CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

Pyrolysis has been addressed as an attractive thermal process for eliminating waste tire problems while allowing energy recovery (gas, liquid fuel, and pyrolysis char). Special attention has been given to the liquid fraction due to a high concentration of valuable mono-aromatic such as petrochemical products. However, the main drawbacks are that the liquid product still highly contains large-size hydrocarbons, especially multi-ring aromatics, and hetero-atom such as sulfur and nitrogen, indicating that it cannot be directly use as the vehicle oil. In order to remove these compounds, the estimation of molecular diameter for designing the oil-upgrading catalysts is necessary needed. Moreover, the solid char has the recovery potential of low grade carbon black or as carbon adsorbent after applying an activation step. Therefore, it is possible that pyrolysis char can be use as a catalyst. The characterization of the obtained products is also reviewed. Details of all mentioned issues are discussed below.

2.1 Drawbacks of Pyrolysis Products

In order to convert waste tires to valuable products, pyrolysis is a feasible renewable technique. Because the degradation of waste tires is not easy, the pyrolysis of along polymer chains needs a heat source to decompose the polymer into small compounds at a high temperature under the absence of oxygen. Gas, oil, and char are the obtained products as seen Figure 2.1.

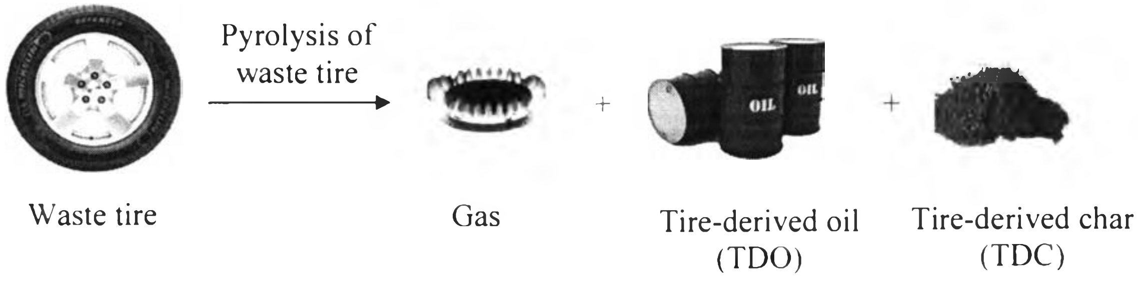


Figure 2.1 Pyrolysis products.

The gaseous product is normally made up to ~ 10-15 wt%, and mostly contain methane, ethane, and mixed C_4-C_5-hydrocarbons. However, its yield does not significantly difference as compared thermal decomposition to catalytic cracking reaction.

Tire-derived oil (TDO) seems to be the attractive product from tire pyrolysis because it can be used as a substance to produce gasoline, kerosene, etc. Furthermore. the petrochemicals (benzene, toluene, ethylbenzene, xylene, styrene, etc.) can be also obtained from this oil. Since asphaltene was still present in liquid product, it needed to be separated prior to analyze by GC. The obtained oil is called maltene. The results can solve the interference of the overlap peak of complex hydrocarbons (Dijkmans *et al.*, 2015). According to Pithakratanayothin and Sirirat (2014), the chemical components in maltene solution, analyzed using GCxGC/TOF-MS, were classified into 8 groups based on their structures; that are, saturated hydrocarbon (SATs), olefins (OLEs), naphthenes (NAPs), terpenes (TERs), mono-aromatics (MAHs), poly-aromatics (PAHs) and polar-aromatics (PPAHs) as shown in Figures 2.2-2.3.

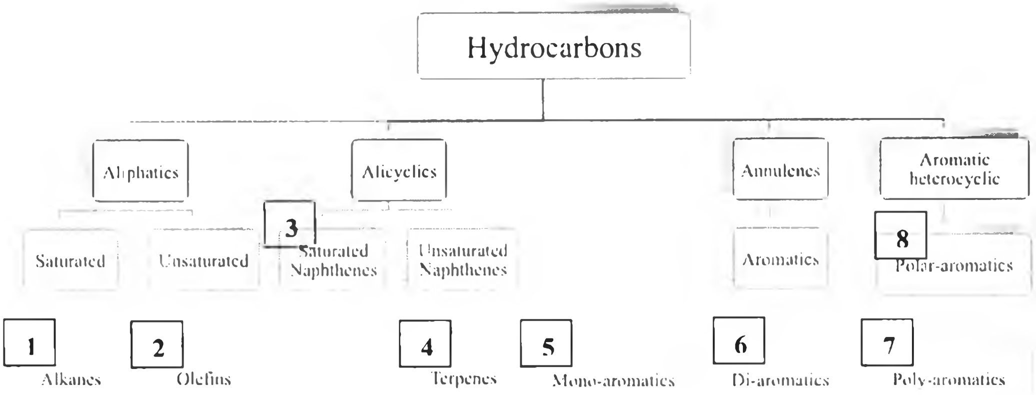


Figure 2.2 Classification of hydrocarbons in tire-derived oil (Pithakratanayothin, 2014).

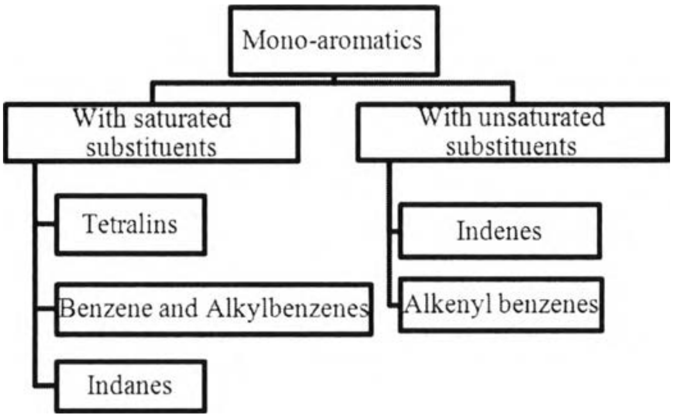


Figure 2.3 Classification of mono-aromatic group (Pithakratanayothin, 2014).

Nevertheless, the improvement of oil qualities is the important issue because heavy compounds especially multi-ring aromatics (DAHs, PAHs, and PPAHs) still remained in tire-derived oil from thermal pyrolysis, indicating that TDO cannot be directly used as vehicle fuel. Thus, TDO should be upgraded prior to use, especially the removal of multi-ring aromatic compounds and heavy fractions. Furthermore, there are some drawbacks from the degradation of waste tires because the obtained oil still contains hetero-atoms such as sulfur and nitrogen atoms. The presence of these atoms results from the degradation of accelerators, activators, retarders, and anti-degradants in tires. They are considered as undesirable products since they affect the environment problems, causing the formation of SOx and NOx. Moreover, they posed the effects in refining procedure in particular fouling, catalyst poisoning, equipment corrosion, and gum formation. The recent research works of (Pithakratanayothin, 2014) has already identified sulfur compounds by using GCxGC/TOF-MS as shown in Figure 2.4. The sulfur compounds can be classified in to 4 main groups; that are, thiophenes, benzothiophenes, dibenzothiophenes, and phenaleothiophene.

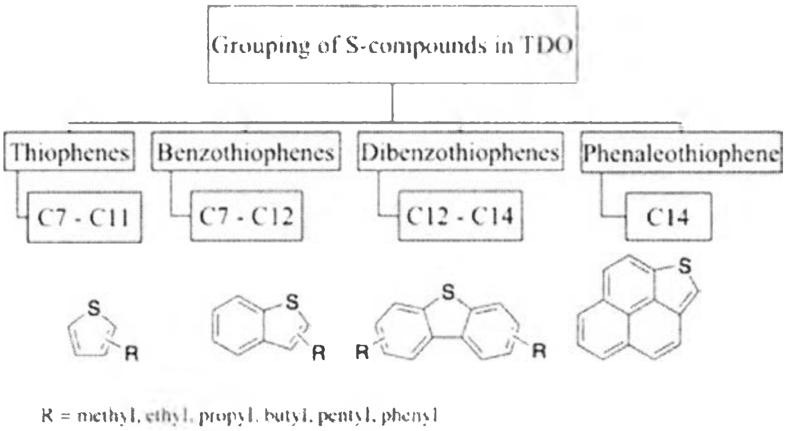


Figure 2.4 Classification of S-compounds in a tire-derived oil obtained from the non-catalyst batch (Pithakratanayothin, 2014).

Additionally, the waste solid or pyrolytic char from pyrolysis process, which is made up to 40-42 wt% of all thermalytic products, has few market outlets, reducing the economic viability. With environmental concern, pyrolytic char can provide valid opportunities to be an alternative resource to produce adsorbents for water and air purification, fuel materials, or catalyst supports after applying an activation step.

2.2 Catalyst Design

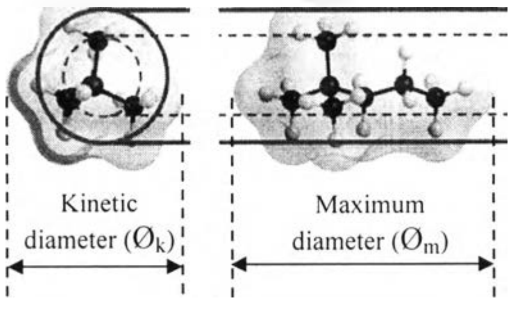


Figure 2.5 Kinetic and maximum diameters of hydrocarbons.

In order to convert heavy fractions into light products, the estimation of molecular sizes of hydrocarbons in tire-derived oil (TDO) is necessary for selecting an oil-upgrading catalyst with an appropriate pore size that can handle all molecules in the feed. Generally, kinetic diameter is commonly referred in catalysis literatures as the size of a molecule, which is used a criterion in selecting pore size of a selective catalyst. Since the TDO is a complex mixture of a large number of bulky molecules, the estimation of average molecular size is not simple, and has not been accomplished. Jae *et al.* (2011) suggested that if the value from literatures has not yet been available, the properties of a compound at the critical point including temperature. pressure, and volume, can be used to calculate its kinetic diameter. The estimation of the molecular size can be also determined from molecular weight; however, the method can be only applicable for a spherical molecule such as aromatic and symmetric compounds (Bird *et al.*, 2007). Furthermore, the molecular sizes can be estimated by using Lennard-Jones calculation (Marcus, 2003). However, Lennard-Jones parameters for evaluation are limited for bulky molecules, like in TDOs. Additionally, kinetic diameter can be observed from commonly available computational programs; for examples, Spartan'02 and GAUSSIAN 98 using quantum mechanic calculation for a complex mixture in gasoline (Jiménez-Cruz and Laredo, 2004), and Turbomole V6.5 electronic structure package using for simulation of kinetic diameter of small gaseous molecules (Mehio *et al.* 2014). For a multi-component mixture, the average kinetic diameter ($Ø_k$) of the compounds in the mixture is absolutely needed to describe the average molecular size. However, the maximum diameter ($Ø_m$) of a molecule, defined as the longest part of a molecule, can indicate the maximum size of catalyst pore that would allow the longest part of a molecule to pass through.

2.3 Mesoporous Materials

Many catalysts used in the pyrolysis process can increase the cracking of hydrocarbons into shorter chain lengths; then, decreasing the liquid products but increasing the gas evolved. Normally, the studies in waste tire pyrolysis require zeolites with a micropore structure. Their structure could imply the shape selectivity of the products (Jae *et al.*, 2011). Indeed, the TDO is the attractive product since it can be used as liquid fuel. However, the recent research work of Yuwapornpanit and Jitkarnka (2015) stated that the improvement of oil qualities was the important issue because 60-65 % of gas oil and vacuum gas oil, and especially 20-25 % of large-size aromatics (di-, poly-, and polar-aromatics) still remained in TDO in thermal decomposition and catalytic cracking (using normal zeolite, pore size < 8 nm) cases. It is reasonable to use mesoporous materials as a cracking catalyst for increasing the molecular diffusion inside the molecular sieve pore, where has a lot of active sites.

2.3.1 Meso-silica Materials

Mesoporous materials are defined as porous inorganic solids with a pore diameter in the range of 2–50 nm (Yang *et al.*, 1998). They have a large variety of properties with respect to composition, pore shape and particle morphology (Zhao *et al.*, 1998). Most mesoporous materials are in oxide forms, such as SiO_2, Al_2O_3, TiO_2 and ZrO_2, and their structures are usually cubic or hexagonal (Kartini *et al.*, 2004). Meso-silica type, which belongs to M41S and SBA families, is one of the molecular sieves as shown in Figure 2.6.

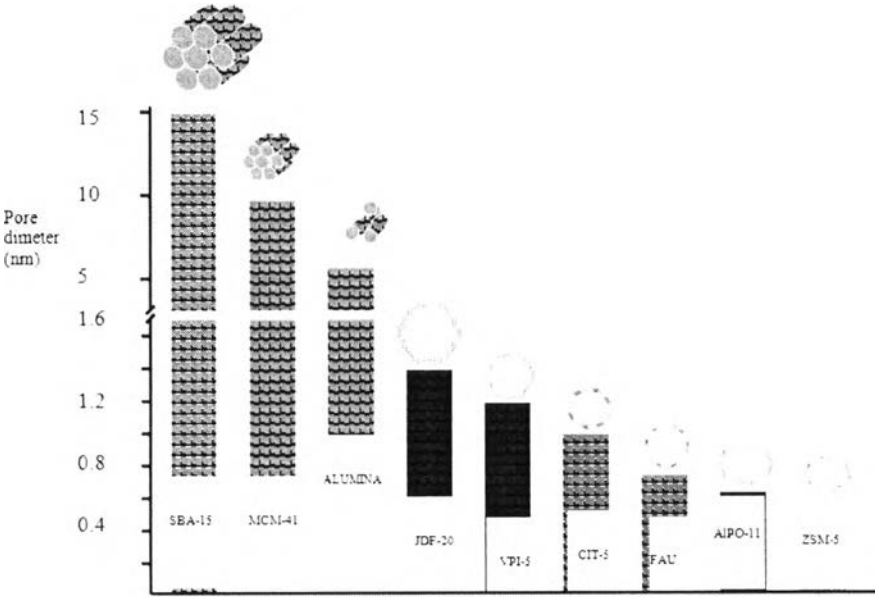


Figure 2.6 Different structural types of molecular sieves (Čejka, 2004).

2.3.1.1 Synthesis Methods and Characterizations of Meso-silica Materials

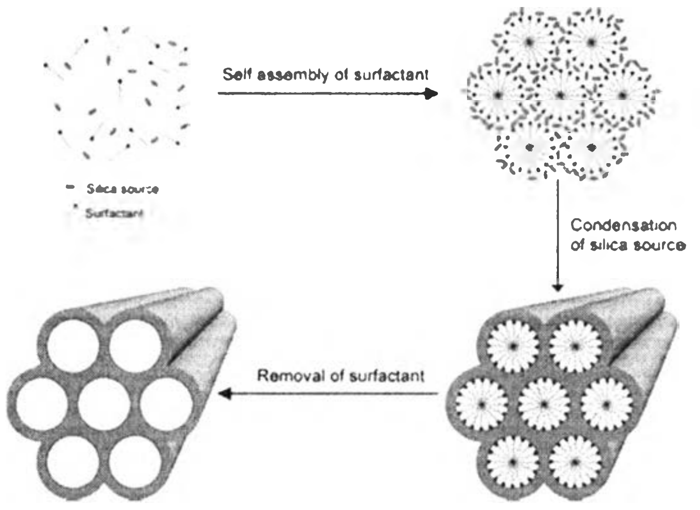
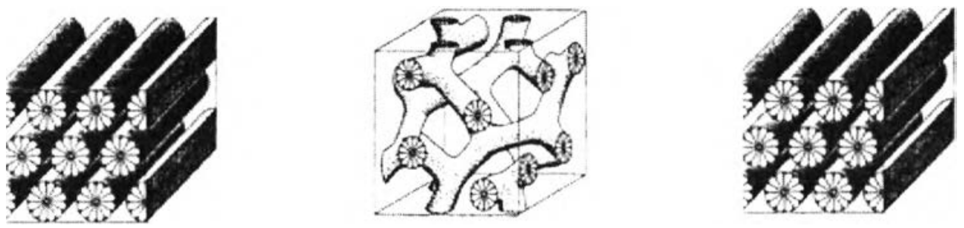


Figure 2.7 Self-assembly of MCM-41 (University of Strathclyde, 2010).

The concept of these approaches is to terminate the synthesis process after the synthesisis complete. The synthesis of mesosilica materials involves the formation of ion pairs between an oligomer silicate and a surface-determining agent. The surface-determining agent with ion pairs is the subsequent self-assembly of these ion pairs into ordered silicate-surfactant composites. Calcination of the silicate gel formed is used to remove the template for a mesoporous creation as shown in Figure 2.7. Normally, two chemical reactions, silicate hydrolysis and polycondensation, occur after the precipitation and liquid-crystalline templating process. The synthesis conditions have an influence on the rate of these reactions that can be accelerated or inhibited in an anisotropic manner of poly-condensation. Two directions could be specified along the pore radius. Moreover, these two reactions are responsible for a variety of material properties, including hydrothermal stability. When a surfactant template is carried out, pore in the material appear. The pores have an average intermediate shape between a cylinder and a hexagonal prism. Aqueous-alkaline solutions result in highly ordered substances with a hexagonal shape. However, the materials are characterized by a low hydrothermal stability. If the surface was coated by TEOS, the increasing wall thickness was observed. The silica species block the pores, making them inaccessible. A solution with a small degree of silica aggregation was applied on the effect of the reconstruction of the defective areas of the pore wall, resulting in increasing hydrothermal stability (Kirik *et al.*, 2014). Furthermore, pH is determined to be the most important of the investigated synthesis parameters in affecting pore ordering and meso-phase. The solubility and the rate of dissolution of silica increases with increasing pH. The increasing pH resulted in a decrease of the total interfacial area and a more long-range pore ordering (Daehler *et al.*, 2005). Voegtlin *et al.* (1997) found that high pH also provided fast and complete hydrolysis, where polymerization can occur within a few minutes. When the pH of the precursor solution decreased (higher acidity), it was observed that the intensity of diffraction peaks in the XRD pattern decreased, suggesting a considerable decrease of pore ordering (Ng *et al.*, 2013).



MCM-41
(Hexagonal Structure)

MCM-48
(Cubic Structure)

SBA-15
(Hexagonal Structure)

Figure 2.8 Structures of MCM-41, MCM-48 (Chena *et al.*, 2013), and SBA-15 (Wang *et al.*, 2001).

M41S is a group of Mobil researchers who discovered MCM-41 in 1992. Materials belonging to this family are hexagonal ordered pores such as MCM-41 and MCM-48, which has cubic ordered pores (Chena *et al.*, 2013) as shown in Figure 2.8. Six years later after MCM-41 was discovered, the University of California, Santa Barbara can produce silica nano particles with much larger pores 3.6 to 15 nm. The material was named "*Santa Barbara Amorphous*"-type material (SBA-15). This family of mesoporous silica is prepared with nonionic block copolymers as templates (Wang *et al.*, 2001). Its structure is hexagonal, which is similar to MCM-41 structure as seen in Figure 2.8.

MCM-41 and MCM-48 are composed of silica wall with uniform mesopore materials. These materials possess large surface areas, which can be up to more than 1,000 m^2g^{-1}. Pore diameter can be controlled within the mesoporous range between 1.5 to 20 nm by adjusting the synthesis conditions or by using surfactants with different chain lengths. Normally, MCM-41 and MCM-48 have been used for catalytic reactions, support of heterogeneous catalysts, and as adsorbents in wastewater treatment. Recently, the synthesis methods of MCM-41 and MCM-48 were developed to synthesize at room temperature by (Meléndez-Ortiz *et al.*, 2014; Kibombo *et al.*, 2014). The advantages are low energy usage, short-time aging, and uniform structure. The conditions were prepared in a base condition at room temperature by adding aq. NH_4OH and ethanol into the solution (surfactant + distilled water). Then, TEOS was added when the solution became homogeneous and subsequently age under continuous stirring condition at room temperature. The obtained solid was filtered with distilled water, dried and then calcined.

The small-angle XRD patterns, SEM, TEM of images MCM-41, MCM-48, and SBA-15 are displayed in Figures 2.9-2.10. MCM-41 is a one-dimensional mesoporous structure. A strong refraction at the (100) plane was used to confirm MCM-41 structure. The other peaks were also well resolved into (110), (200), and (210) planes as shown in Figure 2.9a (Meléndez-Ortiz *et al.*, 2014). Crystallinity of MCM-48 is shown in Figure 2.9b. The small-angle XRD diffractograms displayed the typical reflections at 2θ values of 2.8 (211) and 3.2 (220) and signals between 4.4 and 5.8 corresponding to the planes (321), (400), (420) and (332) (Kibombo *et al.*, 2014). Figure 2.9c showed the crystallinity of SBA-15. The small-angle XRD diffractogram displayed the typical reflections at 2θ values of (100), (110) and (200) (Almuhamed *et al.*, 2014).

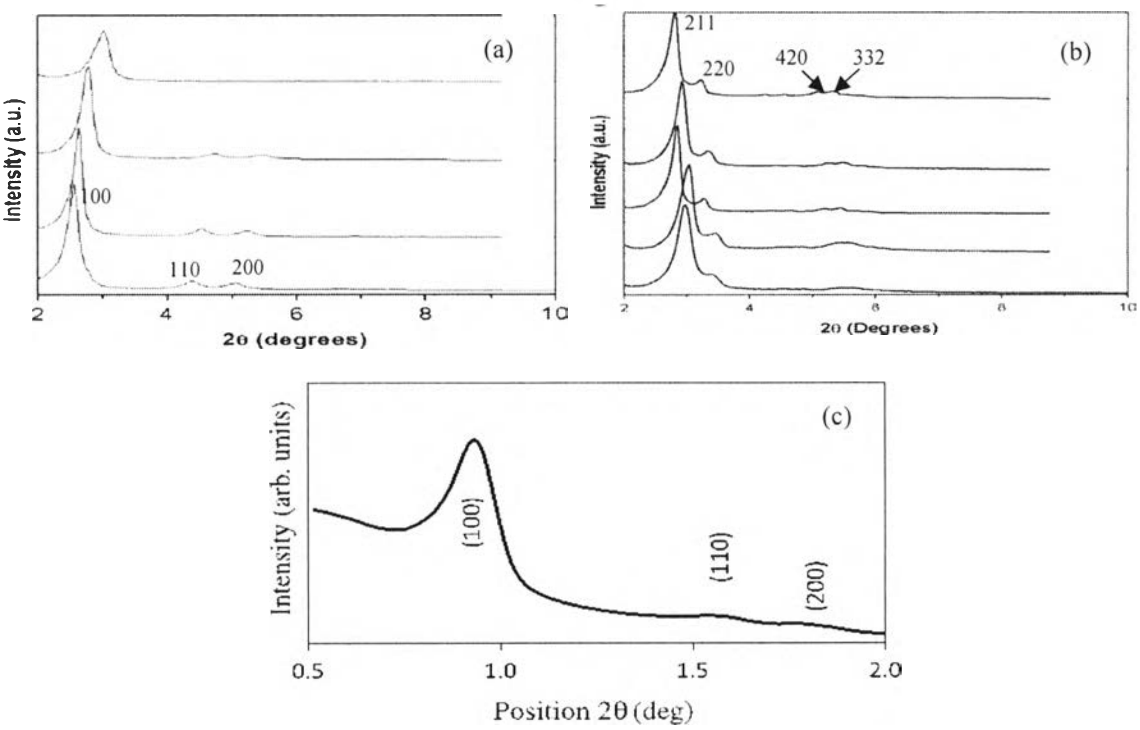


Figure 2.9 Small-angle XRD patterns of (a) MCM-41 (Meléndez-Ortiz *et al.*, 2014), (b) MCM-48 (Kibombo *et al.*, 2014), and (c) SBA-15 (Almuhamed *et al.*, 2014).

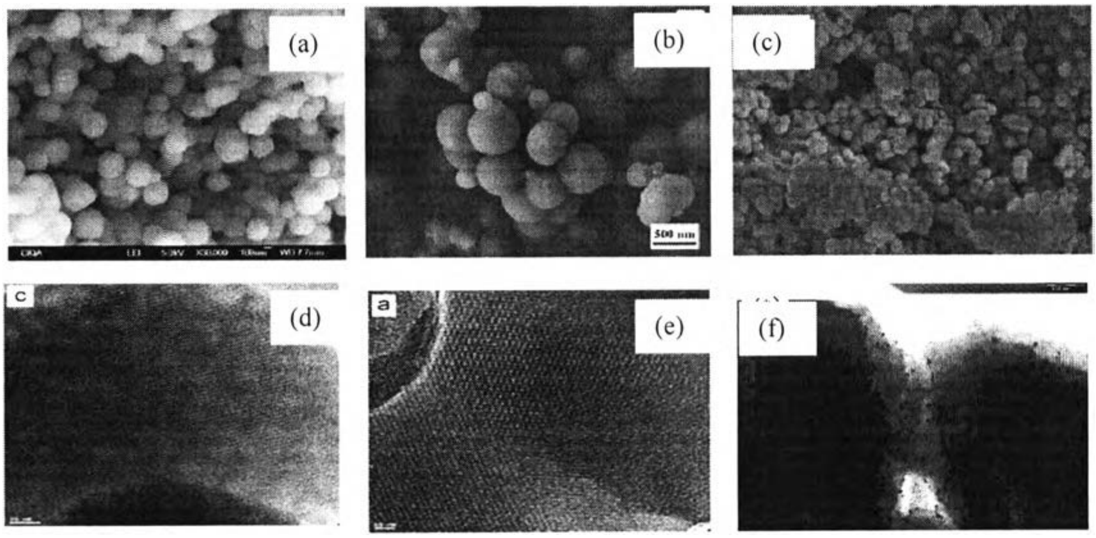


Figure 2.10 SEM images of of (a) MCM-41 (Meléndez-Ortiz *et al.*, 2014), (b) MCM-48 (Kibombo *et al.*, 2014), and (c) SBA-15 (Almuhamed *et al.*, 2014), and TEM images of of (a) MCM-41 (Meléndez-Ortiz *et al.*, 2014), (b) MCM-48 (Kibombo *et al.*, 2014), and (c) SBA-15 (Almuhamed *et al.*, 2014).

2.3.1.2 Catalytic Reactions of Meso-silica Matrials

MCM-41 was synthesized using a hydrothermal method in a NaOH solution with CTAB as a template (Jin *et al.*, 2012). The synthesis MCM-41 gave a high catalytic activity and good selectivity to monomer styrene for the catalytic cracking of polystyrene. The side reaction yields were ethylbenzene, isopropylbenzene, isopropenylbenzene and a secondary cross-linking product. Carrott *et al.* (2001) investigated the adsorption effect by varying the chain length of the surfactant, using TMA in the range of carbon C10-C18, and the molar ratios of reagents used were 1 TEOS: 0.145 surfactant: 2.96 NH_3: 155 H_2O. The results showed that longer chain lengths of surfactants gave a higher adsorption of nitrogen, neopentane, n-hexane, benzene and methanol. Furthermore, Jung *et al.* (2005) investigated the catalytic roles of pores over alkali-treated MFI zeolites. The alkali-treatment resulted in the loss of strong acid sites and the formation of mesoporous structure in the catalytic cracking of naphtha. It was shown that larger pore suppressed the production of longer alkanes to hexane and heptane by reducing further oligomerization. Larger pore size was not effective in enhancing overall alkene selectivity, due to the rapid elution of primary cracking products. Moreover, the effect of acidity was studied by Marcilla *et al.* (2005). They found that the difference of the product depended on the pore size of catalyst used. Another factor was acidity. The activity of catalyst was enhanced when its acidity was increased. Miguel *et al.* (2006) investigated the effect of catalysts on tire products. Three zeolites (standard ZSM-5, mono-crystalline n-ZSM-5 and BETA zeolite) and two mesoporous materials (Al-MCM-41 and Al-SBA-15) were used in this experiment. They found that all zeolites gave selectivity toward mono-aromatic compounds. The mesoporous catalysts gave a wide range of aromatic products, and exhibited stronger aromatization of benzene ring. For waste tire pyrolysis, the pure silica MCM-41 with a pore diameter of 2.61 nm at a catalytic temperature of 350 °C was used as a support because of the size of atomic molecules in TDO (Du˜ng *et al.*, 2009), especially the large molecules of poly-, polar-aromatics and saturated hydrocarbons. It was reported that the gas yield obtained from the MCM-41 was much higher than that produced from thermal pyrolysis. The obtained oil using MCM-41 had higher naphtha and kerosene but lower poly- and polar-aromatics. In addition, saturated hydrocarbons in the derived oil also decreased using MCM-41. These results showed the ability of cracking of MCM-41, which led to a dramatic increase in mono- and di-aromatic groups. Accordingly, MCM-41 caused the shifts of these compound distributions to a higher carbon number, indicating the formation of heavier aromatics. It is well accepted that aromatic hydrocarbons are not easy to be converted in a secondary cracking reaction.MCM-41 was also reported to favor the alkylation reaction of the previously-formed aromatic rings. Therefore, mono- and di-aromatics can be produced from the cracking of poly- and polar-aromatics and the alkylation of saturated hydrocarbons (Du˜ng *et al.*, 2009), which could be explained using the study by Miguel *et al.* (2006).

MCM-48 with a three-dimensional helical pore network and high thermal stability is in the same M41S series as MCM-41. Its pore size had been proven appropriate to crack large molecules of hydrocarbons and preserve light olefins formation (Du˜ng *et al.*, 2009). For waste tire-pyrolysis, MCM-48 was used as a support to improve light olefin and light oil productions as compared with non-catalyst. The results showed hydrocarbons chains tended to be cracked to the monomers, which also improved the content of methane, ethane, and especially C4-, and C5-hydro-carbons. For light olefins, ethylene and propylene in gas, MCM-48 gave a higher selectivity of propylene than that of ethylene. Moreover, MCM-48 increased mono-, and di-aromatics in accordance with decreasing saturated, poly-, and polar-aromatic hydrocarbons. In addition, MCM-48 insignificantly reduced the amount of sulfur in oil. This indicated the mild cracking activity of MCM-48 could break C-S bonds in the pyrolytic oil (Witpathomwong *et al.*, 2011).

SBA-15 with thick pore walls and high pore volume has better thermal and hydrothermal stability, resulting in high temperature resistance as well as acid–base tolerance. It is used in catalytic reactions (Johansson *et al.*, 2009), such asalkylations, oxidations, isomerizations, hydrogenations, esterifications, desulfurization and so on. The cracking behavior of asphaltene in the presence of iron catalysts supported on a mesoporous molecular sieve with different pore diameters was studied by Byambajay and Ohtsuka, (2003). They reported that asphaltene conversion increased almost linearly with increasing pore diameter up to 12 nm, and reached 65% by using Fe/SBA-15 with 10 %wt. loading of Fe. The pore structures of

Fe/SBA-15 catalysts were almost unchanged after cracking and subsequent re-calcination to remove deposited coke. To improve the quality of the oil, which was made from mixing biomass and tire pyrolysis, SBA-15 gave significantly better performance than MCM-41 and HZSM-5 for reducing the density and viscosity of the oil because of its larger pore size. Moreover, it could effectively decompose some large molecular compounds into small ones as well (Cao *et al.*, 2009). The catalytic activity of cumene cracking over AlSBA-15 with pore size of 12.55 nm was investigated by Gobara, (2012). He found that, when increasing the temperature, cumene was cracked to benzene. Ajaikumar *et al.* (2013) studied the effect of various catalysts on the isomerization of α-pinene. The authors showed that α-pinene was changed to 49.1 %wt. mono-aromatics, tricyclene, camphene, terpinolene and limonene, by using SBA-15. The functional group of –OH presented when the SBA-15 surface was used. Its surface could exchange ions with the surfactant, which could provide sulfur compounds attached at the surface as shown in Figure 2.11 (Cesarino *et al.*, 2007).

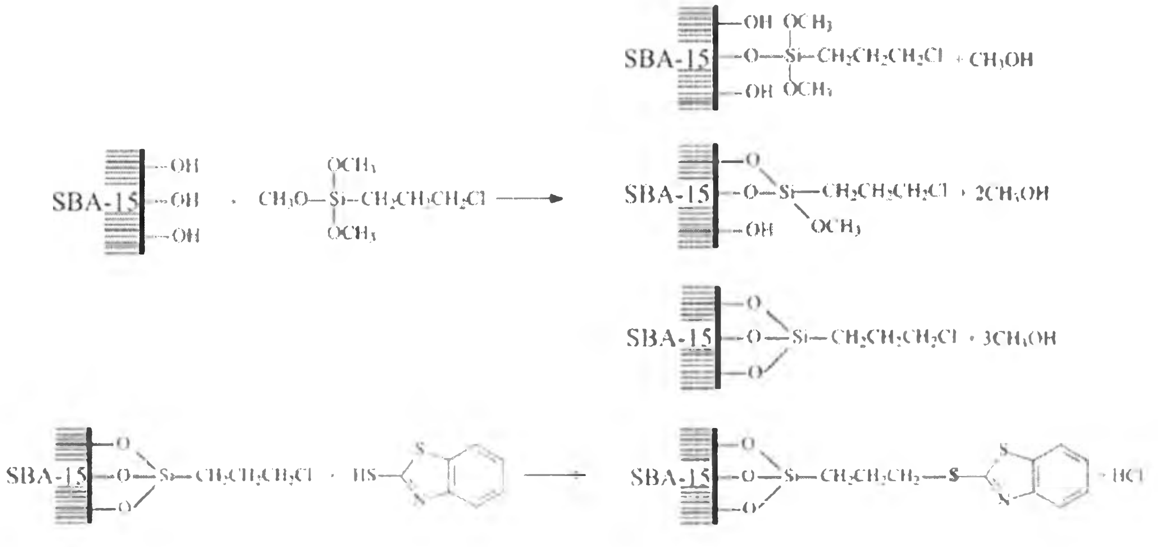


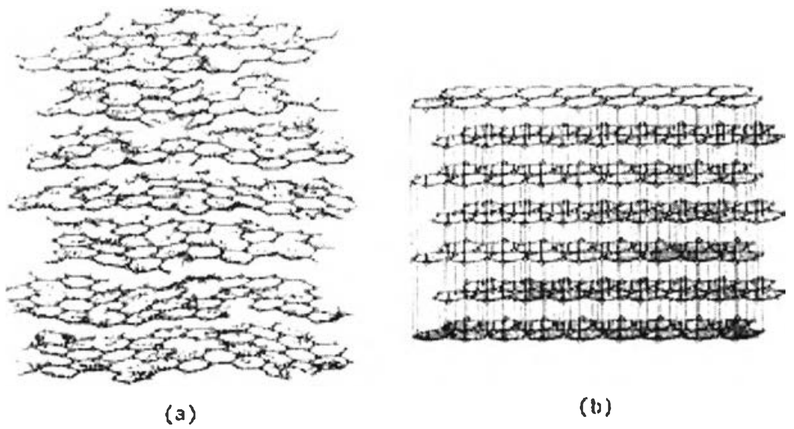
Figure 2.11 Adsorption of sulfur compound on the SBA-15 surface (Cesarino *et al.*, 2007).

From the observations, the effects of pore size between MCM-41 and SBA-15, and the effect of pore structure between MCM-41 and MCM-48 have not been studied in waste tire pyrolysis. To study these effects, MCM-41, MCM-48, and SBA-15 are used to investigate on identifying the deference of species especially the removal of di-, poly-, and polar-aromatics in tire-derived oil.

2.3.2 Pyrolysis Char

Another group of mesoporous material is carbon. The carbon residue of waste tire pyrolysis is one of them. Interesting things about this material are that it is inexpensive, and its activity can give the benefits for industry. It can be modified to have more activity by heat (Helleur *et al.*, 2001), acid, or base treatments (Soltani *et al.*,2014), which depends on the reaction used.

2.3.2.1 Treatment Methods and Characterizations of Pyrolysis Char



(a) (b)

Figure 2.12 Structure of (a) pyrolysis carbon and (b) graphite (On-X Life Technologies Inc, 2013).

Pyrolysis carbon is the solid waste obtained from waste tire pyrolysis. Generally, heating a hydrocarbon, nearly to its decomposition temperature, and permitting the graphite to crystallise produce pyrolysis carbon. Its structure is similar to graphite but covalent bonding between its graphene sheets shows imperfections in its production (Wikipedia, 2014). The crystalline pyrolytic carbon has a distorted lattice structure with random unassociated carbon atoms as seen in

Figure 2.12a, unlike, as an example, graphite as seen in Figure 2.12b. This structure provides it with isotropic properties that are similar in all directions. It exhibits excellent stability, strength, wear resistance, fatigue resistance, and biocompatibility graphite (On-X Life Technologies Inc, 2013).

Bunthid *et al.*(2010) analyzed the element composition of pyrolysis carbon, and found that the element composition mostly consisted of carbon and volatile matter, and contained a little amount of moisture. It was noted that it still contained sulfur compounds that need to be carefully used. The analyzed data are shown in Table 2.1.

Table 2.1 Elemental composition of pyrolysis carbon (Bunthid *et al.*, 2010)

Analysis	Waste Tire Powder (% w/w)
Proximate analysis (as received)	
Moisture	0.40
Volatile matter	67.1
Ash	5.70
Fixed carbon	26.8
Ultimate analysis (dry basis)	
Carbon	84.2
Hydrogen	7.9
Nitrogen	1.0
Sulfur	1.4
Oxygen	5.5
Gross calorific value (Mj/kg)	33.2

(a) Chemical Treatment

Soltani *et al.* (2014) found that mesoporous char from the pyrolysis of used cigarette filters was modified by using nitric acid to enhance its surface acidity. Nitrogen adsorption-desorption was used to confirm an average pore size of 3.24 nm, and a 57.8 % increase in the surface acidity compared to the non-modified char was further confirmed by Boehm titration method. Bernardo *et al.*

(2012) suggested using acidic leaching to increase polarity, which allowed the recovery of significant amounts of the pyrolysis oils trapped in the crude chars and improved the yield of the pyrolysis liquids. In order to decrease the ash content of the chars, a demineralization procedure using hydrogen peroxide was successfully applied, and high efficiency removals of the majority of the metallic elements were achieved. HNO_3-treatment of pyrolysis char resulted in the highest amount of the oxygenated functional groups, and sulfur removal, as compared with the un-treated, and the treatments with HCl, HCOOH, and H_2O_2. Furthermore, HNO_3-treatment was able to maintain pore structure than other acids.

(b) Thermal Treatment

Helleur *et al.* (2001) studied the potential applications of pyrolytic char from used tires. They found that activation using steam at 900 °C for 3 h produced an activated carbon with a good surface area of 302 m^2g^{-1}, and post-carbonization at 600 °C can remove unwanted odor and trace oil. This activated carbon had an excellent adsorption capacity for phenol and metal from the solution. However, Bernardo *et al.* (2012) confirmed the thermal analysis of char from the pyrolysis of mixed plastics, tire rubber, and forestry biomass wastes. They found that the residue non-combusted above 600 °C presented a stable weight that was considered to be ash.

2.3.2.2 Catalytic Reactions of Pyrolysis Char

The waste tire pyrolysis oil contained polycyclic aromatic sulfur hydrocarbons (PASH), which caused the production of toxic and corrosive SO_X in the exhaust gas during combustion (Williams and Bottrill, 1995). Thus, these are the main drawbacks and limits of using waste tire pyrolysis oil in a real combustion process. Firstly, it requires a desulfurization process to upgrade before use as a practical alternative liquid fuel. Activated carbon (AC) is an interesting renewable resource because of its financial and ecological costs in the oxidative desulfurization (ODS) process. Importantly, the problems of waste tire-derived char have been addressed. In order to remove sulfur containing species, same previous papers reported that the addition of AC combining with peroxideand adjusting the pH ~ 4 by formic acid for the ODS could enhance the removal of dibenzothiophenes

(DBT) from 25 % up to 82.3 % (Yu *et al.*, 2005). AC was also proven as an efficient adsorbent of sulfur-containing species in the gas phase, such as hydrogen sulfide, sulfur dioxide, and methyl mercaptans (Bandosz *et al.*, 2006).

2.4 Catalytic Mechanism

The vulcanization process during tire production connects of long chain polymers of isoprene, butadiene, and styrene–butadiene. They are cross-linked with sulfur bonds, and are further protected by additives. One of the earliest studies on the pyrolysis of rubber was done in 1929 when Midgley and Henne found that isoprene and dipentene were the dominating products. The production of these chemicals and other liquids, especially oils, from rubber pyrolysis had been studied over the years under many different conditions.

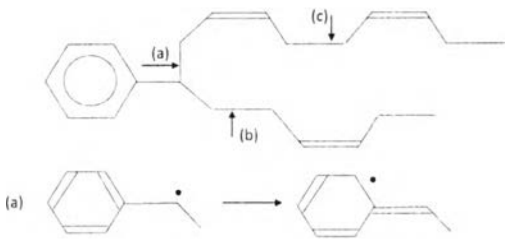


Figure 2.13 Possible scission position for C-C bonds in the SBR chain during pyrolysis and the resultant resonance aromatic structure for Position **(a)** (Choi, 2000).

Many attempts have been made to investigate the thermal degradation mechanism of rubber tires. Rubber polymers can be depolymerized through chain scission and side-group scission. Figure 2.13 shows the possible areas of analysis in a styrene–butadiene rubber polymer. In most cases, chain scission was found to be more preferable during the pyrolysis of natural rubber (Chen and Qian, 2002), polybutadiene (Uhl *et al.*, 2000), and styrene–butadiene rubber (Choi, 2000). Chen and Qian (2002) found that β-scission was preferred in the pyrolysis of natural rubber because of the low bond dissociation energy, leaving the allylic radicals out. Choi (2000) showed that for styrene–butadiene rubber, scission was favored to occur at positions **(a)** than at **(b)** or **(c)**, as shown in Figure 2.13. This is due to the higher stability of the resonance form due to the phenyl ring for the radical with the radical center on styrene, formed from the bond at **(a)**. The scission at position **(b)** and **(c)** does not produce an aromatic compound with resonance. In addition, decomposition reactions also occur concurrently with depolymerization during pyrolysis to produce short chain hydrocarbons (Chen and Qian, 2002).

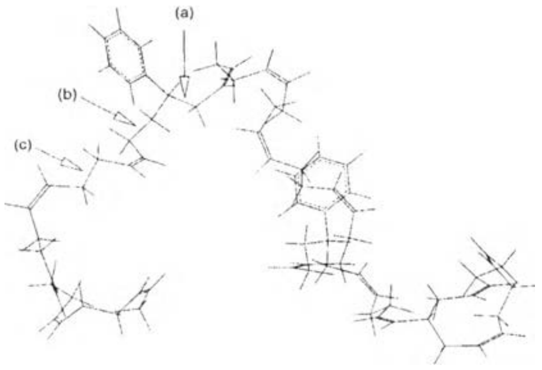


Figure 2.14 Energy-minimized structure of the model SBR (Choi, 2000).

The feasibility of cracking position also depends on the energy bonding as presented in Figure 2.14. Choi (2000) found that the average bond lengths of the **(a)**,**(b)**, and **(c)** linkages were 1.552, 1.545, and 1.543 Å, respectively. The length of the C-C bond formed between styrene and butadiene units was longer than the bond length formed between butadiene units. This suggests that the bond dissociation of the **(a)** linkage is more favorable than **(b)** and **(c)**. Actually, the complex structure of tire still makes it difficult to understand clearly the multi-reactions occurring in the pyrolysis reaction. Selecting a catalyst to depolymerize through chain scission and side-group scission by thermal cracking and hydrogenation reactions is interesting for discussion. Consequently, the size and structure of catalyst pores in the pyrolysis of waste tires should be large enough for the long chain of polymers to pass through inside with a long enough time to hold for thermal cracking and hydrogenation reactions.

In 2002, Seddegi *et al.* studied the catalytic cracking of high-density polyethylene over MCM-41. It was proposed that the acid sites were associated with the silanol groups that linked the channels. The adsorption of the polyethylene on the surface increased the basicity of the hydrocarbon fragment. Then, it promoted the protonation reaction by the silanol groups and stabilized the formation of carbenium ions. This implies that isobutene is a primary product of the cracking reaction because the skeletal isomerization of the butenes normally requires high acidity. Carbenium ion-mediated cracking over MCM-41 indicated the presence of an acidic surface. As the composition is pure silica, the nature of the acid site must be associated with the silanol groups linked the wall of the channels. Therefore, the silanol groups of the MCM-41 materials must be more reactive than in the case of amorphous silica, which could interact between the oxygen atoms and the hydrogen atoms from the linear polyethylenic chain. These interactions made the hydrocarbon fragment more basic. The reactive silanol group is shown in the following scheme.

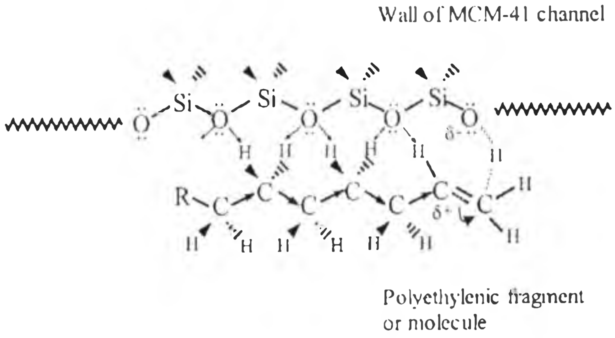


Figure 2.15 Hydrocarbons interaction with silanol group on MCM-41 surface (Seddegi *et al.*, 2002).

2.5 Identification of Nitrogenous Compounds in Tire-derived Oil

Nitrogenous compounds are considered as undesirable products since they affect the environment problems, causing the formation of NOx. Moreover, they posed the effects in refining procedure in particular fouling, catalyst poisoning, equipment corrosion, and gum formation. Thus, the identification of nitrogenous compounds is the first criteria to study prior to further treatment.

Mirmiran *et al.* (1992) characterized the nitrogenous compounds from the naphtha fraction of the used tire vacuum pyrolysis oil. This research divided naphtha fraction into three main groups; that are, hydrocarbon (mainly aromatics), oxygenate compounds, and nitrogenous compounds. The analytical separation technique relied on liquid-solid chromatography using dual packed silica gel and alumina column. The nitrogenous compounds were eluted with methanol. Thirty-one compounds were found by using gas chromatography/mass spectrometry (GC/MS) and confirmed by using gas chromatography/ atomic emission detection (GC/AED). The detected species were reported without grouping. The main nitrogenous compound in the naphtha fraction was pyridine. Furthermore, the fourier transform ion cyclotron resonance mass spectrometry (FTICP-MS) can be used to identify the elemental composition, bond equivalent, and carbon number based on ultra-high-resolution (Tong *et al.,* 2013, Oldenburg *et al.*, 2014, and Sim *et al.*, 2015). However, FTICP-MS is not the quantitative analysis, and its maintenance cost is the limitation on widespread availability. From the observations, the GC/MS might be the proper instrument for the classification of N-containing compounds in TDOs. Although the normal GC/MS can provide the detail on compositional information, the disadvantage is that it cannot interpret and resolve the overlap peaks of the complex hydrocarbon chromatogram. This is due to the several order of magnitudes of hydrocarbon matrix, their fragmentations can interfere with those of other hetero-compounds. Therefore, the comprehensive two-dimensional gas chromatography (GCxGC) is a lot more powerful for characterizing nitrogenous compounds (Flego and coworker, 2011). Even though the GCxGC is more powerful than other instruments, the hetero-atoms can still overlap with the complex hydrocarbons. To solve this interference, Dijkmans *et al.*, 2015 suggested to precipitating asphaltene out of the oil prior to analysis. Previously, Pithakratanayothin and Jitkarnka (2014) attempted to identify sulfur compounds and classify them by using the comprehensive two-dimensional Gas Chromatography with Time of Flight Mass Spectrometer (GC×GC/TOF-MS). The result showed that this method was able to overcome the limitation of chromatogram interpretation, which is better for detection each group of hetero-atom structures.

Furthermore, the obtained oil can be upgraded, aiming to remove the hetero-atoms, by using hydrated iron (III) chloride-clay adsorbent, hydrodenitrogenation (Wei *et al.*, 2015), ultrasound-assisted oxidative desulfurization process (Nunes *et al.*, 2014), and ionic liquid methods (Laredo *et al.*, 2015). Generally, the literature reported the nitrogenous compounds in diesel (Cheng *et al.*, 2004; Laredo *et al.*, 2015; Matzke *et al.*, 2015), crude (Flego and coworker, 2011; Oldenburge *et al.*, 2014; Sim *et al.*, 2015), coker gas (Wei *et al.*, 2015), and shale oils (Tong *et al.*, 2013; Dijkmans *et al.*, 2015). The derivatives of indole, carbazole, aniline, quinoline, pyridine, and benzothiophene were the major of nitrogenous compounds in the oils.

2.6 Research Motivation

According to literature review, Muenpol *et al.* (2015) and Yuwapornpanit and Jitkarnka (2015) reported the effects of HBETA and HY zeolites, respectively, on the yield and composition of products from the pyrolysis process. They found HBETA and HY zeolites reduced oil yield but increased gas yield. HBETA and HY zeolite gave a high total concentration of monoaromatics, especially benzene and styrene. Moreover, Boxieng *et al.* (2006) investigated the activity of USY on the concentration of single-ring aromatics in oil. USY gave a higher activity than ZSM-5 because of its larger pore size. From several studies, the pore size of zeolites is the most important factor for increasing the concentration of valuable light olefin and aromatic compounds. However, normal zeolites have pore sizes in the micro-pore range (< 2 nm), which limit bulky molecular diffusion and inner pore reactions. Thus, mesoporous catalysts that have larger pore sizes (2-50 nm) are investigated to allow the mass diffusion, which are expected of increase the cracking of the bulky molecules (di-, poly-, and polar-aromatics).

There were three main purposes of this study for the effects of the mesoporous materials (MCM-41, MCM-48, SBA-15, and pyrolysis char) on the catalytic pyrolysis of waste tire. Firstly, the average kinetic diameter of each group of molecules in a waste tire-derived product was determined in order to select a suitable pore size and structure of mesoporous materials. Secondly, the effects of various pore sizes and structures on the species in tire-derived oil were investigated.

Mesoporous materials can provide higher diffusion than micropore zeolites, which were expected to enhance the inner pore reactions. Moreover, the cubic structure, that is more complex than the hexagonal one, and its three-dimension structure may hold a longer retention time on the inner pore reactions. Finally, this is the first time that a treated pyrolysis char was used in waste tire pyrolysis in order to recycle waste solid product. If pyrolysis char has the ability to be a catalyst or a support in this process, it will be valuable in terms of cost and economy.

The prediction of possible products could be roughly done by measuring the average size of each group of components in products based on their kinetic diameters. It was found that HBETA zeolite can increase the yield of small groups of molecules, especially gas yield and mono-aromatics (Muenpol *et al.*, 2015). On the other hand, the large molecules of products (di-, poly-, and polar-aromatics) decreased less and gas oil and vacuum gas oil were still remained. There are many papers that have been published on the use of zeolite with micro-pore structure in the catalytic cracking process, which suggested that a micro-pore might be too small to convert large molecules to small molecules (Ajaikumar *et al.*, 2013).

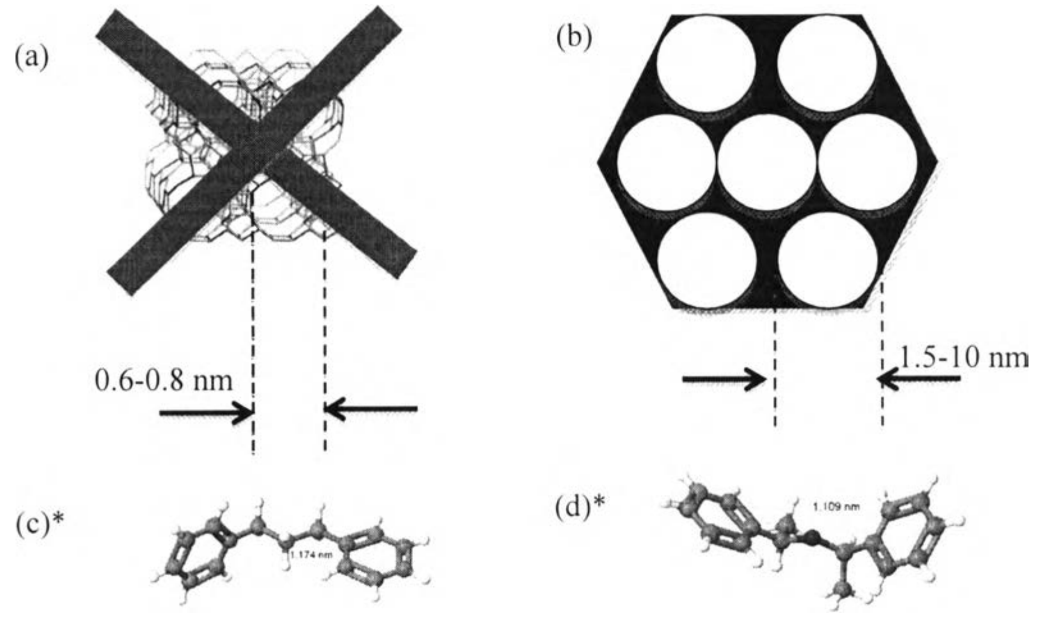


Figure 2.16 Pore sizes of (a) zeoilite and (b) Mesoporous, and the maximum diameter of (c) dibenzylmethane (PAHs) and (d) 1,1'-oxydiethylidene(bis)-benzene (PPAHs) (*Royal Society of Chemistry, 2015).

Consequently, if the smaller pore catalyst of normal zeolites limits the mass diffusion, considered by the kinetic diameter (Figure 2.15), a bigger pore catalyst would rather be used to solve this problem. Therefore, mesoporous materials were expected further enhance the concentration of valuable mono-aromatics (benzene, toluene, ethylbenzene, mixed-xylenes, styrene, and cumene) that are producted from the conversion of large molecules.

2.7 Objectives and Scopes of Research Work

There were 4 main objectives and scopes in this research work; that are,

Part 1: To estimate the average size of each group of molecular species in tire-derived oil based on their kinetic and maximum diameters for oil-upgrading catalyst design.

- The representative components from each group were first selected using the Yamane's method.
- The kinetic diameter ($\varnothing_k$) of all representative molecules were next calculated using its critical volume at critical point based on Joback method.
- The maximum diameter ($\varnothing_m$) were next evaluated using the published data from ChemSpider
- The average kinetic and average maximum diameters were subsequently determined
- The catalysts were finally designed.

Part 2: To investigate the possibility of using molecular sieves in waste tire pyrolysis by studying the effects of pore size and pore structure on product distribution especially the reduction of heavy fractions and multi-ring aromatics.

Pore size (Hexagonal structure)	Al-MCM-41	Commercial materials
	Al-SBA-15	
Pore structure (Pore size ~3 nm)	Si-MCM-41	Synthetic materials
	Si-MCM-48	

Part 3: To study the performance of pyrolysis char as a catalyst in waste tire pyrolysis and its effect on product distribution, especially the reduction of heavy fractions and multi-ring aromatics.

Pyrolysis char	Untreated char
	5MHNO$_3$-treated char

Part 4: To identify the N-containing species in tire-derived oil using the powerful GCxGC/TOF-MS for better understanding in further treatment.

- Three samples of tire-derived oil from thermal pyrolysis were sampled in this scope.
- The obtained liquid was first dissolved in n-pentane with the oil to n-pentane mass ratio of 1:40 for asphaltene separation. The obtained oil was called maltene.
- The 30 µL maltene was diluted in 2 mL carbondisulfide (CS$_2$) prior to analyze.

There were 9 experiments to be performed for this work with the controlled parameters as follows:

- The used tires, Bridgestone TURANZA GR-80, were cut and sieved into particle size range of 20-40 mesh.
- Pyrolysis of scrap tire was performed in a bench-scaled autoclave reactor.
- Process conditions; that are, holding time, N_2 flow rate, heating rate, pyrolysis zone temperature, catalytic zone temperature, and the weights of scrap tire and catalyst were fixed to 30 min, 30 ml/min, 10 ^{o}C/min, 500 ^{o}C, 350 ^{o}C, 30 g and 7.5 g (ratio of tire per catalyst = 4:1), respectively.