

Pyrolysis of scrap tyres with zeolite USY

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Abstract

A zeolite catalyst of ultrastable Y-type (USY) was investigated in the research of two staged pyrolysis–catalysis of scrap tyres. Scrap tyres were pyrolysed in a fixed bed reactor and the evolved pyrolysis gases were passed through a secondary catalytic reactor. The main objective of this paper was to investigate the effect of zeolite USY on the yield of products and the composition of derived oil. The influences of several parameters such as pyrolysis temperature, catalytic temperature, catalyst/tyre ratio, heating rate, etc. on the yield of the derived oil, char and gas were investigated. It showed that the increase of catalytic temperature and catalyst/tyre ratio resulted in high yield of gas at the expense of the oil yield. For example, when the catalyst/tyre ratio increased from 0.25 to 1.0, the yield of gas increased from 30.5 to 49.9 wt.%, and the oil yield decreased nearly two-fold from 31.6 to 12.7 wt.%. The concentration of light naphtha (boiling point < 160 °C) was also investigated in this study. And the high catalyst/tyre ratio favored to increase the concentration of light naphtha (< 160 °C) in oil. In order to study the composition of derived oil, a distilled fraction (< 280 °C), which was 92.5 wt.% of the oil obtained from catalytic pyrolysis of scrap tyre at a pyrolysis temperature, catalytic temperature and catalyst/tyre ratio of 500, 400 °C and 0.5, respectively, was analyzed with gas chromatography/mass spectrometry (GC/MS). The distillate was found to contain 1.23 wt.% benzene, 9.35 wt.% toluene, 3.68 wt.% ethylbenzene, 12.64 wt.% xylenes, 1.81 wt.% limonene and 13.89 wt.% PAHs, etc., where the single ring aromatics represented a significant potential use as chemicals.

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1. Introduction

With the increasing emphasis on the environment and sustainability, recycling of waste is becoming more and more important for many waste streams. Such wastes include scrap tyres, which have the potential to be readily recycled since large tonnages are generated. For example, approximately 150 million scrap tyres are produced in North America and 180 million in European Union [1]. The world production of waste tyres amounts to 5×10^6 tonnes/year, 2×10^6 tonnes of which are produced in Europe, 2.5×10^6 tonnes in North America and 0.5×10^6 tonnes in Japan [2]. China is the biggest consumption country of rubber, which is amount to 4.2×10^6 tonnes in 2004. China is also the second largest country to produce tyres. These tyres are usually dumped in landfills or left in the open air, which result in significant environmental disturbances and dangerous situations such as the risks of fire.

Pyrolysis, the thermal degradation of the waste tyre in the absence of oxygen, generates the oil, char, gas and residual steel product, all of which have the potential to be recycled. 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 a low-grade activated carbon or carbon black [6–8]. The oil may be combusted as a substitute fuel [9–11]. Williams did a lot of job for the analysis of oils derived from the pyrolysis of waste tyres. In the report [9], the fuel properties of the derived oil including calorific values, ultimate analyses, flash point, moisture content, fluorine and chlorine contents were determined. And the concentration of polycyclic aromatic hydrocarbons (PAHs) and lighter aromatic hydrocarbons were also determined. The research of PAHs was also reported in Williams' another paper [12]. Roy et al. [13–15] compared the derived oil from tyre pyrolysis with petroleum naphtha, the conclusion was that the naphtha from the derived oil had a higher octane number than petroleum naphtha but must be hydrofined and reformed in order to be used as a clean fuel. Some other studies about the pyrolysis of tyres were also reported in Refs. [16,17], etc.

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However, the derived oils from tyre pyrolysis without catalyst have been shown to be highly aromatic, which are limited to be used as a substitute liquid fuel. Since the derived oils contain concentrations of valuable chemicals such as benzene, toluene, xylenes, etc., so they can be extracted from the derived oils and used as chemical feedstocks in the chemical industry. So catalysts are used to produce more single ring aromatic compounds during tyre pyrolysis. Williams and Brindle [10,11] used zeolite ZSM-5 and two zeolite Y-type catalysts with different Si/Al ratios and pore sizes to study the influence on the yields of products and the composition of derived oils. The Y-zeolite catalyst had a lower silica/alumina (Si/Al) ratio and therefore higher surface acidity and also possessed a larger pore size than the ZSM-5 catalyst. The Y-zeolite catalyst produced significantly higher concentrations of benzene, toluene, xylenes, naphthalene and alkylated naphthalenes compared to the ZSM-5 catalyst.

Ultrastable Y (USY) is a kind of zeolite with lower Si/Al ratios and larger pore size compared to Y-zeolite and ZSM-5 zeolite. The structure of USY is characterized by large, essentially spherical, internal cavities (supercages) linked tetrahedrally through pore openings, defined by rings of 12 oxygen atoms (12-rings). The protons existed in the zeolite are associated with aluminum atoms that, along with silicon atoms (occupy sites at the centers of apex-linked tetrahedral of oxygen atoms), form the three-dimensional framework of the zeolite. Though USY was commonly used in hydrocracking and fluid catalytic cracking (FCC) catalysts [18,19], few studies about USY applying in tyre pyrolysis were reported. The application of USY in tyre pyrolysis may enhance to obtain more chemical feedstocks. The studies are very interesting.

In this study, the scrap tyres were pyrolysed in a fixed bed reactor and the derived gases passed directly to a second catalytic reactor containing a zeolite USY catalyst. The influences of pyrolysis temperature, catalytic temperature, heating rate and catalyst/tyre ratio on the yield and fraction of the derived oils were investigated in this paper. And the property of the derived oil had also been analyzed by GC–MS for the purpose of potential use as chemical feedstock, such as benzene, toluene and xylenes.

2. Experimental

The tyre material was in the form of finely shredded crumbed tyre derived from discarded cars, which was shredded to produce a size of 8.0–10.0 mm. 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.% for the tyre rubber used.

USY (offered by Qilu Petrochemical Huaxing Company Ltd.) was used as the catalyst with a pore size of 9.0 Å, and silica/alumina (Si/Al) ratio of 5 representing a high acidity. The BET surface area and the concentration of Na₂O are 800 m²/g and 1.5 wt.%, respectively. The catalyst was 1 mm in diameter with about 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 and could contain up to 20 g tyre sample. The pyrolysis reactor was upright with an airproof lid on above. When the lid was moving, the tyre can be

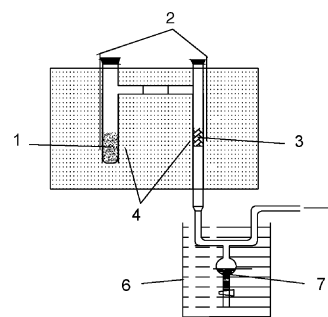


Fig. 1. The schematic diagram of the experimental system. (1) Scrap tyre; (2) thermocouple; (3) catalyst; (4) electric furnace; (5) vent; (6) ice/water condenser; (7) oil.

put into it quickly. The pyrolysis reactor was externally heated via an external electrical heater, and heating rate and final temperature were controlled and temperatures monitored through the reactor using thermocouples. No gas was introduced into the reactor to sweep the evolved gas. The used tyres were contained in a sample cage with dimensions of 2.6 cm diameter × 10 cm high which was removable, allowing the sample to be introduced and post-reaction solid product to be removed easily. The pyrolysis gases produced in the pyrolysis reactor were passed directly to a heated secondary catalyst reactor which was connected with the pyrolysis reactor and its temperature was controlled separately. The derived 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 catalytic reactor was also upright with an airproof lid on above. When the lid was moving, the catalysts can be put into it quickly. The schematic diagram of the experimental system is shown in Fig. 1.

The pyrolysis temperatures, catalytic temperatures and catalyst/tyre ratios and heating rate are considered in this study. The processes for the experiments are described as follows. Before the reactors being heated, the lid of the catalytic reactor was moving and the catalyst was put into the catalytic reactor. After the lid of the catalytic reactor being covered, the temperature of catalytic reactor was heated to the final temperature at a quick heating rate at about 200–250 °C/min. The catalyst was activated at that temperature for 1 h before the pyrolysis of the tyre. After the catalyst being activated, the pyrolysis reactor was pre-heated to a certain temperature. Then, the tyres were put into the pyrolysis reactor and the lid was covered. After that the pyrolysis reactor was heated to final temperature at a certain heating rate and kept at that temperature for 0.5 h. When the influences of parameters of pyrolysis temperatures, catalytic temperatures and catalyst/tyre ratios were considering, the pre-heated temperature for pyrolysis reactor was 400 °C and the heating rate from 400 °C to final temperature was about 200–250 °C/min. When the heating rate for pyrolysis reactor was investigated from 5 to 40 °C/min, the pre-heated temperature for pyrolysis reactor was 150 °C and the final temperature was 550 °C.

The high temperature gaseous products from the pyrolysis and catalytic reactor were introduced into the condenser, the

liquid products were obtained and non-condensed gas was emitted. The yields of char can be obtained from pyrolysis reactor when the reactors were cool.

In order to obtain the influences of some parameters on the light fractions of derived liquid products, the light naphtha (<160 °C) was distilled from the liquid products, and the yields of the light fraction were investigated.

Because of the complexity of the oil derived from the pyrolysis of the tyres, it was fractionated before being analyzed by GC/MS (Gas chromatography–mass spectrometry). Therefore, one oil obtained from the pyrolysis of scrap tyres was distilled and the fraction with the boiling point lower than 280 °C was investigated for its composition by GC/MS, while the pyrolysis condition for this oil was that the pyrolysis temperature, catalytic temperature and catalyst/tyre ratio were 500, 400 °C and 0.5, respectively. 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, and then programmed to 300 °C at 5 K min⁻¹, held for 5 min. Typical mass spectrometer operating conditions were as follows: transfer line 170 °C, ion source 270 °C and electron energy 70 eV.

3. Results and discussion

3.1. Mass balance

In order to eliminate the flow effect, the catalysts were replaced with the inert ceramic beads of similar size in catalytic reactor when considering the experiments without catalyst. Fig. 2 showed the influence of pyrolysis temperature on the yields of products from the pyrolysis of waste tyres in the absence of a catalyst, while the ceramic bead temperature was 400 °C. The pyrolysis in the absence of catalysis produced an oil yield of 52.0 wt.%, gas yield of 11.9 wt.% and char yield of 36.1 wt.% at a pyrolysis temperature of 500 °C. The coke yield also showed a value of 0.4 wt.%. Similar product yields results have been reported by Williams and Brindle [11] in a fixed bed reactor which was introduced with a continuous purge of inert nitrogen. Also, other workers using a variety of reactors have found similar high yield of oil, for example, Benallal et al. [13] using a 19 kg h⁻¹ pilot unit yielded 50 wt.% oil at 510 °C and 2–20 kPa, represented approximately 57 wt.% oil.

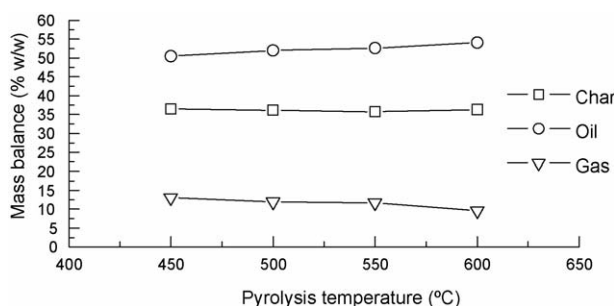


Fig. 2. Effect of pyrolysis temperature on mass balance of gas, oil and char.

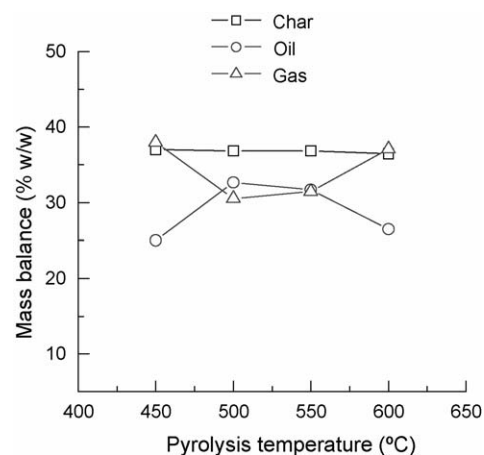


Fig. 3. Effect of pyrolysis temperature on mass balance.

Roy and Unsworth [20] used a vacuum pyrolysis unit to pyrolyse tyres at 415 °C and reported a maximum oil yield of 56.6 wt.%. Kawakami et al. [21] obtained an oil yield of 53 wt.% from the pyrolysis tyres in a rotary kiln at between 540 and 640 °C.

It seemed that there was a slight increase in the yield of oil from 50.47 to 54.10 wt.% as the pyrolysis temperature changed from 450 to 600 °C. The yield of char, as expected remained constant around 36.0 wt.%, since the pyrolysis of the tyres was the same for each experiment. And the yield of gas decreased from 450 to 600 °C. It might have been expected an increase in the amount of gases, and a consequent decrease in the amount of liquids, due to a stronger thermal cracking produced at high temperatures. However, in this experiment, such variation was not produced. There are other similar conclusions concerning the lack of influence of temperature in tyre-pyrolysis yields [22–24].

The presence of zeolite USY catalyst served to reduce the oil yield and increase the gas yield, with formation of coke on the catalyst. Figs. 3 and 4 showed the product yields for the pyrolysis–catalysis of waste tyres in relationship to pyrolysis temperature and catalytic temperature, respectively, while the other parameters were kept at constant. For example, while the pyrolysis temperature was being investigated, the catalytic temperature and catalyst/tyre ratio were kept at 400 °C and 0.5,

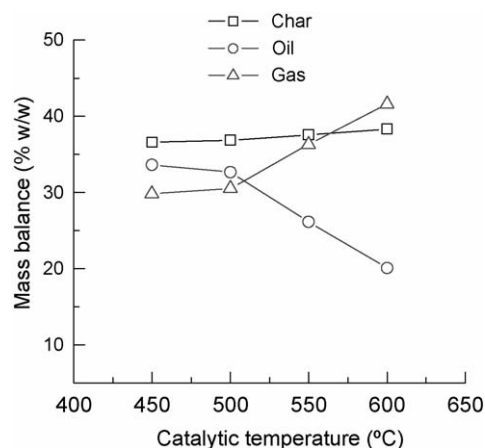


Fig. 4. Effect of catalytic temperature on mass balance.

respectively. And the pyrolysis temperature and catalyst/tyre ratio were kept at 500 °C and 0.5, respectively, while the parameter of catalytic temperature was being investigated. It was apparent that the addition of zeolite USY had the effect of markedly reducing the oil production. Fig. 3 showed that the yield of oil increased first and then decreased as the pyrolysis temperature increased from 450 to 600 °C, and the maximum yield of oil was 32.7 wt.% at a pyrolysis temperature of 500 °C. Fig. 4 showed that increasing the catalytic temperature had the effect of increasing gas production at the expense of oil yield. For example, the gas yield rose from 29.8 to 41.6 wt.% and oil yield fell from 33.6 to 20.1% as the catalytic temperature increased from 350 to 500 °C. The char yield was still kept constant around 36 wt.%. The formation of the carbonaceous coke on the catalyst was about 20 wt.%, which was much higher than the one without catalyst. It was also higher than the one on a catalyst of zeolite ZSM-5 reported by Williams and Brindle [11], which was around 10 wt.%. This was because the Si/Al ratio and pore size were different between zeolite USY and ZSM-5 catalysts. The defined pore sizes were 9 Å for the USY catalyst and 5.6 Å for the ZSM-5 catalyst, respectively. Williams and Brindle [11] found that a smaller pore size would entail less hydrocarbons being of sufficiently small enough size to enter the pore system in the first place, therefore less pyrolysis vapor experienced the zeolite cracking and reformation mechanisms that led to formation of aromatic hydrocarbons. That meant that larger pore size resulted in higher concentration of aromatics. And Venuto and Habib [25] reported that aromatic species had a greater predisposition to being involved in pathways to coke formation because of their ability to easily be involved in hydrogen transfer and cyclization reactions. Therefore, more aromatics were produced with large pore size catalyst to form coke, which was identified in this paper. The Si/Al ratios were 5 for the USY catalyst and 40 for the ZSM-5 catalyst, respectively. The low Si/Al ratio resulted in higher activity [19] and as the Si/Al ratio was decreased, thereby increasing surface activity, there was a clear and significant increase in the yield of aromatic hydrocarbons produced [11]. So, the coke formation of USY catalyst was higher than ZSM-5 catalyst.

The influence of catalyst/tyre ratio was shown in Fig. 5, in which the pyrolysis temperature and catalytic temperature were kept at 500 and 400 °C, respectively. The char yield remained the same throughout the pyrolysis–catalysis experiments as expected since the pyrolysis of the tyres was identical for each experiment. As the catalyst/tyre ratio was increased, there were decrease in the yield of oil and increase in gas yield. For example, when the catalyst/tyre ratio increased from 0.25 to 1.0, the yield of gas increased from 30.5 to 49.9 wt.%, and the oil yield decreased nearly two-fold from 31.6 to 12.7 wt.%. Williams and Brindle [11] showed that there was a reduction in oil yield of 24 wt.% that is from 55.8 to 32 wt.% and gas yield increased by 14–20 wt.% while he used a Y-zeolite (CBV-400) catalyst, the ratio of which to tyre was increased from 0 to 2. Therefore, the higher catalyst/tyre ratio would enable more reactants to be cracked into gases.

In the report of Williams, the yield of tyre pyrolysis oil was about 46 wt.% for ZSM-5 zeolite catalyst, 43 wt.% for

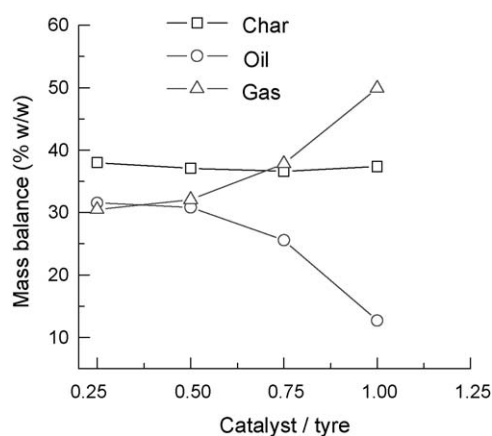


Fig. 5. Effect of catalyst/tyre ratio on mass balance.

the Y-zeolite (CBV-400) catalyst at a catalyst/tyre ratio of 0.5, which was 32.6 wt.% in this study using USY zeolite as a catalyst at equivalent catalyst/tyre ratio, while the other parameters such as the pyrolysis temperature and catalysis temperature were 500 and 400 °C, respectively. Therefore, the derived oil from the pyrolysis–catalysis of scrap tyres with USY zeolite catalyst was lower in yields compared with ZSM-5 zeolite and Y-zeolite (CBV-400) catalyst at the equivalent conditions.

Fig. 6 demonstrated the influence of heating rate of pyrolysis temperature on the product yield of the pyrolysis–catalysis of tyres at the catalytic temperature and catalyst/tyre ratio of 400 °C and 0.5, respectively. The pyrolysis reactor was heated from 150 °C to the final temperature of 550 °C with different heating rate from 5 to 40 °C/min. It was observed that the heating rate of pyrolysis temperature was an important factor during catalysis with zeolite USY catalyst. No big change in the yield of gas was found while the heating rate increased from 5 to 10 °C/min, there was a large decrease in gas yield with the further increase of heating rate to 40 °C/min. In addition, the oil yield increased from 18 to 27 wt.% with the increase of the heating rate from 5 to 40 °C/min. It is supposed that high heating rate is favoring the formation of oil, since the pyrolysis gases and vapors are con-

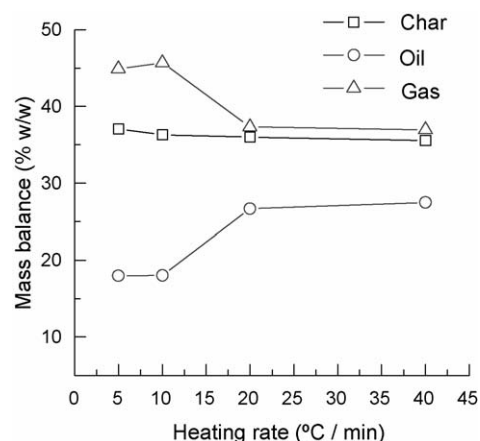


Fig. 6. Effect of heating rate on mass balance.

densed before further reaction breaks down the higher molecular species into gaseous products. There wasn't much influence of heating rate on the char yield. At a heating rate of 40 °C/min, coke deposition was 22.5 wt.%, which increased from 18.7 wt.% at the heating rate of 5 °C/min. A variety of reactions lead to the formation of coke during the catalysis of gases derived from the pyrolysis of tyres. The increasing of catalyst coke illustrated that there may be more aromatic species and alkenes produced at higher heating rate, which have a great predisposition to being involved in pathways to coke formation.

3.2. Distillation

The light naphtha (<160 °C) was distilled from the derived oils. Fig. 7 showed the effect of three parameters (pyrolysis temperature, catalytic temperature and catalyst/tyre ratio) on the yield of light naphtha (<160 °C), in which, PT, CT and C/T stood for pyrolysis temperature, catalytic temperature and catalyst/tyre ratio, respectively. And the pyrolysis temperature was investigated at levels of 450, 500, 550 and 600 °C, respectively, while the catalytic temperature and catalyst/tyre ratio were kept at 400 °C and 0.5, respectively. The catalytic temperature was studied at levels of 350, 400, 450 and 500 °C, respectively, at the pyrolysis temperature and catalyst/tyre ratio of 500 °C and 0.5, respectively. And while the pyrolysis temperature and catalytic temperature were 500 and 350 °C, the catalyst/tyre ratio was investigated at levels of 0.25, 0.5, 0.75 and 1.0, respectively. Fig. 7 illustrated that the concentration of light naphtha decreased first and then increased as the pyrolysis temperature increased from 450 to 600 °C. The minimum value of light naphtha was 55.9 wt.%. As it was seen from Fig. 7 that the catalytic temperature and the catalyst/tyre ratio had the same influences on the light fraction, since the light naphtha increased when these two parameters increased from 350 to 550 °C and 0.25 to 1.0, with two maximum values of 63.9 and 63.2 wt.%, respectively. These concentrations of light naphtha were much higher than

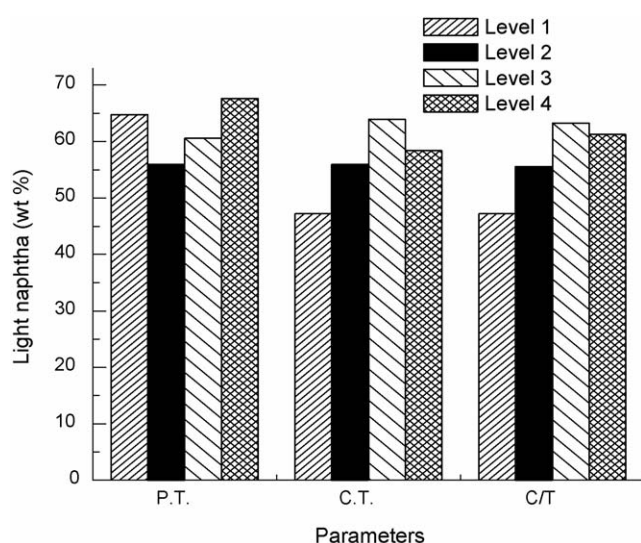


Fig. 7. The influences of pyrolysis temperature (PT), catalytic temperature (CT) and catalyst/tyre ratio (C/T) on the yield of light naphtha (i.b.p. 160 °C).

the result reported by Laresgoiti et al. [24], which was 10 wt.%. Pakdel and Roy [15] used a vacuum pyrolysis unit to pyrolysis tyres at 510 °C, and they got a fraction of 27% (<204 °C) by distillation. The high light naphtha obtained in this study was because the gases produced from the reactor were passed through a catalytic reactor, where the secondary reactions were happened to produce more light components.

3.3. Oil composition

GC/MS analyses were carried out with the pyrolysis oil obtained at the pyrolysis temperature, catalytic temperature and catalyst/tyre ratio of 500, 400 °C and 0.5, respectively. And the yields of char, oil and gas were 36.8, 32.7 and 30.5 wt.% at the above conditions, respectively. The oil was fractionated by distillation, and the distillate (>280 °C), which was about 92.5 wt.% in the oil, was obtained as analyte. The objective was to get an idea of the nature and type of compounds of such oil catalyzed with zeolite USY catalyst. Fig. 8(a) showed the whole GC/MS chromatogram obtained from the distilled oil while Fig. 8(b) and (c) corresponded to enlarged fragments of it, in which many identified peaks had been numbered. The NIST Search software was used to analyze the peaks provided by the chromatogram, from which more than the half was not properly identified. The isomeric structures of the compounds had not been determined, due to the limitation of the GC/MS identification procedure to differentiate isomers. All the peaks after 30 min were not identified, since the ratios of these peaks were few. Anyway such identification was beyond the scope of this paper.

Table 1 showed the tentative compounds assigned and the percentage quantified area for every identified peak. It can be seen that, as expected, tyre pyrolysis oil were a very complex mixture of organic compounds. There were such a great number of compounds in tyre oil that the peak areas were very low. The most abundant products, with peak areas around or higher than 1%, were benzene, toluene, ethylbenzene, xylenes, ethylbenzene, butylbenzene, isopropylmethylbenzene, limonene, isopropylmethylbenzene, ethyldimethylbenzene, ter-amethylbenzene, naphthalene, C₅-benzene, methylnaphthalene and dimethylnaphthalene. As it was shown in Table 1, the total concentration of single ring aromatics was 62 wt.%, among which there were 1.23 wt.% benzene, 9.35 wt.% toluene, 3.68 wt.% ethylbenzene, 12.64 wt.% xylenes and 1.81 wt.% limonene. Benzen, toluene and the xylenes have a major use as chemical feedstocks. The major industrial products from benzene are derivatives such as ethylbenzene, cyclohexane and cumene together with other derivatives. The derivatives are used as basic materials for the production of plastics, resins, fibres and surfactants, etc., which are used as feedstocks in the manufacture of surfactants.

Many analyses of derived oils from the pyrolysis of waste tyres without catalyst were reported. For example, Laresgoiti et al. [24] obtained 4.40 wt.% toluene, 3.48 wt.% xylenes, 5.12 wt.% limonene, etc. in a study of 500 °C pyrolysis oils. Benallal et al. [13] obtained 2.3 wt.% benzene, 15.7 wt.% toluene, 21.2 wt.% xylenes and 6.9 wt.% limonene, etc. in the light naphtha fraction, which was only about 20 wt.% of total

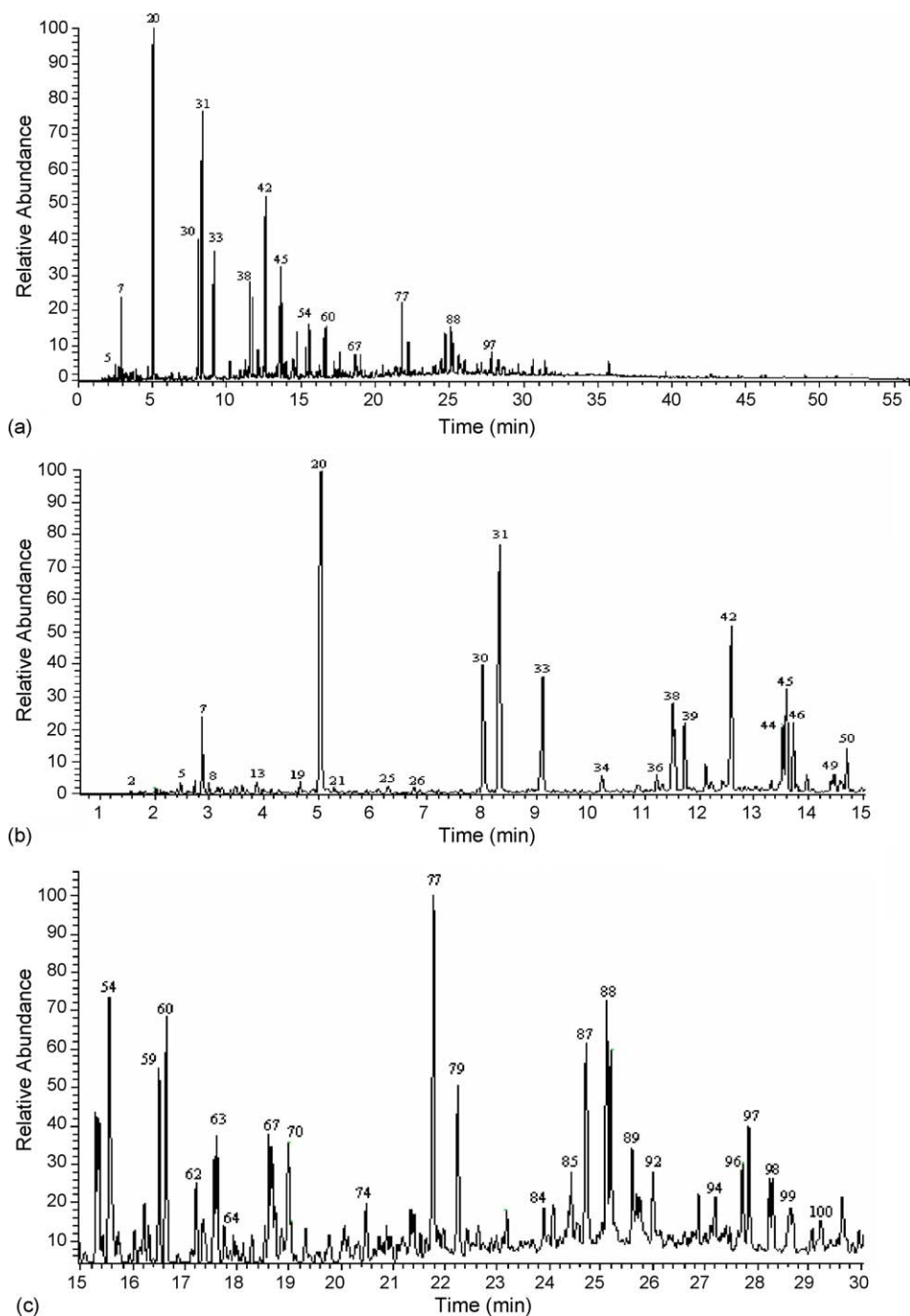


Fig. 8. (a) Total GC/MS chromatogram of the tyre pyrolysis oil; (b) 0–15 min GC/MS chromatogram of the tyre pyrolysis oil; (c) 15–30 min GC/MS chromatogram of the tyre pyrolysis oil.

510 °C pyrolysis oils. And Pakdel et al. [26] presented 1.86 wt.% toluene, 1.60 wt.% xylenes, and 4.00 wt.% limonene. These concentrations of toluene and xylenes were much lower than the one obtained in this study. Therefore, the concentrations of such single ring aromatic are greatly increased with the catalysis of zeolite USY catalyst. It was noticed that the limonene percentage was lower than the one reported by others. Cunliffe and Williams [9], Pakdel et al. [26] and Williams et al. [27] suggested that limonene decomposition to a range of products including benzene, toluene, xylene, trimethylbenzene, styrene and methyl-

styrene at the temperature higher than 500 °C. Therefore, with the high activity of zeolite USY catalyst, most limonene was decomposed in this study.

Williams and Brindle [11] used zeolite ZSM-5 and Y-zeolite (CBV-400) to catalyze the gases derived from the pyrolysis of waste tyres. The total concentration of benzene, toluene and xylenes they obtained was about 10 wt.% for ZSM-5 catalyst and 22 wt.% for Y-zeolite (CBV-400) in the oil at a catalyst/tyre ratio of 0.5, while the pyrolysis temperature and catalysis temperature were 500, 500 °C, respectively. The total concentration

Table 1
Tentative GC/MS characterization of distillate from tyre pyrolysis oil with zeolite USY (concentrations in the distillate, wt.%)

Peak no.	Wt. %	Tentative assignment	Peak no.	Wt. %	Tentative assignment
1	0.04	Dimethylcyclopropane	51	0.15	Methylpropylbenzene
2	0.05	Dimethylcyclopropane	52	0.22	Diethylbenzene
3	0.1	Methylpentene	53	1.59	Ethylidimethylbenzene
4	0.14	Methylpentene	54	1.82	Ethylidimethylbenzene
5	0.24	Methylcyclopentane	55	0.29	Isopropenyltoluene
6	0.21	Hexadiene	56	0.36	C ₅ -benzene
7	1.23	Benzene	57	0.4	Methylpropylbenzene
8	0.17	C ₇ -alkene	58	0.32	C ₅ -benzene
9	0.38	C ₇ -alkene	59	1.09	Teramethylbenzene
10	0.33	Heptadiene	60	1.2	Teramethylbenzene
11	0.19	C ₇ -alkene	61	0.56	Dimethylstyrene
12	0.1	Dimethylcyclopentene	62	0.4	Amylbenzene
13	0.28	C ₇ -alkene	63	1.19	Teramethylbenzene
14	0.16	C ₇ -alkene	64	0.35	C ₅ -benzene
15	0.1	Methylcyclohexane	65	0.27	C ₅ -benzene
16	0.1	Heptadiene	66	0.15	C ₅ -benzene
17	0.12	Heptyne	67	0.91	Naphthalene
18	0.05	Heptyne	68	0.78	Methylbutylenebenzene
19	0.34	Methylhexadiene	69	0.25	Methylbutylenebenzene
20	9.35	Toluene	70	1.03	C ₅ -benzene
21	0.18	Dimethylcyclohexane	71	0.35	C ₅ -benzene
22	0.18	C ₈ -alkene	72	0.31	Cyclopentylbenzene
23	0.07	C ₈ -alkene	73	0.24	C ₆ -alkene-benzene
24	0.2	Dimethylcyclohexene	74	0.35	C ₅ -alkene-benzene
25	0.23	Dimethylhexadiene	75	0.38	C ₅ -alkene-benzene
26	0.19	Dimethylhexadiene	76	0.56	C ₆ -benzene
27	0.08	Dimethylhexadiene	77	2.28	Methylnaphthalene
28	0.21	Ethylcyclohexane	78	0.19	C ₆ -alkene-benzene
29	0.27	Trimethylcyclohexane	79	0.95	Methylnaphthalene
30	3.68	Ethylbenzene	80	0.19	C ₆ -alkene-benzene
31	9.16	<i>m</i> - + <i>p</i> -Xylene	81	0.38	C ₆ -alkene-benzene
32	0.07	Styrene	82	0.11	Ethyltetrahydronaphthalene
33	3.48	<i>o</i> -Xylene	83	0.08	C ₆ -alkene-benzene
34	0.63	Isopropylbenzene	84	0.39	Trimethylindene
35	0.31	Trimethylheptatriene	85	0.65	Ethyl naphthalene
36	0.39	Propylbenzene	86	0.24	Ethyl naphthalene
37	0.3	Trimethylcyclohexene	87	1.48	Dimethylnaphthalene
38	3.65	Ethyltoluene	88	1.5	Dimethylnaphthalene
39	2.06	Ethyltoluene	89	1.05	Dimethylnaphthalene
40	0.73	Trimethylbenzene	90	0.79	Dimethylnaphthalene
41	0.37	Benzonitrile	91	0.2	Ethylquinoline
42	4.97	Trimethylbenzene	92	0.4	Dimethylnaphthalene
43	0.23	Decadiene	93	0.21	C ₁₄ -alkane
44	2.01	Butylbenzene	94	0.52	Isopropyl naphthalene
45	2.58	Isopropylmethylbenzene	95	0.13	Isopropyl naphthalene
46	1.81	Limonene	96	0.62	Trimethyl naphthalene
47	0.62	Indane	97	0.69	Trimethyl naphthalene
48	0.91	Methylpropylbenzene	98	0.78	Trimethyl naphthalene
49	0.54	Methylpropylbenzene	99	0.65	Trimethyl naphthalene
50	1.18	Isopropylmethylbenzene	100	0.14	Trimethyl naphthalene
Total identified				85.11	

of these aromatics was about 23.2 wt.% in the distillate with the USY zeolite catalyst used in this study, which was equal to 21.5 wt.% in the derived oil, at equivalent catalyst/tyre ratio with the pyrolysis temperature and catalysis temperature of 500, 400 °C, respectively. It was apparent that the total concentration of benzene, toluene and xylenes for USY catalyst was higher than the one for ZSM-5 catalyst. Though it was a little higher for Y-zeolite (CBV-400) catalyst than the one for USY catalyst, the

temperature of Y-zeolite catalyst was higher than USY catalyst, which can increase the total concentration of benzene, toluene and xylenes [10]. Therefore, the USY catalyst produced higher concentrations of benzene, toluene and xylenes compared with the ZSM-5 catalyst and Y-zeolite (CBV-400) catalyst. This was because the zeolite USY had a lower Si/Al ratio than ZSM-5 catalyst, which served to increase the surface acidity of the catalyst by increasing the relative surface concentration of aluminium

[11]. And the difference between USY catalyst and Y-zeolite catalyst was most probable due to the lower pore size of Y-zeolite (CBV-400), which is 7.8 Å for Y-zeolite (CBV-400), 9.0 Å for USY catalyst.

The catalytic temperature and catalyst/tyre ratio are very important parameters in the pyrolysis–catalysis of tyres. Higher catalytic temperature and catalyst/tyre ratio can offer higher activity to increase single ring aromatics. This was identified by Williams and Brindle [10,11]. But what exactly influence of catalytic temperature of zeolite USY on the composition of derived oils from the pyrolysis–catalysis of waste tyres will be studied later, since zeolite USY had a different pore size and Si/Al ratio.

From Table 1, we can see the total concentration of polycyclic aromatic hydrocarbons (PAHs) was 13.89 wt.%, where most of them were alkyl naphthalenes. Since the boiling point of the oil determined by GC/MS was below 280 °C, some other naphthalenes such as phenanthrenes and fluorenes, etc., could not be found in this study. PAHs in tyre pyrolysis oils have also been reported by other worker. Cunliffe and Williams [9] studied the concentration of PAHs in a nitrogen purged static-bed batch reactor. He found that the total PAHs content of oils increased from 1.5 to 3.5 wt.% of the total oil as the pyrolysis temperature increased from 450 to 600 °C. Kaminsky and Sinn [28] reported concentrations of 0.85, 0.16, 0.29 and 0.21 wt.% of naphthalene, fluorine, phenanthrene and pyrene, respectively, in the oil derived from the pyrolysis of waste tyres at 750 °C in a fluidized bed reactor. Wolfson et al. [1] pyrolysed scrap tyres in a retort at 500 °C and separated a light and heavy oil fraction. The heavy fraction was shown to contain the PAHs, biphenyl, acenaphthene and alkyl naphthalenes. Laresgoiti et al. [24] also found PAHs such as alkyl naphthalenes, phenanthrenes, fluorenes, diphenyls, etc. It can be concluded that the oil from pyrolysis–catalysis of waste tyres with zeolite USY has high concentration of PAHs, since the presence of catalyst increased the amount of catalytic reactions and therefore promoted cyclization reactions to PAHs.

Two nitrogenated compounds (Benzonitrile and Ethylquinoline) with a concentration of 0.37 and 0.2 wt.% were found in this study, respectively. These compounds are probably derived from the accelerators used in tyre compounding, which are frequently sulphur and nitrogen-based compounds, such as benzothiazoles, thioireas, thiuram, etc. Some other authors had also found nitrogenous compounds in tyre pyrolysis oils [23,24,15,29]. With respect to sulphurated compounds, no one was found in this study. Benzothiazol was the only one compound found by Laresgoiti et al. [24]. Williams and Bottrill [12] used a series of liquid column chromatography fractionations with oxidation and reduction to produce enriched sulphurated compounds, and he found the sulphurated compounds were mainly dibenzothiophene, methyl, dimethyl and trimethyl dibenzothiophenes, and also naphthothiohenes and their emthyl derivatives.

4. Conclusions

(1) Catalytic pyrolysis of waste tyres using zeolite USY catalyst have been investigated in relation to the influence of the pyrolysis temperature, catalytic temperature, cata-

lyst/tyre ratio and heating rate on the yield of the products. The results showed that the influence of the presence of zeolite USY catalyst was to reduce the yield of oil with a consequent increase in the gas yield. The yields of oils decreased largely as the catalytic temperature and catalyst/tyre ratio increased, respectively. It also increased from 18 to 27.5 wt.% as the heating rate of pyrolysis reactor increased from 5 to 40 °C/min. The yield of light naphtha (<160 °C) distilled from the derived oil was found to be influenced by pyrolysis temperature, catalysis temperature and catalyst/tyre ratio, and was around 60 wt.% in the derived oil.

- (2) A distillate (<280 °C) of a derived oil was investigated by GC/MS, the results showed that the oil was a very complex mixture of organic compounds. And the distillate, which was 92.5 wt.% in the derived oil, contained 1.23 wt.% benzene, 9.35 wt.% toluene, 3.68 wt.% ethylbenzene, 12.64 wt.% xylenes, 1.81 wt.% limonene and 13.89 wt.% PAHs.
- (3) Compared with the oil products from the pyrolysis of scrap tyres without catalysts, with ZSM-5 catalyst, Y-zeolite catalyst from literatures and the products with USY zeolite catalyst has higher total concentrations of benzene, toluene and xylenes.

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