

CHAPTER IV

RESULTS AND DISCUSSION

The effects of the addition of the first additives (HBETA and HY) and the second additive (HZSM-5) in the bi-functional catalysts (Pd/HBETA and Pd/HY) on waste tire pyrolysis products are analyzed and discussed in this section. The bi-functional catalyst which can enhance the cracking reaction in order to obtain the lighter products was used as the main catalyst. In addition, a zeolite was added to improve the quality and quantity of pyrolysis products, especially full range naphtha because of its acid property and pore restriction. However, the products obtained from the pyrolysis of waste tire, especially gas and liquid, were investigated on the qualitative and quantitative scenarios.

4.1 Effect of HY as a First Additive in Pd/HBETA

The investigation of HY as an additive in Pd/HBETA for the pyrolysis of waste tire is discussed in this section. The bi-functional catalyst was prepared by incipient wetness impregnation technique, while the additive was physically mixed with the main catalyst at 10 wt% and 20 wt%. All catalysts were sieved in the range of 40-60 mesh and placed in the upper zone (catalytic zone) of the reactor.

4.1.1 Catalyst Characterization

The physical properties of catalysts which were investigated in this section are revealed in Table 4.1. The surface area and specific pore volume were determined by using the BET and Horvath-Kawazoe methods, respectively.

Table 4.1 Physical properties of catalysts with varied percentages of HY in Pd/HBETA

Catalysts	Surface area (m ² /g)	Specific pore volume (cm ³ /g)
HBETA	604	0.49
HY	590	0.58
Pd/HBETA	652	0.64
1%Pd/HBETA+10%HY (1PB10Y)	499	0.55
1%Pd/HBETA+20%HY (1PB20Y)	525	2.96

4.1.2 Product Distributions

The products obtained from pyrolysis process can be separated into gas, liquid or oil, and solid. However, the product distribution can be described using G/L ratio which is revealed in Figure 4.1.

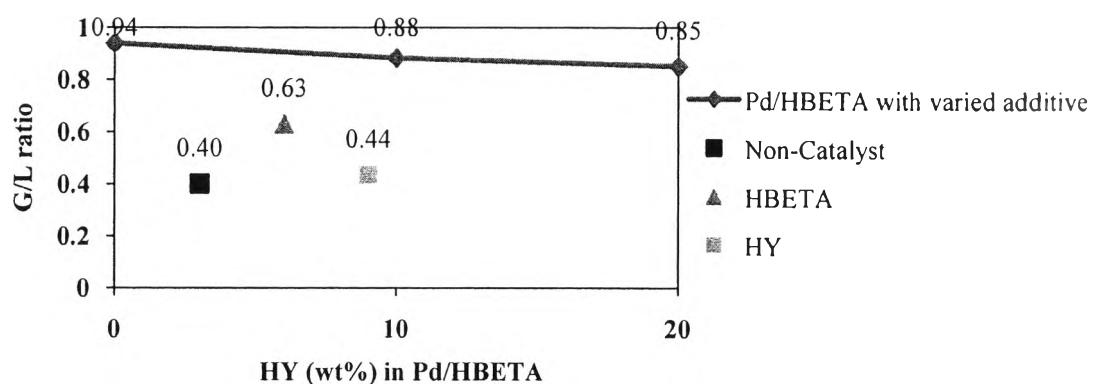


Figure 4.1 G/L ratio obtained from pyrolysis with varied percentages of HY in Pd/HBETA.

This figure exhibits the G/L ratio obtained from pyrolysis with varied percentages of HY as an additive in Pd/HBETA. The results obtained from the pure zeolites, and the non-catalyst cases are also included in the figure as the reference.

Since a higher gas production indicates a higher cracking activity of a catalyst, a high G/L ratio reflects a high cracking activity as well. The results represent that HBETA and HY zeolites can increase the G/L ratio from 0.40 (obtained from pyrolysis without catalyst) to 0.63 and 0.44, respectively, whereas the solid products obtained around 44 wt%. This result is similar to the one of Boxiong *et al*, 2007 who explained that the large molecular materials were cracked into non-condensable gaseous product. The use of Pd/HBETA as a bi-functional catalyst in pyrolysis process drastically increases the value of G/L ratio to 0.94 which indicates the improvement of cracking activity compared to the thermal pyrolysis and pure zeolites. The G/L ratio slightly is reduced to 0.88 and 0.85 with varied percentages of HY in Pd/HBETA at 10 wt% and 20 wt% of HY in Pd/HBETA, respectively. Despite of these slightly reduce in cracking activity, they are expected to lead to the improvement of product qualities which are represented in the next section.

4.1.3 Gas Compositions

Figures 4.2 and 4.3 show the yields of selected gaseous products obtained from the process. The results are illustrated in terms of the yield of light olefins and cooking gases (propane and mixed C4), which are considered as the valuable gas products.

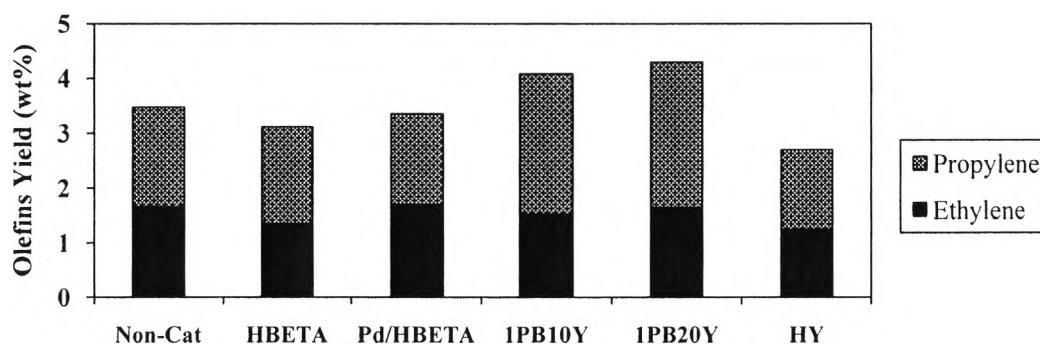


Figure 4.2 Yield of light olefins in the gas products obtained from pyrolysis with varied percentages of HY in Pd/HBETA.

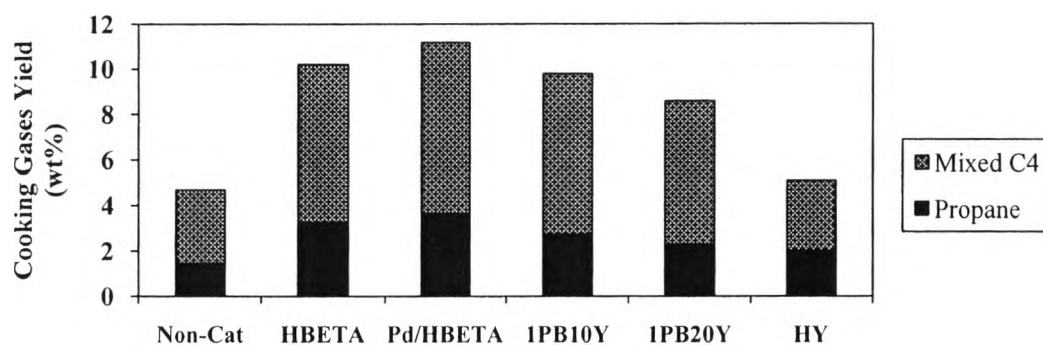


Figure 4.3 Yield of cooking gases in the gas products obtained from pyrolysis with varied percentages of HY in Pd/HBETA.

The results indicate that the pyrolysis without a catalyst can produce the light olefins equal to 3.47 wt%. The pure HBETA and HY zeolites produce less light olefins's yields, which are 3.12 wt%, and 2.70 wt%, respectively, than the non-catalytic case. After Pd/HBETA was used, the yield of light olefins is improved to 3.35 wt% compared to the use of HBETA alone, and then, the yields of light olefins are gradually increased to 4.08 wt% and 4.30 wt% when the HY was added in Pd/HBETA at 10 wt% and 20 wt%, respectively. Moreover, they also produced more olefins than both pure zeolites and the non-catalytic cases.

In case of cooking gases, the pyrolysis without using HBETA gives the lower yield of cooking gases than using HBETA. The pure HBETA zeolite gives higher yield of 10.21 wt% than the non-catalytic (4.68 wt%) and pure HY zeolite (5.08 wt%) cases. After using of Pd/HBETA, the yield of cooking gases is improved to 11.17 wt%. When adding HY in Pd/HBETA at 10 wt% and 20 wt%, the yields of cooking gases are gradually reduced to 9.80 wt% and 8.59 wt%, respectively. Therefore, in this section, it can be concluded that the additive HY in Pd/HBETA helps improving the light olefins yield than Pd/HBETA alone. Despite the yield of cooking gases is reduced, it still produces higher than using pure HY and non-catalytic cases. The concentrations and yields of other gaseous products obtained from the addition of HY in Pd/HBETA are declared in Appendix C1 for further observation. The gas concentrations displayed the same trend as gas yields because, in this case, the yields

of total gaseous products slightly change. In contrast, the concentrations of gases obtained from pyrolysis with pure zeolites and without a catalyst are significantly changed since the total gas yield is lower than using the bi-functional catalysts. Therefore, in this section, it can be concluded that among all Pd-loaded HBETA catalysts, the Pd/HBETA seems to be the best catalysts for cooking gas production since it can produce the highest yield of cooking gas of 11.2 wt%, whereas 20 wt% of HY in Pd/HBETA is the best catalyst combination for light olefins production since it can produce the highest yield of light olefins of 4.30 wt%.

4.1.4 Liquid Products

The liquid or oil products obtained from pyrolysis of waste tire in the form of maltene are further analyzed by a SIMDIST GC for true boiling point curves. Then, they are cut into 5 fractions according to Table 4.2.

Table 4.2 True boiling point cuts and carbon ranges of refinery products (Dũng *et al.*, 2009)

Petroleum Fraction	Carbon Range	Boiling Point (°C)
Full range 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

4.1.4.1 *Quantitative Analysis*

From Figure 4.4, the use of pure zeolites (both HBETA and HY zeolites) help to improve the quantity of lighter products, which are the full range naphtha and kerosene fractions as compared to pyrolysis without a catalyst. Meanwhile, the use of bi-functional catalyst (Pd/HBETA) reduced the naphtha and kerosene fractions which are 33.6 wt% and 15.3 wt%, respectively, as compared to the pure HBETA case. After adding an additive, the full range naphtha is insignifi-

cantly changed at 10 wt% HY in Pd/HBETA (denoted as 1PB10Y) which is 33.7 wt%, but decreased to 30.0 wt% at 20 wt% HY in Pd/HBETA denoted as 1PB20Y (the same as the full range naphtha obtained from the non-catalytic case). However, the quantity of kerosene and light gas oil fractions trend to be improved after 10 wt%, and 20 wt% of HY in Pd/HBETA was used. For the cracking ability of liquid products, both of pure Pd/HBETA and the addition of HY in Pd/HBETA cause the lower cracking performance than the pure zeolites because the long residue fraction remains high as compared to the pure zeolites. Nevertheless, their cracking performance is improved as compared to pyrolysis without a catalyst. Therefore, the use of Pd/HBETA catalysts with and without the addition of HY in Pd/HBETA may not proper for full range naphtha production, as similar as the pure zeolite catalysts do. However, they might be appropriate to be used for gas oils production since they can crack heavy fraction to produce gas oil fractions mainly. Nevertheless, the quality of each fraction must be investigated for the suitable application.

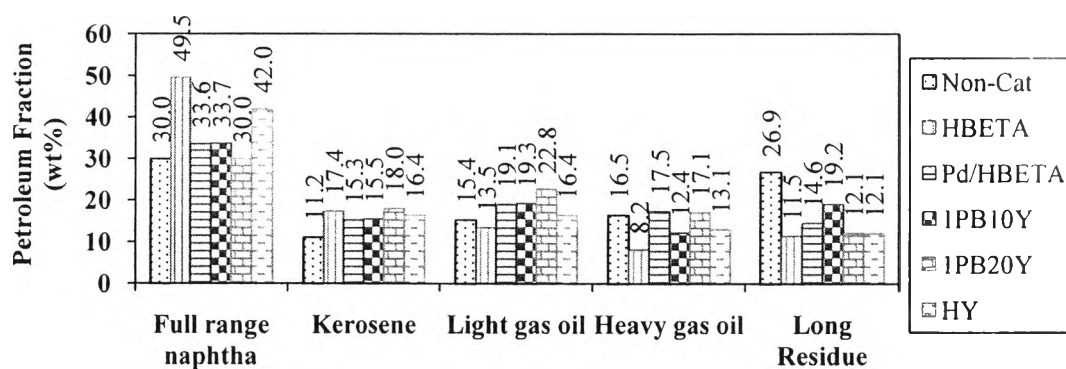


Figure 4.4 Petroleum fractions in derived oils obtained from pyrolysis with varied percentages of HY in Pd/HBETA.

4.1.4.2 Qualitative Analysis

The asphaltene is firstly precipitate from pyrolytic oil by mixing with n-pentane at the ratio of 1:20. It is revealed that the used of bi-function catalyst can drastically reduce the asphaltene in oil product from 0.097 wt% in the case of non-catalyst to 0.014 wt% which is represented in Figure 4.5. After mixing with

HY as additive in Pd/HBETA at 10 wt% and 20 wt%, the asphaltene in pyrolytic oil is gradually increased to 0.054 wt% and 0.078 wt%, respectively. These results confirm that the cracking activities are reduced when the additive was added.

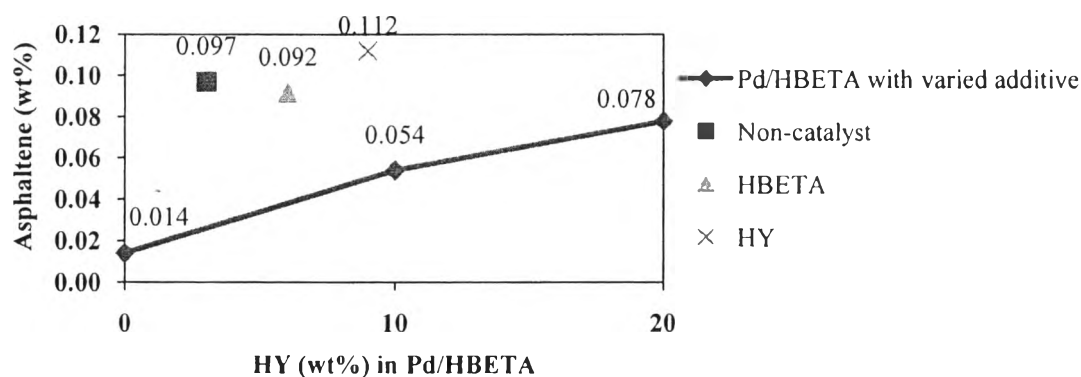


Figure 4.5 Percentage of asphaltene in pyrolytic oils obtained from pyrolysis with varied percentages of HY in Pd/HBETA.

After the precipitation of asphaltene, the remained solution or maltenes were evaluated the chemical compositions via liquid chromatography technique to quantify the amount of hydrocarbon species (saturated hydrocarbons, mono-aromatics, di-aromatics, poly-aromatics, and polar-aromatics) in maltene fractions as in the work of Šebor *et al.* (1999). From Figure 4.6, the result indicates that the use of pure zeolite catalysts can improve the saturated hydrocarbon in the liquid product from 69.8 wt% obtained from the non-catalytic case to 71.7 wt% and 73.7 wt% which obtained from the pure HBETA and pure HY cases, respectively. Moreover, the saturated hydrocarbon reaches to 78.6 wt% when the bi-functional catalyst was used. It can be stated that the use of catalysts can increase the saturated hydrocarbons from the transformation of aromatics, especially di- and poly-aromatic hydrocarbons, which are significantly reduced in the liquid product as compared to the pyrolysis without a catalyst. After adding the additive, the results can clearly show that after adding 10 wt% and 20 wt% of HY in Pd/HBETA, the saturation hydrocarbon content is gradually reduced from 78.6 wt% to 76.5 wt% and 58.1 wt%, whereas the mono-aromatics are increased from 4.1 wt% to 5.3 wt% and 15.4 wt%, respectively. Never-

theless, these compounds must be considered along the range of petroleum fractions to determine the oil quality. For example, the full range naphtha must contain a sufficiently high quantity of saturated hydrocarbons for using as the feedstock for cracking process, or contains a sufficiently high quantity of aromatics compounds for using as the feedstock for aromatics separation or for blending in the gasoline pool.

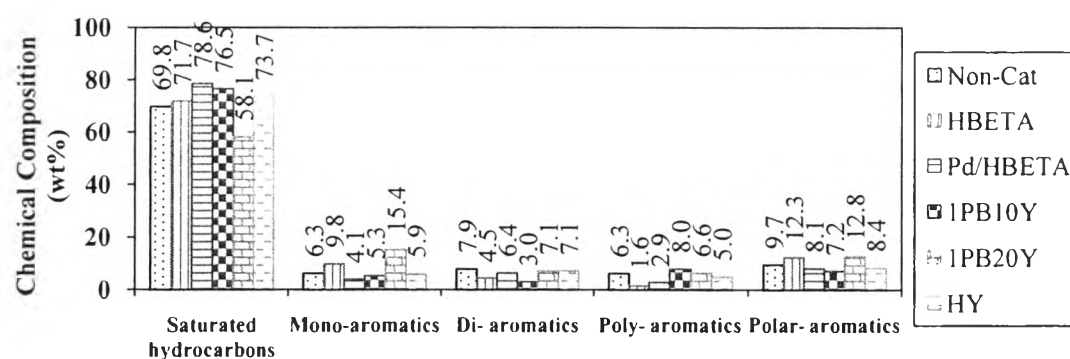


Figure 4.6 Chemical compositions of maltenes obtained from pyrolysis with varied percentages of HY in Pd/HBETA.

Figure 4.7 indicates the distribution of saturation hydrocarbons in oil products. It is found that the use of pure zeolite catalysts (both HBETA and HY zeolites) can increase the saturated hydrocarbons in the naphtha and kerosene fractions as compared to the non-catalytic case. These can be suggested that the pure zeolite catalysts help converting saturated hydrocarbons in heavy fractions to the lighter fractions. After the Pd/HBETA was used, the saturated hydrocarbons in lighter fractions (full range naphtha to light gas oil fractions) are reduced, while the heavier fractions (heavy gas oil and long residue) are increased. And then, the saturated hydrocarbons in naphtha and kerosene fractions are further reduced at 10 wt% HY in Pd/HBETA, but they are enhanced at 20 wt% HY in Pd/HBETA. In contrast, the light gas oil fraction is gradually improved with varied percentages of HY in Pd/HBETA. These can be stated that the addition of HY in Pd/HBETA can improve the quality of light gas oil fraction which can be used for the higher cetane number diesel.

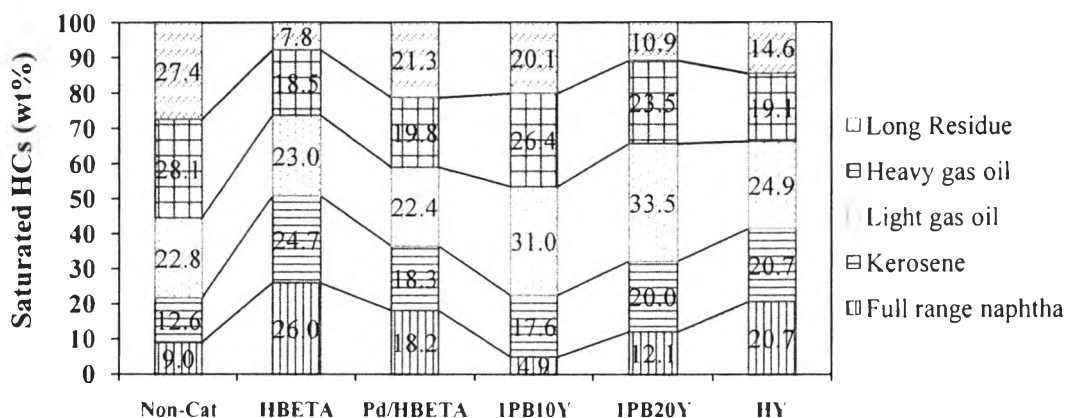


Figure 4.7 Distribution of saturated hydrocarbons in petroleum cuts obtained from pyrolysis with varied percentages of HY in Pd/HBETA.

For the distribution of total aromatics, the results reveal that the pyrolysis without a catalyst generates the total aromatics in various fractions which can be observed in Figure 4.8. For the pure HBETA zeolite, the total-aromatics are slightly reduced in full range naphtha fraction, while they are drastically increased in heavy gas oil fraction. These exhibit the less benefit than the non-catalytic case. However, the total aromatics are remarkably reduced in the kerosene fraction and slightly decreased in the light gas oil fraction. These results can infer that the pure HBETA can suitably be used for the kerosene and light gas oil productions since it can produce high concentration of saturated hydrocarbons in kerosene and light gas oil fractions with a low concentration of total-aromatics in both kerosene and gas oil fractions. For the pure HY zeolite, the result exhibits the advantage from using this zeolite. The pure HY zeolite is suitable for kerosene and light gas oil productions since it can produce high concentration of saturated hydrocarbons in kerosene and light gas oil fractions with a low concentration of total aromatics in these fractions. In addition, it also can be used for the gasoline production since the total aromatics in the naphtha fraction are enhanced; even though, the saturated hydrocarbons in this fraction are still high as compared to the non-catalytic case. With using the Pd/HBETA, the quality of naphtha fraction is improved since the saturated hydrocarbons are reduced, while the total aromatics are enhanced. After adding an ad-

ditive HY in Pd/HBETA, the quality of naphtha fraction is reduced because both of saturated hydrocarbons and total aromatics are reduced. However, the saturated hydrocarbons in the light gas oil fraction are gradually improved with varied percentages of HY in Pd/HBETA. Therefore, it can be concluded that the addition of HY in Pd/HBETA can improve the quality of light gas oil fraction, which can be used for the diesel production. This enhancement of light gas oil fraction by 20 wt% HY in Pd/HBETA can be applicable when the market demand for diesel is reached.

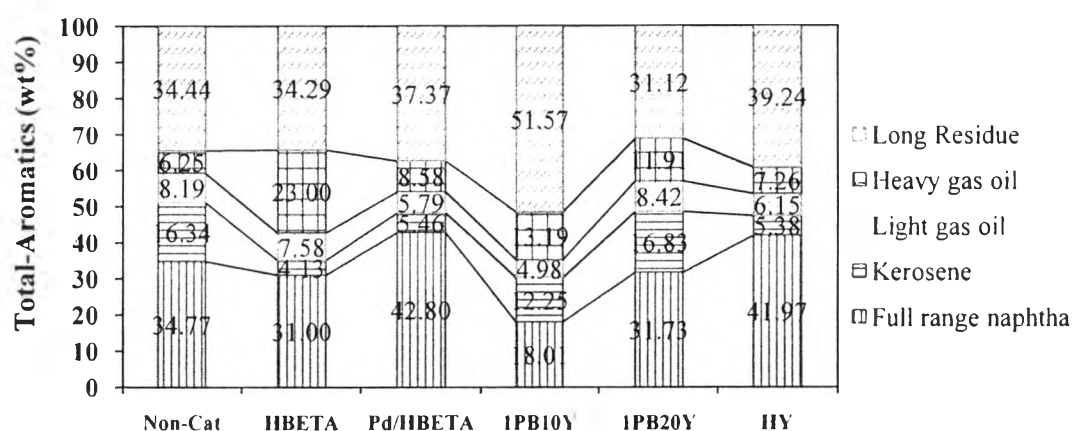


Figure 4.8 Distribution of total aromatic hydrocarbons in petroleum cuts obtained from pyrolysis with varied percentages of HY in Pd/HBETA.

In addition, the coke formation on the catalysts must be evaluated. It can be determined by the TG/DTA technique, which the result is displayed in Figure 4.9. From this result, the coke content on the spent catalysts gradually reduced with the increasing percentages of HY in Pd/HBETA. Therefore, it can support the result of the product distributions which the higher cracking activity produces more coke content on the spent catalysts because the higher cracking activity can create the pathways, which reach to the formation of coke. In the case of pure zeolite, although the HBETA exhibits the higher cracking activity than HY zeolite, the coke formation on HBETA is lower than HY zeolite. It is because the pore structure of these zeolites plays the important role for the amount of coke on the spent catalysts.

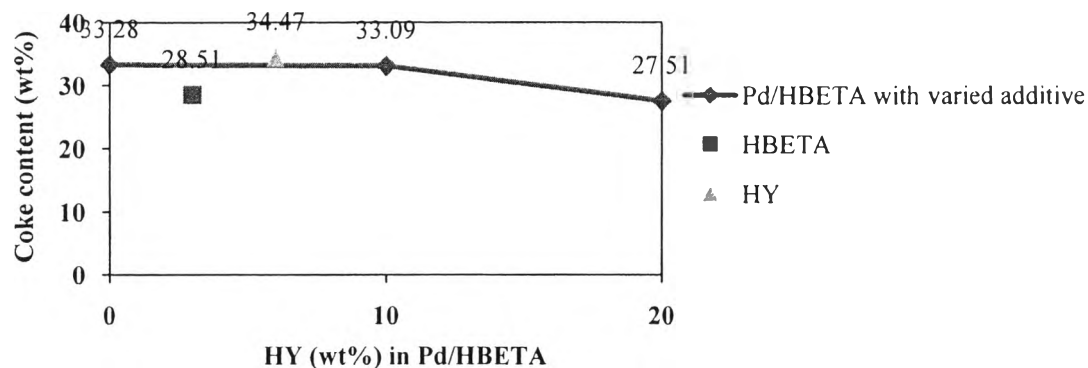


Figure 4.9 Coke formation (wt%) on spent catalysts using in pyrolysis with varied percentages of HY in Pd/HBETA.

4.2 Effect of HBETA as a First Additive in Pd/HY

In this case, HBETA was used as an additive in Pd/HY. The amount of HBETA was varied at 10 wt% and 20 wt%. The catalysts have been prepared in the similar way to the previous case.

4.2.1 Catalyst Characterization

The physical properties of catalysts which were investigated in this section are revealed in Table 4.3. The surface area and specific pore volume were determined by using the BET and Horvath-Kawazoe method, respectively.

Table 4.3 Physical properties of catalysts with varied percentages of HBETA in Pd/HY

Catalysts	Surface area (m ² /g)	Specific pore volume (cm ³ /g)
HBETA	604	0.49
HY	590	0.58
Pd/HY	468	1.43
1%Pd/HY+10%HBETA (1PY10B)	587	1.25
1%Pd/HY+20%HBETA (1PY20B)	501	0.29

4.2.2 Product Distributions

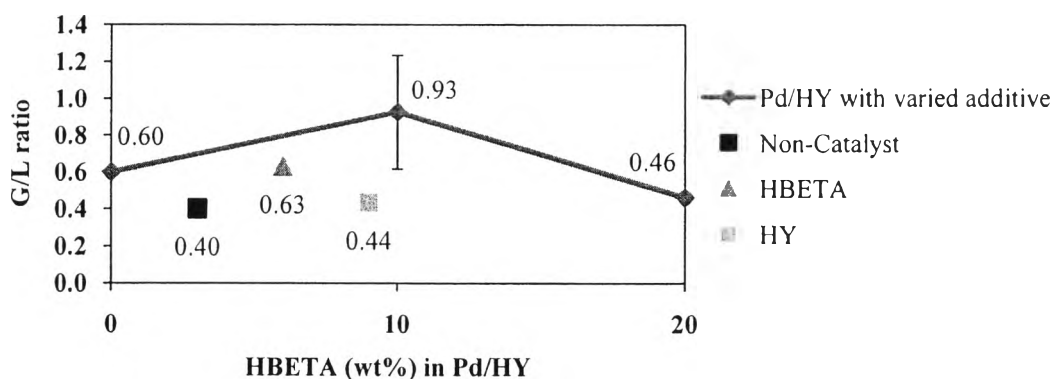


Figure 4.10 G/L ratio obtained from pyrolysis with varied percentages of HBETA in Pd/HY.

The product distribution is represented in term of G/L ratio, which is exhibited in Figure 4.10. The results of pure zeolites have already been discussed in the previous section. In this case, the Pd/HY was used as a main catalyst with varied percentages of HBETA used as an additive. The G/L ratio obtained by using Pd/HY reaches to 0.60, which is higher than that obtained from pyrolysis with HBETA zeolite (0.55), HY zeolite (0.44) and without catalyst (0.40). Moreover, the addition of

10 wt% HBETA in Pd/HY (1PY10B) dramatically increases the G/L ratio to 0.93, which indicates that the cracking activity is significantly improved. In contrast, the G/L ratio is reduced to 0.46 after the 20 wt% HBETA was added in Pd/HY (1PY20B). It means that further addition of HBETA to 20 wt% in Pd/HY gives lower cracking activity. However, it might improve the quality of the liquid products, which is revealed in the next section.

4.2.3 Gas Compositions

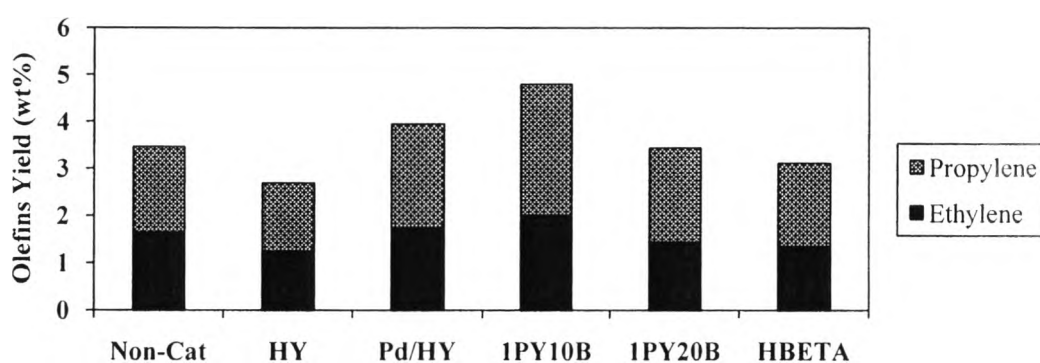


Figure 4.11 Yield of light olefins in the gas products obtained from pyrolysis with varied percentages of HBETA in Pd/HY.

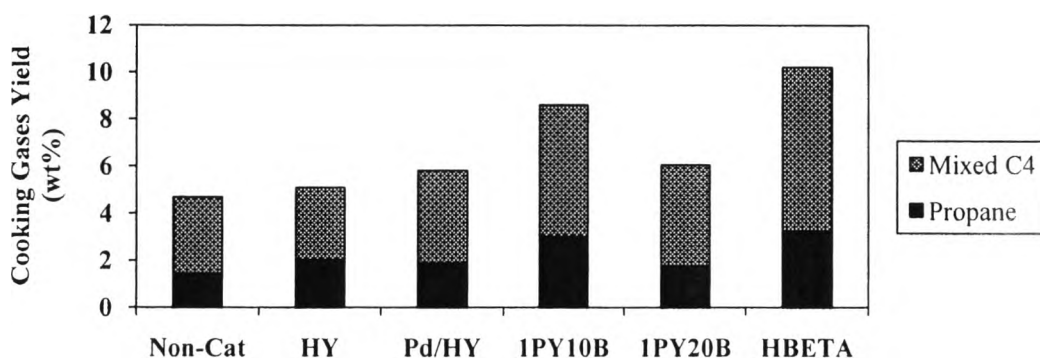


Figure 4.12 Yield of cooking gases in the gas products obtained from pyrolysis with varied percentages of HBETA in Pd/HY.

The yields of light olefins and cooking gas are presented in Figures 4.11 and 4.12, respectively. The results indicate that the Pd/HY improves the yield of light olefins and cooking gases as compared to pure HY and the non-catalytic case. After mixing with 10 wt% HBETA, the yields of light olefins and cooking gas are remarkably enhanced, and then, they are reduced when 20 wt% of HBETA was added in Pd/HY. These outcomes strongly depend on the total yield of gaseous product. Due to the highest gas yield occurring at 1PY10B, the yield of gas compositions reaches the highest value as compared to that of others. Therefore, it can be concluded that the addition of 10 wt% HBETA into Pd/HY is the most outstanding catalyst mixture among all Pd-loaded HY catalysts for light olefins (4.8 wt% yield) and cooking gas (8.6 wt% yield) production. For the compositions of gaseous products, the results exhibit the increase of cooking gases with the increasing amount of HY in Pd/HBETA, which is revealed in Appendix C2. The distribution and yield of all gas compositions are also shown in Appendix C2.

4.2.4 Liquid Products

4.2.4.1 *Quantitative Analysis*

The petroleum fractions in oil are presented in Figure 4.13. The Pd/HY produces 28.3 wt% full range naphtha, which is lower quantity than the pure HY (42.0 wt%) and non-catalytic case (30.0 wt%). Due to the higher cracking activity of 1PY10B, the full range naphtha fraction is enhanced to 37.3 wt%. However, it is still lower than that obtained from pure zeolites. After further adding 20 wt% HBETA in Pd/HY (1PY20B), the naphtha fraction is reduced to 22.2 wt%, which contributes to the reduction of cracking performance. The other fractions illustrate the same trend for both varied percentages of HBETA in Pd/HY. The 1PY10B catalyst produces kerosene and gas oils in a higher quantity than Pd/HY, whereas the use of 1PY20B gives the insignificantly different results from pure Pd/HY. In addition, the cracking performance can be justified by the amount of long residue. The results indicate that the bi-functional catalyst with or without the additive have lower cracking performance than the pure zeolites, but still have the higher activity than the non-catalytic case.

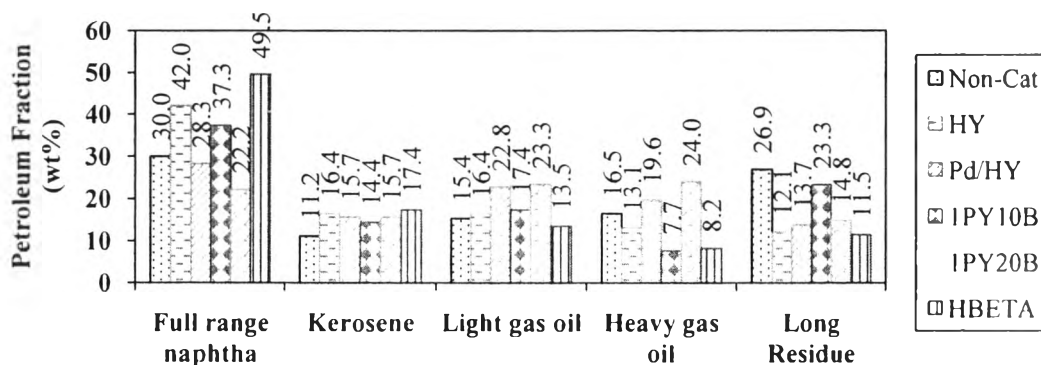


Figure 4.13 Petroleum fractions in derived oils obtained from pyrolysis with varied percentages of HBETA in Pd/HY.

4.2.4.2 Qualitative Analysis

As same as the previous case, the asphaltene is firstly precipitate from pyrolytic oil, which the results are exhibited in Figure 4.14. It is revealed that the use of bi-functional catalyst can drastically reduce the asphaltene in the oil product from 0.097 wt% in the case of non-catalyst to 0.056 wt%. After mixing with 10 wt% and 20 wt% HBETA as the additive in Pd/HY, the asphaltene in pyrolytic oils is 0.092 wt% and 0.054 wt%, respectively. It may be resulted from the higher cracking activity, which allows the catalyst to crack tire compounds, and its intermediates can later re-combine to form complex molecules.

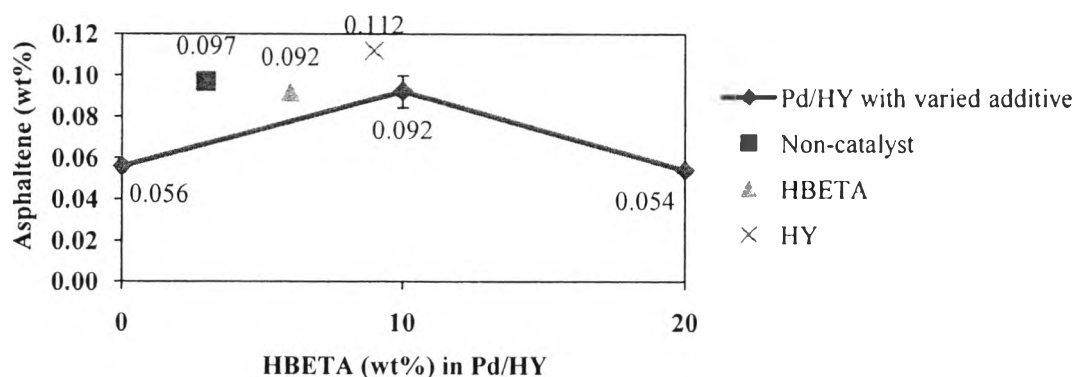


Figure 4.14 Percentage of asphaltene in pyrolytic oils obtained from pyrolysis with varied percentages of HBETA in Pd/HY.

The chemical compositions in Figure 4.15 indicate that the Pd/HY gives the highest concentration of saturated hydrocarbons (75.6 wt%) among all Pd loaded on HY catalysts. In addition, the mono-aromatics content is not significantly different from that obtained from HY. With the additions of 10 wt% and 20 wt% HBETA in Pd/HY, the concentration of saturated hydrocarbons in maltene gradually decreases to 69.2 wt% and 61.6 wt%, respectively, while the mono-aromatics concentration slightly increases. Additionally, the polar-aromatics content gradually increases to 13.3 wt% and 16.9 wt% at 10 wt% and 20 wt% HBETA in Pd/HY, respectively, which might be only caused by the dilution of Pd/HY bed by HBETA addition. Thus, the heteroatom removal reactions which are supposed to take place at the Pd metal sites of catalyst can less occur.

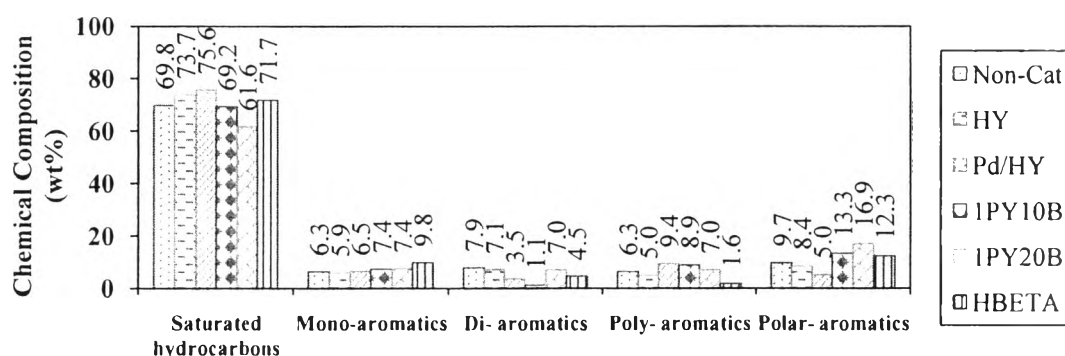


Figure 4.15 Chemical compositions of maltenes obtained from pyrolysis with varied percentages of HBETA in Pd/HY.

In order to determine the quality of petroleum fractions, the saturated hydrocarbons and total aromatics distributed in each fraction must be investigated, which can be observed in Figures 4.16 and 4.17, respectively. As compared to the pure HY zeolite, the Pd/HY can enhance the quality of full range naphtha fraction used for blending in a gasoline pool that has a low octane number and a low total-aromatic content, or for using as a feed for the aromatics separation process. This is because it can produce less saturated hydrocarbons (12.8 wt%) with high total-aromatics (46.1 wt%). Moreover, it can be used for light and heavy gas oil produc-

tions since it increases saturated hydrocarbons in the light and heavy gas oils to 30.5 wt% and 25.7 wt%, respectively, with a low total-aromatic content of 2.3 wt% and 4.8 wt%, respectively. After the additive HBETA was added to the Pd/HY in order to investigate the effect to the product quality, the results illustrate that the addition of 10 wt% HBETA can enhance the saturated hydrocarbons in naphtha and kerosene fractions, whereas the saturated hydrocarbon content in every fraction obtained from the addition of 20 wt% HBETA in Pd/HY is insignificantly different from those produced by the pure Pd/HY.

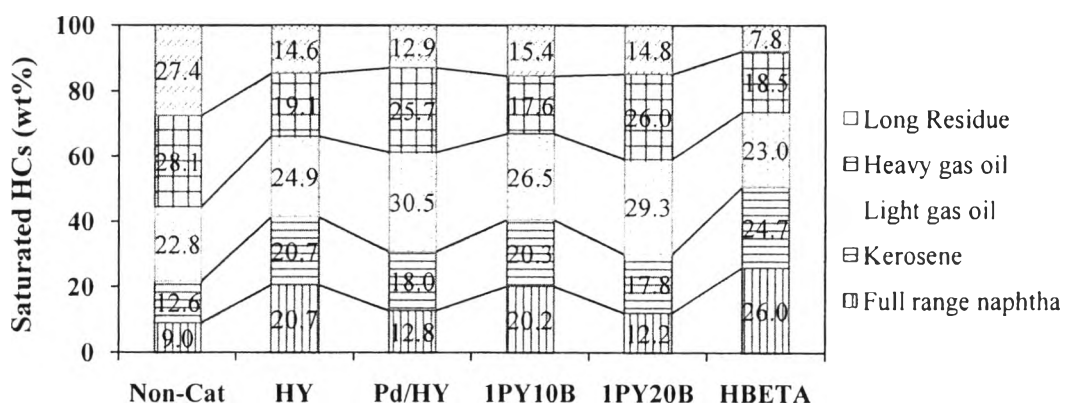


Figure 4.16 Distribution of saturated hydrocarbons in petroleum cuts obtained from pyrolysis with varied percentages of HBETA in Pd/HY.

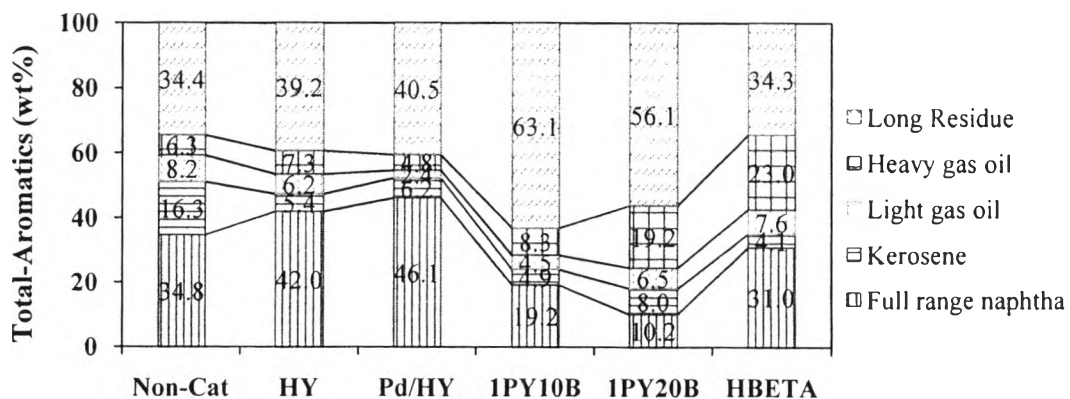


Figure 4.17 Distribution of total aromatic hydrocarbons in petroleum cuts obtained from pyrolysis with varied percentages of HBETA in Pd/HY.

However, the total aromatics in naphtha greatly reduces when the percentage of additive increases. Therefore, it can be concluded that the 1PY10B seems to be a proper catalyst that gives naphtha as a cracking feedstock for olefins production because it produces the large amount of saturated hydrocarbons in naphtha that is preferred in cracking.

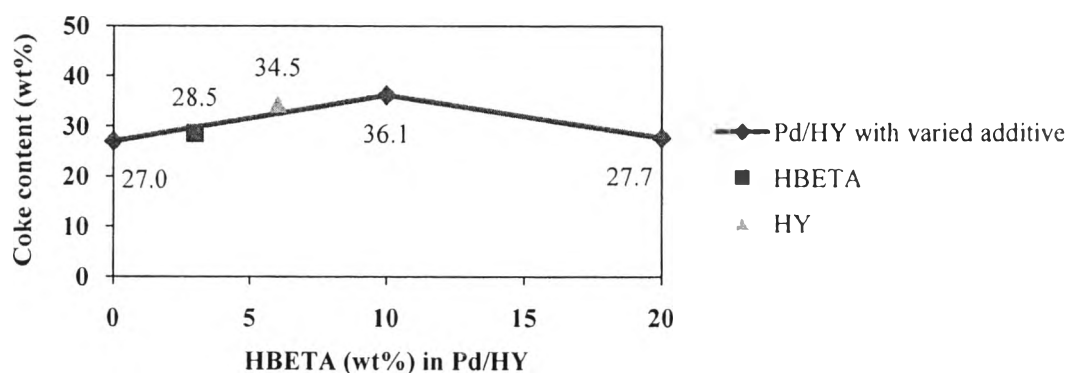


Figure 4.18 Coke formation (wt%) on spent catalysts with varied percentages of HBETA in Pd/HY.

Another parameter is the coke formation on the spent catalysts. The result is illustrated in Figure 4.18. The formation of coke on spent catalysts has a relative to the cracking activity as same as the previous case, which can be explained that the increase of cracking activity can create pathways reaching to the coke formation. Therefore, the results on coke deposition confirm the high cracking activity of 1PY10B catalyst.

4.3 HZSM-5 as a Second Additive in Pd/HBETA + 20 wt% HY

In section 4.1, the addition of HY as an additive in Pd/HBETA can enhance the yield of light olefins, although the cooking gas yields reduce. It was illustrated that the HY addition increased the selectivity for light olefins production. Moreover, both quantity and quality of the light gas oil fraction was enhanced after the HY was

added in the Pd/HBETA. Therefore, the 20 wt% HY in Pd/HBETA was selected to study in this section for the effect of a second additive that is HZSM-5.

4.3.1 Catalyst Characterization

The physical properties of catalysts investigated in this section are revealed in Table 4.4. The surface area and specific pore volume were determined by using the BET and Horvath-Kawazoe method, respectively.

Table 4.4 Physical properties of catalysts with varied percentages of HZSM-5 in 1%Pd/HBETA+20%HY

Catalysts	Surface area (m ² /g)	Specific pore volume (cm ³ /g)
HZSM-5	373	0.25
1%Pd/HBETA+20%HY (1PB20Y)	525	2.96
1%Pd/HBETA+20%HY+10%HZSM-5 (1PB20Y10Z)	490	0.35
1%Pd/HBETA+20%HY+20%HZSM-5 (1PB20Y20Z)	472	0.72

4.3.2 Product Distributions

The product distribution is also displayed in terms of G/L ratio, which is revealed in Figure 4.19. It is found that the using of HZSM-5 alone slightly increases the G/L ratio from those obtained from the non-catalytic case. It can be explained that the very small pore size and low surface area do not allow HZSM-5 to well perform on cracking tire compounds when it was used alone. Meanwhile, the addition of HZSM-5 in 1PB20Y can improve the cracking activity. The G/L ratio obtained from 1PB20Y is 0.85, and further increases to 0.88 and 1.0 at the addition of 10 wt% and 20 wt% HZSM-5 in 1PB20Y, respectively. This result is similar to the one obtained from Qu *et al.*, (2006) who reported that using HZSM-5 alone was not suitable for the first step pyrolysis, but it was suitable for the post catalytic process.

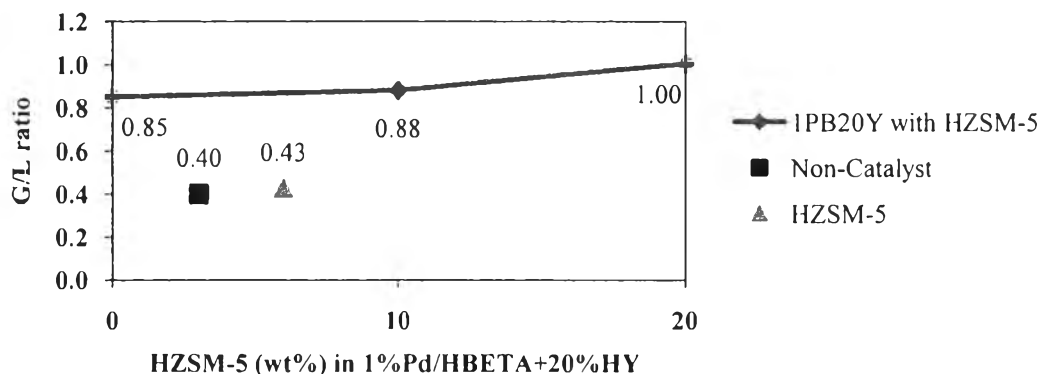


Figure 4.19 G/L ratio obtained from pyrolysis with varied percentages of HZSM-5 in 1%Pd/HBETA+20%HY.

4.3.3 Gas Compositions

The yield of gaseous products obtained from using pure HZSM-5 zeolite is close to that obtained the non-catalytic case which is revealed in Figures 4.20 and 4.21. The yield of light olefins and cooking gases obtained from the non-catalytic case is 3.5 wt% and 4.7 wt%, respectively; while that obtained from the pure HZSM-5 zeolite is 3.3 wt% and 5.4 wt%, respectively.

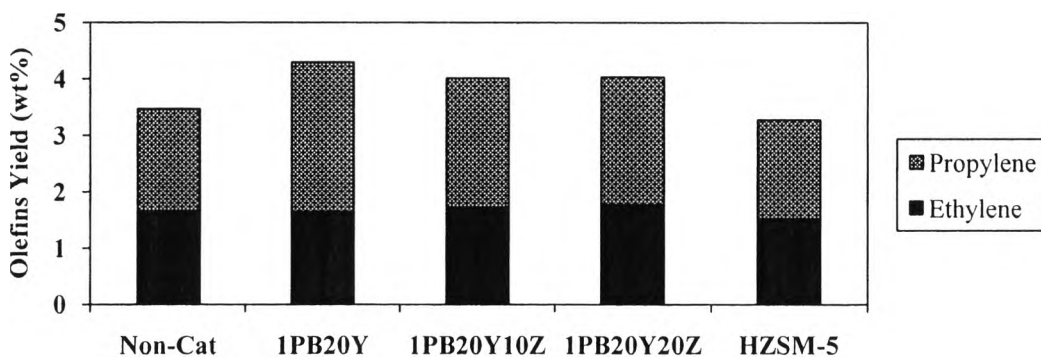


Figure 4.20 Yield of light olefins in the gas products obtained from pyrolysis with varied percentages of HZSM-5 in 1%Pd/HBETA+20%HY.

After 10 wt% and 20 wt% HZSM-5 was mixed in 1PB20Y, the yield of light olefins is slightly reduced from 4.3 wt% obtained from 1PB20Y to 4.0 wt%,

which is insignificantly changed. However, the yield of cooking gases is enhanced from 8.6 wt% obtained from 1PB20Y to 11.5 wt% and 13.4 wt% with adding 10 wt% and 20 wt% HZSM-5, respectively. These results can be explained that the strong acid site of HZSM-5 can protonate the unsaturated molecules to the saturated molecules, and prevent the secondary reactions resulting in the reduction of light olefins and enhancement of cooking gases. The other gaseous compositions and yields are revealed in Appendix C3.

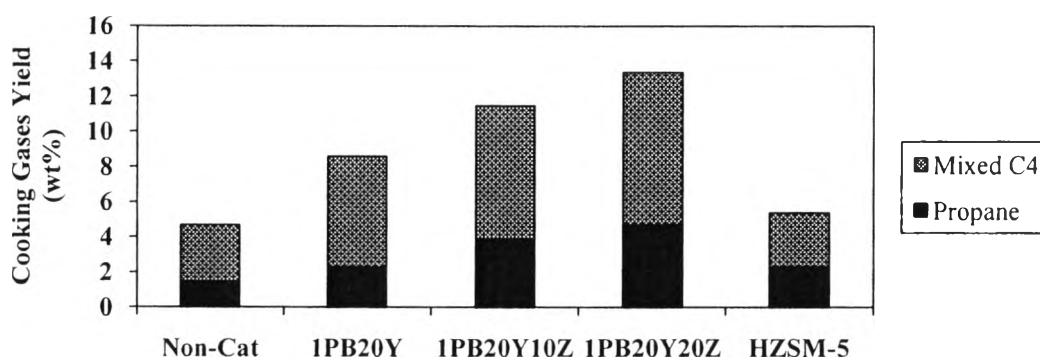


Figure 4.21 Yield of cooking gases in the gas products obtained from pyrolysis with varied percentages of HZSM-5 in 1%Pd/HBETA+20%HY.

4.3.4 Liquid Products

4.3.4.1 Quantitative Analysis

The petroleum fractions of this case are exhibited in Figure 4.22. The result represents that the use of pure HZSM-5 zeolite can potentially convert the heavy fractions (long residue, heavy gas oil and light gas oil fractions) to the lighter fractions (full range naphtha and kerosene fractions) as compared to the non-catalytic case. After HZSM-5 was added into the 1PB20Y, the cracking activity is improved, as compared to the use of 1PB20Y alone, which can increase the amount of full range naphtha. The 1PB20Y can produce 30.0 wt% naphtha, and then, the naphtha increases to 45.3 wt% and 47.7 wt% with adding 10 wt% and 20 wt% HZSM-5, respectively. For the kerosene fraction, 10 wt% HZSM-5 in 1PB20Y

shows the best kerosene production since it can produce at the highest concentration of 23.0 wt%; meanwhile, the light gas oil fraction is further reduced to 14.5 wt% and 11.6 wt% with adding 10 wt% and 20 wt% HZSM-5, respectively.

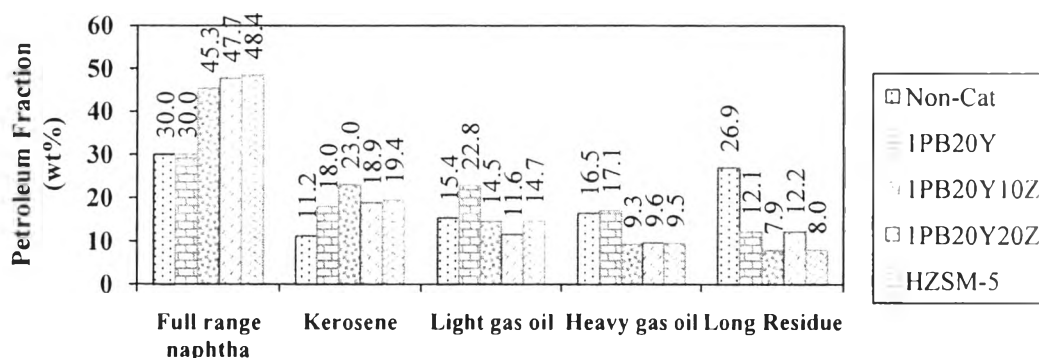


Figure 4.22 Petroleum fractions in derived oils obtained from pyrolysis with varied percentages of HZSM-5 in 1%Pd/HBETA+20%HY.

4.3.4.2 Qualitative Analysis

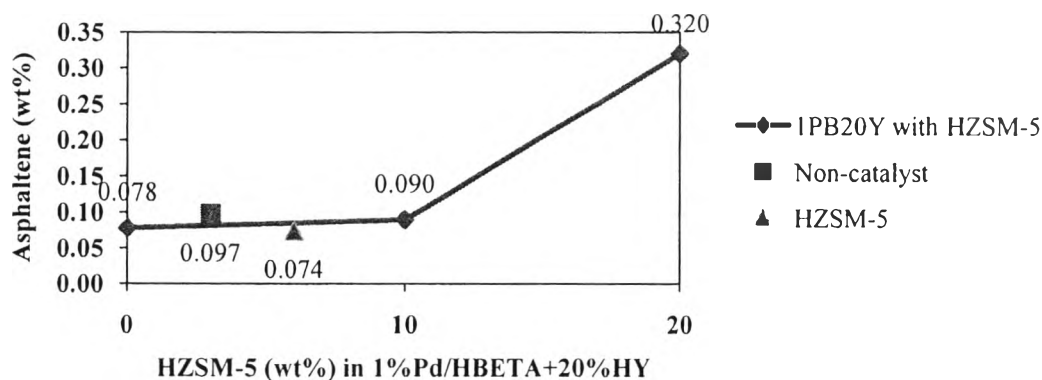


Figure 4.23 Percentage of asphaltene in pyrolytic oils obtained from pyrolysis with varied percentages of HZSM-5 in 1%Pd/HBETA+20%HY.

The asphaltene that is firstly precipitated from liquid product is exhibited in Figure 4.23. The result reveals that the pure HZSM-5 and 1PB20Y produce 0.074 wt% and 0.078 wt% asphaltene in oil, respectively. After 10 wt% and

20 wt% HZSM-5 was added into the 1PB20Y, the asphaltene in oil is 0.090 wt% and 0.320 wt%, respectively. The increases in asphaltene explain the increase in cracking ability of 1PB20Y10Z and 1PB20Y20Z that can cause the re-combination of the intermediates evolved during cracking process.

The chemical composition of oil products is displayed in Figure 4.24. The HZSM-5 reduces saturated hydrocarbons to 56.3 wt%, whereas the mono-aromatics are enhanced to 11.6 wt% as compared to the non-catalytic case. The poly-aromatics obtained from using pure HZSM-5 zeolite are 13.7 wt%, which are higher than that obtained from pyrolysis without a catalyst. After 10 wt% HZSM-5 is mixed with 1PB20Y (1PB20Y10Z), the saturated hydrocarbons content reduces to 50.0 wt%, and then, increases to 58.2 wt% at 20 wt% HZSM-5 mixing, which is close to that of 1PB20Y alone. The mono-aromatics and poly-aromatics gradually reduce with adding 10 wt% and 20 wt% HZSM-5. Moreover, the quality of each petroleum fraction can be examined by taking consideration into the concentration of saturated hydrocarbon and total-aromatics in each petroleum fraction, which can be observed in Figures 4.25 and 4.26, respectively.

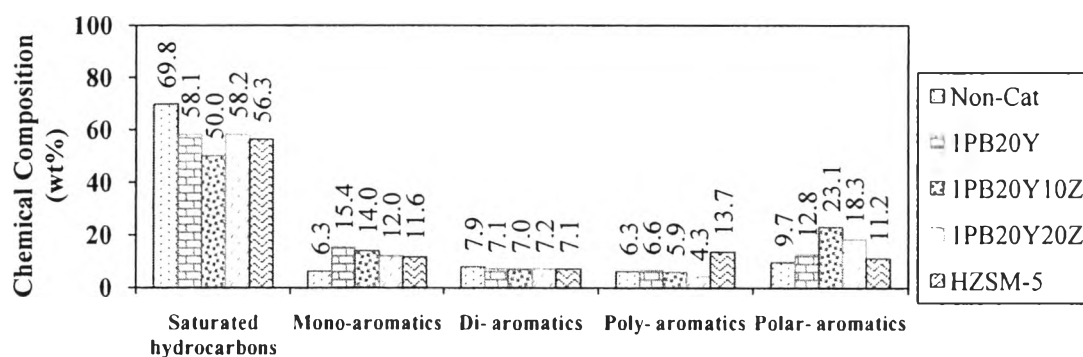


Figure 4.24 Chemical compositions of maltenes obtained from pyrolysis with varied percentages of HZSM-5 in 1%Pd/HBETA+20%HY.

The use of pure HZSM-5 can produce higher saturated hydrocarbons in light fractions (full range naphtha, kerosene, and light gas oil) than the

pyrolysis without a catalyst. The 1PB20Y itself gives 12.1 wt% saturated hydrocarbons in naphtha fraction. After HZSM-5 was added to the 1PB20Y, the saturated hydrocarbons content in naphtha fraction drastically reaches to 40.5 wt% and 40.9 wt% at 10 wt% and 20 wt% of HZSM-5 in 1PB20Y, respectively. Moreover, they are higher than that obtained from pure HZSM-5. The saturated hydrocarbons content in kerosene fraction is also enhanced by mixing HZSM-5 in 1PB20Y. These results can be contributed to the strong acid strength and the pore restriction of HZSM-5 that are selective to the saturated compounds and small molecule. Furthermore, the use of pure HZSM-5 slightly increases total aromatics content in naphtha fraction, while the total aromatics in kerosene and light gas oil fractions drastically reduce, which indicates a better quality of naphtha, kerosene and light gas oil fractions. However, the addition of 10 wt% HZSM-5 in 1PB20Y greatly helps reduce the total aromatics in naphtha fraction from 31.7 wt% (1PB20Y) to 11.0 wt%. Meanwhile, the 1PB20Y mixed with 20 wt% HZSM-5 reduced the total aromatics in naphtha and kerosene fractions to 17.8 wt% and 8.4 wt%. Therefore, the addition of HZSM-5 in 1PB20Y causes the synergy on the distribution of saturated hydrocarbons.

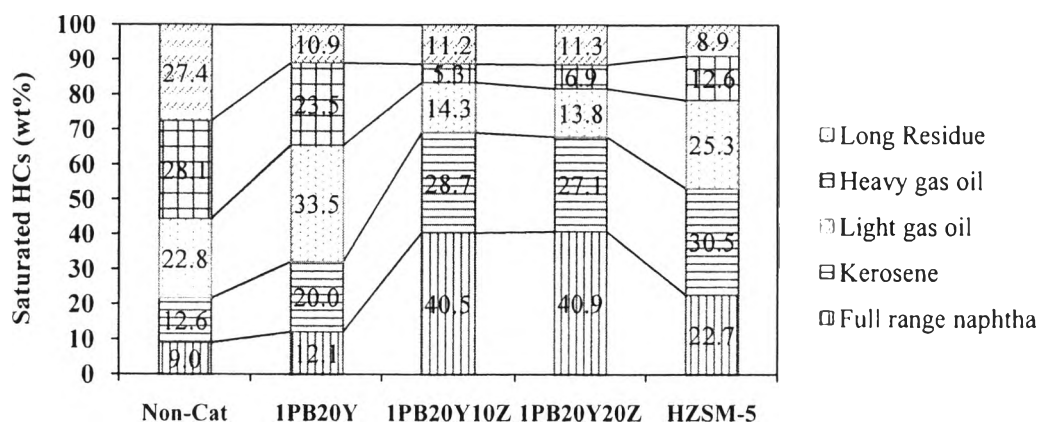


Figure 4.25 Distribution of saturated hydrocarbons in petroleum cuts obtained from pyrolysis with varied percentages of HZSM-5 in 1%Pd/HBETA+20%HY.

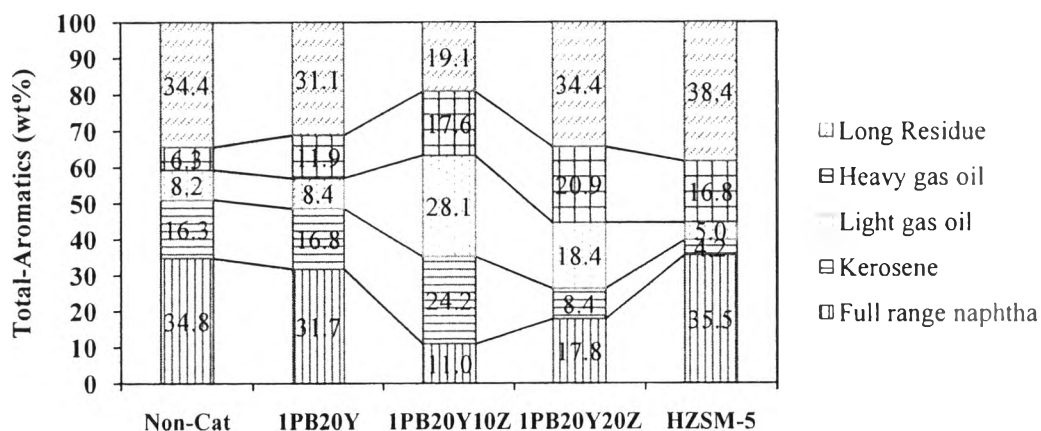


Figure 4.26 Distribution of total aromatic hydrocarbons in petroleum cuts obtained from pyrolysis with varied percentages of HZSM-5 in 1%Pd/HBETA+20%HY.

The coke formation on the spent HZSM-5 is 12.1 wt% as shown in Figure 4.27. The amount of coke on the 1PB20Y catalyst is 27.5 wt%. After it was mixed with 10 wt% and 20 wt% HZSM-5, the coke on the spent catalysts increases to 32.5 wt% and 32.6 wt%, respectively. It can be explained that the increase of coke content is caused by the increase in cracking activity.

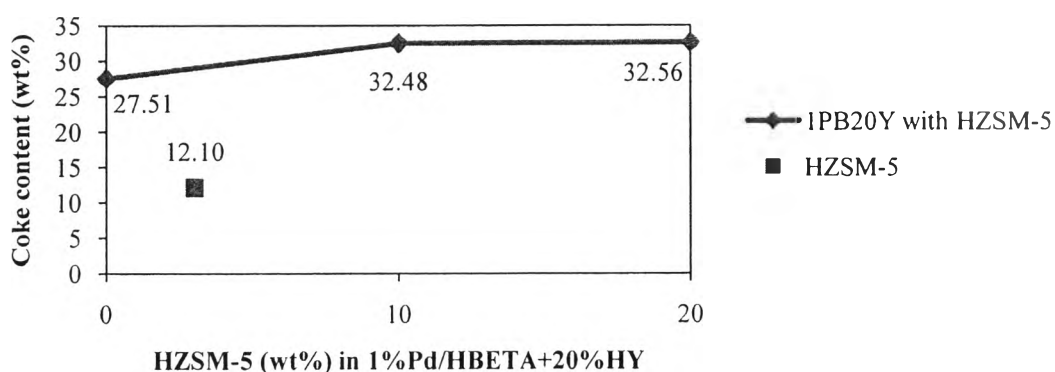


Figure 4.27 Coke formation (wt%) on spent catalysts with varied percentages of HZSM-5 in 1%Pd/HBETA+20%HY.

4.4 HZSM-5 as a Second Additive in Pd/HY + 20 wt% HBETA

In Section 4.2, the addition of HBETA into Pd/HY displayed that the cracking activity reached to the highest at the 10 wt% of HBETA in Pd/HY. Moreover, the catalyst mixture gave the highest yield of light olefins and cooking gases among all Pd loaded on HY catalysts. In addition, it can improve the quantity of full range naphtha fraction, which the quality of this fraction is suitably be used for the cracking process. This can be explained that the synergy occurred at the 10 wt% of HBETA in Pd/HY. Therefore, the mixture of 10 wt% HBETA in Pd/HY was selected to study in this section for the effect of a second additive that is HZSM-5.

4.4.1 Catalyst Characterization

The physical properties of catalysts investigated in this section are revealed in Table 4.5. The surface area and specific pore volume were determined by using the BET and Horvath-Kawazoe method, respectively.

Table 4.5 Physical properties of catalysts with varied percentages of HZSM-5 in 1%Pd/HY+10%HBETA

Catalysts	Surface area (m ² /g)	Specific pore volume (cm ³ /g)
HZSM-5	373	0.25
1%Pd/HY+10%HBETA (1PY10B)	587	1.25
1%Pd/HY+10%HBETA+10%HZSM-5 (1PY10B10Z)	512	0.78
1%Pd/HY+10%HBETA+20%HZSM-5 (1PY10B20Z)	489	0.47

4.4.2 Product Distributions

The product distribution obtained from the varied percentages of HZSM-5 in 1PY10B is shown in Figure 4.28. Using 1PY10B alone produces the gaseous and liquid products in the ratio of 0.93. After mixing with 10 wt% HZSM-5,

the G/L ratio insignificantly changes from using 1PY10B alone; however, it is reduced to 0.71 at 20 wt% HZSM-5 in 1PY10B.

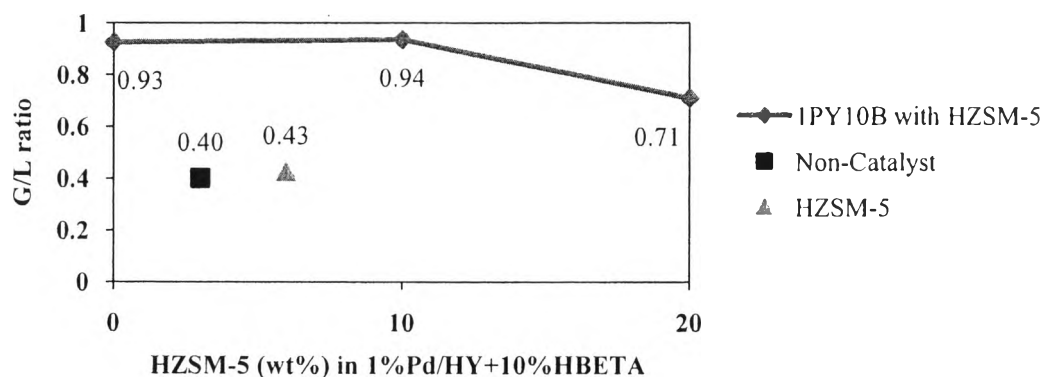


Figure 4.28 G/L ratio obtained from pyrolysis with varied percentages of HZSM-5 in 1%Pd/HY+10%HBETA.

4.4.3 Gas Compositions

The yields of valuable gaseous products are displayed in Figures 4.29 and 4.30. In Figure 4.29, using 1PY10B alone produces 4.8 wt% light olefins. With using 1PY10B mixed with 10 wt% HZSM-5, the yield of light olefins slightly increases to 5.0 wt%, whereas the mixing of 20 wt% HZSM-5 in 1PY10B reduces the light olefins to 4.2 wt%. However, the gas concentrations shown in Appendix C4 indicate that the light olefins concentrations obtained from 1PY10B, 1PY10B10Z, and 1PY10B20Z are similar (17.4 wt% - 17.7 wt%), so the HZSM-5 additive does not change the gas composition. In the case of cooking gases, the use of 1PY10B alone produces 8.6 wt% cooking gases. These gases are raised to 10.0 wt% after mixing 10 wt% HZSM-5 in 1PY10B, and then, they are reduced to 9.2 wt% at 20 wt% HZSM-5 in 1PY10B. However, the gas concentrations illustrated in Appendix C4 also show the increased concentration of cooking gases with the addition of HZSM-5 in 1PY10B. Therefore, the yields of gaseous products strongly depend on the value of G/L ratio.

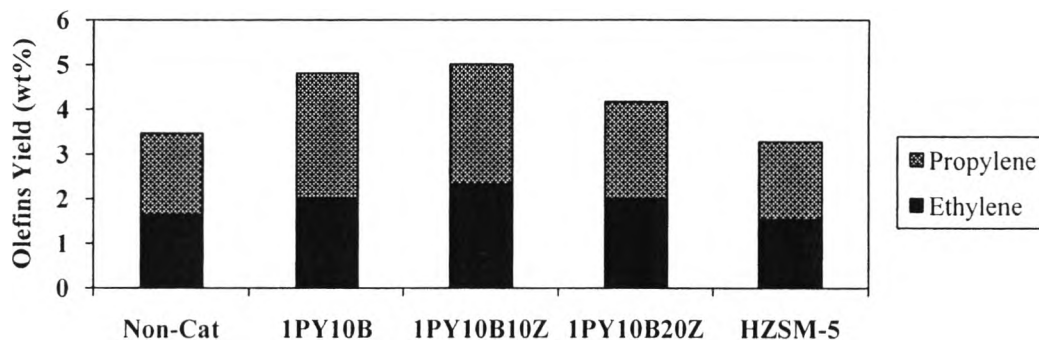


Figure 4.29 Yield of light olefins in the gas products obtained from pyrolysis with varied percentages of HZSM-5 in 1%Pd/HY+10%HBETA.

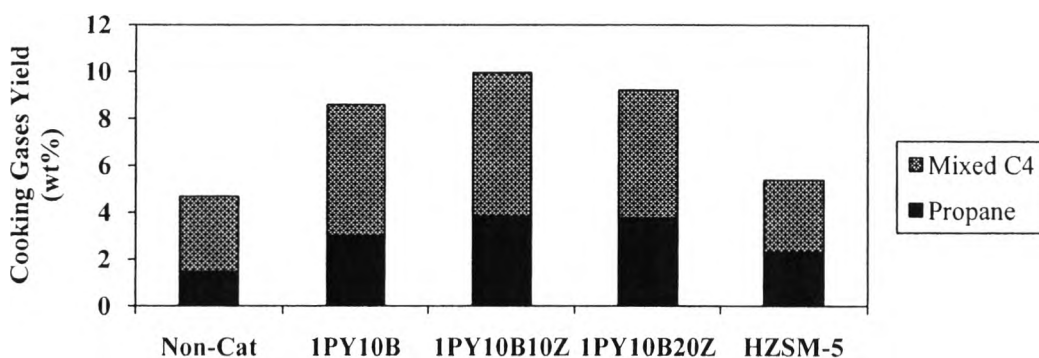


Figure 4.30 Yield of cooking gases in the gas products obtained from pyrolysis with varied percentages of HZSM-5 in 1%Pd/HY+10%HBETA.

4.4.4 Liquid Products

4.4.4.1 *Quantitative Analysis*

The amount of petroleum cuts is revealed in Figure 4.31. The results indicate that the addition of 10 wt% and 20 wt% HZSM-5 in 1PY10B can improve the quantity of light fractions (naphtha and kerosene fractions), whereas the long residue is greatly reduced as compared to the use of 1PY10B alone. However, the quantity of light fractions (naphtha and kerosene fractions) insignificantly changes as compared to the pure HZSM-5 case. In addition, the other fractions ob-

tained from varied percentage of HZSM-5 in 1PY10B tend to be close to the pure HZSM-5 case, which can contribute to the nature of additive HZSM-5.

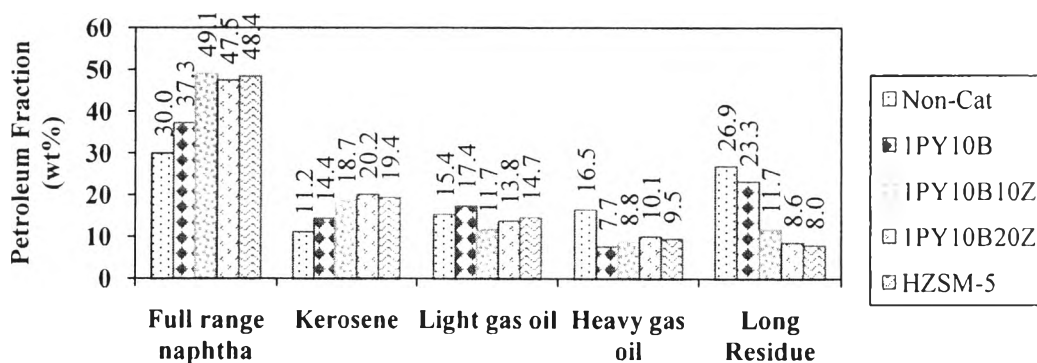


Figure 4.31 Petroleum fractions in derived oils obtained from pyrolysis with varied percentages of HZSM-5 in 1%Pd/HY+10%HBETA.

4.4.4.2 Qualitative Analysis

The percentage of asphaltene in the liquid products obtained from varied percentages of HZSM-5 in 1PY10B is illustrated in Figure 4.32. The addition of 10 wt% HZSM-5 in 1PY10B increases the percentage of asphaltene to 0.106 wt% from 0.092 wt% obtained from using 1PY10B alone. After that, the asphaltene reduces to 0.086 wt% when 20 wt% HZSM-5 was added into 1PY10B.

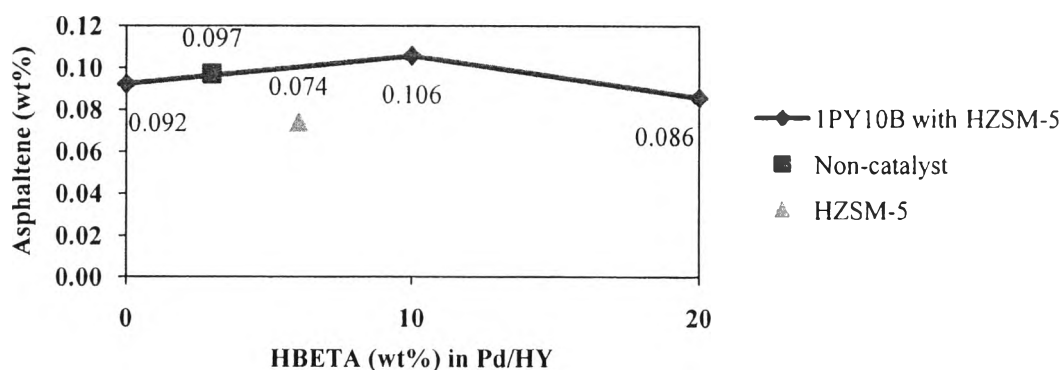


Figure 4.32 Percentage of asphaltene in pyrolytic oils obtained from pyrolysis with varied percentages of HZSM-5 in 1%Pd/HY+10%HBETA.

The chemical compositions of oil products are illustrated in Figure 4.33. The saturated hydrocarbon content in the oil obtained from using 1PY10B alone is 69.3 wt%, which is close to that obtained from pyrolysis without a catalyst (69.8 wt%). When 10 wt% and 20 wt% HZSM-5 was added into 1PY10B, the saturated hydrocarbon content is reduced to 55.3 wt% and 56.4 wt% in oils, respectively. Moreover, the results show that the additions of HZSM-5 in 1PY10B can improve the mono-aromatics approximately by twice as much as that of 1PY10B, whereas the content of poly-aromatic hydrocarbons is lower with the addition of HZSM-5 in 1PY10B than that of the pure HZSM-5 and 1PY10B. From these results, it can be explained that the addition of HZSM-5 can transform saturated hydrocarbons to aromatics hydrocarbons, mostly mono-aromatics, by dehydrogenation and cyclisation reactions, but they cannot transform to poly-aromatics because of the pore restriction of HZSM-5 zeolite.

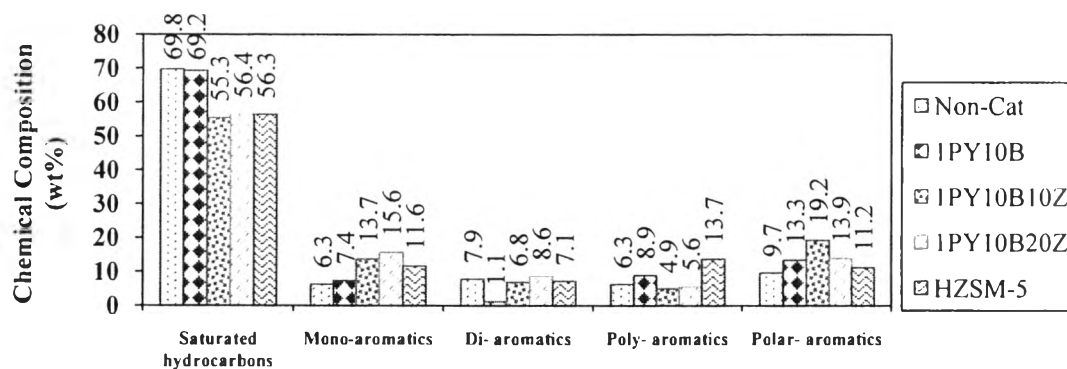


Figure 4.33 Chemical compositions of maltenes obtained from pyrolysis with varied percentages of HZSM-5 in 1%Pd/HY+10%HBETA.

Nevertheless, the reduction of saturated hydrocarbons or improvement of total-aromatics is not as interesting as the distributions of those compositions in each petroleum fraction. The addition of HZSM-5 in 1PY10B helps increasing the saturation hydrocarbons in light fractions (full range naphtha and kerosene fractions). Furthermore, it also improves the total aromatics in naphtha fraction, especially the 1PY10B10Z catalyst. Therefore, 1PY10B10Z seems to be the best cat-

alyst among all hybrid catalysts since saturated hydrocarbons is highly distributed in the naphtha fraction. In addition, the distribution of saturated hydrocarbons in kerosene fraction is higher, although that of the total aromatics is also higher when HZSM-5 was added in 1PY10B. Therefore, the addition of HZSM-5 in 1PY10B, especially 1PY10B20Z, has potential to improve the quantity and quality of the kerosene fraction.

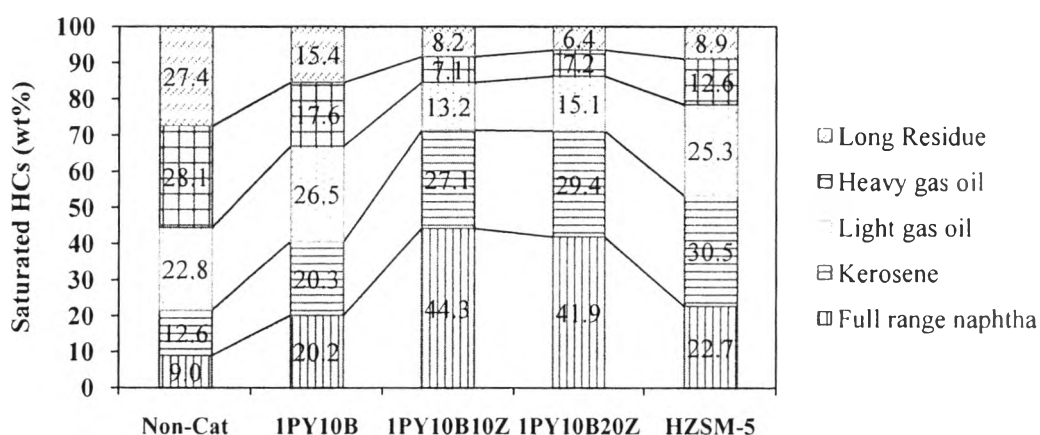


Figure 4.34 Distribution of saturated hydrocarbons in petroleum cuts obtained from pyrolysis with varied percentages of HZSM-5 in 1%Pd/HY+10%HBETA.

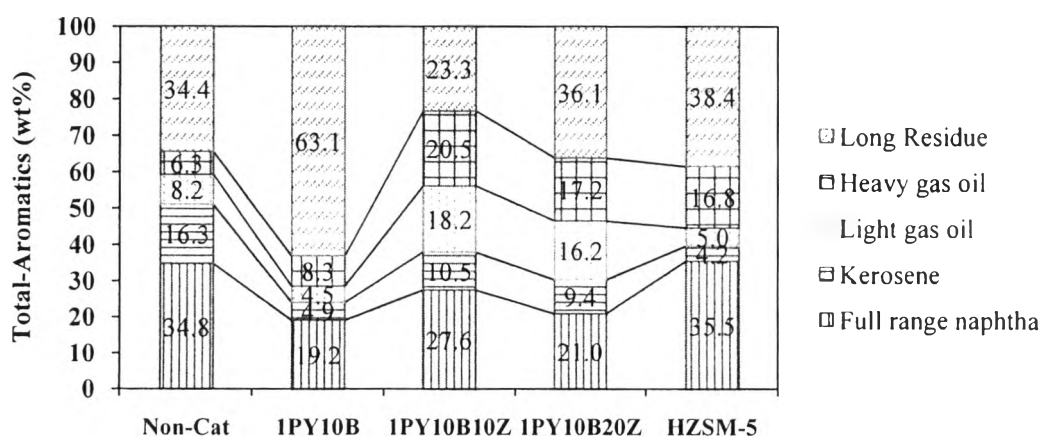


Figure 4.35 Distribution of total aromatic hydrocarbons in petroleum cuts obtained from pyrolysis with varied percentages of HZSM-5 in 1%Pd/HY+10%HBETA.

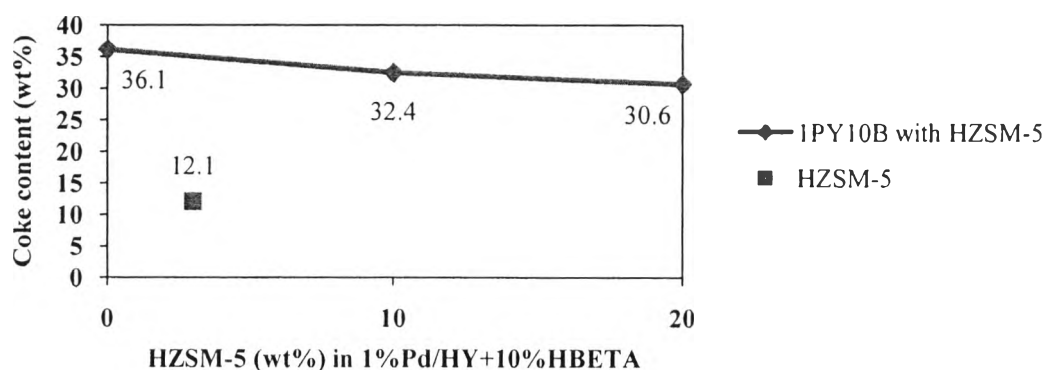


Figure 4.36 Coke formation (wt%) on spent catalysts with varied percentages of HZSM-5 in 1%Pd/HY+10%HBETA.

The coke formation on spent catalysts with varied percentages of HZSM-5 in 1PY10B is revealed in Figure 4.36. The addition of HZSM-5 in 1PY10B can gradually reduce the coke content in the 1PY10B catalyst. It can be explained that the reduction of coke formation on the spent catalysts is caused by the reduction of the cracking activity when HZSM-5 was added into the 1PY10B catalyst.