CHAPTER II
LITERATURE REVIEW

2.1 Waste Tire Pyrolysis Products

The pyrolysis products consist of gas, tire-derived oil, and char. Moreover, the tire-derived oil is a remarkable product in the process. Previously, Pithakratanayothin and Jitkarnka (2014) revealed the components in tire-derived oil that was determined by using comprehensive 2D gas chromatography with time-of-flight mass spectrometry (GC x GC-TOF/MS), which is a powerful instrument to separate the complex mixture. More than 1,500 compounds were found in the maltene solutions. Thus, the components in oils were categorized into 7 groups; that are, paraffins (p), olefins (ole), naphthenes (nap), mono-aromatics (mono), di-aromatics (di), poly-aromatics (poly) and polar-aromatic hydrocarbons (polar). The main components in tire-derived oil are aromatic hydrocarbons. Moreover, sulfur compounds are also present in the tire-derived oil.

2.1.1 Non-Aromatics

Paraffins or saturated hydrocarbons are hydrocarbon compounds that consist of only single bonds. Paraffins that have lower than 5 carbon atoms per molecule are gases such as methane (CH_4), ethane (C_2H_6), propane (C_3H_8) and butane (C_4H_{10}). For liquid phase, paraffins have more than 5 carbon atoms per molecule. Additionally, paraffins have two structures, straight chain and branched chain. Moreover, paraffins and cyclic paraffins are the main compounds in gasoline (Pera et $al.$, 2012). The branched chain structures have a higher octane number, which has a good antiknocking property.

Olefins or unsaturated hydrocarbons contain at least one double bond or triple bond between carbon atoms. Light olefins (e.g. ethylene (C_2H_4), propylene (C_3H_6), butane (C_4H_8)) are widely used in the chemical industry. For instance, ethylene and propylene are used to make a polymer. Butadiene is used to produce tires, plastic, and papers. Moreover, liquid olefins can be used in many applications.

For examples, hexene and octene can be used as comonomers in a polyethylene production. Decene, dodecene, and tetradecene can be used as a lubricant.

2.1.2 Aromatics

Tire-derived oil consists of about 73.2 wt.% aromatic hydrocarbons in maltenes. The group of mono-aromatic hydrocarbons is the main compounds that consist of 34.9 wt.% in maltenes (Yuwapornpanit and Jitkarnka, 2015). Some mono-aromatics in tire-derived oil are valuable products such as benzene (C_6H_6), toluene (C_7H_8), xylenes (C_8H_{10}), ethylbenzene (C_8H_{10}), and cumene (C_9H_{12}) (Figure 2.1) that are widely used in petrochemical industry. For examples, benzene is used for coating, printing and extracting. Furthermore, it is used as a raw material for production of plastics. Toluene is used as an octane booster to improve the performance of machines. Some applications of xylenes are similar to benzene, which are used for printing and painting. Ethylbenzene is primarily used in the manufacture of styrene. Cumene is mainly used as a raw material in the manufacture of phenol and acetone. Moreover, large aromatic hydrocarbons (di- and poly-aromatic hydrocarbons) were found about 25 wt.% in maltenes (Yuwapornpanit and Jitkarnka, 2015). Moreover, Laresgoiti *et al.* (2004) found polycyclic aromatic hydrocarbons such as naphthalene, fluorene, phenanthrene and biphenyl in tire-derived oil by using fluidized-bed pyrolysis units. Furthermore, the amount of polycyclic aromatic hydrocarbons also increased with increasing pyrolysis temperature (Cunliffe and Williams, 1998). The presence of heavy aromatics in fuels is concerned due to incomplete combustion. Thus, they can damage to the health of humans and animals (Environmental Protection Agency, 2008).
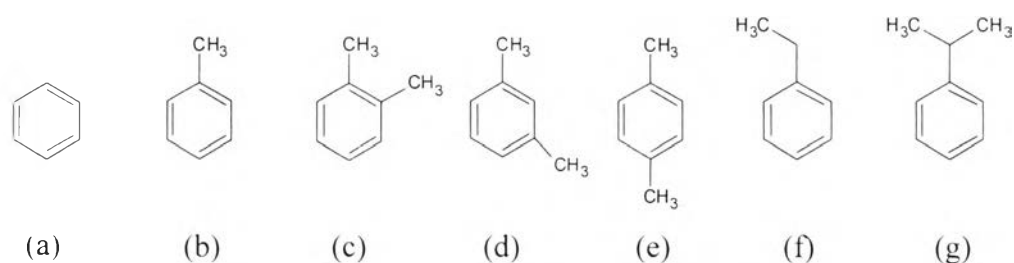

Figure 2.1 Structures of petrochemical (a) benzene, (b) toluene, (c) o-xylene, (d) m-xylene, (e) p-xylene, (f) ethylbenzene, and (g) cumene.
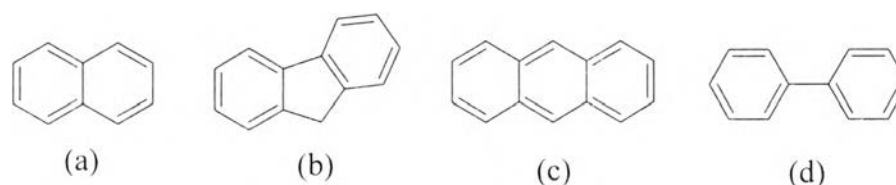
Figure 2.2 Structures of polycyclic aromatic hydrocarbons (a) naphthalene, (b) fluorene, (c) phenanthrene, and (d) biphenyl.

2.1.3 Sulfur Compounds

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. Therefore, sulfur compounds are present in the products of waste tire pyrolysis. Sulfur compounds in pyrolytic gas were found such as SO_2, H_2S, COS, CS_2, and CH_3SH (Zhang *et al.*, 2008; Hu *et al.*, 2014). Moreover, sufur species in tire-derived oil were found such as benzothiophene, dibenzothiophene, 2-methylthiophene, 3-methylthiophene, 2-ethylthiophene, 2,5-dimethylthiophene, 2,4-dimethylthiophene, 2,3-dimethylthiophene, 3-ethylthiophene, 2-isopropylthiophene, 2-tert-butylthiophene and benzothiazole (Williams *et al.*, 1995; Chen *et al.*, 2010; Benallal *et al.*, 1995). The presence of sulfur compounds in tire-derived oil are not proper for using directly as vehicle fuels because of SO_x emission and the worldwide pollution controlling regulation. Thus, hydrotreating or desulfurization is very important to improve the quality of oils.

The sulfur in pyrolytic products can be removed during pyrolysis process. The effect of heating rate and pyrolysis temperature were studied in range of 350-1000 °C and 1–10 °C/min, respectively by Unapumnuk *et al.* (2008). The sulfur was highly removed with increasing temperatures from 350 to 400 °C. In range of 400 to 1000 °C, the desulfurization capability was almost constant. Moreover, heating rate did not affect to the sulfur removal. Thus, the desulfurization of the pyrolytic products can be accomplished by setting up the suitable condition of a pyrolysis reactor.
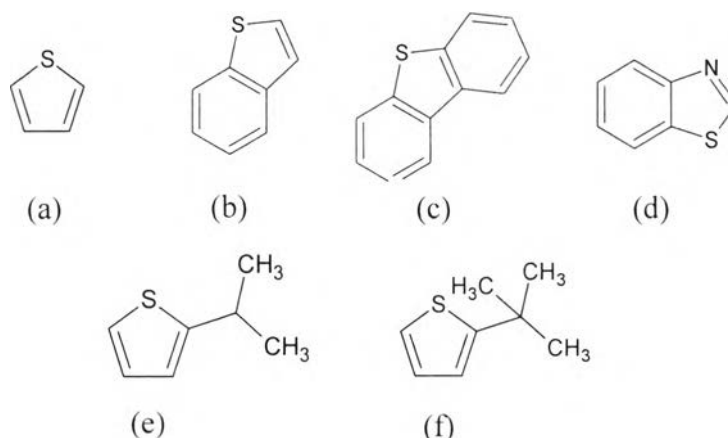
Figure 2.3 Structures of some sulfur compounds in tire-derived oil:

(a) thiophenes, (b) benzothiophene, (c) dibenzothiophene, (d) benzothiazole,

(e) 2-isopropylthiophene, and (f) 2-tert-butylthiophene.

In summary, tire-derived oil has some drawbacks such as high concentrations of large aromatic hydrocarbons and sulfur compounds. In order to increase the quality of oil, catalysts are necessary to enhance the quality and quantity of valuable products.

2.2 Mesoporous Materials

Mesoporous materials have large pore sizes with the diameter range of 2-50 nm. They are widely used in many applications such as separation and catalysis. Normally, MCM-41 and MCM-48 are popular mesoporous materials due to high surface area, pore volumn, and uniform structure. Mesoporous molecular sieves, MCM-41 and MCM-48, were successfully synthesized during 1990s by the researchers at Mobil Oil Corporation. Moreover, the pore diameter was controlled by surfactant as a pore directing agent. The structure of MCM-41 is a one-dimension material that consists of an array of hexagonal channel, and MCM-48 has three-dimension cubic structure (Figure 2.4).
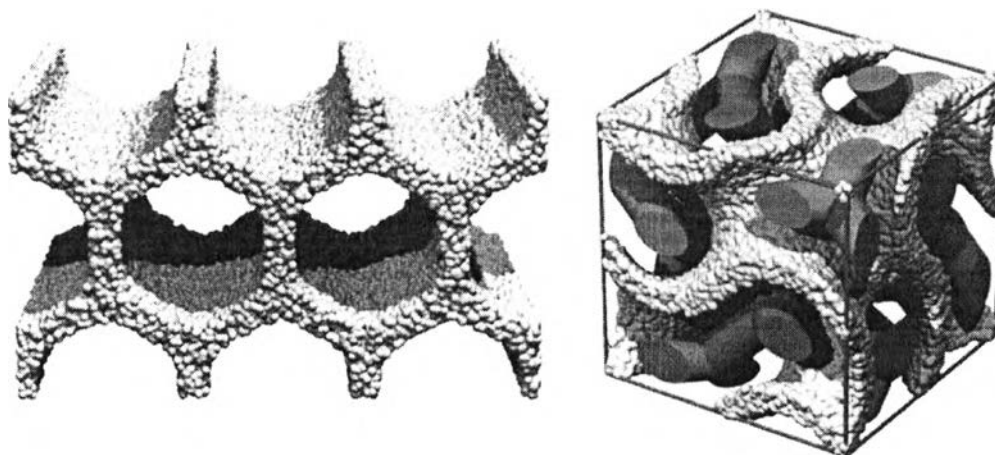
Figure 2.4 Structure of MCM-41without surfactant (left) and MCM-48 with surfactant (right) (Van *et al.*, 2008).

Dung *et al.* (2009a) studied mesoporous silica MCM-41 as a catalyst in waste tire pyrolysis. They found that MCM-41 gave the valuable gas products, which are ethylene and propylene. In tire-derived oil, MCM-41 catalyst decreased the carbon number distribution from C5-C50 for the non-catalytic case to C10-C20. Additionally, the concentration of poly- and polar-aromatic hydrocarbons decreased, resulting in the increasing concentration of mono-aromatics. It can be seen that the MCM-41 catalyst promoted the activity of cracking large molecules due to its large pore size, 26.1Å, 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 in terms of removal of large molecules from the oil. Moreover, MCM-48 has ability to remove sulfur in tire-derived oil, resulting in the increasing sulfur deposited on the spent catalyst. The mild cracking activity of MCM-48 helped C-S to break.

Additionally, Park *et al.* (2008) used Si-MCM-48 and Al-MCM-48 (Si/Al = 30 and 60) as catalysts for the degradation of polypropylene. The introduction of Al atoms creates acid sites on the catalyst so the order of acidity can be ranked as Al-MCM-48 (30) > Al-MCM-48 (60) > Si-MCM-48. The authors found that conversion via catalytic degradation of large molecules of polypropylene was higher than via thermal degradation. Moreover, Al-MCM-48 promoted cracking activity more

greatly than Si-MCM-48, resulting in the narrower carbon number distribution of oil product. Similarly, Jeon *et al.* (2007) used mesoporous MCM-48 as a catalyst for degradation of linear low density polyethylene (LLDPE). In oil products, Al-MCM-48 generated C_7-C_{10} hydrocarbons while Si-MCM-48 generated broader distribution of oil products in the range of C_8-C_{14} hydrocarbons. Therefore, higher acid sites showed the good performance for degradation of large molecules of polymers. On the other hand, mesoporous MCM-48 was used as a catalyst for hydrocracking process (Alsobaai *et al.*, 2007). They found that Al-MCM-48 (25) that has the highest total acidity provided the highest conversion of gas oil to diesel production.

Furthermore, aluminosilicate mesoporous materials with various Si/Al ratios have been used as absorbents to remove sulfur in the 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 depended 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. Moreover, Nasab *et al.* (2014) studied Si-MCM-41 for adsorption of benzothiophene from model oil. They found that the large surface area of mesoporous MCM-41 has a capability to adsorb more than 42% benzothiophene from model oil.

According to above research works, mesoporous can allow the large molecules go through inside the pores and promoted the activity of cracking large molecules into smaller molecules. Moreover, the high acid density of mesoporous is also important to promote a higher cracking activity in the case of degradation of polymers and hydrocracking process. In terms of sulfur removal, mesoporous can highly adsorb sulfur compounds due to its large surface area and acid sites.
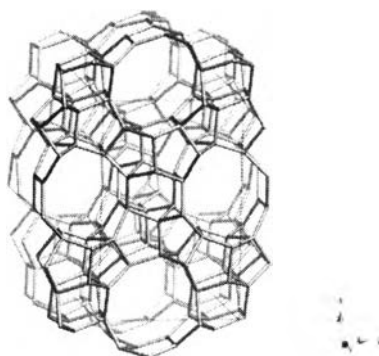
2.3 Zeolite Catalysts

Previously, many researchers studied zeolites as catalysts in waste tire pyrolysis to improve the quality and quantity of pyrolytic products. The valuable mono-aromatic hydrocarbons are desired products for using zeolites as catalysts. The properties of zeolite are shown in Table 2.1.

Table 2.1 Properties of zeolites

Zeolite	Pore Size (Å)	Channel System	Membered Ring
HZSM-5	5.3×5.6	3D	10
HY	7.4	3D	12
HBeta	6.4×7.6	3D	12

HZSM-5 zeolite has the pore size of 5.3 x 5.6 Å. It is a three dimensional channel with 10-membered rings. Olazar *et al.* (2008) reported that HZSM-5 has very strong acid sites, so it highly promotes cracking activity and provides a higher amount of gas. Moreover, in terms of oil, the medium pore size of HZSM-5 promoted the activity of cracking single-ring aromatics C_{10-}, and produced the higher amount of non-aromatic $C_5 - C_{10}$. Additionally, olefins can be condensed to generate cycloparaffins, cycloolefins, isoparaffins, and BTX over HZSM-5 catalyst (Arandes *et al.*, 2000). but HZSM-5 cannot promote the formation of large aromatics due to the limitation of pore size. Muenpol *et al.*, 2015 also studied a medium pore size of HZSM-5 catalysts on pyrolytic products. The author revealed that HZSM-5 reduced mono-aromatic hydrocarbons and sulfur in oil. Moreover it has a high selectivity to produce cyclohexane.

Figure 2.5 HZSM-5 zeolite structure (http://www.iza-structure.org/).

HY zeolite has the pore size of 7.4 Å. It is a three dimensional channel with 12-membered rings. Wehatoranawee (2011) used HY as a catalyst in waste tire pyrolysis. The author found that HY enhanced ethylene and propylene in gaseous products. Moreover, HY enhanced saturated hydrocarbons and reduced di- and polar-aromatic hydrocarbons in oil. Recently, Yuwapornpanit and Jitkarnka (2015) also used HY zeolite as a catalyst in pyrolysis of waste tire. The results showed that HY increased the amount of mono- and di-aromatic with decreasing the amount of poly-aromatic hydrocarbons. Moreover, HY selectively produced petrochemical products, especially benzene and toluene. In terms of sulfur species, HY highly reduced benzothiazoles.
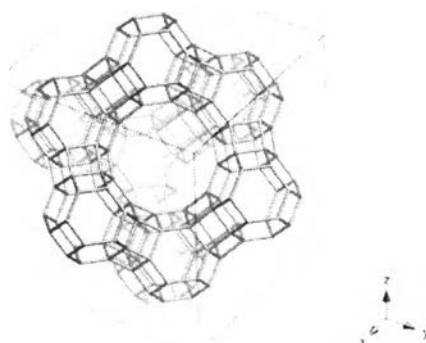
Figure 2.6 HY zeolites structure (http://www.iza-structure.org/).

HBETA zeolite has the pore size 6.4×7.6 Å. It is three-dimension with 12-membered rings. HBETA was used as a catalyst in waste tire pyrolysis by Wehatoranawee (2011). The author found that HBETA promoted the high cracking activity due to the high Si/Al ratio. Moreover, HBETA zeolite gave high amount of polar-aromatics hydrocarbons due to the high acid strength. Choosuton (2007) also used HBETA catalyst in the pyrolysis waste tire. In the gas products, the mixed C_4 and mixed C_5 were highly produced. For liquid products, HBETA reduced di- and poly-aromatics owing to acid sites on catalyst, leading to high the concentration of total aromatics in range of gasoline. Recently, it has been found that HBETA highly

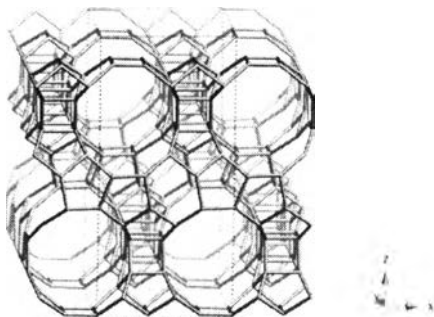produced benzene and ethylbenzene and also reduced sulfur in oils (Yuwapornpanit and Jitkarnka, 2015).

Figure 2.7 HBETA zeolites structure (http://www.iza-structure.org/).

2.4 Research Motivation

According to the literature review, mesoporous can handle large molecules due to its large pore size. In order to improve the quality of tire-derived oil in terms of large aromatic hydrocarbons reductions, mesoporous MCM-48 are necessarily used as a catalyst. Moreover, Al-MCM-48 catalyst that was introduced alumina atoms into silica framework, generating acid sites, was expected to enhance desulfurization in oils. Furthermore, the components such as in tire-derived oil by using mesoporous MCM-48 have not been identified in the previous work.

However, the large pore size of catalyst does not have a shape-selectivity to enhance some desired products. Previously, many researchers found that zeolites highly produced mono-aromatic hydrocarbons, especially HZSM-5, HBETA, and HY, had high selectivity to produce the valuable mono-aromatic hydrocarbons. Therefore, it is interesting to use the combination of mesoporous and microporous as a catalyst. In this work, mesoporous Si-MCM-48 was placed as a lower bed catalyst to promote activity of cracking large molecules. Then, the smaller products from the Si-MCM-48 bed can easily pass through the bed of zeolite. It might be further promoted cracking reaction into valuable mono-aromatic hydrocarbons.
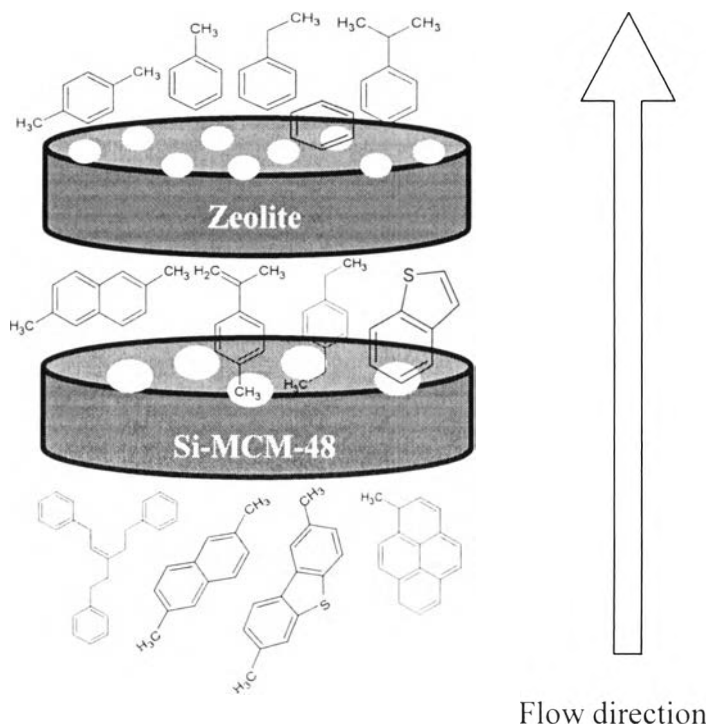
Figure 2.8 Schematic of the double bed of catalyst.

2.5 Objectives

1. To investigate the effect of acid density of mesoporous MCM-48 on tire-derived oil, petrochemicals, and desulfurization

2. To investigate single bed of Si-MCM-48 and double beds of catalysts on tire-derived oil, petrochemicals, and desulfurization.

2.6 Scope of Research

The scope of this research covered as follows:

a.   A waste tire, Bridgestone TURANZA GR-80, was shredded with a particle size range of 40-60 mesh

b.   The pyrolysis of waste tire was conducted in a bench-scale reactor. For reaction condition, N_2 flow rate, particle size of catalysts, heating rate, reaction time, and the amount of waste tire were fixed at 30 ml/min, 40-60 mesh, 10 C/min, 2 h, and 30 g, respectively.

c. For the first part, Si-MCM-48 and Al-MCM-48 catalysts (starting Si/Al of precursors = 50, 75, and 200) were used

Experiments are designed as shown in the Table below:

Mesoporous Material with Different Si/Al Ratios			
Si-MCM-48 (-)	Al-MCM-48 (50)	Al-MCM-48 (75)	Al-MCM-48 (200)

d. For the second part, the single bed of Si-MCM-48 and double beds of catalysts were used. Mesoporous Si-MCM-48 was placed as a lower bed catalyst (first layer) while a zeolite was placed consecutively as an upper bed catalyst (second layer). The effects of zeolites properties; that are, acidity (HBETA and HY) and pore size (HZSM-5 and HBETA), were investigated.

Experiments are designed as shown in the Figure below: