

CHAPTER IV

EFFECTS OF ACIDITY, PORE STRUCTURE, AND BASICITY OF ZEOLITES ON WASTE TIRE PYROLYSIS PRODUCTS

4.1 Abstract

Zeolites have been used as catalysts for the improvement of the quality and quantity of waste tire pyrolysis products; however, their effects on the tire-derived products were not clearly explained, especially on the production of valuable petrochemicals and the formation of sulfur compounds in the oil. This work therefore studied the effects of some zeolites (HBETA, HY, HMOR and KL) properties; namely, Si/Al ratio, pore structure, and acidity/basicity on waste tire pyrolysis products, especially petrochemicals and sulfur compounds in oil, by comparing each pair of zeolites; HBETA-HY, HY-HMOR, and HMOR-KL, respectively. The liquid products were analyzed for chemical compositions and petroleum fractions using GC×GC-TOF/MS and SIMDIST-GC instruments, respectively. Sulfur content in the pyrolysis products was determined by using an S-analyzer. The results showed that the catalyst with higher acid density (HY zeolite) exhibited higher cracking than the one with lower acid density (HBETA zeolite). The catalyst with 3D pore structure (HY zeolite) showed higher cracking activity than the one with 1D (HMOR zeolite). Furthermore, the catalyst with 3D pore structure has higher open space (pore size and volume), resulting in a higher total aromatic production. The acid catalyst (HMOR zeolite) exhibited almost different activities from basic catalyst (KL zeolite). The acid catalyst showed cracking activity, while the basic catalyst did not exhibit cracking ability, but it showed dehydrogenation, alkylation, and ring closure abilities.

4.2 Introduction

Waste tire pyrolysis is quite efficient to solve problems caused by a large number of tires that were produced in several million tons per year. Pyrolysis can not only reduce a large number of waste tires, but also it can recover valuable products that can be used in fuel and chemical applications (Teng *et al.*, 1995;

Williams and Besler, 1995; Chaala and Roy, 1996; Cunliffe and Williams, 1998; de Marco Rodriguez *et al.*, 2001; González *et al.*, 2001; Williams and Brindle, 2003; Zabaniotou and Stavropoulos, 2003; Murillo *et al.*, 2006). Several researchers improved the quality and quantity of pyrolysis products by using zeolites as catalysts because the catalysts exhibited multi-functions, including hydrogenation, dehydrogenation, ring-opening, cracking, aromatization, etc. For examples, HBETA zeolite had high cracking ability and it highly promoted cooking gas production. It also promoted saturated hydrocarbons, and reduced total aromatic content in the oil. It can generate carbenium ions as active species for several reaction such as cracking, hydrogenation, etc. (Wehatoranawee, 2011). Furthermore, she also studied the effect of HY zeolite. HY zeolite increased saturated hydrocarbons, and reduced di- and polar-aromatics in the oil due to large pore volume of it that had high possibility to crack large molecules. Similarly, HMOR zeolite had cracking ability that increased gasoline and decreased vacuum gas oil. Moreover, it produced 2 times of cooking gas as compared with non-catalyst case (Kongkadee, 2008). KL catalyst is a basic catalyst. It had low acid strength resulting in higher saturated hydrocarbons in the oil than non-catalyst case. It also reduced polar aromatics and asphaltene in the oil (Choosuton, 2007). Tire-derived oils were also increased the concentration of valuable petrochemical products such as benzene, toluene and xylene amounts were highly produced from pyrolysis of waste tire using USY, Y and ZSM-5 as catalysts (Williams and Brindle, 2003; Boxiong *et al.*, 2007).

Zeolites are a choice for use in the catalytic pyrolysis of waste tire because they are interesting materials that can be properly selected to improve the quality and quantity of the desired products by considering several parameters such as type, acidity/basicity, Si/Al ratio, pore structure, pore size, etc. This work studies the effect of four different zeolites (HBETA, HY, HMOR and KL) on waste tire pyrolysis products. HBETA and HY were used to study the effect of Si/Al ratio. The effect of pore structure was studied by comparison between HY and HMOR zeolites. Furthermore, the effect of acid and base properties of zeolites was also examined by comparing HMOR with KL. The liquid products in all cases were analyzed for chemical composition and petroleum fractions using GC×GC-TOF/MS and SIMDIST-GC instruments, respectively.

Table 4.1 Calcination conditions of fresh zeolites before uses as catalysts

Zeolite	Calcination Temperature (°C)	Heating Rate (°C/min)	Holding Time at Calcination Temperature (hr)
BETA	600	2	5
Y	500	5	3
MOR	500	5	3
KL	500	10	3

4.3 Methodology

4.3.1 Catalyst Preparation

Four types of zeolites, NH₄-BETA (Si/Al=13.5), HY (Si/Al=7.5), HMOR (Si/Al=9.5) and KL (Si/Al=3), supplied by TOSOH Company (Singapore) were calcined in static air at the conditions shown in Table 4.1. Finally, the catalyst powders were pelletized, crushed, and sieved to the size range of 40-60 mesh. It is noted that HBETA and HMOR zeolites are the same ones used in Dũng *et al.* (2009).

4.3.2 Catalyst Characterization

XRD machine (Rikagu) was used to acquire the XRD patterns of the catalysts using CuK α radiation operated at 40 kV and 30 mA. The scanned angle in the range of 5 - 65° was scanned at a scanning speed of 5°/min. Surface area and pore volume of catalysts were determined by N₂ physisorption using Thermo Finnigan Sorptomatic 1990 equipment. The amount of coke on spent catalysts was determined by using Perkin Elmer/Pyris Diamond (Thermogravimetric/Differential Thermal Analysis, TG/DTA). The temperature was ramped up from room temperature to 900 °C with the heating rate of 10 °C/min. Sulfur content on catalyst surface was determined by using LECO®Elemental Analyzer (TruSpec®S).

4.3.3 Waste Tire Pyrolysis

Pyrolysis diagram is similar to the work of Dũng *et al.* (2009). Catalytic pyrolysis of waste tire was operated at atmospheric pressure from room temperature to a temperature of 500 °C (the pyrolysis zone) and 350 °C (the catalytic

zone) with a ramping rate of $10^{\circ}\text{C}/\text{min}$ and a holding time of 2 hr after the final temperatures were reached. 30 grams of shredded tire (20-40 mesh) and 7.5 grams of a catalyst (40-60 mesh) were packed in the pyrolysis zone and the catalytic zone, respectively. Nitrogen gas was used as a carrier gas. Liquid products were condensed in the condensers immersed in an ice-salt (NaCl) bath, while gas products were collected by using a gas sampling bag.

4.3.4 Product Analysis

Liquid and solid products were weighed for calculating the product yield. Before analysis, asphaltene was firstly precipitated from the liquid products via mixing with *n*-pentane in the oil/*n*-pentane mass ratio of 40:1. After that the precipitated asphaltene was filtered from the solution using a Teflon membrane ($0.45\ \mu\text{m}$) in a vacuum system, and then the maltene solutions were analyzed for the composition and average carbon number by using Gas Chromatography-Mass Spectrometry (GC \times GC-TOF/MS). GC \times GC-TOF/MS apparatus equipped an Agilent gas chromatograph 7890 (Agilent Technologies, Palo Alto, CA, USA), a Pegasus[®] 4D TOF/MS (LECO, St. Joseph, MI, USA) and a thermal modulator was used to analyze oil compositions. The instrument was operated by the cooperation of two GC columns. The 1st GC column was a non-polar Rtx[®]-5Sil MS and the 2nd GC column was an Rxi[®]-17 MS. Furthermore, true boiling point curves of maltene solutions were also analyzed by using a Varian GC-3800 simulated distillation gas chromatograph (SIMDIST-GC) conformed to the ASTM-D2887 method. The instrument equipped with FID and WCOT fused silica capillary column ($15\ \text{m} \times 0.25\ \text{mm ID} \times 0.25\ \mu\text{m}$ film thickness) The true boiling point curves were cut into petroleum fractions according to their boiling points; gasoline ($<149^{\circ}\text{C}$), kerosene ($149\text{-}232^{\circ}\text{C}$), gas oil ($232\text{-}343^{\circ}\text{C}$), light vacuum gas oil ($343\text{-}371^{\circ}\text{C}$) and heavy vacuum gas oil ($>371^{\circ}\text{C}$). The gas products were analyzed for hydrocarbon species and concentrations by using a GC-FID, Agilent Technologies 6890 Network GC system (HP-PLOT Q column: $20\ \mu\text{m}$ film thickness and $30\ \text{m} \times 0.32\ \text{mm ID}$). Furthermore, the liquid and solid products were also analyzed for their sulfur content by using a LECO[®] Elemental Analyzer (TruSpec[®]S); whereas the sulfur content in gas products was calculated via mass balance.

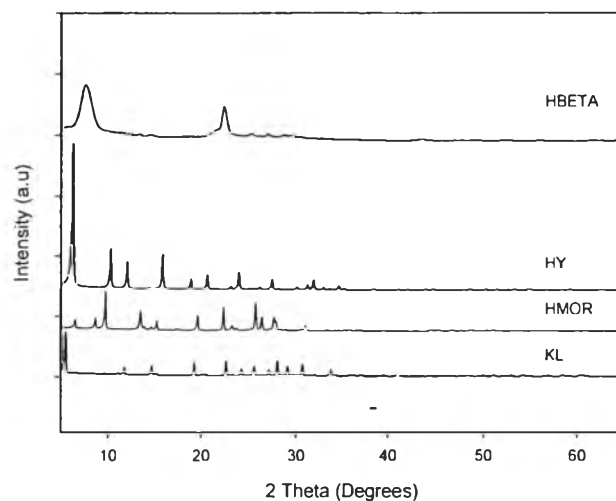


Figure 4.1 XRD patterns of zeolites.

4.4 Results and Discussion

4.4.1 Effect of Acidity

With similar pore openings, pore structures, the results obtained from using HBETA (Si/Al=13.5) and HY (Si/Al=7.5) were compared to examine the effects of acid strength and density on the pyrolysis products.

As compared with the non-catalyst case, HBETA and HY zeolites do not increase the gas production even though liquid yields are decreased while solid yields are constant because the zeolites generate a high amount of coke as seen in

Table 4.2 BET specific surface area and pore volume of catalysts

Catalyst	BET surface area (m^2/g)	Pore Volume (cm^3/g) [*]
HBETA	539	0.257
HY	515	0.266
HMOR	395	0.199
KL	200	0.104

* Horvath-Kawazoe (H-K) Calculations

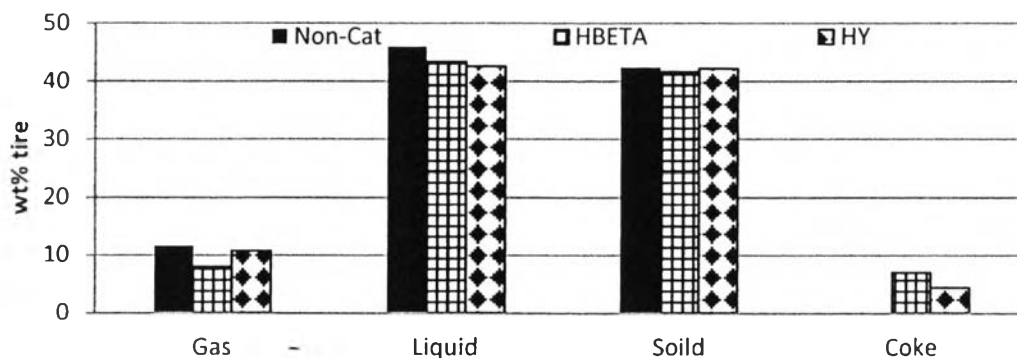


Figure 4.2 Product distribution in the HBETA and HY cases.

Figure 4.2. Figure 4.3 shows that HBETA and HY highly produce mixed-C₄ and mixed-C₅ because the catalysts can promote cracking activity of the tire molecules by generating carbenium ions as active species. The maltene compositions (Figure 4.4a) were classified into 7 groups, consisting of paraffins, olefins, naphthenes, and 4 groups of aromatics (mono-, di-, poly- and polar- aromatics). The two catalysts increase the formations of mono- and di-aromatics while the other groups (except polar-aromatics) are decreased. The catalysts increase cracking activity, resulting in the decreasing concentration of poly-aromatics, and aromatization activity, resulting in the decreasing concentrations of paraffins, olefins, and naphthenes while the concentrations of mono- and di-aromatics are increased. Furthermore, it is confirmed by the overall average carbon numbers of maltenes (Table 4.3) in the HBETA and HY cases that are less than that in the non-catalyst case. These observations can be also supported by the SIMDIST-GC results (Figure 4.4b) that the catalysts increase full-range naphtha fraction. HBETA reduces asphaltene, polar-aromatics and sulfur contents in the oil (Figures 4.4a, 4.4c and 4.5a). Moreover, HY can reduce asphaltene and sulfur contents in the oil as well.

Valuable petrochemicals taken into consideration are benzene, toluene, xylenes, styrene, ethylbenzene, cumene, limonene and cyclohexane shown in Figure 4.4d. It can be observed that HBETA highly produces benzene and ethylbenzene while HY highly produces benzene and toluene.

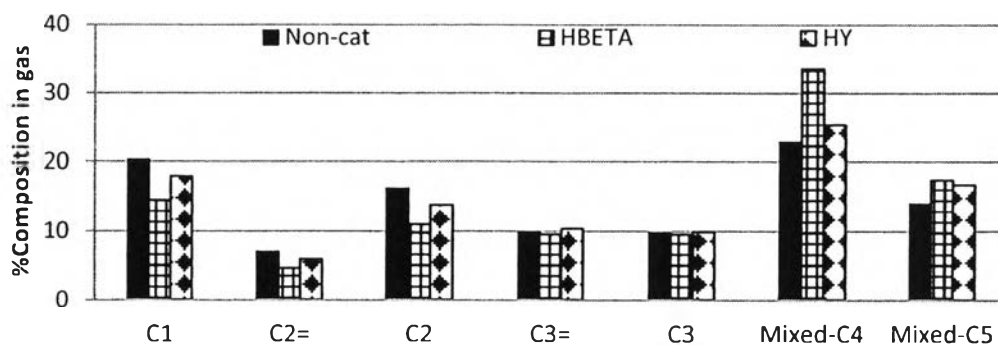


Figure 4.3 Gas compositions in the HBETA and HY cases.

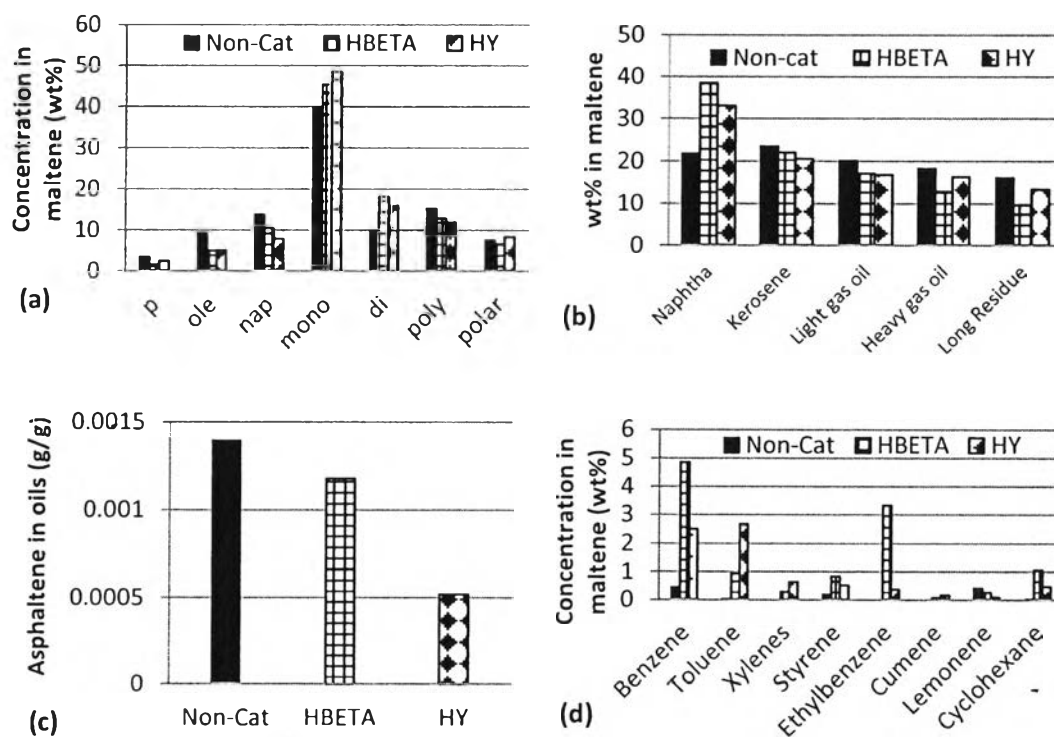


Figure 4.4 Oil analysis in the HBETA and HY cases; (a) Concentrations of each chemical group in maltenes, (b) Petroleum cuts, (c) Asphaltene content in oils, and (d) Valuable petrochemicals in oils.

Major sulfur-containing species in waste tire pyrolysis oils can be grouped into 6 groups; that are, thiophenes (Th), benzothiophenes (BT),

Table 4.3 Average carbon number of each chemical group in maltenes in the HBETA and HY cases

	P	Ole	Nap	Mono	Di	Poly	Polar	Total
No Cat.	15.7	12.2	12.3	11.8	12.1	14.7	11.4	<u>12.5</u>
HBETA	14.9	11.5	11.0	10.8	12.0	14.8	11.0	<u>11.7</u>
HY	15.4	11.8	11.3	11.1	12.0	14.7	11.2	<u>11.8</u>

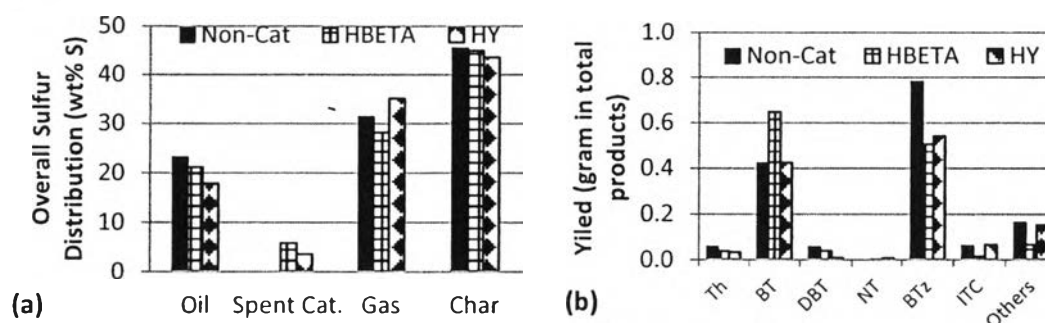


Figure 4.5 Sulfur analysis in the HBETA and HY cases; (a) Overall sulfur distribution, and (b) Distribution of sulfur-containing compounds in maltenes.

dibenzothiophenes (DBT), naphthothiophenes (NT), benzothiazoles (BTz) and isothiocyanates (ITC). Figure 4.5b shows that HBETA and HY selectively reduce benzothiazoles. Furthermore, the average carbon numbers of sulfur-containing compounds (Table 4.4) are decreased in both HBETA and HY cases, indicating that the catalysts also help further remove sulfur for the case in hydrotreating.

As compared with HY, HBETA produces a higher amount of coke and a lower gas yield because HY has higher acid density, causing the higher cracking of long chain molecules, but it has lower acid strength, resulting in lower coke formation. HBETA produces higher full-range naphtha than HY because the lower acid density of HBETA causes a lower cracking activity. Furthermore, HBETA gives a lower polar-aromatic concentration than HY. The higher acid strength of HBETA can convert polar-aromatics into the forms of asphaltene and

Table 4.4 Average carbon number of major sulfur-containing compounds in maltenes in the HBETA and HY cases

	Th	BT	DBT	NT	BTz	ITC
No Cat.	9.86	10.0	12.9	-	7.26	9.16
HBETA	9.59	9.87	13.2	12.0	7.19	7.00
HY	9.31	9.81	12.3	12.4	7.24	7.48

coke. HY exhibits a cracking activity than HBETA, resulting in the higher mono-aromatic concentration, and the lower concentrations of di- and poly-aromatics in the maltene.

4.4.2 Effect of Pore Structure

HY (3D pore structure) and HMOR (1D pore structure) with the similar pore sizes and Si/Al ratios were selected in this work for studying the effect of pore structure on waste tire pyrolysis products.

The valuable petrochemicals in mono-aromatics highly produced are benzene and toluene in the HY case and styrene in the HMOR case as shown in Figure 4.8d. Furthermore, the catalysts also show cracking ability as seen in the decrement of overall average carbon numbers in the maltenes (Table 4.5), and the increment of full-range naphtha (Figure 4.8b). As compared with the non-catalyst case, HY and HMOR can reduce sulfur content in the oils (Figure 4.9a) by converting sulfur-containing compounds in the oils into gas and coke. The increment

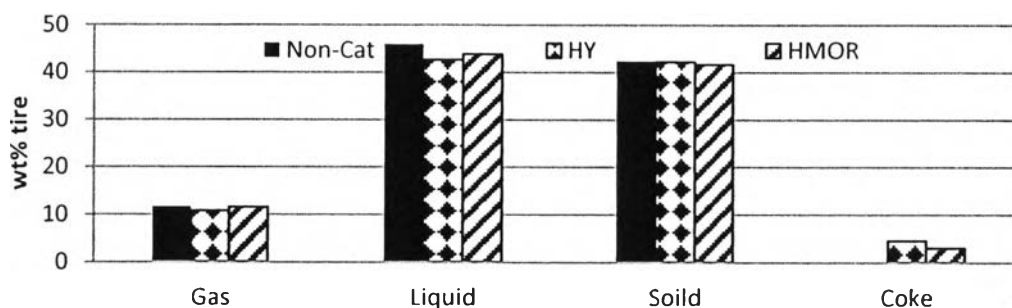


Figure 4.6 Product distribution in the HY and HMOR cases.

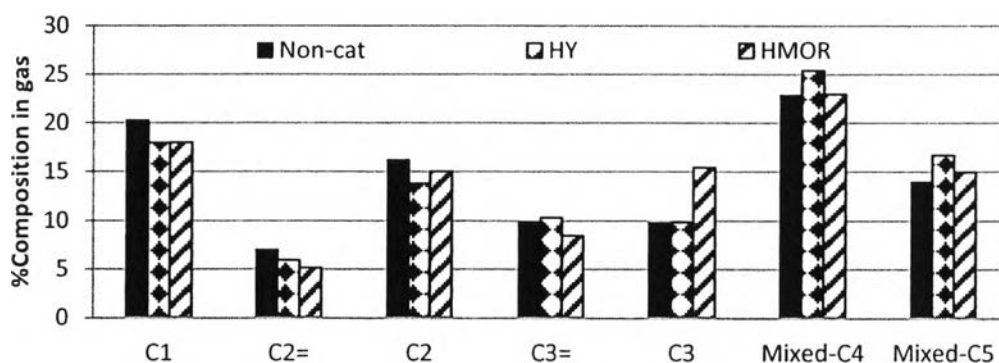


Figure 4.7 Gas compositions in the HY and HMOR cases.

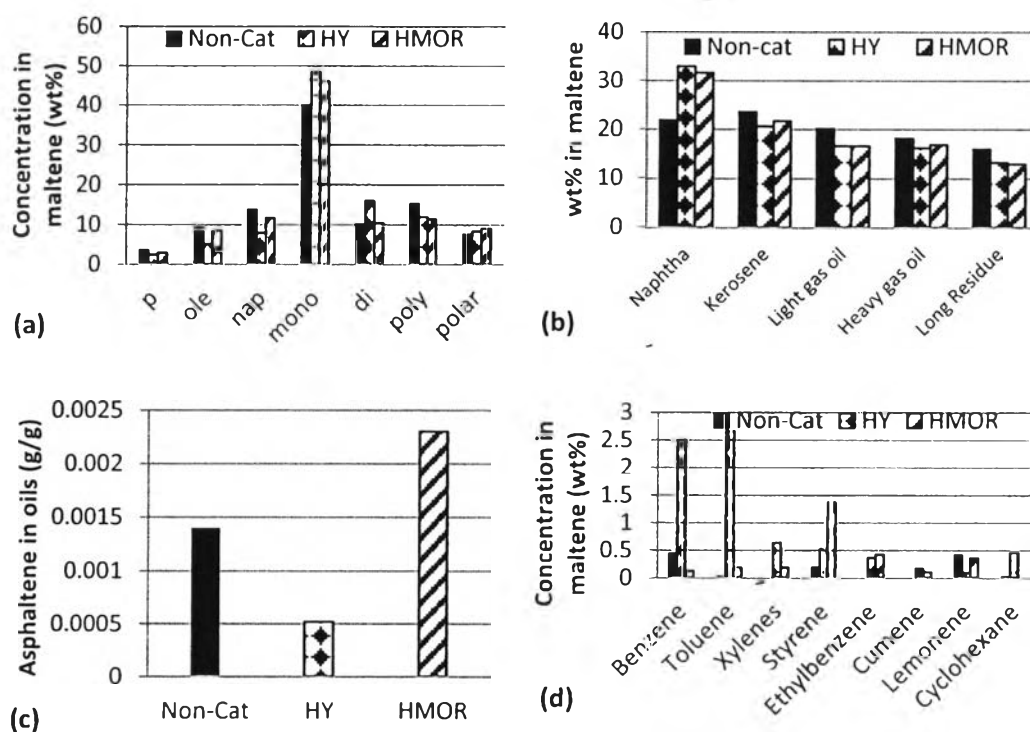


Figure 4.8 Oil analysis in the HY and HMOR cases; (a) Concentrations of each chemical group in maltenes, (b) Petroleum cuts, (c) Asphaltene content in oils, and (d) Valuable petrochemicals in oils.

of sulfur in gas phase indicates that the catalysts exhibit hydrogenolysis ability. Furthermore, the catalysts can reduce the average carbon numbers of almost all groups of sulfur-containing compounds in maltene (Table 4.6), indicating that the

Table 4.5 Average carbon number of each chemical group in maltenes in the HY and HMOR cases

	P	Ole	Nap	Mono	Di	Poly	Polar	Total
No Cat.	15.7	12.2	12.3	11.8	12.1	14.7	11.4	<u>12.5</u>
HY	15.4	11.8	11.3	11.1	12.0	14.7	11.2	<u>11.8</u>
HMOR	16.1	11.9	12.1	11.6	11.9	14.7	11.6	<u>12.2</u>

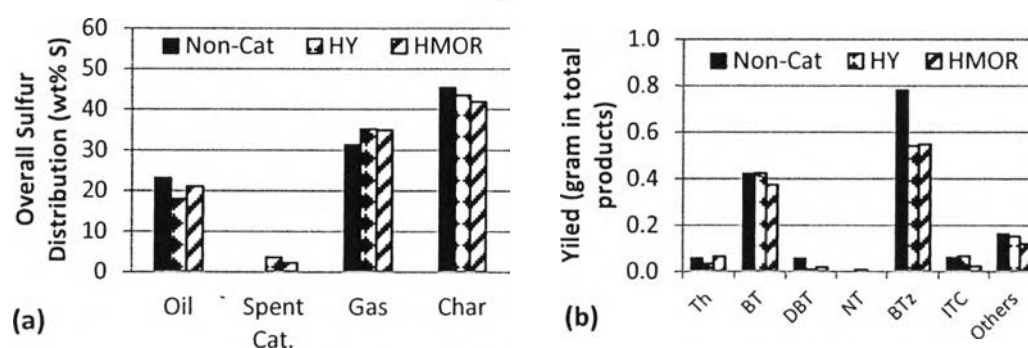


Figure 4.9 Sulfur analysis in the HY and HMOR cases; (a) Overall sulfur distribution, and (b) Distribution of sulfur-containing compounds in maltenes.

sulfur-containing compounds in the oils can be removed easily in the desulfurization processes.

The valuable petrochemicals in mono-aromatics highly produced are benzene and toluene in the HY case and styrene in the HMOR case as shown in Figure 4.8d. Furthermore, the catalysts also show cracking ability as seen in the decrement of overall average carbon numbers in the maltenes (Table 4.5), and the increment of full-range naphtha (Figure 4.8b). As compared with the non-catalyst case, HY and HMOR can reduce sulfur content in the oils (Figure 4.9a) by converting sulfur-containing compounds in the oils into gas and coke. The increment of sulfur in gas phase indicates that the catalysts exhibit hydrogenolysis ability. Furthermore, the catalysts can reduce the average carbon numbers of almost all groups of sulfur-containing compounds in maltene (Table 4.6), indicating that the

sulfur-containing compounds in the oils can be removed easily in the desulfurization processes.

For the effect of pore structure, HMOR produces a higher amount of gas product than HY although the liquid yield in the HMOR case is higher because the 3D pore structure catalyst has a higher space (pore size and architecture) for aromatic production, resulting in more aromatic production and a higher amount of coke deposited on the catalyst surface (Bortnovsky *et al.*, 2005), than the 1D pore structure catalyst. Paraffins, olefins and naphthenes can be reactants for aromatic production; so, these compounds are reduced in the HY case more than in the HMOR case. HY also produces higher full-range naphtha with lower sulfur content and polar-aromatic concentration than HMOR, indicating that HY has a higher cracking activity than HMOR. Moreover, the catalysts can also help remove sulfur more easily. From Figure 4.9b, the percentages of benzothiazoles and isothiocyanates are decreased in the HMOR case while the proportion of isothiocyanates is not decreased in the HY case, indicating that HMOR can promote breaking of C-S and C-N bonds while HY do not break C-N bonds because HMOR might have slightly higher acid strength than HY.

Table 4.6 Average carbon number of major sulfur-containing compounds in maltenes in the HY and HMOR cases

	Th	BT	DBT	-NT	BTz	ITC
No Cat.	9.86	10.0	12.9	-	7.26	9.16
HY	9.31	9.81	12.3	12.4	7.24	7.48
HMOR	9.80	9.95	13.4	-	7.22	7.00

4.4.3 Effect of Acid/Base Zeolites

The results from using HMOR and KL zeolites with the similar pore size and pore structure (1D pore structure) were compared to study the effect of acid and basic catalysts on waste tire pyrolysis products.

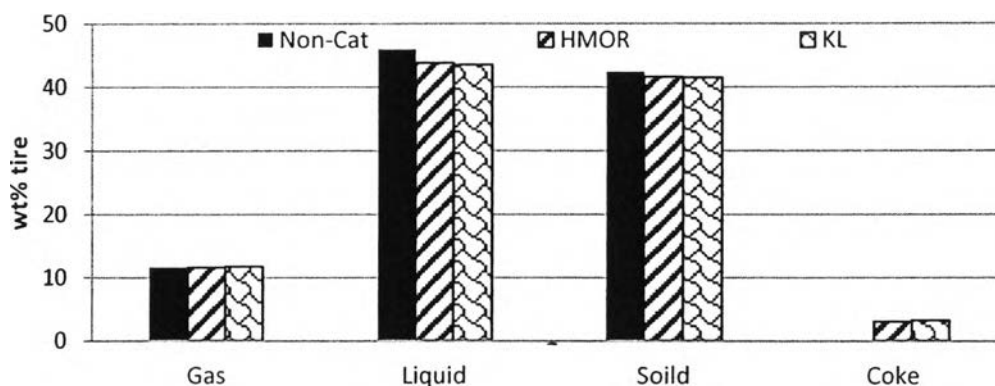


Figure 4.10 Product distribution in the HMOR and KL cases.

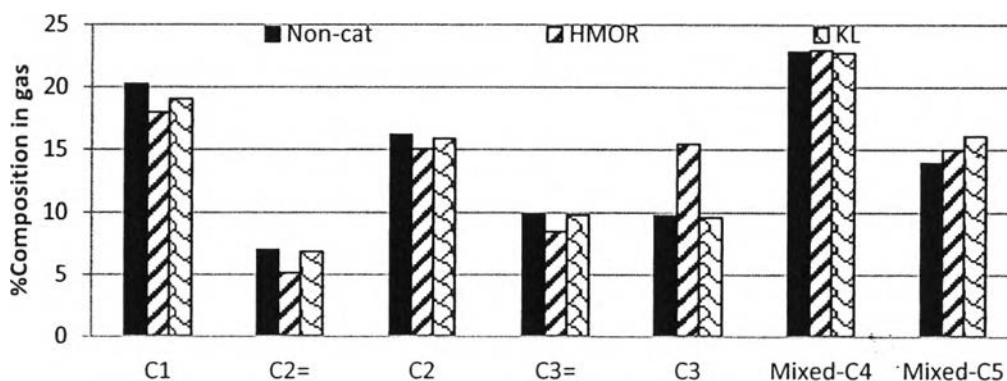


Figure 4.11 Gas compositions in the HMOR and KL cases.

Figure 4.10 shows that the acid and basic catalysts give the same product distribution. The gas compositions in Figure 4.11 show that HMOR enhances propane production while KL does not significantly affect the gas composition as compared with the non-catalyst case. HMOR and KL enhance the production of mono-aromatics and full-range naphtha (Figures 4.12a and b).

As compared with the non-catalyst case, the increasing full-range naphtha in HMOR case and the increasing kerosene in KL case are observed because KL reduces the concentration of polar-aromatics in the maltene. KL gives the lower asphaltene content (Figure 4.12c) and the lower amount of polar-aromatics than HMOR, but KL generates a higher amount of coke that might be formed from

asphaltene and polar-aromatics. Figure 4.12d shows that HMOR highly produces styrene, while KL does not produce any petrochemicals at all.

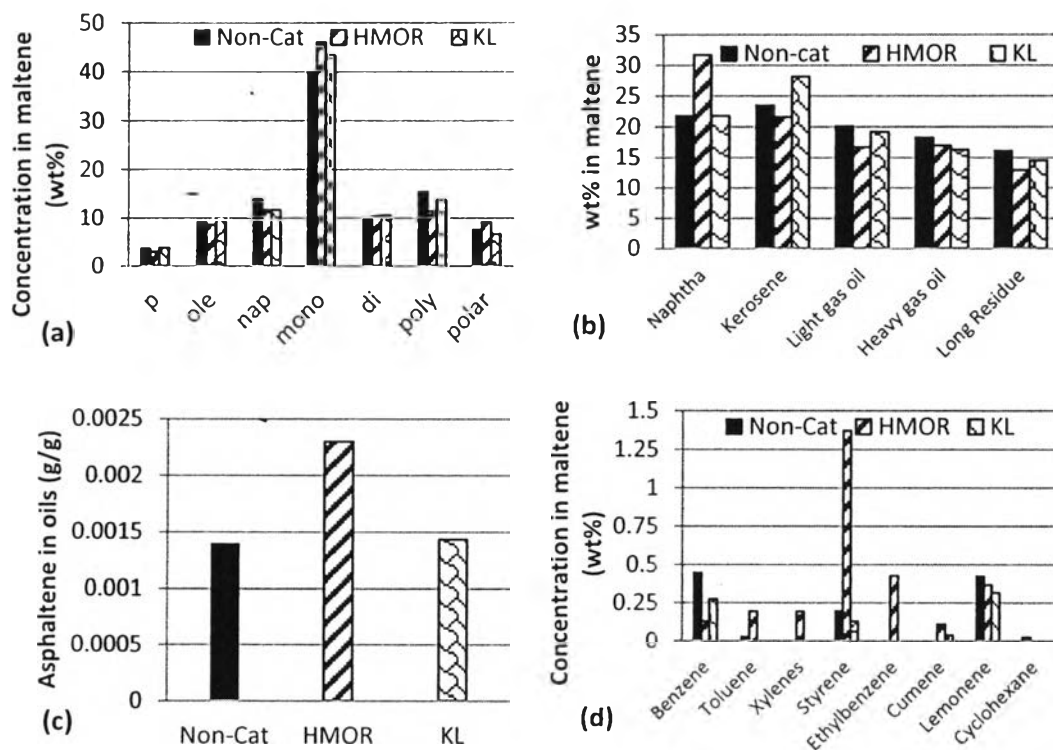


Figure 4.12 Oil analysis in the HMOR and KL cases; (a) Concentrations of each chemical group in maltenes, (b) Petroleum cuts, (c) Asphaltene content in oils, and (d) Valuable petrochemicals in oils.

Table 4.7 Average carbon number of each chemical group in maltenes in the HMOR and KL cases

	P	Ole	Nap	Mono	Di	Poly	Polar	Total
No Cat.	15.7	12.2	12.3	11.8	12.1	14.7	11.4	<u>12.5</u>
HMOR	16.1	11.9	12.1	11.6	11.9	14.7	11.6	<u>12.2</u>
KL	15.0	12.5	12.4	12.1	12.1	14.9	11.4	<u>12.6</u>

In terms of sulfur reduction (Figure 4.13a), both zeolites can reduce sulfur in oils. However, KL zeolite might increase sulfur and nitrogen removal from the oil; which potassium cations might interact with the nucleophilic species (N and S sites in the molecules in the oil), resulting in higher reduction of sulfur in the oil, and lower the concentration of benzothiazoles in KL than that in HMOR (Figure 4.13b).

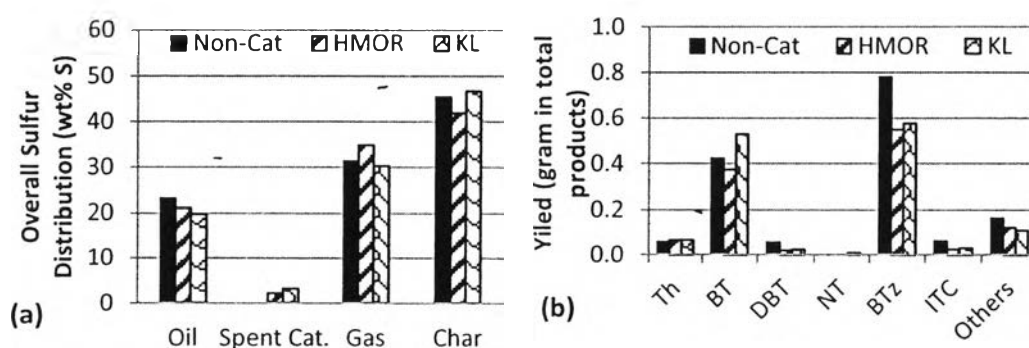


Figure 4.13 Sulfur analysis in the HMOR and KL cases; (a) Overall sulfur distribution, and (b) Distribution of sulfur-containing compounds in maltenes.

Table 4.8 Average carbon number of major sulfur-containing compounds in maltenes in the HMOR and KL cases

	Th	BT	DBT	NT	BTz	ITC
No Cat.	9.86	10.0	12.9	-	7.26	9.16
HMOR	9.80	9.95	13.4	-	7.22	7.00
KL	10.6	10.2	13.5	13.4	7.27	7.33

4.5 Conclusions

The effect of zeolites on waste tire pyrolysis products was studied in this work by comparing between HBETA and HY (Si/Al ratio), HY and HMOR (pore structure), and HMOR and KL (acid/base catalysts). The results showed that the higher acid density catalyst (HY zeolite) exhibited higher cracking activity than the

lower acid density catalyst (HBETA zeolite), resulting in higher gas yield and mono-aromatic concentration in oil, and lower sulfur and asphaltene contents in the oil than HBETA. The 3D pore structure catalyst (HY zeolite) showed higher cracking activity resulting in lower overall carbon number of maltene, higher full-range naphtha, lower sulfur and asphaltene contents in the oil, and lower polar-aromatic concentration in the oil than 1D pore structure catalyst (HMOR zeolite). Furthermore, the 3D pore structure catalyst has bigger open space (pore size and architecture), resulting in higher total aromatic production. The acid and basic catalysts (HMOR and KL zeolites) exhibited cracking ability but HMOR zeolite can produce light oil (full-range naphtha) more than KL (kerosene). So, KL zeolite produced higher overall carbon numbers of maltene than the non-catalyst case. Furthermore, the electrophilic part of KL reacted more with nucleophilic species of sulfur-containing compounds, resulting in higher sulfur reduction than HMOR. The valuable products were differently produced in each zeolite case. HBETA significantly produced more benzene and ethylbenzene. HY selectively produced more benzene and toluene. Styrene was observed in a significant amount using HMOR while KL did not seem to produce any C₆-C₉ petrochemicals at all in oil.

4.6 Acknowledgements

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4.7 References

Bortnovsky, O., Sazama, P., and Wichterlova, B. (2005) Cracking of pentenes to C₂-C₄ light olefins over zeolites and zeotypes: Role of topology and acid site strength and concentration. *Applied Catalysis A: General*, 287, 203-213.

- Boxiong, S., Chunfei, W., Binbin, G., Rui, W., and Liangcai (2007) Pyrolysis of waste tyres with zeolite USY and ZSM-5 catalysts. Applied Catalysis B: Environmental, 73(1-2), 150-157.
- Chaala, A. and Roy, C. (1996) Production of coke from scrap tire vacuum pyrolysis oil. Fuel Processing Technology, 46, 227-239.
- Choosuton, A. (2007) Development of waste tire pyrolysis for the production of commercial fuels: Effect of noble metals and supports. M.S. Thesis, The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Thailand.
- Cunliffe, A.M. and Williams, P.T. (1998) Composition of oils derived from the batch pyrolysis of tyres. Journal of Analytical and Applied Pyrolysis, 44, 131-152.
- de Marco Rodriguez, I., Laresgoiti, M.F., Cabrero, M.A., Torres, A., Chomón, M.J., and Caballero, B. (2001) Pyrolysis of scrap tyres. Fuel Processing Technology, 72, 9-22.
- Dũng, N.A., Wongkasemjit, S., and Jitkamka, S. (2009) Effects of pyrolysis temperature and Pt-loaded catalysts on polar-aromatic content in tire-derived oil. Applied Catalysis B: Environmental, 91, 300-307.
- González, J.F., Encinar, J.M., Canito, J.L., and Rodríguez, J.J. (2001) Pyrolysis of automobile tyre waste. Influence of operating variables and kinetics study. Journal of Analytical and Applied Pyrolysis, 58-59, 667-683.
- Kongkadee, K. (2008) Effect of metals loaded on zeolite supports on tire pyrolysis products: Ru on HMOR and HZSM-5. M.S. Thesis, The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Thailand.
- Murillo, R., Aylón, E., Navarro, M.V., Callén, M.S., Aranda, A., and Mastral, A.M. (2006) The application of thermal processes to valorise waste tyre. Fuel Processing Technology, 87, 143-147.
- Teng, H., Serio, M.A., Whjtowicz, M.A., Bassilakis, R., and Solomon, P.R. (1995) Reprocessing of used tires into activated carbon and other products. Industrial and Engineering Chemistry Research, 34, 3102-3111.
- Wehatoranawee, A. (2011) Catalytic pyrolysis of waste tire over Ag-loaded catalysts. M.S. Thesis, The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Thailand.

- Williams, P.T. and Besler, S. (1995) Pyrolysis-thermogravimetric analysis of tyres and tyre components. Fuel, 74, 1277-1283.
- Williams, P.T. and Brindle, A.J. (2003) Aromatic chemicals from the catalytic pyrolysis of scrap tyres. Journal of Analytical and Applied Pyrolysis, 67, 143-164.
- Zabaniotou, A.A. and Stavropoulos, G. (2003) Pyrolysis of used automobile tires and residual char utilization. Journal of Analytical and Applied Pyrolysis, 70, 711-722.