



## CHAPTER IV

### RESULTS AND DISCUSSIONS

The pyrolysis of waste tire produces gas, liquid and solid products. Especially, liquid products can be produced as the most abundant and valuable fraction. All of these products can be used in wide applications, such as chemical feedstock, and a fuel source. However, the liquid products consist of complex mixtures of chemical components such as asphaltene, saturated hydrocarbons, mono-aromatic, di-aromatic, poly-aromatic, and polar aromatic compounds. Furthermore, there is some limitation to use the liquid or oil product as a high grade fuels due to lower quality, fuel specification, and more seriously environmental emission. High aromatic content in the liquid product is the one problem in real applications.

The pyrolysis products are affected by many parameters (feed properties, types of reactor, and operating conditions), catalysis is the one of technologies which can improve the quality and/or quantity of desired products. Therefore, catalytic pyrolysis is the way to solve this problem. In this work, the effects of catalysts (Pd/H-BETA), metal loading, catalytic temperature, residence time, and metal loading methods on tire pyrolysis products were examined. Especially, the reduction of aromatic contents in liquid products and the increase of desired products were emphasized. The results and discussions are presented as following.

#### 4.1 Effects of Palladium on H-BETA

The effects of noble metal on the liquid product obtained from the pyrolysis of tire were investigated. 30 g of scrap tire was pyrolyzed at atmospheric pressure with the final pyrolysis temperature of 500°C. The 1%wt palladium over H-BETA zeolite was packed at the upper bed in the bench scaled autoclave reactor with the catalytic temperature of 350°C. The liquid product was analyzed by a SIMDIST-GC and classified into 5 petroleum fractions according

to their boiling points as shown in Table 4.1. The results and discussion on the effects of chemical composition of liquid products, and carbon number distributions are presented in this part. All raw data for this part are presented in Table C1, C2, F5, F6, and I4 in Appendix C, F, and I.

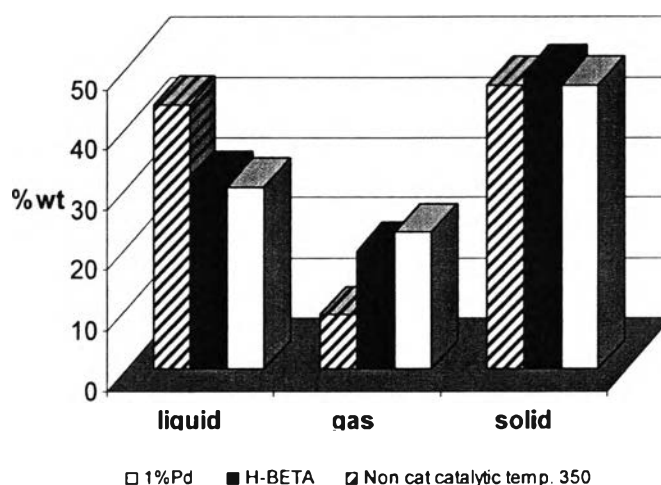
**Table 4.1** The boiling point and carbon range of refinery products (Speight, 2002)

<b>Fraction</b>	<b>Carbon range</b>	<b>Boiling point (°C)</b>
Gasoline	C <sub>5</sub> -C <sub>9</sub>	15.5-149
Kerosene	C <sub>10</sub> -C <sub>13</sub>	149-232
Gas oil	C <sub>14</sub> -C <sub>20</sub>	232-343
Light vacuum gas oil	C <sub>21</sub> -C <sub>23</sub>	343-371
Heavy vacuum gas oil	C <sub>24</sub> -C <sub>50</sub>	371-566

#### 4.1.1 Product Distribution

Figure 4.1 shows the effect of H-BETA and 1 %wt Pd /H-BETA catalyst on pyrolysis products. The results indicate that both catalysts have an influence on the product yields. H-BETA increases the gas yield from 9 to 19.46 %wt and reduces the liquid yield from 47.3 to 31.4 %wt. This is because the acid support (H-BETA) of catalyst cracked liquid products or heavy hydrocarbons into light hydrocarbons or the gas products. Similarly, William *et al.*, (2002) reported that the presence of catalyst in tire pyrolysis helped to reduce the oil yield and increase the gas yield. Moreover, Pd/H-BETA shows a higher gas yield and a lower liquid yield. It is possible that the noble metal or palladium can enhance the hydrogenation and hydrogen transfer reactions. And then, the heavy hydrocarbons were cracked onto lighter products. For, solid product, there was no sig-

nificant difference in solid yield with adding palladium over H-BETA catalyst for tire pyrolysis.

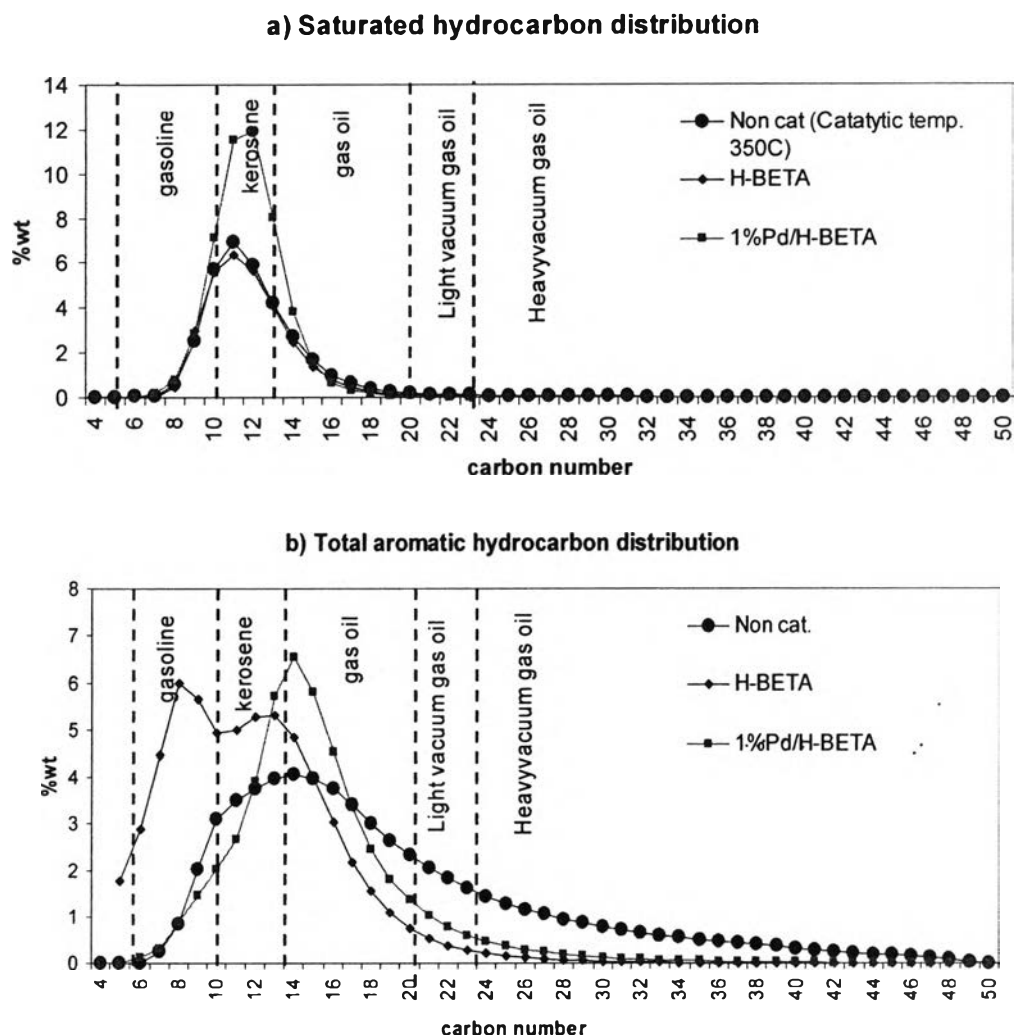


**Figure 4.1** Product distribution of catalytic pyrolysis of scrap tire using H-BETA and 1%wt Pd /H-BETA.

#### 4.1.2 Quality of Pyrolysis Oil

Figure 4.2 shows the carbon number distribution of saturated hydrocarbons and aromatic compounds. This carbon distribution curve can roughly indicate the chemical components in 5 petroleum fractions in the liquid products. It is found that the most saturated hydrocarbons are in the kerosene range. Pd/H-BETA catalyst can produce higher saturated hydrocarbons in the kerosene fraction than the other petroleum fractions as shown in Figure 4.2 (a).

Moreover, Figure 4.2 (b) shows that the catalyst can reduce aromatic compounds in the heavy fractions (light and heavy vacuum gas oil), and decrease the aromatic compounds in kerosene and gasoline fractions. Moreover, it also produces the narrow distribution of aromatic compounds. It might be considered that the bi-functional catalyst can enhance hydrogenation reaction, and crack the high molecular weight into lower molecular weight aromatic compounds. The pores of the catalyst might be selective to produce the narrow range of carbon distribution numbers of aromatic compounds.



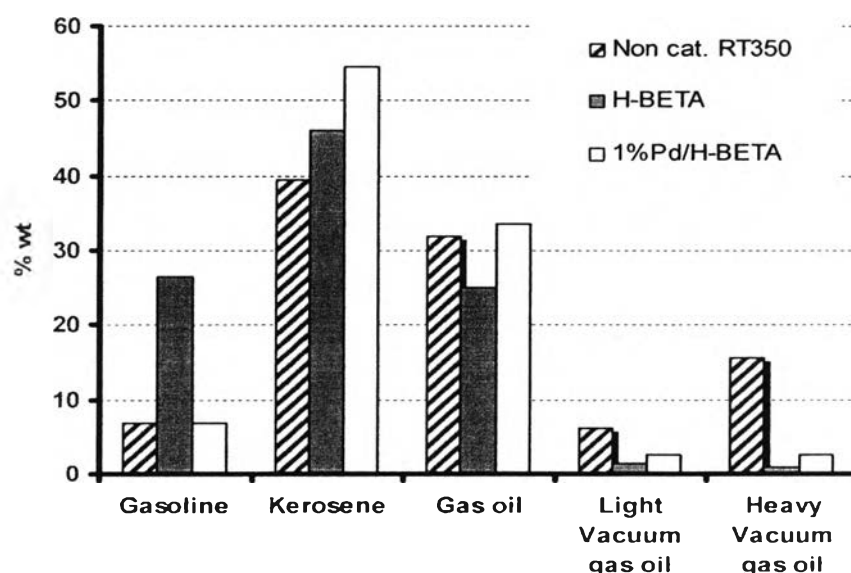
**Figure 4.2** Carbon number distribution of (a) saturated hydrocarbons, (b) total aromatic compounds in maltene fractions obtained from non catalytic and catalytic pyrolysis at the catalytic temperature of 350°C.

#### 4.1.3 Quantity of Petroleum Fractions

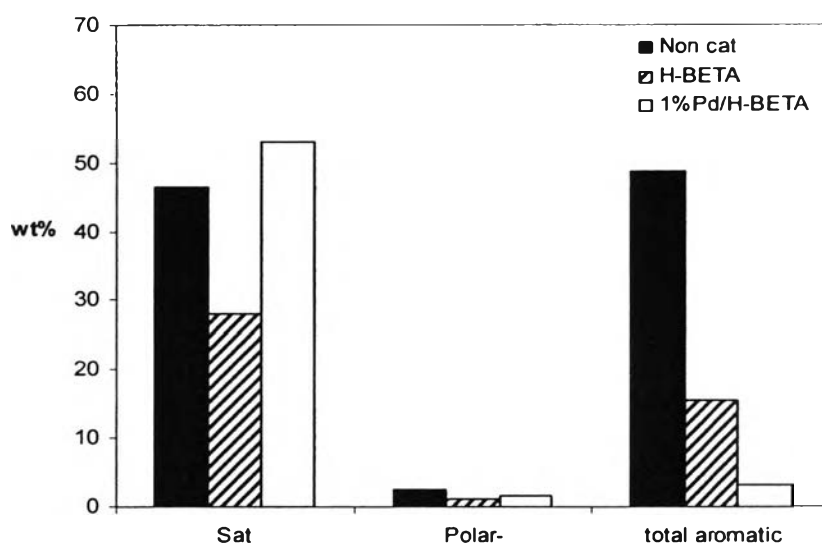
Liquid products obtained from catalytic pyrolysis were separated into 5 petroleum fractions. The effect of Pd/H-BETA catalyst on the petroleum fraction in maltene is shown in Figure 4.3. It can be observed that the heavy hydrocarbons such as light and heavy vacuum gas oil are reduced. Consequently, kerosene and gas oil are increased with the addition of Pd/H-BETA in the system. In the other hand, there is a significant decrease in the gasoline yield as compared with using H-BETA as the catalyst (Figure 4.3). However, the chemi-

cal compositions of gasoline are shown in Figure 4.4. The results show that the Pd/H-BETA zeolite increases the saturated hydrocarbons. Consequently, the total aromatic hydrocarbons are decreased. It can be explained that the Palladium can enhance the hydrogenation activity and ring opening reactions, and then the hydrogenated or ring opening products might be cracked on acid sites to lower molecular weight hydrocarbons or the gas products. Figure 4.5 shows that heavy hydrocarbon gases ( $>C_5$  gases) are increased, and the mixed  $C_4$  and  $C_5$  are decreased, resulting in the increase in light hydrocarbons (Methane, Ethylene, and Ethane) when the Pd/H-BETA was used as the catalyst. These results indicate the trend of hydrocarbon cracking, which heavy hydrocarbons are cracked to lighter hydrocarbons.

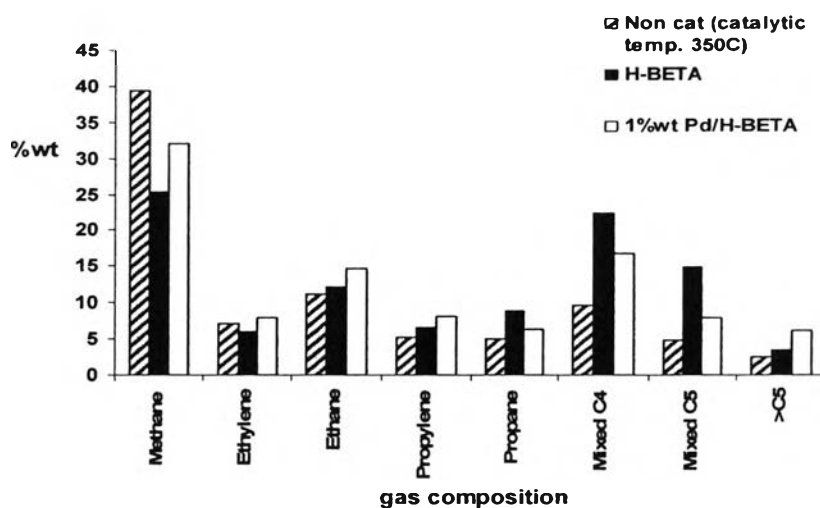
In addition, the Pd/H-BETA catalyst gave the higher yield of kerosene fraction. From these results, it means that the Pd/H-BETA might crack the high molecular weight hydrocarbons to produce those in the kerosene fraction, or the pore size of zeolite support gave the high selectivity to produce kerosene.



**Figure 4.3** Petroleum fractions in maltene obtained from catalytic pyrolysis using H-BETA and 1 %wt Pd /H-BETA at the catalytic temperature of 350°C.



**Figure 4.4** Chemical composition in gasoline fraction obtained from catalytic pyrolysis using H-BETA and 1 %wt Pd /H-BETA at the catalytic temperature of 350°C.



**Figure 4.5** Chemical composition of gas products obtained from catalytic pyrolysis using H-BETA and 1 %wt Pd /H-BETA at the catalytic temperature of 350°C.

From the quantity of 5 petroleum fractions and the quality of pyrolysis oils, it can be concluded that the Pd/H-BETA catalyst can produce the high quantity of kerosene fraction containing the high amount of saturated hydrocar-

bons. Simultaneously, it reduced the aromatic compounds in pyrolysis oil as compared with non-catalytic pyrolysis case. Therefore, The Pd/H-BETA was selected to study further in the effect of palladium loading on the quantity of petroleum products and the quality of pyrolysis oil.

## 4.2 Effect of Pd Loading Amount

The Pd/H-BETA was prepared by an impregnation method, and the amount of palladium loading was varied to 0.25, 0.50, 0.75, 1.00, and 1.25%wt. The final temperature of pyrolysis zone and catalytic zone are 500°C and 350°C, respectively. The influence of loading amount onto the H-BETA onto pyrolysis products are reported in this part.

### 4.2.1 Catalyst Characterization

#### 4.2.1.1 Crystal Structure of Catalysts

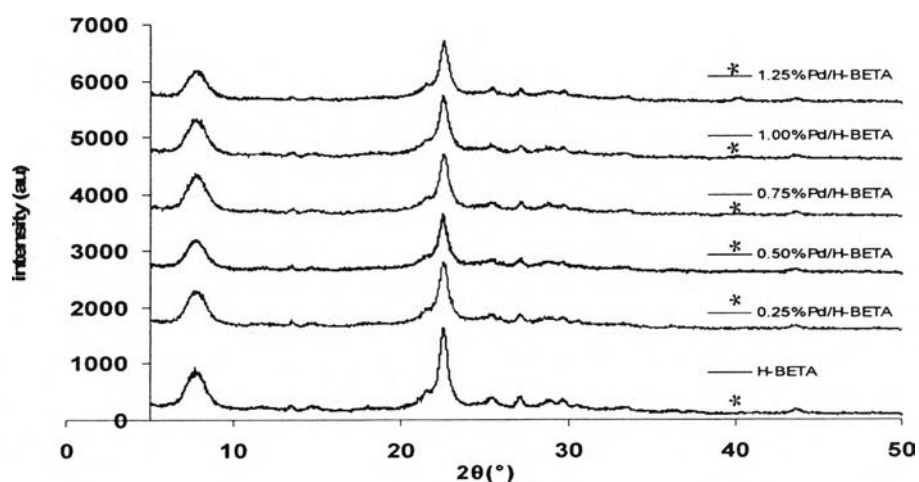
The XRD patterns of various percentages of palladium loading show the typical peaks of all catalysts associated with H-BETA zeolite (Figure 4.6). The addition of palladium and the increase of palladium loading did not affect on the crystal structure of zeolite.

#### 4.2.1.2 Palladium Particle Size

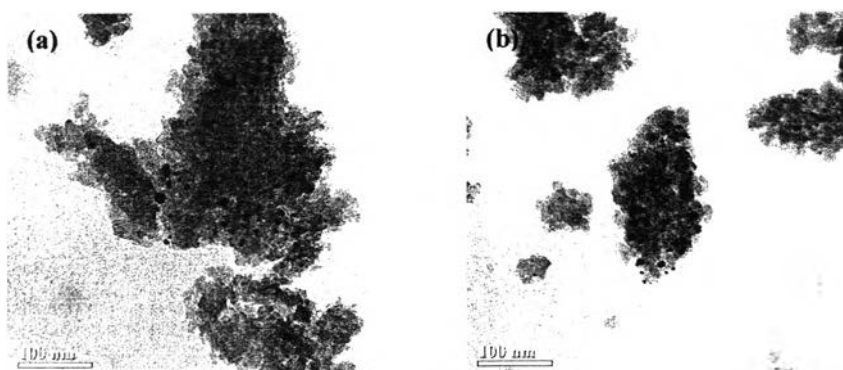
In the XRD patterns, only the diffraction lines of pure H-BETA support were observed (Figure 4.6) because Pd crystals were too small (below the XRD detection limit). This result may also indicate that the formation of well dispersion amorphous phase and/or the crystal smaller than 4 nm (Castano et al, 2006). The TEM image of Pd/H-BETA catalyst with the Pd content of 0.25 wt.% and 1 wt% confirm the small sizes of palladium particles (Figure 4.7). The metal particles are nano-particles, and have a various sizes (3-15 nm). The TEM images also show that larger particle sizes are formed when the amount of metal loading was increased. This same effect has been observed by Lucas et al, in 2005.

#### 4.2.1.3 Surface Area, Average Pore Volume, and Pore Size of Catalysts

The specific surface area of the impregnated catalysts was decreased when palladium was loaded on the zeolite support as shown in Table 4.2. It is possible that the palladium particle might cover the pores of catalyst, and the  $N_2$  gas used in the BET method could not diffuse into the pore. Therefore, the determined surface area was decreased. The effect of palladium loading had no significant change with the increasing amount of palladium loading.



**Figure 4.6** The XRD patterns of various impregnated catalysts with different palladium loading (\* The palladium peak position,  $2\theta = 40.116^\circ$ ).



**Figure 4.7** The TEM image of Pd/H-BETA: (a) 0.25wt% of Pd/H-BETA (impregnated catalyst), and (b) 1.00wt% of Pd/H-BETA (impregnated catalyst).



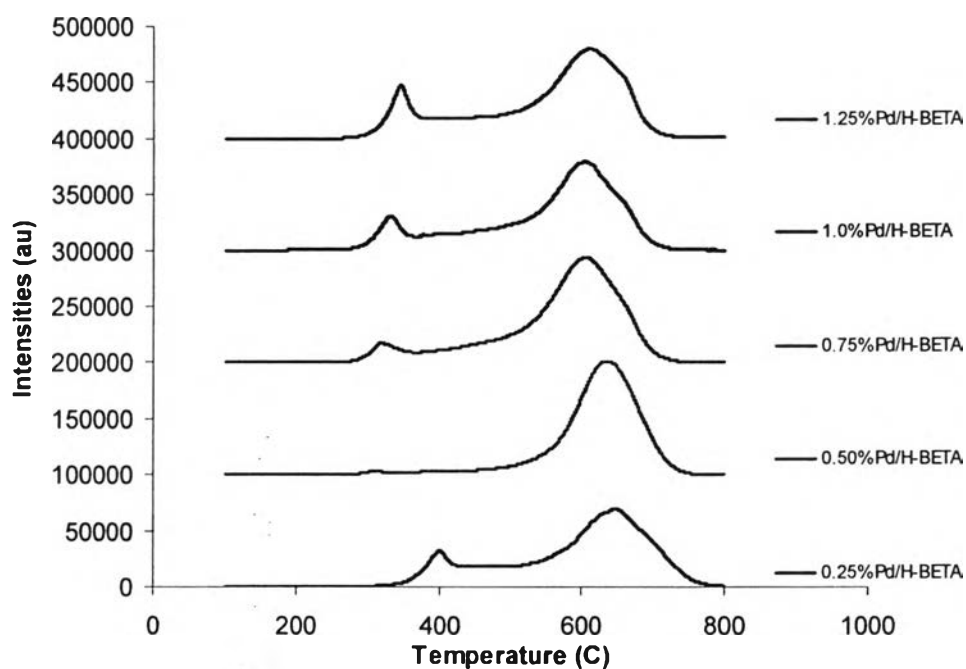
**Table 4.2** Surface area and average pore volume of impregnated catalysts

Sample	Pd loading (wt%)	S <sub>BET</sub> (m <sup>2</sup> /g)	Pore volume (cc/g)
H-BETA	-	629.4	1.539
Pd/H-BETA (Impregnation)	0.25	558.8	0.959
	0.50	597.4	1.147
	0.75	537.8	1.319
	1.00	567.6	2.454
	1.25	519.3	1.436

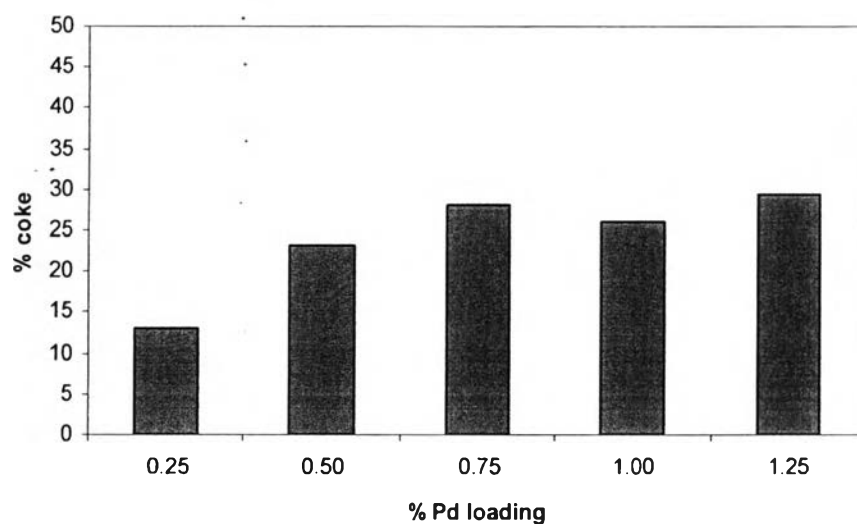
#### 4.2.1.4 Type of Coke and Amount of Coke Formation in Spent Catalysts

The type of coke was observed from the Temperature Programming Oxidation (TPO) patterns. It was found that the superficial carbides (or the heavy hydrocarbons which adsorbed on the catalyst surface) were increased at 250°C - 400°C, and the peak of the pyrolytic carbon (500°C - 750°C) slightly shifts to lower temperature with increasing the palladium loading (Figure 4.8).

The amounts of coke formation on spent catalysts were determined by TPO patterns and calculated from the area under the TPO peak. The results showed that the percentages of coke formation increased at higher palladium loading (Figure 4.9). It is possible that the addition of palladium of catalyst increased the hydrogenation and cracking activity. Therefore, hydrocarbon products were cracked and produced more coke on the catalyst surface.



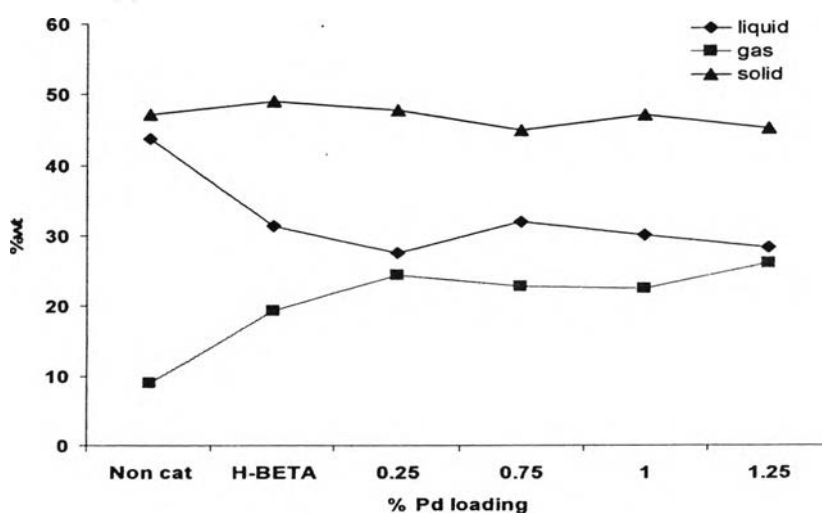
**Figure 4.8** The TPO pattern of various spent catalysts at different palladium loading amounts.



**Figure 4.9** The percentage of coke formation on spent catalysts having different palladium loading amounts.

#### 4.2.2 Product Distribution

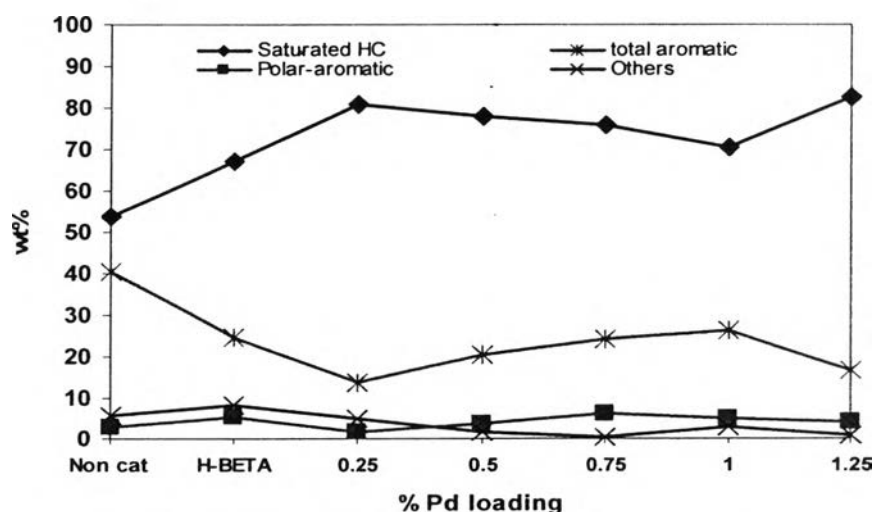
The product yield of catalytic pyrolysis with the different metal contents is shown in Figure 4.10, which shows that the bi-functional catalyst suppresses the liquid yield with the increasing amount of palladium loading. Moreover, the reduction of liquid product is related to the increase of gas product yields. It means that the catalyst cracked the liquid product or high molecular weight hydrocarbons to produce more gas yields. When Pd loading is increased from 0.25 to 0.75 %wt on H-BETA zeolite, the liquid yield rises up. Due to a decrease of specific surface area of the palladium catalysts, it is possible that the increase of palladium loading slightly reduced the strong acid density of catalyst due to metal particles which partially cover on the acid support (Lucus *et al*, 2005). Therefore, the cracking activity of bi-functional catalyst was reduced. And then the yields of liquid product were slightly dropped with increasing metal loading up to 1.25%wt. This is because the metal might play greater important role in hydrogenation or ring opening reactions with higher loading percentages. After that the ring opening products might be cracked to lighter products or the gas products on the acid support (H-BETA) of catalyst. Thus, the liquid product is decreased with increasing gas yield.



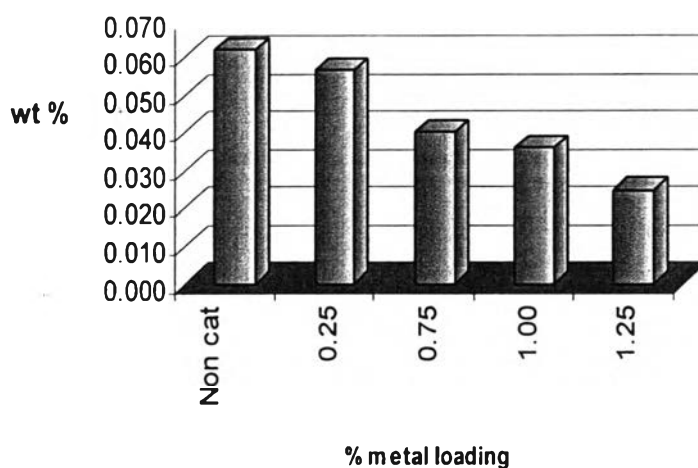
**Figure 4.10** The product distribution of the catalytic pyrolysis of scrap tire at different palladium metal loading amounts.

### 4.2.3 Quality of Pyrolysis Oil

The saturated hydrocarbons and aromatic compounds in maltene fraction were analyzed by using liquid chromatography method. Figure 4.11 shows the effect of palladium loading on chemical composition in the maltene fractions. The results show that Pd/H-BETA catalysts produce a high fraction of saturated hydrocarbons, and reduce the total aromatic hydrocarbons as compared to the non-catalytic pyrolysis. Moreover, the yield of saturated hydrocarbons is slightly dropped with the increase of palladium loading from 0.25wt% to 1.0 wt%. In opposite way, the aromatics are increased with the amount of palladium loading on H-BETA zeolite. From these results, the aromatic compounds might be produced from saturated hydrocarbons. Another supported result is shown in Figure 4.1, which is the influence of palladium loading on asphaltene. The amount of asphaltene fraction is decreased with the increasing percentage of metal loading. For these results, it is possible that the palladium can enhance the hydrogenation and cracking activity of aromatic hydrocarbons. Consequently, the high molecular-weight aromatic compounds (asphaltene) were broken into lower molecular-weight aromatic compounds or the lighter products.



**Figure 4.11** Chemical composition in maltenes obtained from the catalytic pyrolysis of Pd/H-BETA with different Pd loading amounts.



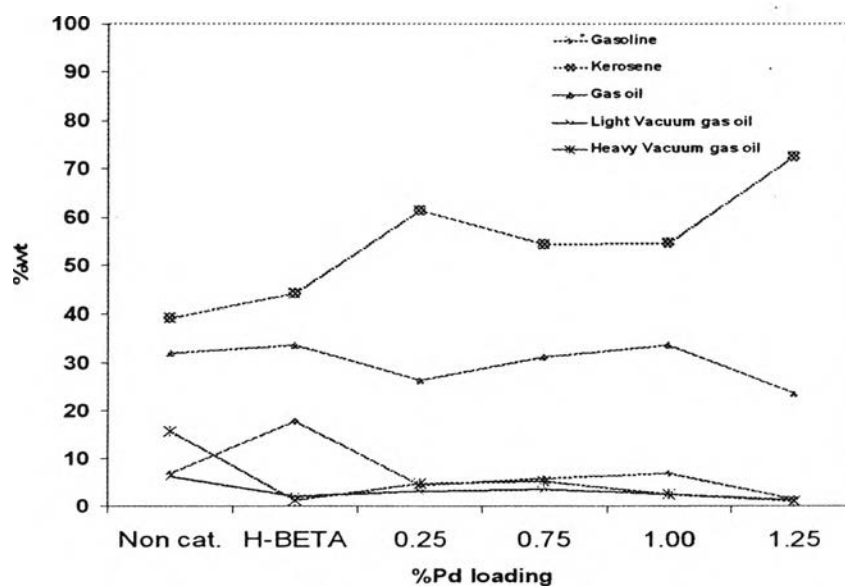
**Figure 4.12** The amount of asphaltene in liquid products obtained from catalytic pyrolysis of Pd/H-BETA with different Pd loading amounts.

The polar aromatics are the hydrocarbon compounds containing N, O or S, mainly associated with the aromatic structures. The polar aromatic might be formed on the bi-functional catalyst surface. The electron-deficient metal particles created by the strong acid site withdraw the electrons from the noble metal. This decreased the strength of bonding interaction between sulfur and metal particle due to lower acidity of catalyst. Thus, sulfur is split-over on metal sites, and might associate with aromatics to form polar aromatic compounds (Du H. *et al*, 2005). In Figure 4.11, the polar aromatic hydrocarbons are slightly increased with a increase of palladium loading from 0.25 wt % to 1.0 wt %. This might be related to the metal particle sizes and the amount of metal particles which pertained to the sulfur adsorption site. However, at 1.25 wt % of Pd loading, the polar aromatic slightly decreases. It is possible that 1.25wt% Pd/H-BETA has a larger metal particle which contributed to lower spill-over activity than the other. This effect can increase the strength of sulfur-metal bonding. Thus, the polar aromatic formation was reduced. From above results, it can be concluded that the metal site and the acid site density had an influence on the polar aromatic formation.

#### 4.2.4 Quantity of Petroleum Fractions

The quantities of petroleum in maltene fraction are shown in Figure 4.13. The bi-functional catalyst can increase the kerosene fractions significantly from 40wt % to 70 wt% because the cracking of heavy hydrocarbons and the pores of the catalyst would be selective with hydrocarbon molecules in kerosene fraction. Similar to Aguado et al.(2000), the study on the catalytic pyrolysis of several polyolefins in a batch reactor using different BETA zeolite, showed that the degradation of HDPE had a good selectivity to C<sub>5</sub>-C<sub>12</sub> hydrocarbons (60-70%). However, the gasoline fraction was decreased with the increasing amount of Pd loading. It is possible that the aromatics in gasoline fraction were hydrogenated by metal sites and further cracked to the gas product on the acid sites of bi-functional catalyst. The light and heavy vacuum gas oil fractions decreased with similar trend as gasoline fractions.

From the results of chemical composition and petroleum fraction in maltene, 0.25wt% is the optimum metal loading, because it produced the highest amount of saturated hydrocarbons and lowest aromatic compounds in maltene. It also produced the higher quantity of kerosene fraction.



**Figure 4.13** Petroleum fractions in maltene obtained from non-catalytic and catalytic pyrolysis at different metal loading amounts.

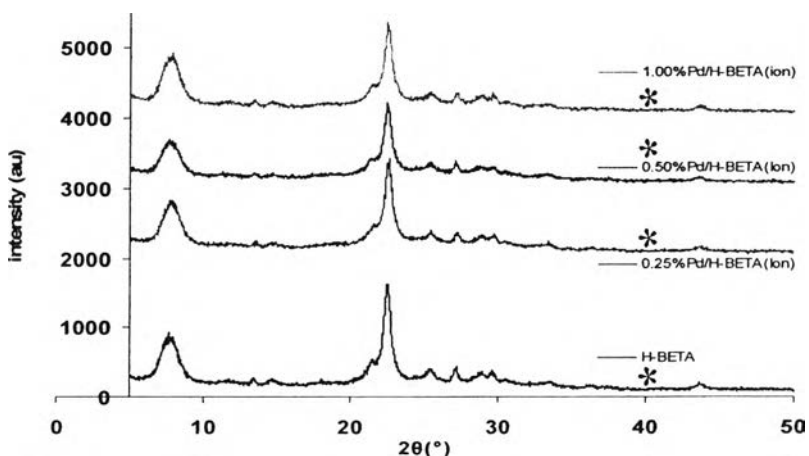
### 4.3 Effect of Metal Loading Method

The properties of noble metal particles are strongly dependent on the preparation procedure such as method for loading metal ion into zeolite (Liu *et al.*, 2007). In this part, the ion-exchange method and incipient wetness impregnation were investigated. The other parameters such as the catalytic temperature, final pyrolysis temperature, the amount of waste tire, and residence time were fixed at 350°C, 500°C, 10 g, and 25 min, respectively. The effect of palladium loading method on the quality of pyrolysis oil and the amount of petroleum fractions are reported and discussed in this part. All raw data for this part are presented in Table C4, H4, I3, and J1 in Appendix C, H, I, and J.

#### 4.3.1 Catalyst Characterization

##### 4.3.1.1 Crystal Structure of Catalysts

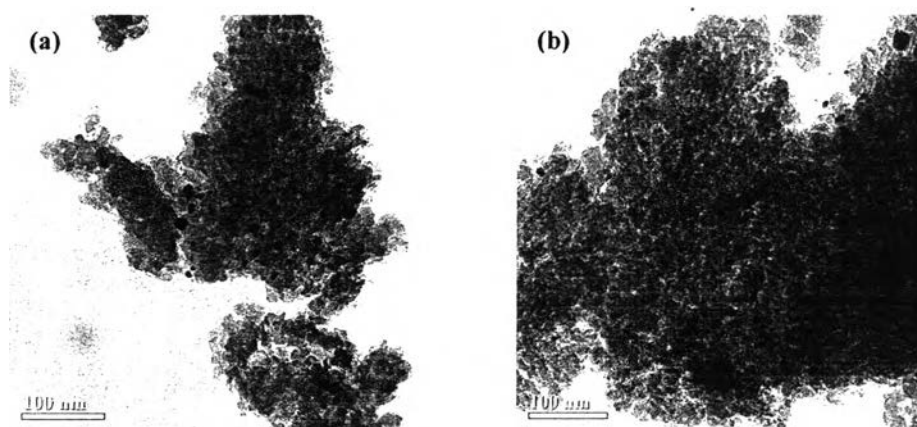
From the XRD patterns, the peaks of all catalysts are similar to that of the H-BETA support. It means that the crystal structure of ion-exchanged catalysts does not change, or the loading of palladium did not affect on the crystal structure. The palladium metal peaks can not be observed. It means that the palladium particles had small sizes as shown in TEM images (Figure 4.14).



**Figure 4.14** The XRD patterns of various ion-exchanged catalysts with different palladium loading amounts (\* The palladium peak position,  $2\theta = 40.116^\circ$ ).

#### 4.3.1.2 Metal Particle Size

The ion-exchange technique can produce the catalysts which have a very fine metal particles and higher metal dispersion on H-BETA than incipient impregnation as shown in the TEM images (Figure 4.15). The impregnated catalyst particles have various sizes in the range of 3 to 15 nm. But, the particle sizes of ion-exchanged catalysts almost had same size (4-8 nm). The stronger metal-support interactions of the ion-exchanged catalysts generally give higher dispersion of metal on zeolite than impregnated catalysts. Similarly, the XRD patterns confirmed that metal particle sizes were small, under the lowest detection limit of XRD technique. Moreover, the TEM images also show the location of metal particles. It was found that the metal particles of impregnated catalysts were deposited mostly on the external surfaces. In the case of ion-exchanged catalysts, they were highly distributed on both inside the pore and a few amounts on external surface. The metal particles possibly deposited in the hidden case of H-BETA due to very small metal particles in case of ion-exchange catalysts.



**Figure 4.15** The TEM images of 0.25 wt % Pd/H-BETA: (a) impregnated catalysts, and (b) ion-exchanged catalyst.



#### 4.3.1.3 Surface Area and Pore Volume of Ion-exchange Catalysts

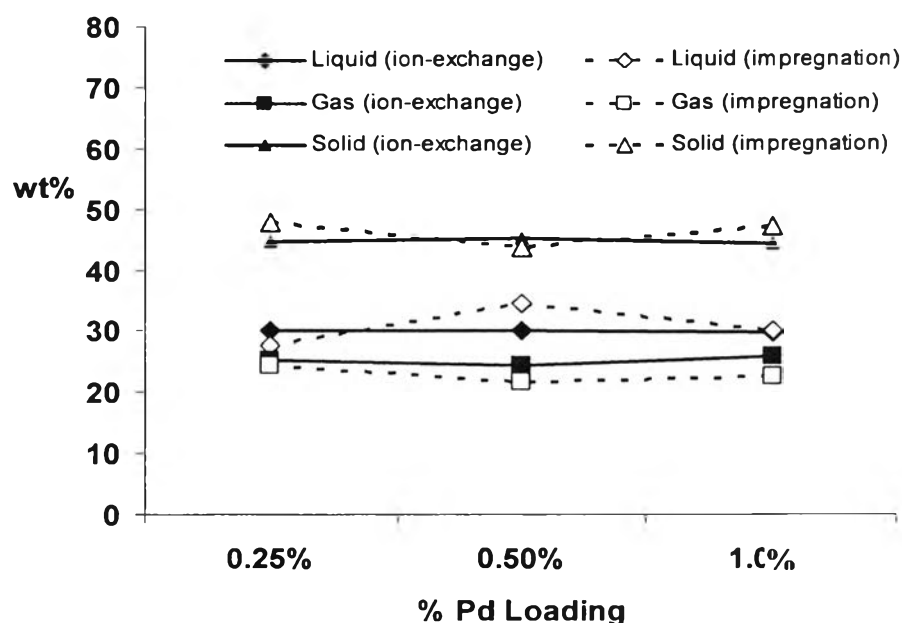
For ion-exchanged catalysts, the amount of palladium loading did not affect the specific surface area, because the Pd ions were exchanged with protons in the zeolite structure, and the exchange created a very small metal particle clusters which did not cover or block the pore of catalyst. They might be located inside the pore or on the catalyst surface.

**Table 4.3** Surface area and the average pore volume of ion-exchanged catalysts

Catalyst	Pd loading (wt%)	$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	Pore volume (cc/g)
<b>Pd/H-BETA (Ion-exchange)</b>	0.25	610.7	2.260
	0.50	610.2	2.899
	1.0	611.5	1.674

#### 4.3.2 Product Distributions

The yield of pyrolysis products obtained from ion-exchanged and impregnated catalysts were similar (Figure 4.16). The ion-exchanged catalyst can produce the gas products more than the impregnated catalyst. It is reasonable to assume that the large molecules of hydrocarbons need to be cracked on the external surface of catalyst first, and then the smaller cracked products diffuse inside the pore and react further on the active sites in the pore. From the surface area of both catalysts, the impregnated catalysts possibly have the metal particles covered the pore of zeolite, which might affect to the cracking reaction of hydrocarbons, because they could not diffuse to be cracked further in the pore. On the other hand, the pores of ion-exchanged catalysts are not blocked by metal particles. Therefore, the gas product is higher than that of impregnated catalysts. The solid, liquid, and solid were about 45, 30, and 25 wt%, respectively. It might be possible that the amount of pyrolysis products did not depend on the way to load the metal on the support.



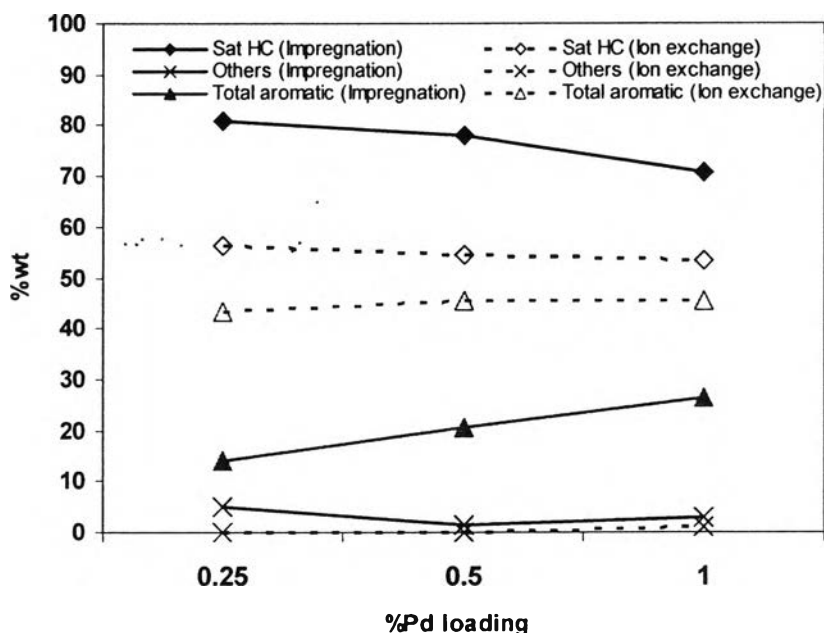
**Figure 4.16** The product distributions of catalytic pyrolysis of scrap tire using the impregnated and ion-exchanged catalysts at different Pd loading amounts.

#### 4.3.3 Quality of Pyrolysis Oil

The quality of pyrolysis was determined by the amount of saturated and aromatic hydrocarbons in the maltene fraction. The effects of metal loading method on quality of pyrolysis oil are shown in Figure 4.17. It can be observed that the ion-exchanged catalysts produce lower saturated hydrocarbons and much higher aromatic hydrocarbons than the impregnated catalysts. In fact, very fine metal particles on the ion-exchanged catalysts can well disperse almost inside micropores or mesopores or the main channel, and few amounts are deposited on the external surface of zeolite (Figure 4.15). Moreover, the main compositions in pyrolysis oil obtained from thermal degradation of tire such as aromatics (phenantrene, heptadiene, fluorine, naphthalene), alkanes and other hydrocarbons (Dai *et al.*, 2001), are large molecules. And, the large hydrocarbon molecules such as pyrene were hydrogenated mainly on the external surface and in mesopores (Tang *et al.*, 2007). It is possible that the thermal pyrolysis products can hardly diffuse inside the pore of catalyst. Therefore, the ion-exchanged

catalysts have less activity on the hydrogenation and ring opening of aromatic compounds than the impregnated catalysts whose metal particles generally deposit on the external surface of zeolite. This might be concluded that the main reactions in reduction of aromatic hydrocarbon are be occurred on the external surface of the catalyst.

The amount of saturated and aromatic hydrocarbons (related to the quality of pyrolysis oil) does not much depend on the amount of metal loading on the ion-exchanged catalysts because these hydrocarbons were not changed with the increasing the palladium loading as shown in the Figure 4.17.

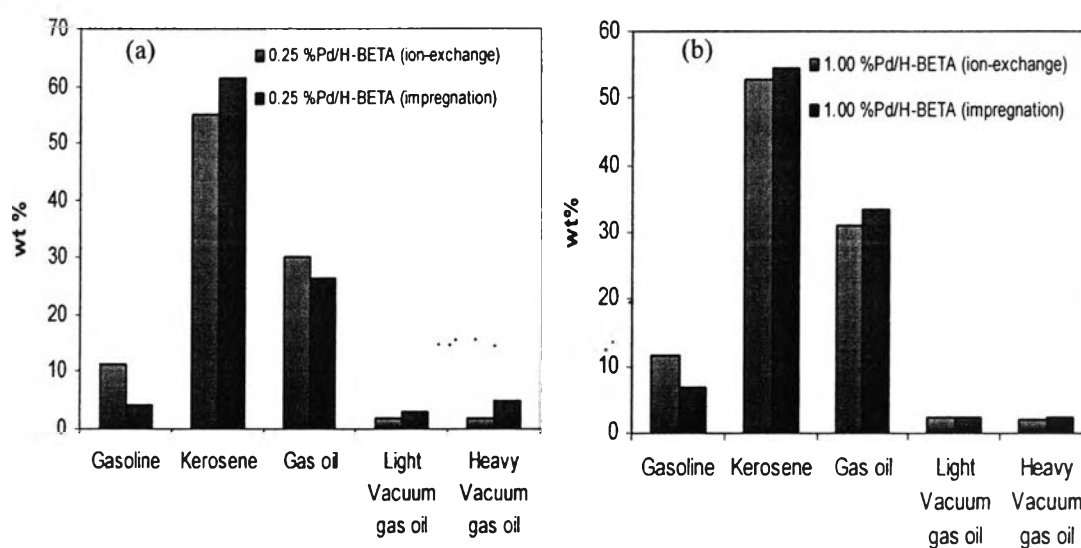


**Figure 4.17** The yield of saturated hydrocarbons and total aromatic in maltene obtained from catalytic pyrolysis using the impregnated and ion-exchanged catalysts at different Pd loading percentages.

#### 4.3.4 Quantity of Petroleum Fractions

The effect of loading method on the quantity of petroleum fractions is shown in Figure 4.18. It was found that the both catalysts prepared by ion-exchanged and incipient wetness impregnation had similar amount of the petroleum fractions. This indicated that the loading method had a little influence on the quantity of petroleum fractions. However, the oils obtained from impreg-

nated catalysts are composed of the kerosene and the other heavy fractions larger than those obtained from the ion-exchanged catalysts. It might be occurred from the effect of where reactions are taking place. For example, for the impregnation catalysts, the reactions mainly occur at the external surface of mesopores. The secondary reactions of the intermediated products might be occurred, and higher molecular hydrocarbons are formed. On the other hand, the products produced in the ion-exchanged case are limited by the pore size.



**Figure 4.18** Petroleum fractions in maltene obtained from catalytic pyrolysis using: (a) 0.25wt% Pd/H-BETA, and (b) 1.00wt% Pd/H-BETA.

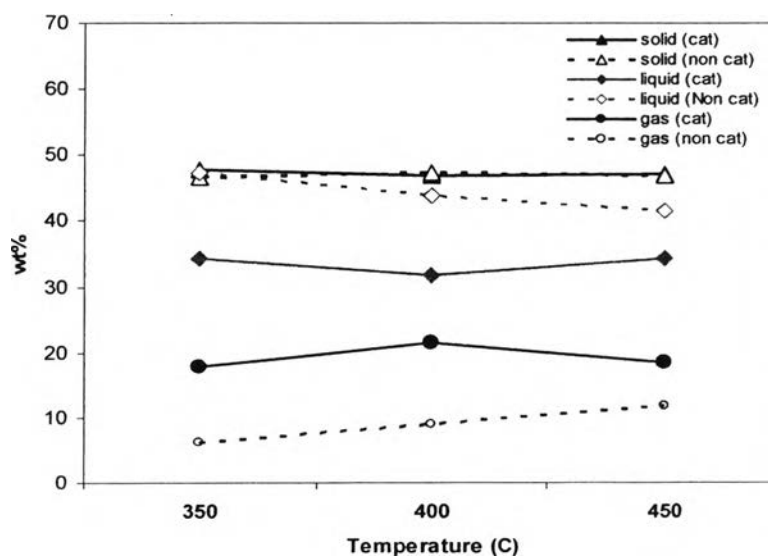
From all of above results, it can be concluded that the chemical compositions in pyrolysis oil are strongly influenced by the metal loading method. Moreover, the impregnated catalysts can produce lower saturated hydrocarbon and aromatic contents in pyrolysis oil. Therefore, the impregnation is the suitable method to prepare the catalyst for upgrading oil obtained from tire pyrolysis using Pd/H-BETA catalysts.

#### 4.4 Effect of Catalytic Temperature

The scrap tire pyrolysis was performed in a bench scale auto-clave reactor at atmospheric pressure. This reactor was divided into 2 zones (Figure 3.1); the pyrolysis zone which the final temperature was fixed at 500°C, and the reaction zone, where a catalyst was loaded. From the last past, the 0.25 wt% of Pd/H-BETA catalyst can produce the highest amount of saturated hydrocarbons and lower aromatic contents in the maltene fraction. In this part, the catalytic temperature was varied from 350°C to 450°C in order to study the effect of catalytic temperature on the liquid product. All raw data for this part are presented in Table C1, D1, H1, H2, I1, and I2 in Appendix C, D, H, and I. It was found that reaction temperature affected on the quality pyrolysis oil and quantity of petroleum fractions as discussed below.

##### 4.4.1 Product Distribution

The effects of temperature in the catalytic zone on gas, liquid, and solid yields in non catalytic and catalytic pyrolysis are shown in Figure 4.19. For the non-catalytic pyrolysis, the liquid yield decreases with increasing reaction temperature whereas the gas yield increases.



**Figure 4.19** The products obtained from the non catalytic and catalytic pyrolysis of scrap tire at the different temperatures of catalytic zone.

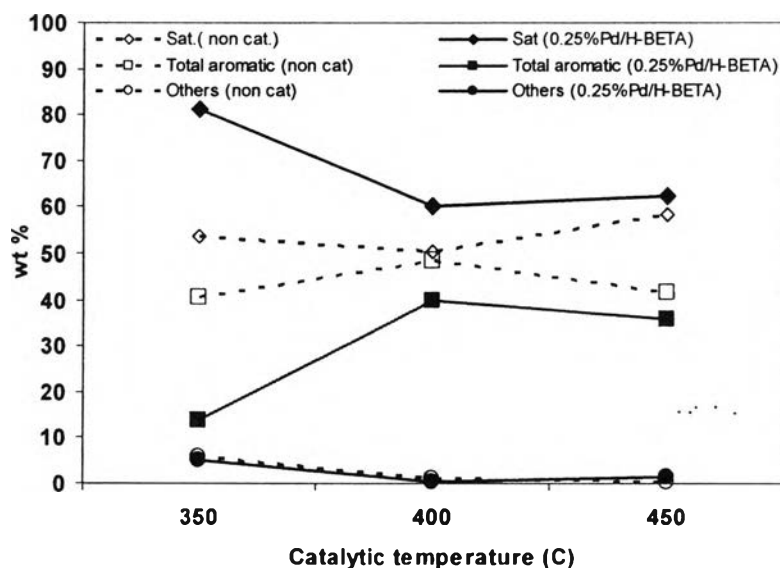
The decline of liquid yield was likely due to the secondary cracking of pyrolysis products to form lighter products or the gas products. However, the liquid yields in the catalytic pyrolysis initially decrease at 400°C, and then increase with the rising of catalytic temperature. It would probably have been caused by the highest cracking activity favored at 400°C, and the coke formation at high temperatures reducing the cracking activity of catalysts. The solid yields of both systems were not influenced by the reaction temperature. It was slightly constant yield, and had similar dimension and shape as appeared in the original scrap.

#### 4.4.2 Quality of Pyrolysis Oil

Based on the chemical compositions in maltene fraction, the reaction or catalytic temperatures affected on the saturated hydrocarbons in the non-catalytic pyrolysis. Especially, at 400°C, the saturated hydrocarbons decrease resulting in an increase of the total aromatic hydrocarbons (Figure 4.20). It was apparent that the saturated hydrocarbons might be converted to the aromatic hydrocarbons and the increase of temperature possibly promoted the aromatic formations (Migule *et al*, 2002). For the catalytic pyrolysis, the saturated hydrocarbons were decreased with increasing the temperature from 350°C to 450°C. The results of the total aromatic hydrocarbons showed a marked increase from 26.5 to 5.6 wt% when the catalytic temperature increased from 350°C to 450°C. It is possible that the increase of temperature promoted the aromatic formations (Migule *et al*, 2002) or the strong acid properties, large pore sized of catalyst support, and the higher catalytic temperature might be boosted the higher amount of coked on catalysts (Figure 4.16). Therefore the activities of catalyst in reduction of aromatic hydrocarbons were suppressed by coke formation at high temperature.

The environmental concerning and fuel specifications limit the quantity of sulfur compounds. Sulfur compounds in pyrolysis oils obtained from tire are representatives of polar aromatics. The effects of catalytic temperature on polar fraction are shown in Figure 4.20. It was found that the polar aromatic decreased with the increasing catalytic temperature. However, in catalytic pyrolysis, the polar aromatic hydrocarbons were higher than in the non-

catalytic pyrolysis. It might be occurred from the effect of metal on the catalyst support which can promote the polar aromatic formation. In addition, the influence of increasing catalytic temperature resulted in the decrease of polar aromatic hydrocarbons. At the higher temperature, it might be difficult for sulfur to adsorb on the metal surface due to a high amount of coke formation on the catalyst surface. Therefore, the polar aromatic formation was reduced.

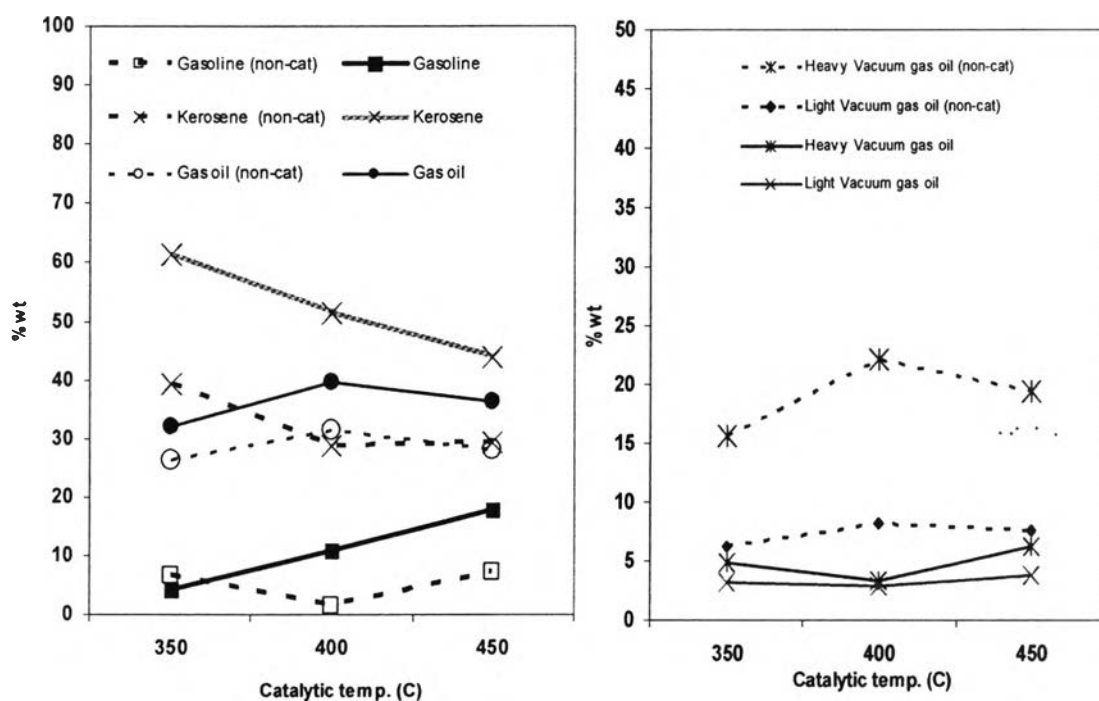


**Figure 4.20** Chemical composition in maltenes obtained from catalytic (0.25wt% Pd/H-BETA) and non-catalytic pyrolysis at different catalytic temperatures.

#### 4.4.3 Quantity of Petroleum Fractions

The effect of catalytic temperature on petroleum fractions in catalytic temperature is similar to that on the petroleum fractions in non-catalytic pyrolysis case as shown in Figure 4.21. The difference of both systems is the amount of 5 petroleum fractions in maltene. The quantities of petroleum products were changed with the increasing catalytic temperature. The presence of the catalyst served to decrease the amount of light and heavy vacuum gas oil resulting in an increase of gasoline, kerosene, and gas oil as compared to the quantity of petroleum products in non-catalytic pyrolysis. When the catalytic temperature was increased, the gasoline increased from 4.2 wt % to 17.8 wt%. The amount of

kerosene decreased at higher catalytic temperatures. This data suggest that the kerosene fraction might be cracked to produce more gasoline fraction. This trend is similar with gas oil fraction and the heavy fractions. The gas oil was increased, but the light and heavy fractions were decreased when temperature was increased from 350°C to 400°C.



**Figure 4.21** Petroleum fractions in maltene obtained from non- catalytic and catalytic pyrolysis (0.25wt% Pd/H-BETA) at different catalytic temperatures.

The optimum temperature in the catalyst zone depends on the desired products. The quality of pyrolysis oil is the main purpose in this work. Therefore, the lowest catalytic temperature (350°C) is the optimum temperature because it can produce highest amount of saturated hydrocarbons and the lowest amount of aromatic hydrocarbons.



## 4.5 Effect of Residence Time

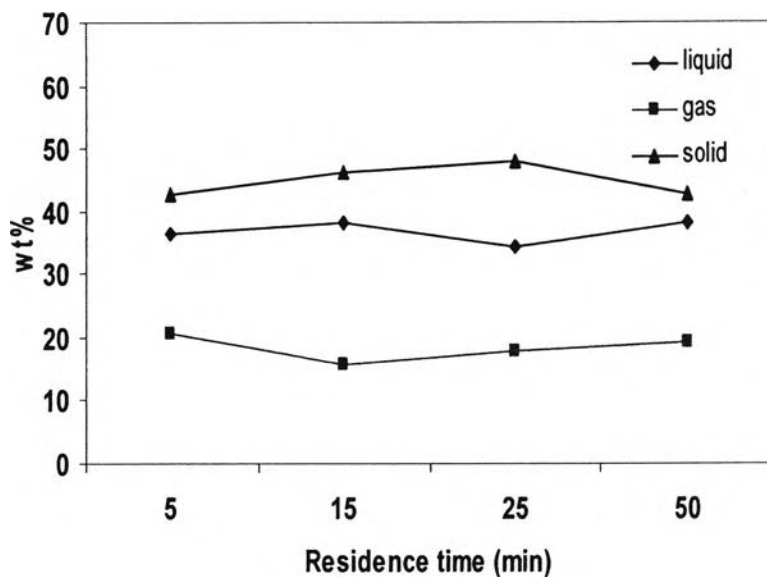
The residence time is the time that hydrocarbon vapor spends in the pyrolysis and catalytic zone of reactor. This residence time was varied from 5, 15, 25, and 50 min by adjusting the N<sub>2</sub> flow rate. The other parameters; the catalytic temperature, the final pyrolysis temperature, and the amount of tire were fixed at 350°C, 500°C, 30 g, and 10 g, respectively. In this part, the 0.25 wt% of Pd/H-BETA prepared by incipient wetness impregnation was packed in the catalytic zone. The effects of residence time on chemical composition in liquid product and the amount of petroleum fraction are reported in this part. All raw data for this part are presented in Table C3, H4, and I5 in Appendix C, H, and I.

### 4.5.1 Product Distribution

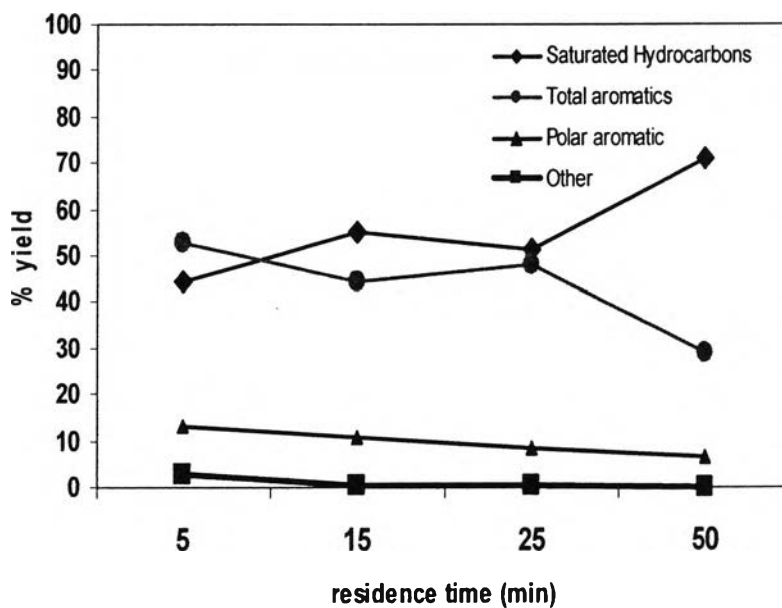
Figure 4.22 shows the effect of residence time on product yields of catalytic pyrolysis. It was found that the yields of the gas, liquid, and solid products did not depend on the residence time in pyrolysis reactor because there was no significant change on the product yields when the residence time increased.

### 4.5.2 Quality of Pyrolysis Oil

The saturated hydrocarbons were increased, resulting in the decline of aromatic hydrocarbons with the increasing residence time (Figure 4.23). It is possible that the pyrolysis vapor has more contact time on the catalyst surface, and the hydrogenation and ring opening activity are increased. The catalyst can convert the aromatic hydrocarbons to produce more saturated hydrocarbons. The sulfur compound or polar aromatic hydrocarbons slightly decreased due to the reduction of aromatic compounds available for reacting with sulfur in the reactions.



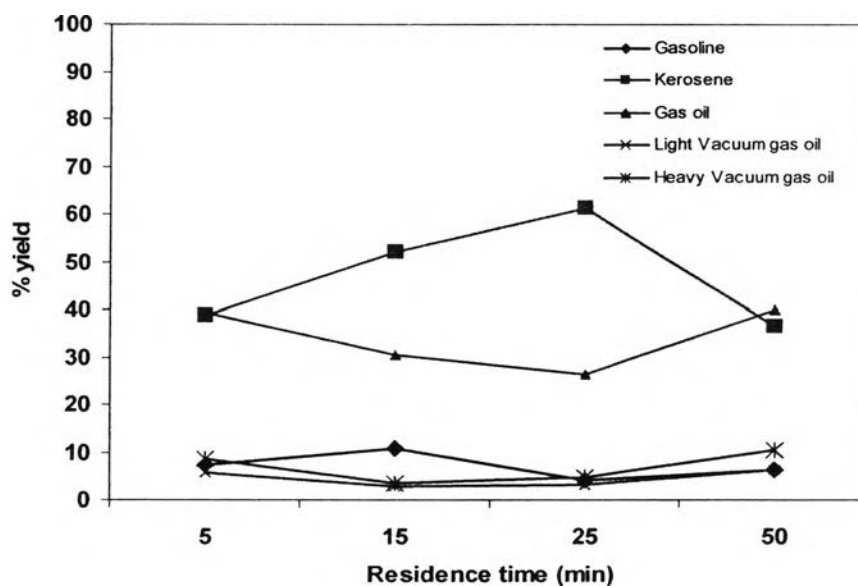
**Figure 4.22** The product distributions of catalytic pyrolysis of scrap tire at different residence time.



**Figure 4.23** The yield of chemical compositions in maltene obtained from catalytic pyrolysis at different residence time.

#### 4.5.3 Quantity of Petroleum Fractions

Residence time has more influence on the quantity of light fractions than heavy fractions (Figure 4.24) due to the limitation of the pore size of the catalyst, especially, kerosene and gas oil fraction whose the size is closed to the pore size of H-BETA support. The kerosene is increased markedly at the expense of gas oil yield with the increasing residence time. For example, kerosene increases from 38.8 wt % to 61.3 %wt when residence time increases from 5 to 25 min. However, at 50 min of residence time, the kerosene yield droppes to 36.5 wt% and the gas oil is increased from 26.3 wt% to 40 wt%. It is possible that the kerosene fractions would have been cracked further by the catalyst or by the thermal effect, and the recombination of cracked products is consequently occurred to produce more gas oil. Similarly, the heavy fractions are slightly the increase of the residence time from 15 to 50 min.



**Figure 4.24** Petroleum fractions in maltene obtained from catalytic pyrolysis at different residence time.