# CHAPTER II
THEORETICAL BACKGROUND AND LITERATURE REVIEW
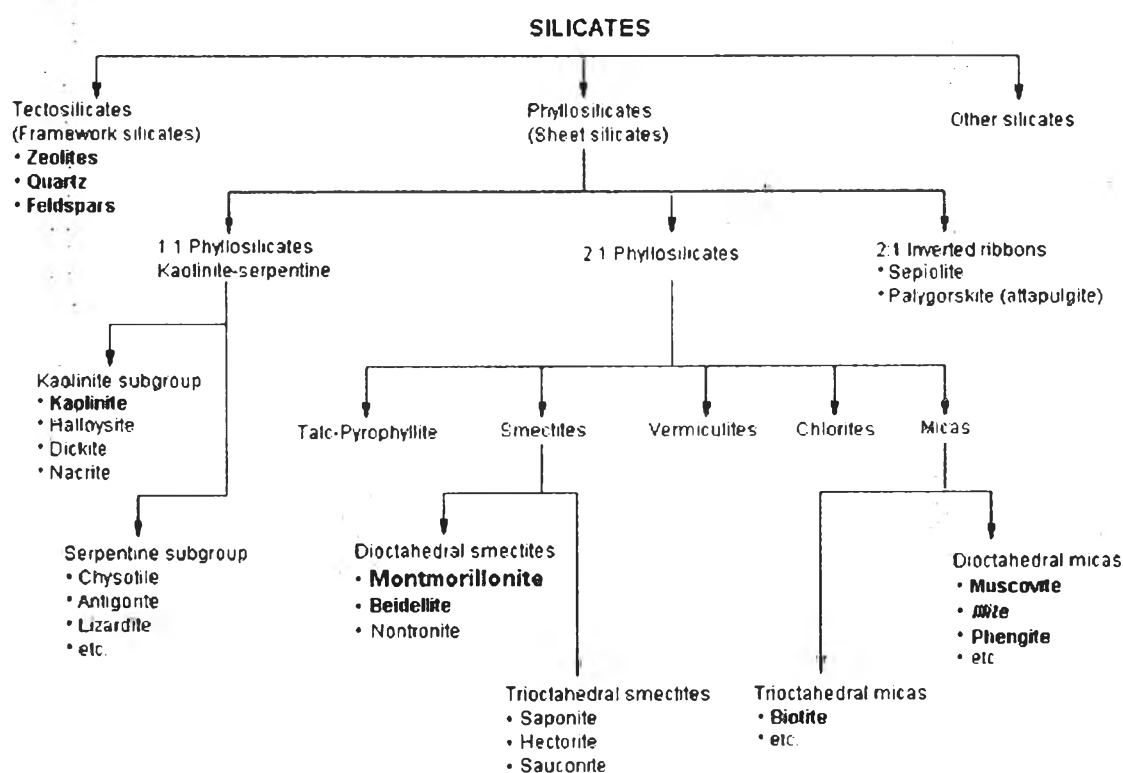
2.1 Theoretical Background

Clay, a naturally occurring material, is a product resulted from the chemical wethering of many kinds of rocks. It is also the most abundant materials on the earth crust. Clay can be simply defined as a rock that comprises of very small size materials. More precisely, the name was generally given to a rock, which at least 50% of the materials contributed in the bulk have a particle size less than 2 micrometers. The major constituents of clay are clay minerals, which are exhibited in a form of a thin flake-like phyllosilicates (sheet silicate). Clay minerals can have no charge on them, although they are more likely found to bear a net electronegative charge surface. However, the charged surfaces are normally eventually balanced by the interlayer cations (e.g. H^+, Ca^{+2}, Na^+ and Mg^{+2}). Regarding to a very small flake-like particle of clay mineral, it gives clay a set of unique properties, for example, a very high specific surface area to volume, the cations exchange capacities, a plastic behavior when exposed to moisture, and a swelling and shrinking due to water absorption and liberation.
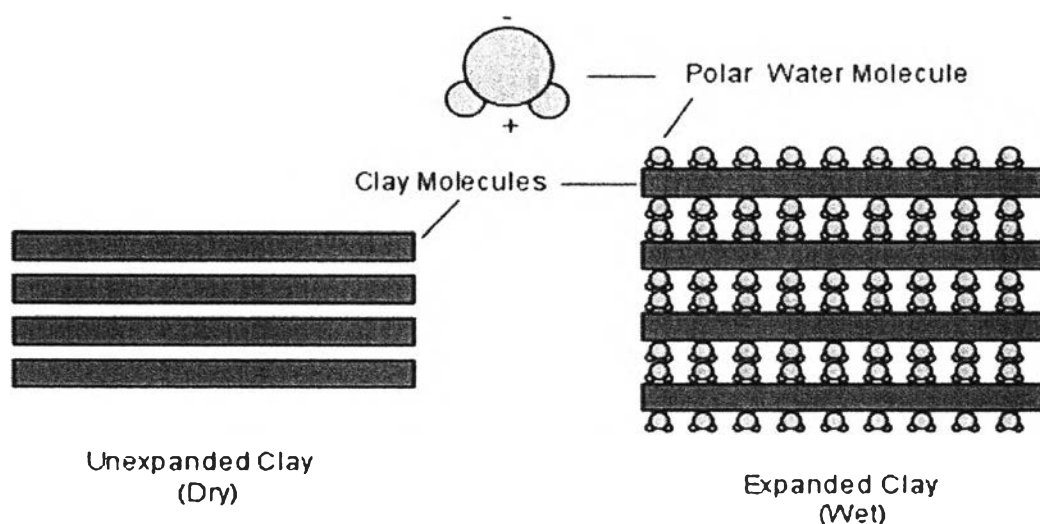
Figure 2.1 Picture demonstrating the swelling and shrinking of clay mineral (http://agronomy.agri.cmu.ac.th/meteo/361212/).

So far, a large number of clay minerals have already been discovered. Many scientist and geologist experts had tried to put them in families to be easier for understanding. Nevertheless, to be able to understand deeply about all the properties and characteristics of each individual clay mineral is extremely difficult. It not only requires a long term study and experiences, but expertises in the geological area of study are also crucially necessary. Figure 2.2 shows the detailed groups and families of silicate minerals.

SILICATES

Tectosilicates
(Framework silicates)
• Zeolites
• Quartz
• Feldspars

Phyllosilicates
(Sheet silicates)

Other silicates

1 1 Phyllosilicates
Kaolinite-serpentine

2 1 Phyllosilicates

2:1 Inverted ribbons
• Sepiolite
• Palygorskite (attapulgite)

Kaolinite subgroup
• **Kaolinite**
• Halloysite
• Dickite
• Nacrite

Talc-Pyrophyllite   Smectites   Vermiculites   Chlorites   Micas

Serpentine subgroup
• Chrysotile
• Antigonte
• Lizardite
• etc.

Dioctahedral smectites
• **Montmorillonite**
• **Beidellite**
• Nontronite

Dioctahedral micas
• **Muscovite**
• *Illite*
• Phengite
• etc

Trioctahedral smectites
• Saponite
• Hectorite
• Sauconite

Trioctahedral micas
• **Biotite**
• etc.

Figure 2.2 Diagram of groups and families of silicate minerals
(http://agronomy.agri.cmu.ac.th/meteo/361212/).

The specific physical and chemical properties of each type of clays are normally related to the species and the quantity of clay mineral contributed inside them. As shown in Figure 2.2, there are a wide variety groups and species of clay minerals; but unfortunately, the authors are lack of expertise to mention all of them. Our interest only lies on the kaolinite and montmorillonite minerals, which are the major constituents in the commercial clays named ball clay and bentonite.

Similar to kaolin clay, ball clay composed mainly of kaolinite clay mineral (up to 70wt %), and exhibited a high plasticity which make it easy to be extruded and form a catalyst extrudates. Kaolinite mineral can be classified as a 1:1 layer type of clay mineral, which means one sheet of silicon tetrahedra and one sheet of alumina octahedra are linked together by oxygen atoms. The chemical formula of kaolinite mineral is $Si_4Al_4O_{10}(OH)_8$. The unique property of kaolinite mineral is that the bondings between each plates or clusters are the strong hydrogen bond, which is resulted in a strong adhesion forces between the crystal grains, and hence, make them incapable to swell and shrink when exposed to water.
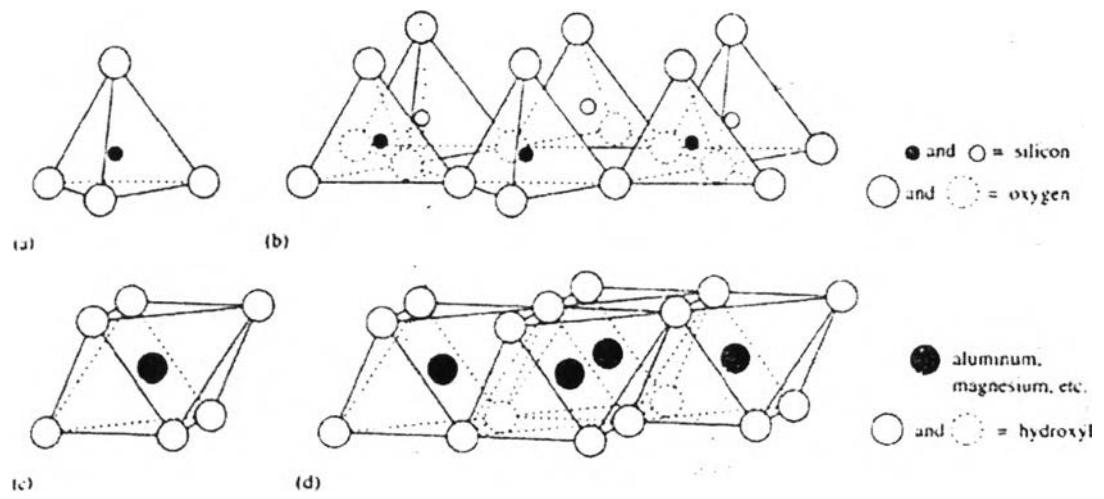

Figure 2.3 Single silica tetrahedron (a), and sheet structure of silica tetrahedra arranged in hexagonal network (b), a single octahedral unit (c), and a sheet structure of octrahedral units (http://accessscience.com/content/Clay%20minerals/139900).

Bentonite can be commonly described as a clay-rich rock that is generated from the chemical weathering of volcanic ash. Generally, the majority of the clay mineral contributed in this type of rock is montmorillonite mineral. Bentonite color normally appears in white, light gray, and cream color. Similar to other kinds of clay, it can also be found in many regions of the world, such as in Europe, North - South America, Australia, and East of China. Uses of bentonite could be said to be very broad. As they can be used in many kinds of applications ranging from the drilling mud for petroleum exploration and drilling, the manufacturing of adhesive and pig-

ment, or even the pharmaceutical area and cosmetics, and etc. Back to the mineralogy of bentonite, as mentioned earlier, bentonite is made up of mainly the montmorillonite mineral, which belongs to the smectite mineral group. Dissimilar to the kaolinite mineral, this type of mineral bear a 2:1 layer type which is denoted as the two silica tetrahedral sheets sandwiching a central octahedral sheet. The bonding type between the clusters of smectite group mineral is the weak oxygen-oxygen linkage, which gives them a distinctive swelling property and allows the interlayer cations exchangeability.

2.2 Literature Review

Tire is a complex material which is composed of numerous kinds of components, e.g., rubber, steel wires, chemical agents, textile and reinforcements. The major part which accounts for approximately 50% is rubbers. Rubbers are known as a type of elastomers, which have many special properties such as great elasticity, high tensile strength, good tear resistance, high abrasion resistance, and good dynamic properties. Rubbers themselves can be divided into two main categories. The first is natural rubber. This type of rubber can be obtained from a natural rubber tree. After passing though some treatment processes and polymerization, it will become a type of polymer called cis-1,4-polyisoprene. Nowadays, natural rubbers are extensively used in many kinds of applications including tire manufacturing. Another type of rubbers is so called synthetic rubbers. These types of rubbers have different unique characteristics depending on the formulation of polymers. They are usually used in a specific application which requires a specialty material. Examples of synthetic rubbers are Styrene-Butadiene Rubber (SBR), Chloroprene Rubber (CR), butadiene Rubber, Butyl Rubber (IIR) and etc.
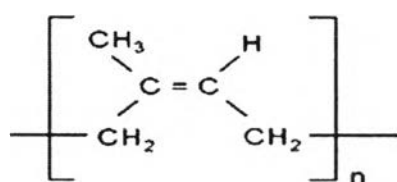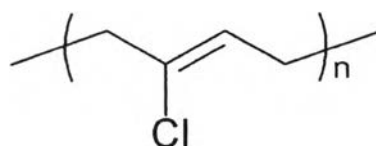

Polyisoprene
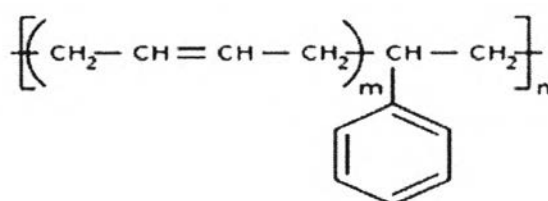
Styrene-butadiene
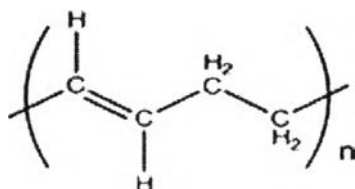
Polybutadiene

Polychloroprene

Figure 2.4 Examples of natural and synthetic rubbers (Phopaisarn *et al.*, 2009).

Even so, rubbers although have some good properties, but their ability is somehow limited. For example, they can deform or degrade easily when exposed long enough to sun light, has low oxidation stability, and can be dissolved easily in a non-polar solvent. Therefore, in order to make them strong and tough enough to be able to handle a harsh use in an automotive application, vulcanization process is required.
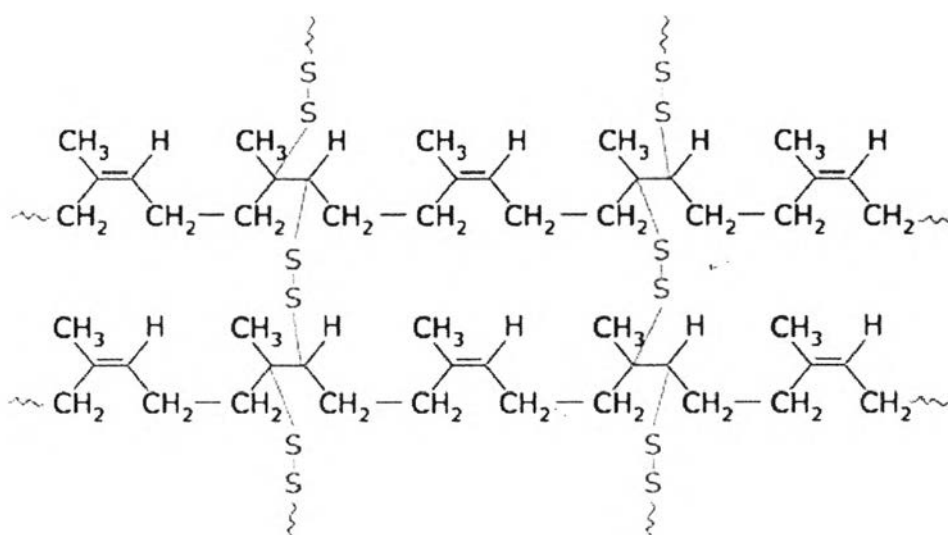
Figure 2.5 Vulcanized poly-isoprene with disulfide cross-links (http://www.chem1.com/acad/webtext/states/polymer-images/vulcanized.png).

Vulcanization was discovered accidentally in the year 1839 by an American inventor named Charles Spencer Goodyear. At that time, his discovery began the new era of rubbers utilization and application. By definition, vulcanization is an irreversible process where long chain polymers in the rubber become cross-linked by some kinds of curative substances such as sulfur. The vulcanized rubbers have a better elasticity, higher thermal resistivity, and also can tolerate more solvents. However, the cross-linked network makes tires impossible to be re-processed. Hence, the different kinds of waste conversion processes were developed in order to solve waste tire disposal problems.

Pyrolysis is one process that gains a particular attention since the products obtained from the process contain valuable chemicals, which can be used as a petro-chemical feed stock and supplement of fossil fuel. Since an ancient time, pyrolysis

technique was mainly used to convert wood into charcoal. But more recently, their application has been broaden especially to an industrial application. Pyrolysis is a type of thermal degradation processes which can be simply described as a process those breakdowns heavy hydrocarbon molecules to lighter product fractions at a high enough temperature. Nowadays, pyrolysis technique has been widely applied as a recycling process in many kinds of waste material recoveries, especially for plastic applications. In most of the cases, the pyrolytic products are normally composed of gas, liquid, and solid. However, the product composition is highly dependent to the feed type and also the process conditions. The key parameters that affect the product distribution in pyrolysis process are listed as follows.

- Feed type
- Operating condition
- Size of the reactor
- Type of the reactor
- Efficiency of heat transfer
- Residence time

In a past few decades, many researchers started to apply pyrolysis technique on waste tire recycling process. A great deal of work has been done to find an optimum process condition in order to enhance the economic feasibility and produce higher value products from waste tire pyrolysis. Williams *et al.* (1997) studied an influence of temperature and heating rate on a product composition of scrap automotive tire pyrolysis in a static-bed reactor. The temperature was varied up to 720 °C, and the heating rate was in between 5 to 80 °C min^{-1} under nitrogen atmosphere. They found that up to 600 °C, gas and oil products increased with an increasing temperature while the mass percentage of the solid char decreased. Additionally, they also reported that beyond 600 °C there was only a small change in the product yield. Finally, they concluded that increasing in pyrolysis temperature also had an effect on the aliphatic and aromatic compositions of the oil product; that is, the higher temperature produced more aromatic, and lowers the aliphatic hydrocarbons. The composition of the pyrolytic products was reported as oil (55 wt %), char (35 wt %) and gas (10 wt %). They also concluded that there was no significant change in product yield while changing the heating rates. In the year 2001, similar experiment was carried

out by Rodriguez *et al.* (2001) Again, the pyrolysis of scrap tire was studied in an autoclave reactor under nitrogen atmosphere. By varying a temperature, they found that above 500 °C there was no significant change in both amount and characteristic of the pyrolytic products. Barbooti *et al.* (2004) studied a waste tire pyrolysis in a fixed-bed batch reactor (1.25 m length and 0.03 m o.d.). They reported that the optimum conditions to maximize the pyrolytic product yields were 430 °C, the nitrogen flow rate of 0.35 m^3h^{-1}, and the particle size of 10 mm.

Berrueco *et al.* (2005) studied scrap tire pyrolysis under nitrogen atmospherere. They analyzed the influence of temperature on the product yields and gas composition. They found that the liquid yield increased with temperatures from 400-500°C; however, above 500 °C, it remained constant. Conversely, the gas yield showed a slight increase with increasing temperature from 400-700 °C. Laresgoiti *et al.* (2004) studied the chromatographic analysis of gases obtained in tire pyrolysis. They reported that above 500 °C there was no significant influence of temperature on the solid, liquid and gas yields. However, they found that there was an influence of the temperature on the gas composition and its evolution. At higher temperatures, they found that more CO and CO_2 were produced from inorganic components, and lighter gases were produced in a secondary reaction. Diez *et al.* (2004) also reported the same way; that is, a higher pyrolysis temperature resulted in higher liquid and gases yields. Furthermore, they also concluded that gases composition strongly depended on the final pyrolysis temperature, which agreed very well to the result from Laresgoiti *et al.* (1999). A year later, Diez *et al.* (2005) studied a pyrolysis of waste tire and made a comparison of the results between a fixed-bed laboratory reactor and a pilot plant rotary reactor. They found that the produced solid chars were similar in both composition and combustibility, but the gas composition showed a significant difference. The laboratory gases were found to have more C2+ hydrocarbon fractions because of shorter residence time whereas the gaseous products from the pilot plant were composed of mainly methane and hydrogen due to longer residence time. Therefore, the gases obtained from the laboratory gave a higher calorific value than those from the pilot plant.

Different types of tires for pyrolysis were also investigated by Ucar *et al.* (2005). They studied the influence of different types of tires, passenger car tire and

truck tire, on the pyrolytic products. They found that the compositions of the pyrolytic products of both tire types were not significantly different, but the passenger car tire had a higher amount of aromatics and sulfur content. Additionally, they also reported that the solid product produced from the truck tire was more suitable for the production of activated carbon.

Nevertheless, conventional pyrolysis alone is not considered to be a good enough technique for handling waste tires by several reasons. Firstly, the majority of the pyrolytic products which are solid char and low-graded oil have low economic values; therefore, it makes the process of tire pyrolysis economically infeasible. Another is the high cost of separation and purification of complex mixture products which are unquestionably necessary. As a consequence, many new methods have been developed in order to improve the effectiveness of the pyrolysis process. Roy *et al.* (1999) performed a pyrolysis experiment of waste tire under vacuum atmosphere. The temperature was varied between 480 °C and 520 °C, under the total pressures of lower than 10 kPa. They found that the advantages of using vacuum pyrolysis were lower temperature and residence time required to pyrolyze the tire sample; thus, it minimized the undesired reactions that might occur such as the formation of carboneous compounds and the secondary decomposition of the high value hydrocarbon products. They also reported that the carbon black produced from this vacuum pyrolysis process had a similar surface chemistry and activity to those commercial carbon black. Murena *et al.* (2000) studied a hydrogenative scrap tire pyrolysis under the liquid phase in a presence of hydrogen donating compound. The experiment has done by using a lab scale autoclave reactor, and the temperature was varied from 380 °C to 400 °C. They found that hydrogenative pyrolysis required lower temperature and gave a higher yield of liquid products as it minimized coke formation and repolymerization reactions. Menendez *et al.* (2002) studied the pyrolysis of sewage sludge by using a microwave furnace. They found that heating by microwave furnace was much faster, and the temperature was much more stable than the conventional electric furnace. Hence, it consumed less time as well as lower energy than the electric furnace.

Catalytic pyrolysis is an alternative that has received a great attention since it can improve the products quality by enhancing the overall process selectivity.

Many catalysts including numerous kinds of zeolytic materials, meso-structured materials and amophus materials have undergone several investigations under different process conditions to observe the effect on a pyrolysis of waste tire. Miguel *et al.* (2006) studied the effect of several acid catalysts in converting waste tire rubber into hydrocarbon products. In their work, five different types of catalyst (standard ZSM-5, monocrystalline n-ZSM-5, beta zeolyte, Al-MCM-41 and Al-SBA-15) were investigated. They found that all the zeolytic materials (standard ZSM-5, monocrystalline n-ZSM-5, beta zeolyte) exhibited a high selectivity toward aromatic species especially for benzene, toluene and m/p-Xylenes. On the other hand, the last two mesoporous materials promoted aromatization and benzene alkylation as they have a larger pore size and weaker acid strength. Boxiong *et al.* (2007) studied the pyrolysis of waste tire with the aid of catalysts, USY and ZSM-5, to obtain higher concentration of single ring aromatics such as benzene, toluene and xylenes. In 2006, Marcilla *et al.* studied the influence of different solid state acid catalysts in the catalytic pyrolysis of different polymers. The catalysts used in pyrolysis were HZSM-5 zeolite and mesoporous aluminosilicates—MCM-41a and MCM-41b (higher acidity). They found that the activity of acid catalysts depended on pore size because reactant molecules can easily access to the active sites located in the interior of the pores. Another factor is acidity. They also found that the activity of catalyst increased as the acidity increased. Wang *et al.* (2006) proposed a scrap tire catalytic co-pyrolysis with a lubricant base oil (LBO). They found that co-pyrolysis under the aid of a catalyst can remarkably increase the pyrolysis rate and also produced higher value oil products. Kittikom *et al.* (2008) studied the pyrolysis of waste tire using ruthenium metal loaded on the HMOR zeolite. The goal of his research was to maximize the light olefins production from catalytic waste tire pyrolysis. In his experiment, the process conditions (temperature and resident time) and the amount of ruthenium metal loading were investigated for the effect on waste tire pyrolysis. The temperature was varied from 500-700°C, and the residence time between 25-75 minutes. The results revealed that the gaseous products increased with an increasing temperature and shorter residence time. He found that high temperature and long residence time promoted the formation of heavy hydrocarbon molecules, especially poly-aromatic hydrocarbon. For the

catalytic case, the production of total light olefins showed the maximum at the 0.7% ruthenium loading.

Choosuton *et al.* (2007) studied the effect of several bi-functional catalysts on waste tire pyrolysis. Again, the experiment was done on a bench scale autoclave reactor. In his study, four types of commercial catalysts were loaded with three kinds of noble metals (Pt, Pd and Ru) using incipient wetness impregnation method to obtain 1%wt metal loaded catalysts. The catalysts were then tested to observe the effect on waste tire pyrolysis, both in qualitative and quantitative aspects. He found that by using bi-functional catalysts, the poly-aromatic contents in oil product were reduced by 50-70 wt%, and the gasoline and kerosene obtained also had higher quality compared to the case of using zeolites alone or non-catalytic process. He reported that the best catalyst for producing gas products was Ru/HMOR; which can produce three times higher gas products than non-catalytic case. Finally, he also concluded that Pd/Beta was the best catalyst for the production of gasoline and kerosene.

Until now, numerous kinds of natural and synthetic matrix or binder have undergone countless of investigations and studies in order to develop a proven catalyst for an industrial-scale application. Lucas *et al.* (2005) studied the hydroisomerisation of n-octane over platinum catalysts with or without a binder (bentonite). Three types of zeolites (MOR, beta, and ZSM-5) with and without the binder (65wt. %) were compared. The platinum content in all samples was fixed at 1 wt. %. The experiment was carried out in an autoclave Engineers (BTRS-Jr) micro reactor. Experimental conditions were as follows: the weight of catalyst to zeolite, 530mg; temperature, 250-410 °C; total pressure, 10 bars; WHSV = 10 g $_{n-C8}$ h^{-1} g$^{-1}_{zeolite}$; and H$_2$/n-C8 molar ratio, 14. They found that the loaded platinum metal on the zeolites did not affect the zeolites acid properties, and the bentonite acidity was found to be very low (no strong acid site was observed). In case of the agglomerate catalysts, the experimental values of strong acid sites were always found to be lower than the predicted one (calculated from the contribution of the raw materials, zeolite and bentonite) and the opposite effect was observed for weak acid sites. They explained that the reduction of the expected strong acid sites may attribute to the solid-state ion exchange between the zeolite protons and sodium ions in the clay during the calcination of the catalysts. The influence of the binder on the dispersion of the platinum was also in-

vestigated. They reported that when MOR and ZSM-5 zeolites were agglomerated with bentonite, the dispersion of metallic species was decreased, and the opposite effect was found on beta zeolite. They explained that the decreasing in the dispersion of the first two catalysts (MOR and ZSM-5 with 65% bentonite) were derived from the increasing of mesoporous material (bentonite), which allowed a better metal growth than a microporous one, and thus decreased the metallic dispersion. On the other hand, the agglomerated beta zeolite showed an opposite effect. They explained that some amount of the clay binder filled up the intercrystalline voids in the beta zeolite, which dramatically decreased their mesoporosity, which consequently, prohibited the metal growth. In the n-octane hydroisomerisation of non-agglomerated catalysts, ZSM-5 was observed to be the most active catalyst. The result was explained in the way that ZSM-5 had acid sites with high density and strength. However, mordenite zeolite (MOR), which has the highest acidity amongst the tree zeolites, showed a lower activity compared to ZSM-5. They explained that the mordenite zeolite presented a high steric hindrance which did not allow the accessibility to all its acid sites. Likewise, according to the acidity and the structure of beta zeolite, n-octane conversion was expected to be higher than ZSM-5, however, the result was shown oppositely. They explained that it may be related to the pore size which caused a difference in the activation energy of the two zeolites, which means activation energy is smaller on ZSM-5 than on the beta zeolite. Similar results was observed on the agglomerated catalysts, which is ZSM-5>BETA>MOR.

In the same year, Lucas *et al.* also studied the influence of the Si/Al ratio in the hydroisomerisation of n-octane over platinum and palladium beta zeolite-based catalyst with or without a binder. Similarly, the percentage of binder used and the metal content were fixed at 65 wt. % and 1 wt. %, respectively. The operating conditions used were also the same as the previous work. They found that the acid site density of the catalyst decreased, and the acid strength of the medium-strong acid sites increased, with an increasing the Si/Al ratio. Concerning the n-octane conversion, the catalytic activity of the beta zeolite catalyst decrease with the increase of Si/Al ratio, as the conversion was related to the acid sites density of the catalyst. Also, the decreased of the metal dispersion was observed when the Si/Al ratio was increased. Moreover, platinum metal showed a better metallic dispersion when com-

pared to the case of palladium. They explained that this effect was resulted from the fact that Pt atoms are less mobile than Pd, because the larger size of the former and their higher polarizability due to the d electron configuration. The catalyst loaded with Pt showed a better n-octane conversion as compared to those loaded with palladium. They explained that the higher Pt dispersion allowed a higher amount of metal sites available for the production of alkenes, which further affect the formation of carbenium ion. The agglomerate catalyst with the 65 wt. % binder (bentonite) showed similar results compared to the non-agglomerated one; that is, higher conversion was observed for the low Si/Al ratio, and the Pt loaded catalyst exhibited a better n-octane conversion. One interesting point is that, the agglomerated catalysts with bentonite were expected to give a lower conversion of n-octane because of the neutralization of the acid sites by the binder, however, the opposite result was observed. They concluded that the higher activity was derived from the cationic aluminium extra-framework species (EFAL) which have a strong Lewis acidity that could interact with the structural Bronsted acid sites, enhancing their acid strength through a synergetic effect and, consequently, making them more active to the n-octane hydroisomerisation.

Sánchez et al. (2007) studied the effect of binder content on the catalytic performance of Pt/Beta-based catalyst. In their work, the different amount of clay, sodium bentonite, was applied as a binder for beta zeolite to investigate the catalytic performance on hydroisomerization of n-octane. The platinum content was fixed at 1wt. % and the binder content was varied in the range of 35-65 wt. %. They found that the agglomeration of the beta zeolite by the clay binder affected the surface area per gram of zeolite, which suggested a blockage of zeolite channels. They reported that the n-octane conversion was decreased with the increasing binder content, and showed the maximum value of 90.8% conversion with the binder content of 35wt. %. Additionally, the non-agglomerated catalyst which had the highest strong acid sites density per gram of zeolite exhibited the lowest conversion of 52.2%. The explanation was similar to those of Lucas et al. (2005), which was related to the cationic aluminium extra-framework species (EFAL). Finally, the isomer selectivity of all the catalysts was reported to be similar, which was around 90%.

Kasture *et al.* (2007) studied the influence of binder on the catalytic performance in the isopropylation of benzene over H/Beta zeolite catalysts. In their work, zeolite beta was synthesized using flyash as a source of silica and alumina. The synthesized zeolite was then mixed with the different amounts of alumina binder (10-50 wt. %), and then shaped by pelletizing and extrution to produce catalyst pellets and extrudates for the isopropylation of benzene. They found that among the different percentages of alumina binder used, the catalyst with 40% alumina was found to be the best catalyst as it gave a stable benzene conversion (19.25 and 18.21, for catalyst pellets and extrudates) and high cumene selectivity (93.52% for pellets and 91.94% for extrudates) . Lastly, they also concluded that the pellet catalyst was the better catalyst formulation as compared to the extrudate catalyst.

Choudhary *et al.* (1997) studied the influence of binder on the acidity and performance of H-Gallosilicate (MFI) zeolite in propane aromatization. In their study, two types of binder (alumina and kaolin) were tested at the concentration of 10 and 50 wt%. From the catalyst characterization, the results revealed that both the total and external acidity of the zeolite catalyst decreased remarkably due to the kaolin binder, whereas alumina binder caused only little or no significant effect on the total acidity, but greatly increased the external acidity of the zeolite catalyst. They explained that the observed increased in the external acidity was resulted from the creation of new zeolitic acid sites (i.e., tetrahedral Al sites) at the external surface of the zeolite crystal by substitution of framework Si by Al from the alumina binder. They also reported that the reduction of both intercrystalline and the external acidity by the kaolin binder were derived from the neutralization of some zeolitic acid by the alkaline and alkaline-earth matal cations on the binder. For the propane aromatization, they found that the total conversion of propane and its conversion to aromatics were decreased remarkably with the increasing kaolin concentration. However, the presence of alumina even at 50% concentration had no effect on the initial activity of zeolite catalyst. They also observed that both types of the binder helped enhance the selectivity toward aromatic species, especially at lower conversion. Concerning the effect of the binder on the deactivation of the catalysts and selectivity, they reported that the deactivation of both catalysts decreased the aromatic selectivity, aromatisation/cracking activity and dehydrogenation/cracking activity ratios, and also shape

selectivity in the propane aromatization; however, the deactivation in the case of alumina binder was observed to be higher.

Goncalves *et al.* (2009) studied the effect of zeolite (Y), kaolin, and alumina on the in a cracking of heavy resedue evaluated by thermogravimetry. The information regarding the coke formation of all three types of catalyst was investigated, and the results were compared together with the conventional thermal process. They found that the kaolin and alumina promoted twofold higher coke formation compared to the thermal process while the Y zeolite gave the highest coke formation of fourfold.

Sritana *et al.* (2009) studied the catalytic pyrolysis of waste tire over HMOR based catalyst. In their work, the agglomerated Ru/HMOR catalyst was synthesized by using the different percentages of clay matrix (40-70% kaolin) and the fixed amount of aliminar binder (10wt. %) to produce catalysts for the catalytic pyrolysis of waste tire. The amount of metal content (Ru) was fixed at 0.7wt % in all samples. They found that Ru/HMOR catalyst can enhance the production of light olefins in the pyrolytic products. They also concluded that the optimum composition of the catalyst was 20 wt% of Ru/HMOR, 70wt% of kaolin, and 10wt% of alumina binder.

Putene *et al.* (2003) studied the influence of the aluminum content in the silica/alumina matrix on the selectivity of FCC catalysts. The cyclohexene conversion was used as a probe reaction for the study. In their work, 30% wt. of USY and USY-A (without extra frame work alumina) zeolite with various matrix types was synthesized. The percentage of alumina (0, 12, and 25wt. %) in the silica/alumina binder and the dealumination time by steaming (1, 3, and 5h) were varied to produce a large amount of samples. They found that the activity of the catalyst increased with the aluminium content in the matrix. Moreover, the results also revealed that the extraction of extraframework aluminium (EFAL) promoted a more active catalysts (USY-A was more active than normal USY catalyst). They also reported that the dealumination by steaming decreased the activity of both type of zeolites catalyst dramatically.

In this study, our objective is to develop the Pd/Beta catalyst for using in the industrial application. Natural clays and synthetic materials are generally introduced as a zeolite matrix in order to provide a necessary mechanical strength and resistance

towards collision and attrition losses. It has been proven that, at an elevated tempera-ture, binders or matrixes are not chemically inert to zeolite nor catalytically inactive (Cañizares *et al.*, 2001). As a result, zeolite-matrix interaction always has strong in-fluences on the catalytic activity, selectivity, and also deactivation of the zeolites. In some cases, the matrixs not only play role in strengthening the catalyst body, but they also act as diluents and heat transfer media for zeolite component which mod-erates their cracking activity and subsequently prevents the over-cracking of the product. Moreover, it has been reported that the binder or the matrix itself could also change the acidic properties of a zeolite by means of changing the protons-exchange efficiency, which may be resulted either by the trapping of coke precursor on the binder surface and/or the blocking of zeolite channels during the pelletizing progres-sion (Sánchez *et al.*, 2007). As a consequence, the information concerning the binder and matrix on the acidity and catalytic performance of the catalyst is, therefore, very crucial for the development of industrialized catalysts.

The objectives of this research work were to further develop the Pd/Beta catalyst for using in tire pyrolysis at the industrial scale. The influence of different matrixes on the quality and quantity of pyrolytic products, the effect of Si/Al ratio of the Pd/Beta zeolite on the product yields, activity, acidity, and selectivity of the pyro-lysis of waste tire, and lastly, the optimum zeolite-matrix ratios on the product yields, and the composition of the pyrolytic products were investigated.

The scope of this research covered as follows: (1) the pyrolysis of scrap tire was operated in a bench-scaled autoclave reactor, (2) N_2 flow rate, heating rate, the amount of sample and the amount of catalysts were fixed at, 50 ml/min, 10°C min, 30 g and 7.5 g, respectively, (3) two different Si/Al ratio of Beta zeolite (13.5 and 250) were used as the noble metal support to investigate the effect on waste tire py-rolysis, (4) two type of natural clay marix were studied for their effect on the pro-duced agglomerated catalyst and the quality and quantity of product obtained from catalytic pyrolysis, (5) the optimum agglomerated catalyst composition with various percentage of active component (5, 20, and, 40 wt %.), 0.25 wt% Pd supported on Beta catalyst, in a presence of alumina binder (10 wt %.) and matrix were also be investigated to find the optimum product yields and compositions on the catalytic pyrolysis of waste tire. The final experimental design is shown in the Table 2.1.

Table 2.1 The experimental design in this research

Active component (wt %)		Batch Number	
		Ball clay	Bentonite
Beta13.5	5%	1	2
	20%	3	4
	40%	5	6
	100%	7	
Beta250	5%	8	9
	20%	10	11
	40%	12	13
	100%	14	
Pure matrixes		15	16
Non-cat/No support		17	