# CHAPTER IV
# RESULTS AND DISCUSSION

In this chapter, the qualities and quantities of the products obtained from using the modified Ni catalysts (Ni, NiMo and NiW on HBETA) and modified Co catalysts (Co, CoMo, and CoW on HBTEA) in waste tire pyrolysis are discussed and compared. The loading percentage of the first metal (Ni or Co) was fixed at 5% by weight, and the percentage of the second metal (Mo or W) was varied as 10% and 20% by weight of the catalyst. Incipient wetness impregnation technique was employed to prepare all catalysts.

## 4.1 Modified Ni/HBETA catalysts

### 4.1.1 Verification of metallic form of modified Ni/HBETA

X-ray Diffraction (XRD) was employed to verify the metallic form of the catalysts.

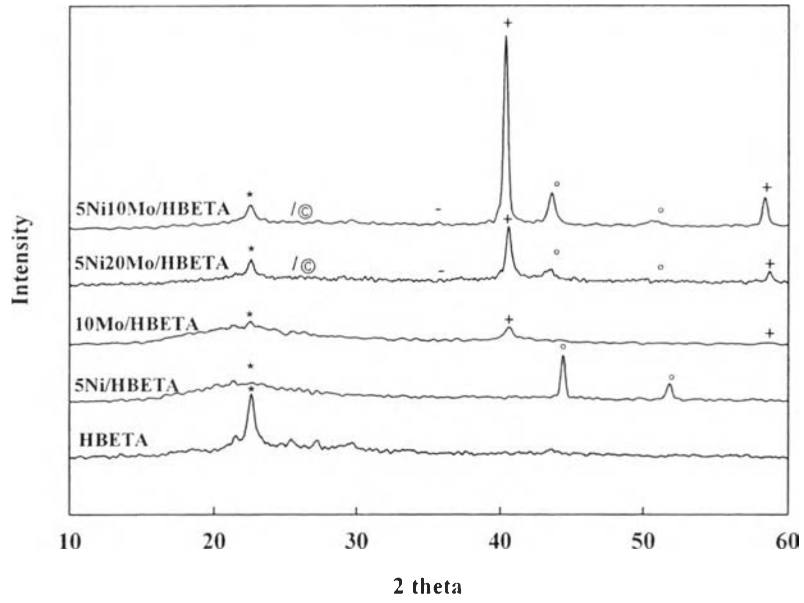

**Figure 4.1 (a)** XRD patterns of Ni and NiMo over HBETA catalysts; (*) HBETA, (°) Ni, (+) Mo, (-) NiO, (/) $MoO_2$, and (©) ($MoO_3$)

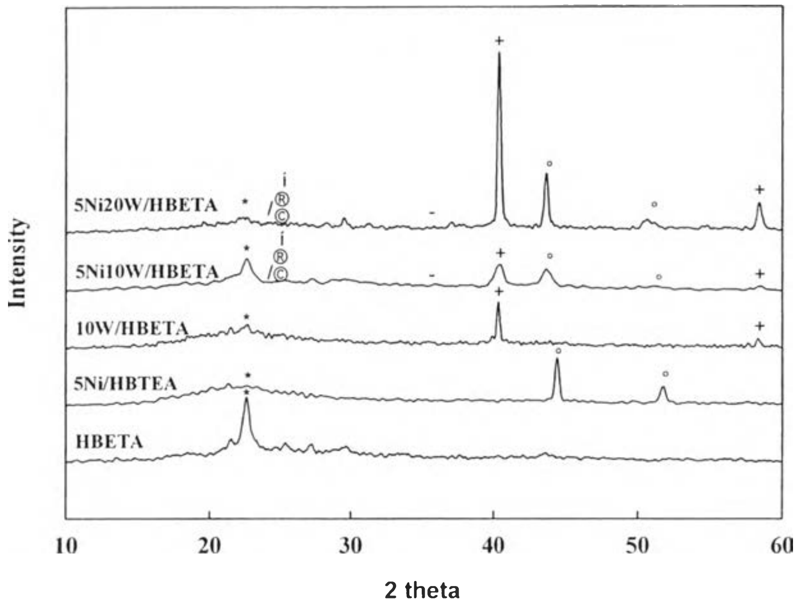

**Figure 4.1(b)** XRD patterns of Ni and NiW over HBETA catalysts; (*) HBETA, (°) Ni, (+) W, (-) NiO, (/) WO, (©) $WO_2$, (®) $WO_3$, and (í) $W_4O_{11}$

Figure 4.1(a) shows the XRD patterns of Ni and NiMo catalysts supported on HBETA zeolite. The result shows that HBETA zeolite gives a peak at 22.6 °. 5%wt of Ni over HBETA gives three peaks at 22.3 °, 44.5 °, and 51.7 °. The peaks at 44.5 ° and 51.7 ° belong to Ni metal. Moreover, 10 %wt Mo over HBETA shows two peaks; that is, the bigger one is at 40.6 °, and the smaller peak is at 58.8 °. From their XRD patterns, it can be confirmed that NiMo/HBETA catalysts are completely reduced from an oxide to the metal form because the XRD peaks of NiMo/HBETA are matched with those of Ni and Mo metals, and any of NiO (-), $MoO_2$ (/) and $MoO_3$ (©) peaks does not appear (after matched with the standard from Joint Committee on Powder Diffraction Standards database) Likewise, Figure 4.1(b) shows the XRD patterns of Ni and NiW supported on HBETA zeolite. The peaks of 10W/HBETA are found at 22.7 °, 40.3 °, and 58.3 °. The reference indicates that the peaks at 40.3 ° and 58.3 ° are the peaks of W in the metal form. The profiles of NiW catalysts do not have any of NiO (-), WO (/), $WO_2$ (©), $WO_3$ (®), and $W_4O_{11}$ (í) peaks (after matched with the standard from Joint Committee on Powder

Diffraction Standards database). Therefore, the NiW/HBETA catalysts were completely reduced to the bimetallic form.

### 4.1.2 Pyrolysis activity

This section exhibits the qualities and quantities of the pyrolytic products from the 5 %wt of Ni with10 and 20 %wtof one of the second metals (Mo and W) supported on HBETA zeolite. The pyrolytic products can be classified into gas, oil, and solid residue (char). The product distribution can be shown by the ratio of gas to liquid in Figure 4.2. The solid product remains constant at about 40 wt%.

#### *4.1.2.1 Gas to liquid ratio (G/L ratio)*

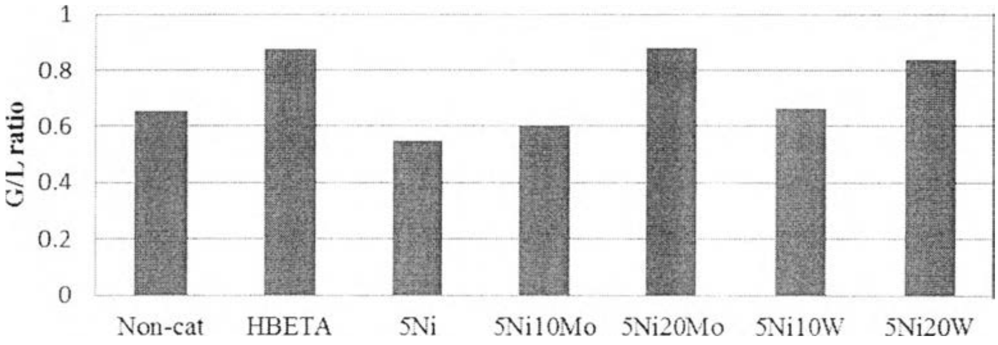

**Figure 4.2** G/L ratio obtained from modified Ni /HBETA catalysts.

* 5Ni = 5 wt% Ni on HBETA

** 5Ni10Mo = 5 wt% Ni- and 10 wt% Mo- loaded HBETA

*** 5Ni20Mo = 5 wt% Ni- and 20 wt% Mo- loaded HBETA

**** 5Ni10W = 5 wt% Ni- and 10 wt% W- loaded HBETA

***** 5Ni20W = 5 wt% Ni- and 20 wt% W- loaded HBETA

Figure 4.2 illustrates the ratio between gas and liquid obtained from the modified Ni/HBETA catalyst as compared to pure that of HBETA zeolite and the non-catalytic case or non-cat (thermal pyrolysis). The higher G/L ratio indicates that the gas yield increases while the liquid yield decreases. This can be described that the higher G/L ratio gave the higher the cracking ability because the heavy molecules can be cracked into lighter molecules over the acid sites of the catalysts. The results show that the pure HBETA gives good cracking ability due to the increasing gas to liquid ratio from 0.65 to 0.87. In the case of Ni/HBETA, the reduction in G/L ratio can be possibly resulted from the interaction between the metal and the support. When the second metal (Mo or W) is added into the catalyst, the G/L ratio increases with the increase of the amount of the second metal loading which indicates that bimetallic NiMo and NiW over HBETA had the higher cracking ability than Ni. In addition, 5%wt Ni with 20 %wt Mo loading gives the highest G/L ratio (0.88).

### *4.1.2.2 Yield of Olefins*

Non-condensable gases are gaseous pyrolysis products composed of gases in the range of $C_1$-$C_5$. Some of these gases are valuable petrochemical products such as olefins (ethylene and propylene), cooking gas, and mixed $C_4$. Figures 4.3-4.4 shows the yield of these petrochemical gases obtained from modified Ni/HBETA catalysts.

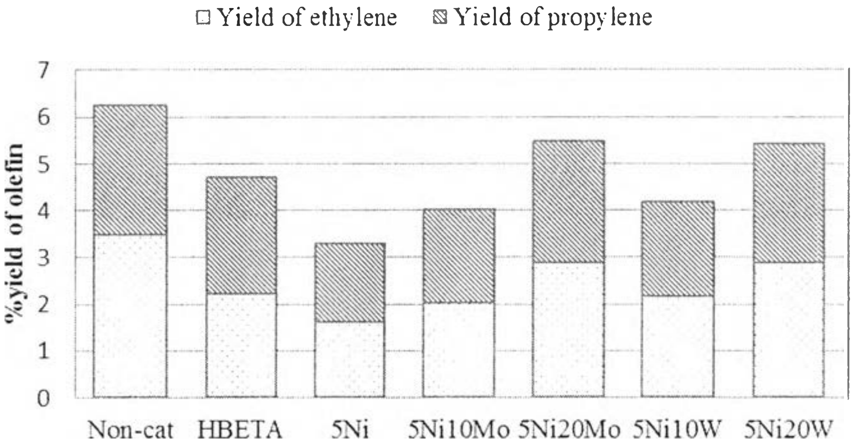

**Figure 4.3** Yield of ethylene and propylene obtained from modified Ni/HBETA catalysts.

From Figure 4.3, the result exhibits that the non-catalytic case gives the higher yield for ethylene and propylene than the pure HBETA zeolite; that are, approximately 3.48% and 2.77%, suspectively 5Ni/HBETA gives the lowest yield of olefins; however, when the bimetallic (NiMo or NiW) catalysts are used, the yields of ethylene and propylene increase significantly. The yield of olefins increases with the increasing contents of Mo and W. Moreover, 5Ni20Mo and 5Ni20W supported on

HBETA give the higher yields of ethylene and propylene than the other catalysts. Nevertheless, all catalysts still give lower olefin yield than non-catalytic case.

### *4.1.2.3 Yield of Cooking Gases*

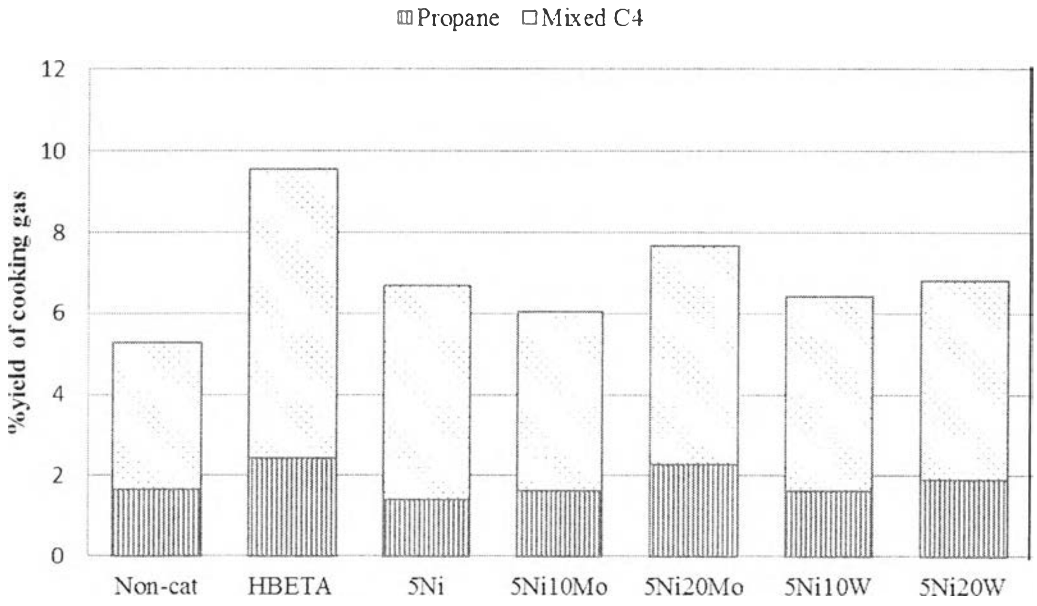

**Figure 4.4** Yield of cooking gas obtained from modified Ni/HBETA catalysts.

Figure 4.4 illustrates the yield of cooking gases (propane mixed with mixed $C_4$) obtained from all modified Ni catalysts, pure HBETA and the non-catalytic. Pure HBETA gives a higher yield of propane and mixed $C_4$compared to the non-catalytic and the other catalysts, which is about 2.4% and 7.2%, respectively. Although all of the modified Ni catalysts have lower activity than the parent BETA zeolite, but they give a higher yield of cooking gases than the non-catalytic case. 5Ni/BETA gives the lowest yield of propane than the others. When using 5Ni20Mo/HBETA, it can increase the yield of cooking gas whereas when other modified Ni/HBETA are used. the yield of cooking gas does not change much when compared with 5Ni/HBETA.

### *4.1.2.4 Liquid Compositions*

After asphaltene was separated from the liquid product of waste tire pyrolysis, the maltene solutions were separated into 5 fractions consisting of saturated hydrocarbons, mono-aromatics, di-aromatics, poly-aromatics and polar-aromatics by using liquid column chromatography (Sebor *et al.*, 1999) as shown in Figure 4.5.

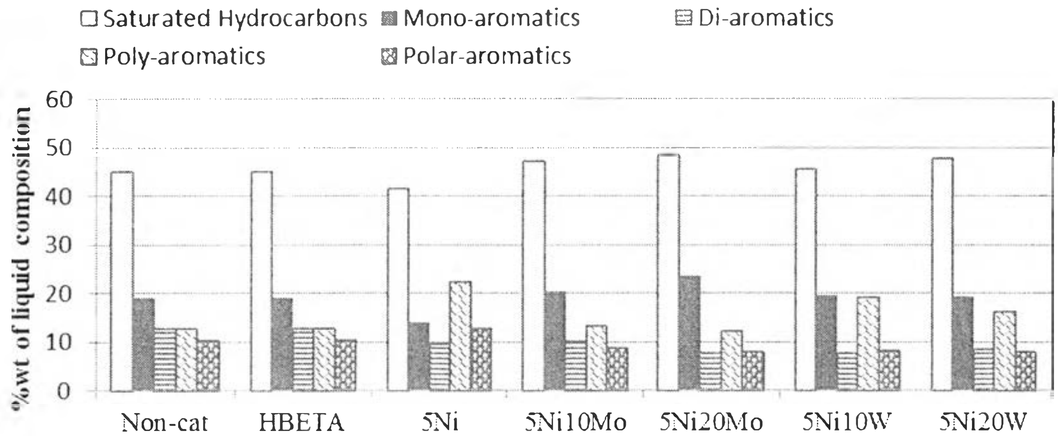

**Figure 4.5** Chemical compositions in maltenes solution from modified Ni/HBETA catalysts.

Figure 4.5 illustrates the chemical compositions of maltenes solutions from using modified Ni/HBETA catalysts as compared to those of the pure HBETA and the non-catalytic case. The result shows that the pure HBETA has lesser effect on the change in concentration of components because it slightly changes what is obtained from the non-catalytic case. With using 5Ni/HBETA, the light components (saturated hydrocarbons and mono-aromatics) decrease with the increase in the heavy components (poly- and polar-aromatics).However, when the bimetallic catalysts (NiMo and NiW on HBETA) are used, the saturated hydrocarbons and mono-aromatics increase dramatically in the same trend in accordance with the decreases in poly- and polar-aromatics, which indicate the good cracking ability. NiMo/HBETA catalysts show the higher cracking ability as compared to NiW/HBETA catalysts because they are more likely to convert heavy components to the light components than NiW/HBETA catalysts. The pyrolytic oils obtained from

5Ni20Mo/HBETA had the highest concentration of saturated hydrocarbons and mono-aromatics, which are about 48.6% and 23.5% by weight, respectively. Therefore in this case, it can be concluded that the doping of Ni/HBETA catalysts with either Mo or W can increase the qualities of the pyrolytic oils because they can help to convert the heavy components such as poly- and polar aromatics to the lighter components (saturated hydrocarbons and mono-aromatics) as compared with the non-catalytic case.

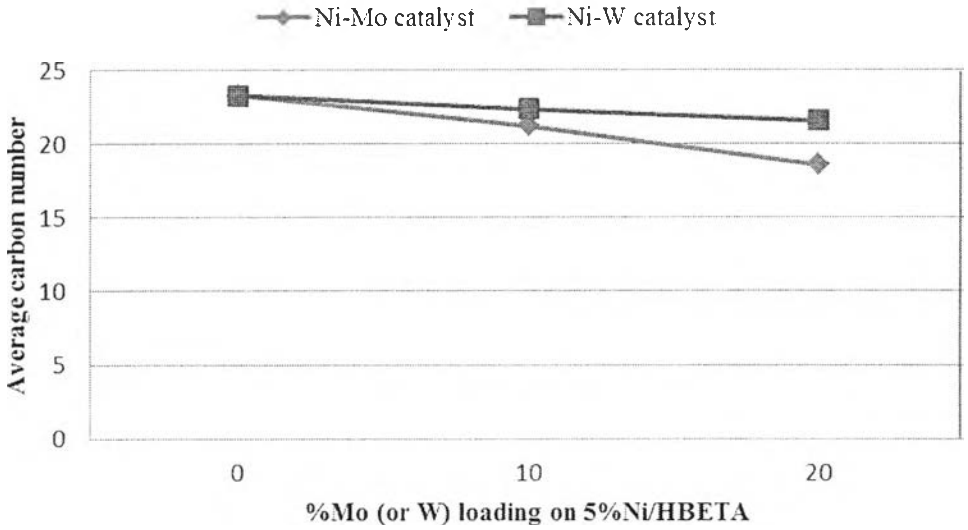

**Figure 4.6** Average carbon number of polar-aromatics fractions obtained from using modified Ni/HBETA catalysts.

Figure 4.6 illustrates the average carbon number of polar-aromatics obtained from using modified Ni/HBETA catalysts. It exhibits that the average carbon number of polar-aromatics slightly decreases in the same trend when the bimetallic catalysts (NiMo and NiW on HBETA) are used. This result shows that modified Ni/HBETA catalysts exhibit good hydrogenation and ring-opening activity on the active sites of these catalysts. In addition, NiMo/HBETA catalysts have the higher hydrogenation and ring-opening activities than the NiW/HBETA one since the polar-aromatics fractions have a lower average carbon number. Moreover, the average carbon numbers of polar-aromatics obtained from using 5Ni20Mo/HBETA is about 18.6, which is significantly lower than that from 5Ni/HBETA (23.3). It can be concluded that the modified Ni catalysts, especially 5Ni20Mo, help improving the production of short chain hydrocarbons by converting heavy hydrocarbons into lighter hydrocarbons via the ring-opening and hydrogenation.

#### *4.1.2.5 Petroleum Fractions*

The maltene solutions were analyzed by a SIMDIST-GC for the true boiling point distillation curves, and then cut to the petroleum fractions; that 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) as shown in Figure 4.7

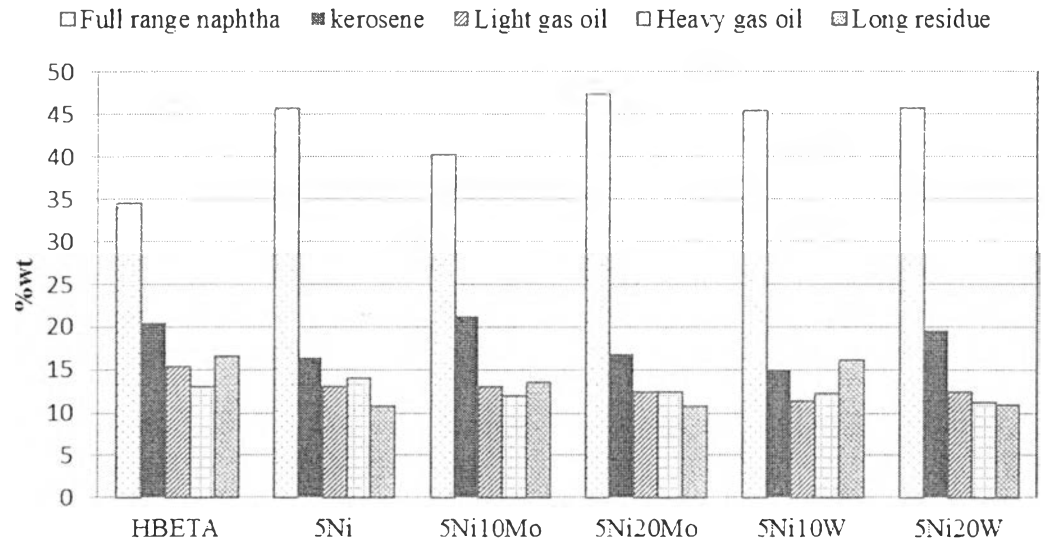

**Figure 4.7** Petroleum fractions in maltenes obtained from modified Ni/HBETA catalysts.

Figure 4.7 illustrates the petroleum fractions in maltenes obtained from using modified Ni/HBETA catalysts. It can be seen that using the 5Ni/HBETA can increase the products in the range of full range naphtha. The results show that the NiMo catalysts are likely to produce the light oil fraction because 5Ni20Mo/HBETA gives the highest quantity of full range naphtha while 5Ni10Mo/HBETA gives the highest amount of kerosene. It can be seen that the higher the amount of the second metal (Mo or W), the higher amount of full range naphtha is obtained. In addition, pure HBETA produces the heavier oils than all other catalysts. Therefore, it can be concluded that modified Ni/HBETA catalysts can be used to improve the qualities of oil.

### 4.1.3 Reducibility of modified Ni catalysts and metal-metal interaction

Temperature-programmed reduction (TPR) was conducted to identify the reducibility of the impregnated catalysts and the metal-metal interaction. TPR profiles of the modified Ni/HBETA catalysts, 10%Mo/HBETA, and 10%W/HBETA are shown in Figures 4.8 and 4.9

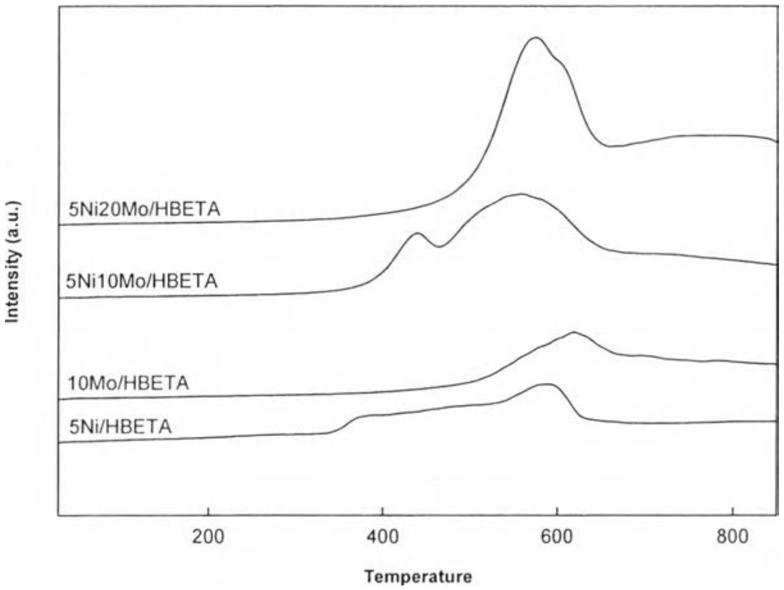

**Figure 4.8** TPR profiles of various bimetallic NiMo catalysts in comparison with that of 10Mo/HBETA.

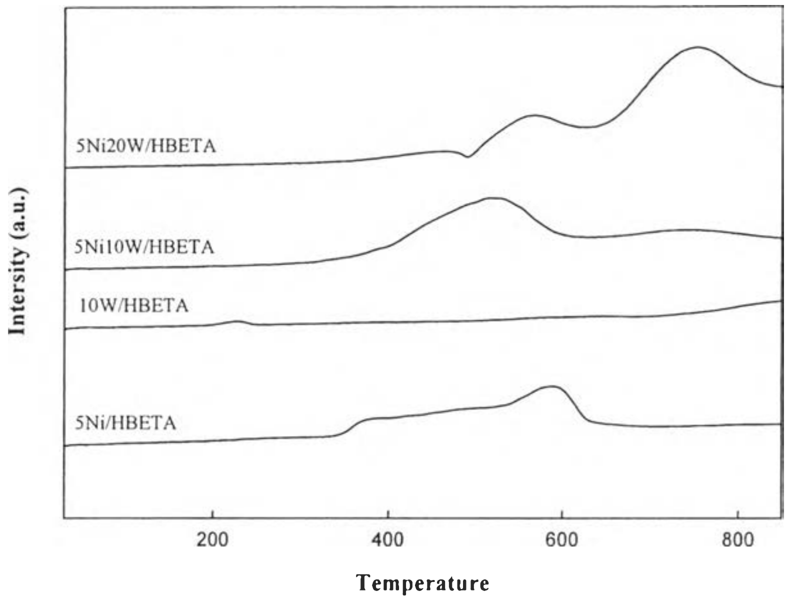

**Figure 4.9** TPR profiles of various bimetallic NiW catalysts in comparison with that of 10W/HBETA.

| Catalysts on HBETA | peak1 (°C) | peak2 (°C) |
|---|---|---|
| 5Ni | 370 | 570 |
| 10Mo | 620 | |
| 10W | 850 | |
| 5Ni10Mo | 440 | 580 |
| 5Ni20Mo | 580 | |
| 5Ni10W | 510 | 730 |
| 5Ni20W | 570 | 750 |

**Table 4.1** Reduction peaks of modified Ni/HBETA catalysts in comparison with those of 10Mo/HBETA and 10W/HBETA.

Table 4.1 shows the reduction temperatures of modified Ni/HBETA catalysts in comparison with those of 10Mo/HBETA and 10W/HBETA. 5Ni/HBETA has two reduction peaks at 370 °C and 570 °C. The reduction peaks of 10Mo and 10W on HBETA are located at 620 °C and 850 °C. The TPR profile of 5Ni20Mo/HBETA shows only one peak at 580 °C, which relates to the strong interaction of between Ni and Mo whereas the TPR profile of 5Ni10Mo has two peaks at 440 °C and 580 °C assigned to the weaker interaction of Ni-Mo that that of 5Ni20Mo/HBETA. It also indicates that some of Ni that do not have interaction with Mo. In addition, TPR profiles of NiW show the weaker interaction between Ni and W than that occurs between NiMo as indicated by two peaks; one at a lower temperature (~500-600 °C), and another one at a higher temperature (~700-800 °C). Moreover, 5Ni20W/HBETA has stronger metal interaction between Ni and W than 5Ni10W/HBETA. Therefore it can be concluded that the higher the content of the second metal, the strong metal interaction between Ni and Mo or Ni and W is observed.

### 4.1.4 Desulfurization ability

#### *4.1.4.1 Sulfur distribution*

Structure of tires contains sulfur, which is crosslink between carbon and sulfur (C-S bonds) of rubber chains are distributed in the pyrolytic oil, pyrolytic gas, char and coke on the spent catalyst as shown in Figure 4.10

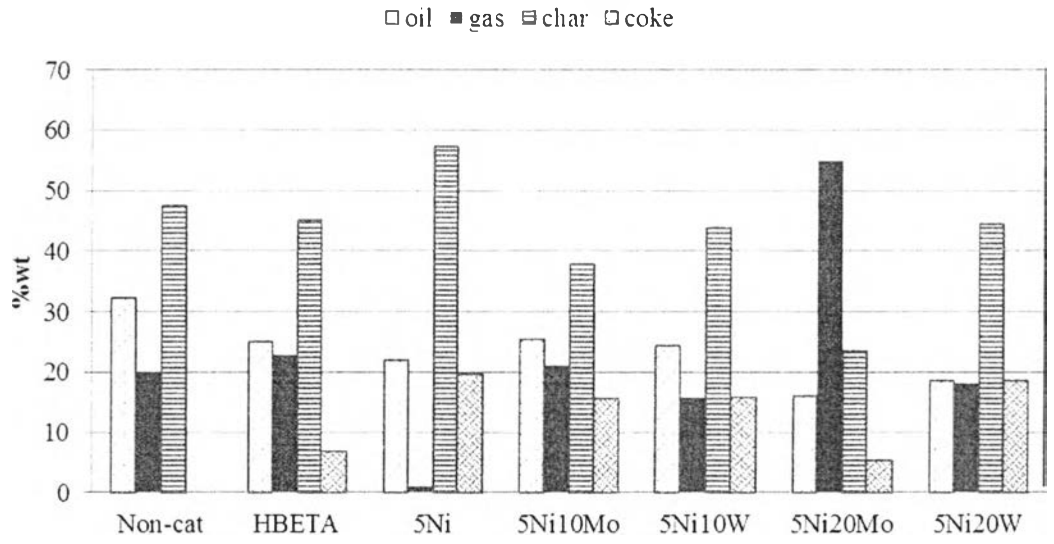

**Figure 4.10** Sulfur distribution in the pyrolytic products obtained from modified Ni/HBETA catalysts.

Figure 4.10 illustrates the sulfur distribution of the pyrolytic products obtained from various catalysts. Using pure HBETA, sulfurs in oil and char decrease in association with the increase in the sulfur content in gas when compared with those in the non-catalytic product. It can be suggested that the pure HBETA catalyst has good cracking ability because the sulfurs in char and oil the decrease with increase in the sulfur in gas. Otherwise, with using 5Ni/HBETA as catalyst, the high sulfur contents in char and spent catalyst are observed together with the low sulfur contents in gas. However using the bimetallic catalysts, the decrease in sulfur content in char and spent catalyst is observed with the increase the sulfur contents in gas. In addition, 5Ni20Mo shows the good catalyst for the sulfur reduction in oil due to the lowest sulfur contents in oil and the highest sulfur contents in gas among those obtained from other modified Ni catalysts.

#### *4.1.4.2 Sulfur contents*

The sulfur contents in pyrolytic oil and sulfur deposition on spent catalysts were determined by a CHNS analyzer.

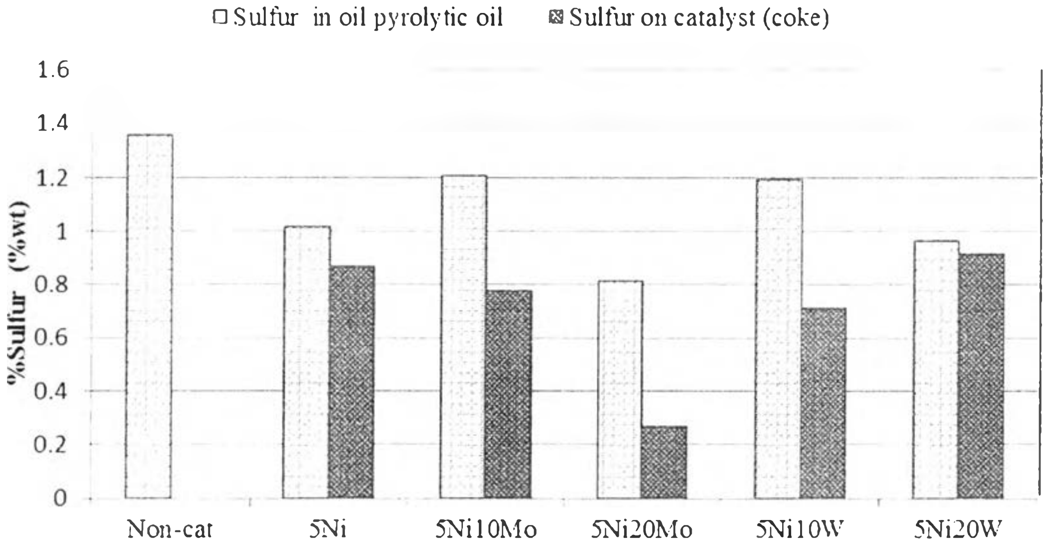

**Figure 4.11** Sulfur contents (%wt) on spent catalysts and in the pyrolytic oils obtained from modified Ni /HBETA catalysts.

Figure 4.11 shows sulfur contents (%wt) on spent catalysts and in the pyrolytic oils obtained from modified Ni/HBETA catalysts. The sulfur content in pyrolytic oil is about 1.36 %wt when none of the catalyst used. 5Ni/HBETA and all of modified Ni/HBETA catalysts show good hydrodesulfurization ability because they can reduce the sulfur content in the pyrolytic oil. When 5Ni/HBETA is used, it can reduce the sulfur content in pyrolytic oil to 1.02 wt%, whereas sulfur content on the spent catalyst (coke) is 0.87 wt%. Using 5Ni10Mo/HBETA and 5Ni10W/HBETA, the sulfur content in the pyrolytic oils increase in conjunction with the decrease in sulfur content on the spent catalyst, whereas when using 5Ni20Mo/HBETA and 5Ni20W/HBETA, the sulfur content in oils further decrease from the lower content of the second metal. 5Ni20Mo/HBETA gives the lowest sulfur contents in the pyrolytic oil (0.82 wt%) and the lowest sulfur contents on the spent catalysts (0.27 wt%) among all others. 5Ni20Mo/HBETA is a good catalyst for the sulfur reduction as indicated by the lowest sulfur contents in oil. This can be suggested that 5Ni20Mo/HBETA can breakdown the C-S bonds due to the hydrodesulfurization activity. Moreover, it can be concluded that 5Ni20Mo/HBETA catalyst can produce high quality of oil that contains low sulfur content.

#### *4.1.4.3 Type of sulfur compounds*

The sulfur compounds in the pyrolytic oils were identified by using GC-MS (TOF). In this case, only C, H, and S elements were considered in the identification of sulfur compounds since the other elements are less in the tire-derived oil. After the sulfur compounds were identified, the sulfur compounds were grouped into the petroleum fractions; according to their carbon number namely gasoline ($C_5$-$C_9$), kerosene ($C_{10}$-$C_{13}$), Gas oil ($C_{14}$-$C_{20}$), light vacuum gas oil ($C_{21}$-$C_{23}$), and heavy vacuum gas oil ($C_{24}$-$C_{50}$). The results are shown in Appendix K. 5Ni20Mo/HBETA gave the lowest sulfur contents in the pyrolytic oil; therefore, in this case, the sulfur compounds from the 5Ni20Mo/HBETA and from the non-catalytic case are compared in terms distribution in petroleum fractions.

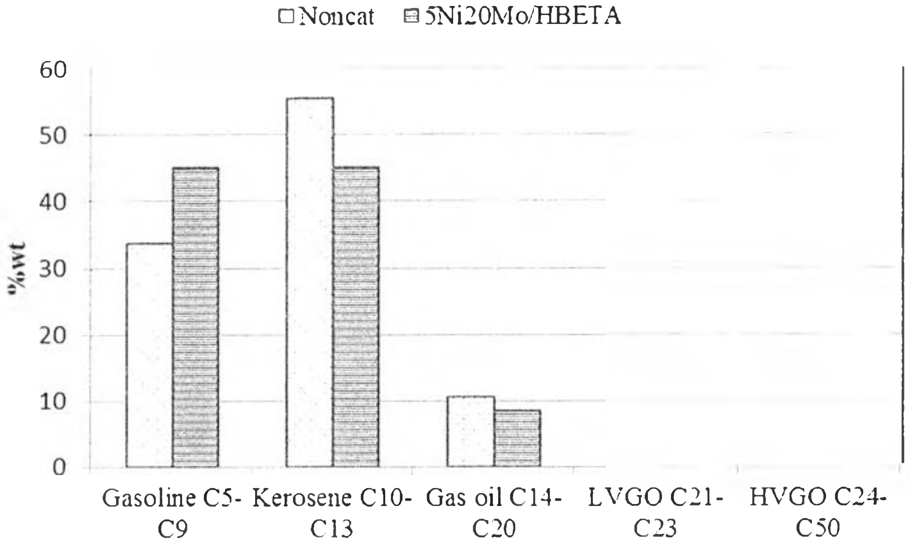

**Figure 4.12** Sulfur distribution in petroleum fractions obtained from 5Ni20Mo/HBETA.

Figure 4.12 illustrates the amount of sulfur compounds in the range of sulfur distribution in petroleum fractions obtained from 5Ni20Mo/HBETA and the non-catalytic case. It was found that the pyrolytic oils contain a low quantity of the heavy fractions (LVGO and HVGO). Therefore, sulfur compounds are hardly found distributed in the VGO fractions. In addition, with using 5Ni20Mo/HBETA, the sulfur compounds in the heavy fractions may be converted into smaller molecules or to light fractions. Furthermore, the sulfur compounds in the oil obtained from 5Ni20Mo/HBETA are mainly in the range of $C_5$-$C_9$, such as such as thiophene, 2-(1-methylethyl)-, benzo[b]thiophene, 4-methyl and benzo[b]thiophene whereas the sulfur compounds from the non-catalytic case are mainly in the range of $C_{10}$-$C_{13}$, such as benzo[b]thiophene, 2,7-dimethyl, benzo[b]thiophene, 2-ethyl-7-methyl- and dibenzothiophene.

## 4.2 Modified Co/HBETA catalysts

From Section 4.1, it was found that the bimetallic Ni-based catalysts with 20 wt% of the second metals (Mo and W) had the higher quality and quantity of the desired products than 10 wt%; therefore, in this part 20 wt% Mo and W were used to modified 5Co/HBETA catalysts. The pyrolytic products in this session were compared with the 5Ni20Mo/HBETA, which has shown the highest performance on the quality and quantity of the pyrolytic products.

### 4.2.1 Pyrolysis activity

#### *4.2.1.1 Gas to liquid ratio (G/L ratio)*

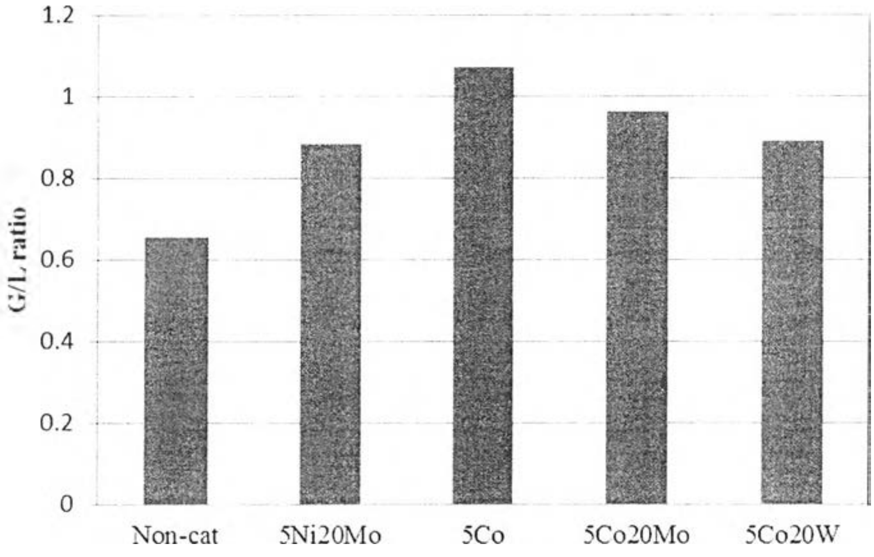

**Figure 4.13** G/L ratio obtained from modified Co/HBETA.
* 5Co = 5 wt% Co on HBETA
** 5Co20Mo = 5 wt% Co- and 20 wt% Mo- loaded HBETA
*** 5Co20W = 5 wt% Co- and 20 wt% W- loaded HBETA

Figure 4.13 illustrates the ratio between gas and liquid from modified Co/HBETA catalysts as compared to that of the 5Ni20Mo/HBETA. The results show that 5Co/HBETA has the higher G/L ratio (1.07) than the other modified Co/HBETA catalysts and 5Ni20Mo/HBETA. It can be suggested that 5Co/HBETA has the higher cracking ability than the others because it shows the highest G/L ratio. When the bimetallic Co catalysts (5Co20Mo/HBETA and

5Co20W/HBETA) are used, the G/L ratio decreases, indicating the lower cracking ability. However, the G/L ratios obtained from 5Co20Mo/HBETA and 5Co20W/HBETA catalysts are close to that from 5Ni20Mo/HBETA.

### *4.2.1.2 Yield of Olefins*

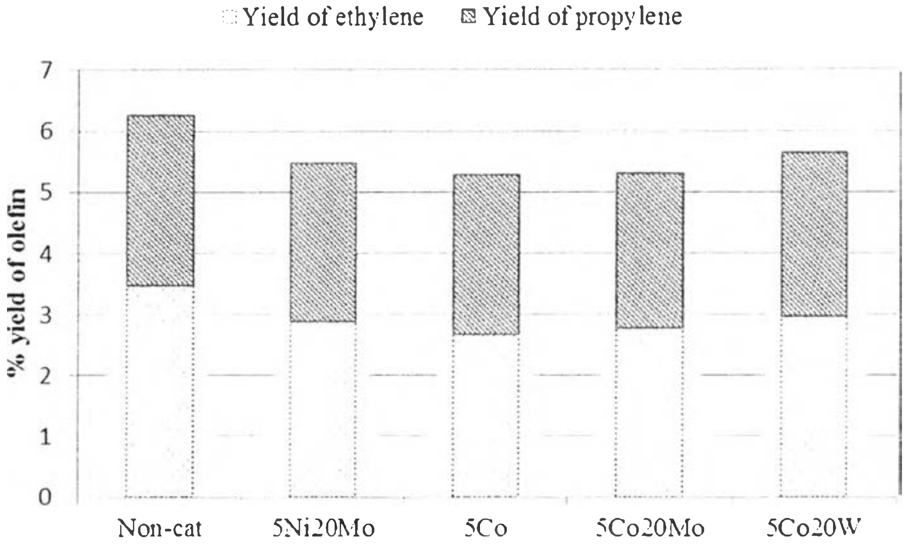

**Figure 4.14** Yield of ethylene and propylene obtained from modified Co/HBETA catalysts.

From Figure 4.14, the result exhibits that yield of olefins obtained from 5Co/HBETA and the bimetallic Co catalysts (5Co20Mo/HBETA and 5Co20W/HBETA) are approximately in the same level, which is 5.3-5.6% approximately. It can be suggested that the cracking activity and yield of olefins do not change when the bimetallic Co catalysts were used.

### *4.2.1.3 Yield of cooking gas*

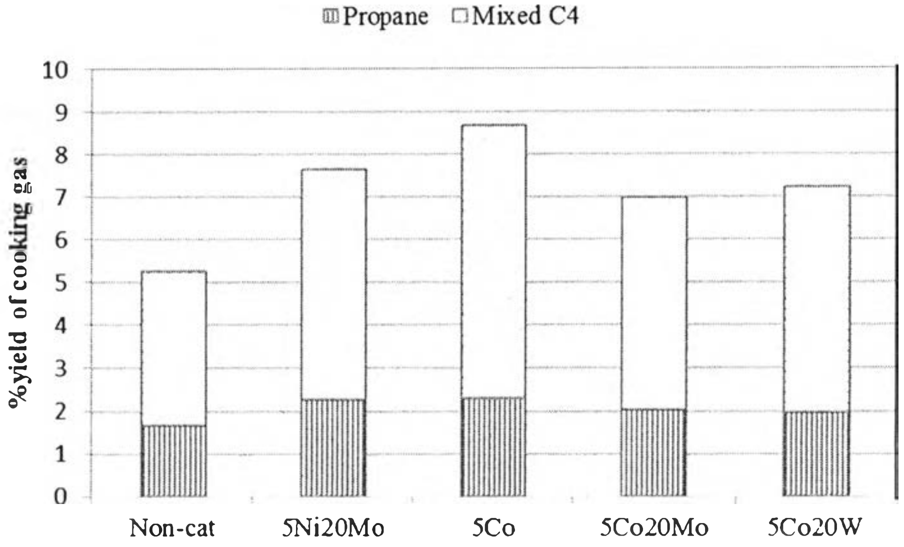

**Figure 4.15** Yield of cooking gas obtained from modified Co/HBETA catalysts.

Figure 4.15 illustrates the yield of cooking gas obtained from 5Co/HBET, and bimetallic Co catalysts in comparison with 5Ni20Mo/HBETA. 5Co/HBETA gives the highest yield of propane and mixed $C_4$ among the other catalysts, which is about 2.3% and 6.4%, respectively. In this case, the bimetallic catalysts have a lower yield of cooking gas than 5Co/HBETA and 5Ni20Mo/HBETA, but they still gave the higher yield of cooking gas than the non-catalytic case.

### 4.2.1.4 Liquid compositions

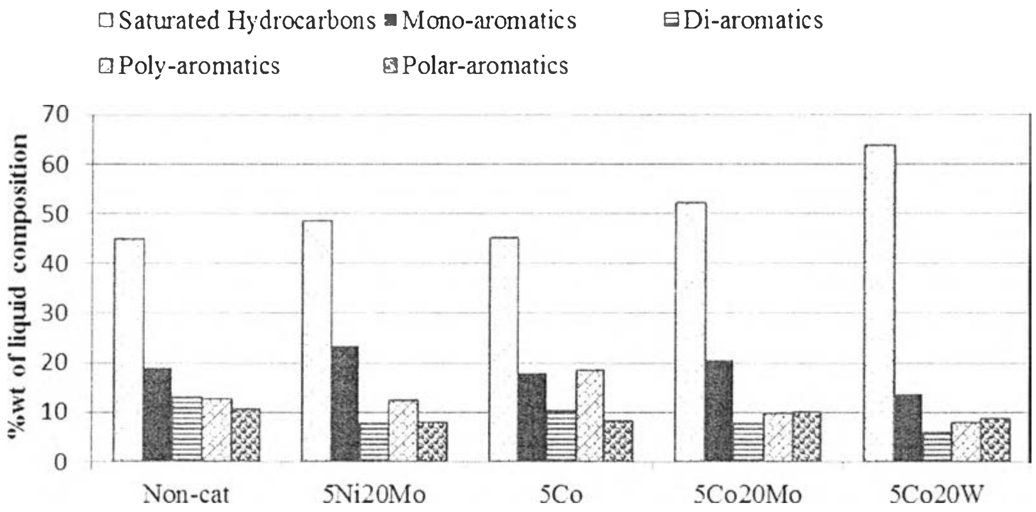

**Figure 4.16** Chemical compositions in maltenes from modified Co/HBETA catalysts.

The chemical compositions in maltenes obtained from modified 5Co/HBETA catalysts as compared to those of 5Ni20Mo/HBETA are shown in Figure 4.16. The results show that 5Co/HBETA can reduce the polar-aromatic content with the increase in the poly-aromatic content in the pyrolytic oil, when compared with the non-catalytic case, whereas the saturated hydrocarbons and mono-aromatics are slightly changed. Therefore, 5Co/HBETA does not help to convert poly- and polar-aromatics to saturated hydrocarbons and mono-aromatics. However, when the bimetallic Co catalysts (5Co20Mo/HBETA and 5Co20W/HBETA) are employed, the saturated hydrocarbons and mono-aromatics increase dramatically with a decrease in the poly- and polar-aromatics. The 5Co20W/HBETA catalyst gives the highest concentration of saturated hydrocarbons (63.8 wt%) among the other catalysts. Therefore, in this case, it can be concluded that bimetallic Co catalysts can increase the qualities of the pyrolytic oils because they can help to convert aromatics to saturated hydrocarbons.

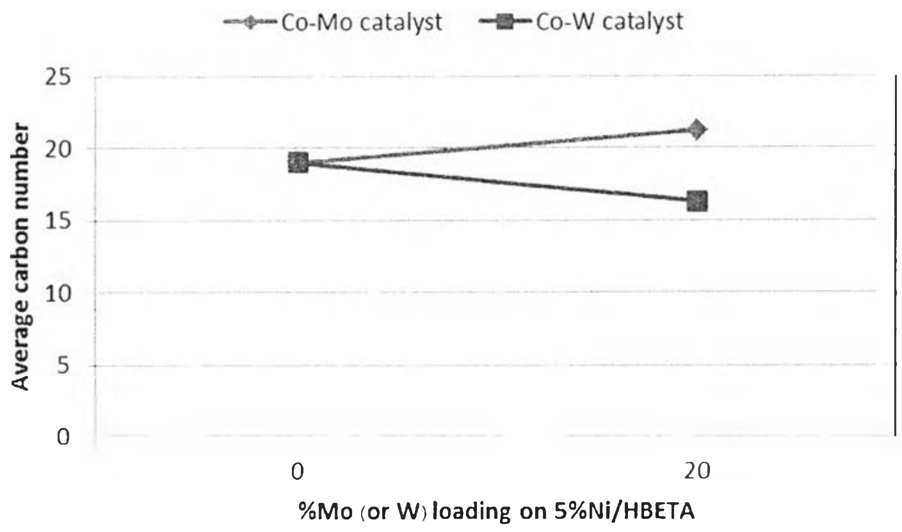

**Figure 4.17** Average carbon number of polar-aromatics fraction obtained from using modified Co/HBETA catalysts.

Figure 4.17 illustrates the average carbon number of polar-aromatics obtained from using modified Co/HBETA catalysts. It exhibits that the average carbon number of polar-aromatics obtained from 5Co/HBETA is about 19. When 5Co20Mo/HBETA is used, the average carbon number of polar-aromatics increases to 21.2. According to the result from Section 4.2.1.4, the pyrolytic oil obtained from 5Co20Mo/HBETA had the higher polar-aromatic contents than that from 5Co/HBETA. In addition, with using 5Co20W/HBETA, the average carbon number of polar-aromatic decreases to 16.3 that is similar to the result from Section 4.2.1.4 and it is also lower than the average carbon number obtained from 5Ni20Mo/HBETA (18.6). This can be suggested that 5Co20W/HBETA shows the higher hydrogenation and ring-opening abilities than the other catalysts. Moreover, it can be concluded that 5Co20W/HBETA is a good catalyst for producing short chain hydrocarbons by converting the heavy hydrocarbons to the light hydrocarbons via the ring-opening and hydrogenation.

### *4.2.1.5 Petroleum Fractions*

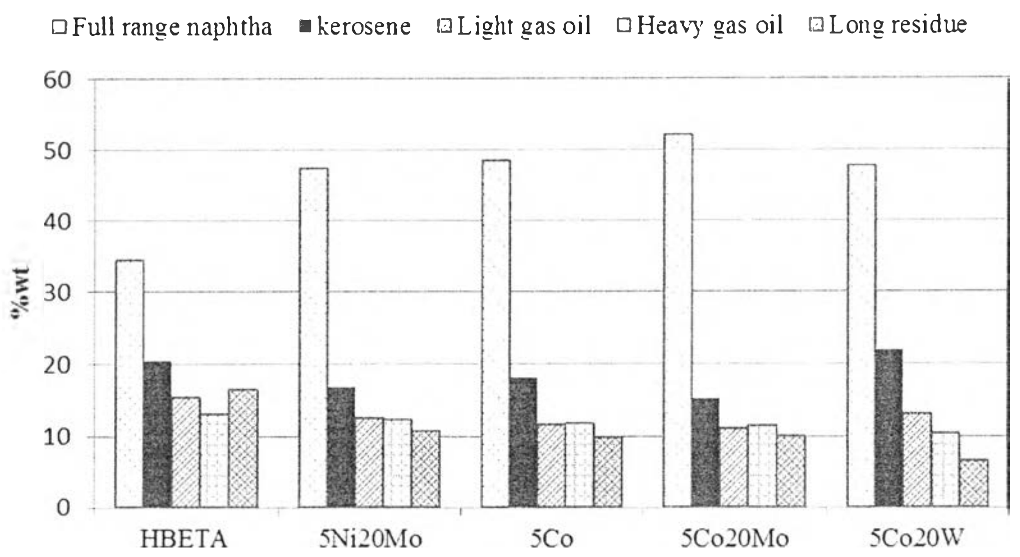

**Figure 4.18** Petroleum fractions in maltenes obtained from modified Co/HBETA catalysts.

Figure 4.18 illustrates the petroleum fractions of maltenes obtained from using modified Co catalysts in comparison with 5Ni20Mo/HBETA and pure HBETA zeolite. The results show that all modified Co/HBETA catalysts can increase the full range naphtha with the decreases in the heavy fractions (gas oil and long residue) as compared to the pure HBETA zeolite. 5Co/HBETA can increase the full range naphtha from 34.5 to 48.5 wt%, and decrease the long residue from 16.5 to 9.8 wt%. Moreover, the products obtained from 5Co/HBETA are similar to those obtained from 5Ni20Mo/HBETA. When 5Co20Mo/HBETA is used, it can further increase the full range naphtha to 52.2 wt%. 5Co20W/HBETA can further decrease the long residue to 6.6 wt%. Therefore, it can be concluded that modified Co catalysts can be used to produce the light oils with low contents of the heavy fractions. It is also found that, among all tested catalysts, 5Co20Mo/HBETA is the best catalyst for the full range naphtha production.

### 4.2.2 Reducibility of modified Co catalysts and metal-metal interaction

TPR profiles of the modified Co/HBETA catalysts, 10%Mo/HBETA, and 10%W/HBETA are shown in Figures 4.19 and 4.20

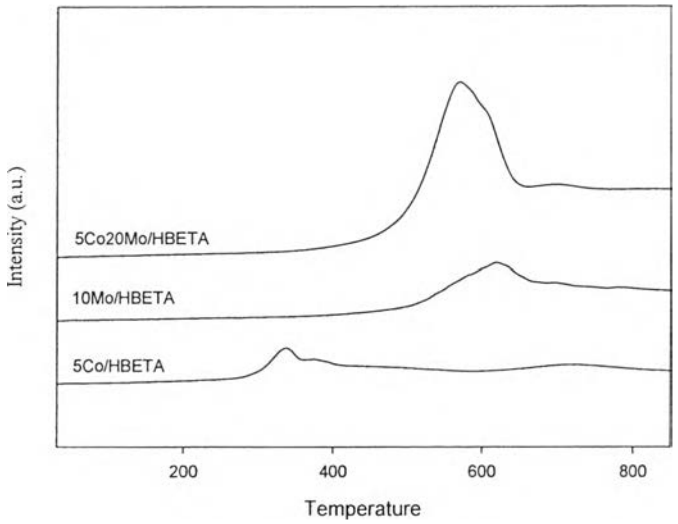

**Figure 4.19** TPR profiles of various modified Co/HBETA catalysts, 10Mo/HBETA, and 5Ni20Mo/HBETA.

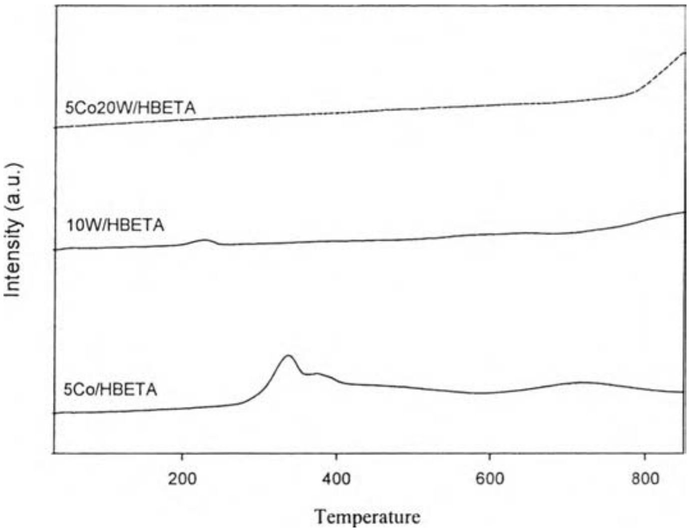

**Figure 4.20** TPR profiles of various modified Co/HBETA catalysts, 10W/HBETA, and 5Ni20Mo/HBETA.

| | Peak (°C) |
|---|---|
| 5Co | 337 |
| 10Mo | 620 |
| 10W | 850 |
| 5Co20Mo | 568 |
| 5Co20W | ➢ 850 |
| 5Ni20Mo | 580 |

**Table 4.2** Reduction peaks of modified Co/HBETA catalysts in comparison with those of 10Mo/HBETA, 10W/HBETA and 5Ni20Mo/HBETA.

Table 4.2 shows the temperature programmed reduction of modified Co catalysts having 10%wt of Mo and W in comparison with those of 5Ni20Mo on HBETA. 5%wt of Co has the reduction peak at 337 °C whereas 5Co20Mo/HBETA has the reduction peak at 568 °C, which means that 5Co20Mo/HBETA exhibits the strong interaction between Co and Mo similar to the peak obtained from 5Ni20Mo/HBETA. For 5Co20W/HBETA, there is no peak at the temperature below 850 °C, but the peak seems to appear at a temperature of higher than 850 °. Referred to the previous results that the pyrolytic oil obtained from 5Co20W/HBETA has high quality and quantity; therefore, it can be suggested that 5Co20W/HBETA has a reduction peak at a temperature of higher than 850 °C, which shows the strong interaction between Co and W.

### 4.2.7 Desulfurization ability

#### *4.2.7.1 Sulfur distribution*

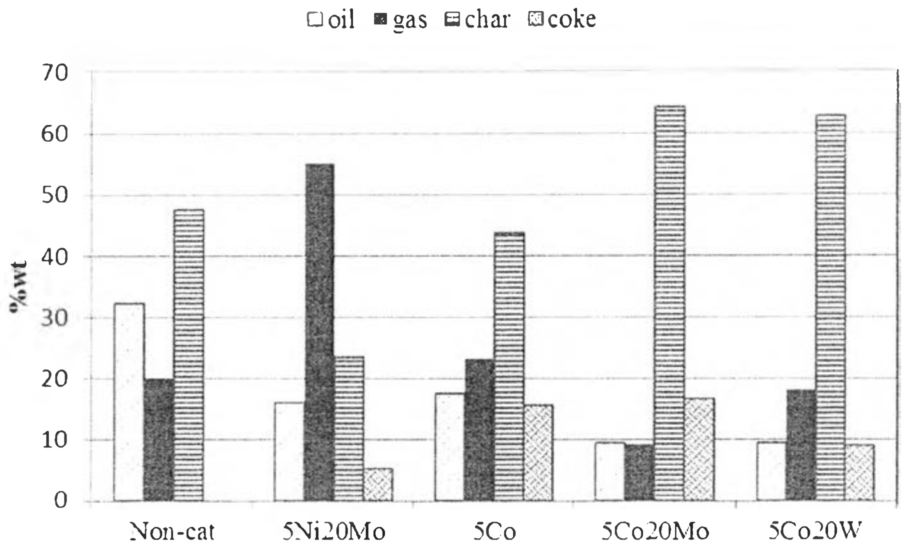

**Figure 4.21** Sulfur distribution in the pyrolytic products obtained from using modified Co catalysts on HBETA zeolite.

Figure 4.21 illustrates the sulfur distribution of the pyrolytic products obtained from modified Co catalysts as compared with that of 5Ni20Mo/HBETA and the non-catalytic case. From the result in Section 4.1.4.1, it has been shown that 5Ni20Mo/HBETA had the greatest desulfurization ability among the other modified Ni catalysts since it has the highest sulfur distribution in the pyrolytic gas. However, for this case when modified Co catalysts are used, the sulfurs are mainly distributed in char whereas the distributions of sulfur in oil and gas decrease. 5Co/HBETA gives the highest sulfur distribution in gas among the other modified Co catalysts. When the bimetallic catalysts are used, the sulfur distributions in oil and gas further decrease with the increase of the sulfur distribution in char and coke. It can be suggested that sulfur compounds in the pyrolytic gas become heavier and then condense into the pyrolytic char after the catalytic reaction occurred.

### *4.2.7.2 Sulfur contents*

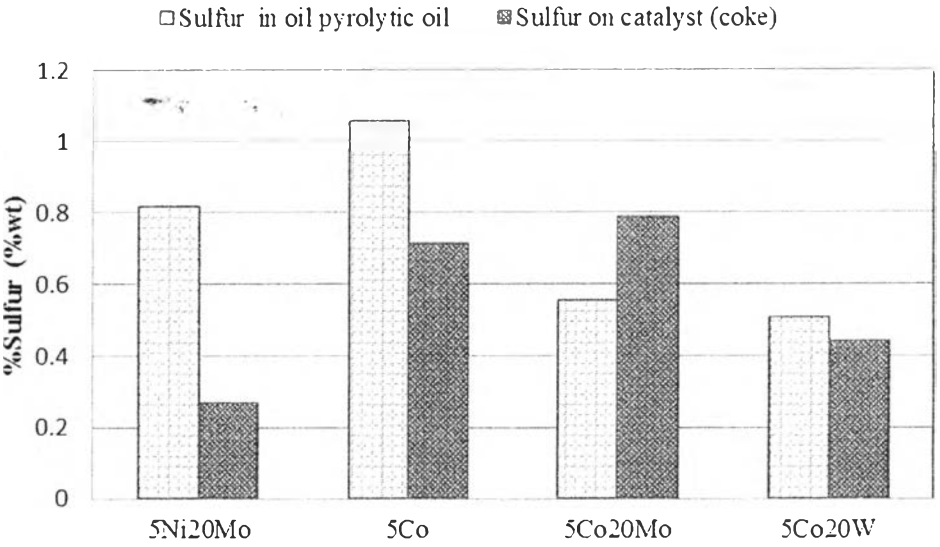

**Figure 4.22** Sulfur contents (%wt) on spent catalysts and in the pyrolytic oils obtained from modified Co catalysts.

Figure 4.22 shows the presence of sulfur contents obtained from modified Co/HBETA catalysts. The result shows that 5Co/HBETA and all of the modified Co/HBETA catalysts have the good hydrodesulfurization ability due to the decrease in sulfur content in the pytolytic oils when compared with the non-catalytic case. Using 5Co/HBETA can help to decrease the sulfur contents in pyrolytic oils from 1.36 (non-cat) to 1.06. When the bimetallic catalysts are used, the sulfur content in pyrolytic oils further decreases. The sulfur content in pyrolytic oils obtained from 5Co20W/HBETA is the lowest among that of the others, that is 0.51 wt%. However, the sulfur content on the spent modified Co catalysts (coke) is still higher than that on 5Ni20Mo/HBETA. Therefore, it can be concluded that the modified Co catalysts can produce high qualities of oils from waste tire pyrolysis that contain low sulfur contents, and it is found that 5Co20W/HBETA is the best catalysts for hydrodesulfurization due to the lowest sulfur content in pyrolytic oil.

*4.2.7.3 Type of sulfur compounds*

From the previous result, the bimetallic Co/HBETA catalysts showed good potential to produce high qualities and quantities of the pyrolytic product; for examples, the pyrolytic oil obtained from 5Co20Mo/HBETA and 5Co20W/HBETA are mainly in the full range naphtha with a low sulfur content. In this part, the sulfur compounds and the sulfur distribution in petroleum fractions were examined to investigate the effect of the second promoters and the catalysts.

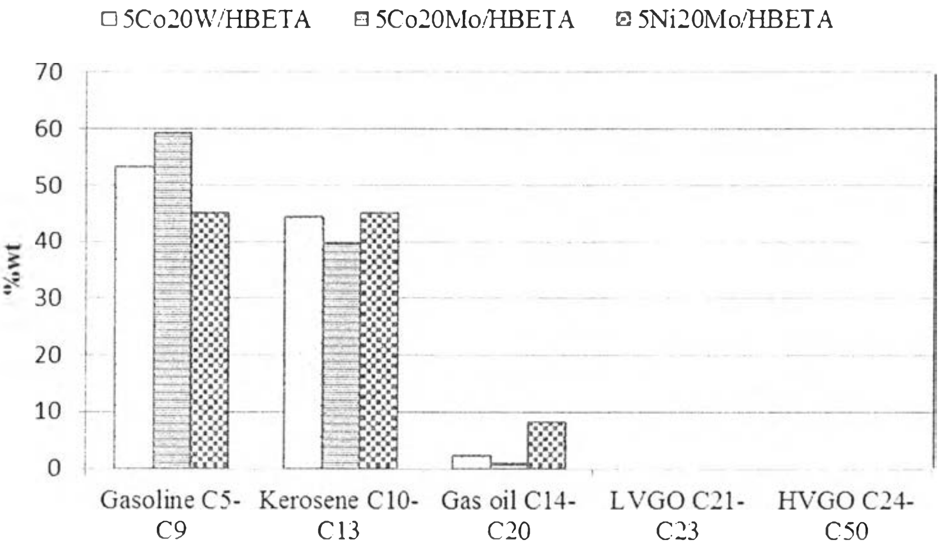

**Figure 4.23** Sulfur distribution in petroleum fractions obtained from 5Co20Mo/HBETA and 5Co20W/HBETA in comparison with 5Ni20Mo/HBETA.

Figure 4.23 illustrates sulfur distribution in petroleum fractions obtained from bimetallic Co/HBETA catalysts as compared with that of 5Ni20Mo/HBETA. It was found that there is no sulfur compound with the carbon numbers higher than 20; therefore, there is no sulfur compound in the heavy fractions (LVGO and HVGO). Furthermore, the sulfur compounds obtained from the bimetallic modified Co catalysts are mainly distributed in the light fractions (gasoline and kerosene). It can be suggested that using 5Co20Mo/HEBTA and 5Co20W/HBETA, it is likely that the sulfur compounds in heavy fractions are converted into the smaller molecules distributed in the light fractions. The results also show that the sulfur compounds obtained from 5Co20Mo/HBETA and

5Co20W/HBETA are mainly distributed in the gasoline range such as thiophene, 2,5-diethyl-, 2-ethyl-5-propyl-, and benzo[b]thiophene whereas the sulfur compounds from 5Ni20Mo/HBETA are mainly distributed in the kerosene range.

From the results, it can be suggested that HBETA zeolite helps to promote cracking ability, which can convert heavy products to light products as observed from the increase of full range naphtha with the decrease of long residue. When the monometallic catalysts were used, it was found that Ni and Co can help to promote hydrogenation and ring-opening because they enhance the quality of the oils by decreasing poly- and polar aromatics and then increasing saturated hydrocarbons and mono-aromatics. The modification of Ni/HBETA and Co/HBETA with Mo and W significantly increase the desulfurization activity due to the desulfurization ability of Mo and W. It was observed that both Mo- and W- modified Ni/HBETA and Co/HBETA can increase the qualities and quantities of the pyrolytic products, indicating that they have better hydrogenation and hydrodesulfurization abilities than the monometallic (Ni/HBETA and Co/HBETA) due to the strong interaction between the two metals.