CHAPTER V
EFFECTS OF ZEOLITIC SUPPORT PROPERTIES ON SULFUR SPECIES AND DISTRIBUTION IN TIRE-DERIVED PRODUCTS

5.1 Abstract

High sulfur content in oils are undesirable due to the emission of pollutants. The use of sulfur removal catalysts to improve the quality of oils has gained high attention. In this work, tire-derived products via catalytic pyrolysis were analyzed in order to investigate the impact of zeolite channel structure and pore size on sulfur content, species, and distribution. To study the effect of channel structure, HMOR (straight) and HBeta (zigzag) were chosen for comparison. For the impact of pore size, HBeta (6.4 Å × 7.6 Å) and HZSM-5 (5.3 Å × 5.6 Å) were chosen for comparison since they have a zigzag channel structure in common. The products were analyzed by using an elemental analyzer for sulfur content, whereas a GC×GC-TOF/MS was used to investigate the sulfur species in oils. The results showed that using all catalysts resulted in the reduction of sulfur content in oils. HBeta (zigzag channel) produced more benzothiophenes than benzothiazoles, whereas HMOR (straight channel) produced more benzothiazoles than benzothiophenes. The larger pore size of HBeta produced more larger sulfur compounds (such as benzothiophenes, dibenzothiophenes, and benzothiazoles) than the smaller pores of HZSM-5. Moreover, the larger pore volume of HBeta caused a higher amount of coke formation.

5.2 Introduction

Tire-derived oils are complex mixtures of aliphatic and aromatic compounds such as benzene, toluene, xylenes as well as limonene (Islam *et al.*, 2008). The fuel properties of tire-derived oils were found similar to those of diesel and gasoline (Banar *et al.*, 2012). Furthermore, they suggested that tire-derived oils can be used as

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feedstocks for chemicals production. However, sulfur in tire-derived oils is the most disturbing problem. Due to vulcanization in the tire production, tire structure is comprised of sulfur in various forms in the large network between sulfidic crosslinks and rubber chains, which can be monosulfidic, disulfidic, and polysulfidic (Bilgili *et al.*, 2001). The release of sulfur from the tire molecules during pyrolysis results in the low quality of oil products. With the similar gross calorific value to fuel oils (about 40.0 MJ/kg), tire-derived oils have a sulfur content of about 1.4-1.5 wt.% (Cunliffe and Williams, 1998), which is lower than that in some grades of fuel oils, but still causes the low quality. In consequence, sulfur is expected to be removed to obtain the light oil with a low sulfur content. Dũng *et al.* (2009) studied the effect of temperature and catalysts on waste tire pyrolysis. They found that sulfur-containing polar-aromatics increased with increasing pyrolysis temperature. Moreover, the results show that polar-aromatics reduction activity can be ranked as follows: Pt/HBETA > Pt/HMOR > HBETA > HMOR. It was explained that the higher acid strength of HBETA resulted in higher cracking ability than the lower strength of HMOR, and the larger pore size of HBETA allowed larger molecules to go inside its pore and to be cracked. The higher dispersion of Pt/HBETA catalyst resulted in better hydrogenation because of the higher surface area and pore diameter of HBETA. They concluded that heavier polar-aromatics were prevented from being formed by hydrogenation to saturated compounds, and then further cracked by the acid supports. Recently, the use of Rh/KL has been studied by Pinket (2011) in order to produce a valuable product with a low sulfur content in oils. The results showed that KL reduced sulfur in the pyrolysis oil from 1.40 to 0.91 wt.%, and it further decreased to 0.35 wt.% with using Rh/KL, meaning that Rh/KL could potentially benefit cracking and sulfur removal simultaneously.

So far, the effects of acid properties of zeolites were studied the most on tire-derived products, but none of researchers has studies the effects of channel structure and pore size on sulfur species and distribution in products The objective of this work was therefore to investigate the effects of channel structure and pore size of zeolite on sulfur distribution, content, and species in tire-derived products. HMOR (2D-straight channel structure) and HBeta (3D-zigzag channel structure) were selected to investigate the effect of channel structure. They are acidic zeolites and

have insignificant difference in pore size, which is 6.5 Å × 7.0 Å for HMOR and 6.4 Å × 6.7 Å for HBeta. To control the acid parameter, both zeolites need to have the same Si/Al ratio; however, since it is difficult to synthesize or find exactly the same Si/Al ratio of both zeolites in the market, HMOR with the Si/Al ratio of 9.5 and HBeta with the ratio of 13.5 were selected to use. Furthermore, HBeta (6.4 Å × 7.6 Å) and HZSM-5 (5.3 Å × 5.6 Å) with 3D-channel structure and a close Si/Al ratio (13.5 and 15, respectively) were employed to investigate the effect of pore size.

5.3 Experimental

5.3.1 Catalyst and Material Preparations

All zeolites, which are HMOR (Si/Al = 9.5), HZSM-5 (Si/Al = 15), and HBeta (Si/Al = 13.5), were obtained from Tosoh Company in Singapore. In order to remove impurity from the zeolite, HMOR and HZSM-5 were calcined at 500 °C for 3 h with the heating rate of 10 °C/min, and HBeta was calcined at 600 °C for 5 h with 2 °C/min. After that, HMOR, HZSM-5, and HBeta powders were pelletized, crushed, and sieved into the particle size range of 400-425 µm. Tire, Bridgestone TURANZA GR-80, was scraped and sieved into the particle size range of 425-850 µm.

5.3.2 Catalyst Characterization

X-ray diffraction (XRD) patterns were taken by using a Bruker X-ray diffractometer system equipped with a 2.2 kW Cu anode in a long fine focus ceramic X-ray tube for generating a CuKα radiation (1.5405 Å). The detector scanned the peak position from the samples as a function of 2θ by starting at the 5 ° to 100 ° (2θ) range with a scan speed of 5 °(2θ)/min. The specific surface area and pore volume were characterized by using a Thermo Finnigan/Sorptomatic1990 equipment. In addition, Thermogravimetric/Differential Thermal Analysis (TG/DTA) was used to determine coke deposited on spent catalysts. The temperature was ramped to 900 °C with heating rate of 10 °C/min.

5.3.3 Pyrolysis of Waste Tire

The reactor has 2 zones, which are catalytic zone (the upper zone) and pyrolytic zone (the lower zone) as in Dũng *et al.* (2009). Firstly, 30 g of the waste tire with sizes in the range of 425-850 μm was loaded into the lower zone, and 7.5 g of pellet catalyst with sizes in the range of 400-425 μm was loaded to the catalytic zone. Then, the pyrolysis was heated with the rate of 10 °C/min from the room temperature to 500 °C, and then kept for 120 min at the atmospheric pressure. The temperature of pyrolytic zone was controlled at 350 °C. The flow rate of N_2 was controlled at 30 ml/min, continuously flown to purge the oxygen out of the system prior to pyrolysis and subsequently for carrying the pyrolysis products to condensers and a gas sampling bag. The product effluent was carried by nitrogen, and then condensed the liquid products by using ice-salt condensers. The incondensable product was passed to the condensers and collected by a gas sampling bag.

5.3.4 Product Analysis

The liquid and solid products were weighed to determine the amount of an incondensable gas and then the product distribution by mass balance. The obtained gas products were analyzed using a Gas Chromatography, Agilent Technologies 6890 Network GC system, with FID detector. A liquid product was first dissolved in *n*-pentane by 40:1 ratio to precipitate asphaltene. After that, asphaltene was filtered using polyamide membrane (0.45 μm of pore size). The obtained maltene was analyzed for the true boiling point curves and the petroleum fractions by using a Varian CP-3800 stimulated distillation gas chromatography (SIMDIST-GC), equipped with an FID according to the ASTM D2887 method. The true boiling point curves were cut into full range naphtha (< 200 °C), kerosene (200-250 °C), light gas oil (250-300 °C), heavy gas oil (300-370 °C), and long residue (> 370 °C) (Dũng *et al.*, 2010). A two-dimensional Gas Chromatography-Mass Spectrometry (Time of Flight), GC×GC-TOF/MS, was used to identify components in maltenes. Helium and nitrogen were used as a carrier and cooling gas. Finally, The product was also analyzed for the sulfur content by elemental analysis (LECO, US).

5.4 Results and Discussion

5.4.1 Effect of Channel Structure

The overall distribution of sulfur in tire-derived products obtained from using HBeta and HMOR is shown in Figure 5.1. It exhibits sulfur mostly distributes into the char for all cases. Using catalysts cause more sulfur distribution in the gas and on the spent catalysts in accordance with the expense of sulfur distribution in oils. Using HMOR gives more sulfur distributed in the gas product than using HBeta, whereas HBeta results in more sulfur distributed on spent catalyst than HMOR. It can be suggested that the zigzag channel of HBeta results in more deposition of sulfur than the straight channel of HMOR. In addition, sulfur content in oils is shown in Table 5.1. The results show that sulfur content in oil is reduced with using both catalysts. Namely, HMOR gives a slightly lower sulfur content in oils than HBeta. It can be explained that the cracking ability of HBeta and HMOR can help to remove sulfur compounds from oils since cracking can occur at C-S bonds in the sulfur compounds.
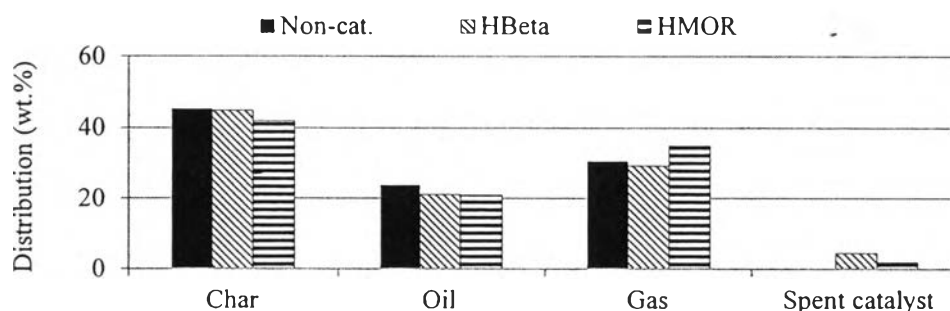

Figure 5.1 Overall distribution of sulfur in pyrolysis products obtained from HBeta and HMOR.

On the other hand, the yield of sulfur species in tire-derived oils is illustrated in Figure 5.2. It can be seen that the zigzag channel of HBeta produces less amount of thiophenes than the straight channel of HMOR. Benzothiophenes dramatically increase with using HBeta, but insigficantly change with using HMOR.

Benzothiazoles sharply decrease with using both catalysts as compared to the non-catalyst case, whereas the mixture heteroatom (O and/or N)-containing sulfur compounds (so-called "the others" in Figure 5.2 and 5.4) is also reduced with using both catalysts.

Table 5.1 Sulfur content on spent catalysts and in oils obtained from HBeta and HMOR

	% Sulfur		
	Non-cat.	HBeta	HMOR
Spent catalyst	-	0.41 -	0.18
Oil	1.17	1.10	1.08

It can be suggested that HMOR and HBeta possibly convert benzothaizoles and the others, to forming hydrocarbon compounds such as derivative of benzenes, or even non-aromatics. Unlike HMOR, HBeta possibly rearranges benzothiazoles to form benzothiophenes inside the zeolite channel. In addition, the zigzag channel of HBeta allows molecules to stay inside its pore with a longer residence time than the straight channel of HMOR; thus, resulting in a high amount of benzothiophenes produced by HBeta, but not by HMOR. Moreover, since using HMOR gives a less amount of benzothiophenes and dibenzothiophenes than using HBeta; thus, it can be concluded that the oil obtained from HMOR is easier to be further desulfurized than those from HBeta.
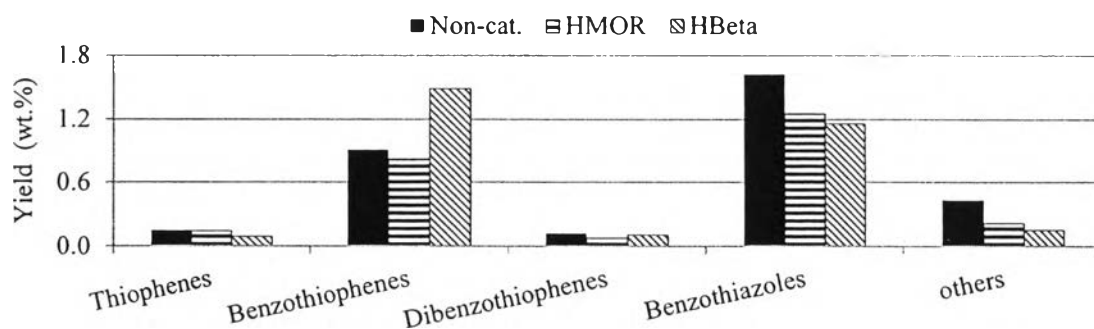

Figure 5.2 Yield of sulfur species in maltenes obtained from HMOR and HBeta.

5.5.4 Effect of Pore Size

Figure 5.3 shows the overall sulfur distribution in tire-derived products obtained from HBeta and HZSM-5 catalysts. The results show that using both catalysts causes the sulfur distribution on the spent catalysts in accordance with the reduction of sulfur distribution in oils. Moreover, sulfur distribution on the spent HZSM-5 (medium pore) is lower than on the spent HBeta (large pore). It can be suggested that the larger pore of HBeta allows a higher amount of sulfur-containing molecules to deposit than the smaller pore of HZSM-5. In addition, the sulfur content on the spent catalysts and in oils obtained from HBeta and HZSM-5 are illustrated in Table 5.2. The results show that HBeta and HZSM-5 slightly reduce sulfur in oils from 1.17 wt.% (the non-catalyst case) to 1.08 wt.% for HZSM-5 and 1.10 wt.% for HBeta. It can be concluded that the oils have a slightly-better quality than the oil from the non-catalyst case.
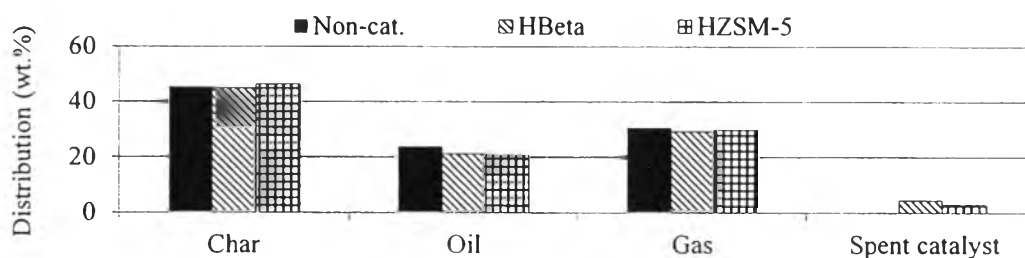

Figure 5.3 Overall distribution of sulfur in pyrolysis products obtained from HBeta and HZSM-5.

Table 5.2 Sulfur content on spent catalysts and in oils obtained from HBeta and HZSM-5

	% Sulfur		
	Non-cat.	HBeta	HZSM-5
Spent catalyst	-	0.41	0.27
Oil	1.17	1.10	1.08

The yield of sulfur species in tire-derived oils from using HZSM-5 and HBeta is illustrated in Figure 5.4. The result shows that thiophenes are slightly reduced with using HZSM-5 and HBeta. The larger channel of HBeta produces a higher amount of larger compounds (benzothiophenes, dibenzothiophenes, and benzothiazoles) than the smaller channel of HZSM-5. In addition, benzothiazoles sharply decrease with using both catalysts, especially HZSM-5, whereas benzothiophenes increase with using HBeta and insignificantly change with using HZSM-5. The mixture of "the others" aromatics also reduces with using both HBeta and HZSM-5. It was explained that HZSM-5 and HBeta possibly convert benzothiazoles and the others to hydrocarbon compounds. In addition, the medium channel of HZSM-5 has less capacity to form large compounds such as benzothiophenes than the larger channel of HBtea. Moreover, the oil obtained from HZSM-5, which has less benzothiophenes, dibenzothiophenes, and benzothiazoles than that from HBeta, is easier to be further desulfurized than that from HBeta, based on the principle in Cottrell (1958) and Garcia-Cruz et al. (2008).
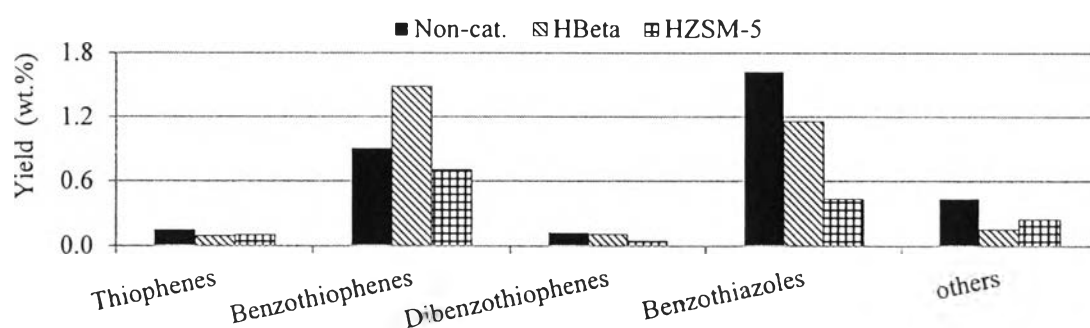

Figure 5.4 Yield of sulfur species in maltenes obtained from HZSM-5 and HBeta.

5.5 Conclusions

The use of all zeolites resulted in the reduction of sulfur in oils. The straight channel of HMOR gaves a better quality of oil than the zigzag channel of HBeta, which consisted of more small molecules of sulfur-containing compounds for further desulfurization in the future. Additionally, the medium pore of HZSM-5 gaves a

slightly-better quality of oil, which has a lower sulfur content, than the larger pore of HBeta. Moreover, the sulfur-containing molecules obtained from HZSM-5 was easier to be further desulfurized than those from HBeta.

5.6 Acknowledgements

5.7 References

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