



CHAPTER IV

RESULTS AND DISCUSSION

The products obtained from catalytic pyrolysis of waste tire using noble metals (Pd and Ru) and non-noble metals (Ni and Fe) supported on acid zeolites (HBeta and HMOR) are quantitatively and qualitatively compared and discussed in this chapter. The percentage of loaded noble metals (Pd and Ru) was fixed at 1% by weight, and that of non-noble metals (Ni and Fe) was varied as 5%, 10% and 20% by weight. All catalysts were prepared by using incipient wetness impregnation technique

4.1 Comparison of Ni with Pd

4.1.1 Using HBeta as a Support

This section compares the effect of the various %Ni loading with 1%Pd supported on HBeta zeolite on waste tire pyrolysis. The product obtained from waste tire pyrolysis consists of gas, liquid, and solid residue (char). The product distributions obtained from waste tire pyrolysis can be explained by plotting the gas to liquid ratio as shown in Figure 4.1.

4.1.1.1 *Gas to Liquid Ratio*

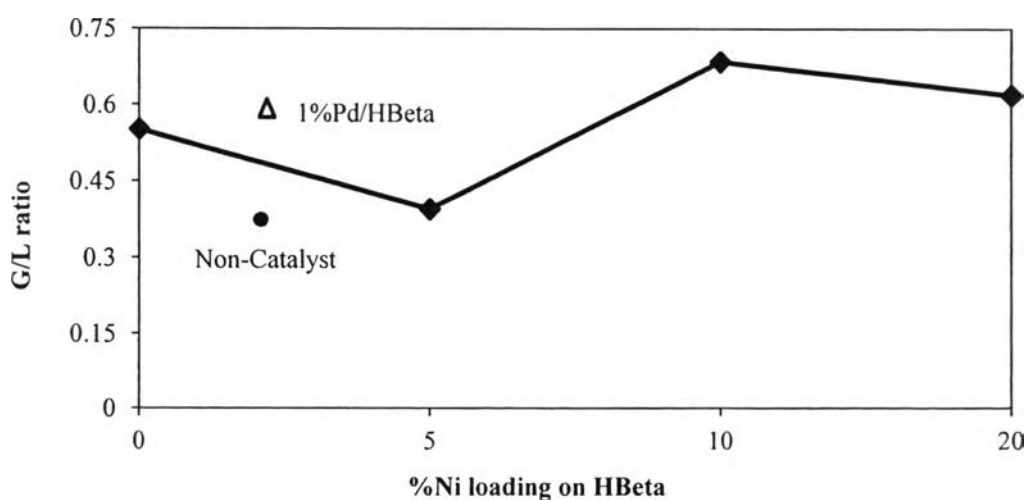


Figure 4.1 G/L ratio obtained from using various % Ni/HBeta in comparison with (●) Non-catalytic and (Δ) 1%Pd/HBeta cases.

In Figure 4.1, the results show that as compared to the non-catalytic case (thermal pyrolysis) and pure HBeta zeolite, 1%Pd/HBeta as the reference increases the G/L ratio. Namely, the G/L ratio increased from 0.4 (catalytic case) and 0.55 (pure HBeta case) to 0.6. The increment of G/L ratio suggests that the gas product increases with the decrease in the liquid product. This result is attributed to the reason that heavy molecules can be cracked into lighter molecules on the metal and acid sites of a catalyst. The presence of all Ni/HBeta catalysts increases the G/L ratio from that of the non-catalytic case, especially 10%Ni/HBeta that gives the highest G/L ratio. The high amounts of Ni (10 wt% and 20 wt%) produce the higher G/L ratios than the non-catalytic and reference cases. The result indicates the high amounts of Ni increase the cracking activity. In addition, 20%Ni/HBeta gives the closest G/L ratio to that of 1%Pd/HBeta.

The non-condensable gases obtained from pyrolysis contain high value petrochemicals such as olefins (ethylene and propylene), cooking gases (hereby presented in terms of propane and mixed C₄), and mixed C₄. The comparisons on the yields of petrochemicals obtained from Ni-loaded catalysts and 1%Pd/HBeta are shown in Figures 4.2-4.4.

4.1.1.2 Yield of Olefins

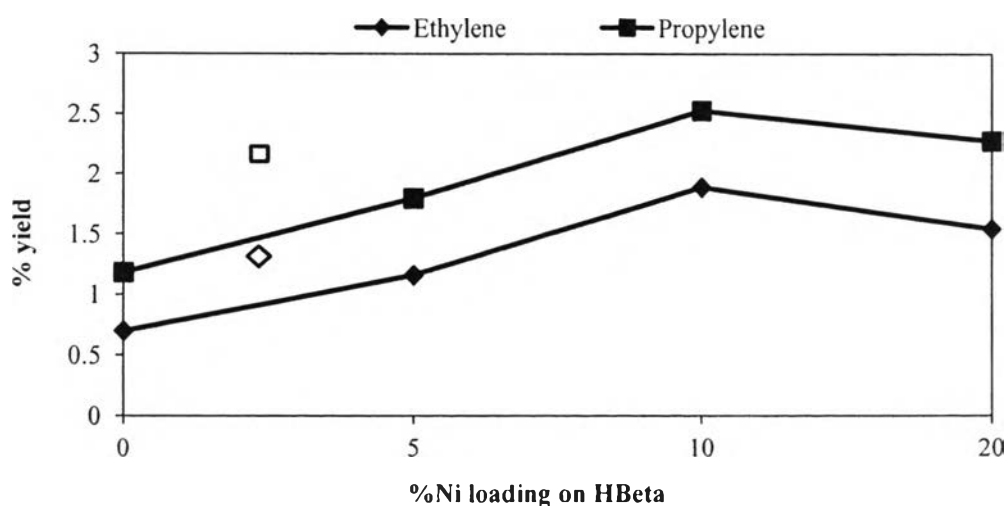


Figure 4.2 Yield of ethylene and propylene obtained from using various % Ni/HBeta in comparison with (◇) ethylene and (□) propylene yields from 1%Pd/HBeta.

For the reference, 1%Pd/HBeta gives higher yields of ethylene and propylene than that of pure HBeta zeolite, which are about 1.4 wt% and 2.2 wt% respectively. Figure 4.2 shows that when the percentage of Ni loading increases, the yields of ethylene and propylene increase in the same trend. Moreover, the Ni catalysts, except at 5%Ni loading, give a higher yield of light olefins than that of pure HBeta zeolite. In addition, 10%Ni/HBeta exhibits the highest yield of light olefins, which are subsequently slightly decreased when the loading increases to 20%Ni. Nevertheless, 20%Ni/HBeta exhibits the yield of light olefins close to that of 1%Pd/HBeta. From this figure, it can be seen that 10%Ni/HBeta gives the higher yield of light olefins than that of 1%Pd/HBeta.

4.1.1.3 Yield of Cooking Gases

The yield of cooking gases (propane and mixed C₄) also increases with Ni loading in the similar trend as the yield of olefins, especially propane. As shown in Figure 4.3, 1%Pd/HBeta gives 2.2 wt% and 6.5 wt% yields of propane and mixed C₄, respectively, which are higher than that of pure HBeta. It is also exhibited that the yield of propane slightly increases whereas the yield of mixed C₄ insignificantly increases with the increased percentage of Ni loading. In case of the propane, the all Ni catalysts show the higher yield of propane than that of pure HBeta zeolite and 20%Ni/HBeta gives the similar yield of propane as 1%Pd/HBeta. Moreover, 10%Ni/HBeta does not only produce the highest yield of light olefins, but also produces the high yields of cooking gases.

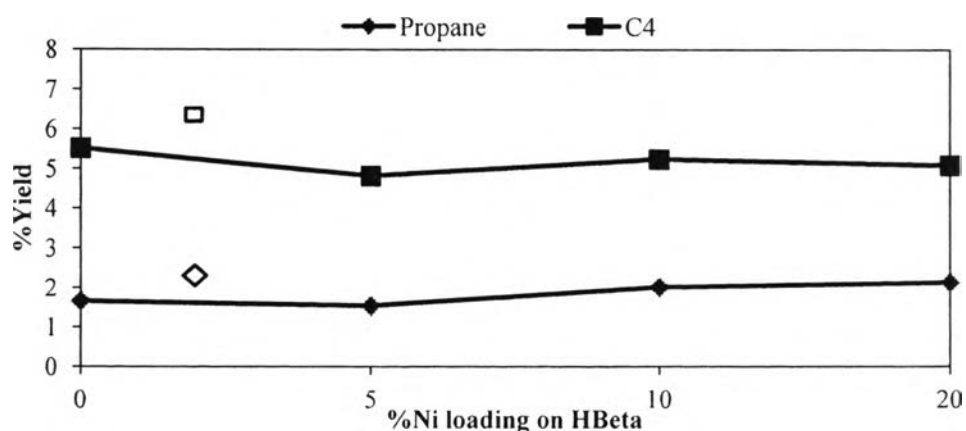


Figure 4.3 Yield of cooking gases obtained from using various %Ni/HBeta in comparison with (◇) propane and (□) C₄ yields from 1%Pd/HBeta.

4.1.1.4 Yield of Mixed C₄

One of high economic value gases is mixed C₄, which is one of the predominant gas products obtained from the pyrolysis of scrap tire. For the reference, 1%Pd/HBeta produces 6.5 wt% yield of mixed C₄. As can be seen in Figure 4.4, as the percentage of Ni loading increases, the yield of mixed C₄ is constant at about 5 wt% for all Ni-loaded catalysts. It can be concluded that Ni catalyst cannot be used as a suitable catalyst as a substitute of 1%Pd/HBeta for mixed C₄ production.

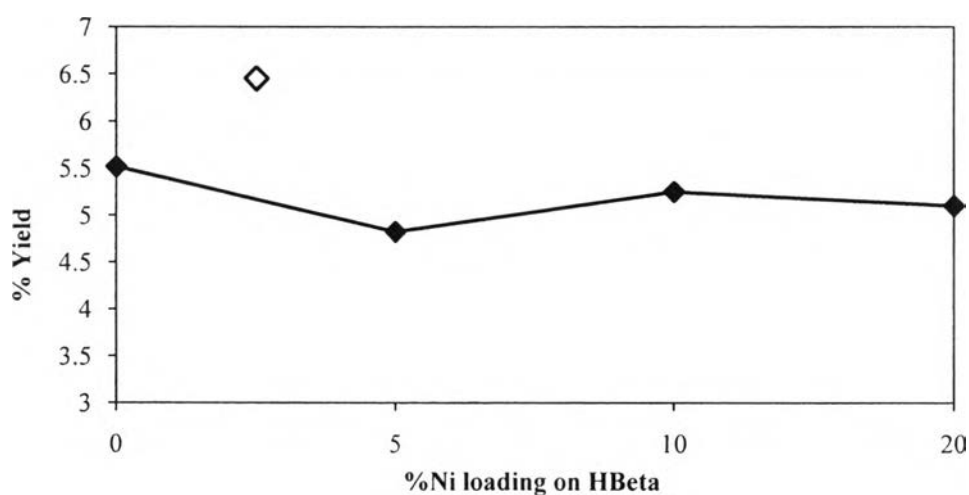


Figure 4.4 Yield of mixed C₄ obtained from using various %Ni/HBeta zeolite in comparison with (◇) Mixed C₄ yield from 1%Pd/HBeta.

As shown in Figures 4.1-4.4, the results exhibit that 10%Ni/HBeta seems to be a potential catalyst to produce light olefins and cooking gases. At the higher loading (20%Ni/HBeta), the yields of light olefins and cooking gases slightly decrease. Nonetheless, 20%Ni/HBeta gives the closest yields of light olefins and propane as 1%Pd/HBeta. For a high amount of Ni loading, the agglomeration of Ni can reduce dispersion and active sites. Furthermore, Eswaramoorthi *et al.*, (2003) studied the Ni loaded on zeolite-β by incipient wetness impregnation (IWI) for the hydroisomerisation of *n*-heptane. They reported when the amount of Ni increases, the total acidity of catalyst continuously falls by reasons of the acid sites covered by Ni species.

4.1.1.5 Temperature-Programmed Reduction (TPR)

Temperature-programmed reductions (TPR) technique was used to identify the reducibility of the impregnated catalysts. TPR spectra of the various percentages of Ni loading are shown in Figure 4.5.

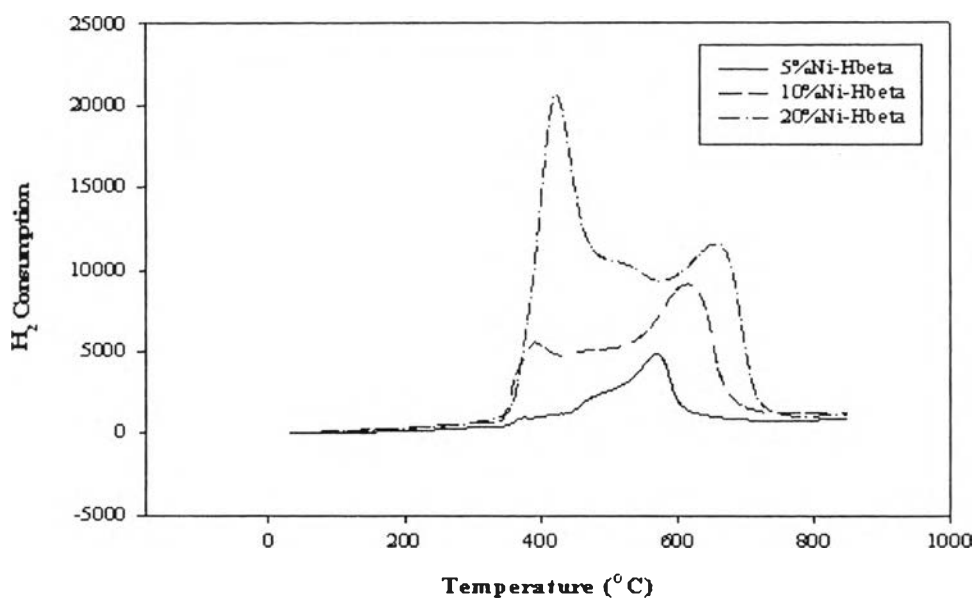


Figure 4.5 TPR spectra of various % Ni loading on HBeta zeolite.

TPR spectra of catalysts with various percentages of nickel show two reduction peaks. 5%Ni/HBeta shows two peaks at 370 °C and 570 °C. 10%Ni/HBeta gives two bigger peaks at the reduction temperatures at 390 °C and 610 °C, whereas 20%Ni/HBeta gives two reduction peaks at temperatures of 420 °C and 650 °C. The peak at the lower temperature could be related to the reduction of NiO to Ni⁰, which located on surface area, whereas the second peak at higher temperature related to the NiO located in zeolite pore (Fúnez *et al.*, 2008). The H₂ consumption depends on the amount of NiO obtained after the calcination of these catalysts. When the percentage of Ni increased, the area of two peaks rapidly increases. As shown in Figure 4.5, at a high amount of Ni loading, the second peak dramatically shifts from 570 °C to 650 °C. The results can be suggested that a higher Ni loading is more difficult to be reduced than a lower loading.

4.1.1.6 Liquid Composition

The liquids obtained from the pyrolysis of waste tire were separated into 5 fractions (Saturated hydrocarbons, Mono-aromatics, Di-aromatics, Poly-aromatics and Polar-aromatics) by using liquid column chromatography (Sebor *et al.*, 1999). All functional compositions were analyzed by a SIMDIST-GC for the true boiling point distillation curves.

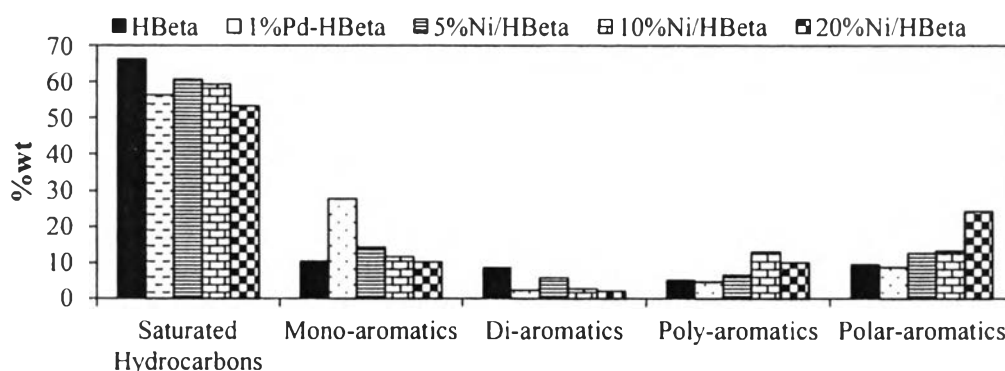


Figure 4.6 Chemical compositions in maltenes obtained from using Ni/HBeta catalysts in comparison with those from 1%Pd/HBeta.

The chemical compositions of maltenes obtained from using varied loading percentages of Ni/HBeta catalysts as compared to pure HBeta and 1%Pd/HBeta are shown in Figure 4.6. HBeta zeolite produces the highest concentration of saturated hydrocarbons of about 66.2 wt%, whereas 1%Pd/HBeta gives the lower concentrations of saturated hydrocarbons of 56.3 wt% in the pyrolytic oil. When the percentage of Ni loading increases, the concentration of saturated hydrocarbons slightly decreases. 5%Ni/HBeta and 10%Ni/HBeta give a higher concentration of saturated hydrocarbons than 1%Pd/HBeta. The results show that 1%Pd/HBeta dramatically increases the mono-aromatics concentrations from 10 wt% to 27.8 wt% when compared to pure HBeta zeolite. On the other hand, the concentration of mono-aromatics is lower with using the Ni-loading catalysts. However, it is still higher than that of pure HBeta, but lower than that of 1%Pd/HBeta. Moreover, the concentrations of poly- and polar-aromatics rapidly increase when all Ni-loaded catalysts are used. It can be suggested that a higher cracking activity catalyst produces a higher concentration of poly-aromatics because the high cracking ability can generate carbocations

which are intermediates to form aromatic compounds (Choosuton, 2007). 1%Pd/HBeta produces a high quality of oil products with a high concentration of saturated hydrocarbons and low concentrations of poly- and polar-aromatics. The Ni-loaded catalyst at a high Ni loading cannot be used as a substitute of 1%Pd/HBeta for the good quality of oil production because it gives the high concentrations of poly- and polar-aromatics.

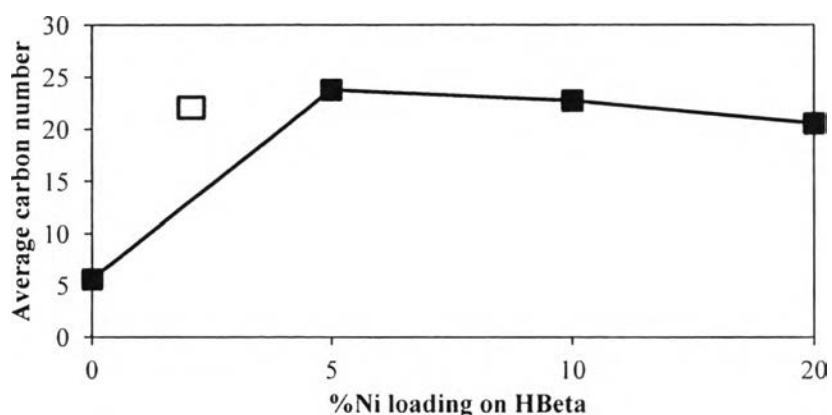


Figure 4.7 Average carbon number of mono-aromatics fractions obtained from using various % Ni/HBeta in comparison with (□) 1%Pd/HBeta.

Figure 4.7 illustrates the average carbon number of mono-aromatics in obtained from using varied loading percentages of Ni/HBeta catalysts as compared to that of 1%Pd/HBeta. It exhibits that the average carbon number of mono-aromatics slightly decreases with the increased percentage of Ni loading. This result is attributed to the reason that the high Ni loading exhibits hydrogenation and ring-opening activity on Ni metal sites. Moreover, pure HBeta gives the lowest of average carbon number of mono-aromatics. Therefore, it can be concluded that Ni loading helps improving the production of short chain mono-aromatics via the ring-opening of di-aromatics. Additionally, 20%Ni/HBeta gives the similar average carbon number of mono-aromatics as that of 1%Pd/HBeta.

In mono-aromatic portion, 10%Ni/HBeta, however, produces the considerably-high concentration of light mono-aromatics (C_6 - C_{11}) as shown in Table 4.1. Additionally, the concentration of light mono-aromatics from 10%Ni/HBeta is as much as a half of those obtained from 1%Pd/HBeta. 5%Ni/HBeta

and 20%Ni/HBeta rarely produce light mono-aromatics (C_6 - C_{11}). The aromatic compounds can be produced via Diels-Alders reactions of olefins obtained from primary cracking reactions and/or the ring-opening of di-aromatics.

Table 4.1 Concentration of light mono-aromatics (BTXs) (%wt)

Carbon No.	Yield of light mono-aromatics (%wt)			
	1%Pd/ HBeta	5%Ni/ HBeta	10%Ni/ HBeta	20%Ni/ HBeta
C_6 - C_8 (BTXs)	4.51	0	1.80	0
C_9	2.16	0	1.01	0.001
C_{10}	2.54	0	1.28	0.023
C_{11}	2.94	0.002	1.59	0.267

4.1.1.7 Petroleum Fraction

The maltenes were analyzed by a SIMDIST-GC for the true boiling point curves, and then cut to petroleum fractions, which are naphtha (<200 °C), kerosene (200–250 °C), light gas oil (250–300 °C), heavy gas oil (300–370 °C), and long residue (>370 °C).

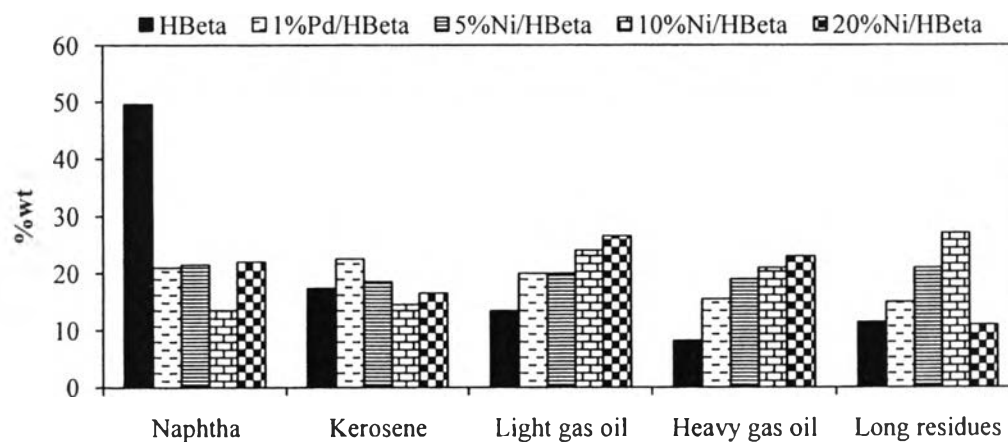


Figure 4.8 Petroleum fractions in maltenes obtained from using various %loading of Ni/HBeta catalysts in comparison with those of 1%Pd/HBeta.

Figure 4.8 shows the petroleum fractions of maltenes obtained from using varied percentages of Ni loading on HBeta zeolite as compared with 1%Pd/HBeta. It can be clearly seen that pure HBeta give the highest concentra-

tion of naphtha and kerosene. The result indicates that pure HBeta produces the lighter oil fraction than that of other catalysts. 1%Pd/HBeta gives the higher concentration of kerosene than that of all Ni/HBeta catalysts. All Ni/HBeta catalysts give the similar concentration of naphtha as that of 1%Pd/HBeta, except 10%Ni/HBeta. The high amount of Ni loaded catalyst produces the higher concentration of light and heavy gas oil. Additionally, the high amount of Ni loading produces the lower concentration of kerosene than that of 1%Pd/HBeta. Moreover, 10%Ni/HBeta produces high poly-aromatics. It can be suggested that 10%Ni/HBeta produces the heaviest oils than the other catalysts. It can be generally concluded that the addition of Ni produces the same amount of naphtha, but the greater in gas oils and long residue in the expense of kerosene reduction.

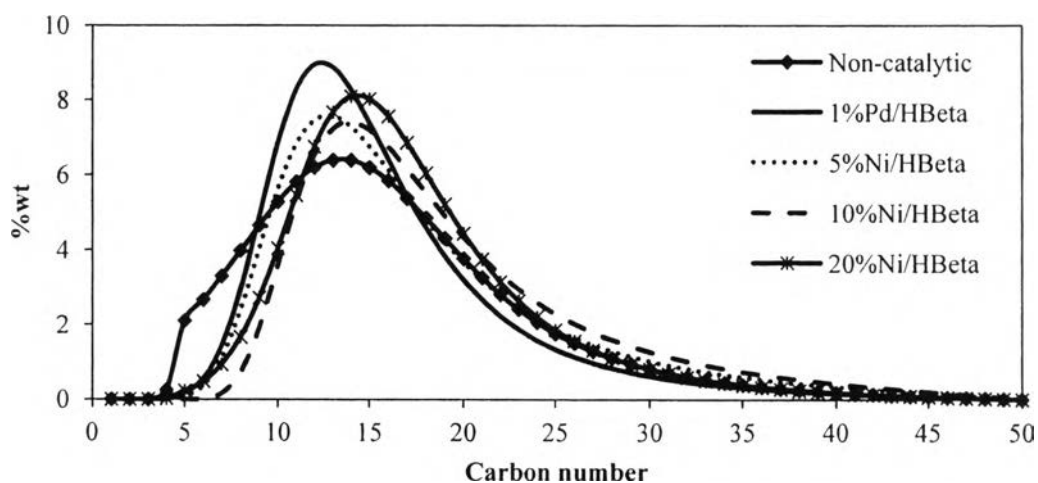


Figure 4.9 Carbon number distribution of maltenes obtained from using various %loading of Ni/HBeta catalysts in comparison with that from 1%Pd/HBeta.

Figure 4.9 exhibits the carbon number distribution of maltenes obtained from using varied loading percentages of Ni/HBeta catalysts as compared to that of 1%Pd/HBeta. It can be observed that the non-catalytic case shows the broad peak, indicating a wide carbon number distribution. The peak becomes narrower with the presence of catalysts. When the percentage of Ni loading increases, the peak seems to shift to higher carbon numbers of maltenes than that of 1%Pd/HBeta. This result relates to the petroleum fraction in maltenes, which shows that the high Ni loading gives the heavy oil fraction.

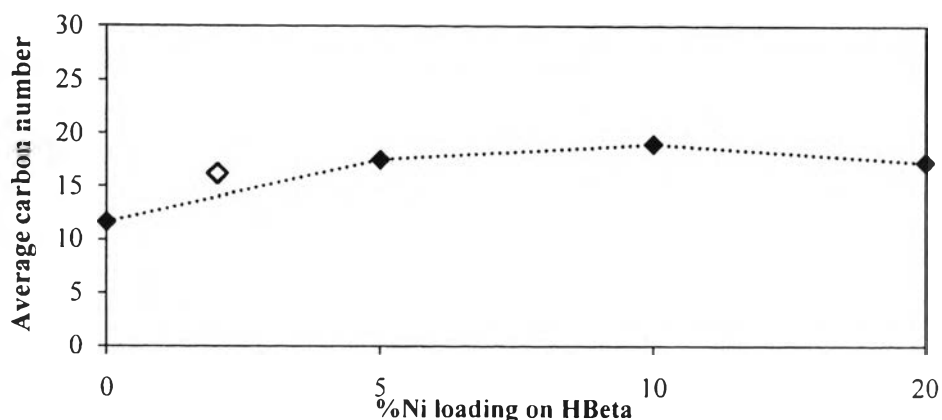


Figure 4.10 Average carbon number of maltenes and mono-aromatics fractions in comparison with (\square) mono-aromatics from 1%Pd/HBeta.

From Figure 4.10, pure HBeta gives the lowest of average carbon number of maltenes additionally, when pure HBeta is compared with 1%Pd/HBeta, the average carbon number of maltenes slightly increases from 11.7 to 15.8. In this figure, it can be observed that the average carbon number of maltenes slightly increases with the increased percentage of Ni loading. Moreover, the average carbon number of 1%Pd/HBeta is the lower than that all Ni catalysts. The results explain that the pure HBeta gives the higher cracking activity than that of 1%Pd/HBeta and all Ni-loaded catalysts. Furthermore, the average carbon number of 1%Pd/HBeta is the smallest among those of the Ni/HBeta catalysts. Nevertheless, 5% Ni/HBeta gives the close average carbon number of maltenes to those of 1%Pd/HBeta. The Sat HCs/Total aromatics ratio can observe the quality of oil products.

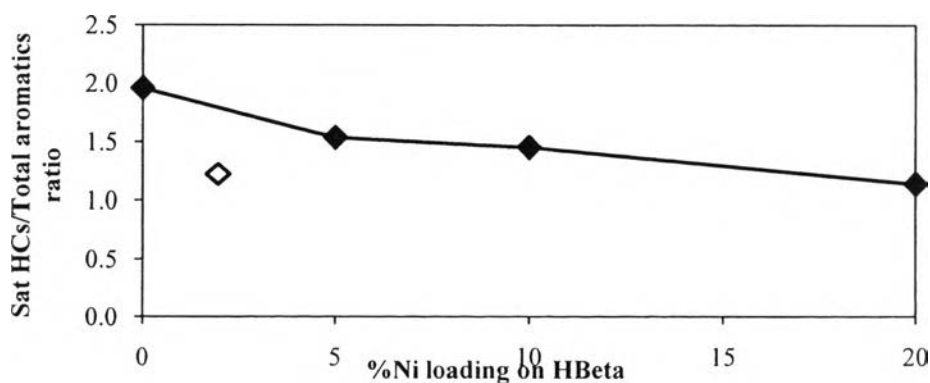


Figure 4.11 Sat HCs/Total aromatics ratio obtained from using Ni/HBeta catalyst in comparison with that from (\diamond)1%Pd/HBeta.

Figure 4.11 shows that the Sat HCs/Total aromatics ratio decreases with increasing the Ni addition. This result is attributed to the reason that the high Ni loading exhibits the high cracking ability on Ni metal sites which can generate carbocations which are intermediates to form aromatic compounds. The 5%Ni/HBeta can be used as a substitute of 1%Pd/HBeta for similar crude oil production since it can produce the similar quantity (same concentration of naphtha) and quality (high Sat HCs/Total aromatics ratio) of oil product to those of 1%Pd/HBeta.

4.1.1.8 Sulfur Formation

The rubber structure of tire contains mostly C-S bonds which are crosslink of rubber chains. The sulfur contents in pyrolytic oil are concerned because of poisoning to an environmental. The sulfur content in pyrolytic oil and sulfur deposition on spent catalysts were determined by a CHNS analyzer.

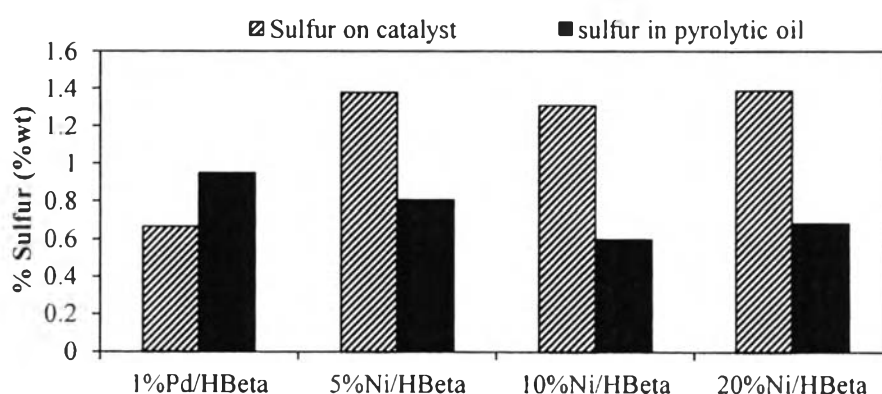


Figure 4.12 Sulfur content on spent catalysts and in pyrolytic oil obtained from Ni/HBeta catalysts in comparison with those from 1%Pd/HBeta.

Figure 4.12 shows that the presence of all Ni/HBeta catalysts, the sulfur content in pyrolytic oil decreases with increasing the sulfur deposits on spent catalysts. The pyrolytic oil obtained from Ni/HBeta catalysts give lower sulfur content than that of 1%Pd/HBeta. It can be suggest that the Ni metal can breakdown the C-S bonds by hydrodesulfurization activity. It can be concluded that the Ni/HBeta catalysts produce a higher quality of pyrolytic oil which contained low sulfur content.

4.1.1.9 Comparison of Catalyst Prices

Since palladium is a noble metal that has a very high price, nickel as an element in the same group (VIII B group) that may be used as a substitute of palladium. Moreover, nickel is a non-noble metal which has a low price. As shown previously, in the case of gaseous products, 10%Ni/HBeta exhibits a good catalyst for light olefins and cooking gases production which produced the yields as high as that of 1%Pd/HBeta. Moreover, 10%Ni/HBeta produces the high valuable mono-aromatics (BTXs) as much as a half of that those obtained from 1%Pd/HBeta. According to these results, 10%Ni/HBeta catalyst may be used as a substitute of 1%Pd/HBeta to produce valuable gas and mono-aromatics products. 5%Ni/HBeta is an eligible catalyst that can be used as a substitute of 1%Pd/HBeta for crude oil production since it provides as similar as quantity and quality of oil products.

Table 4.2 shows the comparison of precursor prices. The precursor of Pd (Palladium (II) nitrate dihydrate) is more expensive than that of the non-noble metal (Nickel nitrate hexahydrate). As shown in Table 4.2, if 5% and 10%Ni/HBeta is used as a substitute of 1%Pd/HBeta, the cost of catalyst is reduced by 18 times and 9 times, respectively.

Table 4.2 Precursor price

Metal	Precursor	Price(Baht)/g	%loaded (wt%)	g of loaded	Price (Baht)
Noble	Palladium(II)nitratedihydrate (Pd(NO ₃) ₂ ·2H ₂ O)	2,600	1	0.253	658
Non-noble	Nickel nitrate hexahydrate (Ni(NO ₃) ₂ ·6H ₂ O)	13.8	5	2.61	36.0
			10	5.5	75.9

4.1.2 Using HMOR as a Support

This section compares the effect of the various %Ni loading with 1%Pd supported on HMOR zeolite on waste tire pyrolysis and investigate whether a non-noble Ni metal can be used as a substitute of a noble metal, Pd, supported on HMOR as a catalyst for waste tire pyrolysis. The products from waste tire pyrolysis which are interested to compare in this section consist of full range naphtha, monoaromatics in maltenes, and petrochemicals gases (olefins, cooking gases and mixed C₄).

4.1.2.1 Liquid to Gas Ratio

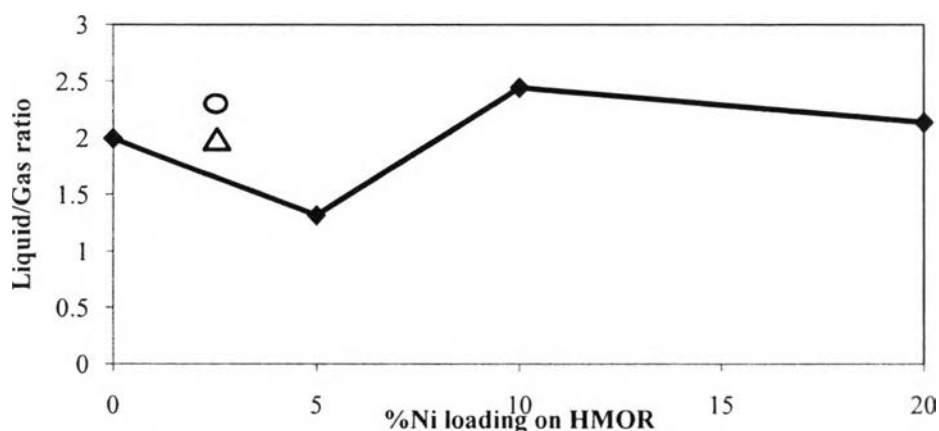


Figure 4.13 L/G ratio from using various % Ni/HMOR in comparison with (○) Non-catalytic and (Δ) 1%Pd/HMOR cases.

The product distribution obtained from waste tire pyrolysis can be illustrated by plotting the liquid to gas ratio as shown in Figure 4.13. It demonstrates the L/G ratio from various % Ni/HMOR in comparison with that of the non-catalytic case (thermal pyrolysis), pure HMOR zeolite (0%Ni), and 1%Pd/HMOR. The results show that 1%Pd/HMOR gives the similar L/G ratio as pure HMOR zeolite (about 2.0) but lower than the non-catalytic case (about 2.5). The L/G ratio increases with the increment of Ni loading from 5 to 10%, and then the L/G ratio slightly decreases from 2.4 to 2.1 at 20%Ni. The L/G ratio from any of catalytic pyrolysis cases is lower than the non-catalytic case. It can be concluded that the metal and acid sites of the catalysts are able to crack the heavy molecules of the liquid fraction into lighter ones in the gaseous fraction. Figure 1 exhibits that 20%Ni/HMOR gives the closet L/G ratio to that of 1%Pd/HMOR. It can be sug-

gested that 20%Ni/HMOR has the similar cracking activity to that of 1%Pd/HMOR, and can produce the yield of liquid fraction approximately close to that of 1%Pd/HMOR.

4.1.2.2 Liquid Composition

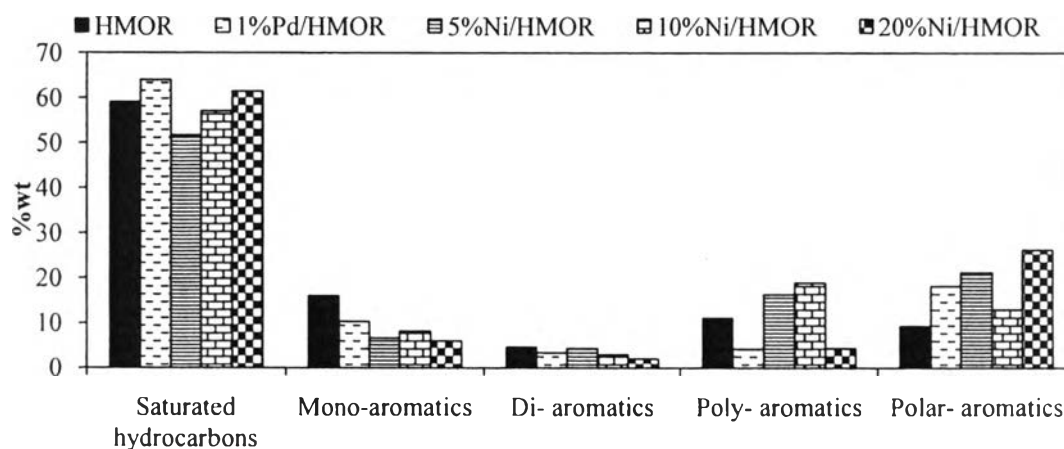


Figure 4.14 Chemical compositions in maltenes from using Ni/HMOR catalysts in comparison with those from 1%Pd/HMOR.

The chemical compositions of maltenes obtained from using varied loading percentages of Ni/HMOR catalysts as compared to those of pure HMOR and 1%Pd/HMOR are shown in Figure 4.14. The results show that 1%Pd/HMOR zeolite produces the highest concentration of saturated hydrocarbons of about 64.0 wt%. The Ni catalysts in general produce less saturated hydrocarbons in maltenes than the 1%Pd catalyst. The percentage of Ni loading increases, the concentration of saturated hydrocarbons increases. As the highest metal loading, 20%Ni gives the concentration of saturated hydrocarbons (about 61.5 wt%) close to that obtained from 1%Pd. It can be explained that in order to obtain the same activity on the hydrogenation of unsaturated hydrocarbons, as high as 20% Ni loading on HMOR is required. The 20%Ni/HMOR not only produces the closest percentage of saturated hydrocarbon to that of 1%Pd/HMOR, but it is also higher than that of pure HMOR zeolite.

In case of mono-aromatics, pure HMOR zeolite gives the highest concentration of mono-aromatics (about 16.0 wt%) due to its favorable dehydrogenation and aromatization activity (Castaño *et al.*, 2006). The 1%Pd/HMOR

produces the higher concentration of mono-aromatics (about 10.3 wt%) than that of all Ni/HMOR catalysts. The concentrations of high-value mono-aromatics, namely benzene, toluene, and xylenes (BTXs) in maltenes are shown in Table 4.3. As a result, the all Ni/HMOR catalysts give a higher yield of C₆-C₈ (BTXs) than 1%Pd/HMOR. Especially, 5%Ni/HMOR gives the highest yield of BTXs in mono-aromatics among all Ni/HMOR catalysts, and it is 7 times higher than that of 1%Pd/HMOR. Furthermore, the poly- and polar-aromatics are enhanced at a high Ni loading due to the high dehydrogenation on Ni metal and further reactions between aromatics and olefins (Williams and Taylor, 1993).

Table 4.3 Yield of benzene, toluene and xylenes in mono-aromatics fraction obtained from using Ni/HMOR catalysts in comparison with those from 1%Pd/HMOR

Carbon number	Yield of BTXs (% by weight) in maltenes			
	1%Pd/HMOR	5%Ni/HMOR	10%Ni/HMOR	20%Ni/HMOR
6	0.04	0.39	0.13	0.30
7	0.07	0.52	0.21	0.43
8	0.13	0.68	0.34	0.61
BTXs	0.23	1.60	0.67	1.35

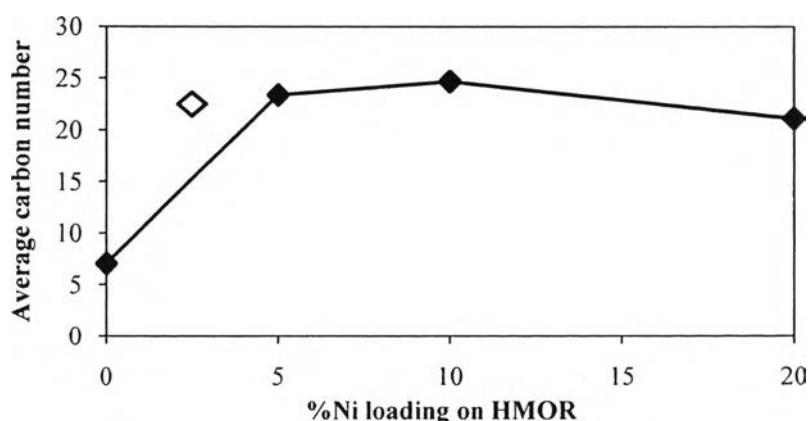


Figure 4.15 Average carbon number of mono-aromatics obtained from using Ni/HMOR catalyst in comparison (◇)1%Pd/HMOR.

Figure 4.15 illustrates the average carbon number of mono-aromatics from using the Ni/HMOR catalysts with varied Ni loading percentages as compared to that of 1%Pd/HMOR. It can be seen that 5%Ni/HMOR and 10%Ni/HMOR give the similar average carbon number of mono-aromatics, namely 23.4 and 24.7, respectively. The average slightly decreases at 20%Ni loading. It can be concluded that the high Ni loading exhibits high hydrogenation and ring-opening activity on Ni metal sites. Additionally, 5%Ni/HMOR exhibits the closest average carbon number of mono-aromatics to that of 1%Pd/HMOR. According to all of the results, it can be suggested that 5%Ni/HMOR seems to be a comparable catalyst to 1%Pd/HMOR to produce light mono-aromatics (BTXs) because it produced the highest yield of light mono-aromatics (BTXs) and the closest average carbon number of mono-aromatics to those given by 1%Pd/HMOR.

4.1.2.3 Petroleum Fractions

The petroleum fractions in maltenes obtained from using varied Ni/HMOR catalysts in compared with that from 1%Pd/HMOR and pure HMOR zeolite is shown in Figure 4.16.

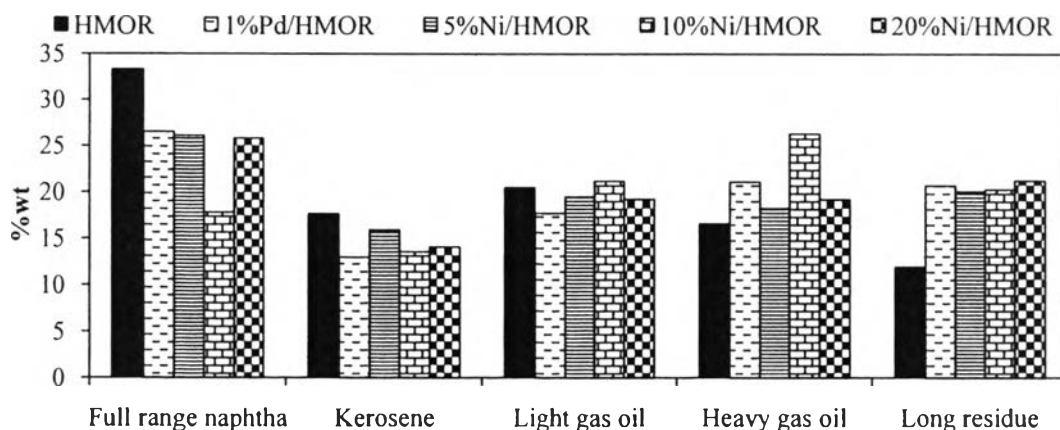


Figure 4.16 Petroleum fractions in maltenes obtained from using Ni/HMOR catalysts in comparison with those from 1%Pd/HMOR.

Therefore, 1%Pd/HMOR has been investigated as a good catalyst for producing full range naphtha and kerosene in waste tire pyrolysis. In Figure 4.16, the pure HMOR zeolite exhibits the highest concentration of full range naphtha and kerosene. Most Ni/HMOR catalysts, except 10%Ni/HMOR give the similar

quantity of full range naphtha as that of 1%Pd/HMOR. In case of kerosene, the presence of Ni on HMOR, especially 5%Ni/HMOR, appears to give a slightly higher concentration of kerosene (15.9 wt%) than that of 1%Pd/HMOR (13.0 wt%). It can be concluded that 5%Ni/HMOR seems to be a suitable catalyst for substituting 1%Pd/HMOR for kerosene production. Figure 4.16, 5% and 20%Ni supported on HMOR catalysts are eligible catalysts that can be used as a substitute of 1%Pd/HMOR for petroleum crude oil production.

The true boiling point curve is one of oil characteristics which can be used for selecting a proper catalyst for substituting 1%Pd/HMOR. The true boiling point curves were obtained from using SIMDIST-GC. The true boiling point curve of maltenes obtained from using varied Ni/HMOR catalysts in comparison with that from 1%Pd/HMOR is shown in Figure 4.17. This figure shows that the 20%Ni/HMOR gives the closest true boiling point curve to that of 1%Pd/HMOR. It can be concluded that 20%Ni/HMOR is an eligible to be used as substituted of 1%Pd/HMOR for petroleum crude oil production.

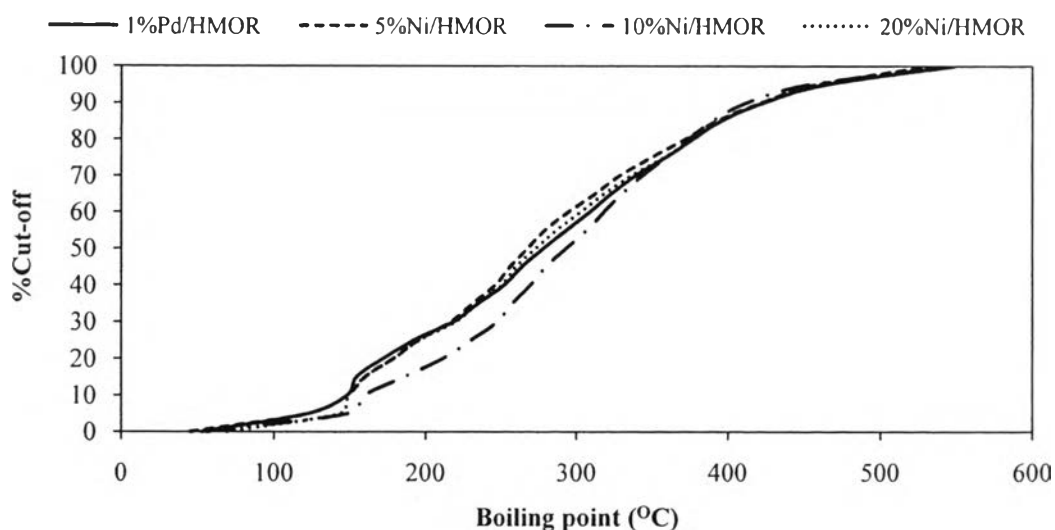


Figure 4.17 True boiling point curves of maltenes obtained from using Ni/HMOR catalysts in comparison with that from 1%Pd/HMOR.

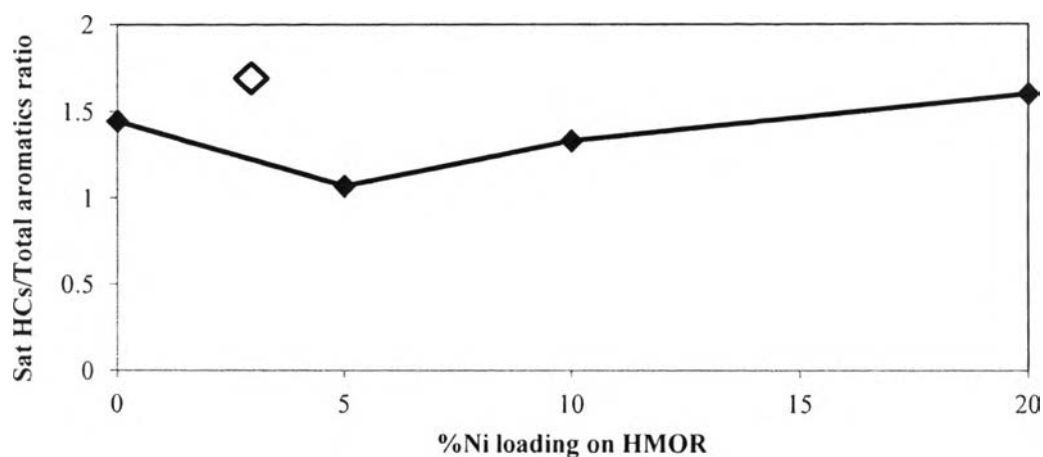


Figure 4.18 Sat HCs/Total aromatics ratio obtained from using Ni/HMOR catalysts in comparison with that from (\diamond) 1%Pd/HMOR.

Figure 4.18 demonstrates the ratio of saturated hydrocarbons to total aromatics obtained from using varied Ni/HMOR catalysts in comparison with that of 1%Pd/HMOR. The result exhibits that the Sat HCs/Total aromatics ratio increases with the increasing Ni addition because of the increasing hydrogenation and ring opening on metal sites. The high percentage of Ni/HMOR (20%Ni) illustrates the highest Sat HCs/Total aromatics ratio than other Ni/HMOR catalysts and pure HMOR zeolite. Furthermore, it gives the closest Sat HCs/Total aromatics ratio to that of 1%Pd/HMOR. It can be suggested that the 20%Ni/HMOR is an eligible catalyst to be used as a substitute of 1%Pd/HMOR in waste tire pyrolysis for oil production since it can produce the similar quality (Sat HCs/Total aromatics ratio) of oil product and quantity of petroleum cuts to those of 1%Pd/HMOR.

According to the results, it can be suggested that the 20%Ni/HMOR is a proper catalyst to be used as a substitute of 1%Pd/HMOR for petroleum crude oil production in waste tire pyrolysis. 20%Ni/HMOR can produce the similar of the quality and quantity of oil product to those of 1%Pd/HMOR. Namely, 20%Ni/HMOR produces the similar concentration of full range naphtha, kerosene, and light gas oil to those of 1%Pd/HMOR, and 20%Ni/HMOR gives the closest true boiling point curve of maltenes to that of 1%Pd/HMOR. Moreover, the oil product

which obtained from 20%Ni/HMOR has as high sat HCs/total aromatics ratio as that of 1%Pd/HMOR.

4.1.2.4 Gas Fractions

The high valuable gaseous products, which can be used as a feed stock in petrochemical plant, consist of olefins (ethylene and propylene), cooking gases (propane and mixed C₄) and mixed C₄. The yields of olefins, cooking gases and mixed C₄ obtained from using varied Ni percentages supported on HMOR zeolite in comparison with those from 1%Pd/HMOR, pure HMOR and non-catalytic cases are shown in Figure 4.19 (a)-(c), respectively.

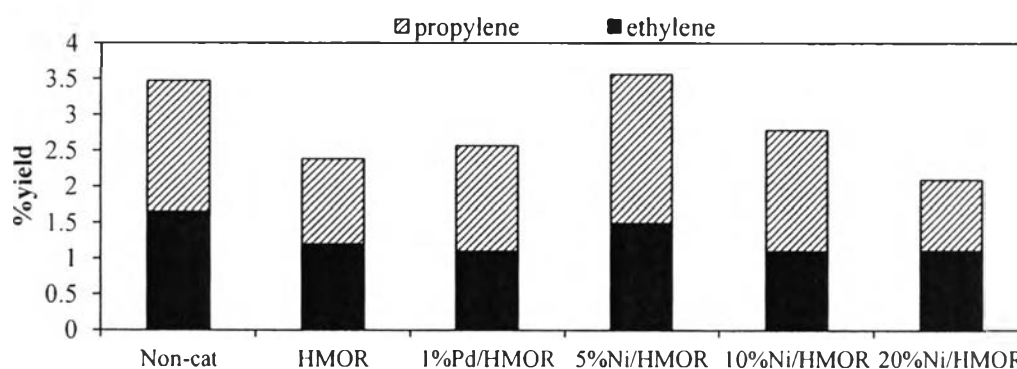


Figure 4.19(a) Yield of ethylene and propylene obtained from using Ni/HMOR in comparison with those from 1%Pd/HMOR, pure HMOR and non-catalytic cases.

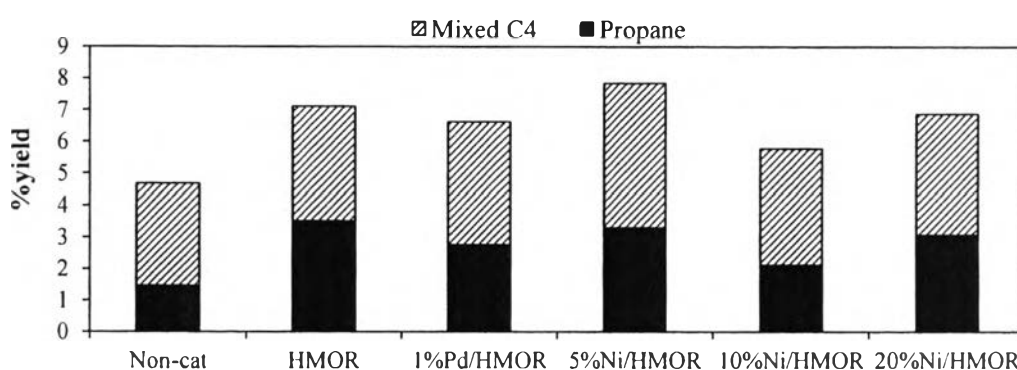


Figure 4.19(b) Yield of propane and mixed C₄ obtained from using Ni/HMOR in comparison with: those from 1%Pd/HMOR, pure HMOR and non-catalytic cases.

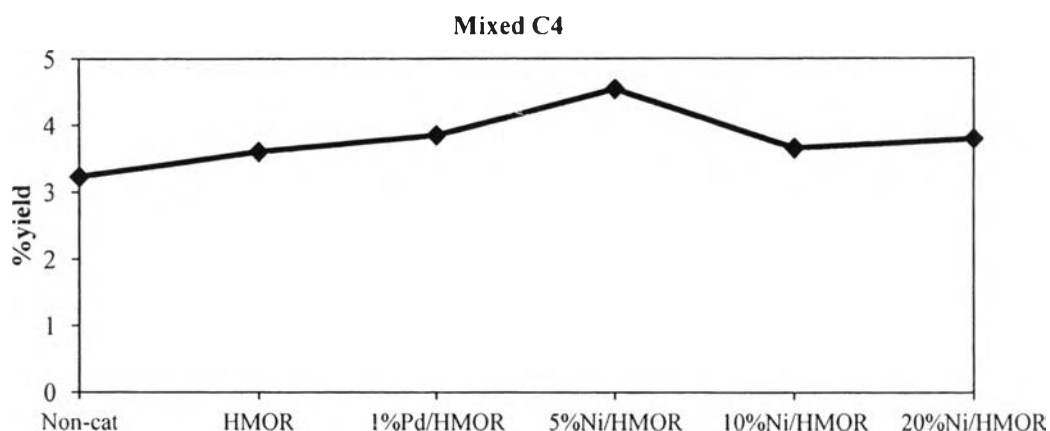


Figure 4.19(c) Yield of mixed C₄ obtained from using Ni/HMOR in comparison with: that from 1%Pd/HMOR, pure HMOR and non-catalytic cases.

Figure 4.19(a)-(c), Its clearly exhibit that 5%Ni/HMOR gives the highest yields of olefins, cooking gases, and mixed C₄ to those of all Ni/HMOR catalysts. Moreover, 5%Ni/HMOR produces the higher yields of olefins, cooking gases, and mixed C₄ than those of 1%Pd/HMOR, pure HMOR zeolite and non-catalytic (thermal pyrolysis). An increasing of amount of Ni loading decreases the yields of olefins, cooking gases, and mixed C₄. These results can be explained that increasing Ni loading enhances dehydrogenation and aromatization via Diels-Alders reaction of olefins products, which consequently decreases the olefins products and increases the aromatics compounds. It can be clearly suggested that 5%Ni/HMOR is a proper catalyst for substituting 1%Pd/HMOR for valuable gaseous production in waste tire pyrolysis.

4.1.2.5 Sulfur Formation

Figure 4.20 shows the sulfur content in derived oil and sulfur deposition on spent catalysts determined by a CHNS analyzer. It can be suggested that the presence of Ni metal can enhance the reduction of sulfur in the pyrolytic oil. Ni metal can crack the C-S bonds, consequently leaving the sulfur atoms on Ni metal. It can be concluded that Ni metal has a high hydrodesulfurization activity of sulfur. Moreover, the pyrolytic oil obtained from Ni/HMOR catalyst has good quality in terms of low sulfur content.

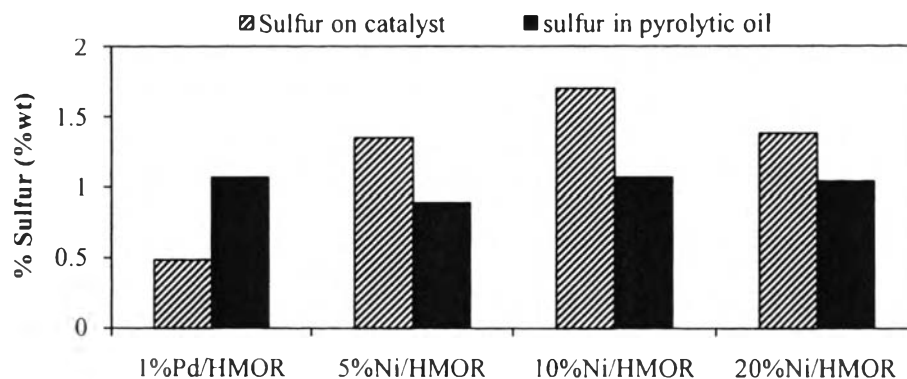


Figure 4.20 Sulfur content on spent catalysts and in pyrolytic oil obtained from Ni/HMOR catalysts in comparison with those from 1%Pd/HMOR.

4.1.2.6 Comparison of Catalyst Prices

In order to reduce the cost of catalyst, the Ni/HMOR catalysts are interested for substituting of 1%Pd/HMOR which a costly noble metal. As mentioned above, 5%Ni/HMOR seem to be a suitable catalyst for substituting of 1%Pd/HMOR for mono-aromatics and high valuable petrochemical gaseous productions. For petroleum oil production, 20%Ni/HMOR produces the similar quality and quantity of petroleum oil product to that of 1%Pd/HMOR.

Table 4.4 shows the comparison of precursor prices. The precursor of Pd (Palladium (II) nitrate dihydrate) is more expensive than that of the non-noble metal (Nickel nitrate hexahydrate). As shown in Table 4.4, if 5% and 20%Ni/HMOR are used as a substitute of 1%Pd/HMOR, the cost of catalyst is reduced by 18 times and 4 times, respectively.

Table 4.4 Precursor price

Metal	Precursor	Price(Baht)/g	%loaded (wt%)	g of loaded	Price (Baht)
Noble	Palladium(II)nitratdihydrate (Pd(NO ₃) ₂ ·2H ₂ O)	2,600	1	0.253	658
Non-noble	Nickel nitrate hexahydrate (Ni(NO ₃) ₂ ·6H ₂ O)	13.8	5	2.61	36.0
			20	12.4	171

4.2 Comparison of Fe with Ru

4.2.1 Using HBeta as a Support

This section compares the influence of the various %Fe loading with 1%Ru supported on HBeta zeolite on waste tire pyrolysis. The valuable products obtained from waste tire pyrolysis such as olefins, cooking gases, mixed C₄, light mono-aromatics (BTXs), and petroleum crude oil are analyzed and compared. The product distributions obtained from waste tire pyrolysis can be illustrated by plotting the gas to liquid ratio as shown in Figure 4.21.

4.2.1.1 Gas to Liquid Ratio

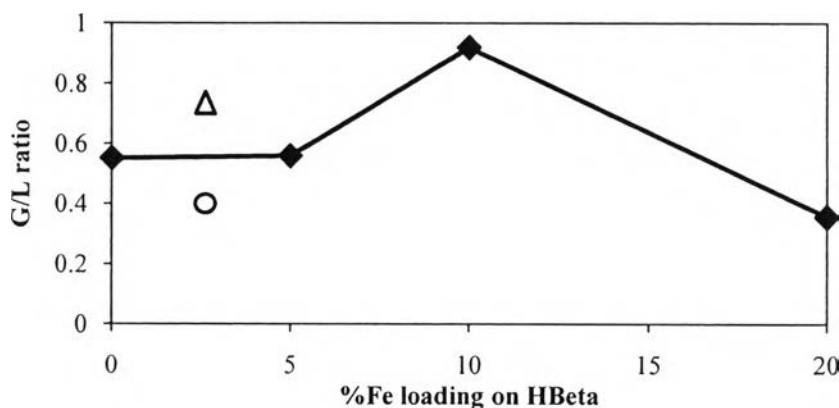


Figure 4.21 G/L ratio obtained from using various % Fe/HBeta in comparison with (○) Non-catalytic and (Δ) 1%Ru/HBeta cases.

The G/L ratio refers to the cracking ability of a catalyst; that is, the large molecules in the liquid fraction can be cracked to lighter molecules that are evolved in the gaseous fraction. Figure 4.21 displays the G/L ratio obtained from using various percentages of Fe loading on HBeta as compared with that of 1%Ru/HBeta, pure HBeta and the non-catalytic case (thermal pyrolysis). The thermal pyrolysis or non-catalytic case exhibits the low G/L ratio (about 0.4) due to the lowest cracking activity among the other cases. The 5%Fe/HBeta gives the similar G/L ratio about 0.55 to that of pure HBeta zeolite (0%Fe). The G/L ratio increases from 0.56 to 0.92 with increasing percentage Fe loading from 5% to 10%, respectively, and dramatically decreases to 0.36 at 20%Fe. From the results, it can be con-

cluded that 10%Fe/HBeta has the highest cracking activity because it gives the highest G/L ratio among all Fe/HBeta catalysts. Moreover, it gives a higher G/L ratio (about 0.73) than that of 1%Ru/HBeta.

4.2.1.2 Gas Fraction

The valuable gases compared in this work consist of light olefins (ethylene and propylene), cooking gases (propane and mixed C₄), and mixed C₄. The valuable gas products obtained from various Fe/HBeta catalysts, the non-catalytic case (thermal pyrolysis), pure HBeta, and 1%Ru/HBeta as the reference are shown in Figures 4.22(a)-(c).

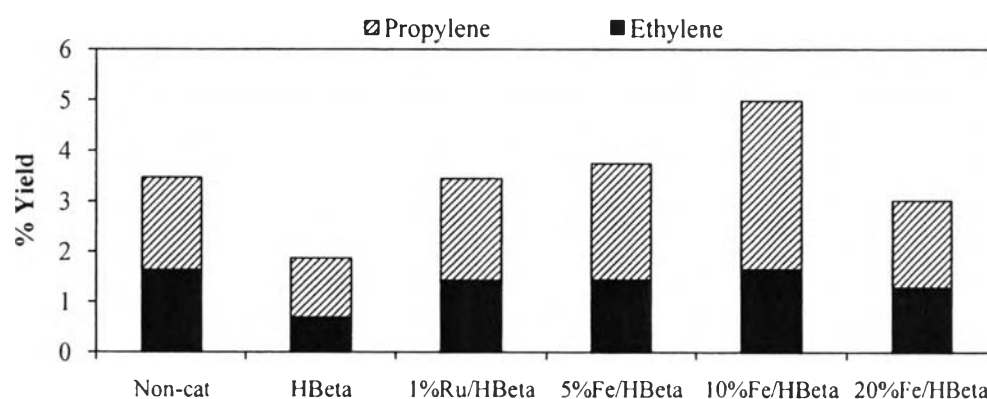


Figure 4.22(a) Yield of ethylene and propylene obtained from using Fe/HBeta in comparison with those from 1%Ru/HBeta, pure HBeta and non-catalytic cases.

The results in Figure 4.22(a) show that the reference 1%Ru/HBeta case gives the yield of light olefins as similar as that of non-catalytic case (thermal pyrolysis), and it gives a higher than that of pure HBeta zeolite. All Fe/HBeta catalysts, except 20%Fe/HBeta, give the higher yield of light olefins than that of 1%Ru/HBeta. The yield of light olefins increases with the increasing Fe loading percentage from 5% to 10%, and slightly decreases at 20%.

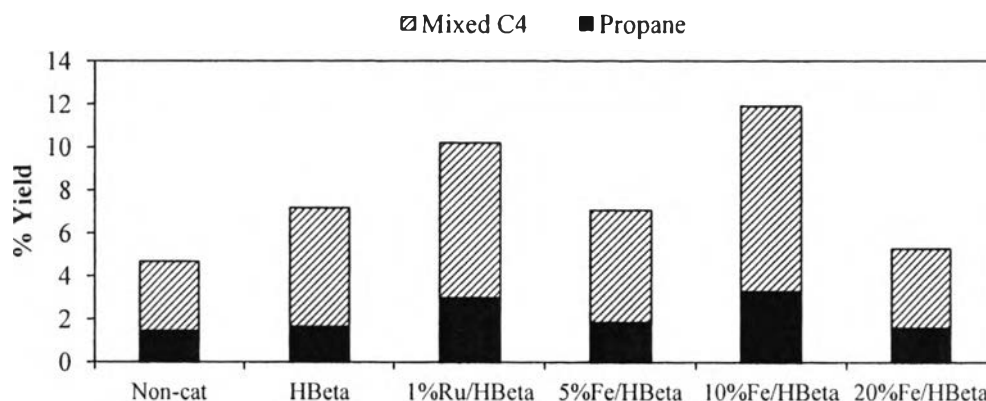


Figure 4.22(b) Yield of propane and mixed C₄ obtained from using Fe/HBeta in comparison with those from 1%Ru/HBeta, pure HBeta and non-catalytic cases.

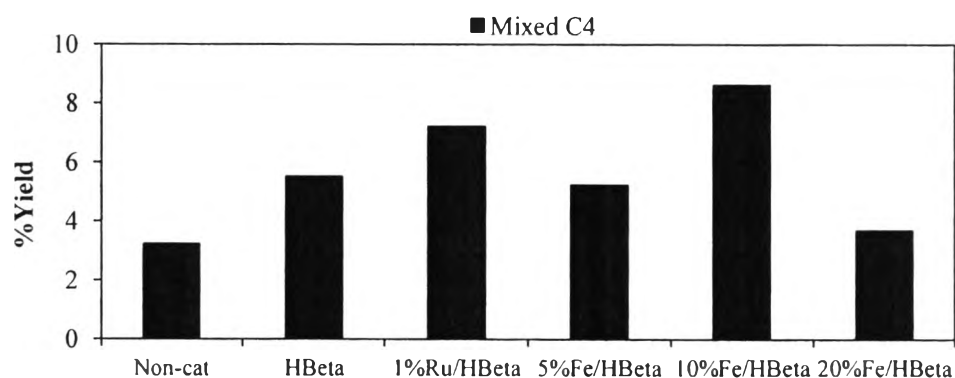


Figure 4.22(c) Yield of mixed C₄ obtained from using Fe/HBeta in comparison with that from 1%Ru/HBeta, pure HBeta and non-catalytic cases.

Figures 4.22(b)-(c) show the yields of cooking gases and mixed C₄ from various % Fe/HBeta in comparison with those of the non-catalytic case (thermal pyrolysis), pure HBeta zeolite (0%Fe), and 1%Ru/HBeta. The results exhibit that 1%Ru/HBeta gives the higher yields of cooking gases and mixed C₄ than those of non-catalytic and pure HBeta cases. When the percentage of Fe loading increases, the yields of cooking gases and mixed C₄ increase in the same trend. Additionally, 10%Fe/HBeta gives not only the highest yields of cooking gases and mixed C₄ among all Fe/HBeta catalysts, but they are also higher than those of 1%Ru/HBeta catalysts. From these results, it can be concluded that the 10%Fe/HBeta catalyst clearly seems to be an eligible catalyst as a substitute of 1%Ru/HBeta for valuable

gases production because it produces the highest yields of light olefins, cooking gases, and mixed C₄ among all Fe/HBeta catalysts, and they are higher than those of 1%Ru/HBeta.

4.2.1.3 Liquid Compositions

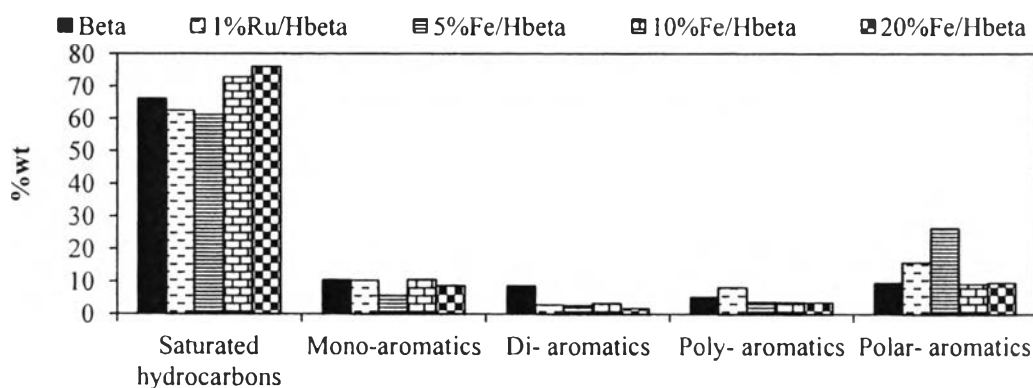


Figure 4.23 Chemical compositions in maltenes from using Fe/HBeta catalysts in comparison with those from 1%Ru/HBeta.

The chemical compositions in maltenes obtained from using varied loading percentage of Fe/HBeta catalyst as compared to those of pure HBeta and 1%Ru/HBeta are shown in Figure 4.23. The results show that the increment of percentage of Fe loading causes to sequentially increase the quantity of saturated hydrocarbons. Additionally, 10% and 20%Fe/HBeta give a higher concentration of saturated hydrocarbons than that of pure HBeta and 1%Ru/HBeta. In case of mono-aromatics, 10%Fe/HBeta gives the similar concentration as that of pure HBeta and 1%Ru/HBeta. The di- and poly-aromatics of all Fe/HBeta cases are insignificantly different from those of 1%Ru/HBeta. In case of polar-aromatics, the high percentages of Fe loading (10-20%) show lower polar-aromatics concentrations than 1%Ru/HBeta. It can be suggested that the high amounts of Fe metal sites play important roles on increasing the hydrogenation and hydrodesulfurization of product molecules. From the quantity of mono-aromatics, 10%Fe/HBeta seems to be the most proper catalyst, which can be used as a substitute of 1%Ru/HBeta since it can produce the similar concentration of mono-aromatics as that of 1%Ru/HBeta. Moreover, 10%Fe/HBeta gives the highest concentration of BTXs, which are the valuable

petrochemical products as shown in Table 4.5. 10%Fe/HBeta produces three times higher yield of BTXs than 1%Ru/HBeta.

Table 4.5 Yields of benzene, toluene and xylenes in mono-aromatics obtained from using Fe/HBeta catalysts in comparison with those from 1%Ru/HBeta

Carbon number	Yield of BTXs (%wt) in maltenes			
	1%Ru/HBeta	5%Fe/HBeta	10%Fe/HBeta	20%Fe/HBeta
6	0.793	0.091	4.02	2.87
7	1.30	0.121	4.25	2.90
8	2.06	0.158	4.38	2.91
BTXs	4.15	0.370	12.7	8.67

The average carbon number is one of effective criteria used to compare the quality of mono-aromatics. The average carbon numbers of mono-aromatics from using various Fe/HBeta catalysts compared with that from 1%Ru/HBeta are shown in Figure 4.24.

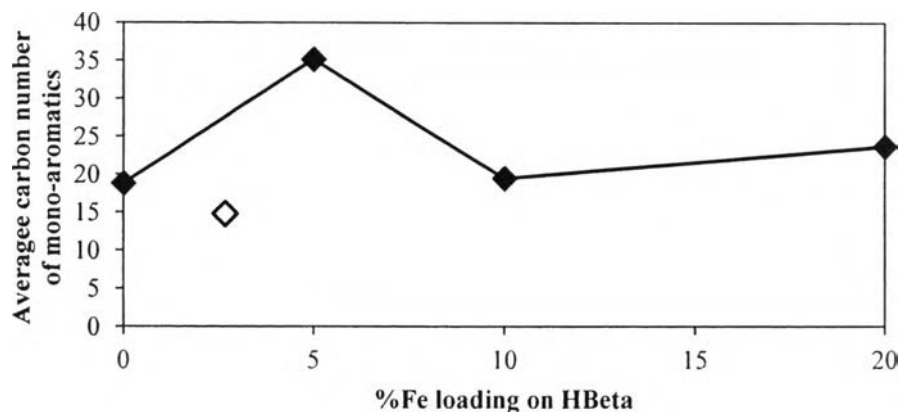


Figure 4.24 Average carbon number of mono-aromatics obtained from using Fe/HBeta catalysts in comparison with (◇) 1%Ru/HBeta.

It can be seen that the average carbon number of mono-aromatics is slightly decreased from C35 to C19 with increasing the percentage of Fe loading from 5% to 10%, respectively, and insignificantly increases at 20%Fe. The 1%Ru/HBeta gives the lowest average carbon number of mono-aromatics of about C15. Additionally, 10%Fe/HBeta gives the closest average carbon number of mono-aromatics to that of 1%Ru/HBeta. From the results, it can be concluded that the

10%Fe/HBeta catalyst is the most capable catalyst that can be used as a substitute of 1%Ru/HBeta for mono-aromatics production since it can produce the similar quality and quantity as those of 1%Ru/HBeta catalyst.

4.2.1.4 Petroleum Fractions

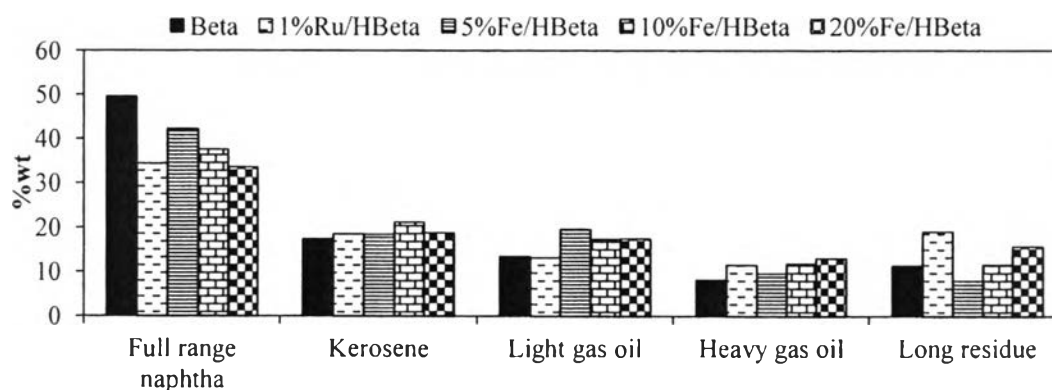


Figure 4.25 Petroleum fractions in maltenes obtained from using Fe/HBeta catalysts in comparison with those of 1%Ru/HBeta.

The influences of Fe/HBeta catalysts on the petroleum fractions as compared to those of 1%Ru/HBeta are shown in Figure 4.25. The results show that as the percentage of Fe loading increases, the concentration of full range naphtha slightly decreases, whereas the concentration of heavy gas oil and long residue sequentially increases. It can be suggested that the increasing Fe loading enhances the heavily oil formation. Iron catalysts are well known as Fischer-Tropsch synthesis (FTS) catalysts. Pour *et al.* (2008) studied the product distribution of iron and iron-zeolite catalysts in FTS. They concluded that the iron-zeolite (bifunctional) catalyst enhanced the secondary reactions, including oligomerization of light olefins, aromatization, and hydrogen transfer. It can be concluded that the heavy fraction in maltenes are produced by secondary reactions such as oligomerization and aromatization of light molecules. Additionally, the presence of Fe on HBeta catalyst gives a higher light gas oil fraction than 1%Ru/HBeta. Another result to be compared in terms of the quantity of petroleum fraction is the true boiling point curve of maltenes as shown in Figure 4.26

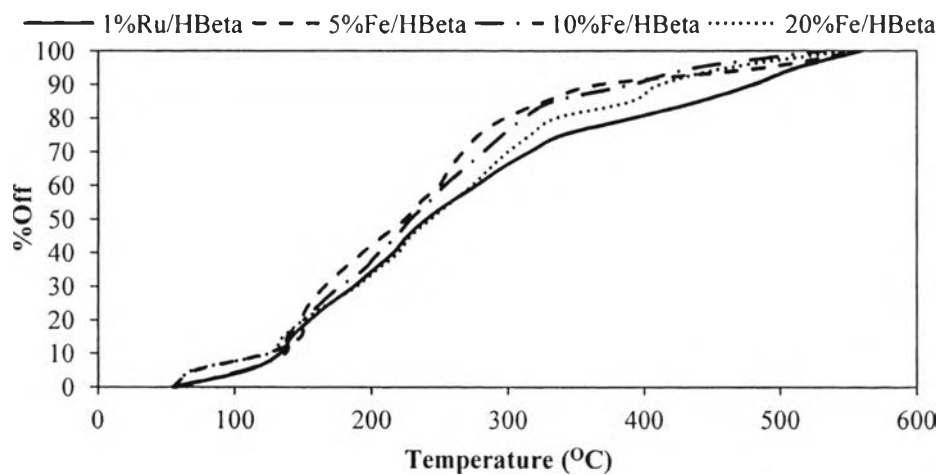


Figure 4.26 True boiling point curves of maltenes obtained from using Fe/HBeta catalysts in comparison with that from 1%Ru/HBeta.

Figure 4.26 illustrates the true boiling point curve of maltenes from using Fe/HBeta catalysts as compared that of 1%Ru/HBeta. This figure exhibits that 20%Fe/HBeta shows the closest true boiling point curve of maltenes to that of 1%Ru/HBeta. It can be summarized that 20%Fe/HBeta produced the similar quantity of petroleum fractions as that of 1%Ru/HBeta. The quality of petroleum fractions are considered by using the average carbon number of maltenes and Sat HCs/Total aromatics ratio as shown in Figures 4.27 and 4.28, respectively.

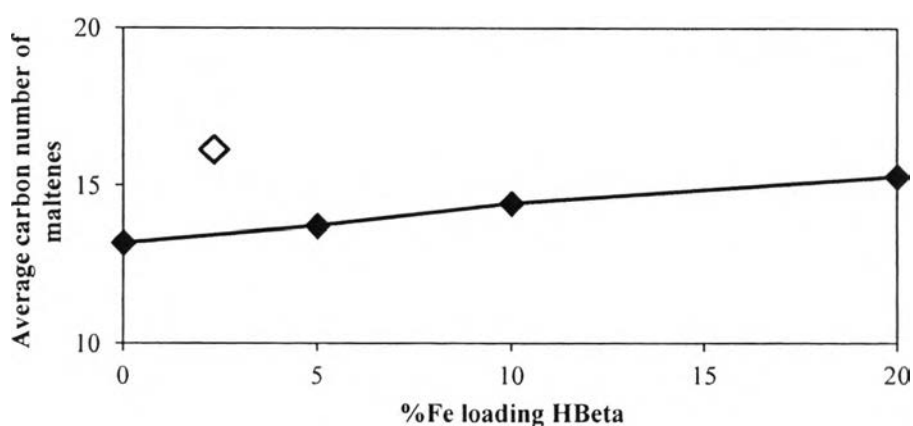


Figure 4.27 Average carbon number of maltenes obtained from using Fe/HBeta catalyst in comparison with that from (◇) 1%Ru/HBeta.

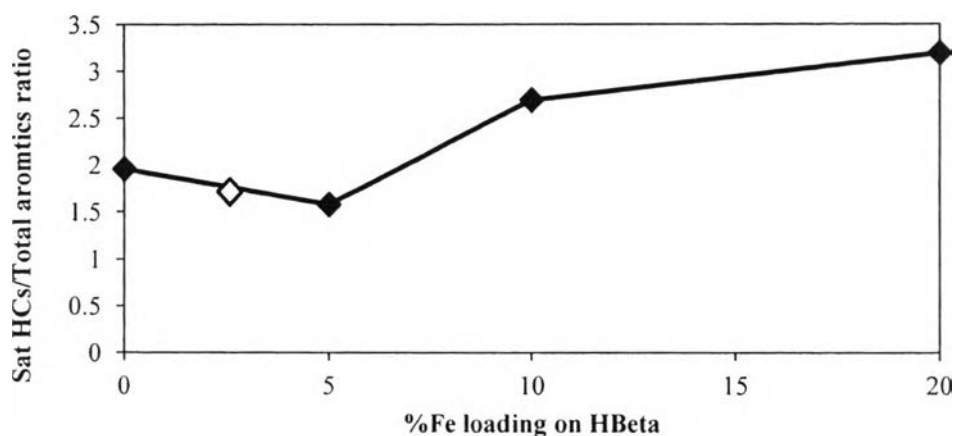


Figure 4.28 Sat HCs/Total aromatics ratio obtained from using Fe/HBeta catalysts in comparison with that from (\diamond) 1%Ru/HBeta.

Figure 4.27 shows that the average carbon number of maltenes increases from 13.7 to 15.3 with the increasing percentage of Fe loading on HBeta from 5-20 %. However, all Fe/HBeta catalysts give a lower average carbon number of maltenes than that of 1%Ru/HBeta (about 15.4). Figure 4.28 shows the Sat HCs/Total aromatics ratio increases with increasing percentage loading of Fe on HBeta. The high amounts of Fe loading on HBeta (10-20 %) give a higher Sat HCs/Total aromatics ratio than that of 1%Ru/HBeta. Additionally, 20%Fe/HBeta gives the highest quality of petroleum production in terms of the highest Sat HCs/Total aromatics ratio. From these results, it can be concluded that 20%Fe/HBeta seems to be a potential catalysts that can be used as substitute of 1%Ru/HBeta for petroleum crude oil production since it can produce the similar quality (high Sat HCs/Total aromatics ratio) of oil product and the similar quantity of petroleum cuts as those of 1%Pd/HMOR.

4.2.1.5 Sulfur Formation

The sulfur content in derived oils and sulfur deposition on spent catalysts were determined by a CHNS analyzer as shown in Figure 4.29. The result shows that for the Fe/HBeta catalysts, the sulfur prefers to deposit on spent catalysts rather than to remain in the pyrolytic oils. Additionally, the sulfur deposition on the spent catalysts increases with the increasing amount of Fe metal.

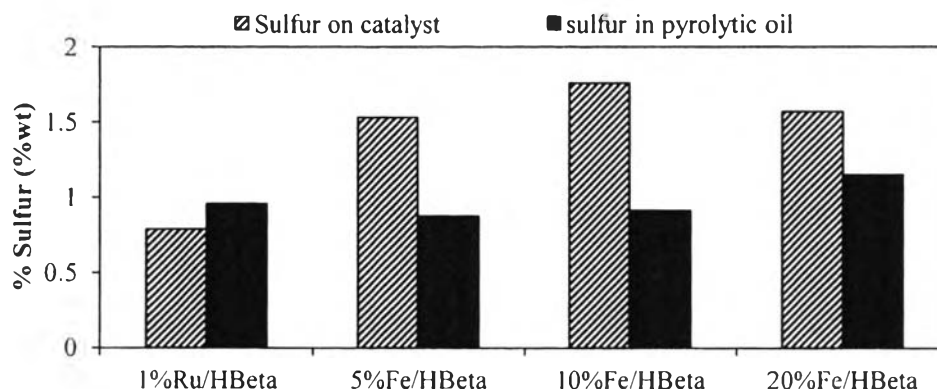


Figure 4.29 Sulfur content on spent catalysts and in pyrolytic oils obtained from Fe/HBeta catalysts in comparison with those from 1%Ru/HBeta.

4.2.1.6 Comparison of Catalyst Prices

As observed above, the non-noble metal Fe/HBeta catalysts have as high activity as the noble metal catalyst (1%Ru/HBeta), which is costly. The precursor of Ru (Ruthenium(III) chloride hydrate) is more expensive than that of the non-noble metal (Iron (III) chloride hexahydrate) as shown in Table 4.6. For examples, if 10%Fe/HBeta is used as a substitute of 1%Ru/HBeta for valuable gaseous and light mono-aromatics (BTXs) production, the cost of catalyst is reduced by 20 times. For the petroleum crude oil production, 20%Fe/HBeta is used as a substitute of 1%Ru/HBeta, the cost of catalyst is reduced by 9 times.

Table 4.6 Precursor prices

Metal	Precursor	Price(Baht)/g	%loaded (wt%)	g of loaded	Price (Baht)
Noble	ruthenium(III) chloride hydrate (RuCl ₃ .aq)	3,700	1	0.207	767
Non-noble	iron (III) chloride hexahydrate (FeCl ₃ ·6H ₂ O)	7.08	10	5.37	38.0
			20	12.1	85.7

4.2.2 Using HMOR as a Support

This section compares the influence of the various %Fe loading with 1%Ru supported on HMOR zeolite on waste tire pyrolysis. The qualitative and quantitative of valuable petrochemical products such as olefins, cooking gases, mixed C₄, light mono-aromatics (BTXs) and petroleum fractions in maltenes are compared and discussed.

4.2.2.1 Gas/Liquid Ratio

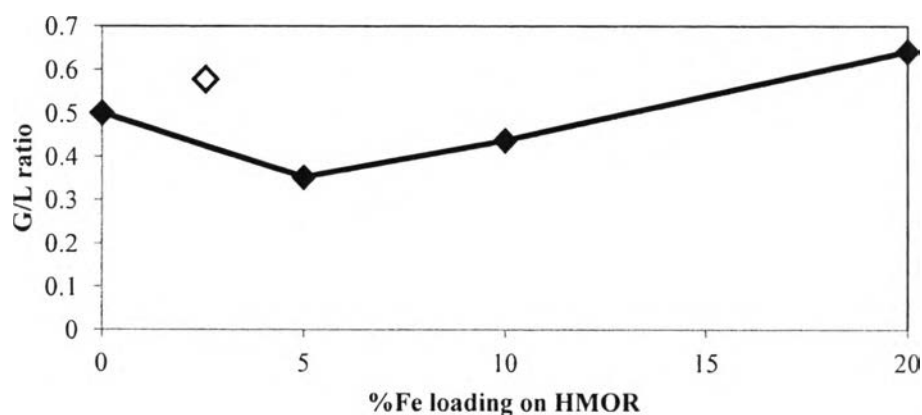


Figure 4.30 G/L ratio obtained from using various % Fe/HMOR in comparison with pure HMOR and (◊) 1%Ru/HMOR cases.

The gaseous products of waste tire pyrolysis were produced by the main reaction, which is cracking reaction, so the cracking activity of catalyst can be explained by G/L ratio as shown in Figure 4.30. The result shows that the G/L ratio gradually increases with the increasing percentage of Fe loading on HMOR. The highest percentage of Fe loading (20%Fe) gives the highest G/L ratio in among of Fe/HMOR. Moreover, 20%Fe/HMOR provides the G/L ratio about 0.64, which is higher than that of pure HMOR (0.5) and 1%Ru/HMOR (0.59). From this result, it can be concluded that the highest percentage of Fe loading on HMOR (20%Fe) has the highest cracking activity among all catalysts.

4.2.2.2 Gas Compositions

The pyrolysis of waste tire produces the gaseous product, namely C_1-C_{5+} , which are analyzed by GC-FID. However, the valuable petrochemical products compared and discussed in this section consist of light olefins, cooking gases, and mixed C_4 as shown in Figure 4.31.

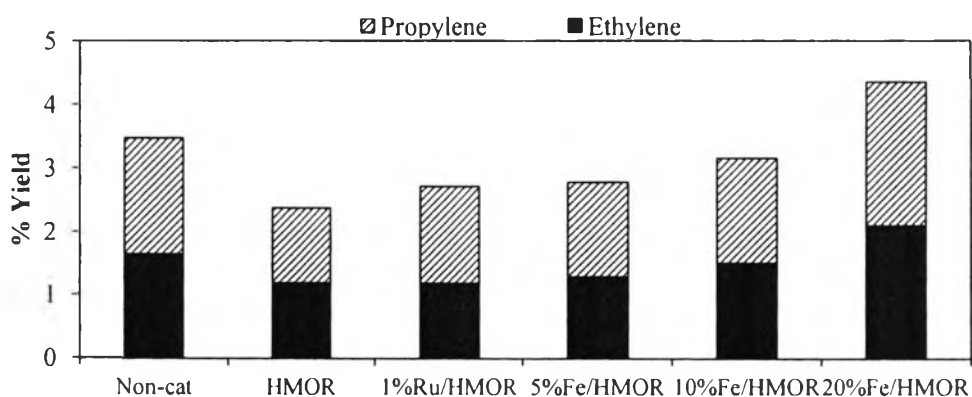


Figure 4.31(a) Yield of light olefins obtained from using Fe/HMOR in comparison with those from 1%Ru/HMOR, pure HMOR and non-catalytic cases.

Furthermore, the light olefins have high value and widely used in petrochemical industries, and they are products from the cracking reaction of waste tire. The result shows that the non-catalytic pyrolysis gives the higher yields of light olefins (ethylene and propylene) than those of HMOR and 1%Ru/HMOR. Dũng *et al.* (2009) stated that the thermal cracking of waste tire pyrolysis (without a catalyst) generated free radicals, which further produce the olefins. Moreover, the catalyst and bifunctional catalysts can enhance the secondary reactions such as oligomerization and aromatization, leading to the reduction of light olefins. Whereas the percentage of Fe loading on HMOR increases, the yields of light olefins increase. 20%Fe/HMOR gives the highest yields of light olefins (ethylene and propylene) due to the high cracking activity.

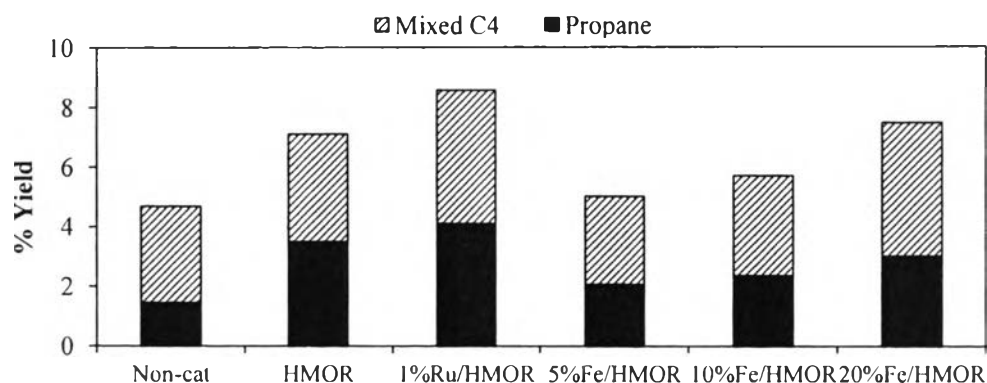


Figure 4.31(b) Yield of cooking gases obtained from using Fe/HMOR catalysts in comparison with those from 1%Ru/HMOR, pure HMOR and the non-catalytic case.

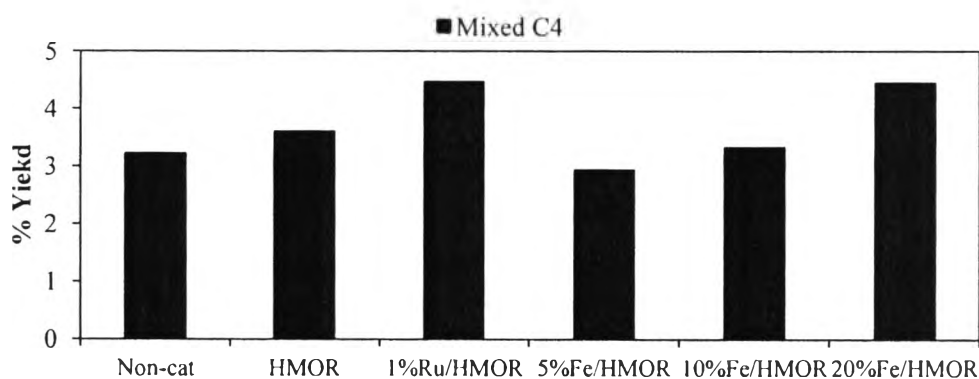


Figure 4.31(c) Yield of mixed C₄ obtained from using Fe/HMOR catalysts in comparison with those from 1%Ru/HMOR, pure HMOR and the non-catalytic case.

Figures 4.31(b)-(c) exhibit the yields of cooking gases and mixed C₄ from using various Fe loading on HMOR in comparison with those of the 1%Ru/HMOR, pure HMOR, and non-catalytic cases. The results show that the 1%Ru/HMOR gives a higher yield of cooking gases and mixed C₄ than those of non-catalytic case and pure HMOR zeolite. From the results, 20%Fe/HMOR gives the closest yields of valuable gaseous products, which are light olefins, cooking gases, and mixed C₄ to those of 1%Ru/HMOR. It can be definitely concluded that 20%Fe/HMOR can be used as a substitute of 1%Ru/HMOR for the valuable gaseous production.

4.2.2.3 Chemical Compositions

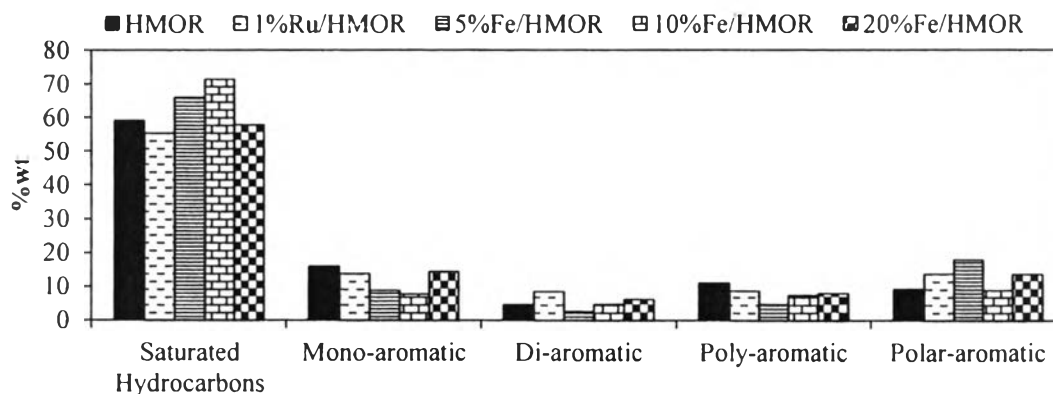


Figure 4.32 Chemical compositions in maltenes from using Fe/HMOR catalysts in comparison with those from 1%Ru/HMOR.

Figure 4.32 exhibits the chemical compositions in maltenes from using various Fe loading on HMOR in comparison with those of 1%Ru/HMOR. The result shows that the saturated hydrocarbon content is increased with the increasing percentage of Fe loading. At the highest percentage of Fe loading (20%Fe), the reduction of saturated hydrocarbons occurs. Additionally, 20%Fe/HMOR gives the lowest saturated hydrocarbons, but its content is still higher than that of 1%Ru/HMOR. At 20%Fe, all types of aromatics compounds increase. It can be explained that the high percentage of Fe loading (20%Fe) has high cracking activity, and generates a high amount of free radicals, which can further undergo the aromatization reactions. Correspondingly, Pour *et al.* (2008) concluded that an iron-zeolite (bifunctional) catalyst enhanced the secondary reactions, including oligomerization of light olefins, and aromatization. The high value chemical composition in maltenes is mono-aromatics, especially light mono-aromatics (C_6 - C_8), or BTXs. The BTXs are widely used as feedstock in petrochemical plants. As shown in Figure 4.32, 20%Fe/HMOR gives the highest concentration of mono-aromatics among Fe/HMOR catalysts and higher than that of 1%Ru/HMOR. In case of light mono-aromatics (BTXs) as shown in Table 4.7, 10%Fe/HMOR produces the highest yields of BTXs among Fe/HMOR catalysts, which is about 20 times higher than that of 1%Ru/HMOR.

Table 4.7 Yields of benzene, toluene and xylenes (BTXs) in mono-aromatics obtained from using Fe/HMOR catalysts in comparison with those from 1%Ru/HMOR

Carbon number	Yields of BTXs (%wt) in maltenes			
	1%Ru/HMOR	5%Fe/HMOR	10%Fe/HMOR	20%Fe/HMOR
6	0.06	0.137	4.75	0.75
7	0.16	0.178	4.53	1.31
8	0.43	0.226	4.32	2.16
BTXs	0.65	0.541	13.6	4.22

The comparison of average carbon number of mono-aromatics from using 5-20%Fe/HMOR, 1%Ru/HMOR, and pure HMOR is shown in Figure 4.33. The results show that the pure HMOR gives the lowest average carbon number of mono-aromatics (about 7.0) due to the high cracking activity. When the percentage of Fe loading increases, the average carbon number of mono-aromatics reduces. 20%Fe/HMOR gives the lowest average carbon number of mono-aromatics among all Fe/HMOR catalysts; moreover, it shows a lower number than that of 1%Ru/HMOR. From the results, it can be concluded that the higher percentage of Fe loading on HMOR produces the smaller molecules of mono-aromatics. However, 10%Fe/HMOR can be used as a substitute of 1%Ru/HMOR for light mono-aromatics production since it can produce the highest yields of BTXs with the closest average carbon number of mono-aromatics.

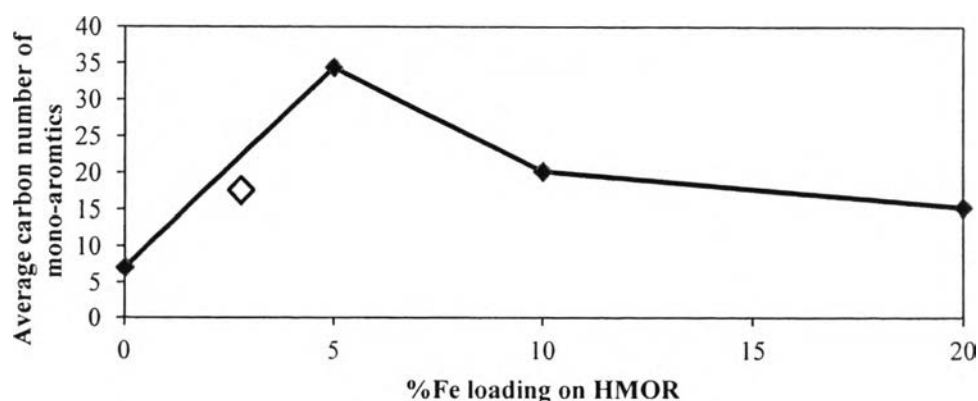


Figure 4.33 Average carbon number of mono-aromatics obtained from using Fe/HMOR catalysts in comparison with that of (◊) 1%Ru/HMOR.

4.2.2.4 Petroleum Fractions

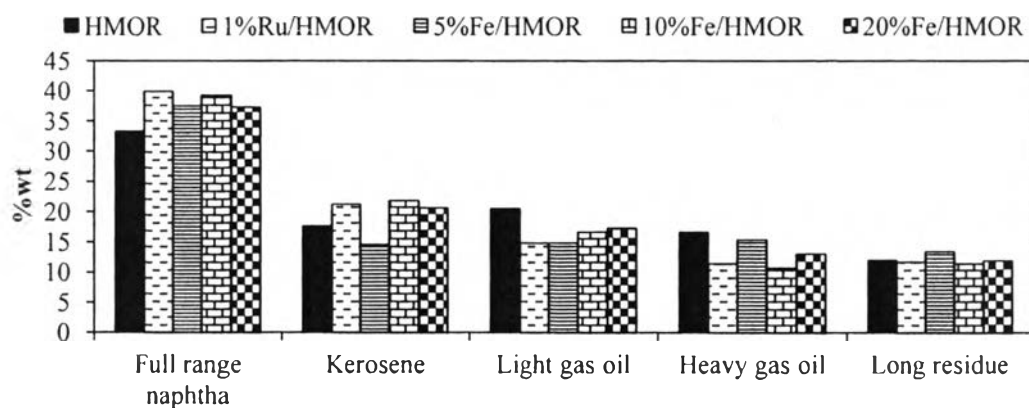


Figure 4.34 Petroleum fractions in maltenes obtained from using Fe/HMOR catalysts in comparison with those of 1%Ru/HMOR and pure HMOR.

The quantity and quality of petroleum fractions in maltenes are compared and discussed as follows. Figure 4.34 shows the quantity petroleum fraction in maltenes obtained from using varied Fe/HMOR catalysts in comparison with those of 1%Ru/HMOR and pure HMOR. The results show that 10%Fe/HMOR exhibits a similar quantity of full range naphtha, kerosene and other fractions as those of 1%Ru/HMOR. 5% and 20%Fe/HMOR give lower full range naphtha and kerosene fractions, while the light gas oil, heavy gas oil, and long residue are higher than those of 10%Fe/HMOR and 1%Ru/HMOR. It can be concluded that 10%Fe/HMOR produces a similar quantity of petroleum crude oil as 1%Ru/HMOR. This result can be confirmed by true boiling point curves as shown in Figure 4.35. Figure 4.35 shows that 10% and 20%Fe/HMOR give the closest true boiling point curve to that of 1%Ru/HMOR.

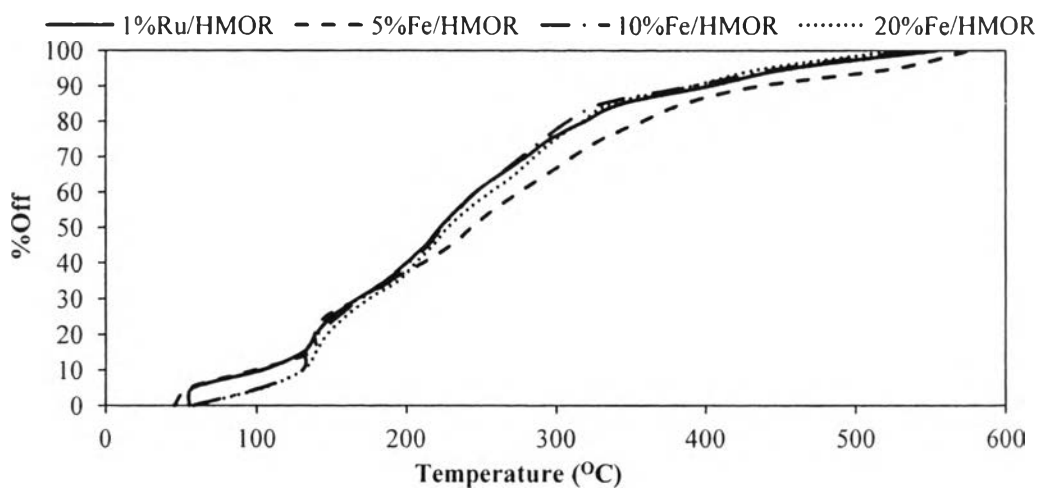


Figure 4.35 True boiling point curve of maltenes obtained from using Fe/HMOR catalysts in comparison with that from 1%Ru/HMOR.

The quality of petroleum crude oil product can be observed by considering the Sat HCs/Total aromatics ratio as shown in Figure 4.36.

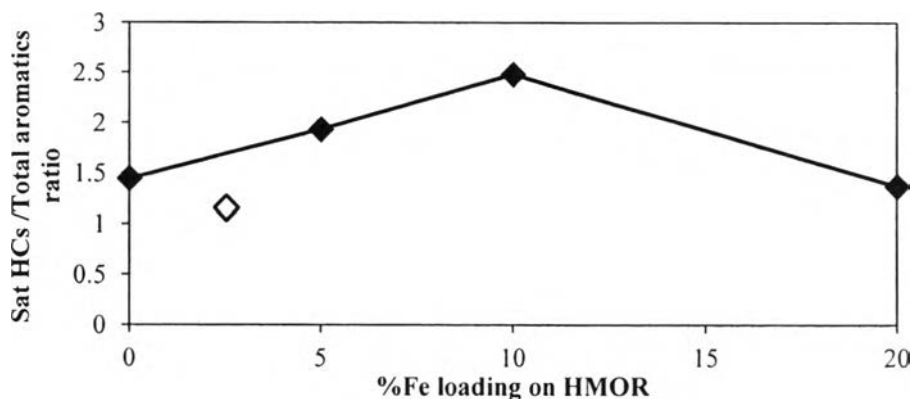


Figure 4.36 Sat HCs/Total aromatics ratio obtained from using Fe/HMOR catalysts in comparison with that from (◇) 1%Ru/HMOR.

This figure shows that the Sat HCs/Total aromatics increases from 1.93 to 2.48 with the increasing percentage of Fe loading on HMOR from 5 to 10%, whereas 20%Fe/HMOR gives the lowest of Sat HCs/Total aromatics (1.37) among all Fe/HMOR catalysts. All Fe/HMOR catalysts give a higher Sat HCs/Total aromatics than that of 1%Ru/HMOR (about 1.23). The results are attributed to the reason that the hydrogenation activity of catalyst can be enhanced by the increasing

Fe metal sites. However, the highest percentage of Fe loading (20%Fe/HMOR) gives the lowest Sat HCs/Total aromatics among all Fe/HMOR catalysts since the high Fe metal loading (20%Fe/HMOR) prefers to produce aromatics compounds by aromatization reactions rather than saturated hydrocarbons by hydrogenation reactions. For petroleum crude oil production, 10%Fe/HMOR is the most proficient catalyst to be used as a substitute of 1%Ru/HMOR since it can produce a similar quantity of petroleum fractions (especially, full range naphtha and kerosene) and similar quality of oil product (high Sat HCs/Total aromatics ratio) as those of 1%Ru/HMOR.

4.2.2.5 Sulfur Formation

Sulfur in an oil product is seriously concerned due to the environmental poisoning ability. The sulfur content in pyrolytic oil and sulfur deposition on spent catalysts obtained from varied Fe/HMOR catalysts in comparison with those from 1%Ru/HMOR are shown in Figure 4.37. The result shows that the increasing Fe loading percentage on HMOR catalysts can reduce the sulfur in pyrolytic oil, and increase the sulfur deposition on spent catalysts. In case of 1%Ru/HMOR, most sulfur elements prefer to remain in the pyrolytic oil rather than on the spent catalyst. From the results, it can be concluded that the pyrolytic oils obtained from Fe/HMOR catalysts, especially a high percentage of Fe loading, have the higher quality than that of 1%Ru/HMOR in terms of lower sulfur content.

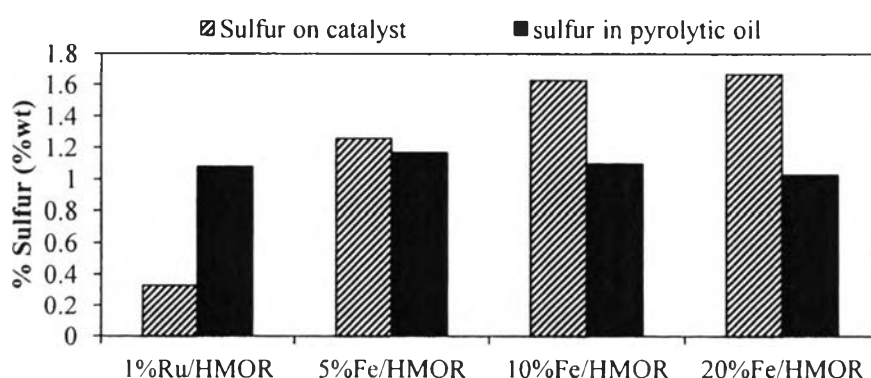


Figure 4.37 Sulfur content on spent catalysts and in pyrolytic oils obtained from Fe/HMOR catalysts in comparison with those from 1%Ru/HMOR.

4.2.2.6 Comparison of Catalyst Prices

Non-noble Fe catalysts were found to have potential to substitute Ru catalysts that are costly ones. As concluded previously, 20%Fe/HMOR seems to be the most capable catalyst to substitute 1%Ru/HMOR for the petrochemical gaseous products since it can produce the highest yields of light olefins, cooking gases, and mixed C₄. As shown in Table 4.8, if 20%Fe/HMOR is used as a substitute of 1%Ru/HMOR, the cost of catalyst is reduced by 9 times. Additionally, 10%Fe/HMOR is eligible catalyst that can be used as a substitute of 1%Ru/HMOR for light mono-aromatics (BTXs) and petroleum crude oil production. If 10%Fe/HMOR is used as a substitute of 1%Ru/HMOR, the cost is reduced by 20 times.

Table 4.8 Precursor prices

Metal	Precursor	Price(Baht)/g	%loaded (wt%)	g of loaded	Price (Baht)
Noble	ruthenium(III) chloride hydrate (RuCl ₃ .aq)	3,700	1	0.207	767
Non-noble	iron (III) chloride hexahydrate (FeCl ₃ ·6H ₂ O)	7.08	10	5.37	38.0
			20	12.1	85.7