CHAPTER IV
RESULTS AND DISCUSSION

In this chapter, the products obtained from catalytic waste tire pyrolysis using bi-functional catalysts, Pd/beta, were analyzed and discussed. The typical products obtained from pyrolysis are distributed in a fraction of gas, solid, and liquid. Up until now, in an attempt to seek the right catalyst to modify each of the products in both qualitative and quantitative perspectives, many research works have already been done. Pd/beta catalyst was one of the proven catalysts which can help upgrade or modify the liquid product. In this work, a further development of Pd/beta catalyst was focused. The purposes of this research were to study the effect of the different silica to alumina ratios of beta zeolite, the type of matrixes, and the percentage of active zeolite (5, 20 and 40 wt. %) contributed in the agglomerated catalyst on the quality and quantity of pyrolytic product.

4.1 Catalyst Characterization

4.1.1 Temperature-Programmed Reduction (TPR)

The temperature programmed reduction (TPR) under the hydrogen gas flow was used to identify the reducibility of the impregnated palladium catalysts. The influence of the Si/Al ratios (13.5 and 250) of Beta zeolite supports on the reduction temperature, and the metal support interaction of palladium were investigated. It has been reported by some authors that the ease of reduction of the catalyst can indirectly indicate the weak bonding of the oxide precursor to the support (Kongsingha *et al.*, 2000). The oxide form of 0.25 wt. % of Pd/Beta catalysts (Si/Al = 13.5 and 250) was first prepared by using the palladium nitrate precursor $Pd(NO_3)_2$ followed by calcination. The temperature programmed reduction at the temperature range of 30-900 °C under the 4.95 % hydrogen gas flow was performed. According to Figure 4.1, the result reveals that the palladium on both types of Beta zeolite support exhibited a very similar reduction temperature, around 77 - 88 °C or 350-361K. The results agree very well with the literatures. Additionally, the similarity of the TPR curves of both Beta zeolites also point out that the difference in the Si/Al ratio of the beta zeolites has a slight or no significant effect on the reduction temperature of palladium. However, many literatures have reported the existence of some palladium oxide species, which interact strongly to the support and require a higher temperature (beyond 300°C) to be reduced. Therefore, in order to confirm the complete reduction of all palladium species in the catalysts, the reduction temperature was selected to perform at 400°C based on the literature (Lucas *et al.*, 2005). In conclusion, as the reduction temperature of Pd/Beta 250 was slightly higher than that of Pd/Beta (Si/Al = 13.5), it is reasonable to conclude that the Pd was bound slightly stronger to the zeolite Beta (Si/Al = 250) support.

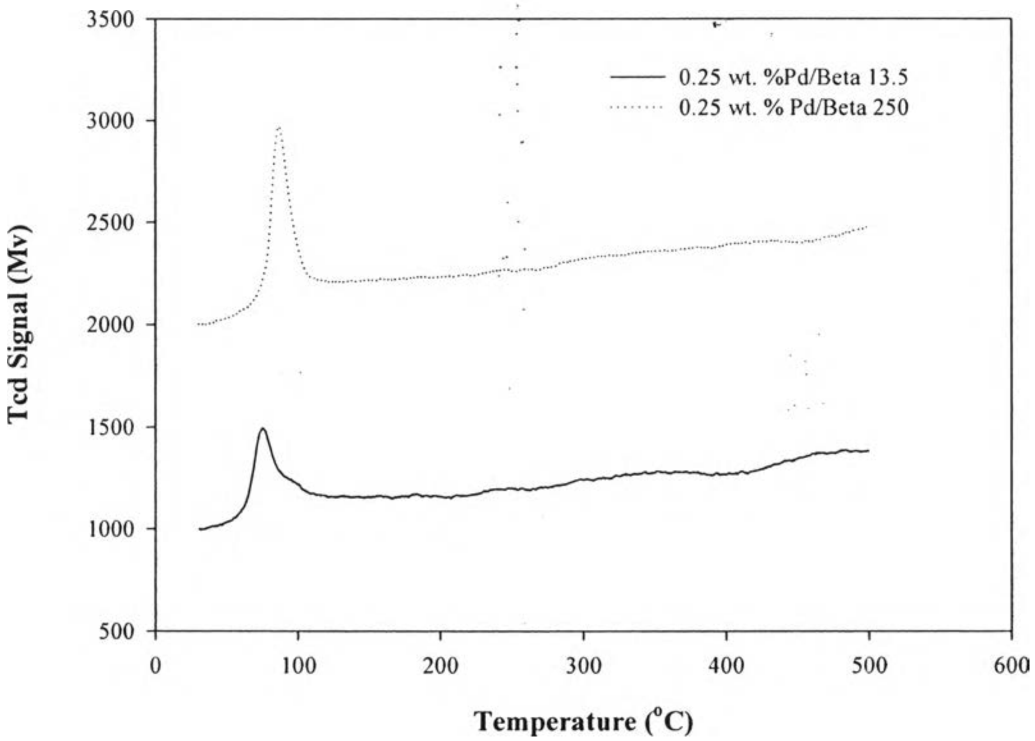


Figure 4.1 TPR profile of the individual active 0.25 wt. % Pd/Beta catalysts (Si/Al = 13.5 and 250).

4.1.2 Physical Properties

Aside from the acidic properties of the zeolite catalysts, the surface area, the pore structure, and the pore volume of a catalyst are also the factors which contribute greatly to its activity and selectivity. Therefore, it is very important to first identify the physical properties and the characteristic of the catalysts used in the experiment. In this work, the physical properties of the extrudate components were analyzed by using the BET method.

Table 4.1 Physical properties of each component used in the catalyst extrudates

Sample	**Surface area (m^2/g)**	**Pore volume (cm^3/g)**
Pd/Beta (Si/Al = 13.5)	652	0.64
Pd/Beta (Si/Al = 250)	469	0.49
Bentonite Clay	42	0.14
Ball Clay	25	0.14
Alumina	73	0.48

4.1.3 CO Pulse Chemisorptions

Dispersion defines as the number of metal atoms exposed to the environment per total number of metal atoms supplied into the catalyst. Pulse chemisorption technique using many kinds of probe molecules (H_2, O_2) has been utilized extensively to identify and determine the extent of metal dispersion on the catalyst. However, unlike some other metals, a commonly used H_2 pulse chemisorption cannot be applied to measure the dispersion of palladium, as H_2 can be diffused and absorbed into the palladium bulk (Kongsingha *et al.*, 2000). Therefore, in order to measure the dispersion of palladium on the prepared catalyst, CO pulse chemisoprtion was carried out using TPDRO/MS 1990. The results in Table 4.1 reveal that the Beta zeolite with the Si/Al ratio of 13.5 exhibits higher palladium dispersion than the one with the Si/Al ratio of 250 due to the higher surface area and the total pore volume of the zeolite.

Table 4.2 Percentage of palladium dispersion using CO chemisorptions

Sample	Si/Al Ratios	% Pd dispersion
Beta Zeolite (1)	13.5	52.3
Beta Zeolite (2)	250	46.5

4.1.4 X-ray Diffraction Patterns

In order to study the crystallinity of the two beta zeolite supports, X-ray diffraction technique was employed. Figure 4.2 represents the XRD patterns of the pure beta zeolites (Si/Al = 13.5 and 250) and the 0.25 wt. % Pd/Beta catalysts (Si/Al = 13.5 and 250). The results reveal that the difference in the Si/Al ratios of the beta zeolite has no effect on their crystal structure, as their XRD patterns are identical. Moreover, for the case of Pd loaded on the Beta zeolites, no peak of palladium was observed as the metal loading percentage is too low. The palladium peak is supposed to locate at 2θ = 40.116° (Pintoo *et al.*, 2008).

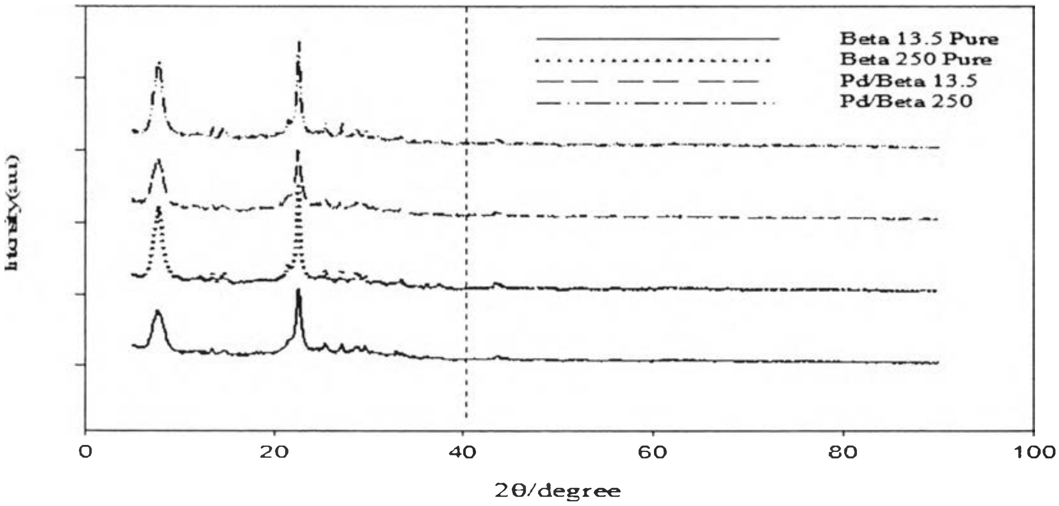


Figure 4.2 XRD patterns of the pure Beta zeolites (Si/Al = 13.5 and 250) and the 0.25 wt. % Pd/Beta catalysts (Si/Al = 13.5 and 250).

4.2 Effect of Different Si/Al Ratio of Beta Zeolite Supports

As mentioned in the previous chapters, the products from waste tire pyrolysis consist of three main parts which are gas, solid, and liquid. Many processing parameters have been proven to have a strong effect on the quantity and the characteristic of the products obtained from catalytic waste tire pyrolysis, e.g., the catalyst per tire ratios, the carrier gas flow rate, and catalytic temperature, and etc. Therefore, for a better concurrence and understanding, it should be made clear first that in this work, our processing conditions are as of those stated in Chapter 3.

Accoding to the previous work, 0.25 wt. % of Pd supported on Beta catalyst has been reported to be a good catalyst in upgrading the liquid product. Nevertheless, in order to further improve the oil and investigate the effect of this particular catalyst, two different type of beta zeolite supports, which have different Si/Al ratios (Si/Al = 13.5 and 250), were then selected for the investigation. The difference in the Si/Al of the zeolites directly relates to their acidic properties. Theoretically, the higher Si/Al ratio represents the lower aluminium content in the zeolite framework (lower acid density), which prolongs the distance between the (AlO_4^-) units, and thereby, results in a higher acid strength of the proton. On the contrary, the lower Si/Al zeolite corresponds to a higher total acid density but lower acid strength of the zeolite (Lucas *et al.*, 2005).

4.2.1 Product Distributions

In this section, the effect of Si/Al ratio of beta zeolite supports (Si/Al ratio of 13.5 and 250) on catalytic waste tire pyrolysis is discussed and compared. The results reveal that both types of Beta zeolite supports promote the production of gaseous product at the expense of liquid product.

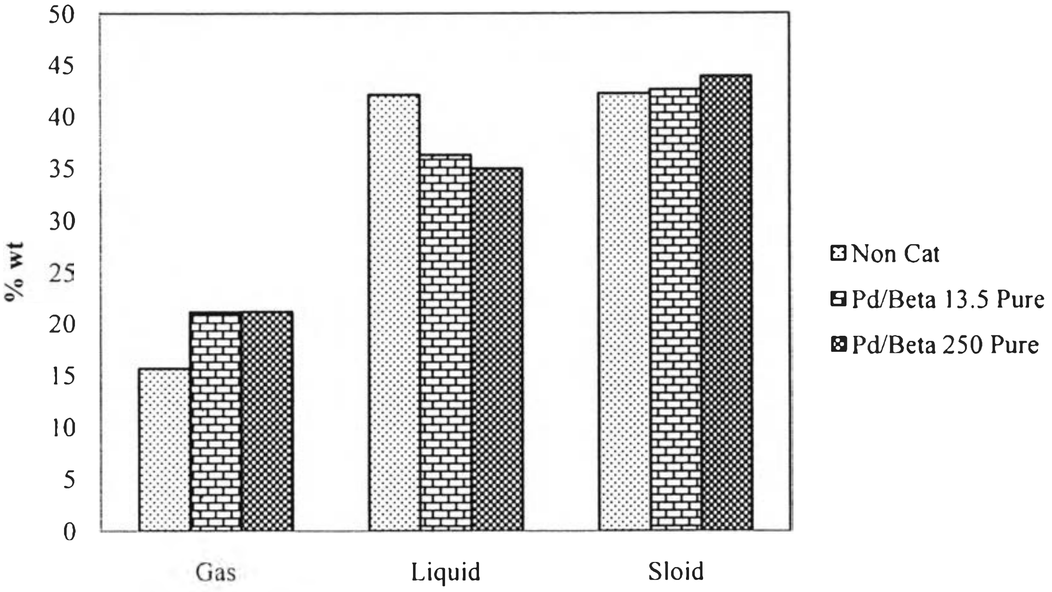


Figure 4.3 Product distribution of catalytic waste tire pyrolysis using 0.25 wt. % Pd/Beta catalysts (Si/Al = 13.5 and 250).

Figure 4.3 demonstrates the product distribution of non-catalytic and catalytic waste tire pyrolysis using two different Si/Al ratios of 0.25 wt. % Pd/beta catalysts. According to the results, the non-catalytic pyrolysis (thermal pyrolysis) shows the highest yield of liquid production (~42 wt. %) as compared to the other catalytic cases. For the case of pure active catalysts; 0.25 wt %Pd/Beta (Si/Al = 13.5 and 250), the higher production of gaseous product was found. Many factors are deemed to play parts in this effect. It has been reported by many authors that the use of catalyst could help crack the heavy hydrocarbons molecule into the lighter fraction via the cracking activity of the active zeolite, which in this case, is the higher gaseous production (Sritana *et al.*, 2009). Moreover, the higher yield of gaseous product may possibly be resulted from the hydrogenolysis reaction favored by the metallic Pd sites of the catalyst (Lucas *et al.*, 2005). Finally, an appropriate pore size and the pore structure of a zeolite have also been reported to play a great role in the activity of some types of reaction. However, in comparing the two catalysts currently used, no significant difference is found on the product distribution.

4.2.2 Gas Compositions

The product obtained from waste tire pyrolysis was first condensed by a series of condensers to collect as a liquid product, and the part of the incondensable hydrocarbons which remains in a gas phase were then collected as the gas product. The collected gas product was analyzed using gas chromatography. It is found that the majority of the hydrocarbon species in the gas product lies in the range of C_1-C_5, although some trace amount of C_{6+} is also detected. The product gas compositions of non-catalytic and catalytic pyrolysis are shown in Figure 4.4

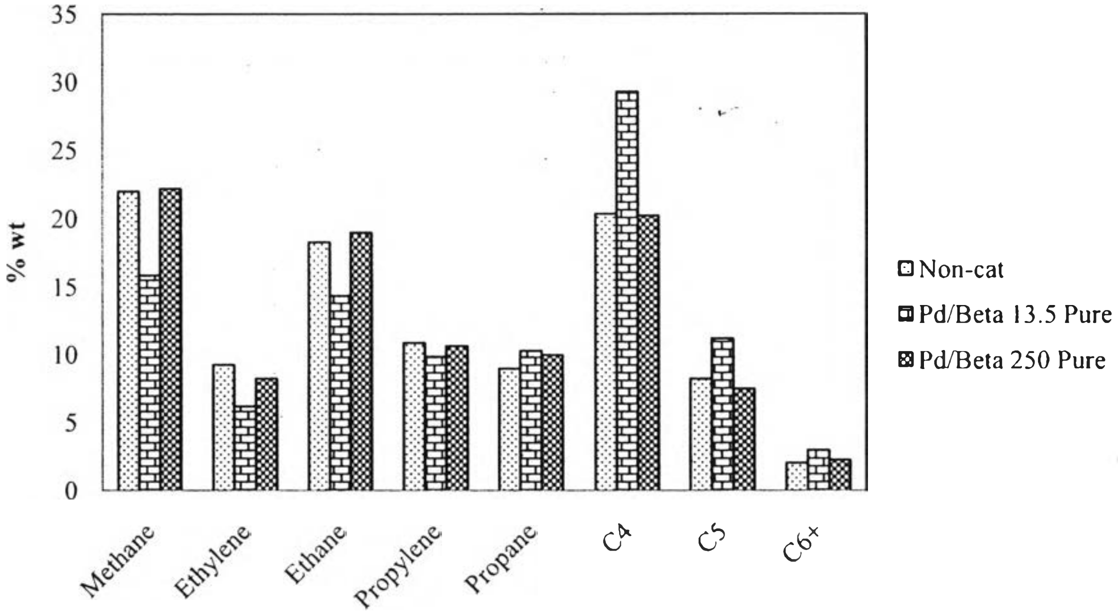


Figure 4.4 Gas composition of catalytic waste tire pyrolysis using Pd/Beta catalysts (Si/Al = 13.5 and 250).

The weight percentage composition of the gas produced from non-catalytic case or the thermal pyrolysis is reported as 22.0% methane, 9.2% ethylene, 18.2% ethane, 10.8% propylene, 8.9% propane, 20.3% mixed-C_4, 8.2% mixed-C_5, and 2.0% of mixed-C_{6+}. The gas product from pyrolysis has a potential to be fractionated and used as a petrochemical feed stock and/or directly used as an energy supplier for any plant unit.

By concerning the two types of Pd/Beta catalysts used, both of the catalytic cases show a minor reduction in the light olefins composition (ethylene and propylene) in the gaseous product. Due to the fact that these light olefins are relatively unstable and quite reactive, the resulted decrease expectedly comes from the hydrogenation activity of the palladium metal cluster impregnated on the surface of the catalysts. The pure 0.25 wt. % Pd/Beta (Si/Al = 13.5) catalyst exhibits a significantly difference in the gas product composition from the other two cases, as it selectively produces a higher concentration of the mixed-C_4, -C_5 and -C_6 hydrocarbons in the gas product. The explanation can be made based on the higher acid density of the Pd/Beta (Si/Al = 13.5) as compared to another one with Si/Al = 250, which makes it more favorable to the occurrence of the secondary reactions such as recombination and/or isomerization of the light hydrocarbons product molecules. On the other hand, the catalyst with Si/Al = 250, which has the similar pore system and specific surface area as those of the one with the Si/Al = 13.5, exhibits only a slight change in the gas composition as compared to the thermal pyrolysis. This can indirectly help confirm that the difference in the gas products composition was mainly resulted from the total acidity difference between the two catalysts having two different Si/Al ratios.

4.2.3 Liquid Products

Amongst the three product fractions obtained from pyrolysis process, it would not be too exaggerated to say that the fraction of liquid is the most important and most valuable product compared to the other two products (solid and gas). The liquid product obtained from waste tire pyrolysis usually appears as a complex mixture, which contains numerous kinds of hydrocarbons species such as parrafins, olefins, napthenes, and a wide verity of aromatic-based products. However, the proportion and quality of each species can be varied by several factors; for examples, the type of tire used, the type of reactor applied, the processing conditions, and etc. Additionally, the type of catalyst used had also been proven to have a strong impact on the type of hydrocarbons species obtained from waste tire pyrolysis.

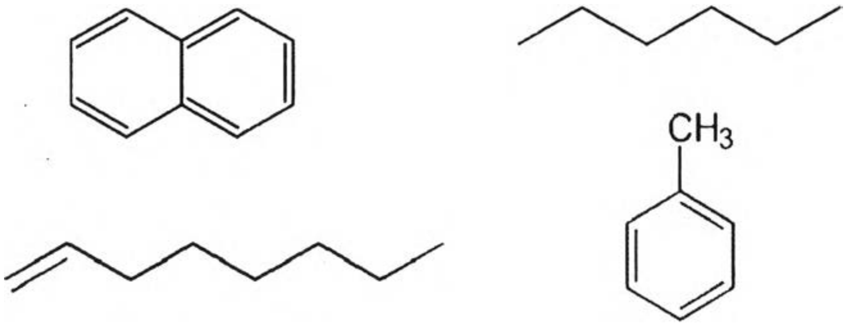


Figure 4.5 Examples of hydrocarbon species obtained from waste tire pyrolysis (http://en.wikipedia.org/).

Apart from the species of hydrocarbons comprising in the oil fractions, the size of hydrocarbons molecules is also one of the most crucial factors to determine the value of the oil product. In general, the heavy oil fractions which has the boiling point over 250-300°C is not a desired fraction, as it has a low economic values and the difficulties in further treatment and processing. Catalytic waste tire pyrolysis using a bi-functional catalyst (a noble metal supported on a zeolite) is one of the proven alternatives which help reduce the average molecular size of the pyrolytic oil through the cracking and hydrogenating activities of the catalyst.

4.2.3.1 Petroleum Fractions

The derived maltene from pyrolytic oil was analyzed by using Simulated Distillation GC, or SIMDIST GC. The true boiling point curve was obtained according to the the ASTM D2887 standard method. The quantity of each oil fraction was classified according to their boiling point cuts, which are the naphtha, kerosene, light gas oil, heavy gasoil, and long residue. The detailed information on the boiling point cuts and carbon ranges of refinery products is shown in the Table 4.3.

Table 4.3 The boiling point cuts and carbon ranges of refinery products (Dũng *et al.*, 2009a)

Fraction	**Carbon range**	**Boiling point (°C)**
Naphtha	C5-C9	<200
Kerosene	C10-C13	200–250
Light gas oil	C14-C20	250–300
Heavy gas oil	C21-C23	300–370
Long residue	C24-C50	>370

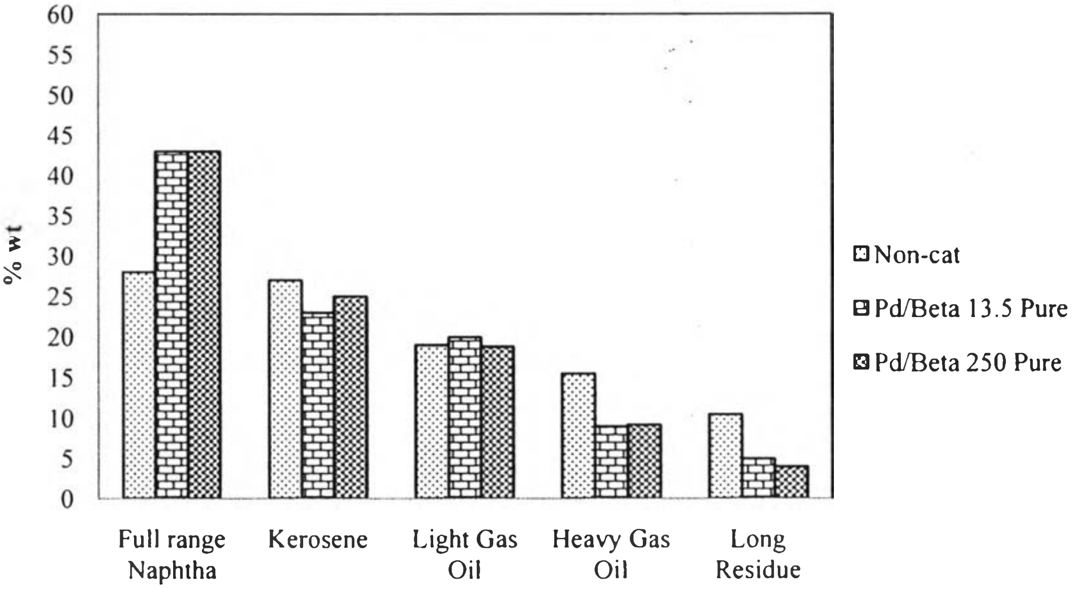


Figure 4.6 Petroleum fraction of the derived maltene from catalytic waste tire pyrolysis using Pd/Beta catalysts (Si/Al = 13.5 and 250).

Figure 4.6 shows the weight percentage of different product fractions of the thermal pyrolysis and the pure active 0.25 wt. % Pd/beta catalysts (Si/Al = 13.5 and 250). Prior to the discussion on any of the catalytic cases, the composition of the oil product from thermal pyrolysis (non-catalytic pyrolysis) is found to be 28% naphtha, 26.5% kerosene, 19% light gas oil, 15.5% heavy gas oil, and 10.5% long residue. According to the results, it can obviously be seen that when both types of pure active catalysts (at Si/Al = 13.5 and 250) are employed, the higher concentration of naphtha is produced at the expense of heavier hydrocarbon fractions such as heavy gas oil and long residue. The appropriate pore size and pore structure of the Beta zeolites are expected to have a contribution for the effect. In general, a Beta zeolite has a relatively large pore size which provides a better accessibility of reactants to diffuse into the pore. Moreover, the zigzag pore structure of Beta zeolite can also retain the reactant to stay longer inside the pore to be further cracked, yielding a naphtha range product. Another reason is expected from the cracking and hydrogenative properties of the Pd/Beta catalysts, which hereby promote the saturation of aromatic-based hydrocarbons that are eventually cracked through the cracking and/or hydrogenolysis reaction yielding naphtha range product. However, no significant effect was found on the naphtha fraction in the oil when the Si/Al of the Beta zeolite was varied.

4.2.3.2 Chemical Compositions

Liquid chromatography technique was used in an attempt to quantify the amount of hydrocarbon species (saturated hydrocarbons, mono-aromatics, di-aromatics, poly-aromatics, and polar-aromatics) in the maltene. Figure 4.7 demonstrates the chemical composition in maltene from the catalytic pyrolysis of waste tire using the Pd/Beta catalysts (Si/Al = 13.5 and 250). The results reveal that the employment of both Pd/Beta (Si/Al = 13.5 and 250) catalysts can distinguishably enhance the production of saturated hydrocarbons. The results also show the reduction in all aromatic fractions. The cracking and hydrogenation activities of the catalyst are mainly attributed to these outcomes.

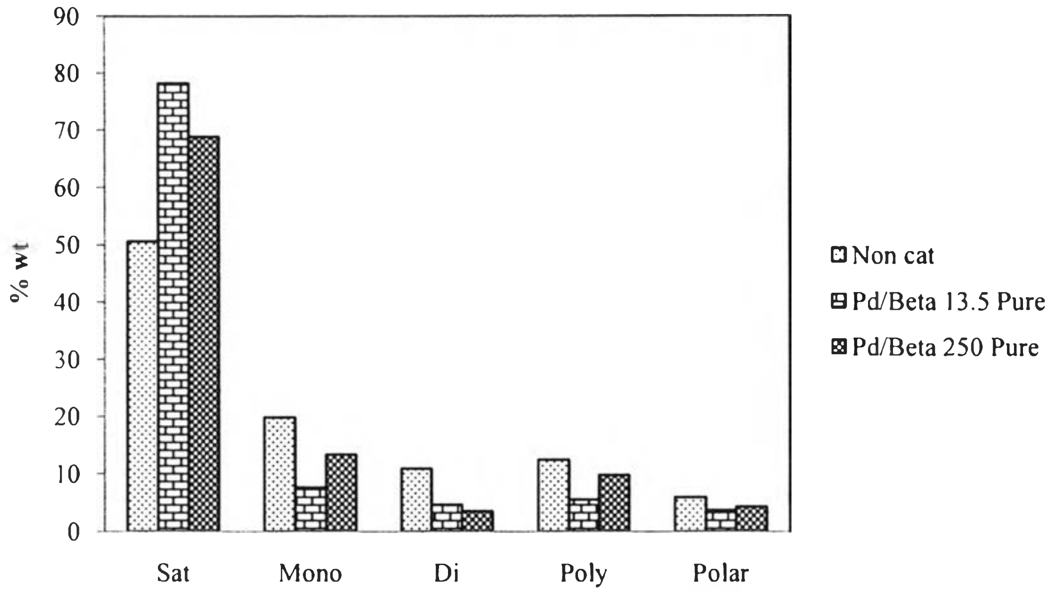


Figure 4.7 Chemical composition in maltene from the catalytic pyrolysis of waste tire using Pd/Beta catalysts (Si/Al = 13.5 and 250).

As demonstrated above, the use of both bi-functional Pd/Beta catalysts can improve the concentration of saturated hydrocarbons in the oil fraction by up to 20-28 wt. %. The results are in a good agreement with Pintoo *et al.* (2008). It has also been reported that the use of metallic function such as Pt can help convert the polar-aromatic and their precursor to saturated hydrocarbons through the hydrogenating activity of the catalyst (Dũng *et al.*, 2009). Palladium was one of the well-known noble metal, which already has been proven for its promising hydroginative activity; therefore, a similar effect on polar-aromatic reduction was expected. Furthermore, according to the previous study, Choosuton *et al.* (2007) reported that the employment of the bi-functional catalysts can greatly reduce the poly-aromatic hydrocarbons in the maltene fraction by up to 50-70%, which corresponds well to the results of the experiments. In comparison, the Beta (Si/Al = 13.5) shows a higher concentration of saturated hydrocarbon content (around 8 wt. %) than the Beta (Si/Al = 250) case. The better dispersion of metallic palladium is mainly responsible for this effect. The results from CO pulse chemisorptions confirm that the Pd/Beta (Si/Al = 13.5) has a higher metallic dispersion of palladium than the

Pd/Beta (Si/Al = 250). This may be resulted from the higher pore volume and specific surface area of the Pd/Beta (Si/Al = 13.5). The higher dispersion of metallic palladium could bring about a greater hydrogenation activity of the catalyst, which consequently promoted a better bond cleavage of the aromatic-based hydrocarbons through the metallic-acid function of the catalyst. Aside from the dispersion effect of palladium, a higher acid density in the case of Pd/Beta (Si/Al = 13.5) may have a contribution in the effect. The higher acid density provides higher acid sites to attack and crack large molecules such as poly-aromatics, yielding a higher saturated hydrocarbons concentration.

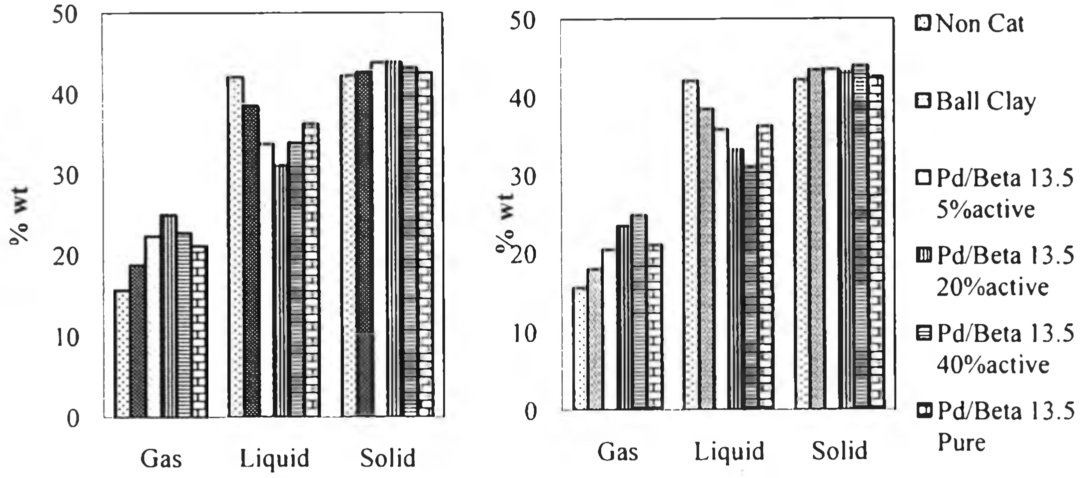
In conclusion, it is reasonable to conclude that the naphtha production in the oil product is mainly resulted from the appropriate pore size, pore structure, and the hydrogenation and hydrogenolysis function of the metallic palladium clusters in the catalyst. The difference in the Si/Al ratio of the Beta zeolite support has only the slight effect on the size of the liquid products (the petroleum fraction) obtained from the waste tire pyrolysis. However, concerning the chemical composition, it is found that a higher in the acid density of the catalyst possibly has a contribution on the chemical composition of the oil products, in which it provides a higher concentration of the saturated hydrocarbons as compared to the lower acid density case.

4.3 Agglomerated Catalysts

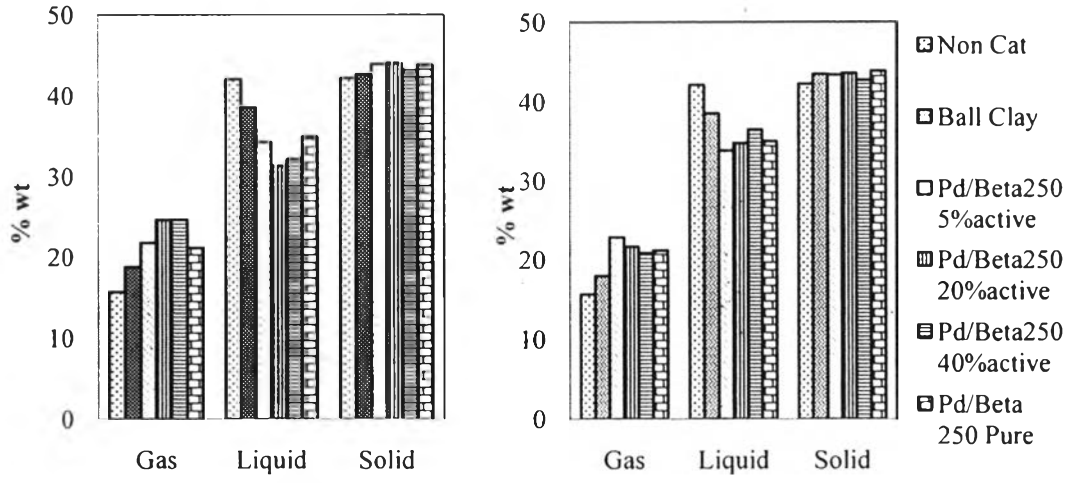
In general, a catalyst used in an industrial scale is usually presented in the form of agglomerated catalyst. The mixing of the pure active component with a binder and a matrix not only could help minimize the pressure drop along the catalytic bed, but it also means the mechanical properties improvement of the finished catalyst. In some cases, a matrix can also act as a diluent and a heat transfer medium for an active zeolite component, which moderates their cracking activity and subsequently prevents the over-cracking of the product (Sritana *et al.*, 2009).

4.3.1 Product Distributions

In this work, two types of natural clay matrixes, which are bentonite clay and ball clay, were used to examine the effect as a catalyst matrix for catalytic waste tire pyrolysis. The optimum extrudate composition that gives the highest naphtha yield and composition from the catalytic pyrolysis of waste tire was determined by using various percentages of active component (5, 20, and 40 wt %. of 0.25 wt. % Pd/Beta catalyst) in the presence of alumina binder (fixed at 10 wt. %) and a matrix. Figure 4.4 shows the product distribution of catalytic waste tire pyrolysis using Pd/Beta-based (Si/Al = 13.5 and 250) extrudates composed of two different clay matrixes. The results reveal that all the extrudates promote a gaseous production at the expense of liquid product. The use of both pure clay matrixes exhibits a similar effect to the product distribution, in which they slightly increase the yield of gaseous and lower the amount of liquid product produced than the non-catalytic case (thermal pyrolysis). This resulted increase in the gas yield primarily come from the mild cracking activity present when the clay matrixes are employed (The effect of matrix to the quantity and quality of the gas and liquid product shall be analyzed and discussed in details later in this chapter). Furthermore, in comparing the two pure clay matrixes used, no significant change in the product distribution is found. This possibly happens because the clay matrixes have relatively low surface area and acid density; therefore, the difference on their catalytic effects is not very well pronounced.



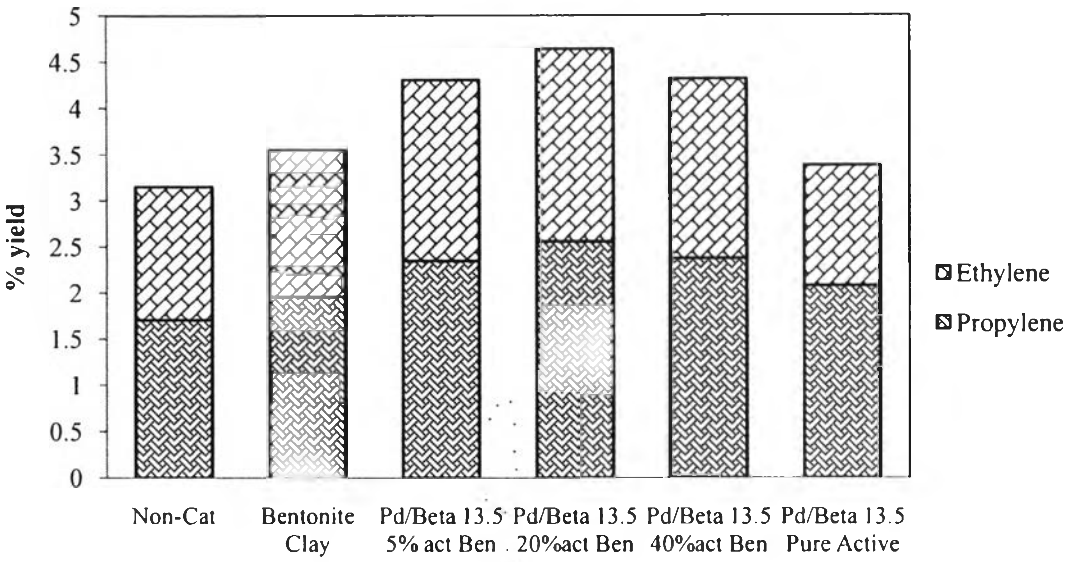
(Si/Al = 13.5)



(Si/Al = 250)

Figure 4.8 Product distribution of catalytic waste tire pyrolysis using Pd/Beta-based extrudates composed of different clay matrixes: Bentonite clay (Left), and Ball clay (Right).

For the case of pure active 0.25 wt % Pd/Beta catalyst, the higher production of gaseous product than that of bentonite and ball clay is found. It has been reported by many authors that the use of catalyst could help crack the heavy hydrocarbons molecule into the lighter product fractions via the cracking activity of the active zeolite, which is in this case higher gaseous production (Sritana *et al.*, 2009). Moreover, the appropriate pore size and pore structure of the zeolite have also been reported to play a great role in the activity on many types of reactions (Lucas *et al.*, 2005). For our cases of 0.25 wt. % Pd/Beta zeolite mixed with the binder (α-alumina) and the matrixes (bentonite and ball clay), all the extruded catalysts are found to produce the higher amounts of gaseous product as compared to all the other pure cases (pure active component, pure matrix and non-catalytic case). The increase in the overall gas production is beneficial in terms of a possible increase in light olefins production (ethylene and propylene), which has a considerably high market demand and economic values. Figure 4.9 demonstrates the increasing in the yield of light olefins produced when the extrudates, 0.25 wt. % Pd/Beta-based (Si/Al = 13.5) catalysts, were employed. Additionally, it has also been found that the increasing in the portion of active component from 5-40 wt. % slightly increases the amount of gas production. However, the information regarding only the product distribution cannot bring about any further logical conclusion. Therefore, the m ore detailed discussion will be done together with the other information, later in this chapter. The synergistic effect between the matrix and the active 0.25 wt. % Pd/Beta active zeolite is expected to responsible for this phenomenon.



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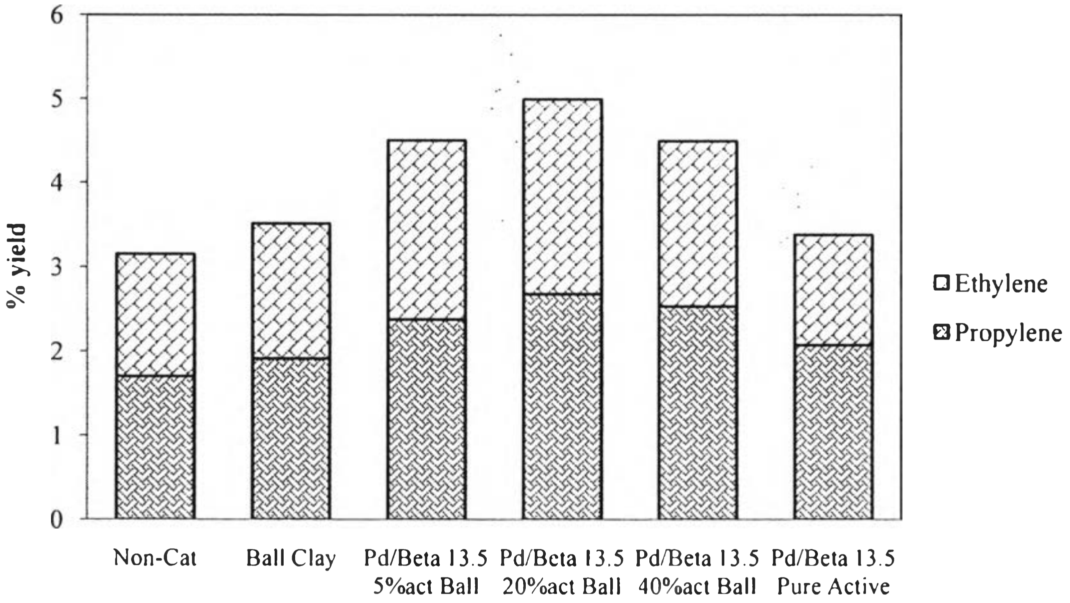


(b)

Figure 4.9 Light olefins production from using the Pd/Beta-based extrudates composed of two different clay matrixes: (a) bentonite clay, and (b) ball clay.

4.3.2 Gas Compositions

Figure 4.10 demonstrates the overall gas composition of the catalytic pyrolysis of scrap tire using the Pd/Beta-based extrudates prepared from mixing with the binder (α-alumina) and bentonite clay matrix. Similar to the pure active component case, the use of agglomerated catalysts exhibits the minor reduction in the composition of light olefins via the hydrogenative function of the impregnated palladium.

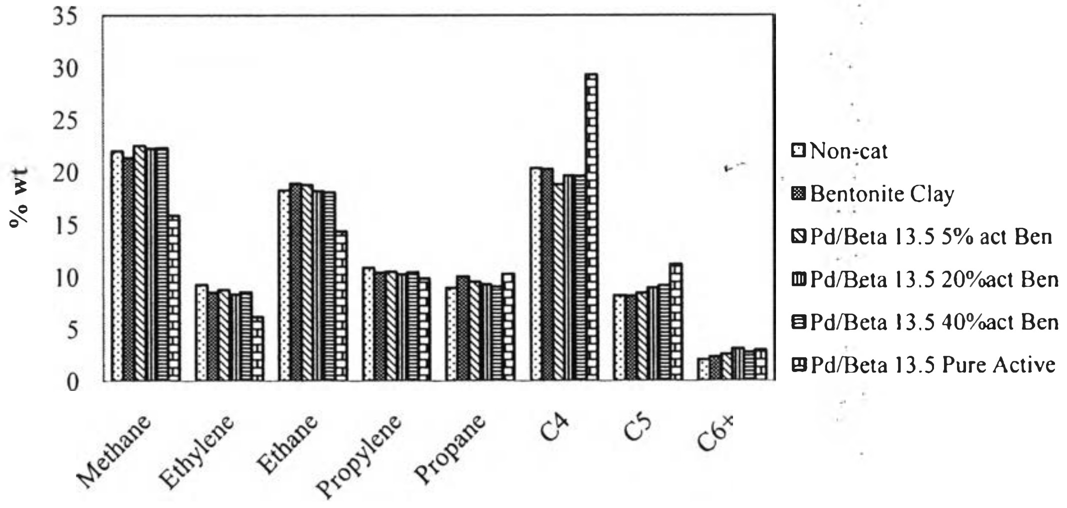
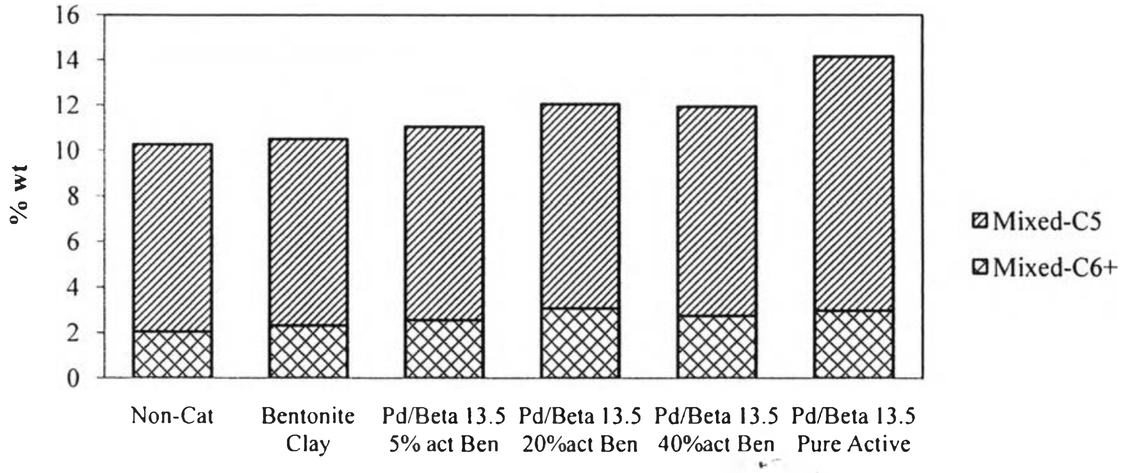


Figure 4.10 Overall gas composition using the Pd/Beta-based extrudates produced from mixing with bentonite clay.

Figure 4.11 demonstrates the composition (by weight) of C_5 and C_{6+} hydrocarbons in the gaseous product from using 0.25 wt. % Pd/Beta (Si/Al = 13.5) zeolite mixed with the binder and two different clay matrixes. The results reveal that the extrudates can slightly enhance the production of C_5 and C_{6+} hydrocarbons in the gaseous composition. In general, a higher concentration of heavy hydrocarbon molecules (C_5 and C_{6+}) in the gas phase has the advantage in terms of greater heating values of the gas product for the direct use as an energy source to any operation unit. The explanation is based on the occurrence of the secondary reactions, which are favored by the higher acid density of the Beta (Si/Al = 13.5) support. However, a similar observation has not been found in the case of the Pd/beta-based extrudates (Si/Al = 250) (See in Appendix C).



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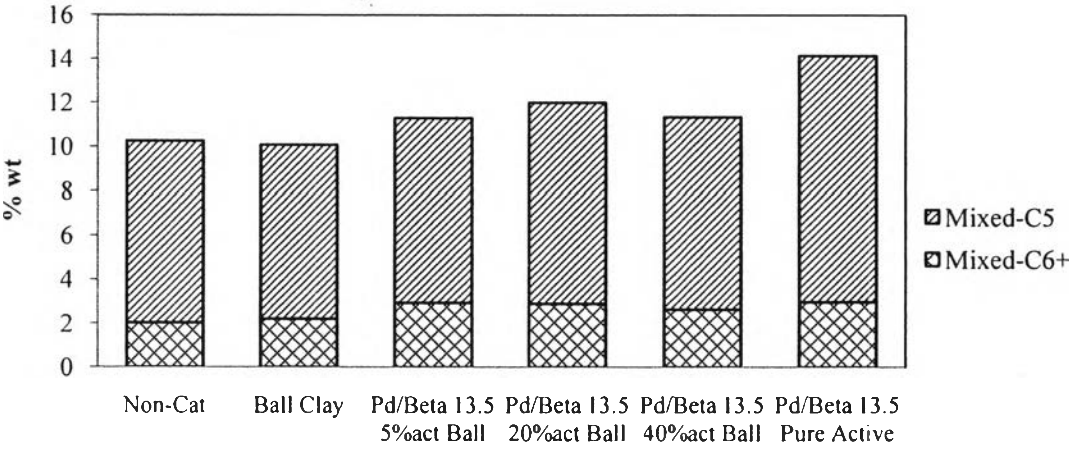


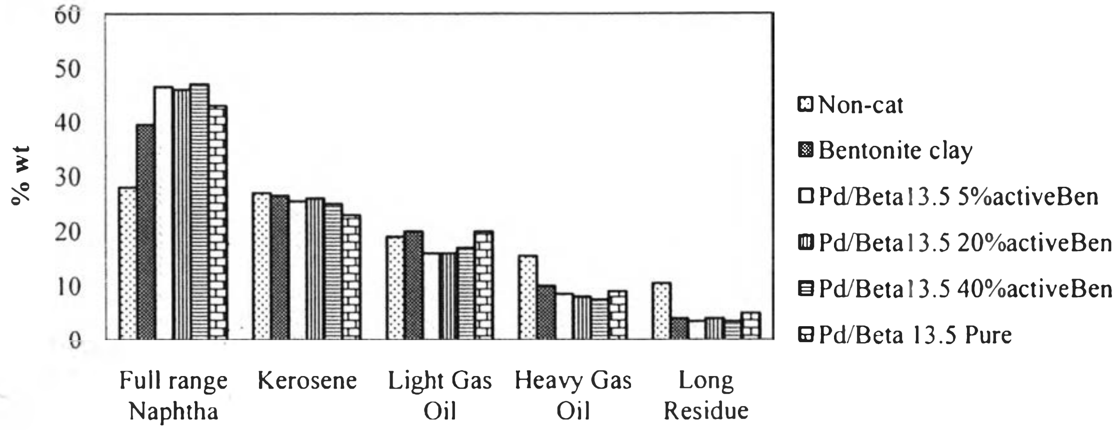
(b)

Figure 4.11 Product compositions of mixed C_5 and C_{6+} hydrocarbons from using Pd/Beta-based extrudates composed of two different clay matrixes: (a) bentonite clay, and (b) ball clay.

4.3.3 Liquid Products

4.3.3.1 Petroleum Fractions

In this part, the petroleum fraction obtained from waste tire pyrolysis using the extrudates is analyzed and discussed. Figures 4.12 and 4.13 show the petroleum fractions in maltene obtained from waste tire pyrolysis using Pd/Beta-based extrudates (Si/Al = 13.5 and 250) prepared from two different clay matrixes. First, for the cases of pure matrix, bentonite and ball clay alone, a higher amount of naphtha is produced at the expense of heavy hydrocarbon fractions such as heavy gas oil and long residue. The result is expected from the cracking of part of the heavy oil products through the mild acid and/or basic sites contained in the natural clays. Likewise, for both cases of pure active components (0.25 wt. % Pd/Beta zeolites with Si/Al = 13.5 and 250), the higher proportion of naphtha is produced (compared to the cases of pure matrix). This is due to the higher total acidity and acid strength of the Beta zeolites, which are superior to the natural clays, and bring about the higher promotion of cracking activity. Furthermore, the lighter hydrocarbons obtained can also be resulted from the hydrogenolysis function of palladium cluster on the catalysts. However, the use of both pure active components, 0.25 wt. % Pd/Beta (Si/Al = 13.5 and 250) even with a higher total acidity and acid strength, does not show the distinctive activity in reducing the heavy hydrocarbon fractions such as gas oil and long residue from that of the pure matrixes (bentonite and ball clays). This phenomenon can be explained by several reasons; for example, in the molecular size perspective. Prior to any further discussion, it should be kept in mind that the hydrocarbons obtained from waste tire pyrolysis are of different sizes and dimensions, ranging from a very small molecule such as methane to a very large poly aromatics, which contain up to forty carbon atoms in the molecule. Therefore, dissimilar to the meso-porous material such as natural clays, zeolitic materials such as Beta zeolite have a much smaller pore system, which acts as a molecular sieve and allows only a small enough molecule of the thermal cracking products to enter the zeolitic pores. As a result, some portion of the heavy products may lack of the possibility to access to the intrinsic acid and/or metallic sites of the zeolite. For this reason, the cracking of the heavy hydrocarbons fractions is supposed to take place mainly at the outer surface of the zeolites, and those, which cannot be diffused in to the zeolite pore, are expected to leave without being cracked, which is resulted in the insufficient reduction in the heavy hydrocarbons fractions.



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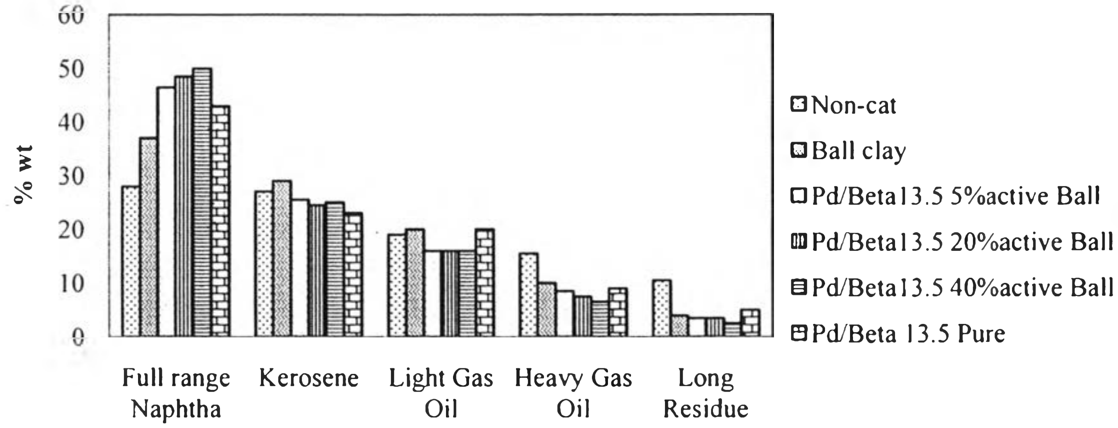
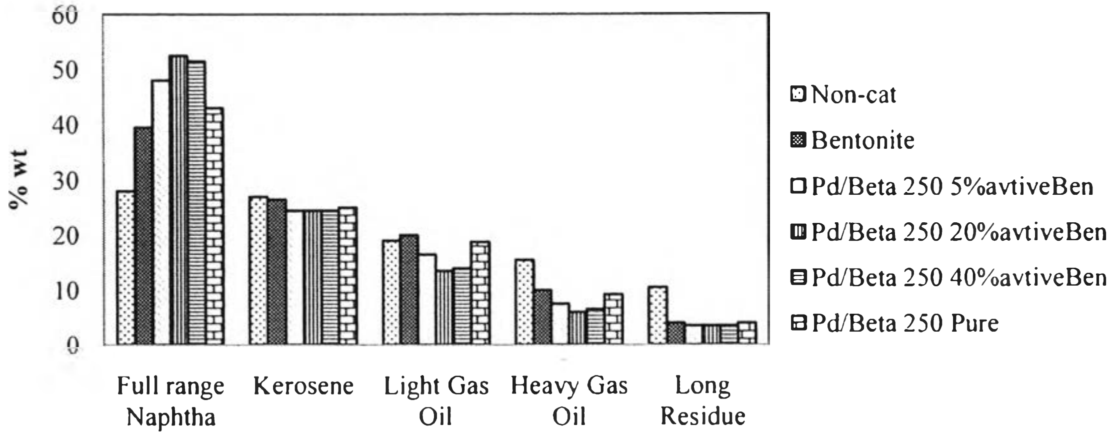
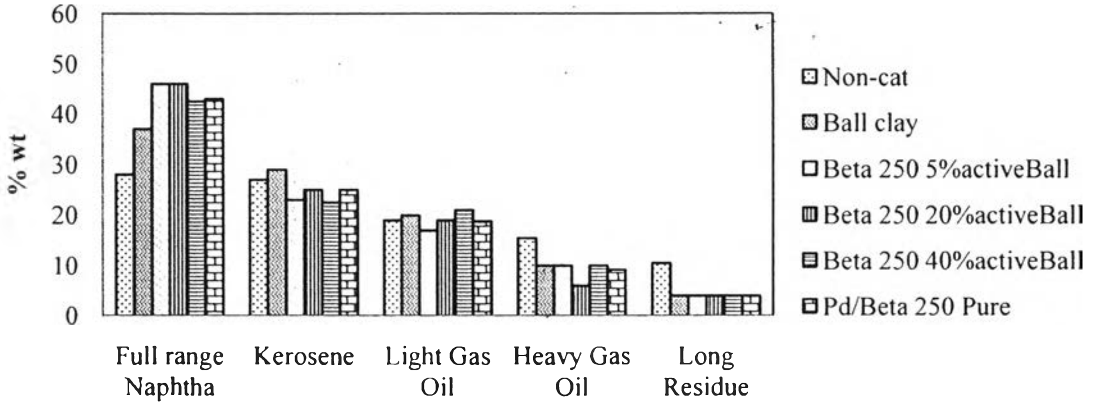


(b)

Figure 4.12 Petroleum fractions in maltene from using Pd/Beta-based extrudates (Si/Al = 13.5) composed of two different clay matrixes: (a) bentonite clay, and (b) ball clay.



(a)



(b)

Figure 4.13 Petroleum fractions in maltene from using Pd/Beta-based extrudates (Si/Al = 250) composed of two different clay matrixes: (a) bentonite clay, and (b) ball clay.

For a series of compounded catalysts, all the extrudates exhibit a higher proportion of naphtha production as compared to the cases of pure matrix and the pure active component. Furthermore, the results also show a relatively lower portion of heavy hydrocarbon content for extrudates. An explanation, which can be attributed to this effect, is the synergistic effect between the mild cracking activity of the meso-porous clay matrix and the cracking activity of active component. It has been reported by several authors that the clay matrix, which bears some mild acid and/or basic sites, can act as a diffusing medium to direct the product from the thermal cracking to the zeolitc framework, and partially crack the heavy hydrocarbon molecules, yielding smaller hydrocarbon fractions (Sritana *et al.*, 2009). On account of that, a part of the resulted smaller product molecules can further be diffused and cracked in the inner pore of the active zeolite resulted in a higher naphtha concentration in the oil product. In addition, some hydrocarbon molecules, which require a stronger acid strength and cannot be cracked readily by the mild acidity or basicity of the clay matrix alone, can possibly be cracked by the exterior acid sites of the zeolite. Based on the results regarding the product distribution, most of the compounded catalysts also show a lower yield of liquid as compared to all the other cases, which can indirectly reflect to their higher overall cracking activity. The increase in the amount of active zeolite contributed in the agglomerated catalysts from 5 to 40 wt % show only a slight increase in the concentration of naphtha range product.

In conclusion, in order to clearly explain the results on petroleum fraction analysis, some hypothesis has been proposed and concluded as follows. As mentioned earlier, it is obvious that the clay matrixes themselves are not catalytically inactive, and some heavy hydrocarbon molecules can be cracked via the mild cracking activity of the meso-porous clay matrix. On the other hand, the active catalyst tends to have the cracking and hydrogenolysis activity on the acid and the supported metal sites through their external surface activity (acid-metal) due to the diffusional limitation concerning the pyrolytic products molecular sizes and dimensions. The combination of the two functions of the materials brings about the existence of the synergistic effect, which further enhances the cracking activity of heavy hydrocarbons. The increase in the active component from 5 to 40 wt. % of Pd/Beta zeolite in the extrudates helps enhance the catalytic activity in terms of increasing the strong acid sites density, which helps crack some hydrocarbon molecules that cannot readily be cracked by the mild acid function of clay matrix. As a result, a slight increase in the content of naphtha range product is achieved.

Apart from the issue on the naphtha concentration in the oil product, the overall yield of naphtha is also a serious concern in terms of economic optimization. According to the results, although the higher concentration of naphtha in the pyrolytic oil can be achieved by using catalysts, but one may recognize that the yield of the liquid product can be considerably dropped as compared to the thermal pyrolysis. So, it is very interesting to see whether the increase in the concentration of naphtha can overcome the considerable drop in the liquid production. Table 4.4 demonstrates the summary of the relative naphtha yield for all the catalytic cases. The results are reported in the terms of the ratio of naphtha yield from a catalytic case to that of the non-catalytic case. It is hereby noted that the yield of naphtha from thermal pyrolysis is reported as 11.8 wt. %. The results reveal that all the catalytic cases can produce a considerably higher yield of naphtha as compared to the non-catalytic case (at about 1.3-1.4 times higher). The extrudates, which give the maximum naphtha yield as well as the highest naphtha concentration, are the series of Pd/Beta with Si/Al = 250 mixed with the bentonite clay. Up to this point it can be concluded that the use of compounded Pd/Beta-based extrudates is an appropriate way for the production of naphtha range product in terms of both naphtha concentration and yield.

Table 4.4 Relative ratio of naphtha yield (Catalytic / Non-catalytic case): (a) Pd/Beta (Si/Al = 13.5), and (b) Pd/Beta (Si/Al = 250)

(a)

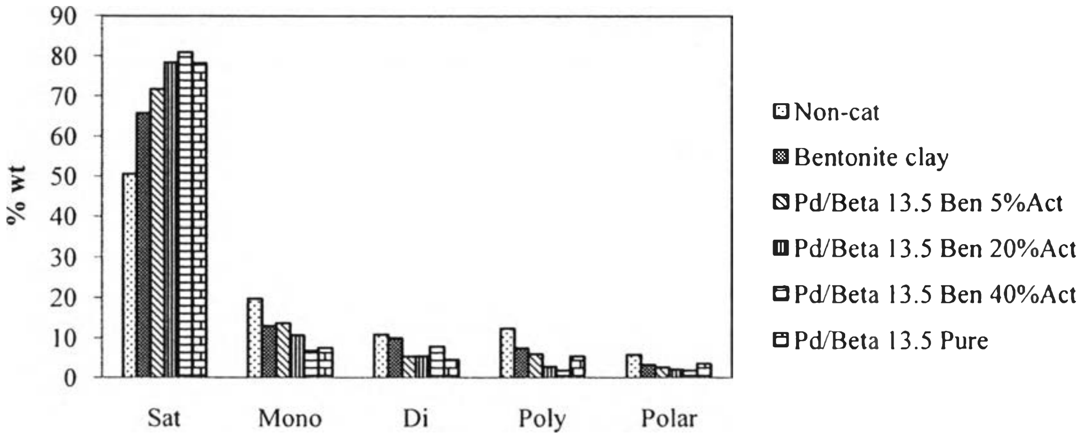
Matrix type	**Pure Matrix**	**5 % active**	**20 % active**	**40 % active**	**100% active**
Bentonite	1.29	1.33	1.22	1.36	1.32
Ball clay	1.21	1.37	1.37	1.32	

(b)

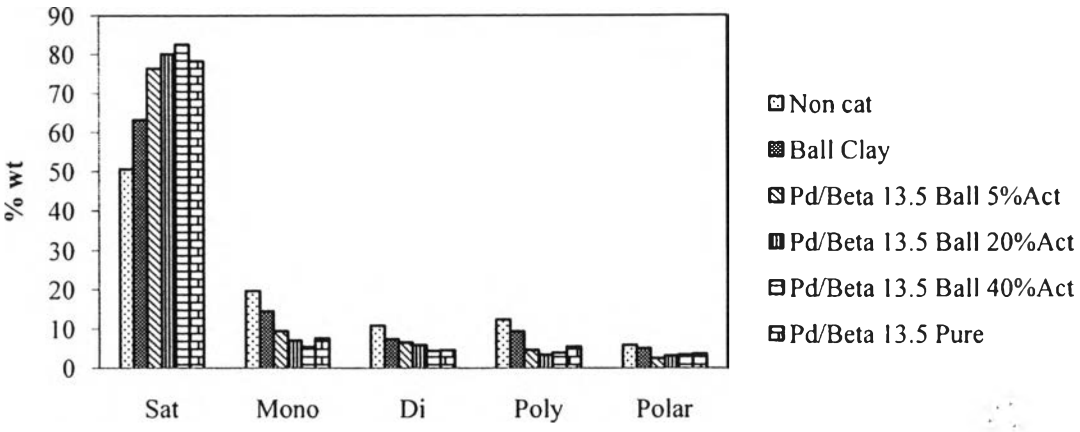
Matrix type	**Pure Matrix**	**5 % active**	**20 % active**	**40 % active**	**100% active**
Bentonite	1.29	1.40	1.40	1.41	1.28
Ball clay	1.21	1.32	1.36	1.31	

4.3.3.2 Chemical Compositions

As stated, the employment of active 0.25 wt. % Pd/Beta catalysts can distinguishably enhance the concentration of saturated hydrocarbons in the oil fraction. Figure 4.13 demonstrates the chemical composition in maltenes from the catalytic pyrolysis of waste tire using Pd/Beta-based catalysts (Si/Al = 13.5 and 250). It is found that the use of clay matrix alone can also help increase the content of saturated hydrocarbons in the oil product. This is probably resulted from the cracking of large aromatic-containing compounds, which gives at least one or more saturated hydrocarbons molecules. For the compounded catalysts, the results reveal that only 5% loading of the active component (Pd/Beta zeolite) can significantly enhance the production of saturated hydrocarbons up to approximately 70 wt. %. Moreover, a further addition of the active component slightly increases the concentration of saturated hydrocarbons which reaches the maximum of around 80 wt. % for the cases of 40 wt. % active component (Pd/Beta zeolite Si/Al = 13.5 mixed with bentonite and ball clay). The results are expected from the synergistic effect between the cracking and the saturation of aromatic-based product through the acid-metallic function of the bi-functional Pd/Beta catalyst. The outstanding hydrogenative property of palladium has been supported by many literatures.



(a)



(b)

Figure 4.14 Chemical compositions in maltenes obtained from using the Pd/Beta-based extrudates (Si/Al = 13.5) composed of two different clay matrixes: (a) Bentonite clay, and (b) Ball clay.

4.3.4 Asphalthene Content in Oil Product

Asphaltene content is one of the factors which represent the quality of the oil product. The lower asphaltene content is preferable for several reasons, such as, the ease of further separation and processing. The asphaltene content in the oil fraction was obtained from the ultrasonic shaking of the pyrolytic oil in the n-pentane solution. The precipitated asphaltexzne was afterward removed out by means of vacuum filtration using nylon membrane filter. The employment of catalyst is one of the proven techniques which can effectively help reduce the asphaltene content in the oil product obtained from waste tire pyrolysis. Figure 4.14 shows the weight percentage of asphalthene fraction in maltenes from using the Pd/Beta-based (Si/Al = 13.5) extrudates. The results reveal that the non-catalytic case gives a very high asphaltene content in the oil product (0.28 wt. %). The use of catalysts can distinguishably reduce the asphatltene content in the pyrolytic oil through the cracking and hydrogenative functions of the catalyst. Similar to the cracking of heavy hydrocarbon molecules, the cracking of asphaltene in the oil product is expected to take place mainly at the outer surface of the catalyst, as the diffusion into the zeolite pores is not possible.

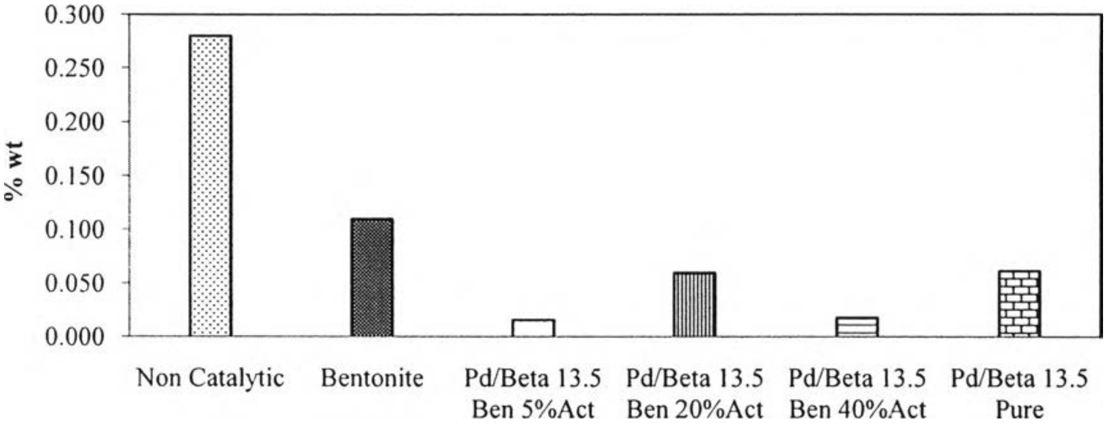


Figure 4.15 Weight percentage of asphalthene in maltenes from using Pd/Beta-based (Si/Al = 13.5) extrudates.

4.3.5 Coke Formation on the Spent Extrudates

The coke formation on a spent catalyst was determined by thermal gravimetric analysis (TGA). The results show that both of the pure active components (0.25 wt. % Pd/Beta with Si/Al = 13.5 and 250) have the high amount of coke, which are approximately 30 wt. % and 22 wt % respectively. The uses of pure active catalysts exhibit a comparatively higher coke formation than the use of pure matrixes (natural clays). Several reasons can be attributed for this effect, for examples, the high cracking activity of the catalyst, which in turn produces some coke through the side reactions, and the over-cracking of the product during the reaction. The other reason is on the high pore volume of the active zeolites, which is capable of retaining the coke inside. Table 4.5 demonstrates the coke formation on the spent catalyst in all the catalytic cases.

Table 4.5 Weight percentage of coke formation on the spent extrudates

Active component (wt %)		**Wt. % Coke**	
		Bentonite clay	**Ball clay**
Beta (Si/Al = 13.5)	5%	12.3	14
	20%	14.4	17.3
	40%	18.3	19.5
	100%	30.4	
Beta (Si/Al = 250)	5%	8.9	10.7
	20%	13.8	13.5
	40%	14.7	18.4
	100%	21.4	
Pure matrixes		11.9	11.5
Non-cat/No support		-	

4.3.6 Sulfur Content in the Oil Products

The sulfur content is one crucial parameter to determine the quality of the derived product. In today's world, more and more strengthen specification on sulfur content in the transportation fuel is being released (e.g., the ultra low sulfur specification in gasoline and diesel oil). In another point of view, the removal of sulfur and hetero-atoms is also aimed for the protection of the catalysts in downstream operations, which can be deactivated easily even in a presence of very low sulfur concentration. Concerning the waste tire pyrolysis, as the reaction was taken place in an oxygen-free atmosphere and the fed tire itself rarely contains nitrogen atoms in its molecules; hence, the elimination of sulfur is the predominant outcome expected here. The sulfur comprising in the feed tire mainly comes from the curative agents, which was used during the vulcanization process. In regards to the tires vulcanization, sulfur can be combined in the tire polymer network by several ways, e.g., mono-, di-, and/or poly sulfide bridges (Dũng *et al.*, 2009a). Sulfur containing compounds are usually found to be hazardous, and sometimes they can be severely corrosive when reacting with water. For this reason, the sulfur content in the feed scrap tire, spent catalysts, and the product derived from waste tire pyrolysis are determined. The sulfur content in the feed tire is found to be approximately 2.3 wt. %. When the tire molecules are ruptured and cracked, the sulfur containing molecules are distributed randomly in the entire derived products, including the spent catalysts. For the non-catalytic or thermal pyrolysis, it is found that the concentration of sulfur in the pyrolytic oil is approximately 1.3 wt. %. The use of both Pd/Beta catalysts (Si/Al = 13.5 and 250) can help reduce the sulfur in the oil product by up to 33 % (the concentration of sulfur is found to drop to 0.88 wt. % when both catalysts are employed). The reduction of sulfur in the oil product is mainly resulted from the cracking and hydrogenating properties of the catalyst. In addition, the cleavage of the C-S, and S-S bonds by the hydrogenolysis function of palladium is also possible. When it comes to the removal of sulfur, it usually refers to the hydro-treating and/or hydro-desulfurization (HDS) process. The typical catalysts practically used in the industry are the molybdenum-based catalysts incooperated with the cobalt and nickel, or so-called CoMo and NiMo catalysts. However, noble metals such as Pd and Pt, or Pt-Pd supported catalysts have also been studied extensively for their activity in hydro-treating and/or hydro-desulfurization (HDS) of many kinds of feed materials (Adeline *et al.*, 2005). However, it is noticeable that the concentration of sulfur in the oil product even with the employment of Pd/Beta catalysts is still rather high (~0.9 wt %). This is expected from the bulkiness of the S-comtaining cyclic compound which makes it more difficult for the S atom to access to the acid or metal sites of the catalyst. A substantial reduction of sulfur is also found when natural clays were employed. The depression of sulfur is primarily resulted from the mild cracking activity of the natural clay.

For the case of compounded catalysts, all the extrudates give the similar sulfur reduction. The concentrations of sulfur are found to be at approximately 1 wt. % for all extrudates. This suggests the dilution effect, on the sulfur reduction, of the active component in the catalysts. Figure 4.15 shows the weight percentage of sulfur in the pyrolytic oil using various extrudates.

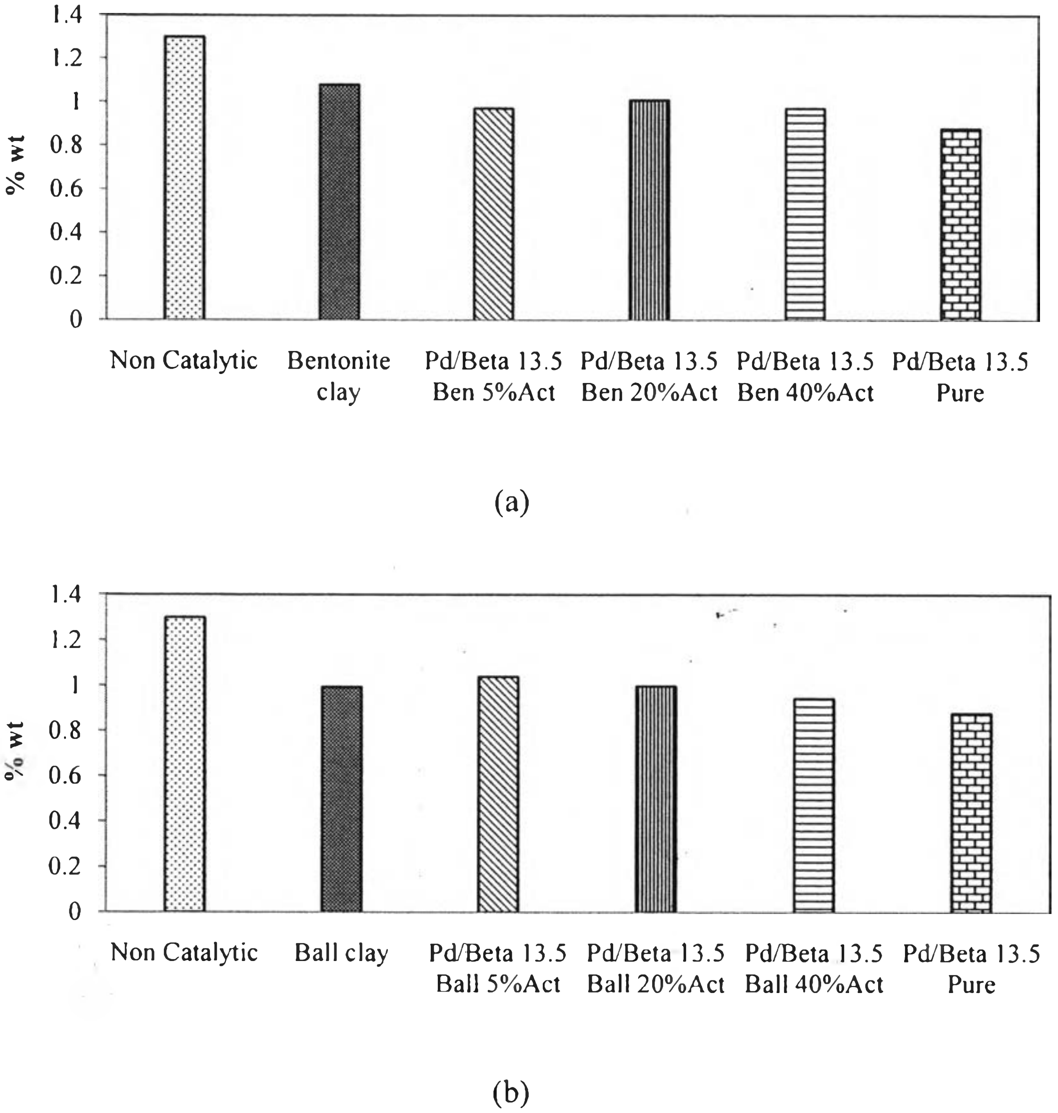


Figure 4.16 Weight percentage of sulfur in the pyrolytic oils from using various extrudates composed of two with different clay matrixes: (a) bentonite clay, and (b) ball clay.