated to make a comparison. So the oil obtained from the pyrolysis of waste tyres could be used as a chemical feedstock rather than a liquid fuel, and the process economics of pyrolysis of tyres have the potential to be improved.

2. Experimental

The tyre material was shredded and crumbed to produce a size of 8.0–10.0 mm without steel in it. The tyre had a typical volatile content of 62.2 wt%, fixed carbon of 29.4%, ash content of 7.1% and a moisture content of 1.3 wt%.

USY (offered by Qilu Petrochemical Huaxing Company Ltd.) was used as the catalyst with a pore size of 9.0 Å, and Si/Al ratio of 5 representing a high acidity. For ZSM-5 catalyst, the pore size and Si/Al ratio are 5.6 Å and 38, respectively, which was offered by the Catalytic Industry of Nankai university. The catalysts were 1 mm in diameter with 3–5 mm length.

The tyre was pyrolysed in a fixed bed reactor constructed of quartz and was 3.0 cm diameter × 16 cm high. The pyrolysis reactor could contain up to 20 g tyre sample. The reactor was externally heated via an external electrical heater, and heating rate and final temperature were controlled. No gas was introduced into the reactor to sweep the evolved gas. The pyrolysis gases produced in the pyrolysis reactor were passed directly to a heated secondary catalyst reactor whose temperature was controlled separately. The flue gases passed through an ice/water condenser later, where oil was obtained. The catalyst reactor was constructed of quartz and was 1.9 cm diameter × 31 cm high. Up to 15 g zeolite catalyst could be used. The schematic diagram of the experimental system is shown in Fig. 1.

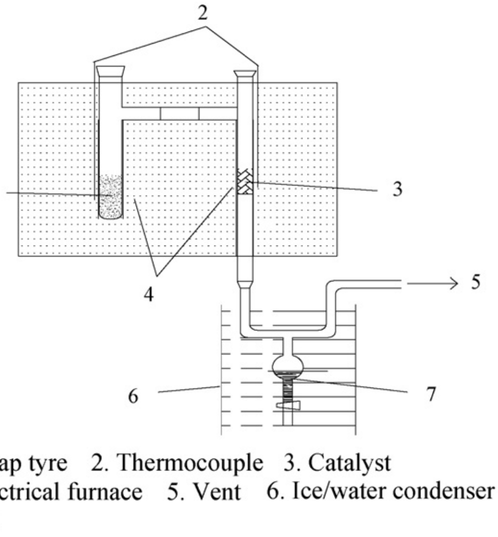

Fig. 1. The schematic diagram of the experimental system.

The influence of catalytic temperature was investigated. Both the zeolite USY catalyst and ZSM-5 catalyst were studied at temperatures of 350, 400, 450 and 500 °C. All other parameters such as pyrolysis temperature, catalyst/tyre ratio were kept constant. The catalyst was heated to the final temperature and held at that temperature for 1 h to activate the catalyst prior to the commencement of the pyrolysis of the tyre sample. While the parameter of catalytic temperature was investigated, the pyrolysis reactor was heated to 400 °C before the addition of sample, and then it was controlled to give the added sample a ramped heating rate of 10 °C min^{-1} to the final tyre pyrolysis temperature 500 °C, and held at this temperature for 30 min to complete the pyrolysis of waste tyres.

The concentration of derived oil was investigated to examine the differences among un-catalysed oil, oil catalysed with USY catalyst and catalysed with ZSM-5. Therefore, waste tyres were pyrolysd at the pyrolysis temperature, catalytic temperature and catalyst/tyre temperature of 500, 400 °C and 0.5, respectively. Then, the derived oil was distilled to obtain a fraction, whose boiling point was below 220 °C. The light fraction (<220 °C) was analyzed with GC/MS to examine the composition. The GC was equipped with a split injector at 250 °C, using a 50:1 split ratio and helium carrier gas at 0.8 ml min^{-1} flow rate. The analysis was performed on a 30 m × 0.25 mm capillary column coated with a 0.25 μm film of DB-5. The oven temperature was set at 40 °C for 2 min, then programmed to 300 °C at

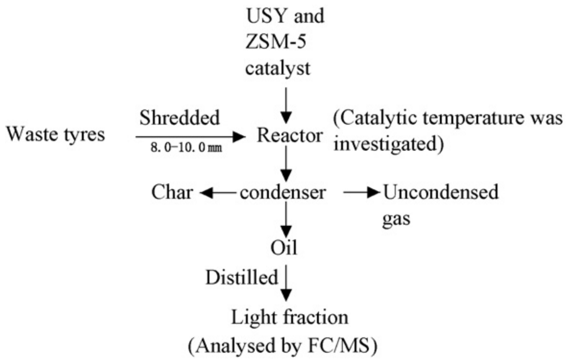

Fig. 2. Flow chart of the study in this paper.

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