

# Impact of Zeolite Channel Structure on Structure of Hydrocarbon Compounds and Petrochemicals in Waste Tyre-Derived Oils

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Waste tyre, a hydrocarbon-based material, exhibits potential to be used for a derivation of petrochemicals. Valuable chemicals such as benzene, toluene, and xylenes were observed in pyrolytic oils. Furthermore, sulphur compounds causing the low quality of oil products and environmental problem were also found. HBeta and HMOR acidic zeolites whose pore sizes are very close, which are 6.4x7.6 Å and 6.5x7.0 Å have different channel structures. The channel structure of HBETA is zigzag whereas that of HMOR is straight. Since the channel structure of zeolites may affect the residence time of molecules to stay in the pores; therefore, the objective of this work was to investigate the channel structure of zeolites that affect the structure and the size of pyrolysis products. The products were analyzed by using a SIMDIST-GC, GC and elemental analyser, whereas a GCxGC-TOF/MS was used to investigate species in oils. The catalysts were characterized by using XRD, TGA, and SAA. The results showed that the compositions of pyrolytic oils classified in terms of paraffins (P), olefins (O), naphthenes (N), and aromatics (A) were different with using different zeolites. Catalytic pyrolysis caused the decreases in olefins and naphthenes with the increases of aromatics. Furthermore, HBeta gave the higher amount of aromatics than HMOR, and gave the lower amounts of olefins and naphthenes than HMOR. It can be explained that the complex pore of HBeta converted more olefins and naphthenes to aromatics inside the pore than the straight pore of HMOR. In addition, HBeta gave a higher amount of light fractions in oils than HMOR that gave a higher amount of heavy fractions such as gas oil and long residue. However, these two zeolites can reduce sulphur in oils, and the species of sulphur were different. Moreover, both HBeta and HMOR catalysts caused the increment in the group of benzothiophenes and the reduction in the group of benzothiazoles.

## 1. Introduction

Conventionally, all petrochemicals are produced from petroleum. Olefins and aromatic hydrocarbons are important petrochemicals. Light olefins include ethylene, propylene and butylenes, which are produced from fluid catalytic cracking unit in oil refineries and steam cracking of natural gas. Ethylene and propylene are important olefins used as raw materials in plastic and chemical industries. Butadiene is dominated in rubber and elastomer industries. Useful aromatic hydrocarbons such as benzene, toluene, and xylenes are derived from the catalytic reforming of naphtha. They are used in a wide range of raw materials. Tyres are hydrocarbon-based materials, which exhibit potential to be used as a source for petrochemical production. In addition, tyres have long-life and complication to recycle, resulting in a large amount of waste tyres discarded. Pyrolysis of waste tyres is an interesting process to treat and recover valuable products (Piyawongpinyo, 2013). Islam et al. (2008) studied waste tyre pyrolysis products, especially liquid products. They found that pyrolytic oils were complex mixtures, which consisted of aliphatic and aromatic compounds. Limonene was the most abundant species in pyrolytic oils as well as benzene, toluene, and xylenes. Moreover, the results showed that pyrolytic oils can be directly used as fuels for furnace, power

plant, and boilers. It can be used as diesel fuel after improving the quality such as desulphurization or blending with commercial fuels. Banar et al. (2012) studied pyrolytic oil from waste tyre pyrolysis. They found that the fuel properties (H/C, HHVs, and density) of pyrolytic oil was similar to those of the diesel and gasoline. Additionally, they suggested that the pyrolytic oil can be used as chemical feedstocks for aromatic production. Dŭng et al. (2009) used HMOR catalyst in waste tyre pyrolysis. The result showed that the presence of HMOR increased the light products, which caused the increment of gas yield and the reduction of oil yield. In addition, the introduction of HMOR led to the increasing amounts of gasoline and kerosene and the decreasing amounts of fuel oil and heavy vacuum gas oil due to the good cracking performance of catalyst. They mentioned that HMOR favoured to produce gasoline, which was selective to pore size. Olazar et al. (2008) studied the effect of using HY and HZSM-5 catalysts on waste tyre pyrolysis. The gas product increased with using HZSM-5 due to cracking of heavy fractions, and it slightly decreased with using HY because HY favoured the activation of olefin alkylation and condensation to form heavy products. Additionally, olefins which consisted of ethylene and propylene increased with the use of both catalysts. Poly-aromatics in oil products increased with using catalysts, especially HY. Thus, it was suggested that larger pore size and more hydrogen transfer capacity of HY caused more cyclization, aromatization, and condensation reactions to occur inside the pore to form aromatics. Recently, the pyrolysis of waste tyre using HBeta and KL zeolites was studied by Saeng-arayakul (2013) in order to compare the effect of acid and basic supports (HBeta and KL, respectively). The results showed that using HBeta produced higher gas yield than using KL, and HBeta zeolite reduced the concentration of heavy liquid fractions (long residues and heavy gas oil) more greatly than KL zeolite. The results demonstrated that long-chain hydrocarbons were more easily cracked by HBeta.

Currently, no study has been conducted on the impact of zeolite on the structure and distribution of hydrocarbon in oil. Thus, the effect of zeolites channel structure on the structure and species of hydrocarbon compounds and petrochemicals in waste tyre-derived oil was studied in this work. HMOR and HBeta zeolites that have different channel structures, which are 2D and 3D channel structure, respectively, were selected in this study. They are acidic zeolites and have no difference in pore size, which is  $6.5 \times 7.0 \text{ \AA}$  for HMOR and  $6.4 \times 6.7 \text{ \AA}$  for HBeta. 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.

## 2. Experiment Section

### 2.1 Catalyst Preparation

HMOR and HBeta zeolites were obtained from Tosoh Company in Singapore. In order to remove impurity from zeolites, HMOR zeolite was calcined at  $500 \text{ }^\circ\text{C}$  for 3 h with the heating rate of  $10 \text{ }^\circ\text{C}/\text{min}$ , and HBeta was calcined at  $600 \text{ }^\circ\text{C}$  for 5 h with  $2 \text{ }^\circ\text{C}/\text{min}$ . After that, HMOR and HBeta powders were pelletized, crushed, and sieved into the particle size range of 20-40 mesh.

### 2.2 Catalyst Characterization

X-ray diffraction patterns were taken 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 CuK $\alpha$  radiation ( $1.5405 \text{ \AA}$ ). The detector scanned for the diffractive peaks from the sample as a function of  $2\theta$  by starting at the  $5^\circ$  to  $100^\circ(2\theta)$  range and a scan speed of  $5^\circ(2\theta)/\text{min}$ . The specific surface area and pore volume were characterized by using a ThermoFinnigan/Sorptomatic1990 equipment. In addition, Thermogravimetric/Differential Thermal Analysis (TG/DTA) was used to determine coke deposited on spent catalysts. The temperature was ramped to  $900 \text{ }^\circ\text{C}$  with heating rate of  $10 \text{ }^\circ\text{C}/\text{min}$ .

### 2.3 Pyrolysis of Waste Tyre

There were 2 zones of the pyrolysis reactor, which are catalytic zone (the upper zone) and pyrolytic zone (the lower zone). Firstly, 30 g of the waste tyre with sizes in the range of 20-40 mesh was loaded into the lower zone, and 7.5 g of pellet catalyst was loaded to the catalytic zone. Then, the pyrolysis zone was heated with the rate of  $10 \text{ }^\circ\text{C}/\text{min}$  from the room temperature to  $500 \text{ }^\circ\text{C}$ , and then kept for 120 min at the atmospheric pressure. The temperature of pyrolytic zone was controlled at  $350 \text{ }^\circ\text{C}$ . The flow rate of  $\text{N}_2$  was controlled at  $30 \text{ ml}/\text{min}$ , 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. These condensers were placed into an ice bath in order to collect the liquid product. A gas sampling bag collected the incondensable products.

### 2.4 Product Analysis

The liquid products were dissolved in *n*-pentane to precipitate asphaltene, and then asphaltene was filtered using polyamide membrane (pore size:  $0.45 \mu\text{m}$ ). Then, the maltenes were analysed for true boiling

point curve and petroleum fractions using a Simulated Distillation Gas Chromatography (SIMDIST-GC) conformed with ASTM D-2887. Finally, the chemical composition of maltenes was analysed using a two-dimensional Gas

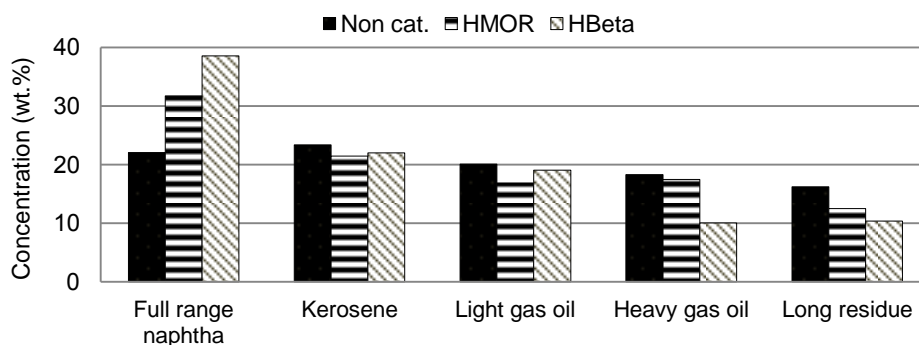


Figure 1: Petroleum fractions in maltenes obtained from HMOR and HBeta catalysts

Chromatography with Time of Flight Mass Spectrometer (GC×GC-TOF/MS). The gas products were analysed for their compositions using a Gas Chromatography (GC-FID). In addition, an elemental analyser was used to analyse the sulphur content in solid products and spent catalysts.

### 3. Result and Discussion

#### 3.1 Petroleum Fractions

Figure 1 illustrates the petroleum fractions in maltenes obtained from HMOR and HBeta catalysts. It shows that full range naphtha in maltenes obtained from HMOR and HBeta increases with the use of both zeolites, whereas the heavier fractions including kerosene, light gas oil, heavy gas oil, and long residue accordingly reduce. In addition, using HBeta gives a higher amount of the light fraction and then a less amount of heavier fractions than using HMOR. Thus, it can be concluded that using HBeta (3D-channel structure) results in the lighter liquid product than using HMOR (2D-channel structure). It may be possible that the 3D-channel structure allows molecules to stay inside the zeolite channel with a longer residence time, and then heavy fractions can be cracked into light fractions more effectively than in the 2D-channel structure. However, using both zeolites give a higher quality of liquid products as compared to the non-catalytic pyrolysis.

#### 3.2 Liquid Compositions

The concentrations of chemical components in maltenes are illustrated in Figure 2. They exhibit that HMOR and HBeta increase the amount of total aromatics with the decreases in paraffins, olefins, and naphthenes as compared to the non-catalytic pyrolysis. Moreover, using HBeta, 3D-channel structure, gives the higher amount of overall aromatics than HMOR, 2D-channel structure, and consequently gives the lower amount of paraffins, olefins, and naphthenes than those from HMOR. It can be explained that aromatic compounds can be formed via Diels-Alder reaction of light olefins (ethylene, propylene, and butene), which occur from thermal degradation of tyre, to cyclic hydrocarbons, and subsequently aromatics are formed via condensation reaction (Cypres, 1987). Moreover, Meng et al. (2013) reported that large intermediate olefins, such as octenes and multi-branched octenes, were favoured to drive cyclization reaction to occur, forming naphthenes. After that, aromatization of naphthenes produces aromatics, followed by condensation of aromatics, forming polycyclic aromatics. These are confirmed by the decreases of light olefins in the gas products, which are illustrated in Figure 3, as well as the decreases of olefins and naphthenes in accordance with the increase of aromatics in maltenes. In addition, it can be seen that the most abundant species of aromatic compounds are mono-aromatics. HBeta gives a higher yield of mono-aromatics, di-aromatics, and poly-aromatics than HMOR, and it gives a lower yield of paraffins, olefins, and naphthenes than HMOR. In addition, the results obtained from the surface area analyser reveal that HBeta has higher surface area and bigger pore volume than HMOR. A bigger pore volume allows molecules to go and stay inside HBeta (3D-channel structure) longer than HMOR (2D-channel structure); thus, molecules can be more easily transformed to mono-, di-, and poly-aromatics via cyclization and condensation reactions inside the zeolite channel.

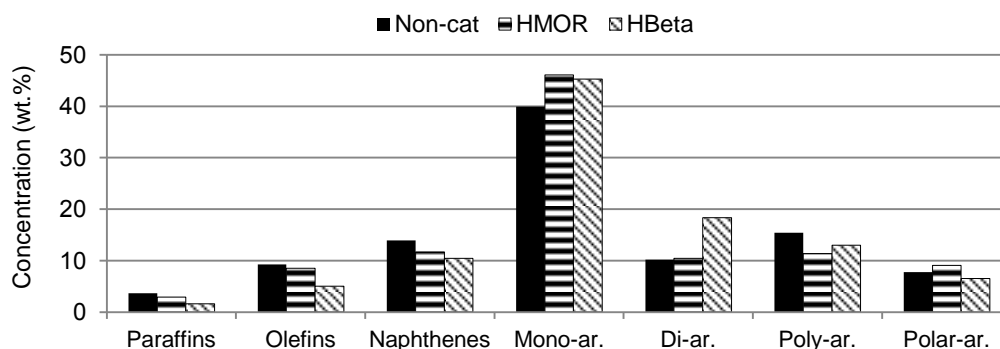


Figure 2: Concentration of components in maltenes obtained from HMOR and HBeta catalysts

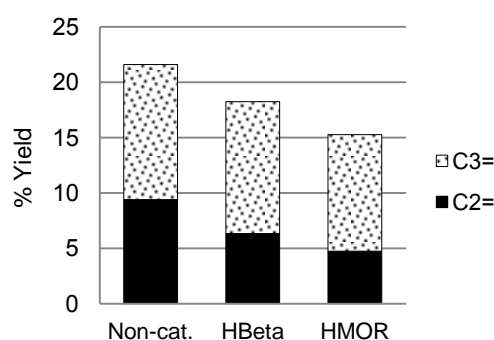


Figure 3: Yield of light olefins in gas products obtained from HMOR and HBeta catalysts

### 3.3 Hydrocarbons in maltenes

Valuable hydrocarbon compounds in maltenes are shown in Table 1. HBeta can produce a higher amount of benzene, ethylbenzene, toluene, and cyclohexane than HMOR and the non-catalytic pyrolysis. The non-catalytic pyrolysis does not produce xylenes, whereas *o*-xylene and *p*-xylene are produced by HBeta, and only *m*-xylene is produced by HMOR. In addition, styrene is increased from 0.189 wt.% (the non-catalytic pyrolysis) to 1.31 wt.% (HMOR), and the amount of cumene is not significantly changed for all cases. Additionally, the amount of all valuable hydrocarbons in maltenes can be ranked as HBeta (10.8 wt.%) > HMOR (2.32 wt.%) > the non-catalyst case (1.57 wt.%). It can be indicated that HBeta gives the highest value of liquid products, followed by HMOR and the non-catalyst case.

Table 1: Valuable compounds in maltene (wt.%)

Valuable compounds	Catalyst		
	1. Non-cat.	2. HMOR	HBeta
Benzene	3. 0.430	4. 0.124	5. 4.81
6. Toluene	7. 0.0274	8. 0.184	9. 0.917
10. Ethylbenzene	11. 0.833	12. 0.408	13. 3.31
14. <i>m</i> -xylene	15. -	16. 0.185	17. -
18. <i>o</i> -xylene	19. -	20. -	21. 0.161
22. <i>p</i> -xylene	23. -	24. -	25. 0.129
26. Styrene	27. 0.189	28. 1.31	29. 0.320
30. Cyclohexane	31. 0.0239	32. -	33. 1.05
34. Cumene	35. 0.0660	36. 0.105	37. 0.0771
38. Total	39. 1.57	40. 2.32	41. 10.8

Table 2: Sulphur content (wt.%) on spent catalysts and in oils obtained from HMOR and HBeta

	Sulphur content (wt.%)		
	42. Non-cat.	43. HMOR	HBeta
Spent catalyst	44. -	45. 0.41	46. 0.18
Oil	47. 1.17	48. 1.10	49. 1.08

### 3.4 Desulphurization activity

The results show the higher sulphur distribution in the gas and on the spent HMOR and HBeta catalysts in the expense of sulphur distribution in oils. In addition, the sulphur content in oils is reduced when the catalysts are applied as shown in Table 2. HMOR gives a slightly-lower sulphur content in oils than HBeta. It can be concluded that both zeolites exhibit the activity on sulphur reduction in oils.

Moreover, sulphur species are determined. Figure 4 exhibits the distribution of sulphur compounds in maltenes. It can be seen that the 3D-channel structure of HBeta produces less amount of thiophenes than the 2D-channel structure of HMOR. Benzothiophenes dramatically increase with using both catalysts, and benzothiazoles tend to decrease with using these catalysts. It can be suggested that S-compounds in the oil, obtained from HBeta, are easier to be desulphurized than those in oil obtained from HMOR (García-Cruz et. al., 2008). Benzothiophenes are easier to be desulphurized than benzothiazoles because C-N bond has a higher bond dissociation energy than C-S bond (Cottrell, 1958). In addition, dibenzothiophenes are slightly decreased with the use of these two catalysts. The mixture of all other heteroatom (S, O and N)-containing aromatic and aliphatic hydrocarbons (so-called "the others") is reduced with using both catalysts.

## 4. Conclusions

HBeta (3D-channel structure) gives the lighter liquid products than using HMOR (2D-channel structure). Since the 3D-channel structure allows molecules to stay inside the zeolite channel with a longer residence time, and then heavy fractions can be cracked into light fractions more effectively than in the 2D-channel structure. For components in maltene, the use of HBeta exhibited a higher yield of mono-aromatics, di-aromatics and poly-aromatics than the use of HMOR, and consequently gave a lower yield of paraffins, olefins, and naphthenes than HMOR. Since a bigger pore volume and higher surface area allows molecules to pass through and stay inside HBeta longer than HMOR; thus, molecules can be more easily transformed to mono-, di-, and poly-aromatics via cyclization and condensation reactions inside the zeolite channel. Additionally, the amount of all valuable hydrocarbons in maltenes obtained from HBeta (10.8 wt.%) was significantly higher than that from HMOR (2.32 wt.%). Both zeolites have a good activity in sulphur reduction in oils. However, HBeta exhibited slightly-better desulphurization activity than HMOR.

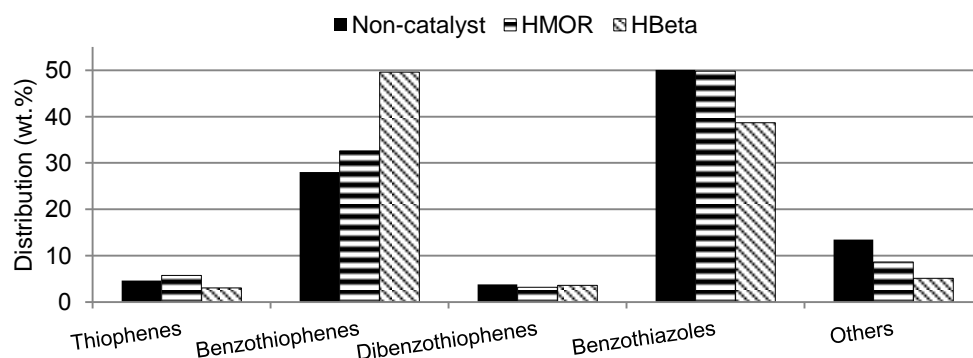


Figure 4: Distribution of sulphur species in maltenes obtained from HMOR and HBeta catalysts

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