

## CHAPTER IV

### IMPACT OF ZEOLITE PROPERTIES ON STRUCTURE OF HYDROCARBON COMPOUNDS IN WASTE TIRE-DERIVED OILS

#### 4.1 Abstract

Waste tire, 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, sulfur compounds causing the low quality of oil products and environmental problem were also found. Many kinds of zeolites were used in pyrolysis process, but the effects of zeolite properties on structure of pyrolysis products have not been explained clearly. The objective of this work was to investigate the properties of zeolites, which are pore channel, pore size, and acidic properties of supports, that could affect the structure of pyrolysis products. The products were analyzed by using a SIMDIST-GC, GC and elemental analyzer, whereas a GC×GC-TOF/MS was used to investigate species in oils. The catalysts were characterized by using XRD, TGA, and SAA.

#### 4.2 Introduction

Conventionally, all petrochemicals are produced from petroleum. Olefins and aromatic hydrocarbons are important petrochemicals. Light olefins including ethylene, propylene and butylenes 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. Tires are hydrocarbon-based materials, which exhibit potential to be used as a source for petrochemical production. In addition, tires have long-life and complication to recycle, resulting in a large amount of waste tires discarded. Pyrolysis of waste tires is a interesting

process to treat and recover valuable products. Islam *et al.* (2008) studied waste tire pyrolysis products, especially liquid products. They found that pyrolytic oils were complex mixtures, which consisted of aliphatic and aromatic compounds. Moreover, the results showed that pyrolytic oils can be directly used as fuels for furnaces, power plants, and boilers. It can be used as diesel after the qualities such as sulfur content or blending with commercial fuels have been improved. Banar *et al.* (2012) studied pyrolytic oil from waste tire 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. Dũng *et al.* (2009) used an HMOR catalyst in waste tire 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 favored 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 tire pyrolysis. The gas product increased with using HZSM-5 due to cracking of heavy fractions, and it slightly decreased with using HY because HY favored 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 tire 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 properties, which are acidic and non-acidic of supports, pore channel, and pore size on the structure and species of hydrocarbon compounds in waste tire-derived oil was studied in this work. HMOR and HBeta were chosen to studied the effect of pore channel, which are 1D and 3D pore channel, respectively. HBeta and HZSM-5 were selected to studied the effect of pore size. In addition, the effect of acidic properties of support was study by using HMOR and KL.

### 4.3 Experimental

#### 4.3.1 Catalyst Preparation

HMOR (Si/Al=13.5), HBeta (Si/Al=9.5), KL (Si/Al=3), and HZSM-5 (Si/Al=15) were obtained from Tosoh Company in Singapore. In order to remove impurity from zeolites, HMOR, KL and HZSM-5 zeolites 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, zeolite powders were pelletized, crushed, and sieved into the particle size range of 20-40 mesh.

#### 4.3.2 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 Å). The detector scanned for the diffractive peaks from the sample as a function of  $2\theta$  by starting at the 5 ° to 100 °( $2\theta$ ) range and a scan speed of 5 °( $2\theta$ )/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 °C with heating rate of 10 °C/min.

#### 4.3.3 Pyrolysis of Waste Tire

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 tire 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 °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<sub>2</sub> 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. These condensers were placed into an ice bath in order to collect the liquid product. A gas sampling bag collected the incondensable products.

#### 4.3.4 Product Analysis

The liquid products were dissolved in *n*-pentane to precipitate asphaltene, and then asphaltene was filtered using polyamide membrane (pore size: 0.45µm). Then, the maltenes were analyzed 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 analyzed using a two-dimensional Gas Chromatography with Time of Flight Mass Spectrometer (GC×GC-TOF/MS). The gas products were analyzed for their compositions using a Gas Chromatography (GC-FID). In addition, an elemental analyzer was used to analyze the sulfur content in solid products and spent catalysts.

### 4.4 Results and Discussion

#### 4.4.1 Catalyst Characterization -

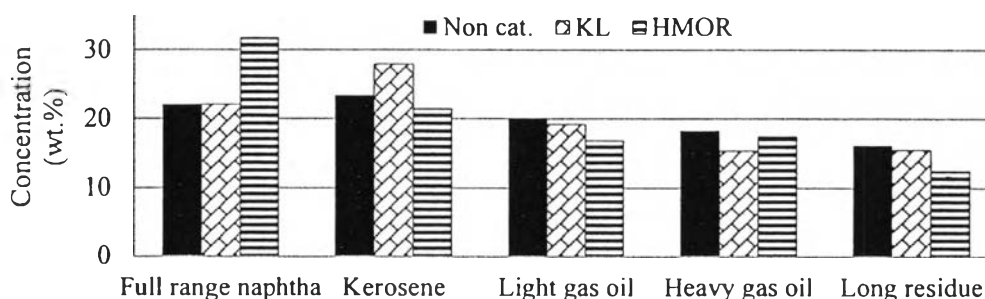
The catalyst properties obtained from surface area analyzer of HBeta, HMOR, HZSM-5, and KL zeolites are revealed in Table 4.4. Figure 4.16. exhibits the XRD patterns, and confirms crystallinity of the zeolites

#### 4.4.2 Comparison between Acid and Non-acid Supports

The acidic and non-acidic properties of zeolites affecting the products are investigated. So, the pair of zeolites, HMOR and KL, were chosen to eliminate the effects of pore size, pore dimension, and pore structure, since both zeolites have the same pore channel, which is one-dimensional.

#### 4.4.2.1 Petroleum Fractions

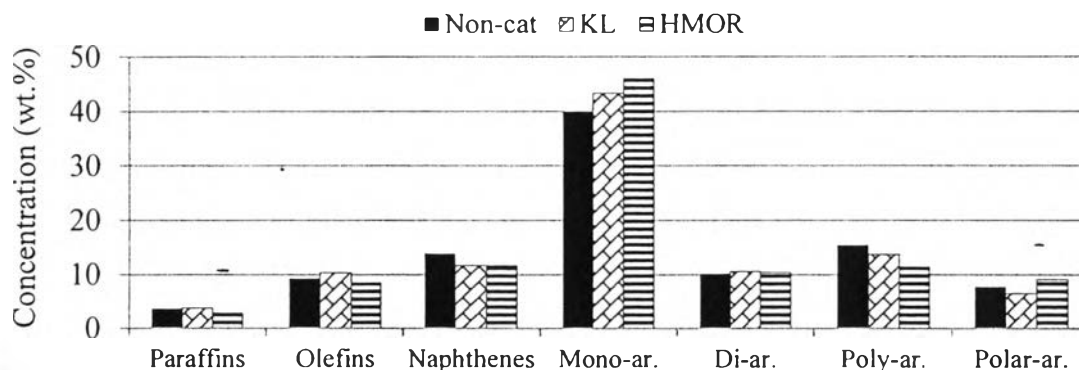
Petroleum fractions in maltenes are classified according to boiling point distillation conformed with ASTM D-2887 into five fractions: full range naphtha (< 200 °C), kerosene (200-250 °C), light gas oil (250-300 °C), heavy gas oil (300-370 °C), and long residue (> 370 °C). The result in Figure 4.1 exhibits that the use of KL, which is a non-acid support, gives the same amount of full range naphtha as the non-catalyst case does. In addition, it gives a higher amount of kerosene than the non-catalyst case, whereas the heavier fractions obtained from KL are lower than that from pyrolysis without catalyst.



**Figure 4.1** Petroleum fractions in maltenes obtained from HMOR and KL catalysts.

On the other hand, the use of HMOR, which is an acid support, increases the amount of full range naphtha to 31.74 wt.%, and also decreases the amount of kerosene, light gas oil, heavy gas oil and long residue. The liquid products obtained from using KL zeolite, non-acid support, contain a highest amount of kerosene fraction furthermore, it contains a lower amount of all heavier fractions as compared to the non-catalyst case. However, it is heavier as compared to the liquid products obtained from using HMOR. From the results, it can be seen that both HMOR (acid support) and KL (non-acid support) can crack the heavy fractions into lighter fractions additionally, using HMOR gives a better cracking ability than using KL. Thus, it can be concluded that liquid products obtained from the acid support (HMOR) is lighter than the liquid products obtained from the non-acid support (KL).

#### 4.4.2.2 Liquid Components



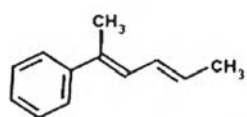
**Figure 4.2** Concentration of chemical components in maltenes obtained from HMOR and KL catalysts.

Furthermore, the chemical components in maltenes are classified into seven groups: paraffins, olefins, naphthenes, mono-aromatic, di-aromatic, poly-aromatic, and polar-aromatic hydrocarbons, as illustrated in Figure 4.2. The results exhibit that using HMOR gives a slightly-lower paraffins than using KL. It can be suggested that olefins produced by the thermal cracking are further converted to aromatics via carbenium ions generated on the acid catalyst. These agree with Meng's results that olefins, which are generated from thermal degradation, are converted to the bigger compounds like naphthenes or aromatics via aromatization and Diels-Alder reactions with using acidic catalyst (Meng *et al.*, 2013). Thus, the amounts of olefins and naphthenes generated by using those catalysts are lower than those from the non-catalytic pyrolysis, resulting in the increase in total aromatics. It is also confirmed by the reduction of light olefins (ethylene, propylene) as compared to the non-catalytic pyrolysis (see in Table 4.5). The amount of mono-aromatic hydrocarbons is 34.94 wt.% for the non-catalytic case, and increases to 43.36 wt.% and 46.06 wt.% with using KL and HMOR, respectively. The amount of di-aromatic hydrocarbons does not change for both cases, which are constant as about 10 wt.%, whereas that of poly-aromatic hydrocarbons decreases with using both catalysts. Moreover, using HMOR gives a lower amount of poly-aromatic hydrocarbons than KL. These can be suggested that

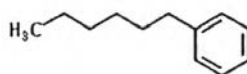
both catalysts enhance the ring opening reaction, that converts polycyclic aromatic hydrocarbons to mono-aromatic hydrocarbons. For polar-aromatic hydrocarbons, which are S, O, and N containing-aromatic hydrocarbons, the yield increases with using HMOR, but decreases with using KL.

#### 4.4.2.3 Valuable Hydrocarbons in Maltenes

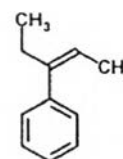
The liquid products were analyzed by using a comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometer (GC×GC-TOF/MS) to determine valuable hydrocarbons in maltenes, which is shown in Figure 4.3. It is found that dominant mono-aromatic hydrocarbons are comprised of benzene, toluene, ethylbenzene, xylenes, cumene, and styrene. Moreover, another value-added compound, cyclohexane, is also found in maltene. HMOR has a potential to produce more petrochemicals, styrene, ethylbenzene, toluene, *m*-xylene, and cumene, than using KL. Moreover, HMOR gives a higher amount of styrene and a lower amount of ethylbenzene and benzene than the non-catalyst case. It can be explained that styrene might be produced by cracking of tire molecules and dehydrogenation of ethylbenzene. Additionally, HMOR may catalyze a tranalkylation reaction of benzene with olefin, results in the increasing of styrene (Sudha *et al.*, 2007). Moreover, KL produces a higher mono-aromatics than the non-catalyst case, but the overall amount of petrochemicals is decreased with using KL (see in Figure 4.2). It can be explained that KL might be converted the petrochemicals to form other mono-aromatic species. From the results, it can be concluded that using HMOR not only gives a light liquid products, but also gives a higher valuable hydrocarbons than KL and the non-catalyst case. It is noted that mono-aromatics are produced significantly by KL are 1-methylpenta-1,3-dienyl benzene, hexylbenzene, and 3-phenyl-2-pentene as depicted below.



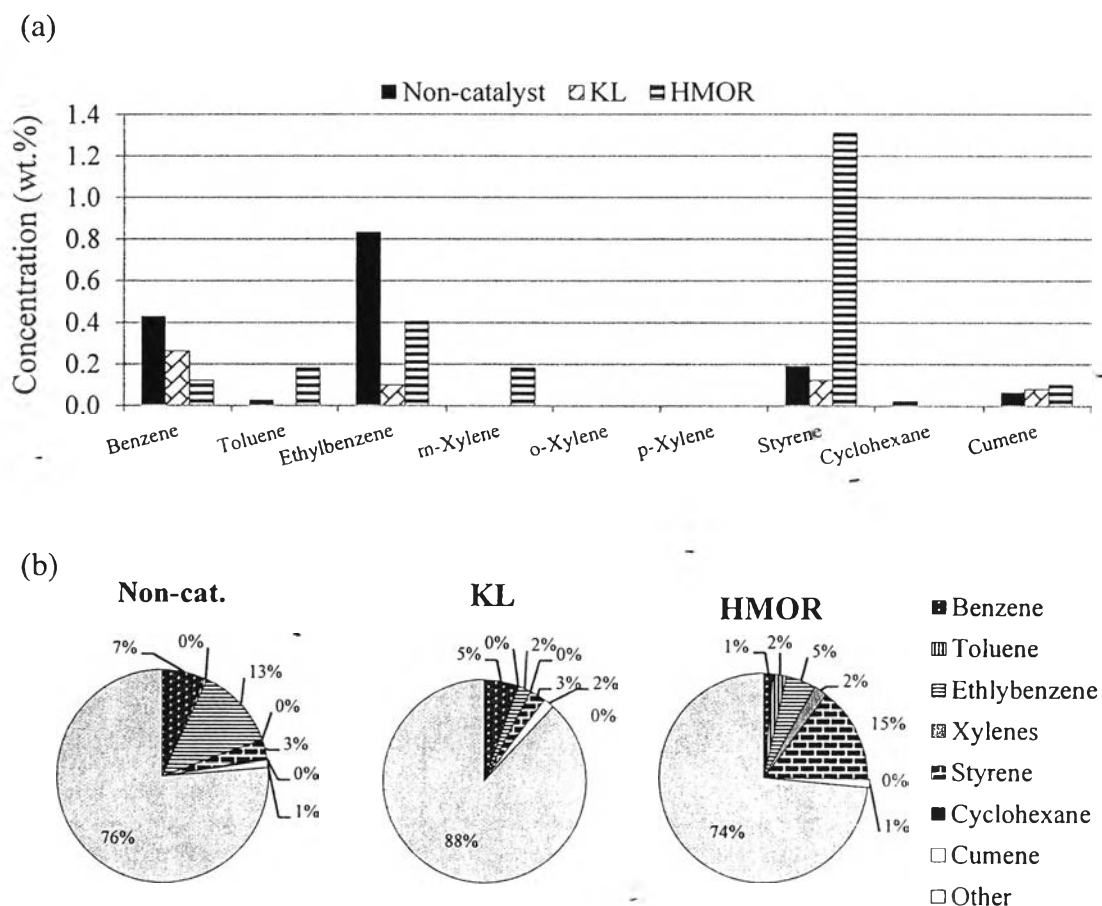
1-methylpenta-1, 3-dienyl benzene



hexylbenzene



3-phenyl-2-pentene

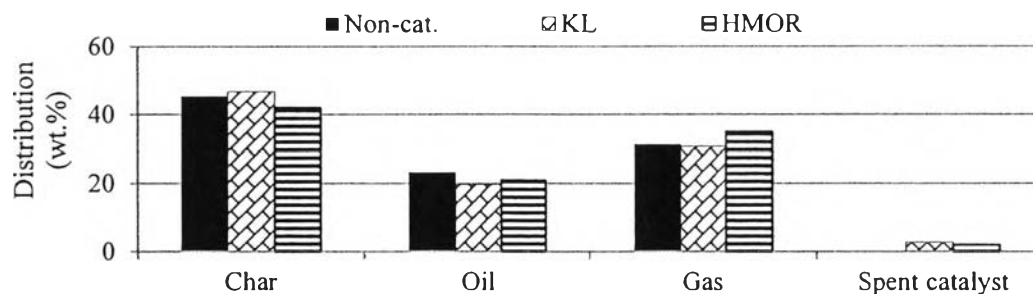


**Figure 4.3** Concentration of petrochemicals in (a) maltenes and (b) gasoline obtained from KL and HMOR catalysts.

#### 4.4.2.4 Desulfurization Activity

Figure 4.4 exhibits the overall sulfur distribution in pyrolysis products from KL and HMOR. The result shows that the sulfur mostly distributes in char for all cases, and KL gives a higher sulfur content in char than HMOR. Using catalysts result in the reduction of sulfur distribution in oils from 23.9 wt.% for the non-catalytic case to 19.7 wt.% and 21.1 wt.% for KL and HMOR, respectively in accordance with the larger increment of sulfur content in gas for HMOR than for KL. In addition, 2.8 wt.% and 2.0 wt.% sulfur are found on the spent KL and HMOR catalysts, respectively.





**Figure 4.4** Overall distribution of sulfur in pyrolysis products obtained from KL and HMOR catalysts.

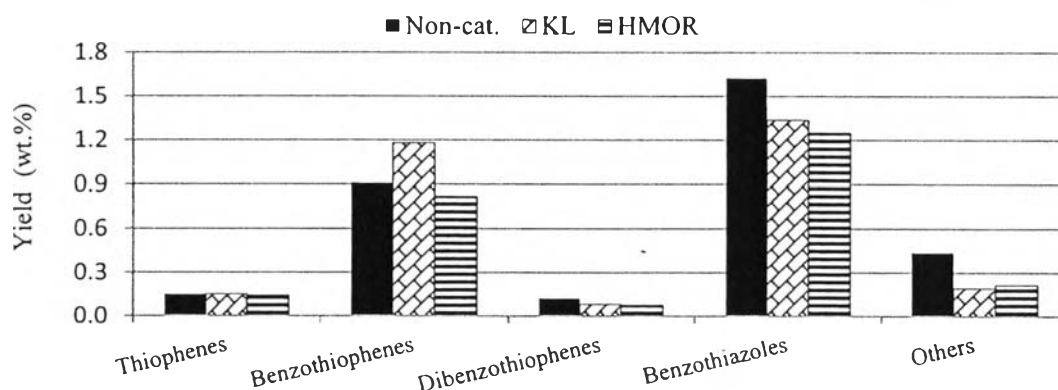
In addition, Table 4.1 reveals the sulfur content on spent catalysts and in oils obtained from KL and HMOR. It exhibits that sulfur content in oil can be reduced by using the catalysts. HMOR gives the sulfur content in pyrolytic oils higher than KL, which are 1.08 wt.% for HMOR and 1.02 wt.% for KL. It can be suggested that KL has better sulfur removal activity than HMOR.

**Table 4.1** Sulfur content on spent catalysts and in oils obtained from KL and HMOR catalysts

	Sulfur (wt.%)		
	Non-cat.	KL	HMOR
<b>Spent catalyst</b>	-	0.25	0.18
<b>Oil</b>	1.17	1.02	1.08

Additionally, the yield of sulfur species in maltenes is shown in Figure 4.5. The sulfur-containing compounds are classified into five groups: thiophenes, benzothiophenes, dibenzothiophenes, benzothiazoles, and a mixture of heteroatom (O and/or N)-containing sulfur compound or so-called “others”. It can be seen that using both catalysts decrease benzothiazoles, especially using acidic support (HMOR). Benzothiophenes increase with using KL, but insignificantly change with using HMOR. Moreover, the amount of “others” is reduced with using both catalysts. It can be suggested that HMOR (acid support) possibly converts

benzothiazoles to forming hydrocarbons such as aromatic hydrocarbons or even non-aromatic hydrocarbons such as derivative of benzene better than using KL (non-acid support). Moreover, benzothiazoles possibly rearrange to form benzothiophenes. In addition, the amount of dibenzothiophenes and thiophenes do not change significantly. In common, benzothiophenes are easier to be desulfurized than benzothiazoles due to C-N bond (770 kJ/mol) has a high bond dissociation energy. Therefore, using HMOR gives better quality of the oils to be further desulfurized than those from KL.



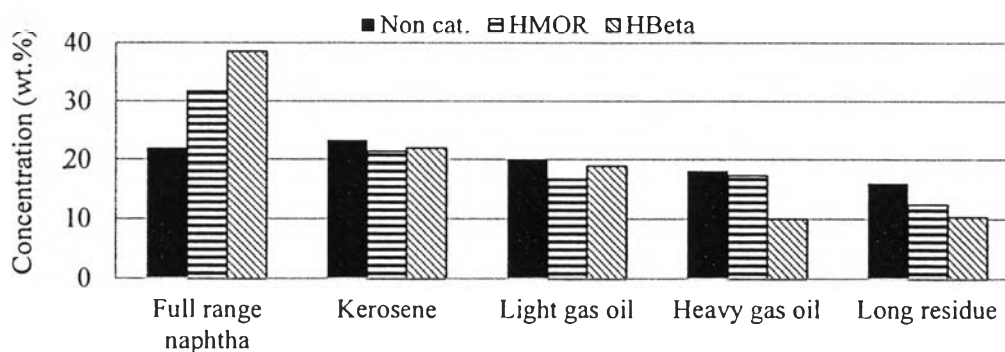
**Figure 4.5** Yield of sulfur species in maltenes obtained from KL and HMOR.

#### 4.4.3 Comparison between the Pore Channel (1D and 3D) of Zeolite

HMOR and HBeta zeolites have different channel structures, which are 1D and 3D pore channel, respectively. They are acidic zeolites, and they have no difference in pore size, which are  $6.5 \text{ \AA} \times 7.0 \text{ \AA}$  for HMOR and  $6.4 \text{ \AA} \times 6.7 \text{ \AA}$  for HBeta. In order to study the effect of pore channel on pyrolysis products, both zeolites need to have the same Si/Al ratio. Since it is difficult to synthesize or find 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 for investigating the effect of zeolites channel structure on the structure and species of hydrocarbon compounds obtained from waste tire pyrolysis.

#### 4.4.3.1 Petroleum Fractions

The petroleum fractions in maltenes obtained from HMOR and HBeta are illustrated in Figure 4.6 in order to elucidate the effect of 1D and 3D pore channel. It shows that full range naphtha in maltenes obtained from HMOR and HBeta increases with using 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 full range naphtha and then a less amount of heavier fractions than using HMOR. Thus, it can be concluded that using HBeta (3D pore channel) results in the lighter liquid product than using HMOR (1D pore channel). It may be possible that HBeta may has a higher acid strength than HMOR, and the 3D pore channel of HBeta allows molecules to stay inside the zeolite channel with a long residence time, and then heavy fractions can be cracked into light fractions more effectively than in the 1D pore channel. However, using both zeolites give a lighter oil as compared to the non-catalytic pyrolysis.

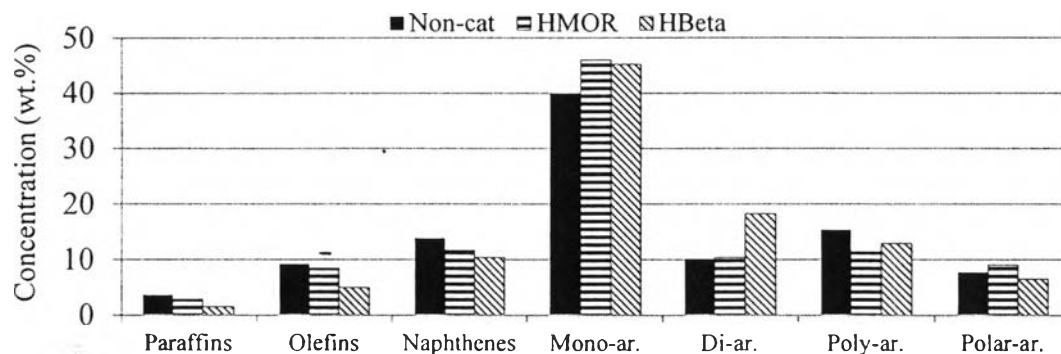


**Figure 4.6** Petroleum fractions in maltenes obtained from HMOR and HBeta catalysts.

#### 4.4.3.2 Liquid Components

Figure 4.7 presents the compositions in maltenes obtained from HMOR and HBeta catalysts. It exhibits 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 with 3D pore channel gives the higher amount of total aromatics than HMOR that has 1D pore

channel, and consequently gives the lower paraffins, olefins, and naphthenes than those from HMOR.



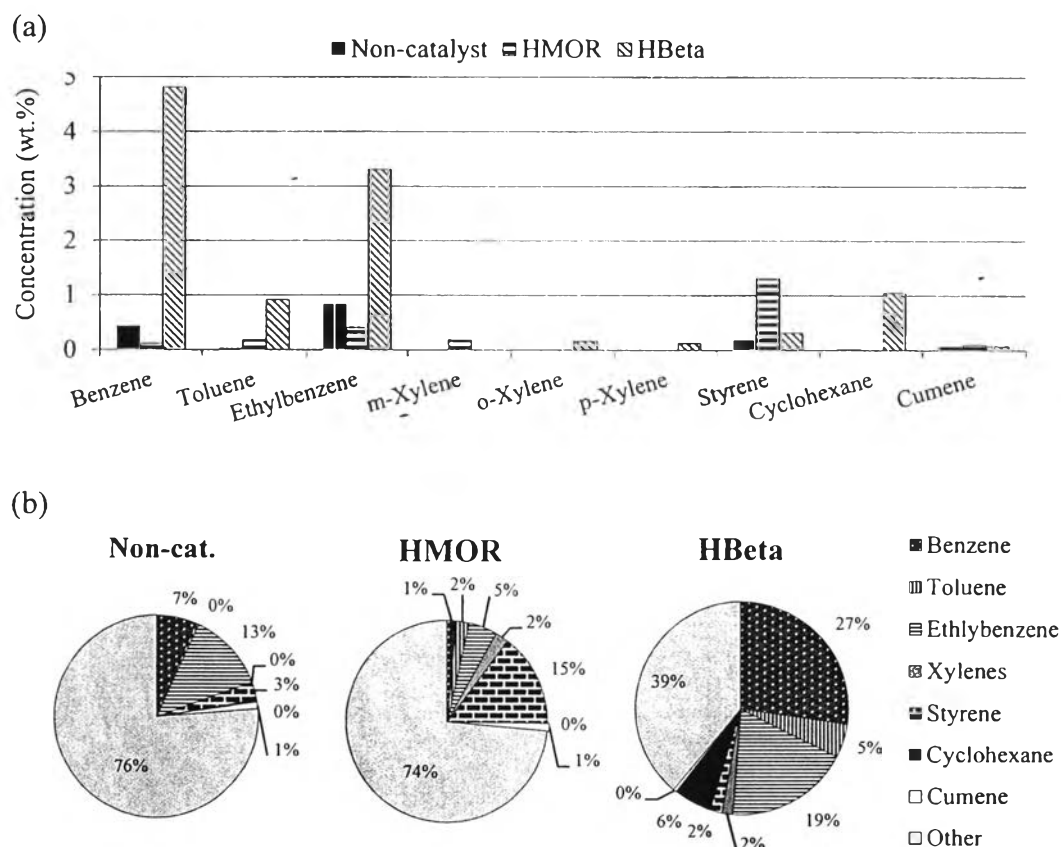
**Figure 4.7** Concentration of chemical components in maltenes obtained from HMOR and HBeta catalysts.

It can be explained that aromatic compounds can be formed via Diels-Alder reaction of light olefins (ethylene, propylene, and butylenes), which occur from thermal degradation of tire, 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 favored 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 (see in Table 4.5) as well as the decreases of olefins and naphthenes in accordance with the increase of aromatics in maltenes. Moreover, the aromatics are classified into five groups as illustrated in Figure 4.7. The aromatic compounds can be classified into mono-aromatics, di-aromatics, poly-aromatics and polar-aromatics. It can be seen that the most abundant species of aromatic compounds are mono-aromatics, (~ 45 wt.% yield). 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 analyzer reveal that HBeta has higher surface area and bigger pore volume than HMOR (see in Table 4.4). A bigger pore

volume allows molecules to go and stay inside HBeta (3D pore channel) longer than HMOR (1D pore channel); thus, molecules can be more easily transformed to mono-, di-, and poly-aromatics via cyclization and condensation reactions inside the zeolite channel.

#### 4.4.3.3 Valuable Hydrocarbons in Maltenes

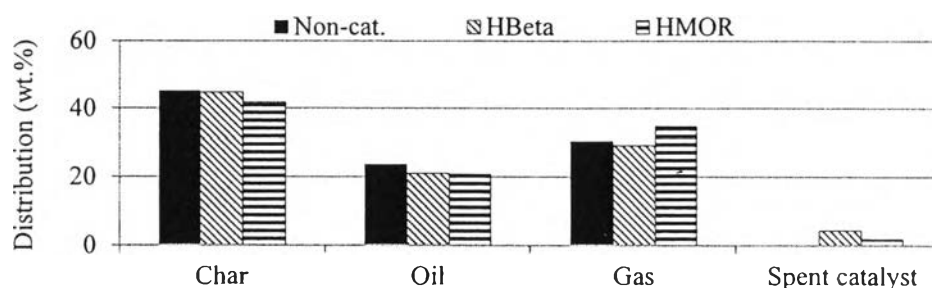
Valuable hydrocarbon compounds in maltenes are shown in Figure 4.8. It exhibits that HBeta can produce a higher amount of benzene, ethylbenzene, toluene, and cyclohexane than HMOR and the non-catalytic case. Moreover, a small amount of *o*-xylene and *p*-xylene are produced by using HBeta, and *m*-xylene is produced by using HMOR. In addition, the amount of styrene sharply increases with using HMOR, and the amount of cumene is not significantly changed for all cases.



**Figure 4.8** Concentration of petrochemicals in (a) maltenes and (b) gasoline obtained from HMOR and HBeta catalysts.

It possible that HBeta, which has a higher acid strength than HMOR, catalyzes the cyclization reaction of paraffins or olefins to form cyclic hydrocarbon such as cyclohexane, and then convert to benzene via cabenium ion mechanism (Joshi and Thomson, 2005). Moreover, both zeolites may catalyze tranalkylation reaction of benzene with an olefin to styrene and ethylbenzene for HMOR and HBeta, respectively (Sudha *et al.*, 2007). Additionally, the amount of overall valuable hydrocarbons in maltenes are shown in Table 4.6. It can be ranked as HBeta (10.8 wt.%) > HMOR (2.32 wt.%) > the non-catalyst case (1.57 wt.%). It can be indicated that oil obtained from using HBeta has a higher value than that from using HMOR.

#### 4.4.3.4 Desulfurization Activity



**Figure 4.9** Overall distribution of sulfur in pyrolysis products obtained from HMOR and HBeta catalysts.

The overall distribution of sulfur in pyrolysis products is shown in Figure 4.9. 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 the spent catalyst than HMOR. It can be suggested that the 3D-channel of HBeta results in more deposition of sulfur than the 1Dchannel of HMOR.

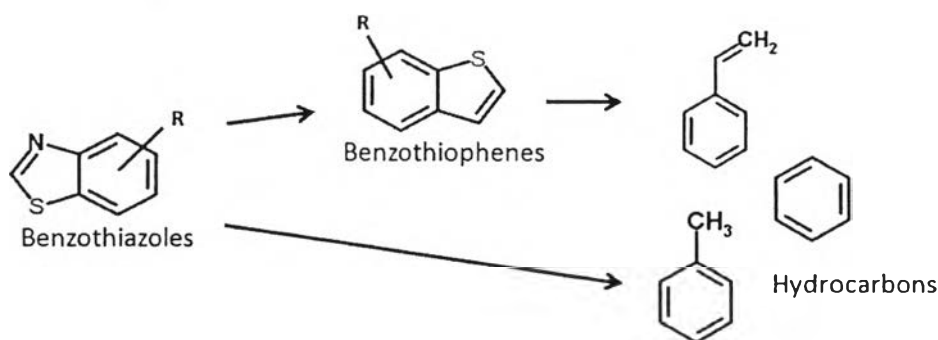
The sulfur content in oils is reduced when the catalysts are applied as shown in Table 4.2. The results show that sulfur content in oil is reduced

with using both catalysts. Namely, HMOR gives a slightly-lower sulfur content in oils than HBeta. It can be concluded that both zeolites exhibit the activity on sulfur removal in oils.

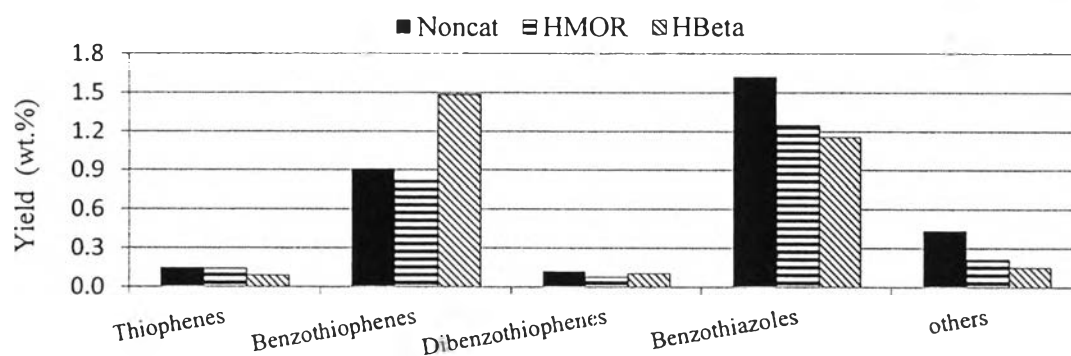
**Table 4.2** Sulfur content on spent catalysts and in oils obtained from HBeta and HMOR catalysts

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

On the other hand, the yield of sulfur species is illustrated in Figure 4.10. It can be seen that 3D pore channel of HBeta produce less amount of thiophenes than the 1D pore channel of HMOR. Benzothiophenes dramatically increase with using HBeta, but insignificantly change with using HMOR. Benzothiazoles sharply decrease with using both catalysts as compared to the non-catalyst case, whereas the heteroatom (O and/or N)-containing sulfur compounds (so-called “the others”) is reduced with using both catalysts. It can be suggested that HMOR and HBeta possibly convert benzothiazoles and the others, forming hydrocarbon compounds such as derivative of benzenes, or even non-aromatics, as illustrated below.



Unlike HMOR, HBeta possibly rearranges benzothiazoles to form benzothiophenes inside the zeolite channel. In addition, 3D pore channel of HBeta allows molecules to stay inside its channel with a longer residence time than 1D pore 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 4.10** Yield of sulfur species in maltenes obtained from HMOR and HBeta catalysts.

#### 4.4.4 Comparison between Two Pore Sizes of Zeolites

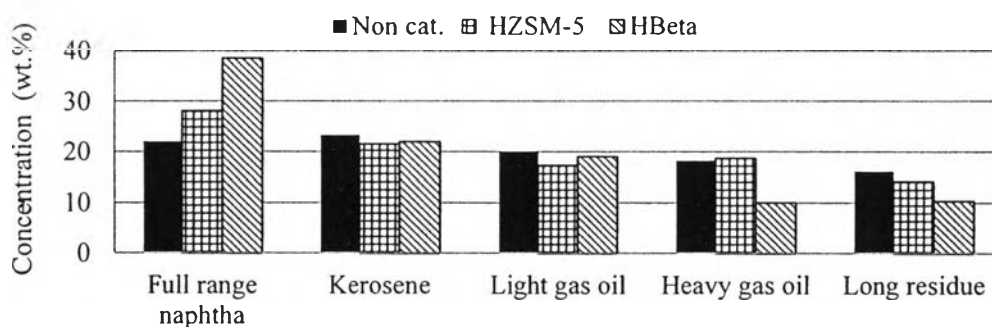
For this part, the effect of pore size of zeolite is considered with employing HZSM-5 and HBeta zeolites. Both of them are acidic zeolites and they have 3D-pore channel. In addition, the Si/Al ratios of these zeolites are not significantly different, which are equal to 15 for HZSM-5 and 13.5 for HBeta, but they have a significant difference in pore size, which are  $5.3 \text{ \AA} \times 5.6 \text{ \AA}$  and  $6.4 \text{ \AA} \times 7.6 \text{ \AA}$  for HZSM-5 and HBeta, respectively.

##### 4.4.4.1 Petroleum Fractions

Figure 4.11 illustrates the petroleum fractions obtained from using HZSM-5 and HBeta zeolites. It shows that both catalysts increase full range naphtha, and decrease the heavier fractions (kerosene, light gas oil, heavy gas oil,



and long residue), except for HZSM-5 that slightly increases heavy gas oil. Using HBeta, which has a larger pore size than HZSM-5, exhibits a higher amount of full range naphtha (38.55 wt.%) than HZSM-5 (28.16 wt.%) and the non-catalytic pyrolysis (22.05 wt.%). It indicates that the effect of large pore size of HBeta allows a higher amount of molecules to go inside the pore to crack than the medium pore size of HZSM-5.

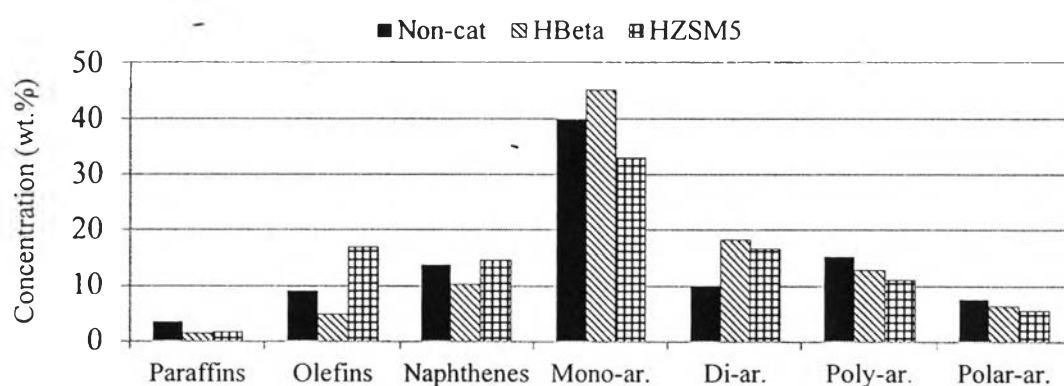


**Figure 4.11** Petroleum fractions in maltenes obtained from HZSM-5 and HBeta catalysts.

#### 4-4.4.2 Liquid Components

The chemical components in maltenes are illustrated in Figure 4.12. The results exhibit that using HBeta gives a higher amount of total aromatics as well as a lower amount of paraffins, olefins, and naphthenes than the non-catalytic pyrolysis. On the other hand, using HZSM-5 results in the reduction of total aromatics and paraffins with the increase of olefins as compared with the non-catalytic pyrolysis. Moreover, the amount of naphthenes does not change significantly with using HZSM-5 as compared to the non-catalytic pyrolysis. It may be caused by the medium pore size of HZSM-5 ( $5.3 \text{ \AA} \times 5.6 \text{ \AA}$ ) that allows a less amount of molecules to go inside the zeolite pore than the large pore of HBeta. Moreover, the surface area analyzer reveals that HZSM-5 has a lower pore volume ( $0.1780 \text{ cm}^3/\text{g}$ ) than HBeta ( $0.2570 \text{ cm}^3/\text{g}$ ); thus, resulting in the reduction of the transformation of olefins to cyclic hydrocarbons and aromatic hydrocarbons (Olazar *et al.*, 2008). In addition, it can be seen that mono-aromatic hydrocarbons increase

with the use of HBeta, but decrease with the use of HZSM-5 as compared to the non-catalytic case. Moreover, both HBeta and HZSM-5 zeolites have the same trend on producing the other aromatic types; that is, they increase di-aromatics, and decrease poly- and polar-aromatic hydrocarbons. Using HZSM-5 gives a lower amount of all aromatic types than using HBeta. It can be explained that the medium pore size of HZSM-5 has the lower cyclization and condensation activity than the large pore size of HBeta.

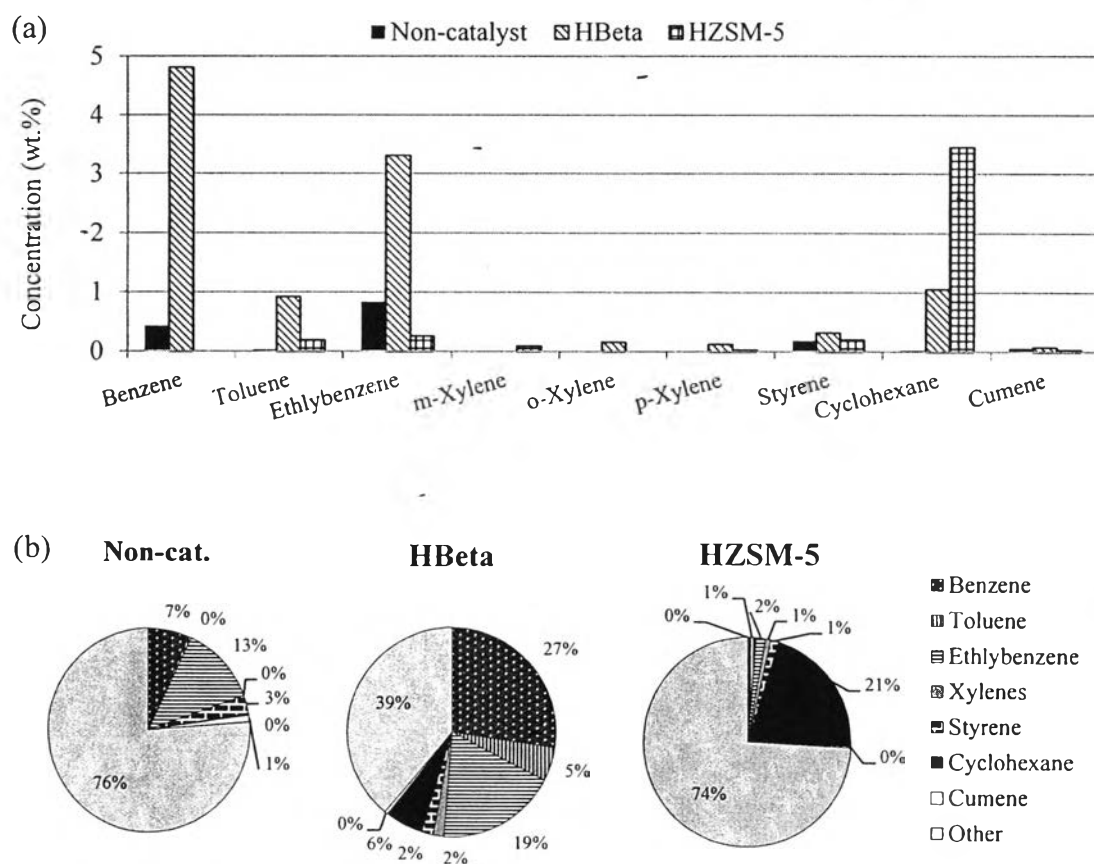


**Figure 4.12** Concentration of chemical components in maltenes obtained from HBeta and HZSM-5 catalysts.

#### 4.4.4.3 Valuable Hydrocarbons in Maltenes

The value-added hydrocarbons obtained from catalytic waste tire pyrolysis using HBeta and HZSM-5 are shown in Figure 4.13. HBeta sharply increases amount of benzene (4.81 wt.%) and ethylbenzene (3.31 wt.%). Moreover, it can produce toluene slightly higher than the non-catalytic pyrolysis. Using HZSM-5 does not produce benzene; however, it gives a small amount of ethylbenzene and toluene. In addition, both catalysts give a large amount of cyclohexane, which are 3.46 wt.% and 1.05 wt.% for HZSM-5 and HBeta, respectively. Moreover, styrene, xylenes, and cumene were found with using HMOR and HBeta. It should be noted that using HBeta gives a higher amount of valuable aromatics, such as benzene, ethylbenzene, and toluene, than using HZSM-5. These observations agree with the Roldan's results, which showed that the medium pore of HZSM-5 was inactive for

the transformations of benzene and xylenes, whereas the larger pore of HBeta was active toward those reactions. It was due to medium pore zeolite that hinders the process through steric restriction in the pore (Roldán *et al.*, 2004). Moreover, these are consistent with the result from surface area analyzer; that is, HZSM-5 has a lower specific surface area and pore volume ( $366.3 \text{ m}^2/\text{g}$ ,  $0.1780 \text{ cm}^3/\text{g}$ ) than those from HBeta ( $539.2 \text{ m}^2/\text{g}$ ,  $0.2570 \text{ cm}^3/\text{g}$ ).

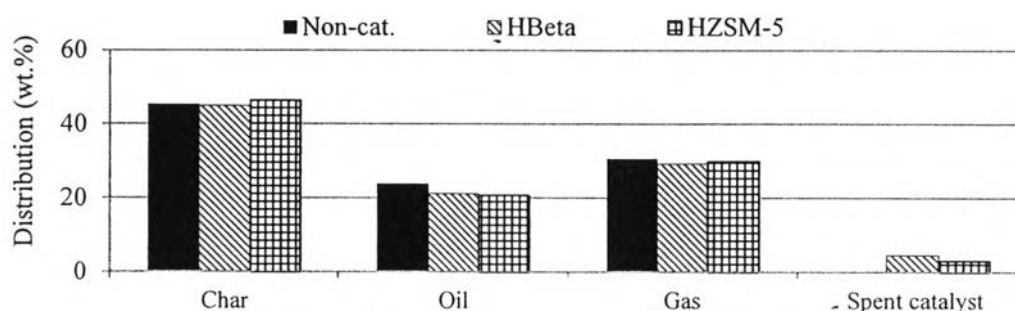


**Figure 4.13** Concentration of petrochemicals in (a) maltenes and (b) gasoline obtained from HBeta and HZSM-5 catalysts.

#### 4.4.4.4 Desulfurization Activity

Figure 4.14 shows the overall sulfur distribution in pyrolysis products obtained from HBeta and HZSM-5 catalysts. The results show that using both catalysts causes the sulfur distributed 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 4.3. The results show that HBeta and HZSM-5 slightly reduce sulfur in oils from 1.17 wt.% (non-catalytic pyrolysis) to 1.08 wt.% for HZSM-5 and to 1.10 wt.% for HBeta. It can be concluded that oils have a slightly-better quality than the oil from the non-catalyst case.



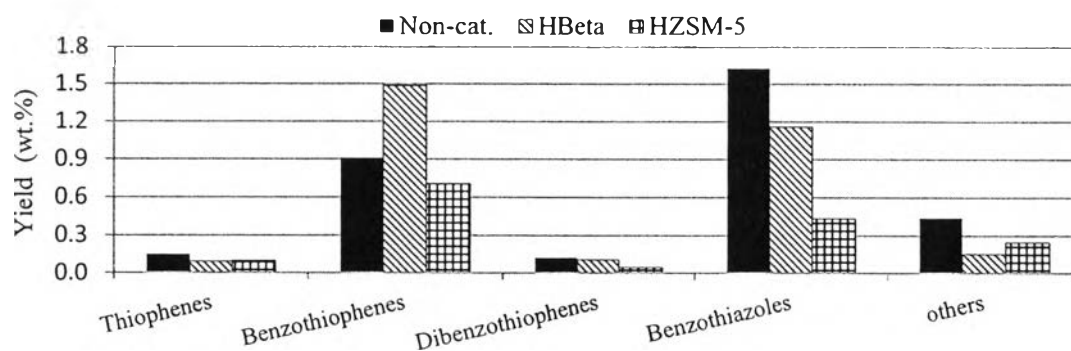
**Figure 4.14** Overall distribution of sulfur in pyrolysis products obtained from HBeta and HZSM-5 catalysts.

**Table 4.3** Sulfur content on spent catalysts and in oils obtained from HBeta and HZSM-5 catalysts

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

The yield of sulfur species is illustrated in Figure 4.15. 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 S-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 heteroatom (O and/or N)-containing sulfur compounds ( so-called “the others”) also reduces with using both HBeta and HZSM-5. It was explained that HZSM-5 and HBeta possibly convert benzothiazoles and the others to form hydrocarbon compounds such as derivative of benzene. In addition, the medium channel of HZSM-5 has less capacity to form large compounds such as benzothiophenes than the larger channel of HBeta. 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 described in Cottrell (1958) and García-Cruz *et al.* (2008).



**Figure 4.15** Yield of sulfur species in maltenes obtained from HZSM-5 and HBeta.

#### 4.5 Conclusions

Pore channel affected the contact time of molecules to stay inside the pore. 3D pore channel (HBeta) exhibited a better cracking ability and petrochemicals production than 1D pore channel (HMOR). Pore size controlled the size of obtained products. Large pore (HBeta) exhibited a better cracking ability and petrochemicals production than the medium pore (HZSM-5) In addition, the acidic properties of support governed reaction activity. Acid support (HMOR) had a higher reaction

activity than non-acid support (KL). A high amount of benzene, toluene, ethylbenzene, and cyclohexane were produced by using HBeta. The highest amount of styrene was produced by using HMOR. In addition, HZSM-5 was selective to produce cyclohexane. The use of catalysts increased the value of oil and also reduced sulfur content in oil for all cases.

#### 4.6 Acknowledgements

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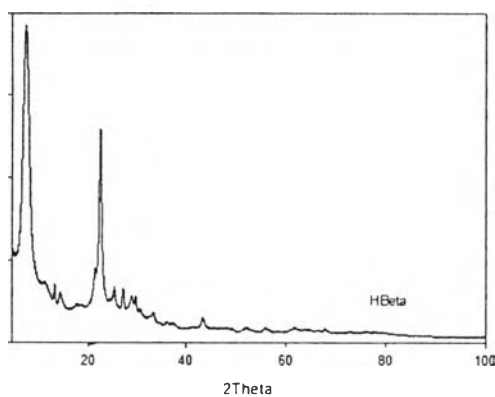
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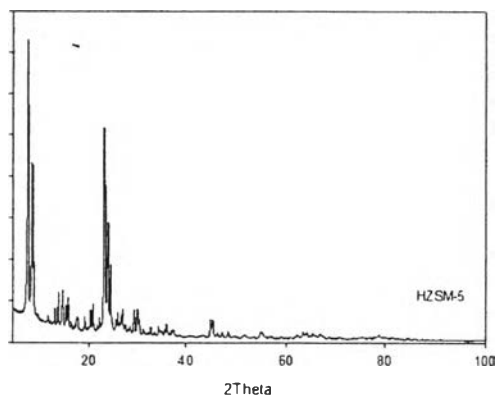
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**Table 4.4** Surface and Pore Volume of Catalysts

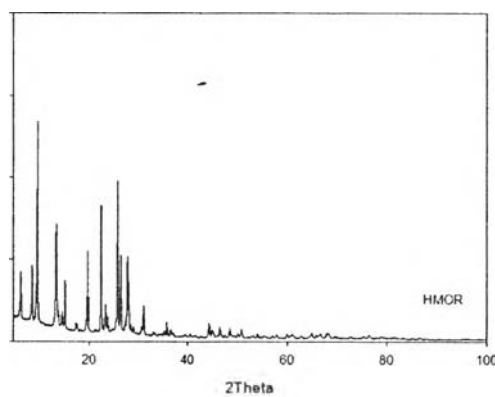
Catalyst	Surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Maximum pore width (Å)	Median pore width (Å)
HBeta	539.3	0.2570	8.148	8.351
HMOR	394.3	0.1990	8.392	8.422
HZSM-5	366.3	0.1780	7.774	7.443
KL	218.0	0.1130	6.954	7.078



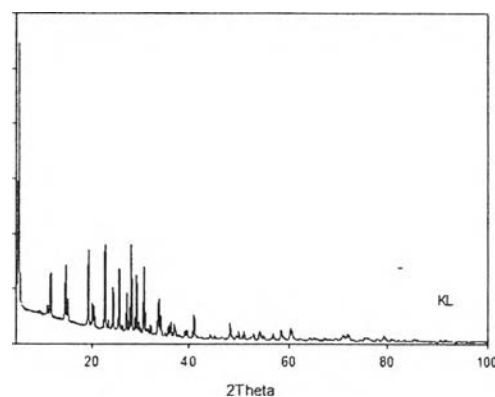
(a) HBeta



(b) HZSM-5



(c) HMOR



(d) KL

**Figure 4.16** XRD patterns of (a) HBeta, (b) HZSM-5, (c) HMOR, and (d) KL.



**Table 4.5** Yield of gas components obtained from waste tire pyrolysis

Catalyst	Methane	Ethylene	Ethane	Propylene	Propane	Mixed-C4	Mixed-C5
Non-catalyst	20.3	9.38	15.9	12.2	9.06	19.6	13.5
HMOR	18.2	4.73	14.9	10.6	16.7	19.4	15.5
KL	19.5	6.7	15.9	12.4	9.13	19.9	16.4
HBeta	14.8	6.31	11	11.9	8.98	29.2	17.8
HZSM-5	13.6	5.2	10.7	10.5	19.7	26.5	13.7

**Table 4.6** Petrochemicals obtained from waste tire pyrolysis using HMOR, HBeta, HZSM-5, and KL

Chemicals	Catalysts				
	Non-catalyst	HMOR	HBeta	HZSM-5	KL
Benzene	0.430	0.124	4.81		0.265
Toluene	0.0274	0.184	0.917	0.196	0.00497
Ethylbenzene	0.833	0.408	3.31	0.258	0.102
<i>m</i> -Xylene	-	0.185	-	0.0981	-
<i>o</i> -Xylene	-	-	0.161	-	-
<i>p</i> -Xylene	-	-	0.129	0.0304	-
Styrene	0.189	1.31	0.320	0.207	0.125
Cyclohexane	0.0239		1.05	3.46	-
Cumene	0.0660	0.105	0.0771	0.0348	0.0827
<b>Total</b>	<b>1.57</b>	<b>2.32</b>	<b>10.8</b>	<b>4.28</b>	<b>0.580</b>