Waste tire pyrolysis is the alternative way to produce oil from a low cost hydrocarbon-containing material. This section discusses the effect of three different catalysts sets of; individually catalysts (%MoO₃/KL and %Re/KL) and co-loaded catalysts (%Re-1%MoO₃/KL) on the pyrolytic products. The different percentages of MoO_3 and Re were the parameters in this studied.

4.1 Effect of MoO₃/KL Catalysts on Pyrolysis Products

4.1.1 Pyrolysis Yields

The weight percentage of MoO_3 based on KL zeolite was 1%, 2%, 3%, 5% and 10%. Scrap tire was pyrolyzed at 500 °C which was the complete decomposition temperature (Rodriguez *et al.*, 2001). The pyrolytic yields from pyrolysis are shown in Figure 4.1.
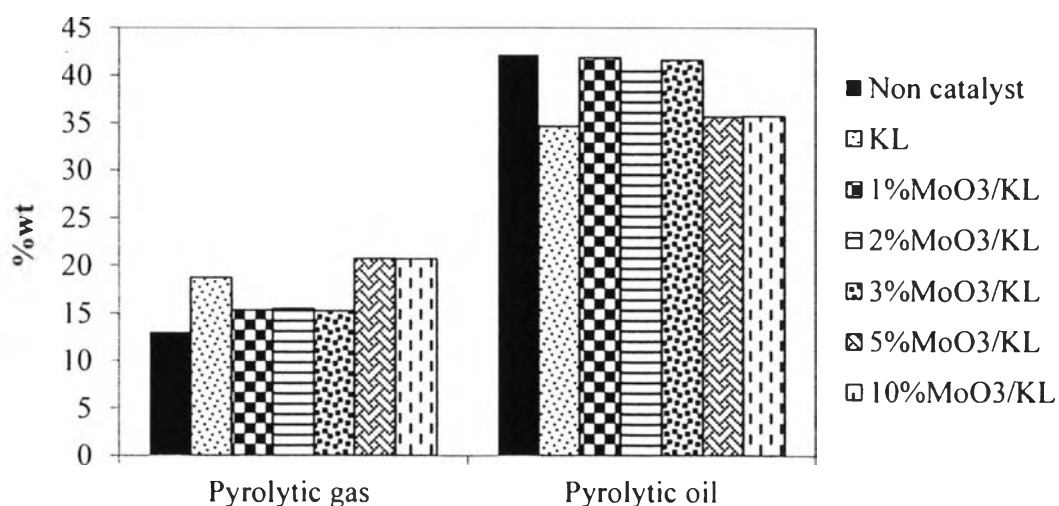

Figure 4.1 Pyrolysis products from waste tire pyrolysis obtained from using MoO₃/KL with varied MoO₃ loading.

Waste tire was decomposed into three products; pyrolytic oil, pyrolytic gas, and char. Non-catalytic pyrolysis produces 42.2% pyrolytic oil, and 13.0% pyrolytic gas. Moreover, it was found that the amount of char remained constant at about 44%wt for both non-catalytic and catalytic cases. Catalytic pyrolysis strongly influences on pyrolytic gas. Using KL zeolite and different percentages of MoO_3/KL gives a high production of pyrolytic gas in comparison to the non-catalytic case. These higher amounts of gas product are evolved from the combination of thermal and catalytic decomposition to breakdown tire structures to various kinds of light hydrocarbons. Moreover, the macromolecules of tire material were easily broken down into light hydrocarbon productions owing to the high reaction activity of catalysts (Choosuton, 2007). According to the experiment, KL zeolite reduces the production of pyrolytic oil with the consequent increase in pyrolytic gas. However, after loading at 1-3 wt% MoO_3, the amount of pyrolytic oil is increased to which was given by the non-catalytic case. With increasing the MoO_3 loading at 5-10 wt%, it can produce the higher amount of pyrolytic gas than the lower MoO_3 loading due to the enhancement of their cracking activity.

The pyrolytic gas was analyzed by using gas chromatography to determine the compositions of gas product. The result with different percentages of MoO_3 loaded on KL zeolite on pyrolytic gas is shown in Figure 4.2.
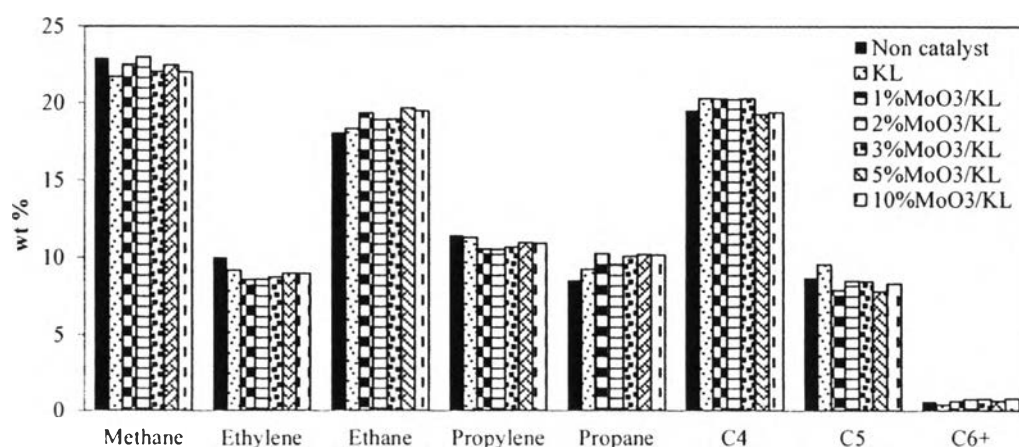

Figure 4.2 Gas compositions obtained from using MoO_3/KL with varied MoO_3 loading.

The gas products from waste tire pyrolysis consist of methane, ethylene, ethane, propylene, propane and mixed C4s and C8 hydrocarbons. These results imply that the cross-linked polymer in tire structures (styrene butadiene rubber, butadiene rubber, isoprene rubber etc.) is cracked into the lighter hydrocarbons. The possible pyrolysis reaction of both thermal pyrolysis and base-catalyzed pyrolysis can occur via the carbon-carbon bond scission at β positions (Choosuton, 2007; Shah *et al.*, 2008). The results obtained in this way agree with the previous studies by Berrueco *et al.* (2005) and Dai *et al.* (2001). Besides the above described components, they found that the main gas components were H_2, CO and CO_2. The mechanism of catalytic cracking via β-scission for styrene-butadiene rubber is shown in Figure 4.3, which illustrates the formation of a C4 hydrocarbon from SBR cracking.
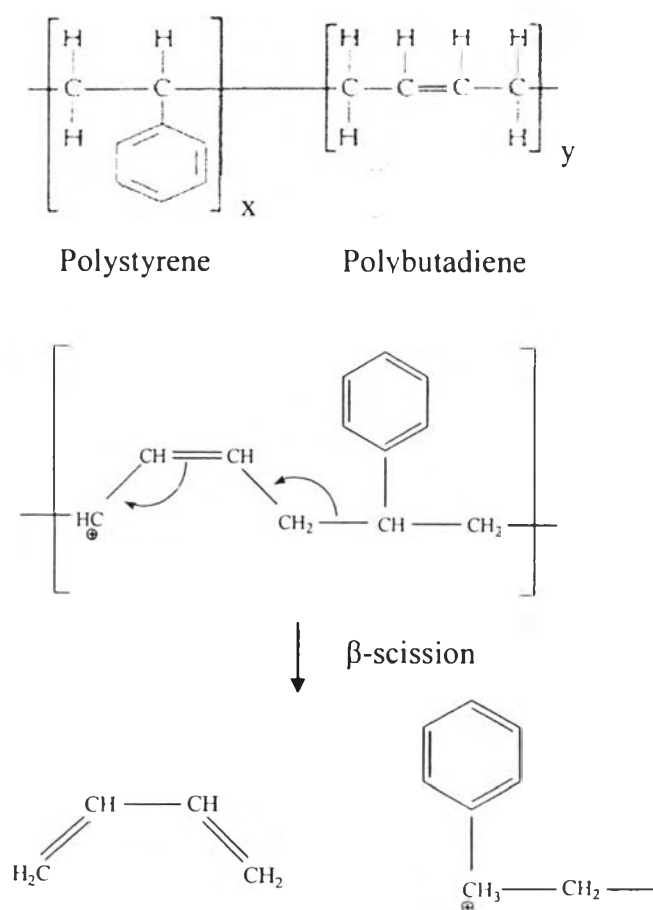

Polystyrene   Polybutadiene

β-scission

Figure 4.3 Catalytic cracking via β-scission obtained from Styrene-Butadiene rubber (Choosuton, 2007).

According to the experiment, thermal pyrolysis and catalytic pyrolysis produce methane as a major product ($\approx$ 22.4 %), followed by mixed C4s ($\approx$ 19.9 %) and ethane ($\approx$ 19.0 %). In addition, Figure 4.2 shows no significant change of gas composition with increasing MoO_3 loading.

4.1.2 Pyrolytic Oil

Oil product was added with n-pentane to precipitate asphaltene before liquid adsorption chromatography step. Asphaltene is the macromolecules, and it contains a great number of polar-aromatics consisting atoms such as O and S. The amount of asphaltene in the liquid products obtained from different percentages of MoO_3 on KL is shown in Figure 4.4. The results show that the non-catalytic pyrolysis produces the highest amount of asphaltene in the pyrolytic oil, which drastically decreases with using both KL zeolite and MoO_3/KL catalysts. It is possible to conclude that the complex and high molecular weight structures of asphaltene are partially broken down on the active site of catalysts to lighter molecular weight structure. These results were supported by Choosuton (2007) having stated that KL zeolite can improve the products from waste tire pyrolysis by reducing the asphaltene in oil products.
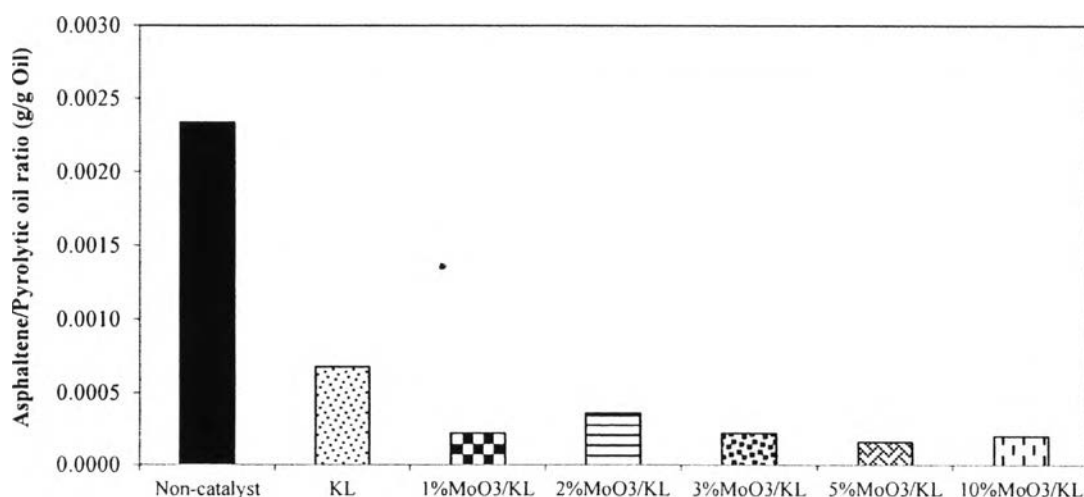

Figure 4.4 Weight fraction of asphaltene in pyrolytic oil obtained from using MoO_3/KL with varied MoO_3 loading.

The pyrolytic oil after asphaltene precipitation with n-pentane is called maltenes. The petroleum fractions in maltenes are classified as shown in Table 4.1 using the true boiling point curve obtained from SIMDIST-GC analysis

Table 4.1 Boiling point ranges of petroleum fractions (Dũng, 2009)

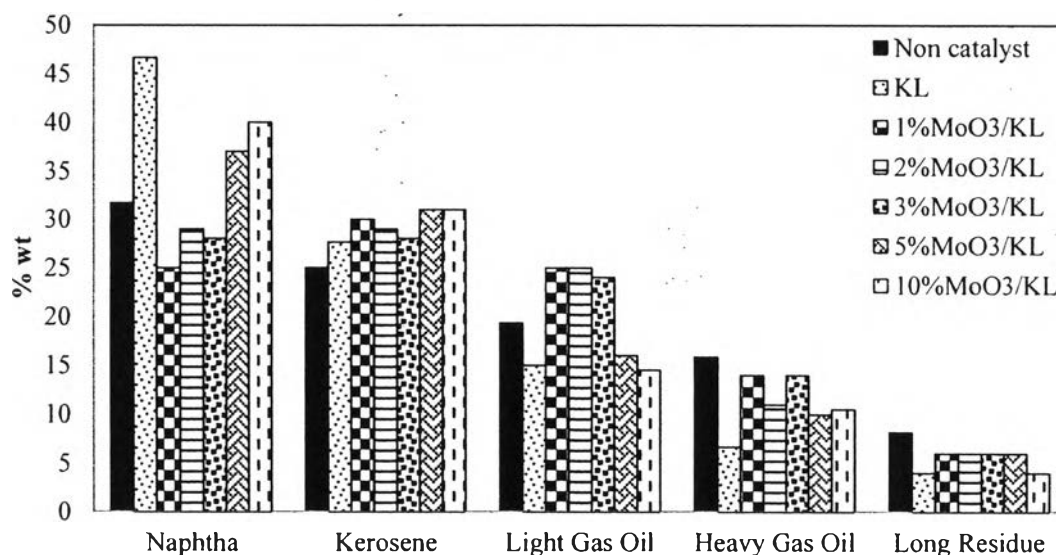| Fraction	Boiling point (°C)
Naphtha	< 200
Kerosene	200 – 250
Light gas oil	250 – 300
Heavy gas oil	300 – 370
Long residue	> 370

Figure 4.5 Petroleum fractions in maltenes obtained from using MoO_3/KL with varied MoO_3 loading.

According to Figure 4.5, the thermal degradation case produces the high amounts of heavy products such as heavy gas oil and long residue. Using KL zeolite gives the highest activity toward the naphtha production (46.7 wt%) in conjunction with the lowest productions of heavy gas oil and long residue. The

percent yield for petroleum fraction is shown in Appendix D4 which among all catalysts KL zeolite also shows the highest yield for naphtha at 16.18 %.

The addition of 1-3 wt% of MoO_3 loading on KL zeolite highly increases the concentration of the light gas oil fraction (about 25 wt%) at the expenses of naphtha range product. This may possibly result from the inhibition effect on the cracking activity of the KL zeolite by the addition of low amount of MoO_3. The reduction in the overall gas yield in the cases of low MoO_3 loading can indirectly reflect the lower cracking activity of the catalyst since the catalyst with high cracking activity tends to promote a higher gas production. However the further increasing MoO_3 loading tends to bring back the naphtha yield with the decrease in heavy fractions such as light gas oil, heavy gas oil, and long residue. Moreover, kerosene production is gradually increased with increasing MoO_3 loading.
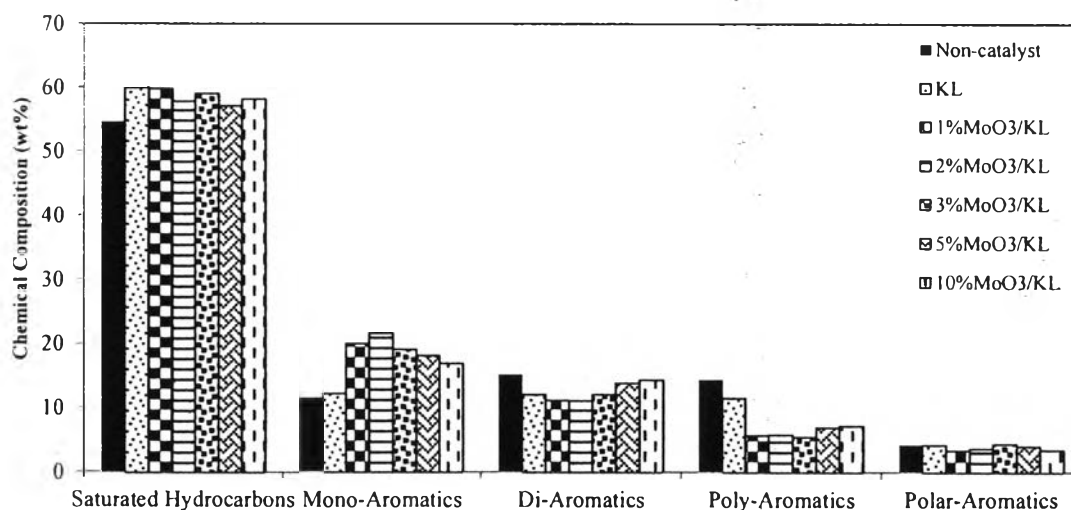

Figure 4.6 Chemical compositions in maltenes obtained from using MoO_3/KL with varied MoO_3 loading.

Figure 4.6 shows that the non-catalytic pyrolysis gives the lowest amount of saturated hydrocarbons in the pyrolytic oil as compared to catalytic case. The presence of KL zeolite produces the high amount of saturated hydrocarbons while other heavy products such as di-, and poly-aromatics are decreased. These

results implied that KL zeolite provides the cracking activity via carbanions to break down the long chain of tire, leading to the higher amount of light molecules such as saturated hydrocarbons. Other supported results indicate the dramatic reduction of asphaltene, the increasing of gas product, and the high production in light fraction such as naphtha and kerosene, which is also influenced by KL zeolite. All MoO_3-loaded KL catalysts give the insignificantly different amount of saturated hydrocarbons in the oils. The amount of mono-aromatics is slightly increased with using KL zeolite in comparison to the non-catalytic case. The presence of MoO_3 loaded on KL zeolite leads to a significant increase in mono-aromatics production. Especially, 1-3 wt% of MoO_3 loading provide the high production of mono-aromatics. The dramatic reduction of poly-aromatics is possibly influenced by cracking reaction and then the high amount of mono-aromatics is produced. Furthermore, the increase in pyrolytic oil and the decrease in pyrolytic gas at 1-3 wt% of MoO_3 loading might be from the aromatization and dehydrogenation reactions of light gas products to produce mono-aromatics.

Wang *et al.* (2004) studied the methane aromatization over MoO_3 supported on HMCM-49. The results showed that MoO_3 loaded on HMCM-49 exhibited the excellent performance for aromatization of methane to give high benzene selectivity around 90%. Similarly, Solymosi *et al.* (1995) studied the dehydrogenation of methane on supported molybdenum oxides. The several products from theirs results were the small amounts of ethylene, ethane, propane, and toluene, while benzene was produced as a main products from the reactions. As mentioned above, it is possible to conclude that MoO_3 species act as the active species for the transformation of light hydrocarbon gases into light aromatic hydrocarbons, especially mono-aromatics. However, the aggregation of MoO_3 species might be occurred when increased MoO_3 loading amounts. Moreover, MoO_3 at the high loading may block the channel entrances of KL zeolite (Xu *et al.*, 1995). Therefore, the activity of MoO_3 species in the conversion of light gas molecules to the aromatic products was also decreased.

4.1.3 Coke and Sulfur Formation

Coke is generated by two basic mechanisms (Chaala and Roy, 1996); the first one is via dealkylation-precipitation reactions of high molecular weight compounds like asphaltene and resins. The second mechanism is produced via condensation of poly-aromatic compounds. According to the experiments, the result of coke deposited on the catalysts is illustrated in Figure 4.7.
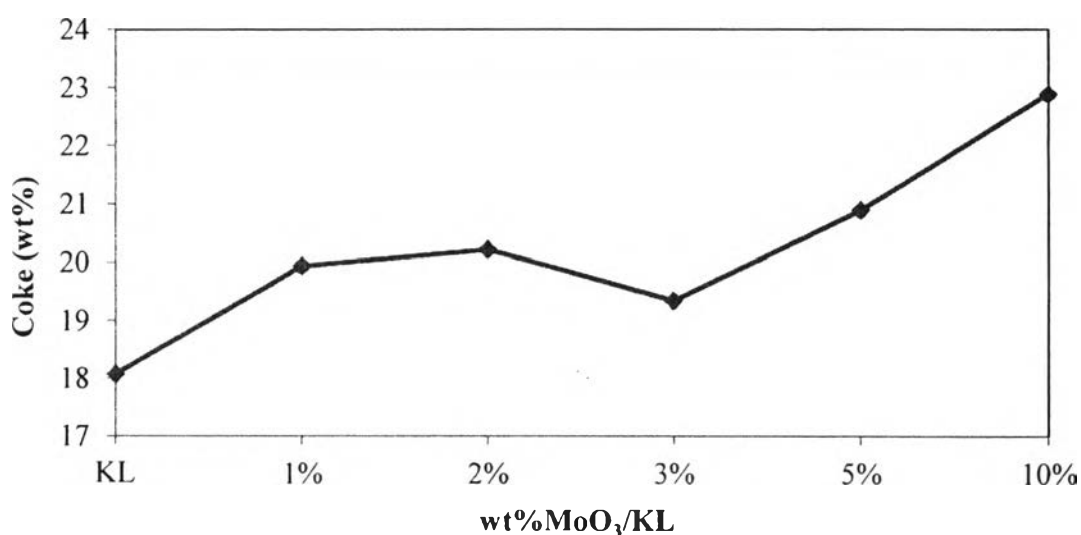

Figure 4.7 Coke formation obtained on spent KL zeolite and spent MoO_3/KL with varied MoO_3 loading.

The results show that MoO_3/KL catalysts produce the high amount of coke, which is also higher than using KL zeolite alone. The increasing MoO_3 loading also tends to increase the amount of coke deposited on the catalysts. The cracking activity is also suggested from the amount of coke deposited on catalysts as the high cracking activity catalyst tends to produce the high amount of coke. The highest amount of coke formation (22.9 wt%) is produced at the highest MoO_3 loading. Moreover, the reduction of poly-aromatics obtained from MoO_3/KL catalysts might be resulted from the condensation of poly-aromatics to produce coke.

The amounts of sulfur in the pyrolytic oil and on the spent catalysts are illustrated in Figure 4.8. The results indicate that the non-catalytic pyrolysis gives

the highest amount of sulfur in the pyrolytic oil (1.31 wt%), whereas using all catalysts highly reduced the sulfur amounts in oils. KL zeolite shows the highest activity to decrease sulfur in the pyrolytic oil. The sulfur deposited on spent KL zeolite exists in the low amounts; thus, the sulfur in oil may be present in the gas phase. At 1-3 wt% of MoO_3 loaded on KL zeolite, no significant difference of the sulfur contents in oils is found, whereas the sulfur content on the spent catalysts dramatically increases as compared to KL zeolite. It is possible to conclude that the sulfur molecules in the gas product are first adsorbed on MoO_3/KL catalysts and then the C-S bonds break, leading to the high amount of sulfur deposited on catalysts. The increasing MoO_3 loading of higher than 3 wt% further reduces sulfur amounts in the oil to the same extent as KL zeolite does. According to the results, overall MoO_3/KL catalysts have a significantly high amount of sulfur deposited on the catalysts in conjunction with the decrease of sulfur in the oil, indicating the decrease of sulfur contents in the gas products.
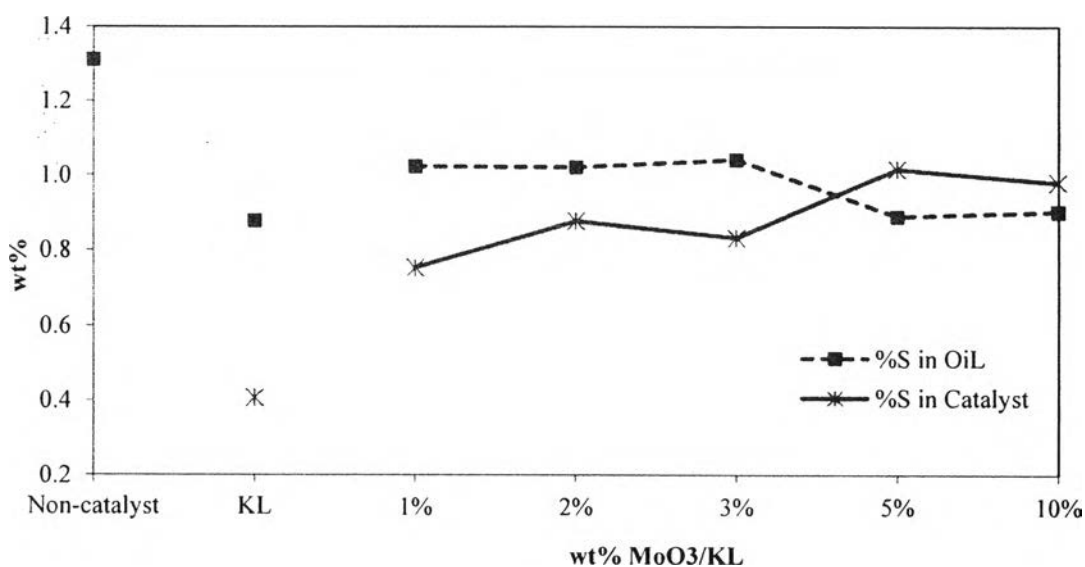

Figure 4.8 Sulfur contents in pyrolytic oil and spent on MoO_3/KL with varied MoO_3 loading.

It can be concluded that all different MoO_3 loadings gave the higher amount of mono-aromatics than the non-catalytic and KL zeolite cases. Especially, 1-3 wt%

of MoO_3 loading can promote the dehydrogenation of some gaseous products followed by aromatization to produce mono-aromatics. Furthermore, the dramatic reduction of poly-aromatics was found after MoO_3 was loaded on KL zeolite. These results can imply that the production of mono-aromatics might be enhanced from the cracking of poly-aromatics. The high amounts of MoO_3 loading of 5-10 wt% can enhance the cracking activity according to the high production of pyrolytic gas. The increase of MoO_3 loading tends to increase the amount of sulfur deposited on the catalysts via the C-S bond cleavage. According to the results, if the amount of MoO_3 loaded on KL zeolite had been loaded more than 10 wt% the catalysts would have produced the higher amount of gas products and higher sulfur deposited on the catalysts due to the enhancement of cracking activity. Moreover, the amount of naphtha and kerosene fraction might have been also increased.

4.2 Effect of Re/KL Catalysts on Pyrolysis Products

4.2.1 Pyrolysis Yields

The percentages applied to Rhenium (Re) in this experimental section were 0.25, 0.50, 0.75, and 1 wt%. The pyrolytic products obtained from Re/KL catalyst are shown in Figure 4.9. The presence of KL zeolite shows a significant decrease in the pyrolytic oil, and then the increase in the pyrolytic gas. The addition of Re on KL zeolite slightly enhances in the cracking activity leading to the increment of pyrolytic gas. Weigh average of char formation from both non-catalytic and catalytic cases is about 44 wt%.
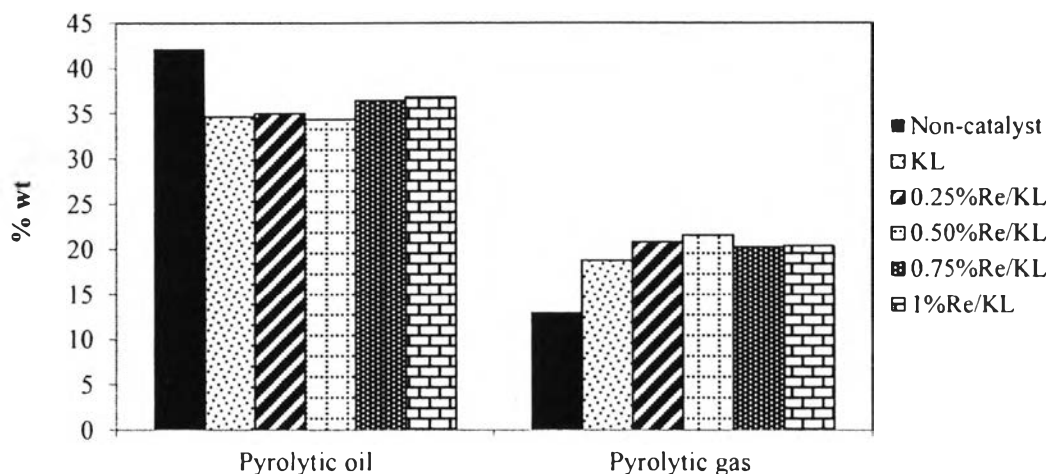
Figure 4.9 Pyrolysis products from waste tire pyrolysis obtained from using Re/KL with varied Re loading.

The gas products obtained from various Re/KL catalysts show no significant difference in the gas compositions as shown in Appendix C. Methane, mixed C4s, and ethylene are still the dominant compositions.

4.2.2 Pyrolytic Oil

The influences of Re/KL catalysts on the petroleum fractions are illustrated in Figure 4.10. According to the results, KL zeolite gives the high cracking activity which leads to the high concentration of naphtha fraction. However, its activity, was found to decrease after 0.25 wt% of Re was loaded resulting in the low amount of naphtha fraction and the increment of light gas oil from the negative effect of Re loading. The increasing Re loading from 0.25 to 0.75 wt% can improve the amount of naphtha fraction, especially at 0.75 wt% of Re loading, which gives the similar results as KL zeolite. In addition, these increased loading shows the significant increase in kerosene fraction and the decrease in light gas oil. The highest Re loading at 1wt% does not promote the light fractions in oil, but instead produces the heavy fractions as the non-catalytic case does.
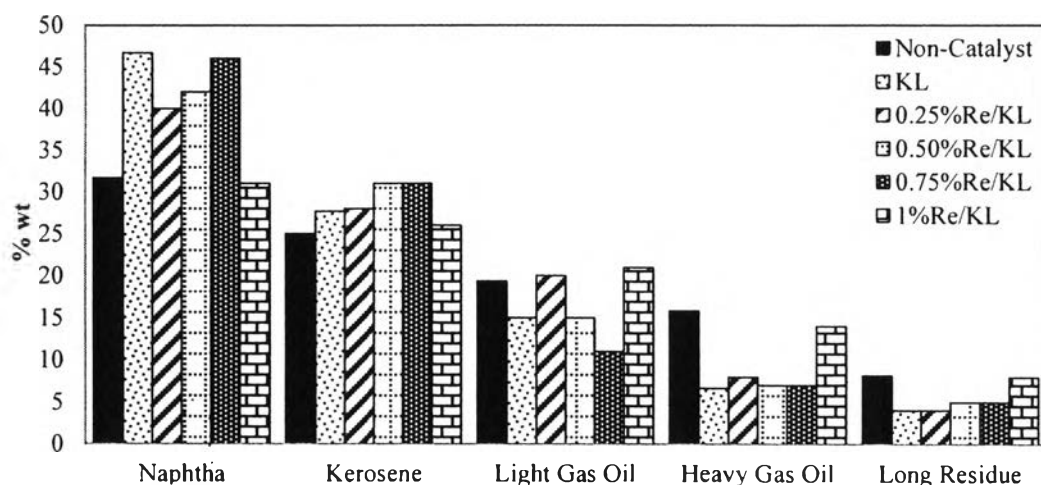
Figure 4.10 Petroleum fractions in maltenes obtained from using Re/KL with varied Re loading.

The compositions of pyrolytic oil after asphaltene separation were analyzed by liquid adsorption chromatography. The effect of Re/KL catalysts on the chemical compositions in maltenes is shown in Figure 4.11.
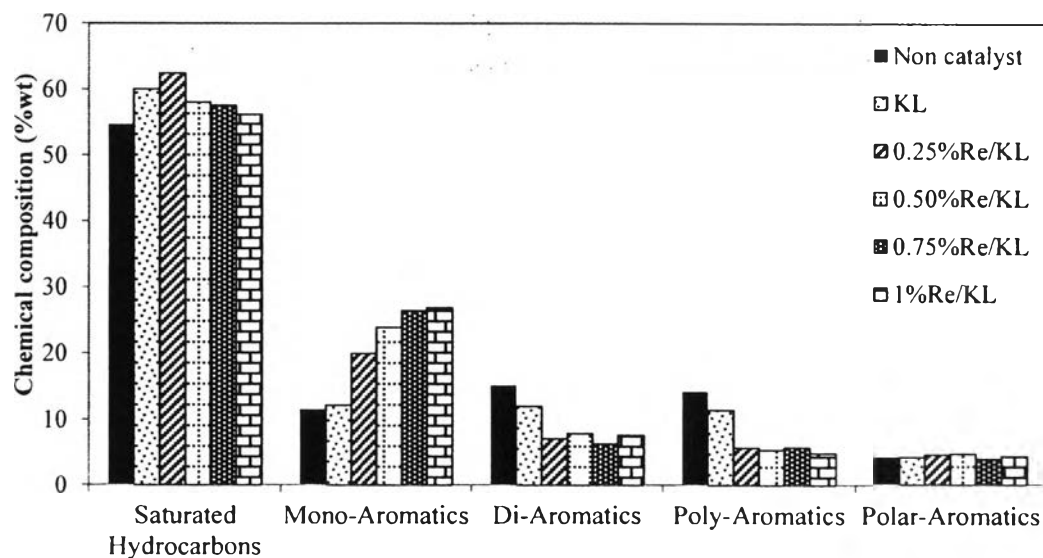

Figure 4.11 Chemical compositions in maltenes obtained from using Re/KL with varied Re loading.

It was found that the addition of Re loading highly increases the amount of mono-aromatics associated with the significant reduction of di- and poly-aromatics. Rhenium catalysts showed the high activity in hydrogenolysis and ring-opening (Carter *et al.*, 1982). Therefore, it is possible that di- and poly-aromatics can be converted to the lighter products such as mono-aromatics via the hydrogenolysis and then the ring-opening function of the catalysts. The high amounts of Re loading at 0.75-1 wt% produce the highest amount of mono-aromatics at around 27 wt%.

According to the mono-aromatic yields stated in Appendix D2, 1 wt%Re loaded on KL zeolite exhibits the highest yield at around 9.9 %. However, it is similar to that obtained from 1 wt% and 2 wt%MoO$_3$/KL catalysts (8.4 %yield and 8.7 %yield, respectively). The carbon number distribution of oil obtained from 1%Re/KL, 1%MoO$_3$/KL and 2%MoO$_3$/KL is compared in Figure 4.12.
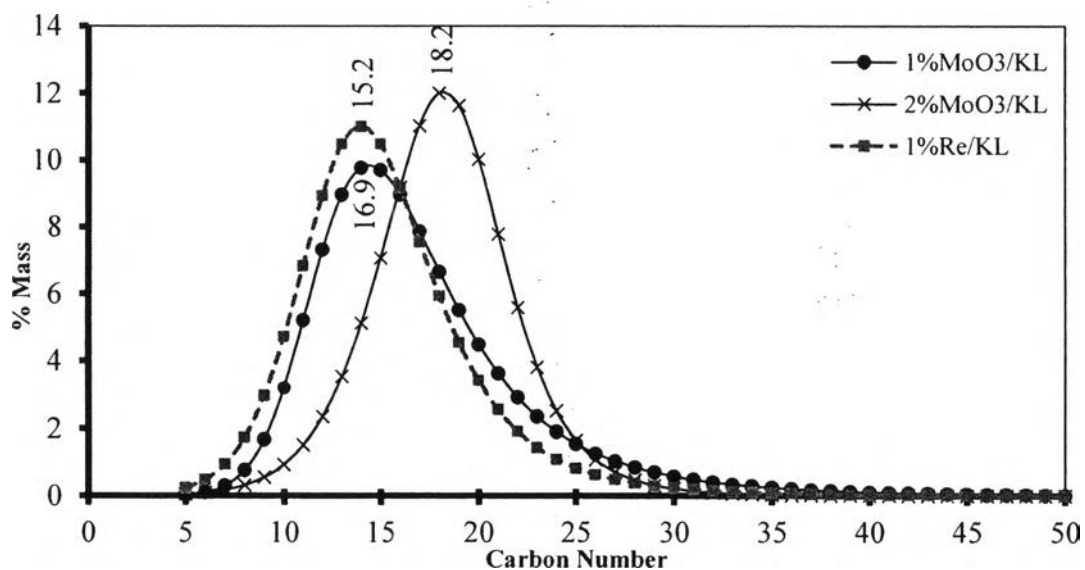

Figure 4.12 Carbon number distribution of mono-aromatics obtained from 1%MoO$_3$/KL, 2%MoO$_3$/KL, and 1%Re/KL.

The results indicate that 1%Re/KL and 1%MoO$_3$/KL give the similar carbon number distribution with the average carbon number in the range of C12-C17 (15.2 and 16.9, respectively). The increase of MoO$_3$ loading from 1 wt% to 2 wt% tends to shift the peak to higher carbon numbers the average of 18.2. However, the

precursor used in preparing a MoO_3/KL catalyst is apparently less expensive than that for Re/KL catalysts, whereas the yields of mono-aromatics obtained from these two catalysts are not significantly different. The prices of precursor are shown in Table 4.2.

Table 4.2 Precursor Prices

Precursor	Amount	Price* (Bath)
Ammonium Molybdate Tetrahydrate $(NH_4)_6Mo_7O_{24} \cdot 4H_2O)$ ACS Grade ($\geq$ 99.0%)	100 g	3,790
Ammonium Perrhenate (NH_4ReO_4) 99.999%	1 g	4,940

*S.M. Chemical Supplies Co., Ltd., Thailand (26 April 2010)

In addition, Re/KL catalysts can help improve the quality of pyrolytic oil by reducing the amount of asphaltene in the oil product. The result revealed that 0.25 and 0.50 wt% of Re/KL catalysts show the drastic reduction of asphaltene. The amount of asphaltene formation obtained from Re/KL catalysts is illustrated in Figure 4.13.
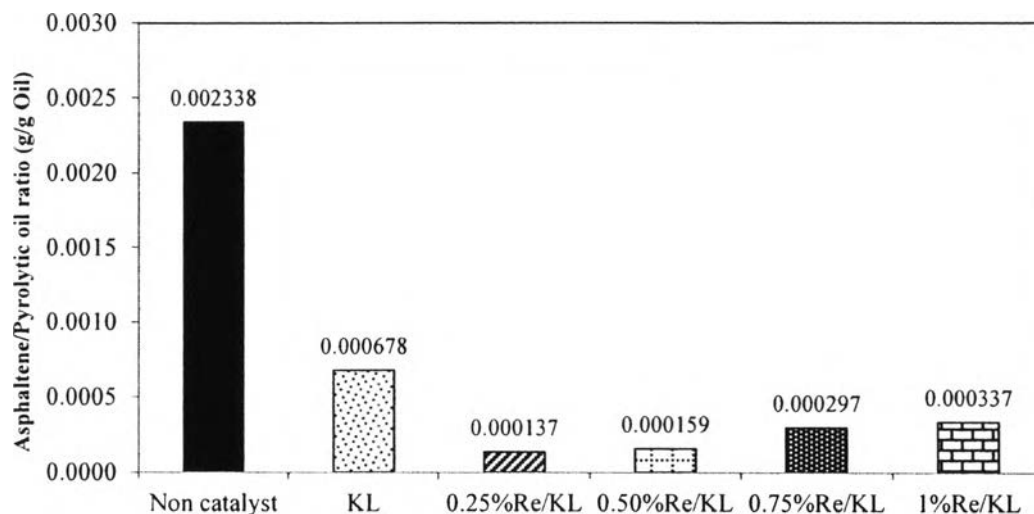
Figure 4.13 Weight fraction of asphaltene in pyrolytic oils obtained from using Re/KL with varied Re loading.

4.2.3 Coke and Sulfur Formation

The amount of coke deposited on the spent Re/KL catalysts is shown in Figure 4.14. The results show that all the different Re loading catalyst gives the low amount of coke formation, which is insignificantly different from KL zeolite.
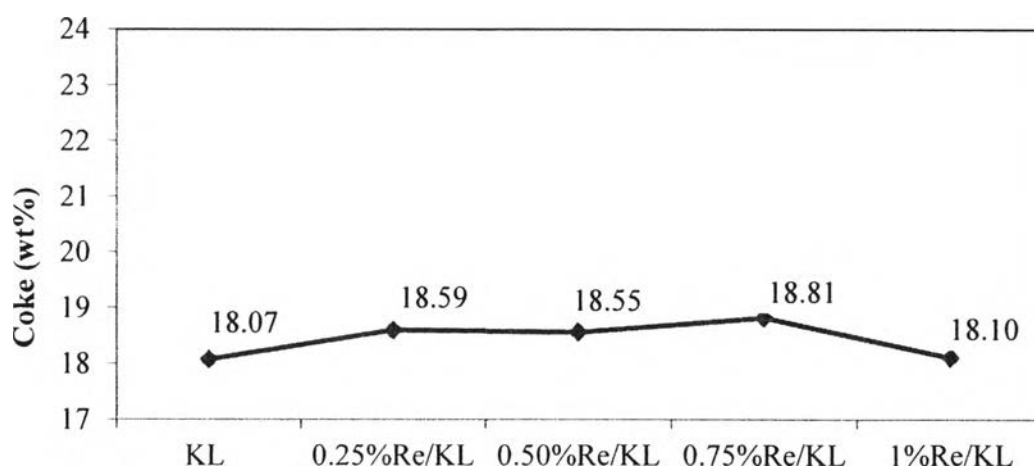

Figure 4.14 Coke formation obtained on spent KL zeolite and spent Re/KL with varied Re loading.

The sulfur contents in the pyrolytic oil and the spent catalysts are shown in Figure 4.15. The result shows no significant difference in the sulfur contents, both on catalysts and in oils obtained from Re/KL catalysts.
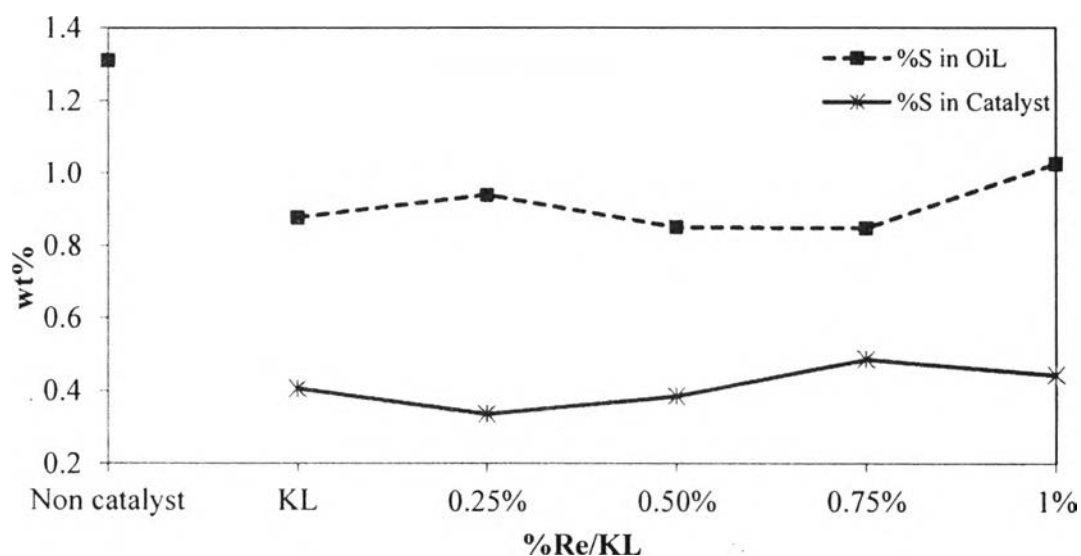

Figure 4.15 Sulfur contents in pyrolytic oil and spent Re/KL with varied Re loading.

On the effects of Re/KL catalysts, it can be concluded that the di- and poly-aromatics in the oil might be converted into mono-aromatics via the hydrogenolysis and ring-opening activities. Moreover, Re/KL catalysts also had the higher activity to produce mono-aromatics than MoO_3/KL catalysts. Especially, 0.75-1 wt% of Re loadings gave the highest amount of mono-aromatics at around 27 wt%, and they also promoted the naphtha production with the decrease of heavy fractions such as light gas oil, heavy gas oil, and long residue.

4.3 Effect of %Re-1%MoO₃/KL on Pyrolysis Products

This section discusses the effect of co-loaded catalysts; that is, various Re percentages were loaded on 1wt% of MoO₃/KL. The goal was to study the effect of co-loaded catalysts (%Re-%MoO₃) on KL zeolite as compared to the individually-loaded catalysts (MoO₃/KL and Re/KL). The amount of MoO₃ content was fixed at 1 wt% at all cases with the additional loading of Re from 0.25-1wt% on KL zeolite. Table 4.3 display the co-loaded catalysts used in this section.

$$\emptyset_{Re} = \frac{W_{Re}}{W_{Re} + W_{MoO_3}} \quad ; \quad \emptyset_{MoO_3} = 1 - \emptyset_{Re}$$

Table 4.3 The weight fraction of catalysts

Catalyst	Ø
1%MoO₃/KL	0
0.25%Re-1%MoO₃/KL	0.20
0.50%Re-1%MoO₃/KL	0.33
0.75%Re-1%MoO₃/KL	0.43
1%Re-1%MoO₃/KL	0.50
1%Re/KL	1

4.3.1 Pyrolysis Yields

The pyrolytic products in terms of Ø are illustrated in Figure 4.16. According to the results, the yields of pyrolytic gas and pyrolytic oil obtained from co-loaded catalysts lie in between those of individually-loaded catalysts (1%MoO₃/KL and 1%Re/KL). These results suggest the dilution effect of co-loaded catalysts. Char production obtained from co-loaded catalysts is shown in Appendix B, and it remains constant at about 44 wt%, indicating the complete decomposition of waste tire material at 500 °C.
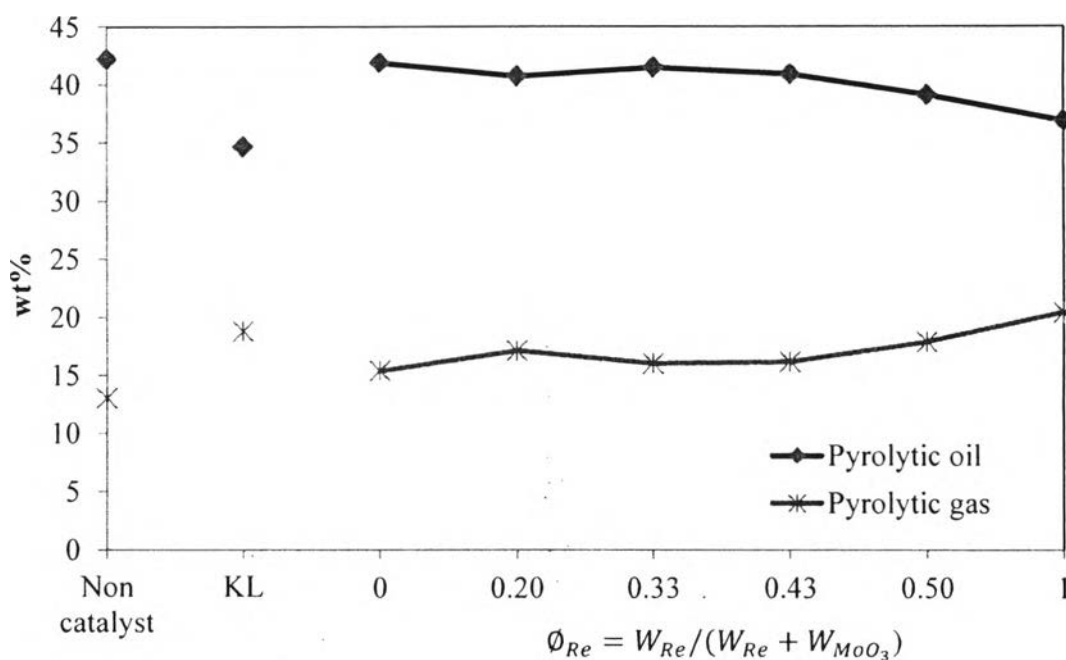
$$\varnothing_{Re} = W_{Re}/(W_{Re} + W_{MoO_3})$$

Figure 4.16 Pyrolytic products obtained from using Re-1%MoO₃/KL with varied Re loading.

All of the Re catalysts loaded on 1 wt% of MoO₃/KL show no significant difference in gas compositions. They also show the same tendency as the individually-loaded catalyst (Re/KL and MoO₃/KL), which can be seen in Appendix C.

4.3.2 Pyrolytic Oil

Figure 4.17 demonstrates the petroleum fractions in maltenes obtained from different percentages of Re loaded on 1 wt% of MoO₃/KL. The presence of KL zeolite produces the significantly high amount of naphtha fraction as compared to the other catalysts. The co-loaded catalysts (at $\varnothing$ = 0.20 to 0.50) give the negative impact on cracking activity since they do not promote the light petroleum fractions such as naphtha or kerosene, but instead, they increase the heavier fractions, like light gas oil.
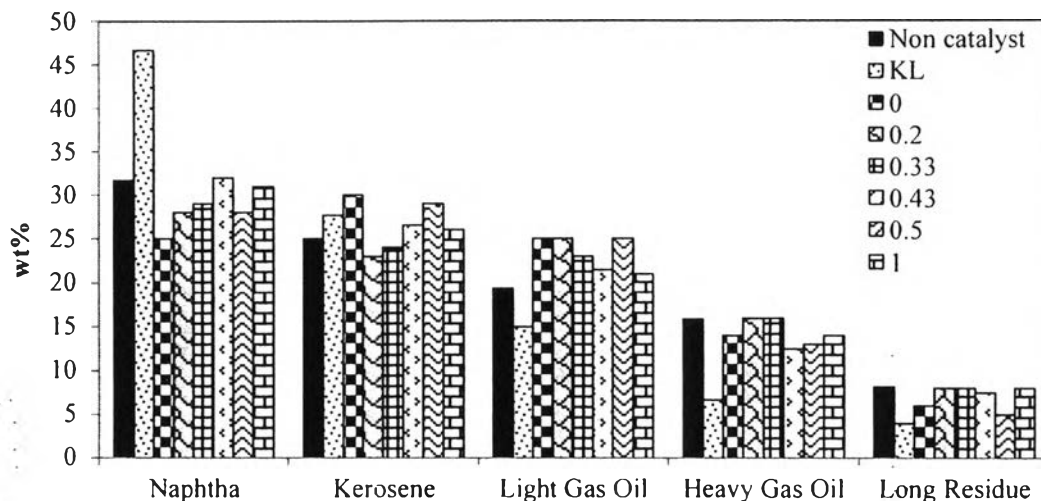
Figure 4.17 Petroleum fractions in maltenes obtained from using Re-1%MoO₃/KL with varied Re loading.

Petroleum fractions in the pyrolytic oil obtained from different percentages of Re loading on 1wt% of MoO_3/KL was analyzed in details for their compositions as presented in Figure 4.18. 1 wt% of MoO_3/KL catalysts at $\varnothing_{Re} = 0$ gives the similar amount of saturated hydrocarbons in the pyrolytic oil about 60 wt% as KL zeolite. The presence of Re in the co-loaded catalysts does not promote the formation of mono-aromatic as the individually-loaded catalysts do, but instead, it enhances the concentration of saturated hydrocarbons. The co-loaded catalyst at $\varnothing_{Re}$ = 0.2 (0.25%Re-1%MoO₃/KL) is found to produce the maximum concentration of saturated hydrocarbons (about 74 wt%). The presence of co-loaded catalysts dramatically reduces the content of di-, and poly-aromatics, while saturated hydrocarbons are shifted to the high production. It is possible to conclude that co-loaded catalysts may promote the cracking and hydrogenation activities to convert di- and poly-aromatics to saturated hydrocarbons. The asphaltene formations obtained from all co-loaded catalysts show the same tendency as MoO_3/KL and Re/KL catalysts. Namely, the co-loaded catalysts produce the low amount of asphaltene in the oil, which helps improve the oil quality. The results are shown in Appendix F.
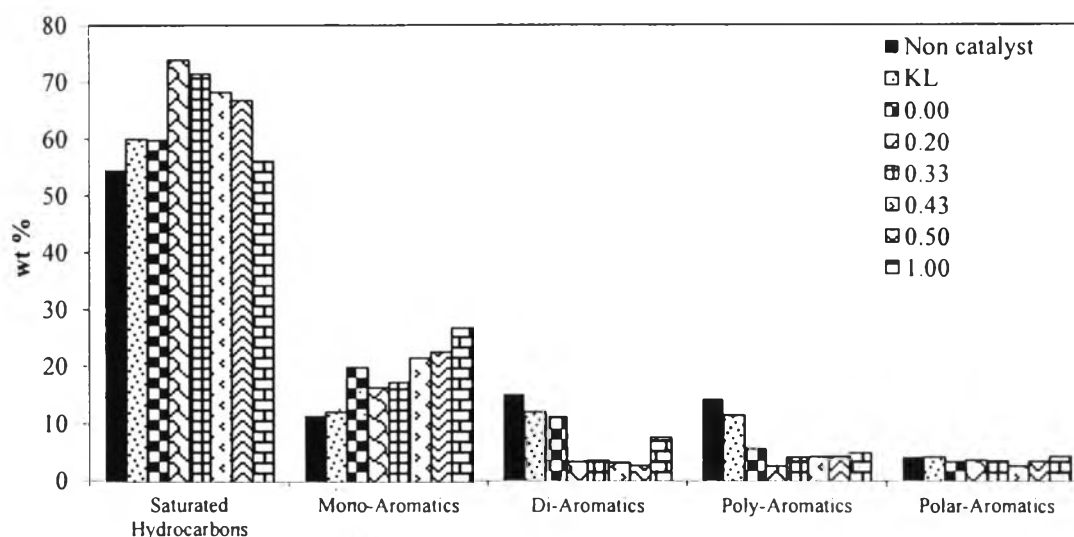
80

70

60

50

wt % 40

30

20

10

0

■ Non catalyst
☐ KL
◙ 0.00
☑ 0.20
⊞ 0.33
⊠ 0.43
☒ 0.50
☐ 1.00

Saturated
Hydrocarbons

Mono-Aromatics

Di-Aromatics

Poly-Aromatics

Polar-Aromatics

Figure 4.18 Chemical compositions in maltenes obtained from using Re-1%MoO₃/KL with varied Re loading.

4.3.3 Coke and Sulfur Formation

The coke formation on the co-loaded catalysts is presented in Table 4.4. The increasing amount of Re on 1wt% of MoO_3/KL tends to increase the amount of coke deposited on the catalysts

The amounts of sulfur in the pyrolytic oil and on the spent catalysts are shown in Table 4.5. According to the results, the co-loaded catalysts show the dilution effect on the sulfur content on the spent catalysts. The dilution effect occurs when the two species are co-loaded, and then they give the sulfur content or any other outcome that lie proportionally in between those obtained from the individuals. Re loading gives a lower amount of sulfur deposited on KL zeolite than MoO_3 loading alone. Moreover, the sulfur content in oil obtained from co-loaded catalysts is also not significantly different from that of the individually-loaded catalysts. The average of sulfur in the pyrolytic oil is 1.04 wt%.

Table 4.4 Coke formation on the spent catalysts

Catalyst	Ø	Coke (wt%)
KL		18.1
1%MoO₃/KL	0	19.9
0.25%Re-1%MoO₃/KL	0.20	17.2
0.50%Re-1%MoO₃/KL	0.33	18.3
0.75%Re-1%MoO₃/KL	0.43	18.9
1%Re-1%MoO₃/KL	0.50	20.0
1%Re/KL	1	18.1

Table 4.5 Sulfur content in the pyrolytic oils and on the spent catalysts

Catalyst	Ø	%Sulfur	
		Catalyst	Oil
Non catalysts	-	-	1.31
KL	-	0.41	0.88
1%MoO₃/KL	0	0.75	1.02
0.25%Re-1%MoO₃/KL	0.20	0.55	1.10
0.50%Re-1%MoO₃/KL	0.33	0.62	1.06
0.75%Re-1%MoO₃/KL	0.43	0.64	1.01
1%Re-1%MoO₃/KL	0.50	0.69	1.02
1%Re/KL	1	0.44	1.03

According to the results, the co-loaded catalysts had the negative impact on naphtha production in oils. Even though the individually loaded catalysts (MoO₃/KL and Re/KL) can promote the mono-aromatics, but the co-loaded catalysts instead promoted the saturated hydrocarbons. It might be resulted from the enhancement of cracking activities and then hydrogenation, which can help convert di- and poly-aromatics to saturated hydrocarbons, by co-loading of the two co-loaded species.