

CHAPTER V

ENHANCEMENT OF PETROCHEMICALS IN TIRE-DERIVED OIL USING ALUMINOSILICATE MCM-48

5.1 Abstract

Waste tire pyrolysis is one of processes that can alternatively produce petrochemicals, such as benzene, toluene, xylene, ethylbenzene, styrene, and cumene. They are widely used as raw materials in petrochemical industry. Tire-derived oil is an aromatic-based hydrocarbon mixture that can be used as a substitute fuel or source of petrochemicals. This work studied petrochemical products in tire-derived oil from using Al-MCM-48, synthesized via a hydrothermal method, as a catalyst. Al-MCM-48 is a cubic-structured mesoporous material, which is commonly used in the applications of separation and catalysis. The results from GCxGC-TOF/MS showed the use of Al-MCM-48 catalyst increased the concentration of petrochemicals in maltene (from 3.4 wt.% to 7.6 wt.%). It enhanced the selectivity of benzene (from 0 wt.% to 1.2 wt.%), toluene (from 0.9 wt.% to 2.0 wt.%), ethylbenzene (from 1.2 wt.% to 2.6 wt.%), p-xylene (from 0.6 wt.% to 0.8 wt.%), and cumene (from 0.7 wt.% to 1.0 wt.%). The enhancement of petrochemicals using Al-MCM-48 was possibly resulted from cracking of bulky molecules caused by the large pore size and acid sites of the catalyst.

5.2 Introduction

Petrochemicals, such as benzene, toluene, xylenes, ethylbenzene, and cumene are used to manufacture several products that people use everyday. For examples, benzene and xylenes are used for coating, printing and extracting. Furthermore, they are used as raw materials for production of plastics. Toluene is used as an octane booster to improve the performance of engines. Ethylbenzene is primarily used in the manufacture of styrene. Normally, styrene is used to make plastic materials via polymerization reaction. Cumene is mainly used as a raw material in the manufacture of phenol and acetone. The petrochemicals can be

produced from several processes such as the catalytic reforming of naphtha in a petroleum refinery. Moreover, many researchers studied waste tire pyrolysis as an alternative process to produce petrochemicals. Tire-derived oil is an aromatic-based hydrocarbon mixture that is not suitable for direct use as vehicle fuels. Muenpol *et al.* (2015) studied the impact of zeolite properties on petrochemical products in tire-derived oil. When the zeolites with two pore sizes (HBETA and HZSM-5) were compared, HBETA that has a larger pore size gave a higher quantity of petrochemical products, especially benzene, toluene, and ethylbenzene than HZSM-5 because the medium pore of HZSM-5 cannot allow large molecules pass inside the pores. Moreover, the 3D pore channel of HBeta provided a higher amount of petrochemicals than the 1D pore channel of HMOR due to a high contact time of molecules in the pores. As a result, HBETA produced a high amount of benzene, toluene, ethylbenzene, and cyclohexane. HMOR and HZSM-5 produced the highest amount of styrene and cyclohexane, respectively. Additionally, Yuwapornpanit and Jitkarnka (2015) used Cu-loaded zeolites in waste tire pyrolysis. The authors found that Cu/HY and Cu/HMOR highly enhanced the petrochemical productivity from 31.2 and 10.6 kg/ton of tire (HY and HMOR) to 52.3 and 43.0 kg/ton of tire (Cu/HY and Cu/HMOR). Furthermore, the petrochemicals in tire-derived oil in both Cu/HY and Cu/HMOR cases might be partially formed from the conversion of sulfur-containing compounds (benzothiazoles and isothiocyanates), because the Cu-loading promoted the dealkylation activity of HY and HMOR. Therefore, it is evident that the use of microporous (HBETA, HMOR, and HZSM-5) and bi-functional catalysts (Cu/HY and Cu/HMOR) in waste tire pyrolysis provided better selectivity to produce petrochemicals in oil. Furthermore, mesoporous materials (MCM-41 and MCM-48) have also been used as catalysts in waste tire pyrolysis (Dũng *et al.*, 2009a; Witpithomwong *et al.*, 2011). The authors found that the concentration of poly- and polar-aromatic hydrocarbons decreased, resulting in the increasing concentration of mono-aromatic hydrocarbons, but the production of petrochemicals in tire-derived oil has not been reported. The purpose of this work was therefore to investigate the potential of Al-MCM-48 catalyst in waste tire pyrolysis on the production of petrochemicals in tire-derived oil. The analysis of petrochemicals and the carbon number distribution in tire-derived oils were done by using GCxGC-TOF/MS.

5.3 Methodology

5.3.1 Catalyst Preparation

Al-MCM-48 (starting Si/Al of precursors = 75) was synthesized via hydrothermal synthesis method (Huang *et al.*, 2008). Tetraethoxysilane (TEOS) and aluminum isopropoxide as silica and alumina sources, respectively, were added into a mixture of hexadecyltrimethyl ammonium bromide (CTAB), sodium hydroxide (NaOH) and deionized water with the composition of TEOS: 0.34Al: 0.6NaOH: 0.2CTAB: 72H₂O. The resulted mixture was stirred for 2 h. After that, it was transferred to a Teflon-lined autoclave heated at 120 °C for 40 h. The obtained product was filtered and washed with deionized water. Then, the solid was dried at 80 °C overnight and calcined at 540 °C with heating rate 2 °C/min for 6 h. Finally, the catalyst powder was pelletized, crushed, and sieved into the particle size range of 40-60 mesh.

5.3.2 Catalyst Characterization

The XRD pattern of a sample was obtained using a Rikagu TTRAXIII diffractometer equipped with Cu K α radiation at 50 kV and 300 mA. The experimental conditions were as follows: 0.02° of sampling width, 2°/min of scan speed, and 2.0-6.0° of scan angles. The 27Al MAS NMR spectrum was analyzed by a Bruker DPX-300 NMR spectrometer. The spectrum was recorded at a frequency of 78 MHz. The experimental conditions were set as follows: 800 numbers of scan (NS), a relaxation delay of 4 second, spin rate of 5 kHz and spectral size 4 K with 2 K time domain size.

5.3.3 Pyrolysis of Waste Tire

The same pyrolysis system was employed in the experiments, following the method set by Dũng *et al.* (2009b). There were two zones of reactor; that are, catalytic zone and pyrolytic zone. 30 g of waste tire sample was loaded into pyrolytic zone, and 7.5 g of catalyst was loaded into the catalytic zone. Nitrogen was flown through the reactor at 30 ml/min. Heated with the heating rate of 10 °C/min

from room temperature, the pyrolytic zone was operated at 500 °C, and the catalytic zone was operated at 350 °C catalytic zone. The liquid product was collected in condensers immersed in an ice bath. The gas product was collected in a gas sampling bag, whereas the solid product remained in the pyrolytic zone of reactor.

5.3.4 Product Analysis

A liquid product was dissolved in n-pentane in the liquid product/n-pentane at the weight ratio of 40:1 for 18 h to precipitate asphaltene. Then, asphaltene was filtered by using a 0.45 μm Teflon membrane in a vacuum system, and then obtained maltene solution. The maltene solutions were characterized by using a two-dimensional Gas Chromatography with Time-of-Flight Mass Spectrometry (GC \times GC-TOF/MS) to identify compounds in maltenes.

5.4 Results and Discussion

5.4.1 Catalyst Characterization

Al-MCM-48 was successfully synthesized via a hydrothermal method based on the Huang's method (Huang *et al.*, 2008) proven by the small-angled XRD pattern. Figure 5.1a shows the diffraction peaks at approximately $2\theta = 2.5^\circ$ and $2\theta = 3.0^\circ$, corresponding the d-spacing of d211 and d220 plane, respectively, which are the characteristic of the parent MCM-48. Figure 5.1b shows the ^{27}Al MAS NMR spectra of Al-MCM-48. The signal intensities of peak present unique resonance at approximately 51 ppm, which is assigned to tetrahedrally-coordinated alumina. However, the octahedrally-coordinated alumina, which is resonance around 5 ppm, is absent in the ^{27}Al MAS NMR spectrum (Kosslick *et al.*, 1998). It can be explained that the alumina atoms have been completely incorporated into the Si-MCM-48 framework.

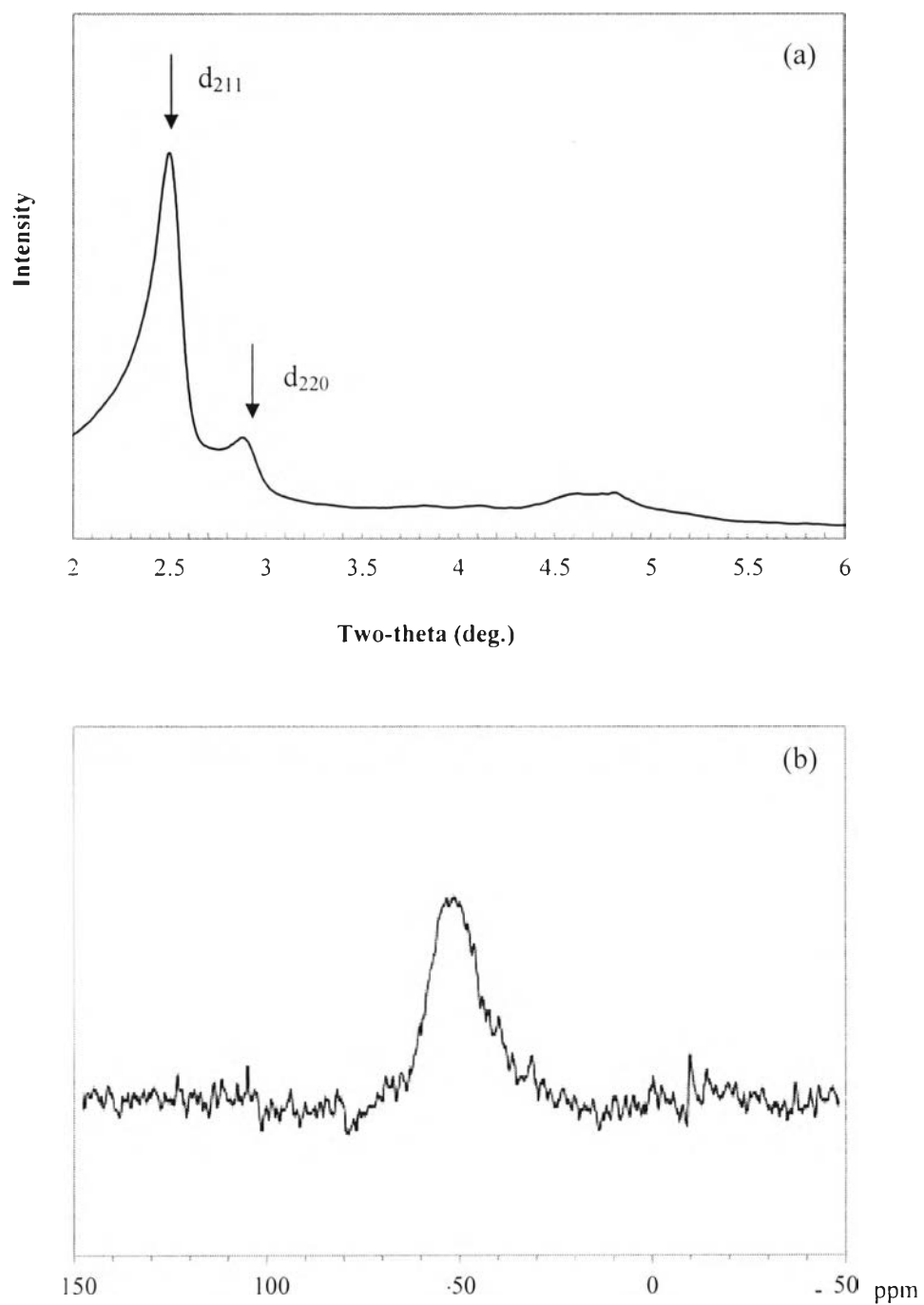


Figure 5.1 (a) XRD pattern of Al-MCM-48, and (b) ^{27}Al MAS NMR spectrum of Al-MCM-48.

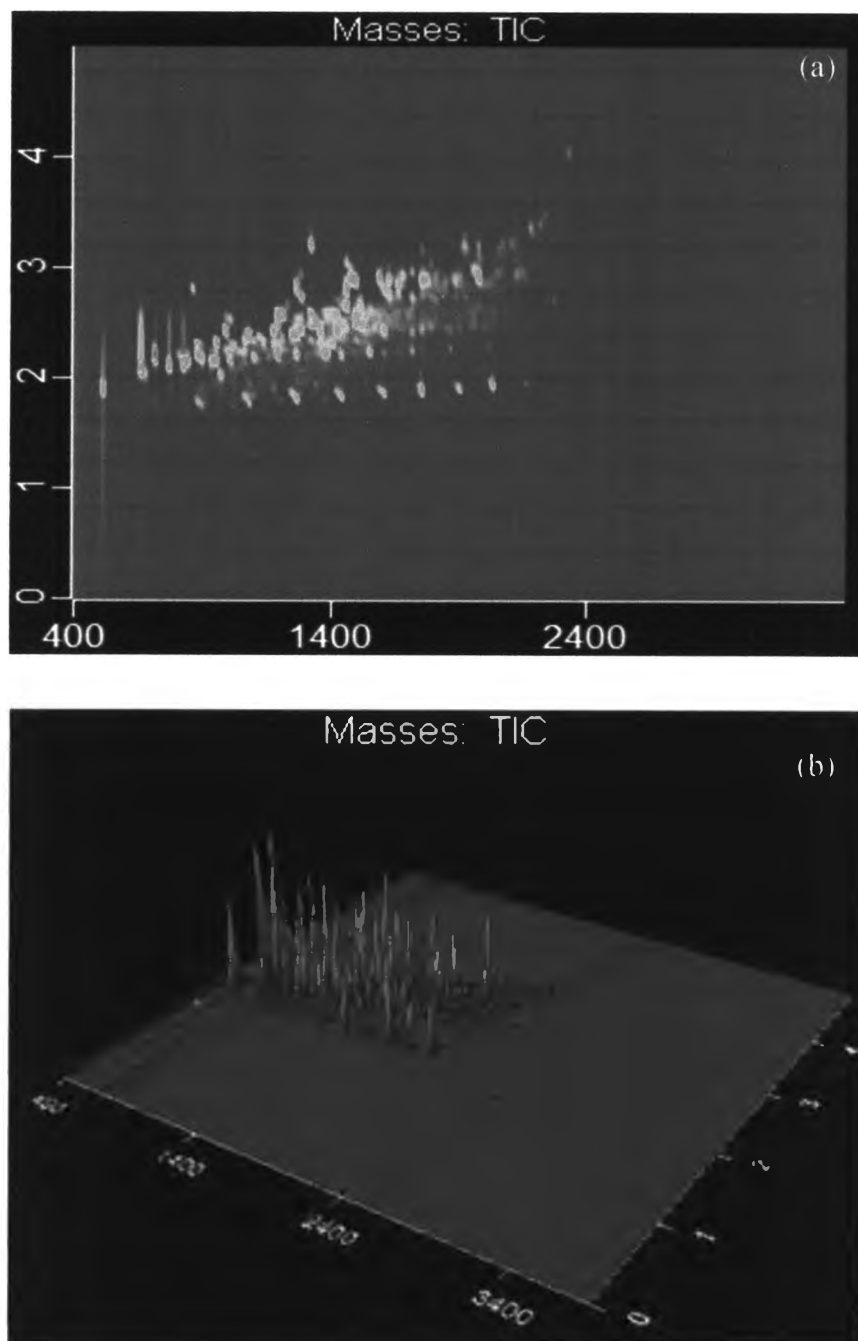
5.4.2 Tire-derived Oil

Figure 5.2 Total ion chromatogram of the maltene from using Al-MCM-48 case :
(a) contour plot and (b) surface plot.

The liquid product was examined by using a GC×GC-TOF/MS, which is a powerful instrument to separate the complex mixture. Figure 5.2 shows the contour and surface plots of maltene solution from using Al-MCM-48. It exhibits the good separation of compounds. In addition, the carbon number distributions in maltenes are shown in Figure 5.3a. It exhibits that tire-derived oil mainly contained the carbon number distributed in the range of C6 to C17. Moreover, the use of Al-MCM-48 as a catalyst can highly reduce C10 and C15 hydrocarbons whereas C6, C7, C9, C13, and C14 hydrocarbons are enhanced. Additionally, the hydrocarbons in the range of C6-C9 are mainly mono-aromatics and petrochemical compounds. The petrochemicals such as benzene (C₆H₆), toluene (C₇H₈), xylenes (C₈H₁₀), ethylbenzene (C₈H₁₀), and cumene (C₉H₁₂) are remarkable products that are widely used as raw materials in petrochemical industry. As a result, the concentration of petrochemicals in tire-derived oil is increased from 3.4 wt.% for non-catalytic case to 7.6 wt.% for the Al-MCM-48 catalyst. Figure 5.3b shows the concentration of petrochemical products in tire-derived oil. It illustrates that Al-MCM-48 significantly enhanced the selectivity to benzene (from 0 wt.% to 1.2 wt.%), toluene (from 0.9 wt.% to 2.0 wt.%), and ethylbenzene (from 1.2 wt.% to 2.6 wt.%), whereas the concentration of p-xylene and cumene slightly is increased from 0.6 wt.% to 0.8 wt.% and from 0.7 wt.% to 1.0 wt.%, respectively. The enhancement of petrochemicals in tire-derived oil by using Al-MCM-48 is possibly occurred from the conversion of C10 and C15 hydrocarbons to petrochemicals. Table 5.1 reports the reduction of some compounds in the carbon number range of C10 and C15. For instances, 1-butyn-1-ylbenzene, 1-isopropenyl-4-methylbenzene, 1,4-diethylbenzene, and cyclopropyl-phenylmethane (Figure 5.4) are mono-aromatic hydrocarbons, which have alkyl group substituents on a benzene ring. Thus, petrochemicals might be formed from the cracking alkyl groups. Moreover, 4-isopropyl-1,6-dimethylnaphthalene and 9,9-dimethyl-9H-fluorene are di- and poly-aromatic hydrocarbons, whose aromatic rings might be cracked in the pores of Al-MCM-48 to form petrochemicals, since Al-MCM-48 has large pore size that can allow large molecules to pass through the pores.

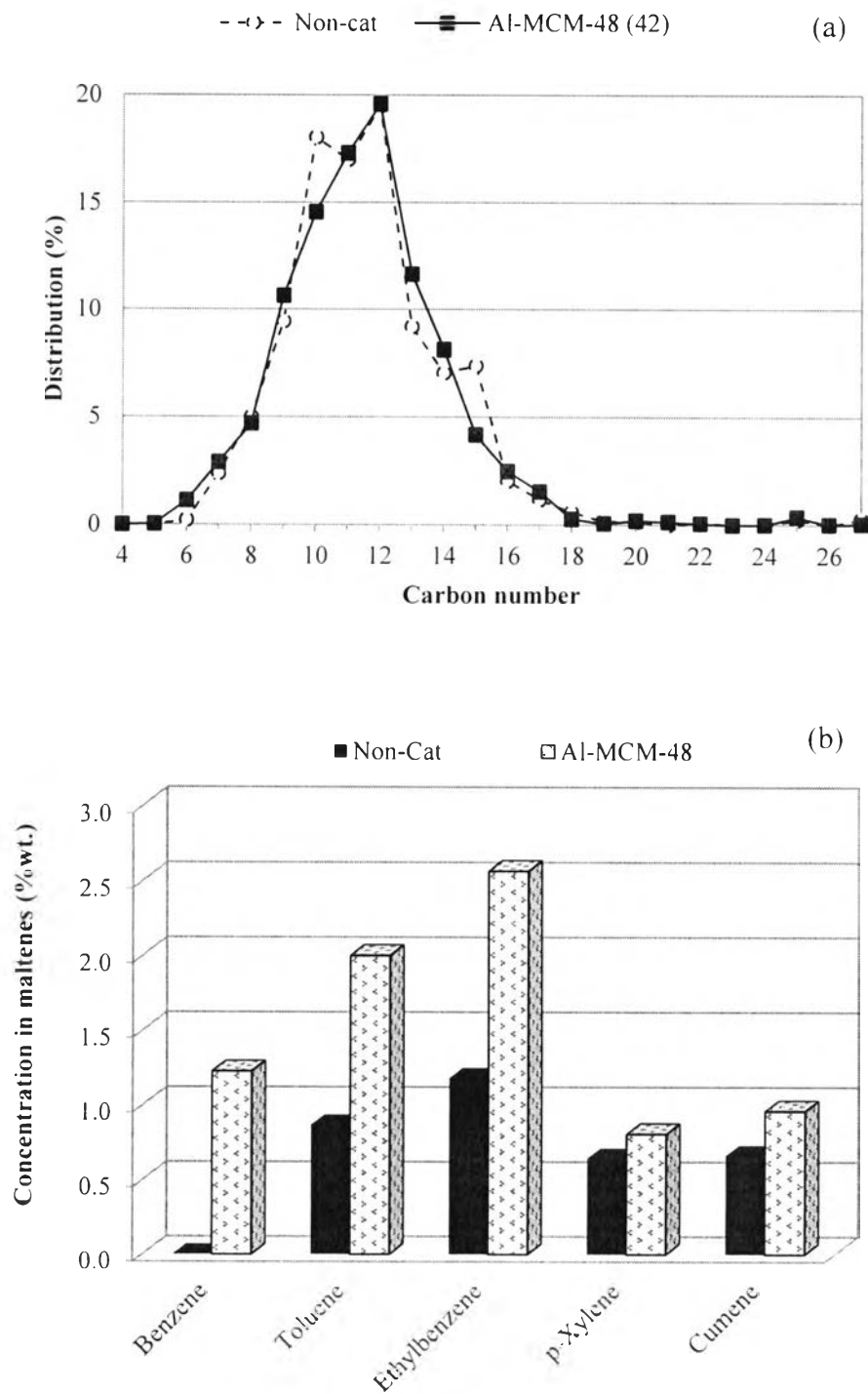
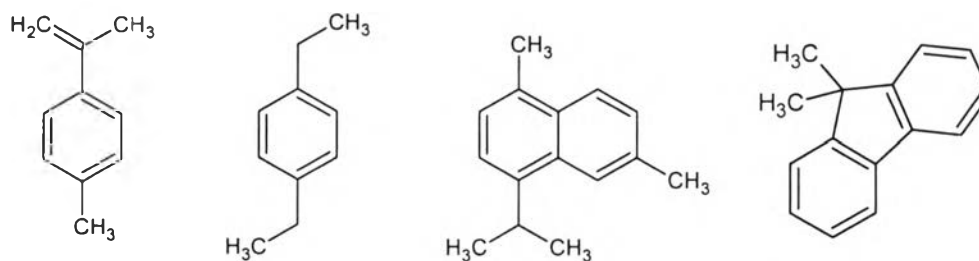


Figure 5.3 (a) Carbon number distributions in maltenes, and (b) Concentration of petrochemicals in maltenes.

Table 5.1 Some C10 and C15 hydrocarbons in maltenes

Compounds	Formula	%Area*	
		No catalyst	Al-MCM-48
1,2-dihydronaphthalene	C ₁₀ H ₁₀	0.26	0.14
1-butyn-1-ylbenzene	C ₁₀ H ₁₀	1.01	0.85
1-isopropenyl-4-methylbenzene	C ₁₀ H ₁₂	0.17	0.00
Cyclopropylphenylmethane	C ₁₀ H ₁₂	0.11	0.00
1,4-diethylbenzene	C ₁₀ H ₁₄	0.14	0.07
1-isopropyl-2-methylbenzene	C ₁₀ H ₁₄	1.45	0.68
1-methylphenanthrene	C ₁₅ H ₁₂	0.15	0.13
9,9-dimethyl-9H-fluorene	C ₁₅ H ₁₄	0.22	0.19
4-isopropyl-1,6-dimethylnaphthalene	C ₁₅ H ₁₈	0.07	0.03
1-phenyl-1-nonyne	C ₁₅ H ₂₀	0.13	0.00

*% Area of compounds in the carbon number of C10 and C15 in maltene determined by GCxGC-TOF/MS

**Figure 5.4** Examples of C10 and C15 hydrocarbons found in maltenes.

5.5 Conclusion

The use of Al-MCM-48 catalyst resulted in the enhancement of petrochemicals in tire-derived oil (from 3.4 wt.% to 7.6 wt.%). Moreover the Al-MCM-48 enhanced the selectivity of benzene, toluene, and ethylbenzene. The enhancement of petrochemicals production was possibly resulted from cracking of C10 and C15 hydrocarbons on the acid sites.

5.6 Acknowledgements

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5.7 References

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