CHAPTER IV

ENHANCED SULFUR REMOVAL FROM TIRE-DERIVED OIL USING ALUMINOSILICATE MCM-48 WITH PYROLYSIS OF WASTE TIRES

4.1 Abstract

MCM-48 (Mobil Composition of Matter number 48) is a cubic-structured mesoporous silica material widely used in many applications such as separation and catalysis. The addition of alumina atoms into the framework of MCM-48 can generate the acid sites suitable for cracking reaction. This work investigated the waste tire pyrolysis by using Al-MCM-48 synthesized via a hydrothermal method as a catalyst. The pyrolysis of waste tire was conducted in a bench-scale reactor. The catalyst was characterized by using small- angle XRD, BET, XRF and TGA. In addition, the products were analyzed by using GC-FID and S analyzer, while a GC×GC-TOF/MS was used to analyze the species in oils. The components in pyrolytic oil were classified into 7 groups; that are, paraffins (p), olefins (ole), naphthenes (nap), mono-aromatics (mono), di-aromatics (di), poly-aromatics (poly) and polar-aromatics (polar). The results showed that Al-MCM-48 decreased the concentration of naphthene and di-aromatics in the oil. It indicates that Al-MCM-48 promoted ring-opening of di-aromatics and aromatization of naphthenes. In addition, Al-MCM-48 catalyst gave 5 percent sulfur reduction in oil. Moreover, sulfur species can be devided into groups of thiophenes (Th), benzothiophenes (BT), dibenzothiophenes (DBT), benzothiazoles (BTz), and isothiocyanates (ITC). An outstanding result Al-MCM-48 can reduce all groups of sulfur-containing compounds, except BTs.

4.2 Introduction

Waste tires, indegradable materials, are difficult to manage. The lifetime of waste tires in a landfill span in the period of 80 -100 years (Martínez et al., 2013). Therefore, pyrolysis of waste tires is an interesting process to transform waste tires to valuable products, such as gas and oil. Normally, vulcanization is one of tire

manufacturing steps, which the addition of sulfur compounds, such as benzothiazole (Llompart *et al.*, 2013), into rubbers is performed to form bonds between rubbers chains to improve the mechanical properties of tires. As a result, sulfur compounds are present in the products of waste tire pyrolysis. Previously, it was found that tire-derived oil has a sulfur content of 1.22 wt.% (Yuwapornpanit and Jitkarnka, 2015). Tire-derived oil, comprised of a high sulfur content, are not proper for using directly as vehicle fuels because of SO_x emission and the worldwide pollution controlling regulation. Therefore, several researchers studied desulfurization in oils. Unapumnuk *et al.* (2008) investigated two parameters: temperature and heating rate, affecting the sulfur removal from tire-derived oil. They observed that the heating rates did not affect on sulfur content whereas desulfurization increased with increasing the temperature from 350 to 400 °C. Furthermore, the zeolites (HMOR, HZSM-5, and HBETA) can reduce sulfur content in tire-derived oil, reported by Muenpol *et al.* (2015). The authors found that the straight channel of HMOR can remove sulfur from tire-derived oil better than the zigzag channel of HBeta. Additionally, the medium pore of HZSM-5 gave a high sulfur removal than the larger pore of HBeta. Moreover, mesoporous molecular sieves, Al-MCM-41 with various Si/Al ratios, were used as adsorbents to desulfurize the commercial diesel fuel (Liu *et al.*, 2007). The authors observed that sulfur removal can be ranked in the order: Al-MCM-41(50) > Al-MCM-41(30) > Al-MCM-41(100), indicating that the adsorption capacity of sulfur-containing compounds depends on the amount of Lewis acidic sites. A strong interaction between sulfur-containing compounds with Lewis acidic sites help to increase the adsorption capacity over Al-MCM-41. The introduction of alumina atoms into the framework of Si-MCM-41 can generate the acid sites. In addition, mesoporous molecular sieves, such as MCM-48 and MCM-41 have been used as catalysts in pyrolysis of waste tire. Dũng *et al.* (2009a) observed that MCM-41 improved the valuable gas products, ethylene and propylene. The MCM-41 gave a narrow carbon number distribution in tire-derived oil in the range of $C_{10}-C_{20}$, whereas the carbon number distribution of non-catalytic case was broad in the range of C_5-C_{50}. Additionally, the concentration of poly- and polar-aromatic hydrocarbons decreased, resulting in the increasing concentration of mono-aromatics. The MCM-41 catalyst promoted the activity of cracking large molecules due to its large pore

size, similar to MCM-48 catalyst as reported by Witpithomwong *et al.* (2011). MCM-48 also improved the yield of ethylene and propylene, and promoted activity of cracking bulky molecules, indicating that mesoporous can improve quality of tire-derived oil. The purpose of this work was therefore to investigate the potential of Al-MCM-48 catalyst in waste tire pyrolysis in terms of the quality and quantity in tire-derived oil. Additionally, sulfur compounds in oils were determined by using GCxGC-TOF/MS.

4.3 Methodology

4.3.1 Waste Tire Sample and Catalyst Preparation

A waste tire, Bridgestone TURANZA GR-80, was prepared as the samples in pyrolysis. It was shredded by a cutting machine, and sieved for tire samples with a particle size range of 40-60 mesh. The Al-MCM-48 (starting Si/Al of precursors = 75) was synthesized via hydrothermal synthesis method (Huang *et al.*, 2008), with tetraethoxysilane (TEOS), aluminum isopropoxide, and cetyltrimethylammonium bromide (CTAB) as the silica source, alumina source, and templating agent, respectively. 9.56 g of CTAB was dissolved in 170 ml of deionized water at 35 °C. Then, 3.15 g of NaOH was added into previous solution and stirred for 10 min. After that, 29.07 ml of TEOS and 0.34 g of alumina source were added and stirred for 2 h at 35 °C. Then, the gel composition was transferred to a Teflon-lined autoclave and heated at 120 °C for 40 h. The solid product was filtrates and washed with deionized water. Next, the catalyst 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.

4.3.2 Catalyst Characterization

The X-ray diffraction pattern of a sample was obtained using a Rikagu TTRAXIII diffractometer equipped with Cu Kα radiation at 50 kV and 300 mA. The experimental conditions were set with 0.02° of sampling width, 2°/min of scan speed, and 2.0-6.0° of scan angles. The nitrogen adsorption/desorption isotherm, pore size distribution, pore diameter, specific surface area, and pore volume were

measured by using a ThermoFinnigan/Sorptomatic 1990 instrument. The Si/Al ratio of catalyst was determined by the X-ray fluorescence (XRF) instrument combined with AXIOS&SUPERQ version 4.0 systems. The IQ+ program was used to analyze the composition of catalyst. Thermogravimetric/Differential Thermal Analysis, TG/DTA was used to determined the amount of coke formation on spent catalyst. The temperature was ramped from 50 to 900 °C with heating rate 10 °C/min. LECO®Elemetal Analyzer (TruSpec®S) was used to measure the sulfur content in spent catalyst.

4.3.3 Pyrolysis of Waste Tire

The same pyrolysis system was employed in the experiments, following the method set by Dũng et al. (2009b). 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.

4.3.4 Product Analysis

The composition of gas was analyzed by using a Gas Chromatography, Agilent Technologies 6890 Network GC system, using HP-PLOT Q column: 30 m x 0.32 mm ID and 20 µm film thickness. A detector used was FID type. n-pentane was added into a liquid product in the liquid product/n-pentane weight ratio of 40:1 for 18 h to separate asphaltene out using a 0.45 um Teflon membrane in a vacuum system, and then obtained maltene solution. The components in maltenes were characterized by using a two-dimensional Gas Chromatography with Time of Flight Mass Spectrometer (GCxGC-TOF/MS) instrument, Agilent gas chromatograph 7890 system, combinded with a cryogenic modulator and a LECO Pegasus 4D TOF/MS. The simulating true boiling point curves of maltene solutions were determined by using a Varian GC-3800 simulated distillation gas chromatograph (SIMDIST-GC),

using ASTM D2887 method. The true boiling point curves were cut into petroleum fractions; that are, 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).

4.4 Results and Discussion

4.4.1 Catalyst Characterization

Figure 4.1 shows the small-angled XRD (SAX) pattern of Al-MCM-48. There are two peaks at $2\theta = 2.5°$ and $2\theta = 3.0°$, corresponding to (211) and (220) diffractions, which indicates that the Ia3d group (Kosslick et al., 1998). Moreover, the d_{211}/d_{220} ratio of 0.86-0.87 can confirm that the catalyst has a cubic symmetry (Danumah et al., 2001). The nitrogen adsorption/desorption isotherm and pore size distribution are shown in Figures 4.2a and 4.2b. Figure 4.1a illustrates that Al-MCM-48 has type IV isotherm that corresponds to mesoporous material. Moreover, Al-MCM-48 has pore size distribution in the range of 2-10 nm, whereas the average pore diameter calculated from the BJH method is 2.69 nm. In addition, the Si/Al ratio, specific surface area, pore volume, and pore diameter of Al-MCM-48 catalyst are shown in Table 4.1.

Table 4.1 Si/Al ratio and physical properties of Al-MCM-48

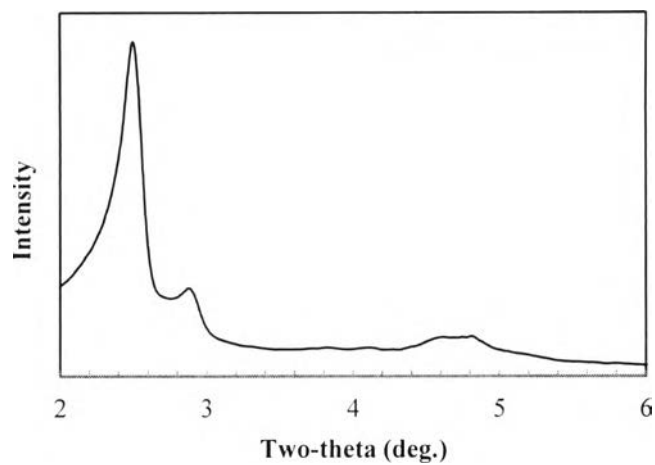| Catalyst	XRF	N_2 Sorption		
	Si/Al Ratio	Specific Surface Area (m^2/g)	Pore Volume (cm^3/g)	Pore Diameter BJH (nm)
Al-MCM-48	42	1,468.4	1.1	2.69

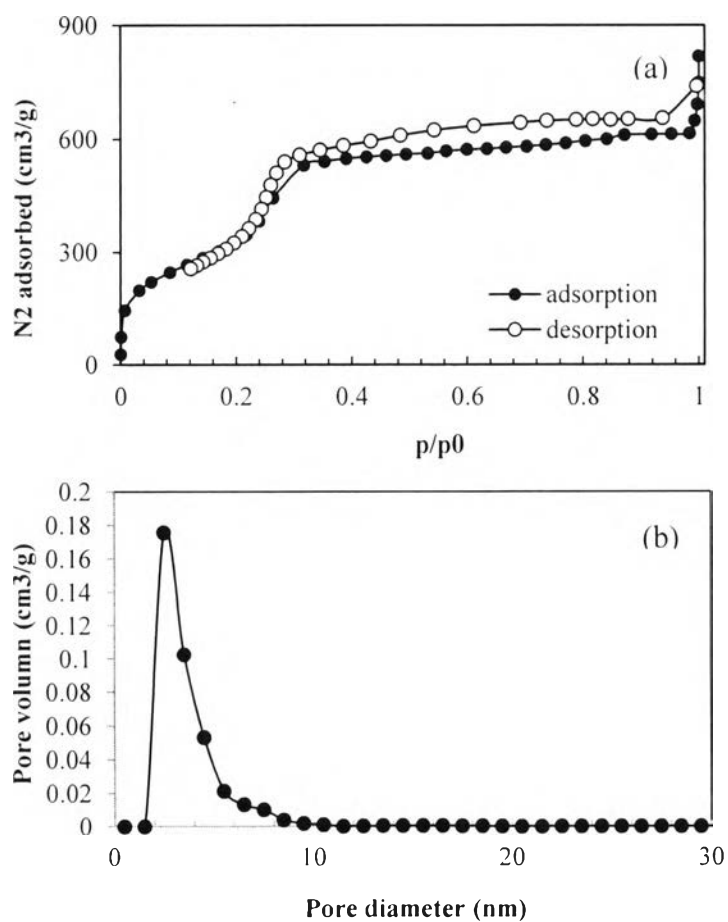**Figure 4.1** SAXS pattern of Al-MCM-48.

Figure 4.2 (a) Adsorption and desorption isotherms of nitrogen on Al-MCM-48 catalyst, and (b) Pore size distribution curve of Al-MCM-48.

4.4.2 Effect of Al-MCM-48 on Pyrolysis of Waste Tire

The distribution of pyrolysis products is shown in Figure 4.3a. It can be observed that Al-MCM-48 decreased the liquid yield due to the coke formation on the spent catalyst. Figure 4.3b shows petroleum cuts in maltene obtained from Al-MCM-48. It illustrates that the light fractions, including full range naphtha, kerosene, and light gas oil increased, whereas the heavy fraction, including heavy gas oil and long residue decreased. It can be ascribed that Al-MCM-48 promoted cracking of heavy liquid product into lighter liquid products. Figure 4.3c shows the components in maltene, which were classified into 7 groups; that are, paraffins (p), olefins (ole), naphthenes (nap), mono-aromatics (mono), di-aromatics (di), poly-aromatics (poly) and polar-aromatics hydrocarbons (polar). The Al-MCM-48 reduced the concentration of naphthenes and di-aromatics, whereas the concentration of mono-aromatics is increased, indicating that Al-MCM-48 promoted ring-opening of di-aromatics and aromatization of naphthenes. In the gas, the yield of methane decreases, whereas that of the others does not change significantly as compared to non-catalytic case.
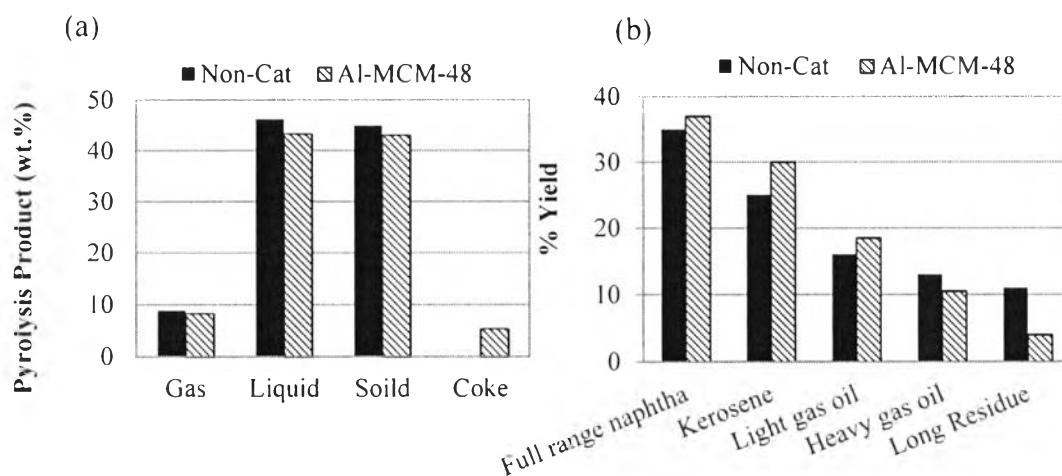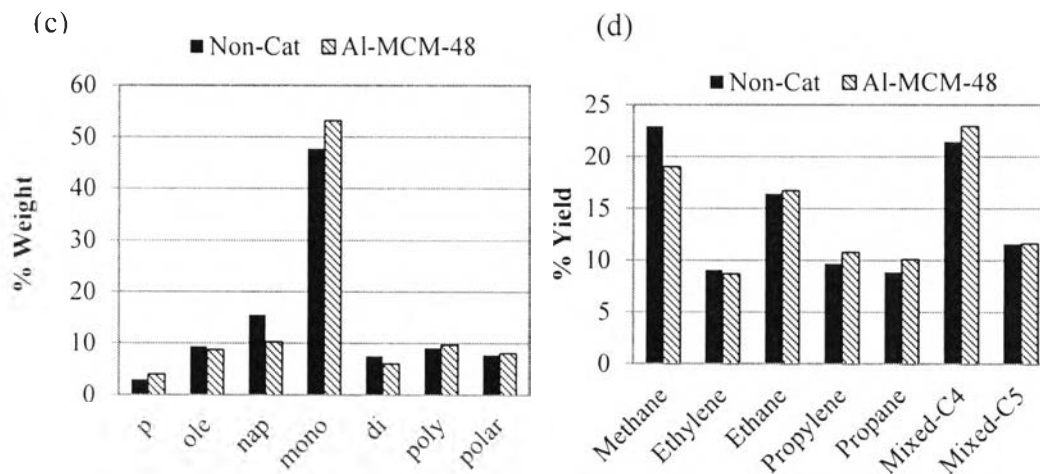
Figure 4.3 (a) Product distribution, (b) Petroleum cuts, (c) Concentration of each group of components in maltene, and (d) Gas composition.

4.4.3 Sulfur Removal Activity

Table 4.2 reports that the sulfur content in oil is reduced from 1.27 to 1.12 wt.% by using Al-MCM-48 catalyst. In addition, the sulfur distribution in pyrolytic products are shown in Figure 4.4a, which illustrates that for thermal pyrolysis more than 50 % of sulfur from tire is distributed in char whereas 30 % of sulfur is distributed in oil, and 18 % is distributed in gas. The use of Al-MCM-48 catalyst can help to reduce 5 % of sulfur in oil, with the increasing percentage of sulfur distributed on the spent catalyst, indicating that Al-MCM-48 can help C-S bond to break. Sulfur-containing compounds in maltenes were categorized into five groups; that are, thiophenes (Ths), benzothiophenes (BTs), dibenzothiophenes (DBTs), benzothiazoles (BTz), and isothiocyanates (ITC). It can be noticed that Al-MCM-48 can reduce all groups of sulfur-containing compounds (except BTs) as shown in Figure 4.4b. Table 4.3 reports the dominant sulfur-containing compounds in each group determined by GCxGC-TOF/MS. It is found that benzothiazole and isothiocyanato-benzene are the main sulfur compounds in the tire-derived oil, which is similar to Choi *et al.* (2014). The presence of sulfur compounds in tire-derived oil is caused by sulfur compounds used in the vulcanization process in the manufacture of tires. In addition, the presence of nitrogen compounds in the oil is resulted from

the degradation of accelerators, such as N,N-diisopropyl-2-benzothiazole-sulfenamide (Quek *et al.*, 2013) during pyrolysis of waste tire.

Table 4.2 Weight percentage of sulfur content in oils and spent catalyst

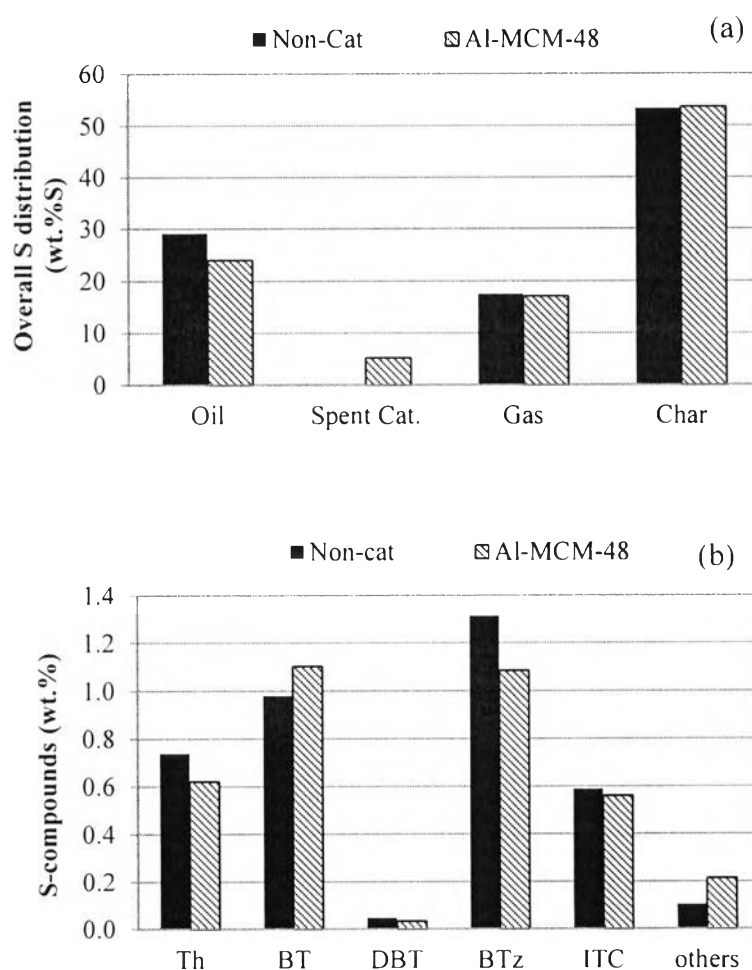| Catalyst	wt.% Sulfur	
	Oil	Spent Catalyst
No catalyst	1.27 ± 0.04	-
Al-MCM-48	1.12 ± 0.03	0.34 ± 0.01

Figure 4.4 (a) Overall sulfur distribution in pyrolytic products, and (b) Sulfur-containing compounds in maltenes.

Table 4.3 Dominant sulfur-containing compounds of each group

Group of Sulfur-containing Compounds	Compounds	Formula	%Area* No catalyst	%Area* Al-MCM-48
Th	Thiophene, 2-(1-methylethyl)-	$C_7H_{10}S$	0.1949	0.1284
	Thiophene, 2-methyl-5-propyl-	$C_8H_{12}S$	0.0785	0.0709
BT	3-Methylbenzothiophene	C_9H_8S	0.2893	0.3350
	Benzo[b]thiophene, 2,7-dimethyl-	$C_{10}H_{10}S$	0.2230	0.2641
DBT	Dibenzothiophene, 4-methyl-	$C_{13}H_{10}S$	0.0165	0.0155
	Dibenzothiophene	$C_{12}H_8S$	0.0125	0.0084
BTz	Benzothiazole	C_7H_5NS	1.0768	0.8480
	Benzothiazole, 2-methyl-	C_8H_7NS	0.2065	0.2180
ITC	Benzene, isothiocyanato-	C_7H_5NS	0.5504	0.4781
	Benzene, 1-isothiocyanato-2-methyl-	C_8H_7NS	0.0216	0.0215

4.5 Conclusions

Aluminosilicate MCM-48 catalyst was used in waste tire pyrolysis to investigate its effect on the quality of tire-derived oil. It was illustrated that Al-MCM-48 gave lighter liquid product due to the increase of full range naphtha and kerosene fractions. Moreover, Al-MCM-48 increased the selectivity of mono-aromatics due to ring-opening of di-aromatics and aromatization of naphthenes. In addition, the sulfur content in oil of Al-MCM-48 was reduced from 1.27 to 1.12 wt.%.

4.6 Acknowledgements

4.7 References

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