CHAPTER IV
RESULTS AND DISCUSSION

This chapter discusses about the effects of noble metal (Rh) and non-noble metals (Ni and Co) with various metal loading supported on KL zeolite and then the effect of bimetallic catalysts (Rh-Ni/KL and Rh-Co/KL) on the qualitative and quantitative of pyrolysis products.

4.1 Effect of Monometallic Catalysts

4.1.1 Effect of 1%Rh Supported on KL Catalyst

This section discusses about the investigation of Rh supported on KL zeolite in the catalytic pyrolysis of waste tire. 1%wt of Rh was loaded on KL zeolite by the mean of incipient wetness impregnation. The influence of supported noble metal, Rh/KL, is discussed as follows.

Figure 4.1 illustrates the product distribution obtained from the use of 1%Rh/KL in the pyrolysis process which includes the results from using non-catalyst and pure KL cases for comparison purpose. The result shows that the presence of KL provides an increase in the gaseous fraction as compared to the non-catalytic pyrolysis. As expected, 1%Rh/KL catalyst results in an increment of gas yield in accordance with a decrease in the yield of liquid product. This result is attributed to the reason that heavy compounds can be attached to the metal sites leading to easier decomposition into lighter compounds. Because the same condition in all experiments was conducted, almost constant in solid yields are observed at around 43%.
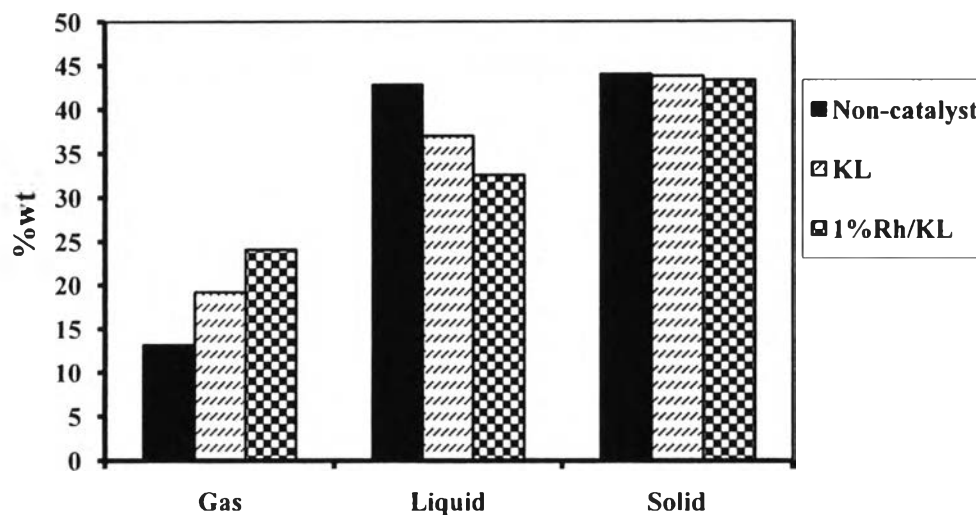
Figure 4.1 Product distribution obtained from pyrolysis using 1%Rh/KL.

The effect of Rh/KL catalyst on gas compositions can be explained by Figure 4.2. It is shown that the role of Rh loaded on KL has the impact on light hydrocarbons; C1, C2, C3 and C4s. Namely, slight increases in C1 as well as C2 and C3 are observed as compared to using KL zeolite. Meanwhile, the amount of unsaturated light hydrocarbons, C2= and C3=, is decreased with using the treatment of 1%Rh/KL. Berrueco et al. (2005) reported that tire is mainly composed of the rubbers which are polybutadiene and polybutadiene-styrene (SBR). Therefore, light hydrocarbon gases from pyrolysis mostly consist of C1 and C4s as the predominant products, which is in agreement with the observed result as well. However, the presence of Rh results in a decrease in C4s, which might be due to the reason that it is converted to lighter gas like C1. There are several types of reaction take place in the pyrolysis especially decomposition reaction at an elevated temperature which lead to the formation of the fragment of a molecule and free radical species. During pyrolysis, the presence of H free radical as reactive species can also be formed and then intermediately adsorbed on the active site of catalysts which further undergo the reaction involving H transfer such as hydrogenation and hydrogenolysis. It was found that Rh has the ability in C-C bond breaking at terminal positions and also ability in hydrogenolysis leading to methane formation (Teschner et al., 2000). In

addition, it is worthy mentioned that this metal exhibits activity in hydrogenation reaction, which can be explained by the hydrogenation of unsaturated light hydrocarbons, C2= and C3=, resulting in a slight increase in hydrogenated products like C2 and C3. However, the gas yield obtained by using Rh/KL is higher than the use of KL alone, which causes a slight increase in C1 as well as C2= and C3= yields and a significant increase in the yield of C2 and C3 as can be seen in Appendix C1.
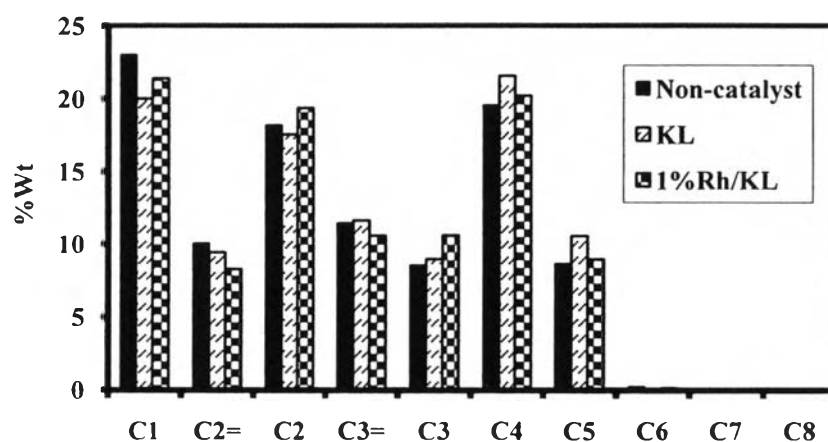

Figure 4.2 Gas composition obtained from pyrolysis using 1%Rh/KL.

Figure 4.3 shows the simulated distillation of maltene which were cut, according to the boiling points, into full range naphtha (<200°C), kerosene (200-250°C), gas oil (250-370°C) and long residues (>370°C) (Dũng *et al.*, 2009). As observed, the derived oil from the non-catalytic pyrolysis are mainly distributed in the range of gas oil. The use of KL results in the conversion to a range of lighter fractions, especially naphtha. The introduction of 1%Rh/KL causes an increase in gas oil with a subsequent decrease in naphtha fraction. It might be ascribed that Rh/KL does not promote cracking of heavy liquid products into lighter one distributed in a range of naphtha fraction.
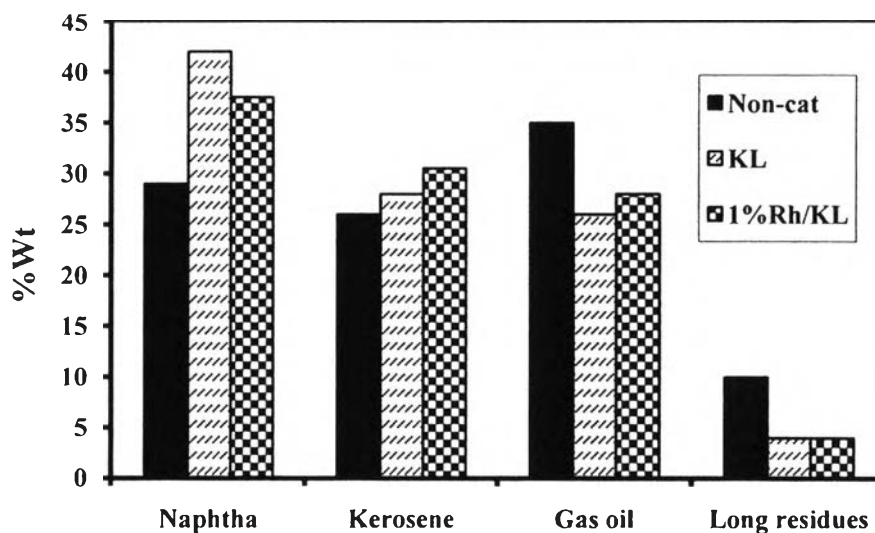
Figure 4.3 Effect of 1%Rh/KL on petroleum fractions.

Fractionations of maltene into chemical classes via the mean of liquid column chromatography are shown in Figure 4.4. It reveals that the presence of pure KL results in an increase in the concentration of saturated hydrocarbons and single-ring aromatic compounds accompanied by a decrease in multi-ring aromatic compounds. When 1%Rh was loaded on KL, the saturate content is slightly increased, and the great amount of mono-aromatics is observed with a consequent lower di- and poly aromatics content compared to KL. It has been reported that oil aromaticity is formed by the aromatization of alkene such as C2=, C3= and butadiene produced during tire pyrolysis (Cypres *et al.*, 1987). Then, these compounds are converted to cyclic alkene via cyclisation followed by the dehydrogenation of six carbon atoms to form simple aromatic compounds and subsequent condensation reactions to form higher poly-aromatics by Diels-Alder reaction, resulting in high C1 and H_2 contents as by products. Moreover, they also reported that at high temperatures, light olefins generated by the deep decomposition of heavier fractions could combine with butadiene to form aromatics and then form high molecular-weight poly-aromatic species by some further reactions of aromatics combined with olefins. It is widely known that mono-aromatic hydrocarbons have attracted interest in petrochemical industries whereas the presence of poly-cyclic aromatic hydrocarbons is disadvantageous in the view of fuel application and hazardous

chemicals. As one can see from the result, the introduction of Rh plays a major role on the formation of mono-aromatic compounds in accordance with the reduction in concentration of multi-ring aromatics. It was noted that Rh metal showed activity in hydrogenation and/or ring opening of hydrocarbons (Albertazzi *et al.*,2003) while the basic property of KL has shown effect on aromatization reaction (Wakui *et al.*, 1999). For base-catalyzed reaction, it is found that the reactants can act as acid toward catalyst which act as base. KL zeolite which is base catalyst also shows the same activity as explained above. It can abstract H^+ from reactants to form cabanion species and subsequently react with intermediate compounds to form products by several reactions such as isomerization, aromatization and alkylation. For ring-opening reaction, there was no report about the ability of basic catalyst in C-C bond cleavage thus the influence of metal site in those ability is dominant in this study. It can be assumed that the hydrogenation of poly-aromatics on active site of Rh is the predominant reaction followed by ring opening reaction which leads to a decrease in poly-aromatic compounds. Additionally, it was found that the hydrogenation of poly-cyclic compound is easier than that of single ring aromatics (Corma et al., 1997). This is the reason why the mono-aromatics content continues to increase as the catalysts is applied.
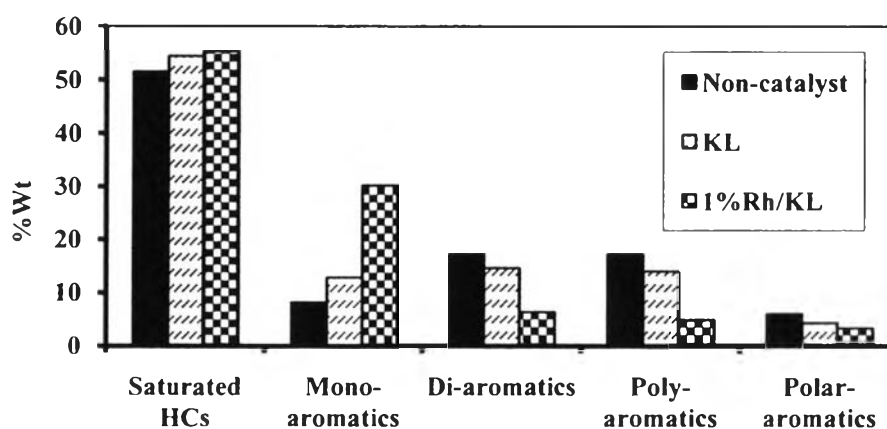

Figure 4.4 Chemical composition in maltene obtained from using 1%Rh/KL.

Moreover, the presence of Rh/KL also results in a slight decrease in the concentration of polar-aromatics compared to non-catalytic and pure KL case. It is proven that polar-aromatics found in waste tire pyrolysis is mostly aromatics

containing a sulfur because oxygen is not allowed in the pyrolysis (Williams *et al.*,1994). Dũng *et al.*, 2009 studied the formation of polar-aromatics in waste tire pyrolysis, and proposed the ways the fraction can be formed. They reported that polar-aromatics can be formed by the combination of olefins with free sulfur or sulfur-containing compounds by Diels-Alders reaction. Moreover, the direct cracking of tire molecules at linked sulfur positions can be occurred. However, the presence of a catalyst can reduce the polar-aromatic formation by the hydrogenation of olefins and unsaturated hydrocarbons to other intermediate products. The reduction in polar-aromatic compounds, when Rh/KL is present, could be attributed to high activity in the hydrogenation property of Rh and the ability in C-S-C bond breaking in the oil molecules. This result is well consistent with the amount of sulfur contents in the oil detected by the elemental analysis technique, which shows the reduction in sulfur with using Rh. It is clearly seen from Appendix H1 that the use of KL and 1%Rh loaded on KL helps decrease sulfur content in the oil by approximately 36 and 75%, respectively, as compared to the non-catalytic case. Additionally, the amount of coke and sulfur deposition on spent Rh/KL catalyst in Appendix G1 is found higher than using KL alone. These results might be the higher activity for Rh catalyst in polar-aromatics reduction as well as sulfur-containing compound in oil which are either cracked or condensed leading to coke formation. However, these phenomena can cause the catalyst deactivation due to the loss of active sites which is resulted from the formation of aromatic/polymeric type of carbon deposited on Rh and sulfur adsorbed on Rh sites. (Lakhapatri et al., 2009)

4.1.2 Effect of Ni and Co Catalysts with Varying Metal Loading

The catalytic pyrolysis of waste tire was conducted with the two non-noble metals, Ni/KL and Co/KL (1, 5, 10, 15 and 20%wt). All were prepared by incipient wetness impregnation technique. The influence of the catalysts on pyrolysis products is discussed as follows.

The product distribution can be explained by plotting the liquid to gas ratio (L/G) as shown in Figure 4.5, which shows the L/G ratio from the non-catalytic, pure KL zeolite, and catalytic cases. The results show that pyrolysis with using the catalysts gives lower L/G ratio than the non-catalytic case, which is due to the fact

that the active sites are available for secondary reactions leading to the reduction of the oil fraction and a consequent increase in the gaseous fraction. From Figure 4.5, a slight decrease in the ratio is found in the increment of Ni loading from 1 to 15% supported on KL zeolite, and then the ratio is slightly increased when using 20%Ni. It can be suggested that the use of high Ni loading provides ability in gas production. On contrary, only 1%wt of cobalt loading produces the highest amount of gas product as can be seen from the lowest L/G ratio in Figure 4.6, and subsequently it starts to increase with increasing metal loading up to 15%wt. followed by a drop in the ratio when 20%Co is used. Meanwhile, 5% and 10%wt of both nickel and cobalt catalysts show the similar result to KL zeolite alone. It can be suggested that the catalysts used in waste tire pyrolysis play an important role in the product yields because of their unique properties promoting the remarkable results.

Furthermore, no significant difference in solid fraction (around 43%wt.) from pyrolysis with and without catalysts is found, which is resulted from the complete decomposition of tire in the process at 500°C.
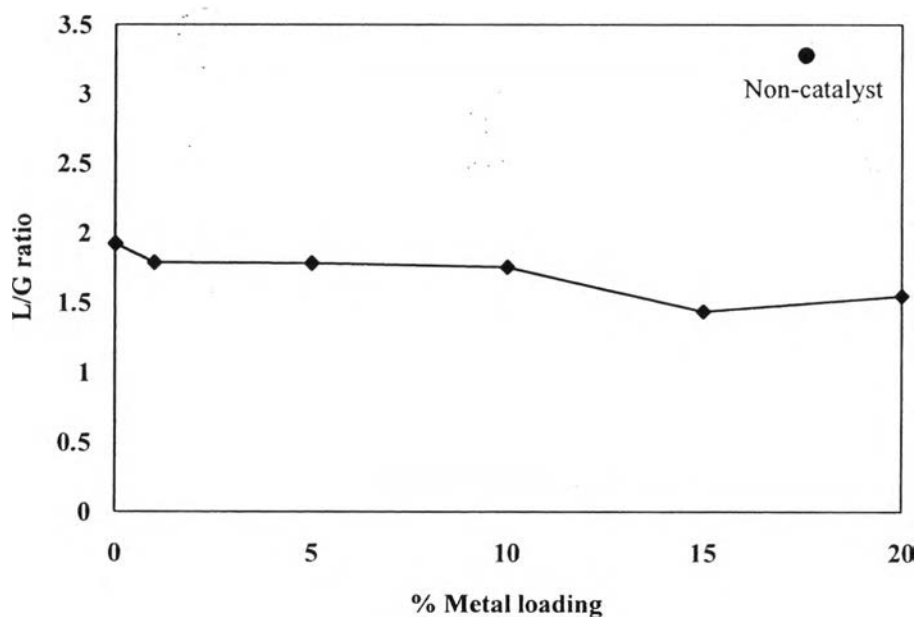

Figure 4.5 L/G ratio obtained from pyrolysis with using various %Ni loading on KL zeolite.
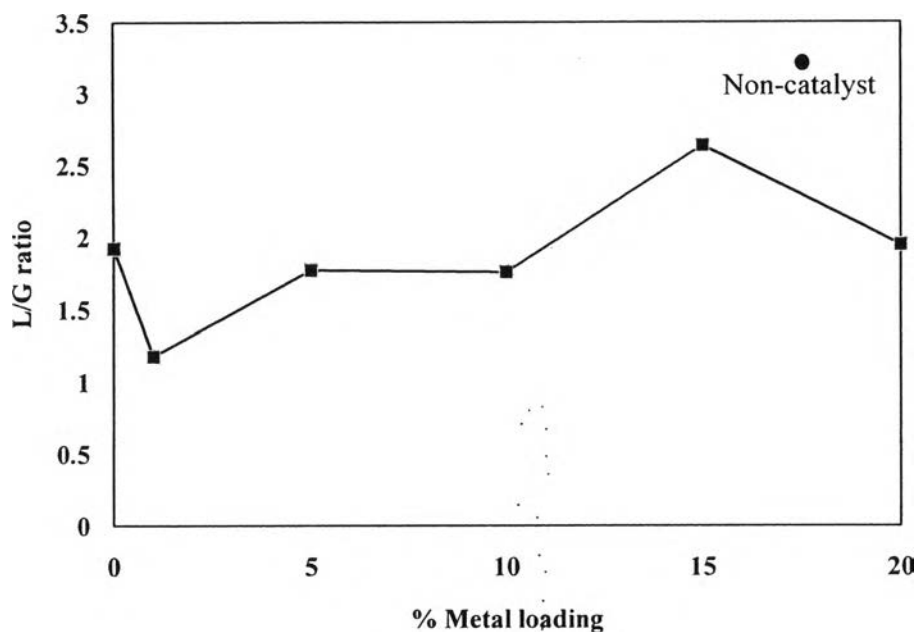
Figure 4.6 L/G ratio obtained from pyrolysis with using various %Co loading on KL zeolite.

As observed above, the presence of catalysts resulted in an increase in the gaseous fraction at the expense of liquid fraction compared to non-catalytic case. From Appendix C2, the use of pure KL zeolite gives the higher gas yield than using no catalyst. The presence of Ni loaded on KL zeolite causes a significant increase in the gas yield as high Ni contents up to 15% loading is used. Namely, the production of light hydrocarbons such as C1, C2, C3 and C4 is likely to increase in yields, which is worthy mentioned that the high amount of Ni could promote cracking ability of high molecular weight materials into low molecular weight products. In contrast, as low as 1%Co loading on KL exhibits the highest performance in gas production since it shows the maximum yield of all light hydrocarbons as compared to the other catalysts. However, further increasing Co content supported on KL zeolite resulted in a decline of gaseous fraction as can be seen from Appendix C3.

Light olefins, which is the important chemical feed stock in petrochemical industry, is also found in the pyrolysis products. Figure 4.7 demonstrates the effect of various metal loadings of Ni and Co supported on KL zeolite on the formation of light olefins consisting of ethylene and propylene. The

result shows that among loaded Ni catalysts, 15% Ni loading gives the highest yield to total light olefin production but not as much as the cases of cobalt catalysts, which show the highest amount of light olefins when 1%wt Co is used in the process. Similarly, 1%wt Co/KL catalyst seems to be a good catalyst for cooking gas production because it provides the highest yield of cooking gas, which is hereby composed of propane and mixed-C4, as can be seen from Figure 4.8.
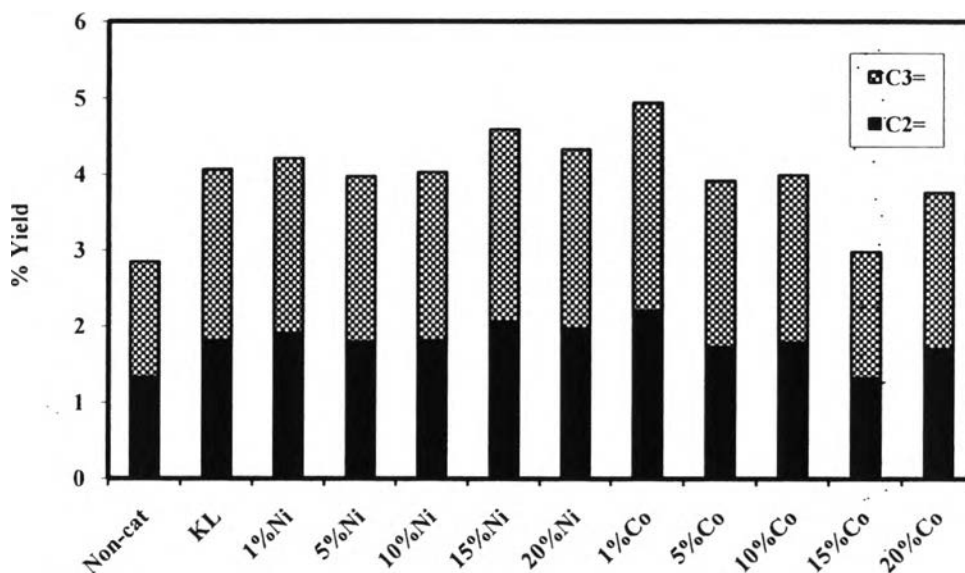

Figure 4.7 Yield of light olefins obtained from pyrolysis with using various metal loading.
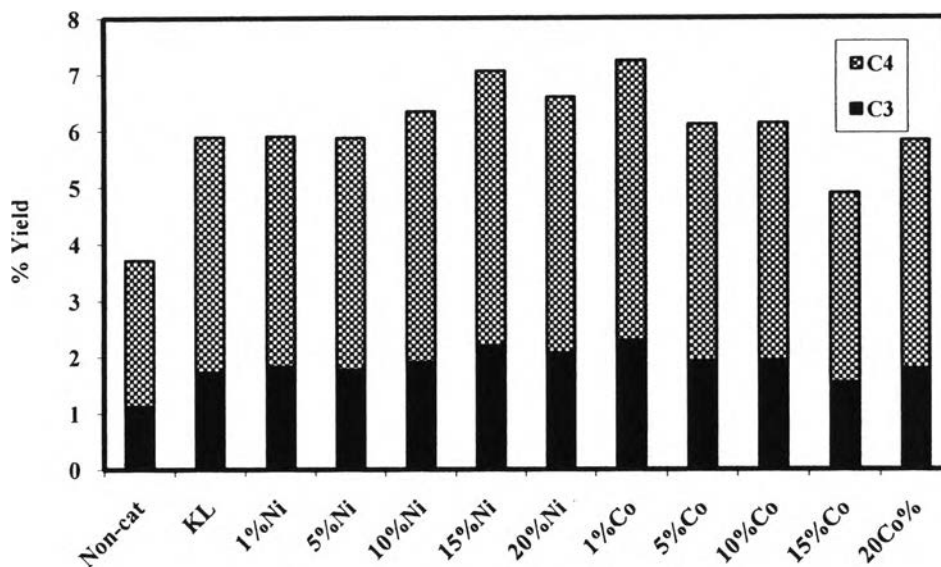
Figure 4.8 Yield of cooking gas obtained from pyrolysis with using various metal loading.

The chemical compositions in maltenes were analyzed via liquid chromatographic separation using specific solvents to obtain saturated hydrocarbons, mono-aromatic, di-aromatics, poly aromatics and polar-aromatics. The result from Figure 4.9 shows that the presence of catalysts results in the reduction in poly-aromatics content in maltene with the increment of mono-aromatics as compared to the non-catalytic case. In the case of Ni supported on KL zeolite, it is found that the higher loading, the lower multi-ring aromatics content is obtained, leading to the increase in mono-aromatics. However, this assumption cannot support the case of 15%Ni which shows rather high poly-aromatics content. Due to the complex mixture of passenger tire, there are several reactions which might occur in the pyrolysis such as Diels-Alders reaction, aromatization, cracking and hydrogenation (Dũng et al., 2009). As observed above, a high metal loading, especially 20%Ni, significantly affects the amount of mono-aromatics. The high amount of metal loading has high tendency to locate both outside and inside the zeolite structure. As a result, these active sites are accessible for multi-ring aromatics produced from tire pyrolysis and these compounds then rapidly undergo further reaction on the basic site of KL zeolite. Additionally, a high Ni content is likely to provide the slight reduction in

saturated hydrocarbons. These results might be ascribed to the terminal C-C bond breaking ability of Ni metal which was reported by Kikuchi *et al.* (1970). It can be explained that the saturates might be further cracked at the terminal C-C bond via hydrogenolysis reaction and then formed light hydrocarbons such as C1 and C2. By this assumption, Ni cluster might be formed, promoting the cracking ability of heavy fraction to gaseous or lighter fractions.

Because polar-aromatic species are present, mostly as sulfur-containing aromatics, it can be explained using the result of sulfur analysis in derived the derived oils as shown below. Elemental analysis shows that the sulfur content in waste tire is about 1.4%. It is clearly seen that the incorporation of Ni on KL zeolite influents the reduction in sulfur in the derived oil by approximately 47-71%. Similarly, Park *et al.*,2008 studied the reactive adsorption of sulfur on supported Ni catalysts for sulfur removal form diesel. They reported that the one-dimensional pore structure of support was more preferable for sulfur diffusion than the three-dimensional one. At this point, sulfur-containing compounds can be removed by strong bonding between metal and sulfur atom leading to sulfur deposition on the spent catalysts as can be seen in Appendix G1. These results show that the use of bifunctional catalysts give similar coke content compared to using pure KL alone. Phopaisarn *et al.* (2009) studied the effect of basic and acid zeolites, which are KL and Y respectively, on waste tire pyrolysis. They found that acid property of Y zeolite have influence on the formation of coke more than KL zeolite which exhibited higher amount of coke deposition on spent catalysts for Y zeolite than KLcatalyst. It can be implied that the lacking of acid sites results in a little effect on coke deposited on the catalysts. However, it was reported that coke deposition can deactivate the active sites by many mechanisms such as encapsulation of a metal particle, deposition in pore and blocking of the entrance to metal surface sites by chemisorptions as a monolayer or physisorption in multilayers. In addition, the formation of aromatic and unsaturated species as a precursor have tendency to increase the coke formation on the surface leading to catalyst deactivation. These could explain the case of 15%Ni/KL, which exhibits the higher concentration of poly and polar-aromatics than the other Ni/KL catalysts. It might be possible that

15%Ni/KL catalyst is deactivated by the condensation of poly-aromatics and bonding with sulfur at the surface, leading to rather high coke and sulfur deposition.
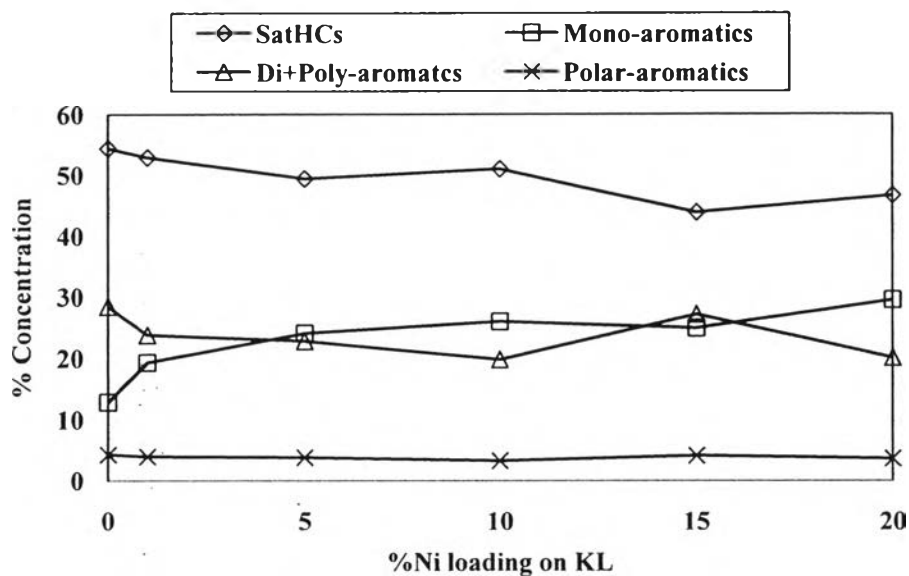

Figure 4.9 Chemical composition in maltene obtained from using varied %Ni loading on KL.

The fractionated liquid products obtained from the use of Co loaded on KL catalysts apparently exhibit high mono-aromatics contents in the maltene fractions in conjunction with a decrease in multi-ring aromatic compounds. As one can see in Figure 4.10, the amount of Co loading affects the content of aromatics. Namely, considerable mono-aromatics are increased in concentration as increasing Co content from 1 to 10%. Consequently, a slight drop in the concentration is observed with a higher loading, but it is insignificantly different. A fluctuation of saturated hydrocarbons is found due to the presence of Co/KL; however, it shows a slight decrease, as compared to using KL alone, when a higher loading is used. As mentioned previously, many reactions take place in the pyrolysis, including aromatization via Diels-Alders reaction by the combination of olefins produced from thermal cracking, which leads to the increases in aromatic hydrocarbon compounds; mono-, di-, poly- and polar-aromatics. However, multi-ring aromatic species are limited in petrochemical uses because they are quite useless. The way to get rid of these species is to convert them to mono-aromatic compounds, which are valuable chemicals. At this point, multi-ring aromatic species can be transformed to single-

ring aromatics by the presence of catalyst providing the ability in hydrogenation and ring opening. As shown in Figure 4.10, Co/KL plays an important role in the increment of mono-aromatics in association with the reduction in di- and poly-aromatics. These results could be explained that the available active sites of Co can promote hydrogenation activity to hydrogenate multi-ring aromatic compounds to other products with a subsequent ring opening reaction involving C-C bond breaking. In addition, the hydrogenation of mono-aromatics is not preferred (Corma *et al.*, 1997). Thus, the increment in mono-aromatics is obviously detected rather than in saturated hydrocarbons. Moreover, the similar concentrations of polar-aromatics are observed except using high Co content, which can be suggested that the low Co loading insignificantly affects the reduction in aromatics containing sulfur. Moreover, it is found from Appendix G1 and H1 that increasing Co concentration leads to the reduction in sulfur compound in derived oil with subsequently high amount of sulfur deposition on spent catalysts suggesting the high C-S bond breaking ability with high loading.
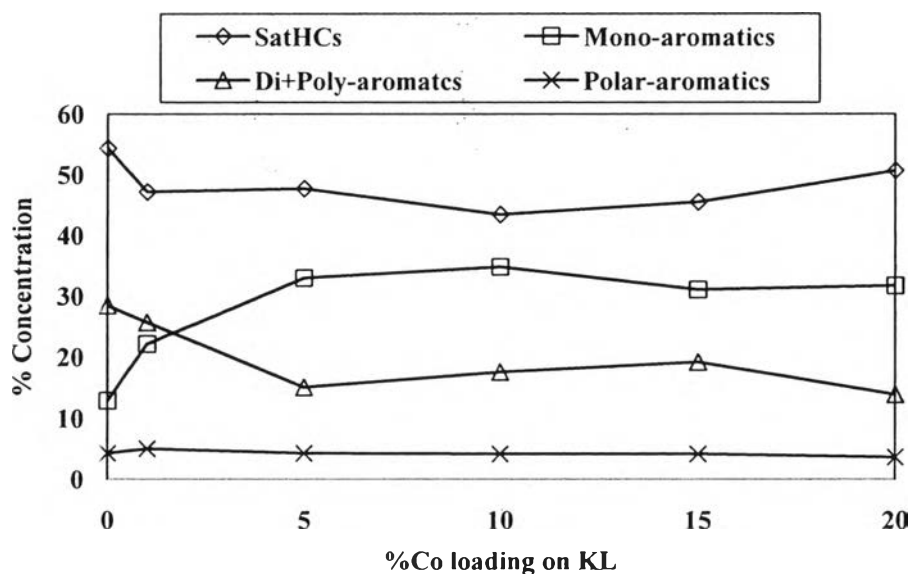

Figure 4.10 Chemical composition in maltene obtained from using varied %Co loading on KL.

The oil products obtained from waste tire pyrolysis are separated into maltene fraction and then further analyzed by using a SIMDIST Gas Chromatography (SIMDIST). The analyzed maltene are cut into 5 fractions

according to their true boiling point range, 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) (Dung et al., 2009). From Figure 4.11, it can be seen that the light fractions such as naphtha, kerosene and light gas oil are increased with using KL zeolite alone whereas the heavy fractions such as heavy gas oil and long residue are decreased as compared to the non-catlytic case. It is possible that the catalysts are available and prolong the reaction for the the reactants to be decomposed to light fractions. The presence of Ni supported on KL has the impact on petroleum fraction. Namely, 1%Ni content results in the reduction in naphtha fraction and the subsequent increase in gas oil fraction. It can be suggested that the introduction of Ni loaded on KL catalysts cause a dramatic decrease in naphtha content. The greater addition of Ni content can only help to bring back naphtha content with the reduction in gas oil fraction while kerosene contents are slightly different. It is likely that the gas oil fraction is converted to lighter fractions, especially naphtha, with using high Ni loading.
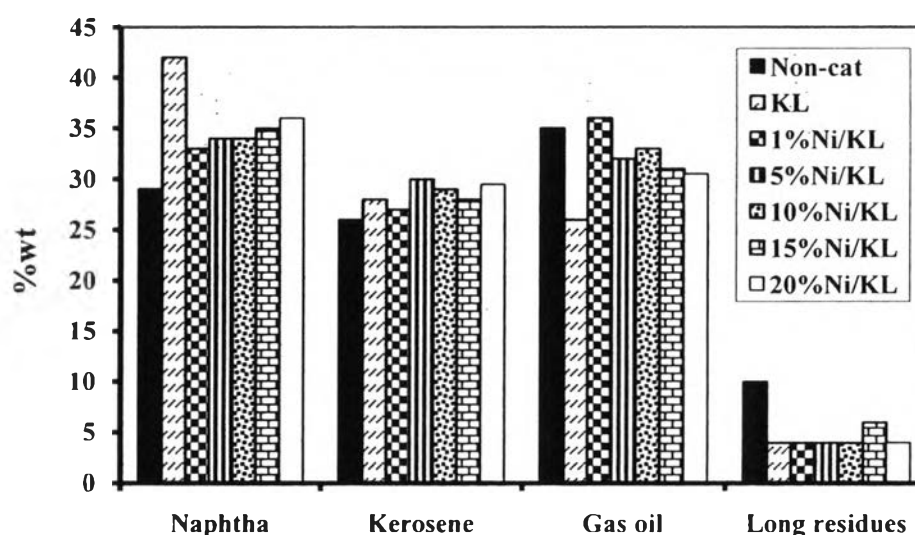

Figure 4.11 Effect of varied %Ni/KL on petroleum fractions

Figure 4.12 illustrates that the introduction of 1%Co loaded on KL exhibits higher gas oil at the expense of naphtha content as compared to KL. Among the loaded Co catalysts, 5% Co gives the maximum content of light fractions; naphtha and kerosene. It is likely that further addition of Co loading change the

distribution to a range of heavy fractions; gas oil and long residues. It can be suggested that the activity of in cracking of heavy liquid product, to some lighter is suppressed when a high Co loading is used.
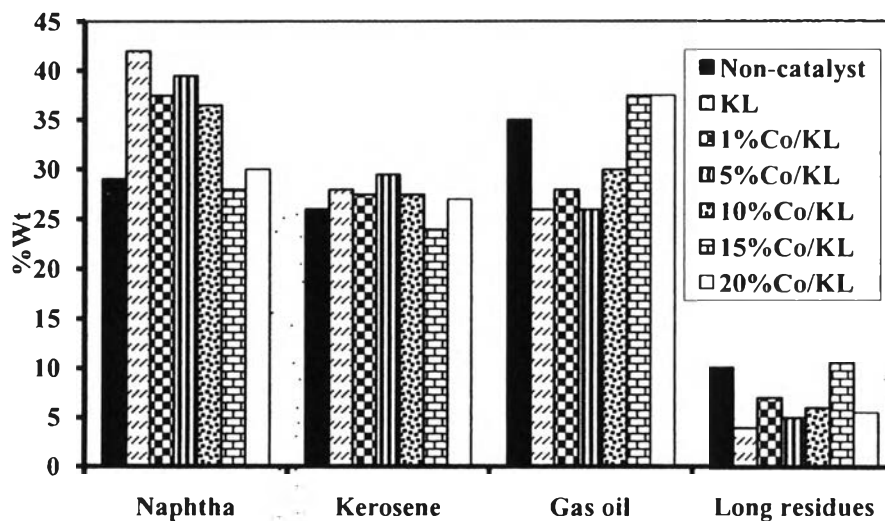

Figure 4.12 Effect of varied %Co/KL on petroleum fractions.

4.1.3 Mono-aromatics from Using Noble and Non-noble Metals

Among fractionations of chemical compositions, mono-aromatic fraction gains greatest attention due to their valuable chemicals. Thus, it is worthy to point out the formation of mono-aromatic compounds which are considerably produced from the catalytic pyrolysis especially from the present study. There have been reported that there are various mono-aromatic species can be produced from the decomposition of tire such as benzene, toluene, xylene and their alkyl-substituted compounds which have ability to compete with the chemical substances produced from refining. The influence of catalysts on the production of them can be further depicted from carbon number distribution shown in Figure 4.13(a-d). Figure 4.13a indicates the distribution curve of mono-aromatics fractionated from liquid adsorption chromatography. It is observed that the non-catalytic oil has very broad and wide distribution peak, which is mainly located in the range of C15-C25. The presence of KL zeolite shows a narrower peak which tends to shift to a low carbon number. The further shift of peak to a lower carbon number with a tall peak is observed when 1%Rh is incorporated into KL zeolite. This trend suggests that the

use of supported Rh results in the formation of lighter single-ring aromatic compounds. Figure 4.13b exhibits the distribution curve of using Ni supported on KL with varying metal contents. It is found that all of loaded Ni catalysts have a shift of the peak to a lower carbon numbers compared to KL alone. Additionally, increasing Ni loading tends to shift the peak to lower carbon numbers. Particularly, 20%Ni results in the highest and narrowest peak among loaded Ni catalysts, which suggests the formation of single- aromatics with the lowest molecular weight. In the case of Co supported KL catalysts, it is obviously found from the previous results that the introduction of Co significantly affects the increment of mono-aromatics concentration with increasing Co content from 5-20%. Figure 4.13c shows that the peak of using 1%Co shift back to a higher carbon number compared to KL. Consequently, increasing Co concentrations cause the shift of peaks to a lower carbon number. The peak which reaches the smallest carbon number corresponds to using 5%Co/KL with the average carbon number of around 14.6, whereas the highest peak among Co catalysts belongs to the use of 10%Co/KL whose the average carbon number is 15.8. The tall peak of the latter results from its narrower distribution of carbon number, which are mainly located in the range of C12-C16. The shorter peak of using 5%Co/KL refers to the wider distribution of carbon number, which are in the range of C10-C15.

Figure 4.13d illustrates the comparison of carbon number distribution obtained from using noble and non-noble metals for the investigation of ability in the mono-aromatics production. In addition, the compounds of mono-aromatic hydrocarbons found in the pyrolytic oil are shown in the figure as examples, and the average carbon number are also given for comparison purpose. From the figure, the 5%Co and 1%Rh are comparable in terms of average carbon number and the shift of peak to low carbon number, which reaches to the smallest carbon number of around C6-C8 corresponding to benzene, toluene and xylene for instances. Moreover, using 20%Ni also gives similar average carbon number, but shows a lower trend of carbon number with the highest peak indicating that they are mostly located in a narrower distribution of around C14. Table 4.1 shows the concentration of light mono-aromatics which are distributed in the range of C6-C11 obtained from this study as examples. These carbon number ranges are expected to be comparable with the

useful mono-aromatics from petrochemical industry. The activity in mono-aromatics production can be ranked in the order; 5% Co > 1%Rh >20%Ni. However, the identification of the compounds is limited so the further study is needed in order to specify the type of species.
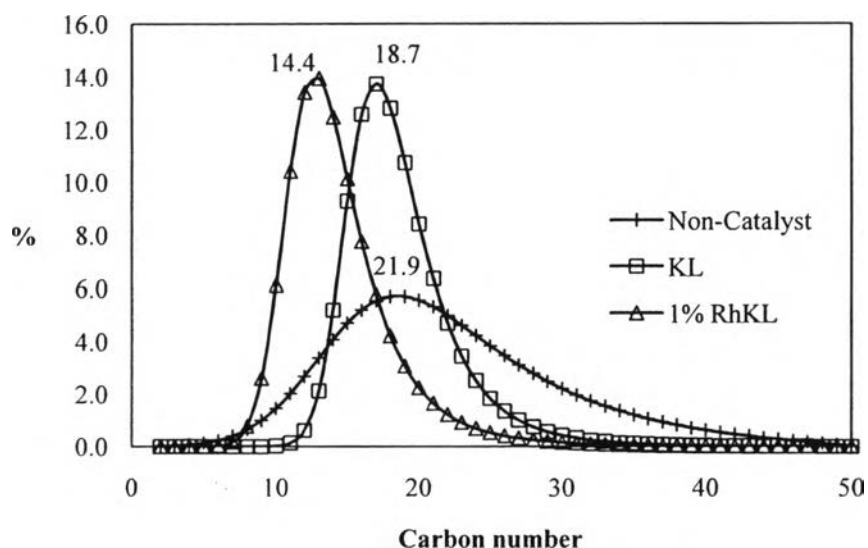

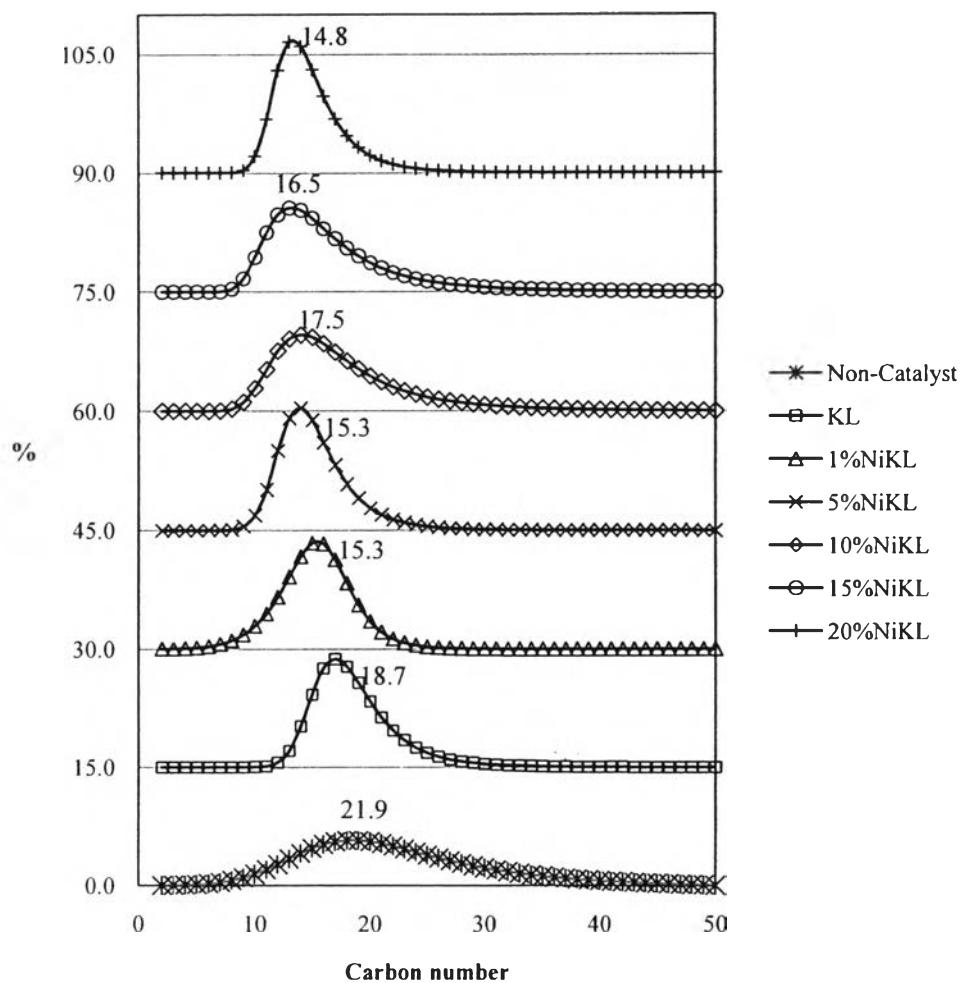**Figure 4.13(a)** Carbon number distribution of mono-aromatics using 1%Rh/KL.

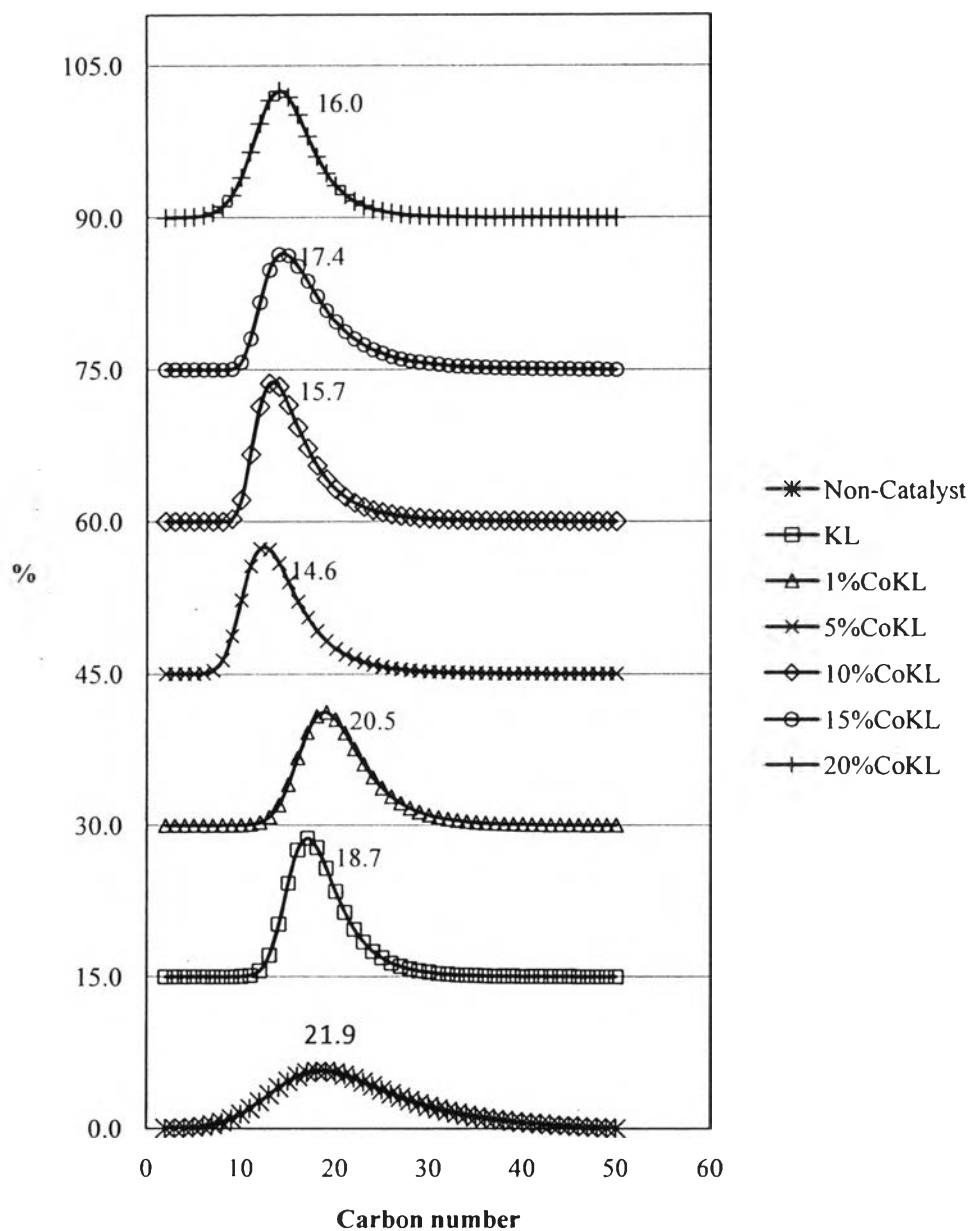**Figure 4.13(b)** Carbon number distribution of mono-aromatics using varied %Ni/KL.

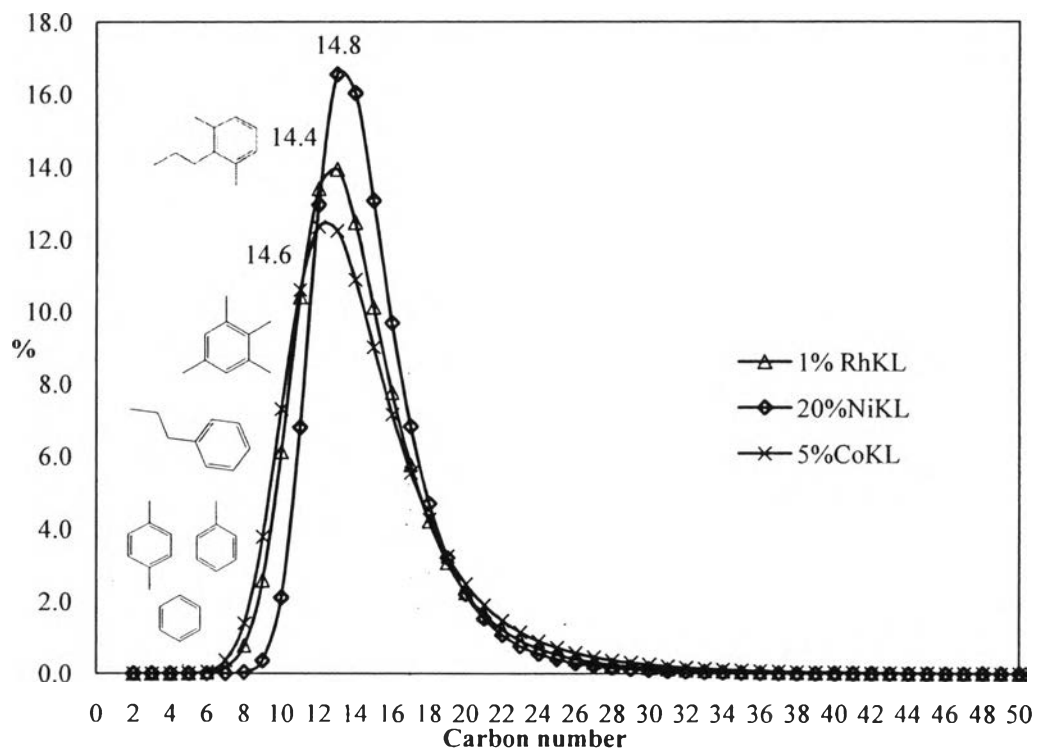**Figure 4.13(c)** Carbon number distribution of mono-aromatics using varied %Co/KL.

Figure 4.13(d) Carbon number distribution of mono-aromatics using 1%Rh, 20%Ni and 5%Co.

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

Carbon number	1% RhKL	5%CoKL	20%NiKL
C6-C8	0.97	1.83	0.04
C9	2.59	3.78	0.36
C10	6.12	7.30	2.11
C11	10.41	10.60	6.79

4.2 Effect of Bimetallic Catalysts

The addition of a second metal is investigated in the catalytic pyrolysis of waste tire in order to investigate whether the products obtained from waste tire pyrolysis can be improved. The bimetallic catalysts supported on KL zeolite (RhNi/KL and RhCo/KL) were prepared by co-impregnation technique with a total metal content of 1 %wt with the varied amounts of Rh from 0.05 to 0.75 %wt. The compositions of non-noble metals, Ni and Co, modified with noble metal, Rh, are expressed in terms of the α ratio, which is determined in the following equation.

$$\alpha_{Metal} = \frac{\%Metal}{\%Rh + \%Metal} \; ; \text{Metal} = \text{Co or Ni}$$

4.2.1 Effect of RhNi/KL

The influence of α ratio on pyrolysis products is shown in Figure 4.14, which exhibits the gas and liquid yields obtained from pyrolysis. The pyrolysis without a catalyst gives the yield of gas, liquid, and solid about 13 %, 43 %, and 44 %, respectively. The presence of pure KL gives the higher gas yield than the non-catalytic case. In addition, the gas and liquid yields of monometallic Ni and Rh supported on KL are also given for comparison purpose. The metal compositions of the catalysts have the impact on the product yields. Namely, increasing the α_{Ni} ratio from 0 to 1 results in the fluctuation of gaseous yield at the expense of liquid yield around the yields of both monometallic catalysts. The increase in gas yield might be attributed to the activity of catalyst in the decomposition of heavy fractions into lighter fractions. The bimetallic catalyst at α_{Ni} = 0.5, consisting of 0.5%Rh and 0.5%Ni, shows the positive effect on the gas formation resulted from the enhancement in cracking reaction. An increase in the liquid yield is observed at α = 0.25 and 0.95. It can be explained that at these ratios the ability of cracking is decreased leading to a higher amount of liquid fraction as compared to the corresponding monometallic catalysts. Moreover, the similar amount of solid fraction around 43% in all runs confirms that tire is completely decomposed at 500 °C, since the experiments were carried out at the same condition.
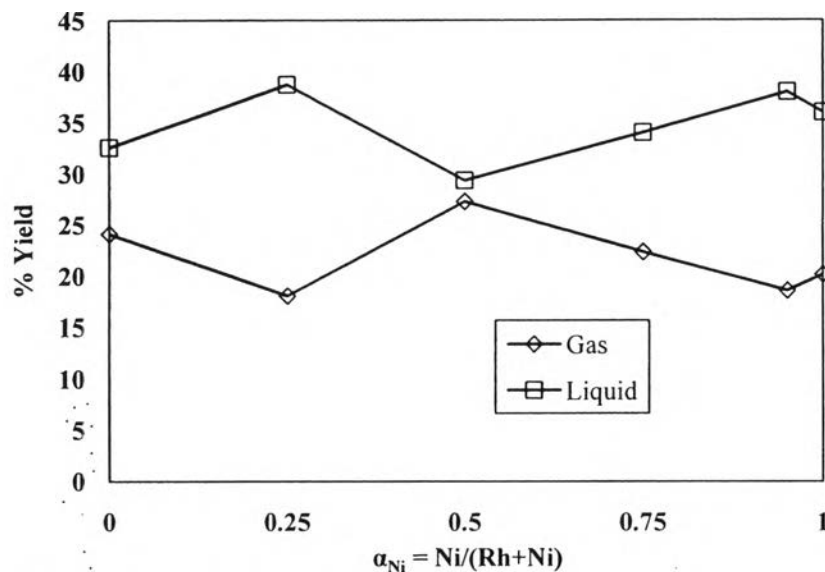
Figure 4.14 Gas and liquid yields obtained from pyrolysis using RhNi/KL.

Appendix C4 illustrates the gas composition obtained from the use of Rh-Ni supported on KL. It is found that at α_{Ni} = 0.5 exhibits a significantly greater yield of light hydrocarbon gases than the use of non-catalytic and all prepared catalysts. Additionally, the bimetallic catalysts also affects the light olefins and cooking gas production as shown in Figures 4.15 and 4.16, respectively. With increasing the composition of Ni content up to 0.50%, the yield of light olefins reaches the highest, and then decreases due to the further addition of 0.75%-1%Ni into the mixed metals. Similar trend is found in the yield of cooking gas formation which exhibits the maximum yield at α_{Ni} = 0.50. This suggests that the suitable composition of bimetallic catalysts to produce the highest yields of light olefins and cooking gas is 0.5%Rh mixed with 0.5% Ni, which indicates the synergy between Rh and Ni.
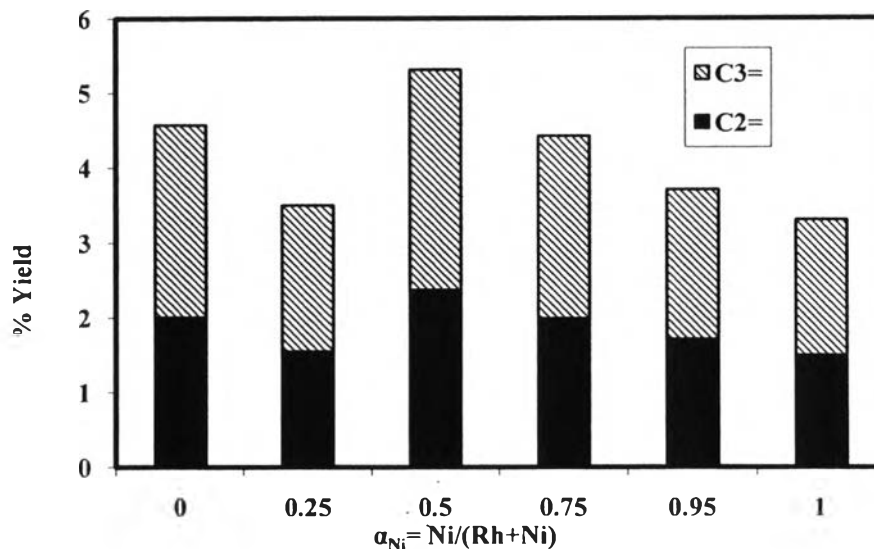
Figure 4.15 Yields of light olefins obtained from pyrolysis with using RhNi/KL.
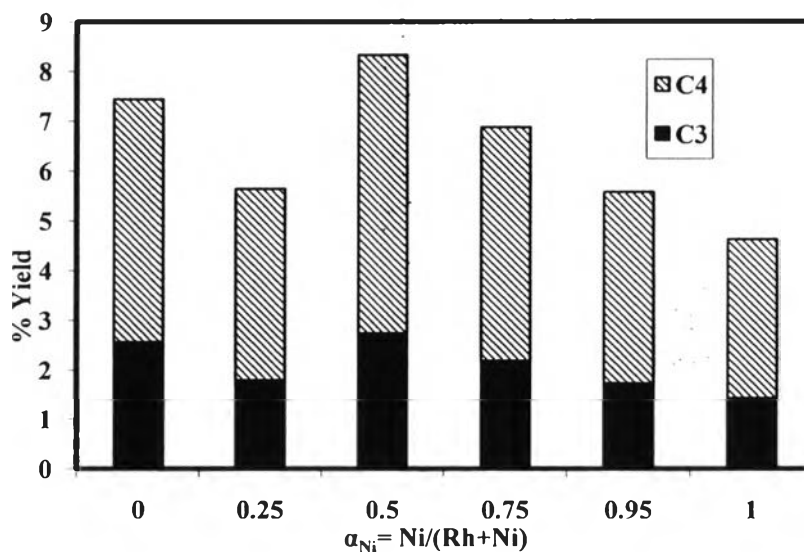

Figure 4.16 Yield of cooking gas obtained from pyrolysis with using RhNi/KL.

Maltene fractionation after asphaltene separation was performed by liquid chromatography to obtain 5 fractions, which are saturated hydrocarbon, mono-, di-, poly-, and polar-aromatic compounds. The results from Figure 4.17 show that the incorporation of Ni helps to promote an increase in saturated hydrocarbons. Especially, the bimetallic catalyst at $\alpha=0.25$ exhibits the highest concentration among the others including monometallic catalysts, 1%Ni and 1%Rh. This result occurs in association with the reduction of total aromatics as observed in Figure 4.18, which

demonstrates that the ratio of saturated hydrocarbons per total aromatics (the sum of mono-, di-, poly- and polar-aromatics) is the highest at the α_{Ni} ratio of 0.25 at which the synergistic effect of Rh and Ni occurs. It can be suggested that the mixed metal sites are available for converting aromatic compounds to saturated hydrocarbons via hydrogenation reaction. The incorporation of Ni to Rh at the appropriate amount could provide an enhancement in hydrogenation and/or ring opening activity. It is in agreement with Taillades-Jacquin *et al.*, 2008, who investigated the hydrogenation of naphthalene by using Pd-Rh catalyst and found that the bimetallic catalyst showed activity and selectivity to the formation of hydrogenated and ring opening products.
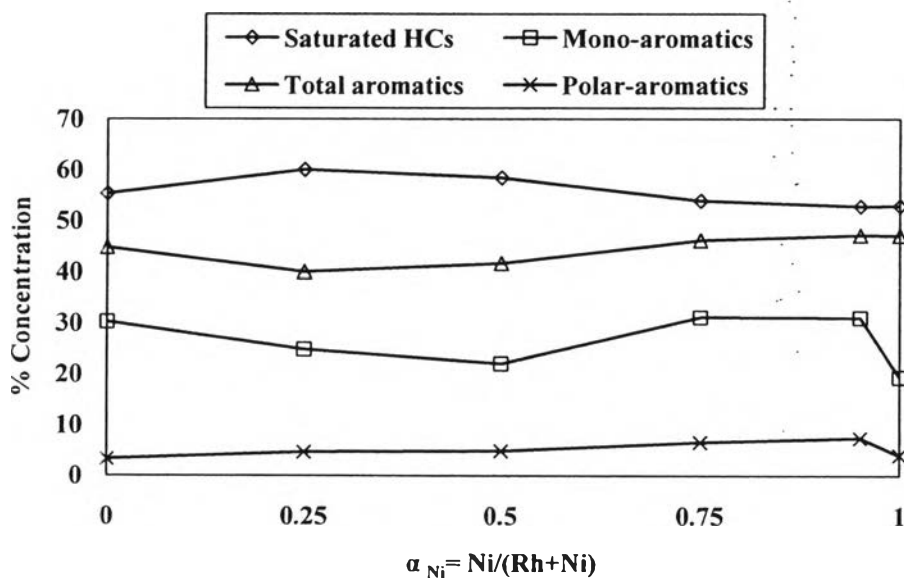

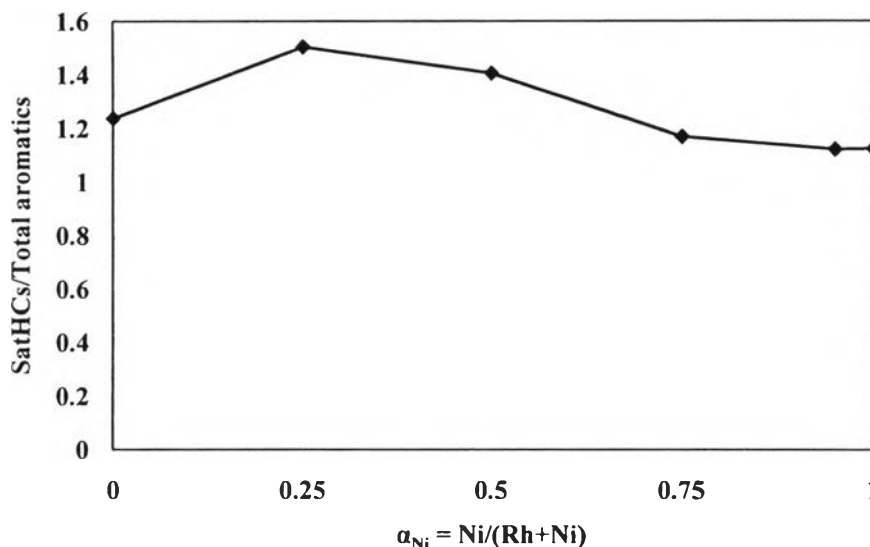**Figure 4.17** Chemical composition in maltenes obtained from using RhNi/KL.

Figure 4.18 Saturated hydrocarbons/total aromatics ratio from using RhNi/KL.

Mono-aromatics, which can be used as valuable substances, are also the target of this research. It is found from Figure 4.17 that the bimetallic catalysts at α_{Ni} = 0.75 and 0.95 exhibit a higher concentration of mono-aromatics than the other two bimetallic catalysts, but both give the similar value as compared to the use of 1%Rh/KL catalyst. The effect on mono-aromatics production can be further explained by Figure 4.19, which illustrates the carbon number distribution with average carbon number obtained from using co-loaded catalysts and their monometallic catalysts. The result shows that the addition of Ni results in the shift of peak to a higher carbon number as compared to using the monometallic Rh/KL catalyst or even the Ni/KL catalyst itself. This can be suggested that co-loading the two metals, Ni and Rh, on the catalysts as bimetallic catalysts have the negative impact on mono-aromatics formation since it gives heavier mono-aromatics basically undesired for petrochemical feed stock. It is only attributed, again, to the catalytic activity in ring-opening and hydrogenation reaction, leading to a decrease in total aromatics content when the Ni ratio is lower than 0.5.
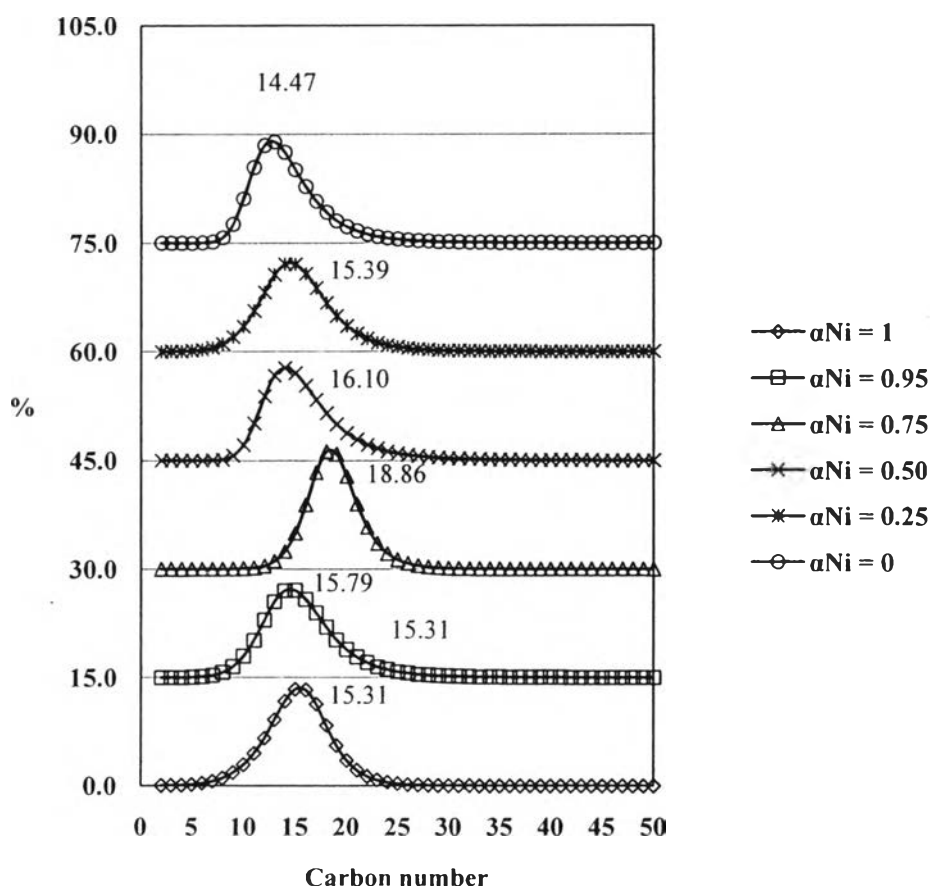
Figure 4.19 Carbon number distribution of mono-aromatics from using RhNi/KL.

Nevertheless, the polar-aromatics content in the oil product is found higher than the use of both monometallic catalysts. It is in accordance with the amount of sulfur in oil as shown in Appendix H2, which is also found higher than using both mono-metallic catalysts. Polar-aromatics are mostly in the form of sulfur-containing aromatics compounds. This can be concluded that the bimetallic catalysts of Rh mixed with Ni supported on KL show the low ability to cleavage C-S-C bond in the molecules of derived oil, resulting in a low quality of oil products.

For petroleum fraction, it is found from Figure 4.20 that among co-loading catalysts, α_{Ni} = 0.5 exhibits the highest naphtha content but, still lower than that obtained from both corresponding monometallic catalysts. However, increasing α_{Ni} from 0.25 to 0.75 results in an increment in gas oil fractions and a further decrease at α_{Ni} = 0.95. These results suggest that the introduction of Rh-Ni as mixed

catalysts have the impact on the higher production of gas oil, which is resulted from the reduction in cracking ability.
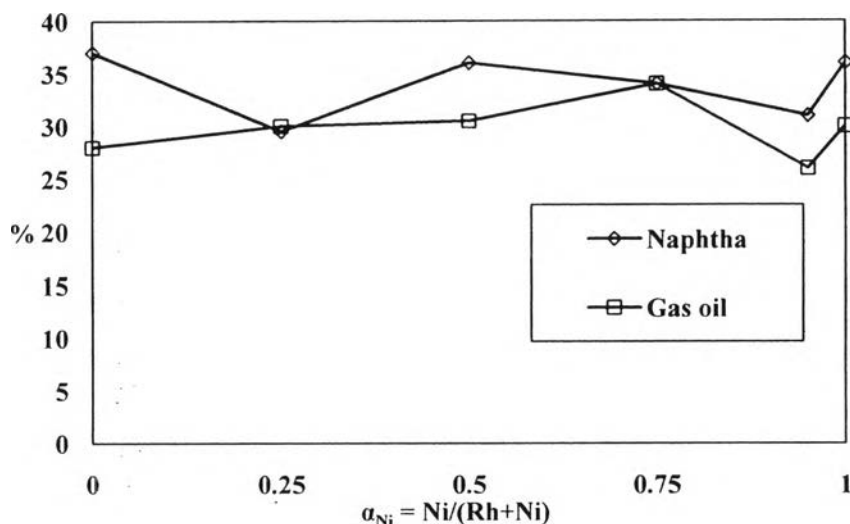

Figure 4.20 Naphtha and gas oil fractions from using RhNi/KL.

4.2.2 Effect of RhCo/KL

The combination of Co and Rh as bimetallic catalysts supported on KL zeolite is also investigated in the catalytic pyrolysis of waste tire. The composition of co-loaded catalysts is presented as the α_{Co} ratio according to the above equation. The product yield of non-catalyst case is 43 % liquid, 13 % gas and 44 % solid. Figure 4.21 illustrates the gas and liquid yields of bimetallic catalysts at various α_{Co} ratios compared to that of monometallic catalysts. The result shows that co-loading on the catalysts have the effect on the product yields. Namely, at α=0.25 the liquid yield reaches the maximum, which shows the highest value compared to the other bimetallic and the monometallic catalysts, and then slightly decreases with increasing α_{Co} up to 0.75. Consequently, the liquid yield starts to increase again at α_{Co} = 0.95. These results suggest that the co-loading is likely to increase the production of liquid product. In addition, the similar value of solid yield is observed in all experiments around 43% which is due to the same reason as discussed previously that tire is completely decomposed at 500°C.
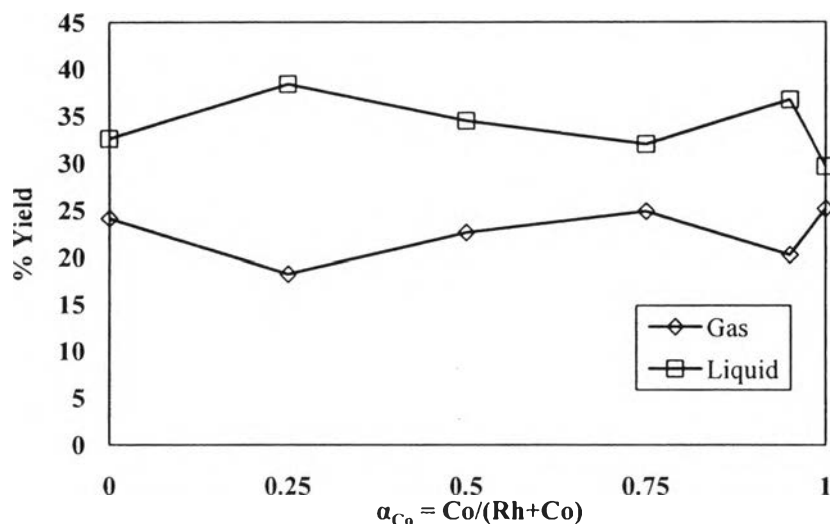
Figure 4.21 Gas and liquid yield obtained from pyrolysis using RhCo/KL.

The use of Rh modified with Co on KL zeolite in catalytic pyrolysis causes a significant effect on the formation of saturated hydrocarbons as can be seen from Figure 4.22. The concentration of saturated hydrocarbons is likely to increase at a higher α_{Co} ratio. The combination of 0.05% Rh with 0.95%Co shows a marked increase in saturates in the oil product, which reaches the highest value at $\alpha_{Co} = 0.95$. These might be ascribed to the fact that the hydrogenation reaction is dominant at the active sites of bimetallic catalysts at the high α_{Co} ratio. Figure 4.23 demonstrates the ratio of saturated hydrocarbons per totals aromatics. The highest peak is obviously seen at $\alpha_{Co} = 0.95$, which can be implied that the saturated hydrocarbons is formed via the hydrogenation of aromatic compounds, leading to a decrease in total aromatics. For mono-aromatics formation, it is found from the result that co-loading catalysts with $\alpha_{Co} = 0.5$ exhibits the highest concentration as compared to their bimetallic catalysts, but gives the similar value as that obtained from using the monometallic Rh/KL catalyst. Additionally, the combination of Rh and Co has no impact on the reduction of polar-aromatics as well as the sulfur-containing compounds in the derived oil as can be seen in Appendix H2.
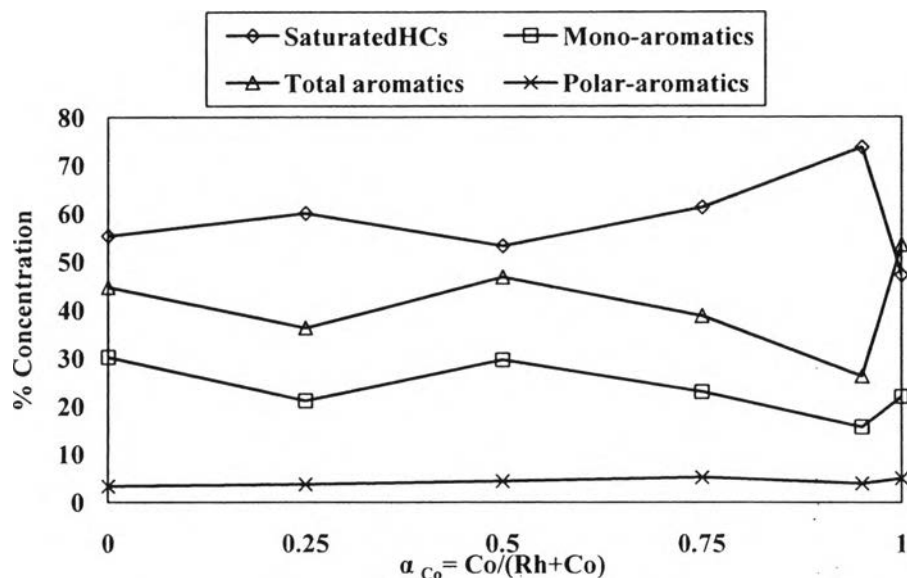
Figure 4.22 Chemical composition in maltenes obtained from using RhCo/KL.
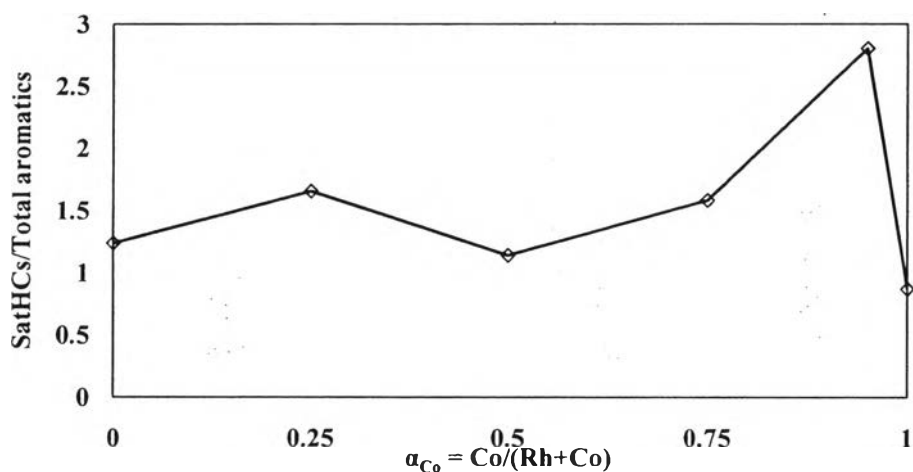

Figure 4.23 Saturated hydrocarbons/total aromatics ratio from using RhCo/KL.

Figure 4.24 exhibits the full range naphtha and gas oil contents in maltenes. It is apparently seen that the naphtha contents from all bimetallic catalysts are lower than that of the corresponding monometallic catalysts, whereas the incorporation of two metals provides a significant impact on the gas oil production which reaches the maximum at α_{Co} = 0.5. The amount of naphtha fraction can indicate the cracking ability of the catalysts in decomposition heavy liquid fraction. Therefore, the introduction of bimetallic catalysts using Co modified with Rh have the negative impact on naphtha fraction in the derived oil, which is attributed to a decrease in cracking ability, resulting in an increment of gas oil fraction.
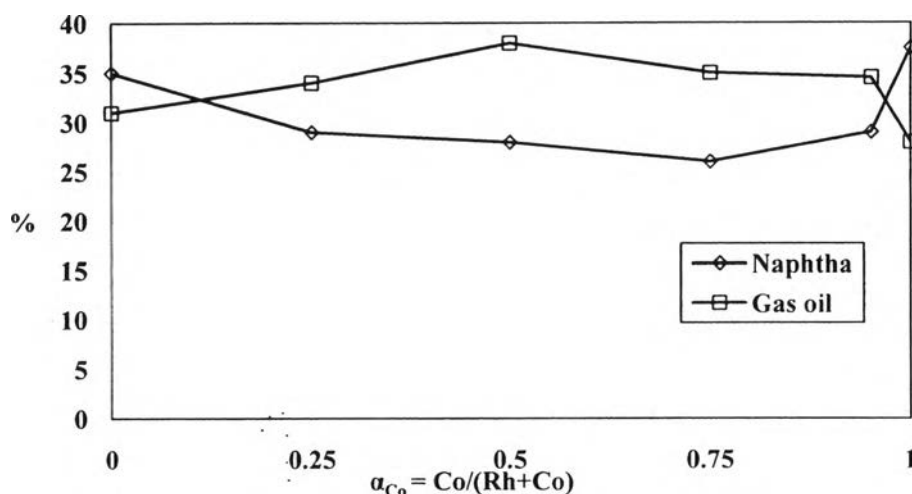
Figure 4.24 Naphtha and gas oil fraction from using RhCo/KL.

In conclusion, the incorporation of 0.5%Rh mixed with 0.5 % Ni as co-loading catalysts have the synergistic impact on the formation of pyrolytic gas, providing the higher yield of cooking gas and light olefins as compared to their corresponding monometallic catalysts. For liquid product, increasing α_{Ni} from 0.5-0.75 results in the increment of saturated hydrocarbons, which leads to the reduction in aromatic content. Moreover, the effect on gas oil production is found when using the small amount of 0.05%Rh addition in 0.95%Ni as the bimetallic catalyst.

In the case of RhCo/KL catalysts, it is obviously shown that the addition of two metals has influence on the production of liquid product, except at α_{Co} = 0.75, which is due to the decrease in cracking ability leading to the formation of heavy fraction, such as gas oil, instead of naphtha fraction. In addition, as low as 0.05%Rh modified with Co gives a distinguishable amount of saturates in the derived oil.

It can be concluded from the above results that the introduction of co-loaded catalysts have the potential on the production of saturated hydrocarbons with the reduction in total aromatic compounds. It is might be attributed to the dominant reactions of hydrogenation and/or ring opening reactions which undergo deeply in the process. However, the bimetallic catalysts have little impact on the production of mono-aromatics because they gave the similar content as compared to their monometallic catalysts. Moreover, sulfur-containing compounds in the derived oil

are found higher than using the mono-metallic catalysts, which is probably due to low activity in C-S bond breaking.