



CHAPTER IV

RESULTS AND DISCUSSION

In this work, the effects of Co supported on SAPO-34, the effects of Co supported on SAPO-34 on acid zeolites (HY, HMOR, HBETA and HZSM-5), and the effects of Co-supported acid zeolites mixed with SAPO-34 as an additive on the qualitative and quantitative of pyrolysis products are analyzed and discussed.

4.1 Effects of SAPO-34 as a Catalyst

The effects of SAPO-34 and 5 %Co/SAPO-34 on the products obtained from the pyrolysis of tire are discussed in this section. 5 wt% of Co was loaded on SAPO-34 by incipient wetness impregnation method.

4.1.1 Physical Properties of Catalysts

SAPO-34 is a silicoaluminophosphate microporous zeolite, and its chemical formula is $(\text{Si}_{0.09}\text{Al}_{0.50}\text{P}_{0.41})\text{O}_2$. Table 4.1 shows the physical properties of SAPO-34. The results show that loading Co on SAPO-34 reduces the surface area and pore volume of SAPO-34.

Table 4.1 Physical properties of SAPO-34 loaded with 5 %Co

Catalysts	$\text{SiO}_2/\text{Al}_2\text{O}_3$ (mol/mol)	Dimension	Pore size (Å)	Specific surface area (m^2/g)	Total pore volume (cm^3/g)
SAPO-34	0.44	3D	9.43	662.6	0.449
5 %Co/SAPO-34	0.44	3D	7.96	220.7	0.088

4.1.2 Product Distribution

The products obtained from waste tire pyrolysis are distributed into gas, liquid, and solid. After pyrolysis, the products were condensed by a series of condensers to collect as a liquid product. And, the incondensable hydrocarbons which are in a gas phase were collected as the gas product. The product distribution from the catalytic pyrolysis of waste tire using Co supported on SAPO-34 as shown in Figure 4.1.

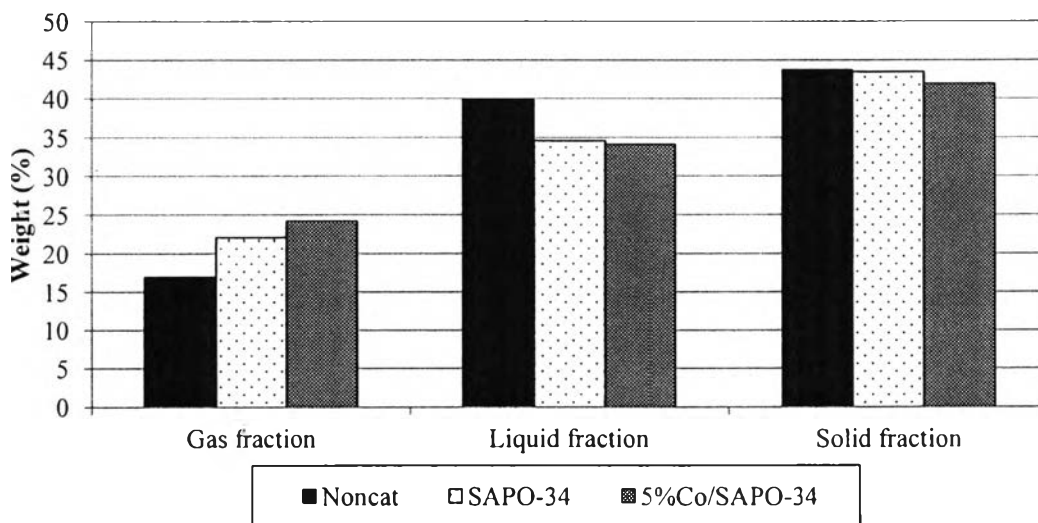


Figure 4.1 Product distribution obtained from the catalytic pyrolysis of waste tire using SAPO-34 and 5 %Co/SAPO-34.

The results show that using SAPO-34 as catalysts in pyrolysis gives a higher amount of gaseous products and a consequent lower amount of liquid products than the non-catalytic case because the acid sites of the catalyst can crack large molecules of products to smaller molecules such as gases. With Co loading, 5 % Co/SAPO-34 gives a higher gas yield than using pure SAPO-34. The liquid yield obtained from the 5 %Co/SAPO-34 catalyst decreases from 34.5 wt% to 34.1 wt%, whereas the gaseous yield increases from 22.3 wt% to 24.2 wt%. This result shows that the metal sites of Co can also break heavier compounds to lighter compounds.

4.1.3 Gaseous Products

The gaseous products obtained from the pyrolysis of waste tire consist of the hydrocarbon species in the range of C1-C5 and some of C6+. The product gas compositions are shown in Figure 4.2. The result shows that using SAPO-34 increases methane, ethane, propane and C4 as compared to the non-catalytic case. The addition of Co on SAPO-34 insignificantly increases ethylene and propylene contents in gas. Figures 4.3 and 6.4 show light olefins (ethylene and propylene) and cooking gas (propane and mixed-C4) obtained from pyrolysis. The presence of SAPO-34 gives higher yield of light olefins and cooking gas than the non-catalytic case, but they are not as much as those of the 5 %Co/SAPO-34 case, which gives the highest yield of light olefins and cooking gas.

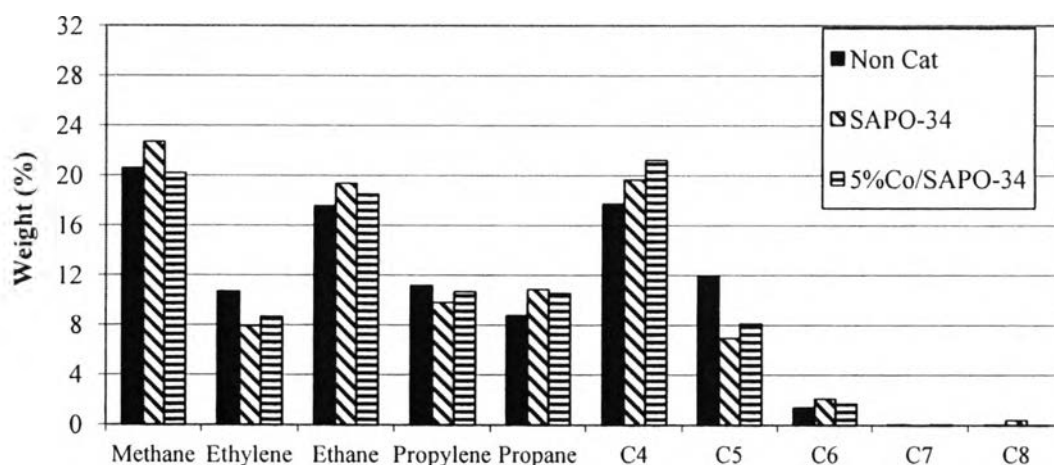


Figure 4.2 Gas compositions obtained from waste tire pyrolysis using SAPO-34 and 5 %Co/SAPO-34.

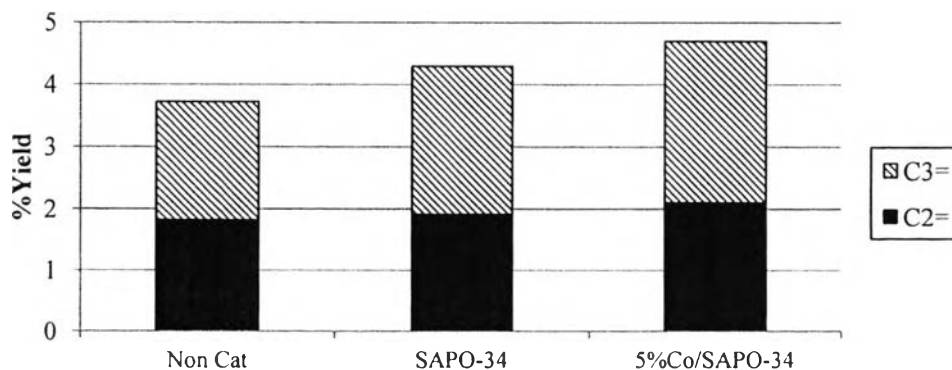


Figure 4.3 Light olefins production from using SAPO-34 and 5 %Co/SAPO-34.

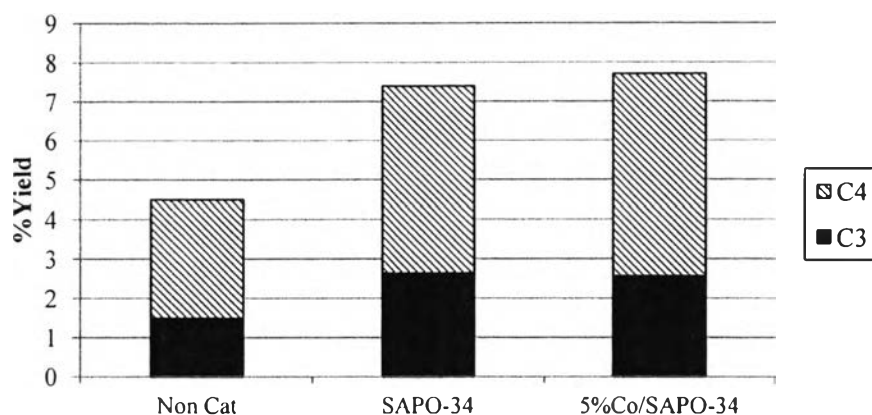


Figure 4.4 Cooking gas production from using SAPO-34 and 5 %Co/SAPO-34.

4.1.4 Oil Products

4.1.4.1 Qualitative Analysis

The liquid products were separated into 5 fractions: saturated hydrocarbons, mono-aromatic, di-aromatic, poly-aromatic, and polar aromatic compounds via liquid column chromatography. The results are shown in Figure 4.5.

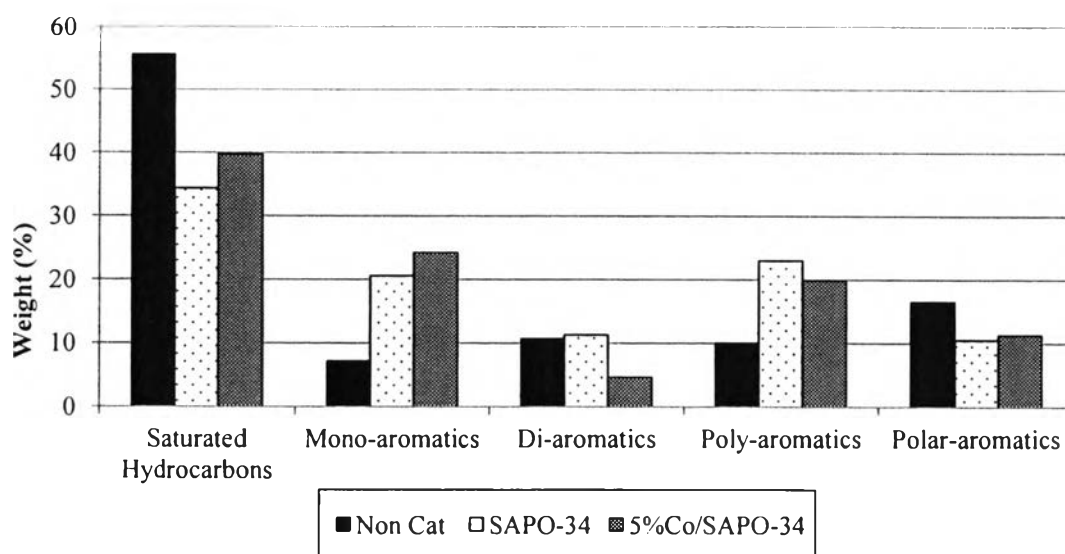


Figure 4.5 Chemical composition in maltenes obtained from using SAPO-34 and 5 %Co/SAPO-34.

The results show that SAPO-34 remarkably increases mono-aromatic and poly-aromatic compounds in the maltene whereas saturated hydrocarbons are remarkably decreased as compared to the non-catalytic case. Using 5 %Co/SAPO-34, mono-aromatics production is further enhanced, whereas di- and poly- aromatics slightly drop when compared with those of SAPO-34. It can be suggested that the active sites of Co promote the activity in hydrogenation and ring opening reaction that can reduce the concentration of multi-ring aromatics (Pedrosa *et al.*, 2006). Moreover, Co leads to aromatization via Diels-Alders reaction, which increases mono-aromatics (Pinket, 2010). This is the reason why the mono-aromatics in oil increase when Co is added.

Asphaltene is a group of substances found in the pyrolytic oil. It is the heaviest and the most viscous part in oil. So, oil that has a higher quantity of asphaltene has lower quality. Figure 4.6 shows the weight fractions of asphaltene in pyrolytic oils. It reveals that as compared to the non-catalytic case, the weight fraction of asphaltene in pyrolytic oils drastically reduces with using SAPO-34. Moreover, it is reduced further with using 5 % Co/SAPO-34.

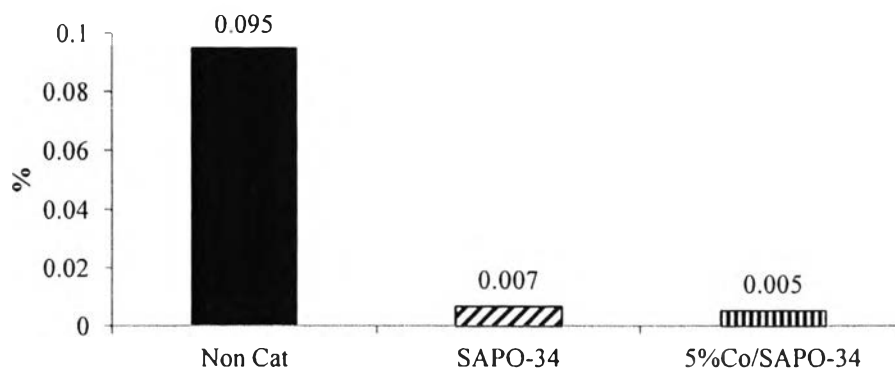


Figure 4.6 Weight fraction of asphaltenes in pyrolytic oils obtained from SAPO-34 and 5 %Co/SAPO-34.

The sulfur content in the oil products is analyzed by CHNOS elemental analysis technique. If the sulfur content in an oil product is low, it indicates that the oil has high quality. Figure 4.7 shows the sulfur content in the oil products and on the spent catalysts. The use of pure SAPO-34 gives a lower content

of sulfur (0.973 wt%) in the oil than that the non-catalytic case (1.08 wt%). 5 %Co/SAPO-34 gives the lowest content sulfur (0.808 wt%) in the oil among all cases.

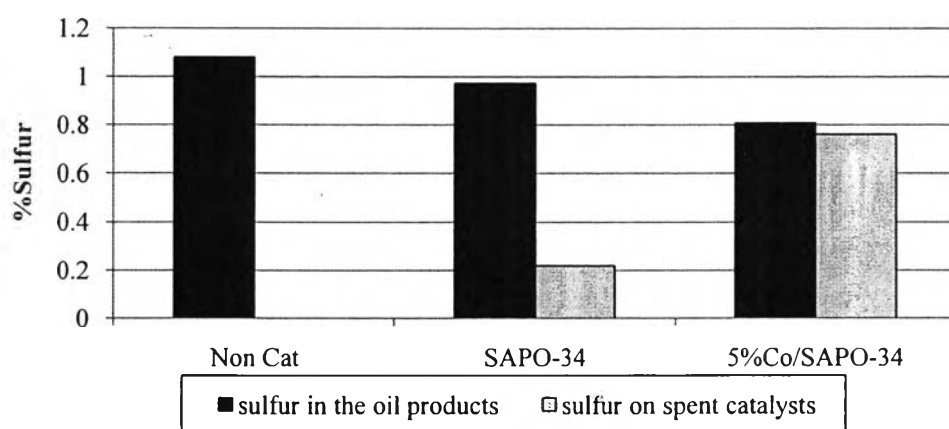


Figure 4.7 Sulfur content in the oil product and on spent catalysts obtained from SAPO-34 and 5 %Co/SAPO-34.

4.1.4.2 Quantitative Analysis

Oil products obtained from the waste tire pyrolysis are classified into petroleum fractions as shown in Table 4.2.

Table 4.2 Petroleum cut (Chaiyavech and Grisadanurak, 2000)

Fractions	Boiling point (°C)	Carbon range
Full range naphtha	<200 °C	C5-C10
Kerosene	200-250 °C	C10-C14
Light gas oil	250-300 °C	C14-C19
Heavy gas oil	300-370 °C	C19-C35
Long residue	>370 °C	>C35

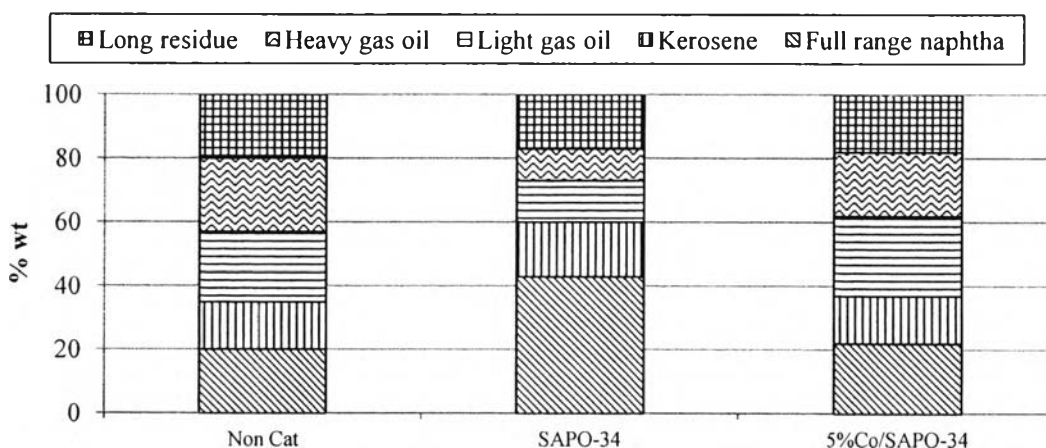


Figure 4.8 Petroleum fractions in maltenes obtained from using SAPO-34 and 5 %Co/SAPO-34.

Figure 4.8 shows petroleum fractions in maltenes. It is found that the maltene from using SAPO-34 contains higher quantity of full range naphtha than the maltene from the non-catalytic case. SAPO-34 seems to be a good catalyst for naphtha production because of its high quantity of full range naphtha. Maltene from using 5 %Co/SAPO-34 has light gas oil fraction greater than that obtained from using pure SAPO-34.

Figures 4.9 and 4.10 show the carbon number distribution of maltenes and mono-aromatics, respectively, from using SAPO-34 and 5 %Co/SAPO-34. It is observed that the oil from the non-catalytic pyrolysis has a wide distribution. The presence of SAPO-34 gives a narrower peak, which tends to shift to a lower carbon number.

Table 4.3 shows the average carbon numbers of maltene and mono-aromatics obtained from using SAPO-34 and 5 %Co/SAPO-34. The result shows that the carbon number shifts to a lower number with using SAPO-34 as a catalyst. However, when 5 %Co is introduced, the average carbon number is higher.

Table 4.3 Average carbon number of maltenes and mono-aromatics obtained from using SAPO-34 and 5 %Co/SAPO-34.

Samples	Carbon number average of maltene	Carbon number average of mono-aromatics
Non Cat	17.1	21.1
SAPO-34	13.8	13.1
5 %Co/SAPO-34	16.9	17.9

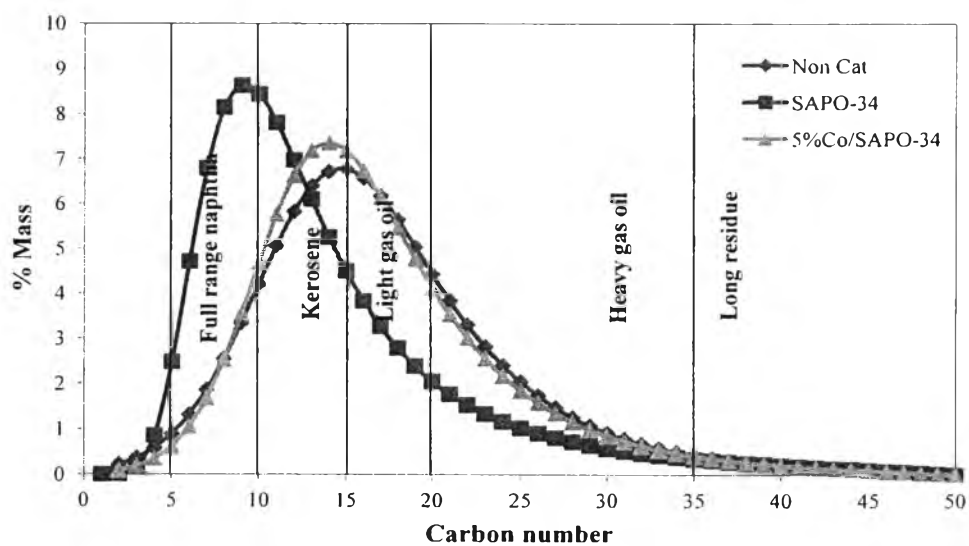


Figure 4.9 Carbon number distribution of maltene from using SAPO-34 and 5 %Co/SAPO-34.

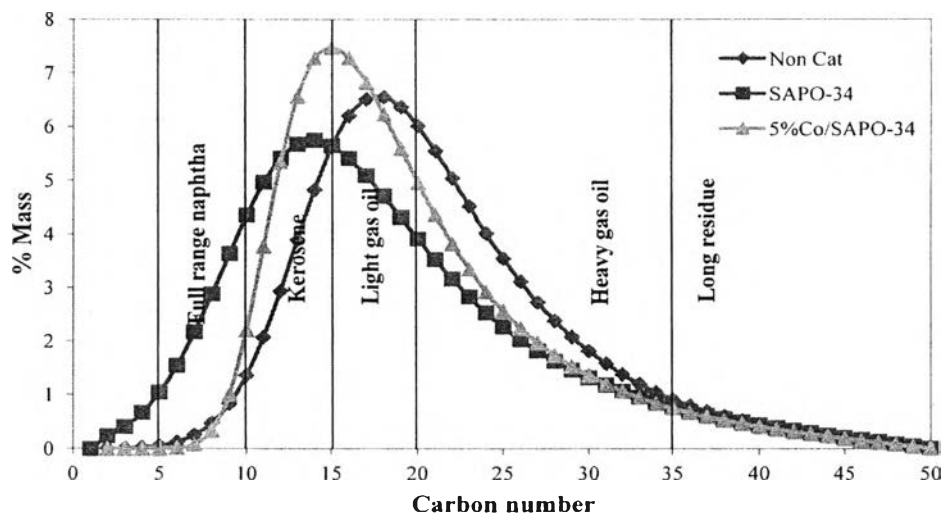


Figure 4.10 Carbon number distribution of mono-aromatics from using SAPO-34 and 5 %Co/SAPO-34.

4.2 Effects of Co-loading on Acid Zeolites

In the catalytic waste tire pyrolysis, the amount of Co supported on acid zeolites (HY, HMOR, HBETA and HZSM-5) was fixed at 5 wt%. The influence of the catalysts on pyrolysis products is discussed as follows.

4.2.1 Physical Properties of Catalysts

Table 4.4 shows the physical properties of catalysts used in the experiments. The order of pore size and pore volume of catalysts are as follows: HY>HBETA>HMOR>HZSM-5. The order of surface area is as follows: HBETA>HY>HMOR>HZSM-5. The acid strength of catalysts (according to $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio) is as follows: HZSM-5>HBETA>HMOR>HY. With Co loading on all zeolite supports, the surface area of supports is lower than those of the corresponding pure zeolites because Co partially blocks the pore opening of the zeolite.

Table 4.4 Physical properties of different zeolites loaded with 5 %Co

Catalysts	SiO ₂ /Al ₂ O ₃ (mol/mol)	Dimension	Pore size (Å)	Specific surface area (m ² /g)	Total pore volume (cm ³ /g)
HY	15	3D	7.4	590.4	0.576
HMOR	19	1D	6.5 x 7.0	462.5	0.359
HBETA	27	3D	6.4 x 7.6	604.3	0.492
HZSM-5	40	3D	5.3 x 5.6	373.4	0.245
5 %Co/HY	15	3D	6.81	365.1	0.144
5 %Co/HMOR	19	1D	6.26	382	0.253
5 %Co/HBETA	27	3D	6.71	545.8	1.037
5 %Co/HZSM-5	40	3D	5.84	251.8	0.21

4.2.2 Product Distribution

The product distributions obtained from the catalytic pyrolysis of waste tire using Co supported on acid zeolites are shown in Figure 4.11. The results show that using acid zeolites leads to the reduction of the oil fraction and the increase in the gaseous fraction due to the acid sites of catalysts. 5 %Co supported on acid zeolites results in an increasing gas yield with a decrease of liquid product.

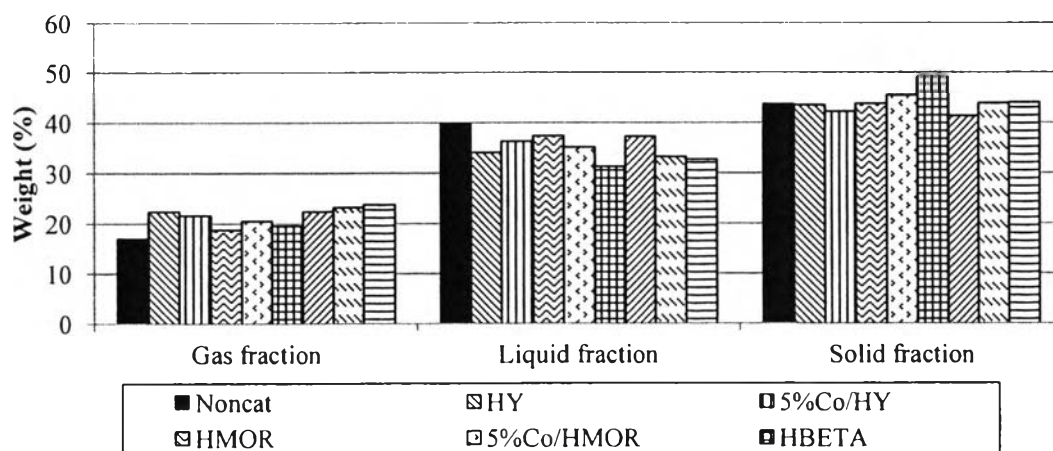


Figure 4.11 Product distribution obtained from the catalytic pyrolysis of waste tire using acid zeolites and 5 %Co supported on acid zeolites.

4.2.3 Gaseous Products

The gas compositions obtained from 5 %Co supported on acid zeolites can be illustrated in Figure 4.12. The presence of acid zeolites results in a decrease in C5, but an increase in propane and C4 as compared to the non-catalytic case. The introduction of Co loaded on acid zeolites increases in methane and ethane, whereas the amounts of C4+ hydrocarbons are decreased with using 5 %Co supported on acid zeolites.

Figures 4.13 and 4.14 show light olefins (ethylene and propylene) and cooking gas (propane and mixed-C4) obtained from pyrolysis. The results show that HY gives the highest amount of light olefins, and HZSM-5 zeolite gives the highest amount of cooking gas among the other zeolites. With Co loaded on all zeolites, the light olefins and/or cooking gas yields insignificantly change. 5 %Co/HY insignificantly increases light olefins production from 4.82 wt% to 4.84 wt%. 5 %Co/HBETA insignificantly increases cooking gas production from 7.71 wt% to 7.77 wt%.

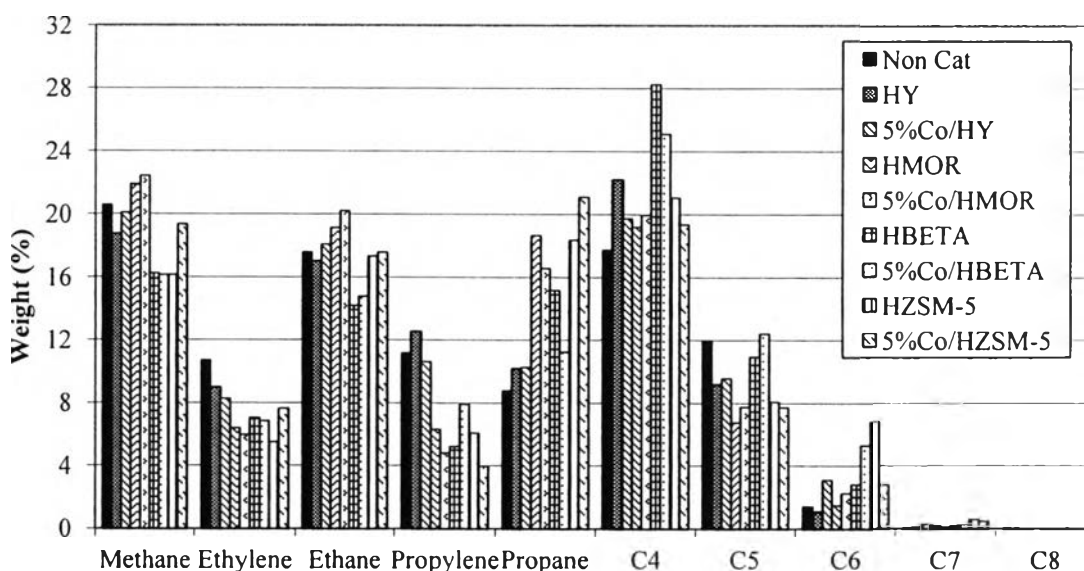


Figure 4.12 Gas compositions obtained from waste tire pyrolysis using acid zeolites and 5 %Co supported on acid zeolites.

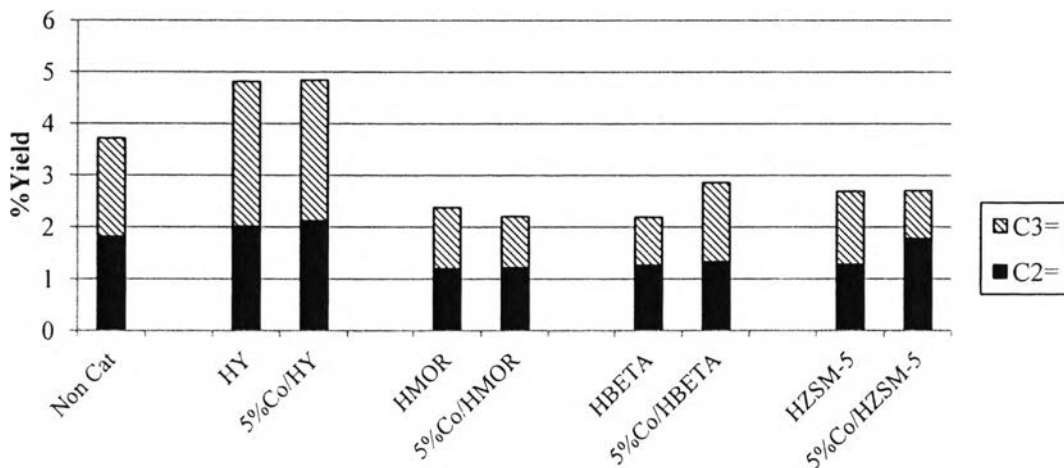


Figure 4.13 Light olefins production from using acid zeolites and 5 %Co supported on acid zeolites.

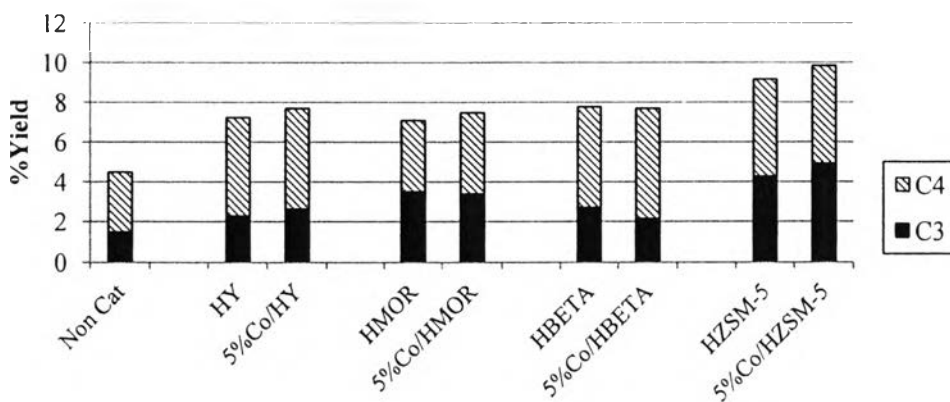


Figure 4.14 Cooking gas production from using acid zeolites and 5 %Co supported on acid zeolites.

4.2.4 Oil Products

4.2.4.1 Qualitative Analysis

The liquid products obtained from pyrolysis are classified into five fractions: saturated hydrocarbons, mono-aromatics, di-aromatics, poly-aromatics, and polar-aromatics by using liquid chromatography. Figure 4.15 shows the chemical compositions in maltenes obtained from using acid zeolites and 5 %Co supported on acid zeolites. It is found that HY and HMOR increase saturated hydrocarbons as compared to the non-catalytic case. The use of all acid zeolites increases mono-aromatics in the maltene as compared to the non-catalytic case, and

HZSM-5 gives the highest amount of mono-aromatics among the other zeolites. It is possibly caused by pore structure of HZSM-5. HZSM-5 has pore size around 5.58 Å (in Table 4.4) that can fit the majority of single-aromatics, that are found in tire-derived oil as shown in Table 4.5. Using 5 %Co supported on all zeolites, mono-aromatics increase, whereas saturated hydrocarbons decrease when compared with those of pure zeolites. Additionally, poly-aromatics decrease with using 5 %Co supported on HMOR and HBETA. It can be suggested that the active sites of Co promote the activity in hydrogenation and ring opening reaction that can reduce concentration of multi-ring aromatic (Pedrosa *et al.*, 2006). Moreover, Co leads to aromatization via Diels-Alders reaction, which increases mono-aromatics (Pinket and Jitkarnka, 2010). This is the reason why the mono-aromatics in oil increase when Co is added. 5 %Co/HZSM-5 gives the highest amount of mono-aromatics among of the other catalysts.

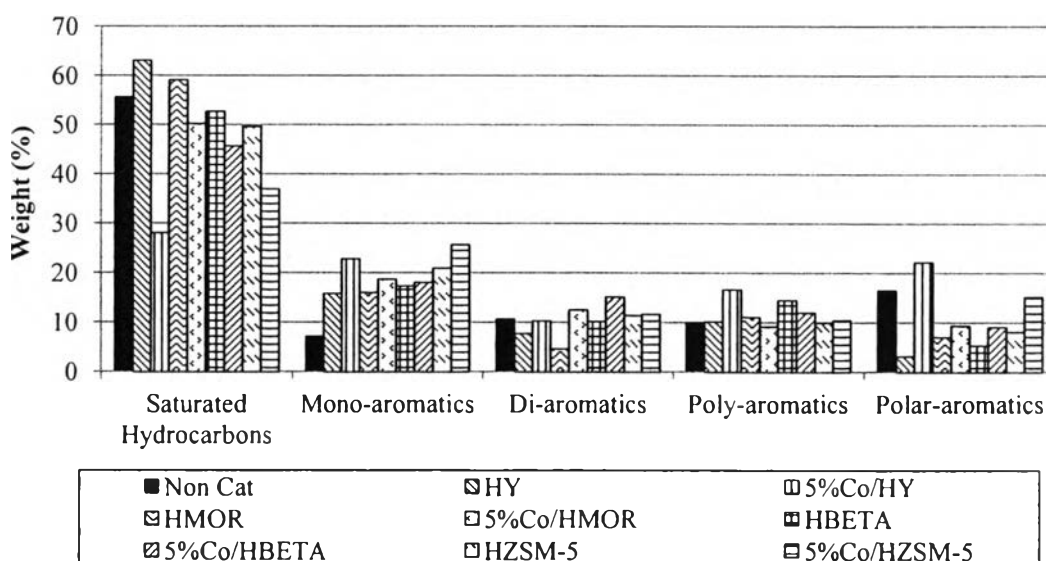


Figure 4.15 Chemical composition in maltenes obtained from using acid zeolites and 5%Co supported on acid zeolites.

Table 4.5 Single-ring aromatic hydrocarbons in oil (Jae *et al.*, 2011)

Aromatic hydrocarbons	Kinetic diameter (Å)
Toluene	5.85
Benzene	5.85
Indane	6.30
Trimethylbenzene (TMB)	8.62
1,3,5-TMB	8.60
1,2,4-TMB	7.60
1,2,3-TMB	6.60
Ethyl benzene	6.00
2-Ethyl toluene	6.60
3-Ethyl toluene	6.60
4-Ethyl toluene	6.60
p-Xylene	5.85
m-Xylene	6.80
o-Xylene	6.80

Figure 4.16 shows the amount of asphaltene in the pyrolytic oils obtained from acid zeolites and 5 %Co supported on acid zeolites. It reveals that as compared to the non-catalytic case, the weight fraction of asphaltene in pyrolytic oils drastically reduces with using the zeolite supports. Moreover, it is further reduced with using 5 %Co loading. It is possibly caused by Co that can promote cracking of heavy parts in oil, and then can improve the oil product.

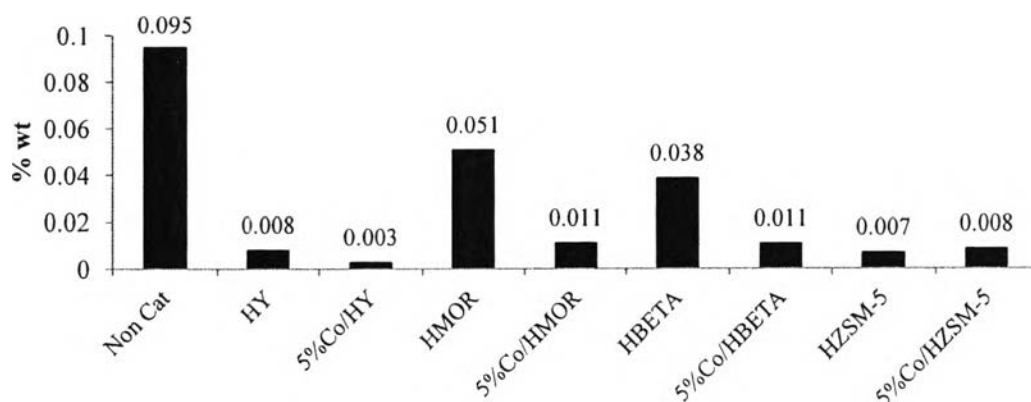


Figure 4.16 Weight fraction of asphaltenes in the pyrolytic oils obtained from using acid zeolites and 5 %Co supported on acid zeolites.

Figure 4.17 shows the sulfur content in the oil product obtained from acid zeolites and 5 %Co supported on acid zeolites. The result shows that HY decreases the amount of sulfur in the oil product from 1.08 wt% (the non-catalytic case) to 0.98 wt%. The presence of 5 %Co/HY promotes the decrease of sulfur concentration in the oil product. It can be suggested that the Co metal has the ability to break C-S-C bond with using 5 %Co/HY as a support. With using 5 %Co supported on HMOR, HBETA, and HZSM-5, the sulfur content in oil products slightly increases.

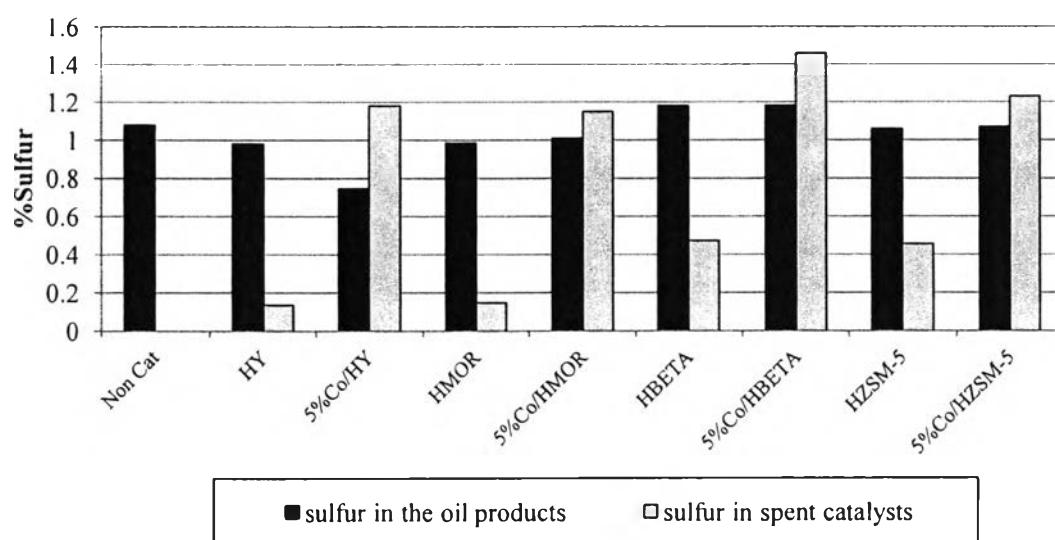


Figure 4.17 Sulfur content in the oil products obtained from using acid zeolites and 5 %Co supported on acid zeolites.

4.2.4.2 Quantitative Analysis

Figure 4.18 shows the petroleum fractions in maltenes obtained from using acid zeolites and 5 %Co supported on acid zeolites. Using the zeolite supports, the light fractions such as naphtha and kerosene increase whereas the heavy fractions such as gas oils and long residue decrease. The results show that HY gives the highest naphtha and kerosene among the pure zeolites. With loading 5 %Co on zeolite supports, oil exhibits higher gas oils as compared to those obtained from the pure zeolites, except 5 %Co/HZSM-5. The results indicate that using Co loading on some supports (HY, HMOR, and HBETA), light fractions (naphtha and kerosene) are transformed to heavier fractions; gas oils and long residue. In the case of 5 %Co/HZSM-5, naphtha is increased.

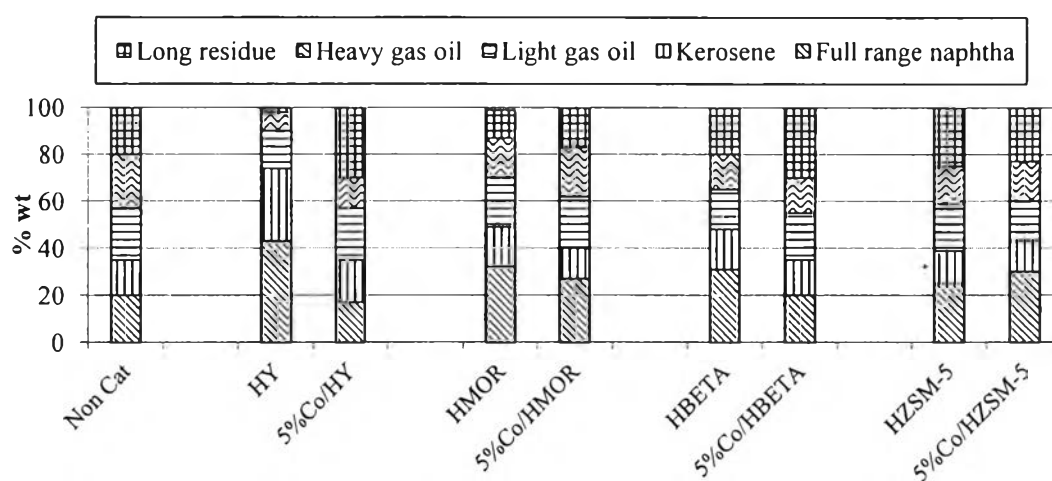


Figure 4.18 Petroleum fractions in maltenes obtained from using acid zeolites and 5 %Co supported on acid zeolites.

The carbon number distributions of maltenes and monoaromatics using acid zeolites and 5 %Co supported on acid zeolites are shown in Figures 4.19 and 4.20. From Figures 4.19, the results show that liquid products are classified into petroleum fractions by carbon numbers. It can be seen that the heavy fractions such as heavy gas oil (C₁₉-C₃₅) and long residue (>C₃₅) are decreased with using catalysts from those produced by the non-catalytic case. The liquid products obtained from using no catalyst are highly distributed in the range of light

gas oil (C14-C19). With using HY, HMOR and HBETA, and HZSM-5 the liquid products are highly distributed in the range of kerosene fraction (C10-C14). With Co loading, most liquid products are distributed in the range of gas oil fraction, except 5 %Co/HY. The main fraction in the oil from using 5 %Co/HY is full range naphtha (C5-C10). This suggests that 5 %Co/HY has the highest cracking activity which results in the formation of lighter products. From Figure 4.20, it is found that using zeolites tends to shift of the peak to a lower carbon number as compared to the non-catalytic case. Using 5 %Co supported on HY, the peak shifts to the smallest carbon number, which means the oil products tend to have the highest concentration of single-ring aromatics such as benzene, toluene and xylene (low carbon numbers) and less multi-ring aromatics (high carbon numbers). The concentration of light mono-aromatics, which are in the range of C6-C8, can be ranked in the order; 5 %Co/HMOR (6.24 wt%) > 5 %Co/HZSM-5 (4.73 wt%) > 5 %Co/HY (2.17 wt%) > 5 %Co/HBETA (1.22 wt%). Although 5 %Co/HMOR seems to give the highest light mono-aromatic (C6-C8), the quantity is roughly estimated from the carbon number distribution. Further measurement using a standard equipment is needed to confirm the result.

Table 4.6 shows the average carbon number of maltenes and mono-aromatics from using acid zeolites and 5 %Co supported on acid zeolites. The results show that the non-catalytic oil has a high value. The presence of all zeolites tends to shift to a lower carbon number. Using Co loading tends to shift back to a higher carbon number as compared to those of pure zeolite, except 5 %Co/HY and 5 %Co/HZSM-5.

Table 4.6 Average carbon number of maltenes and mono-aromatics obtained from using HY and 5 %Co/HY

Samples	Carbon number average of maltene	Carbon number average of mono-aromatics
Non Cat	17.1	21.1
HY	12.9	15.4
5 %Co/HY	13.8	14.8
HMOR	15.2	10.0
5 %Co/HMOR	16.3	20.9
HBETA	16.7	14.3
5 %Co/HBETA	18.7	22.8
HZSM-5	17.7	20.8
5 %Co/HZSM-5	17.4	18.0

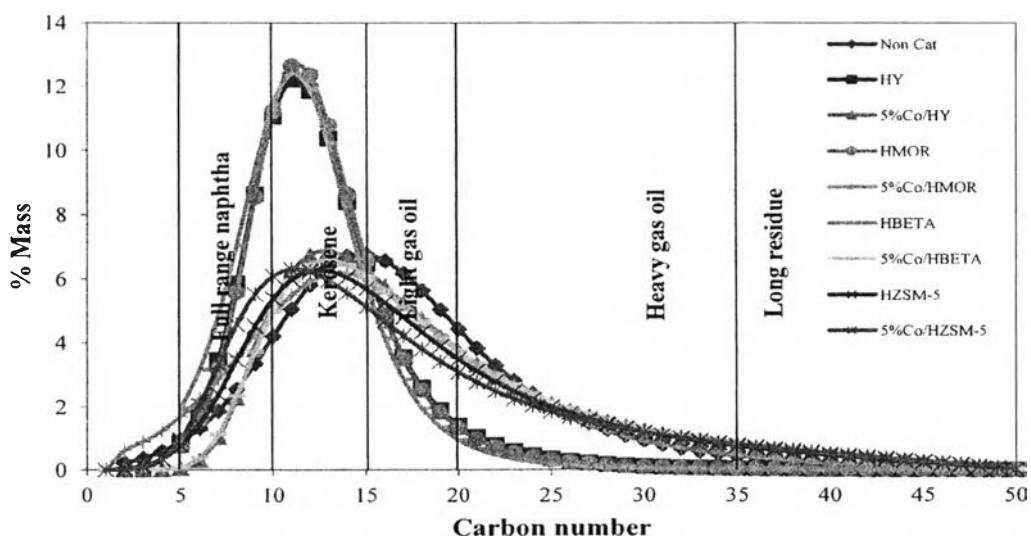


Figure 4.19 Carbon number distribution of maltene from using acid zeolites and 5 %Co supported on acid zeolites.

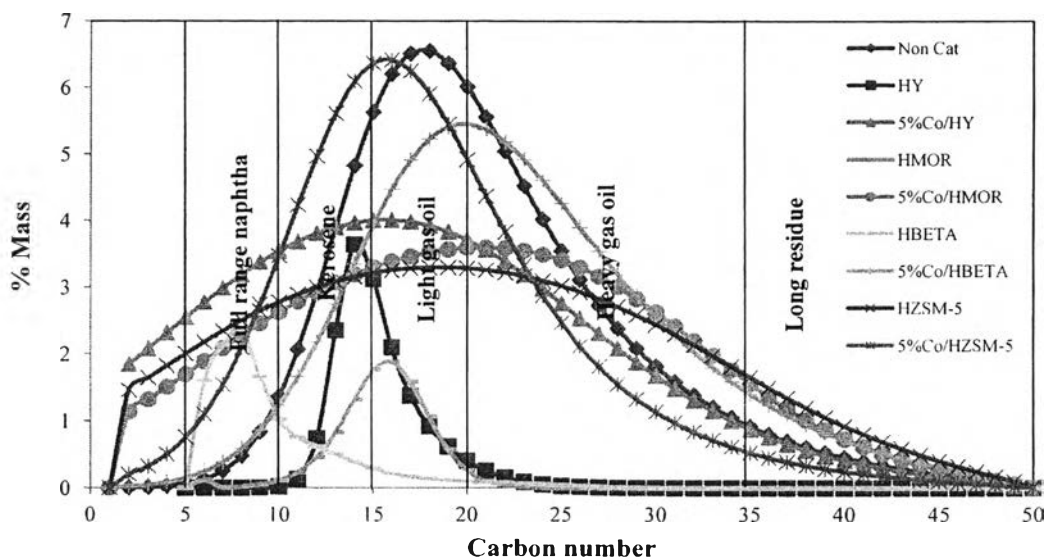


Figure 4.20 Carbon number distribution of mono-aromatics from using acid zeolites and 5 %Co supported on acid zeolites.

4.3 Effect of SAPO-34 as an Additive in Acid Zeolites

In this section, SAPO-34 is used as an additive in acid zeolites (HY, HMOR, HBETA and HZSM-5).

4.3.1 Physical Properties of Catalysts

To prepare binary supports, 50 % of acid zeolites (HY, HMOR, HBETA and HZSM-5) was mixed with another 50 % of SAPO-34. Likewise, 50 % of 5 %Co-supported acid zeolites (HY, HMOR, HBETA and HZSM-5) was mixed with another 50 % of 5 %Co/SAPO-34. Table 4.7 shows the physical properties of the binary supports. The results show that Co supported on the binary supports reduces the surface area and pore volume of binary catalysts.

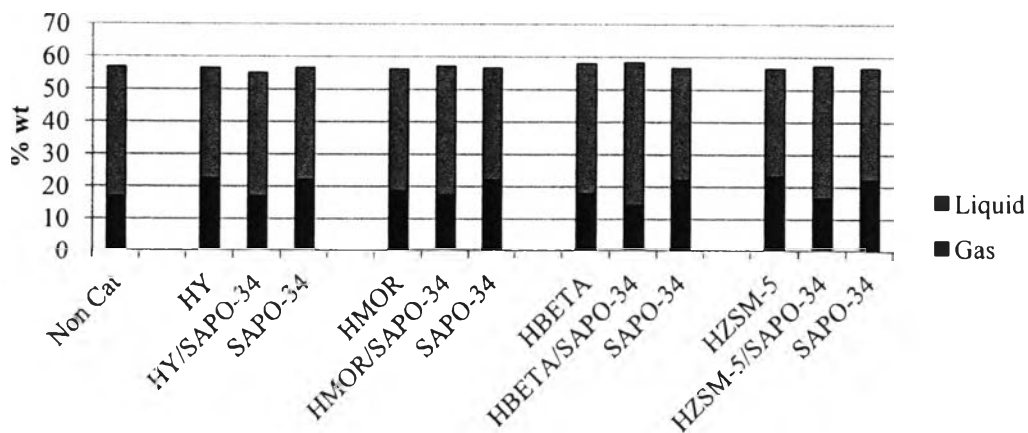
Table 4.7 Physical properties of binary catalysts with and without 5 %Co

Catalysts	Average Pore size (Å)	Specific surface area (m ² /g)	Total pore volume (cm ³ /g)
HY/SAPO-34	6.81	408.6	0.433
HMOR/SAPO-34	6.75	313.9	0.056
HBETA/SAPO-34	6.01	283.3	0.166
HZSM-5/SAPO-34	4.58	157.6	0.159
5 %Co/(HY+ SAPO-34)	7.07	465.9	0.749
5 %Co/(HMOR+ SAPO-34)	7.37	178.9	0.437
5 %Co/(HBETA+ SAPO-34)	7.11	959.5	0.659
5 %Co/(HZSM-5+ SAPO-34)	7.22	264.4	0.532

4.3.2 Product Distribution

The products obtained from waste tire pyrolysis are distributed into gas, liquid, and solid as shown in Figure 4.21. The results show that binary catalysts do not significantly increase the gaseous fractions. Using binary catalysts, the gaseous fractions decrease as compared to those of single support catalysts. For the cases of using Co loaded on all binary supports, all catalysts show a decrease in the gaseous fraction as compared to the corresponding single support catalysts.

a)



b)

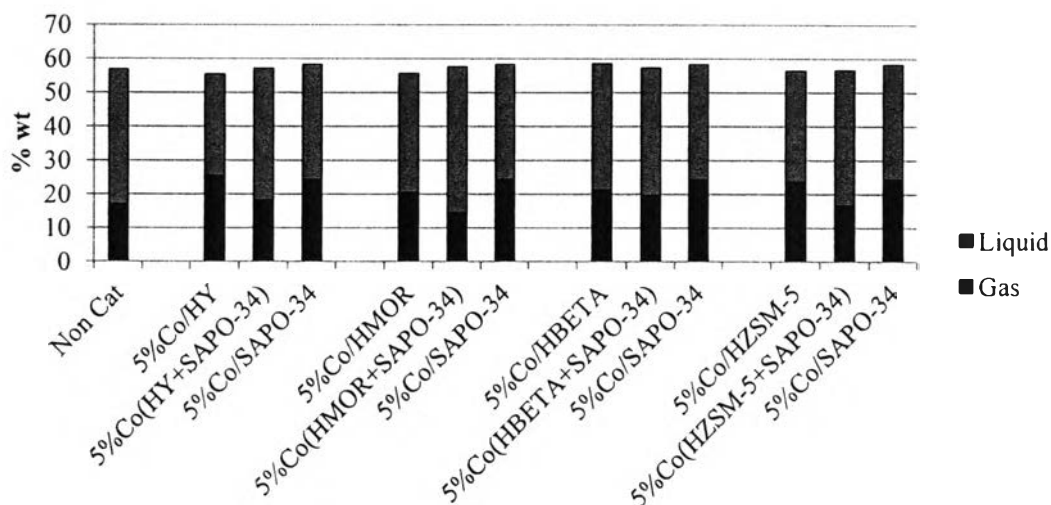
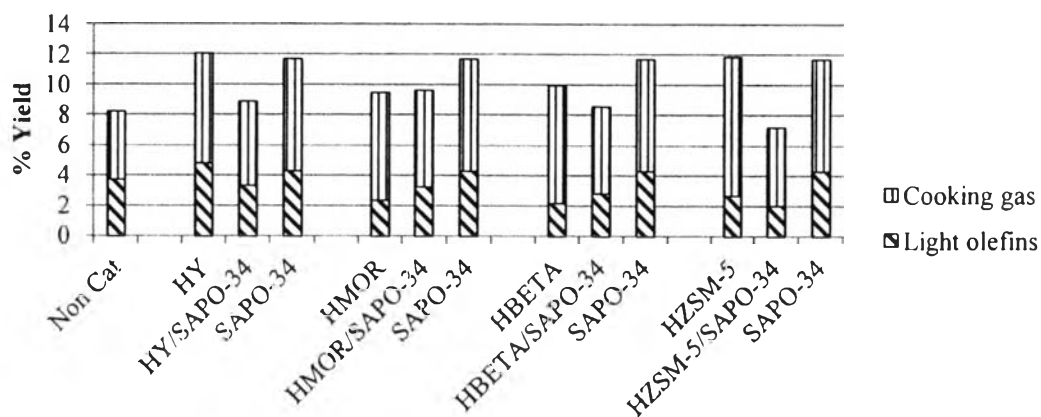


Figure 4.21 Product distribution obtained from the catalytic pyrolysis of waste tire using a) binary supports, and b) 5 %Co supported on binary supports.

4.3.3 Gaseous Products

The gaseous products were analyzed for their valuable components such light olefins and cooking gas as shown in Figure 4.22. The results show that using the binary supports do not help to promote light olefins and cooking gas production. The use of a single support is a better choice. For the comparison between Co loaded on all single supports and on all binary-supports, the results show the same way as the binary supports and the single supports without Co-loading.

a)



b)

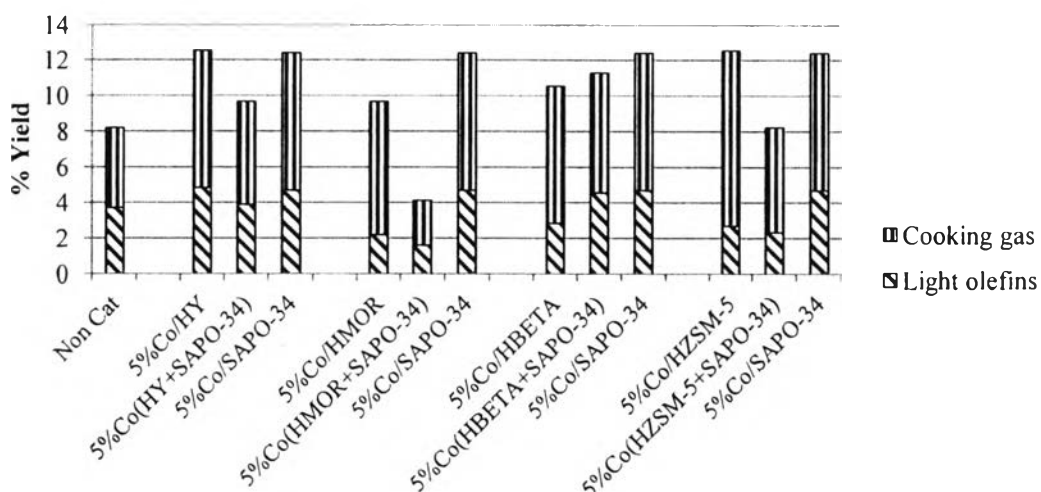


Figure 4.22 Light olefins and cooking gas production from using a) binary supports, and b) 5 %Co supported on binary supports.

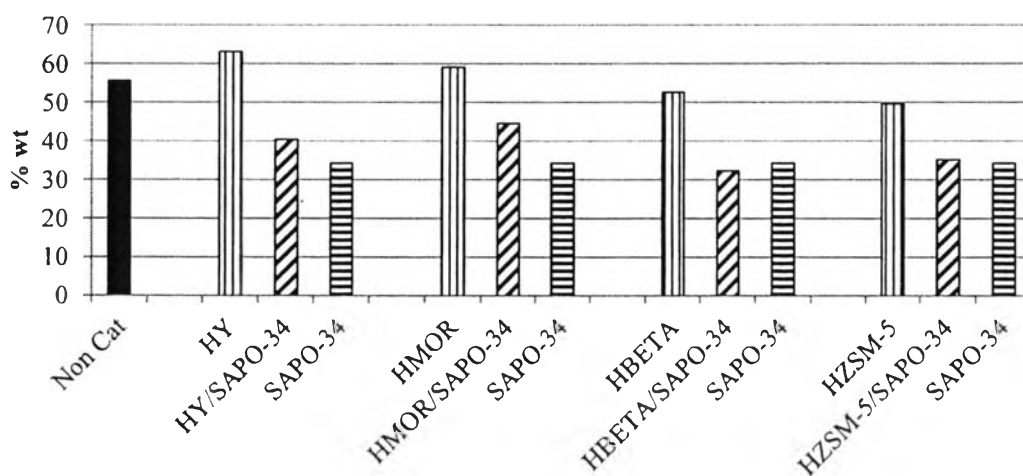
4.3.4 Oil Products

4.3.4.1 Qualitative Analysis

The liquid compositions are classified into five fractions including saturated hydrocarbons, mono-aromatics, di-aromatics, poly-aromatics, and polar-aromatics. But, in this section, only saturated hydrocarbons and mono-aromatics are discussed. Figures 4.23 and 4.24 show the chemical composition in the oil products. Figures 4.23 shows that the amount of saturated hydrocarbons obtained from the binary supports is a value between those obtained from acid zeolites and SAPO-34. The results indicate that it is resulted from the dilution between each pair

of acid zeolites and SAPO-34. In case of Co loading on the binary supports, the content of saturated hydrocarbons in maltenes decreases as compared to the Co loading on the corresponding single support cases, indicating a negative effect of using a binary support.

a)



b)

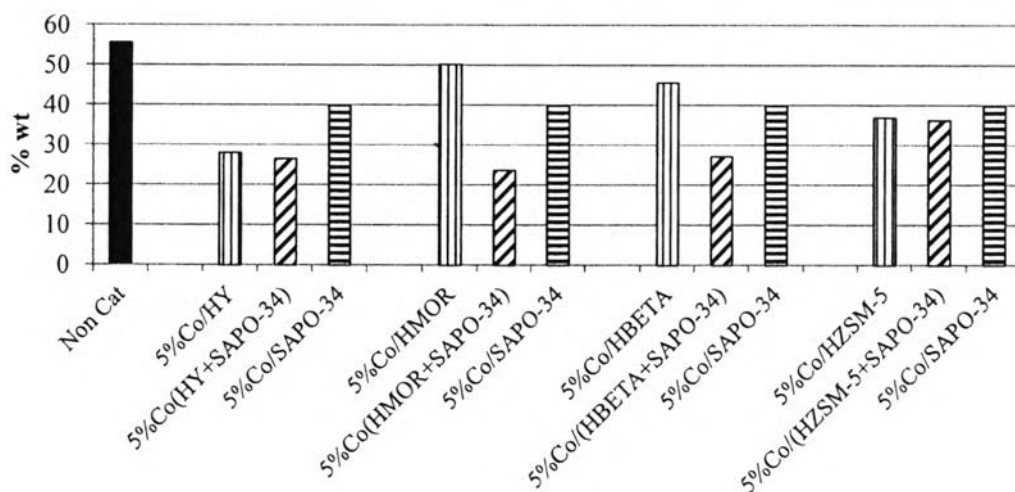
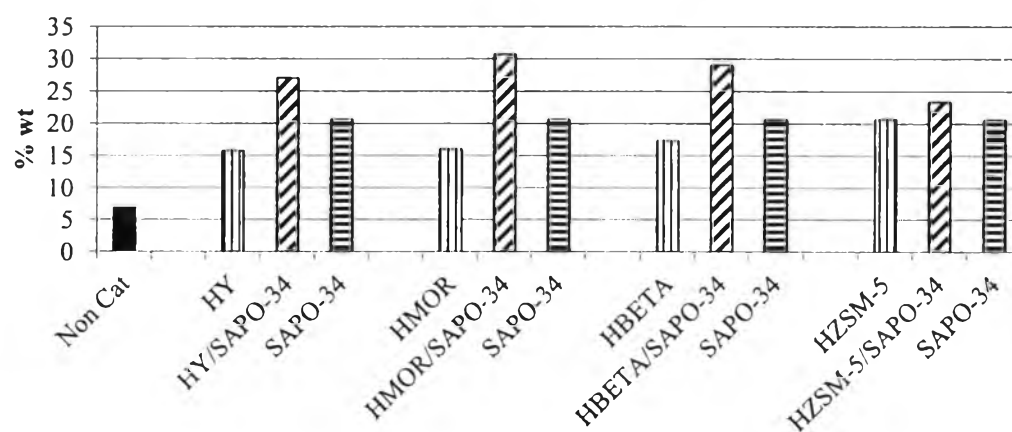


Figure 4.23 Saturated hydrocarbons in maltenes obtained from using a) binary supports, and b) 5 %Co supported on binary supports.

From Figure 4.24, it is found that the binary supports apparently increase mono-aromatics in maltenes to a higher value than those of the two corresponding single supports, indicating the synergy effect occurring between

the two supports. With Co loading, the synergy effect between 5 %Co/(HY+SAPO-34) and 5 %Co/(HMOR+SAPO-34) also occurs, which results in an increase in the mono-aromatics production. However, 5 %Co/(HBETA+SAPO-34) and 5 %Co/(HZSM-5+SAPO-34) give a lower mono-aromatics production than 5 %Co supported on the two corresponding single supports, reflecting the case of dilution effect and negative effect, respectively.

a)



b)

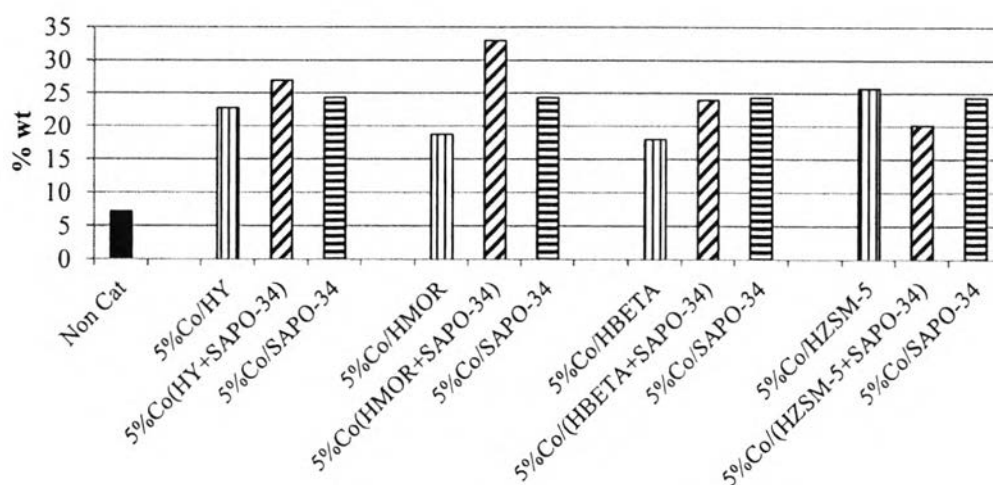
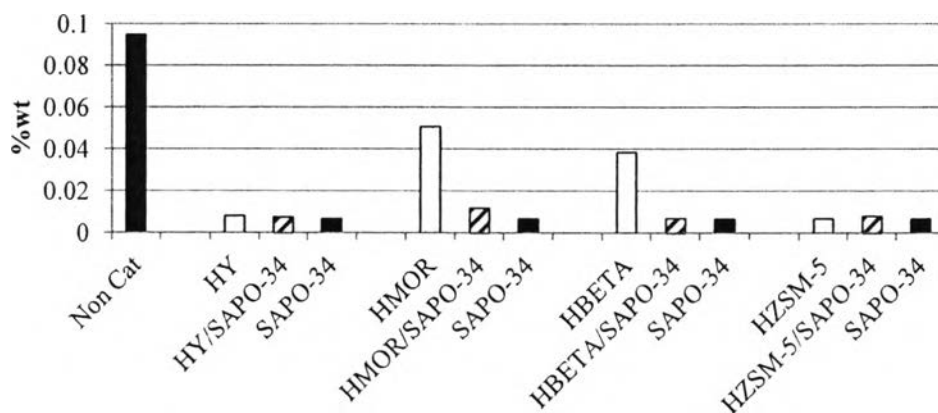


Figure 4.24 Mono-aromatics in maltenes obtained from using a) binary supports, and b) 5 %Co supported on binary supports.

Figure 4.25 shows the weight fraction of asphaltenes in the pyrolytic oils. The results show that using the binary supports leads to the dilution

between the two supports, giving the asphaltene content that lies in between those of the single supports. Moreover, the Co loading cases give a lower asphaltene content in oils. However, the Co-loaded binary catalysts do not give different results.

a)



b)

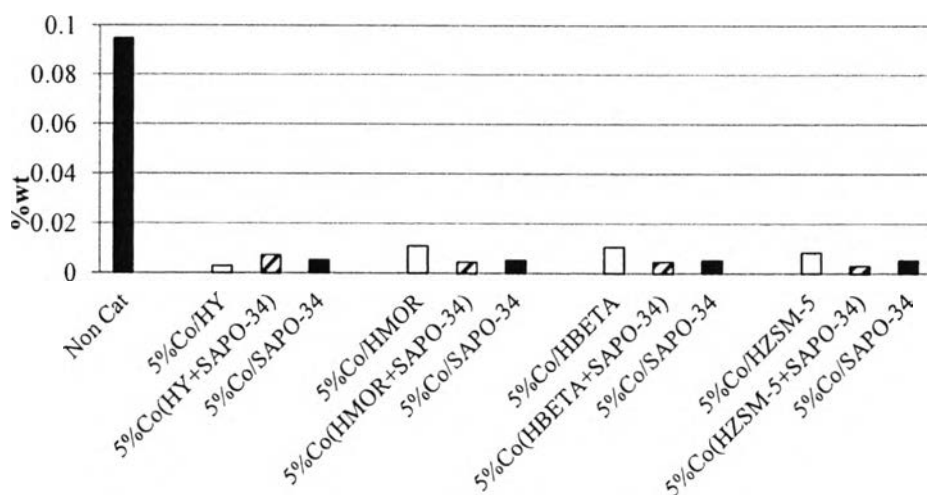
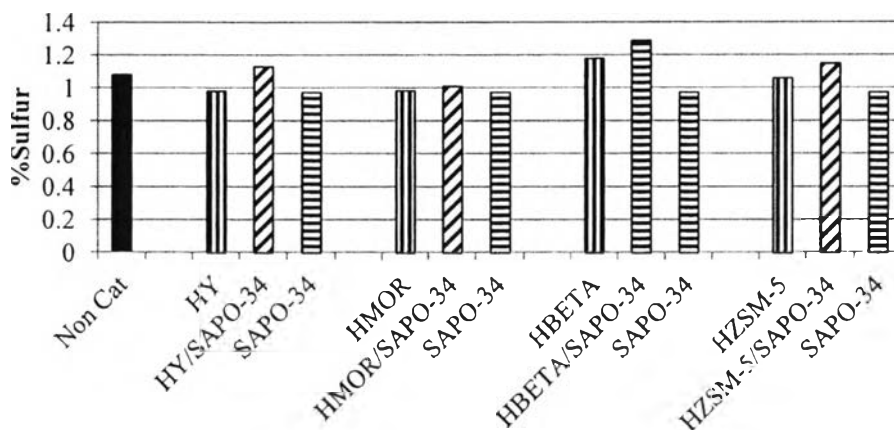


Figure 4.25 Weight fraction of asphaltenes in the pyrolytic oils obtained from using a) binary supports, and b) 5 %Co supported on binary supports.

Figure 4.26 shows sulfur content in the oil products. The results reveal that using the binary supports and 5 %Co supported on binary-supports do not promote low sulfur content in oil. They all give higher sulfur content in oil than a single support, no matter what the support is.

a)



b)

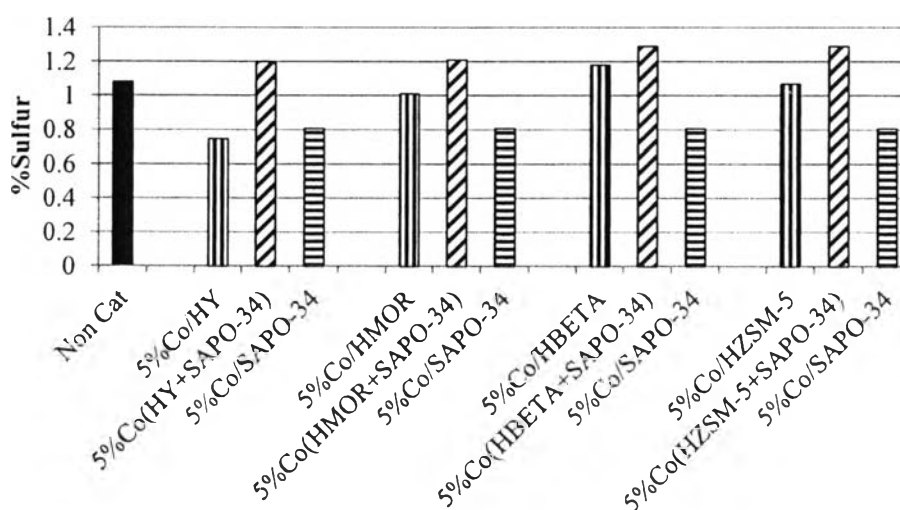


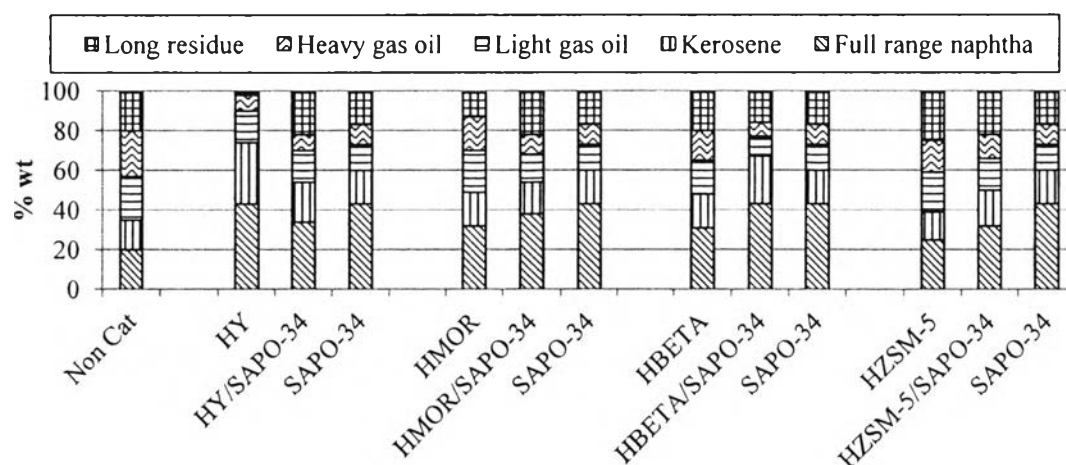
Figure 4.26 Sulfur content in the oil products obtained from using a) binary supports, and b) 5 %Co supported on binary supports.

4.2.4.2 Quantitative Analysis

The oil products were into petroleum fractions, which are full range naphtha (<200 °C), kerosene (200-250 °C), light gas oil (250-300 °C), heavy gas oil (300-370 °C), and long residue (>370 °C) Figure 4.27 shows petroleum fractions obtained from using different catalysts. The result shows that the quality of oil obtained from the binary supports is in general still similar to that from the two corresponding single supports. The quantities of the light fractions (full range naphtha+ kerosene+ light gas oil) and heavy fractions (heavy gas oil+ long residue)

did not significantly change. Furthermore, the use of Co-supported binary support catalysts gave a similar result as the corresponding case without Co loading.

a)



b)

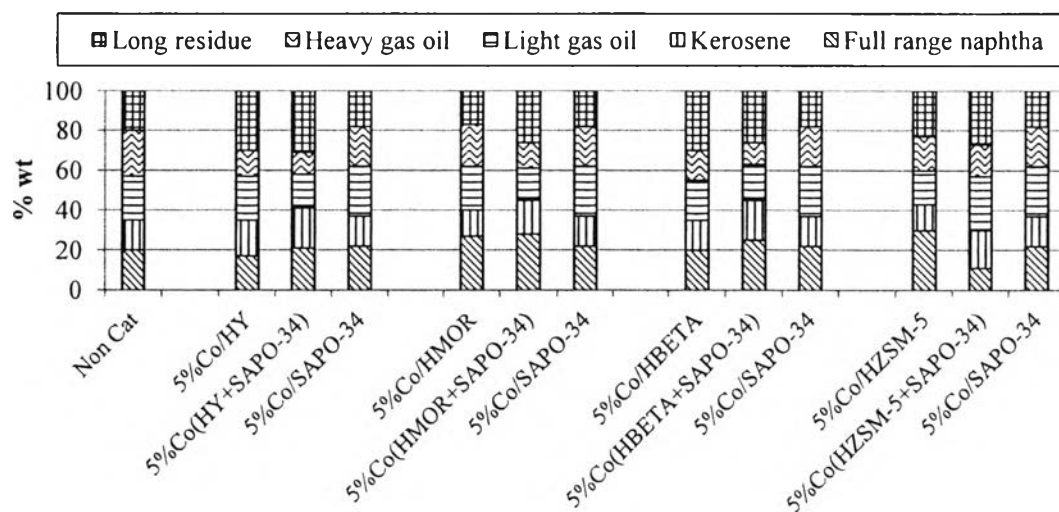
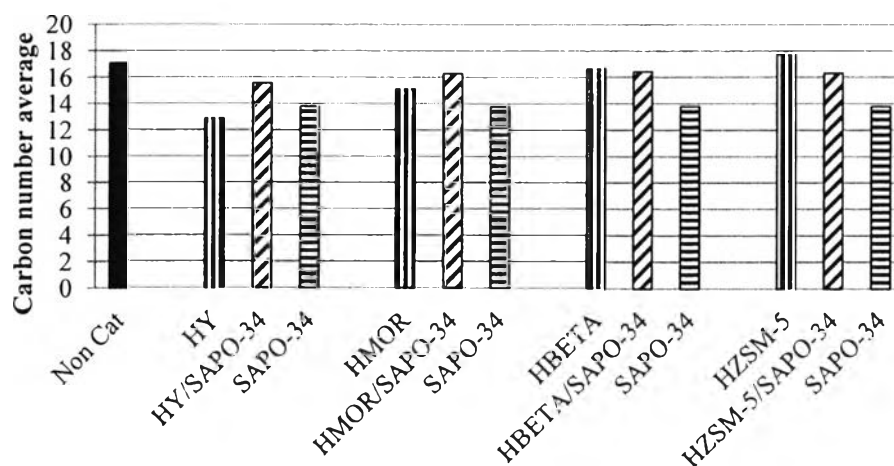


Figure 4.27 Petroleum fractions in maltenes obtained from using a) binary supports, and b) 5 %Co supported on binary-supports.

Figures 4.28 and 4.29 show the carbon number of maltenes and mono-aromatics. From Figure 4.29, the results show that the carbon number of maltenes increases, except those of HZSM-5/SAPO-34 and 5 %Co/(HBETA+SAPO-34). The carbon number of HZSM-5/SAPO-34 lies in between that of

HZSM-5 and SAPO-34, and the carbon number of 5 %Co/(HBETA+SAPO-34) lies in between that of 5 %Co/HBETA and 5 %Co/SAPO-34.

a)



b)

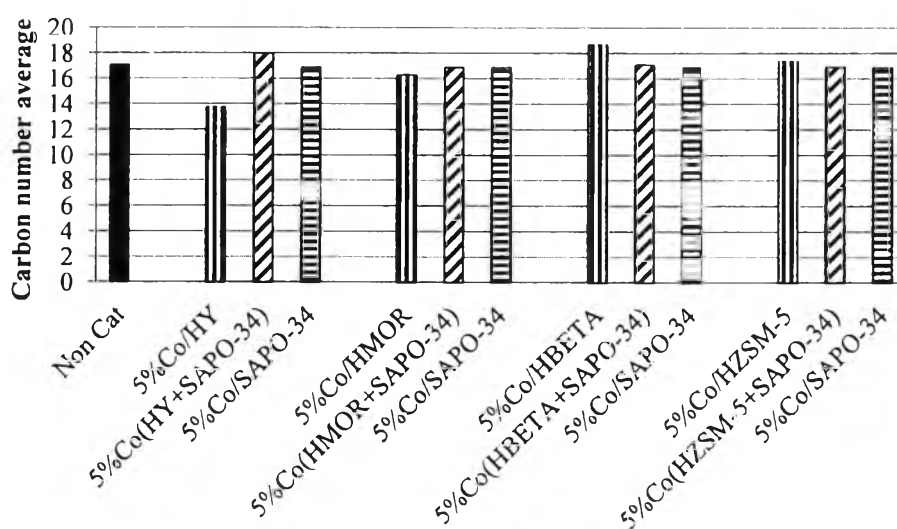
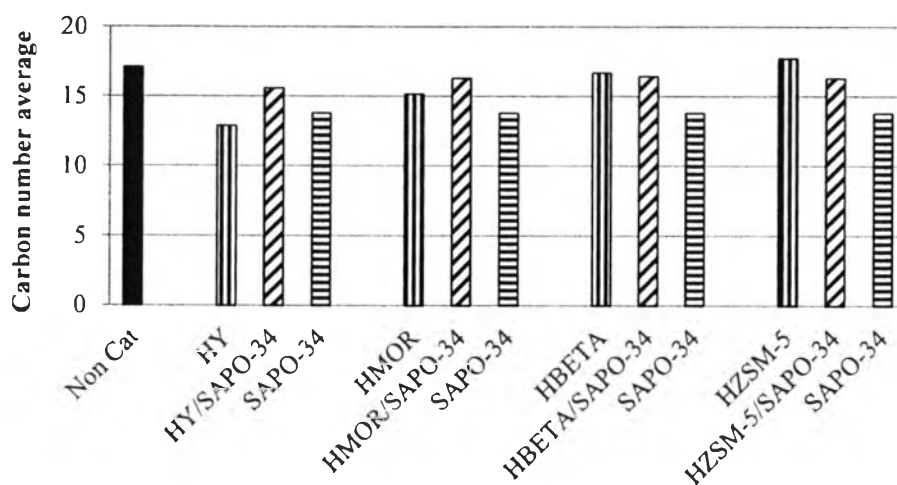


Figure 4.28 Average carbon number of maltenes obtained from using a) binary supports, and b) 5 %Co supported on binary supports.

From Figure 4.29, using the binary supports increase the carbon number of mono-aromatics, except HZSM-5/SAPO-34 that gives the carbon number in between that of HZSM-5 and SAPO-34. In the case of Co supported on

the binary supports, 5 %Co/(HMOR/SAPO-34) and 5 %Co/(HBETA/SAPO-34) give a lower carbon number than 5 %Co/HMOR, 5 %Co/SAPO-34, or 5 %Co/HBETA.

a)



b)

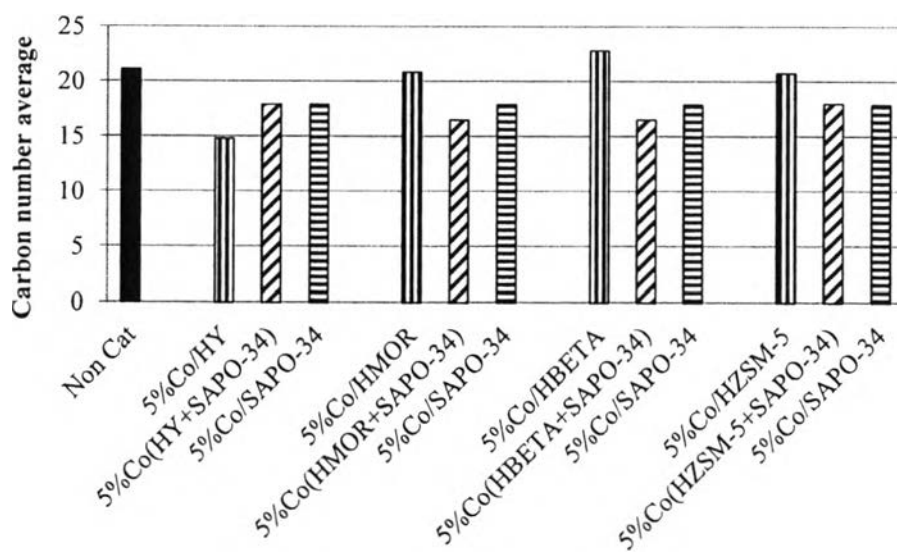


Figure 4.29 Average carbon number of mono-aromatics obtained from using a) binary supports, and b) 5 %Co supported on binary supports.