

CHAPTER IV

RESULTS AND DISCUSSION

This chapter discusses the effect of Ag supported onto zeolite catalysts on the pyrolysis products of waste tire. Furthermore, this chapter also discusses the effect of Ag supported onto zeolite catalysts on desulfurization in oil products.

4.1 Effects of Silver Supported onto Y Zeolite on Pyrolysis Products

4.1.1 Product Distribution

The products obtained from waste tire pyrolysis are distributed into gas, liquid, and solid. Figure 4.1 shows the products distribution obtained from Ag supported on Y zeolite which is varied the weight percent of Ag-loaded as 1, 2, and 3%. As one can see from the figure, the solid yield from all runs is similar. This is attributed to the reason that the all compositions in tire sample are completely decomposed to lower molecular weight products at 500°C (Miguel *et al.*, 2006).

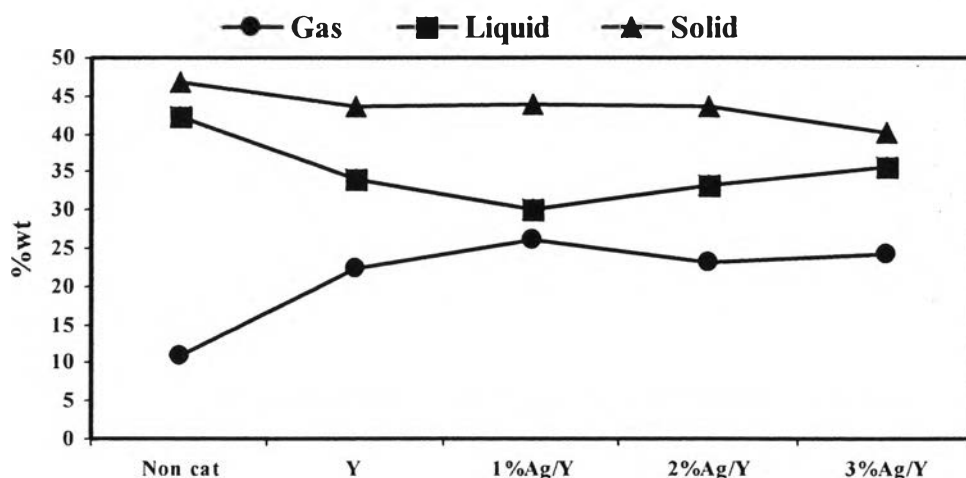


Figure 4.1 Product distribution obtained from the catalytic pyrolysis of scrap tire using Ag supported on Y zeolite.

The results indicate that the catalysts have the influence on the products. The use of Y zeolite as a catalyst decreases the liquid product while the gaseous product increases as compared to the non-catalytic case. It is due to the

cracking activity of Y zeolite resulting in large molecule of products (liquid product) is cracked to smaller molecular size (gas products). In the case of using Ag supported on Y zeolite, 1%Ag/Y decreases liquid yield as compared to using Y zeolite only. The liquid yield obtained from the 1%Ag/Y catalyst decreases from 34.1 wt% to 30.1 wt%, in the relation to the increase of gas yield from 22.4 wt% to 26.1 wt% as compared to the case of using Y zeolite alone. The large molecules are cracked into incondensable-gaseous product due to the high reaction activity of catalysts. Similarly, William *et al.* 2003 explained that catalysts provided other pathways to other products and decreased the amount of oil yields. 2% and 3%Ag/Y have the influence on the increase of liquid yield whereas the gases yield decrease. On the other hand, 2% and 3%Ag/Y give higher liquid yield than that obtained from 1%Ag/Y. It is possible that the amounts of Ag higher than 1 wt% decrease the active site of support (corresponding to BET results, see Table 4.2) resulting in lower cracking activity.

4.1.2 Gaseous Products

The compositions of gaseous product are shown in Figure 4.2. Gases obtained from waste tire pyrolysis consist of methane, ethane, ethylene, propane, propylene, mixed-C4, and mixed-C5. The result shows that the use of catalysts

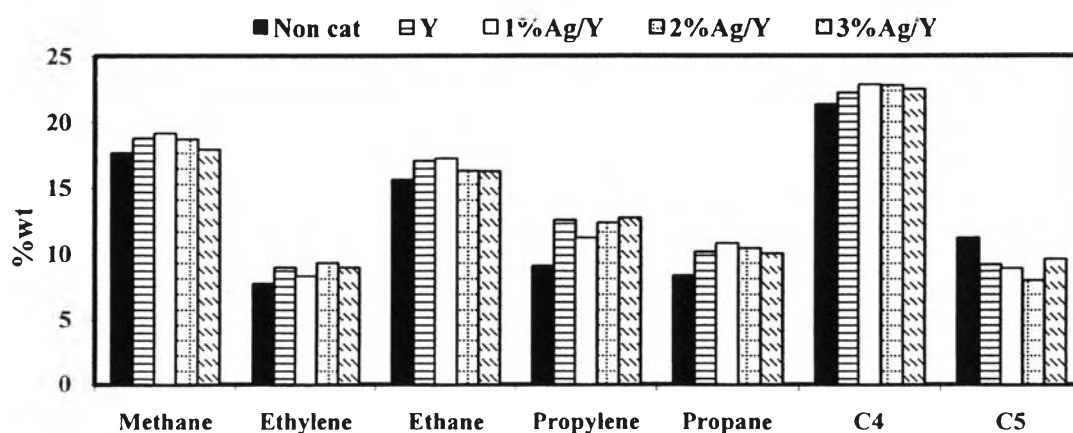


Figure 4.2 Gas compositions obtained from waste tire pyrolysis using Ag supported on Y zeolite.

slightly increases propane, propylene, and mixed-C₄ while mixed-C₅ is decreased as compared to non-catalytic case. The increase of gaseous product is resulted from the cracking activity of studied catalysts.

From the results, the main fraction obtained in all cases is that containing C₄ hydrocarbons. The main substance in this fraction may be butadiene which is the primary cracking products obtained from the breakdown of polymer chains in the waste tire. The primary cracking products are further cracked to light gas products as light olefins (ethylene and propylene) and cooking gas (hereby defined as the mixed gas of propane and mixed-C₄) production. Light olefins and cooking gas are important commercial products and widely used in petrochemical industries. The analysis of the gaseous product shows that 1%Ag/Y zeolite gives the highest amount of cooking gas production (Figure 4.3). Approximately 2.9 times higher cooking gas are obtained as compared to those from non-catalytic pyrolysis.

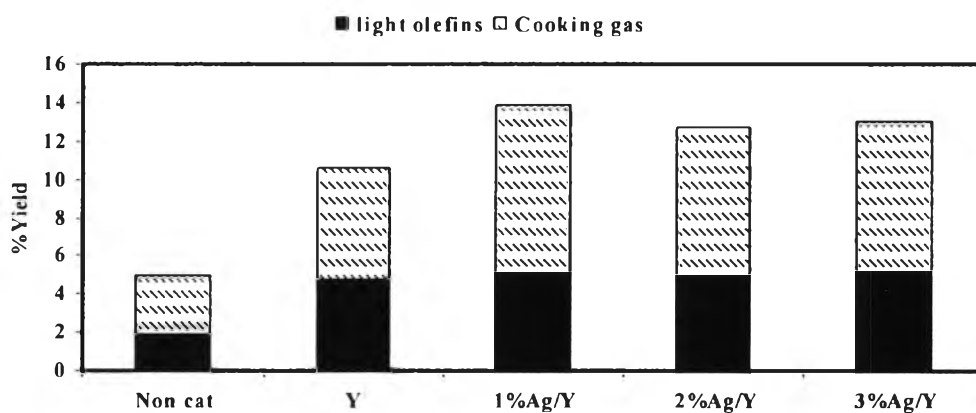


Figure 4.3 Effect of amount of Ag loaded onto Y zeolite on light olefins and cooking gas production

4.1.3 Oil Products

4.1.3.1 Liquid Compositions

The liquid products after asphaltene separation were separated into 5 fractions (saturated hydrocarbons, mono-aromatic, di-aromatic, poly-aromatic, and polar aromatic compounds) according to the chemical composition using liquid adsorption chromatography.

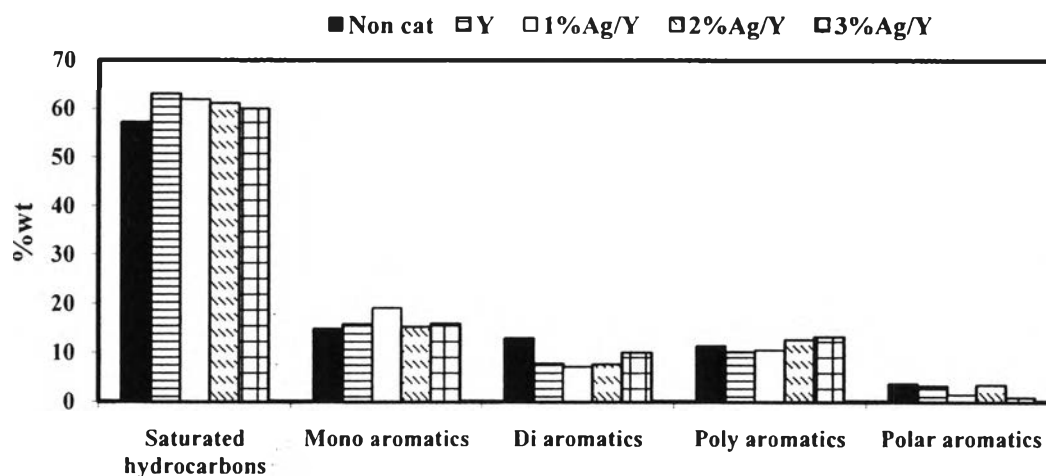


Figure 4.4 Liquid compositions obtained from waste tire pyrolysis using Ag supported on Y zeolite.

Figure 4.4, shows that Y zeolite increases saturated hydrocarbons while di-aromatics are decreased as compared to the non-catalytic case. The use of 1%Ag/Y zeolite as a catalyst gives a lower saturated hydrocarbon than that obtained from using Y zeolite alone. And, it also produces the highest amount of mono-aromatics (19.0 wt %) as compared to other catalysts. The increased amount of Ag loading decreases saturated hydrocarbons whereas di-aromatics and poly-aromatics are increased.

3%Ag/Y gives the high concentrations of di-aromatics and poly-aromatics, and shows low saturated hydrocarbons production. It is possible that the large amount of Ag loading might cover the active sites of Y zeolite resulting in lower activity on cracking. Polar-aromatic compounds are a representative group of sulfur-containing compounds in pyrolytics oil. Figure 4.4 also shows the polar-aromatics concentration obtained from waste tire pyrolysis. The use of Ag supported on Y zeolite gives a lower concentration of polar-aromatics than that obtained from using Y zeolite only. 1%Ag/Y can decrease the polar-aromatics by approximately 2.3 times lower than that obtained from using Y zeolite.

4.1.3.2 Petroleum Fractions

The oil products obtained from catalytic pyrolysis were analyzed by using a SIMDIST Gas Chromatography (SIMDIST GC). From Table 4.1, each fraction is identified according to its boiling point range and carbon number range. These fractions can indicate the quality of pyrolytic oils obtained from waste tire pyrolysis.

Table 4.1 Petroleum fractions (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

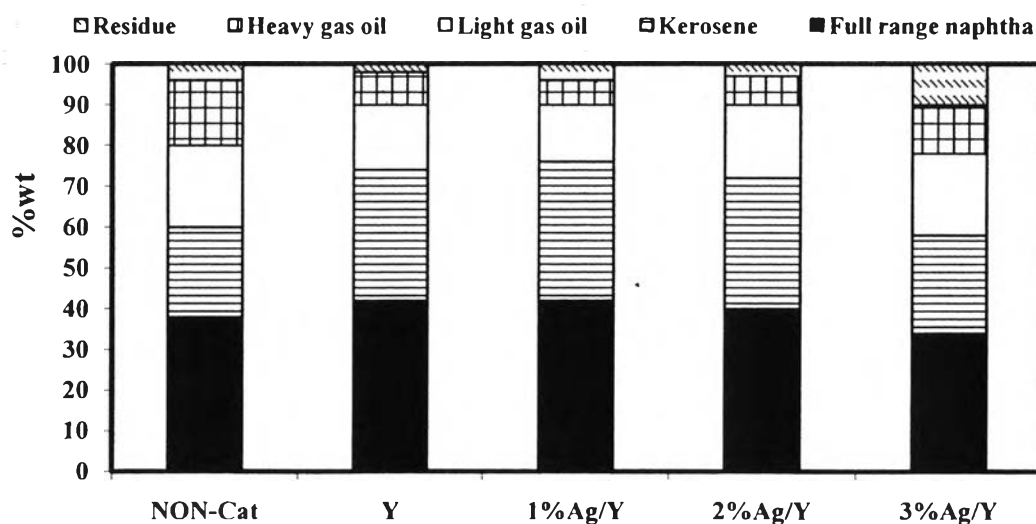


Figure 4.5 Effect of the amount of Ag loaded onto Y zeolite on liquid petroleum fractions.

In the case of petroleum fraction, the result shows that the increased amount of Ag loaded onto Y zeolite has the negative effect because it

increases long residue fraction. 1%Ag/Y slightly decreases light and heavy gas oil fractions whereas kerosene fraction is increased. The production of naphtha, kerosene, and light gas oil is decreased when 2%Ag/Y and 3%AgY were used as catalysts. It can be indicated that the Ag metal may block some active sites of support resulting in lower activity on cracking large molecules to lower molecular-weight molecules. The increased amount of Ag loading on Y zeolite increases the particle size of Ag metal from 3.09 to 6.80 nm. (as presented in Figures 4.6(a)-4.5(c)). The large particle size of Ag covers the active surface of Y zeolite resulting in a decrease in surface area as observed from the BET results in Table 4.2

Table 4.2 Physical properties of Ag loaded on Y zeolite

Samples	Surface area (m²/g)	Total pore volume (cm³/g)	Metal dispersion (%)
Y zeolite	590.4	0.5763	-
1%Ag/Y	579.2	0.3802	29.6
2%Ag/Y	550.5	0.2325	18.6
3%Ag/Y	494.7	0.0614	18.1

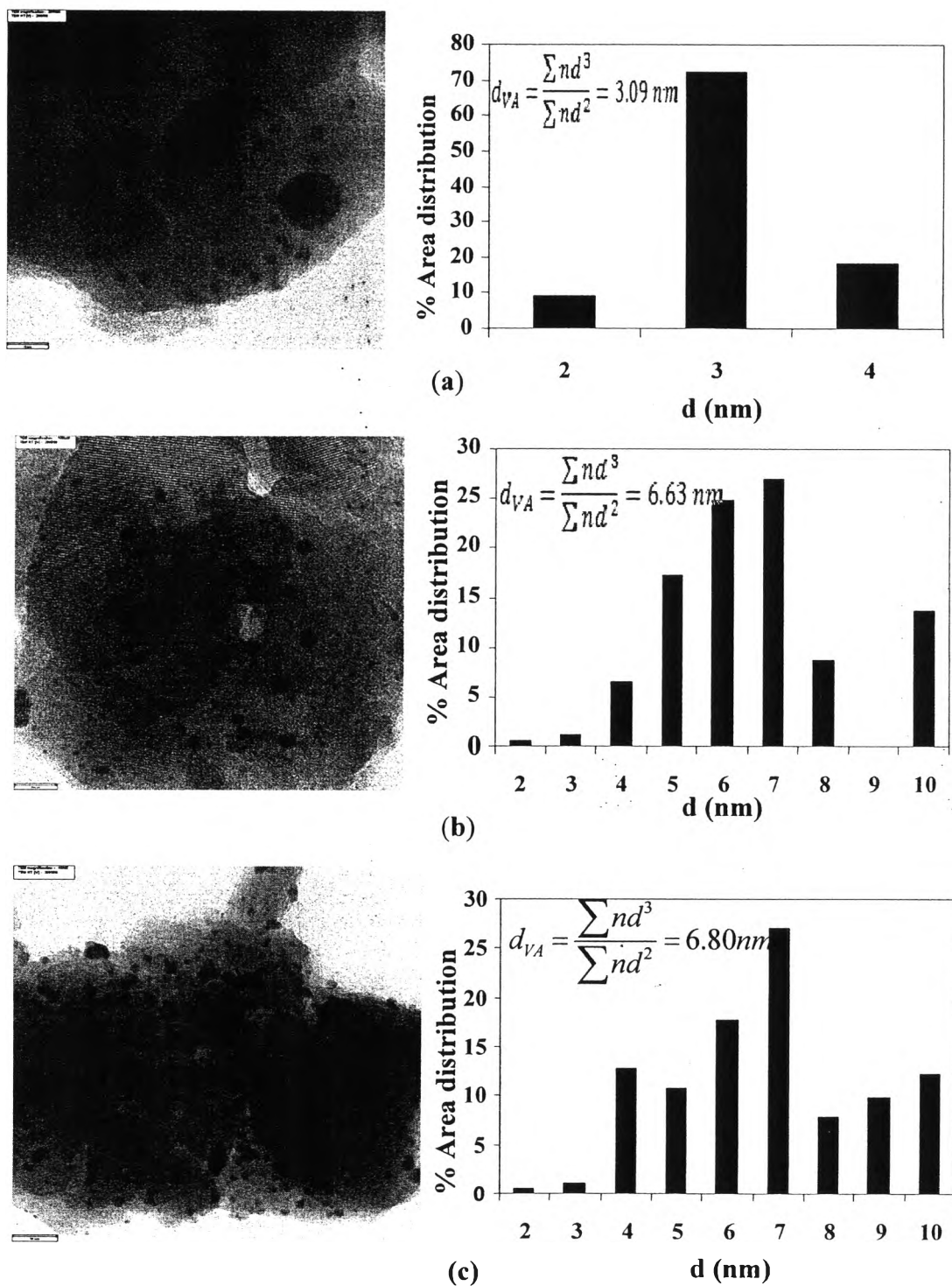


Figure 4.6 TEM images and the size distribution of catalysts: **(a)** 1%Ag/Y, **(b)** 2%Ag/Y, and **(c)** 3%Ag/Y.

4.1.4 Effect of Ag on Desulfurization

Desulfurization is an important process in industry to remove sulfur from petroleum fuels. Due to the fuel quality, it is difficult to satisfy the practical requirement because the environment regulations request a low content of sulfur in oil products. Sulfur content in oil products is an environmental concern because it leads directly to the emission of SO_x when combustion is occurred. Generally, sulfur-containing compounds in oils obtained from waste tire pyrolysis are present in the forms of polar aromatic compounds. In tire manufacture after vulcanization process, sulfur is combined in rubber chains and linked together. Sulfur content in oil products might be present as mono-sulfide, di-sulfide, poly-sulfide, cyclic-sulfides and dependent sulfides. Figure 4.5 shows several types of polar-aromatics in pyrolytic oils which are found in several literatures. (Pakdel *et al.*, 2001, Rodriguez *et al.*, 2001, Laresgoiti *et al.*, 2004, and Unapumnuk, 2008)

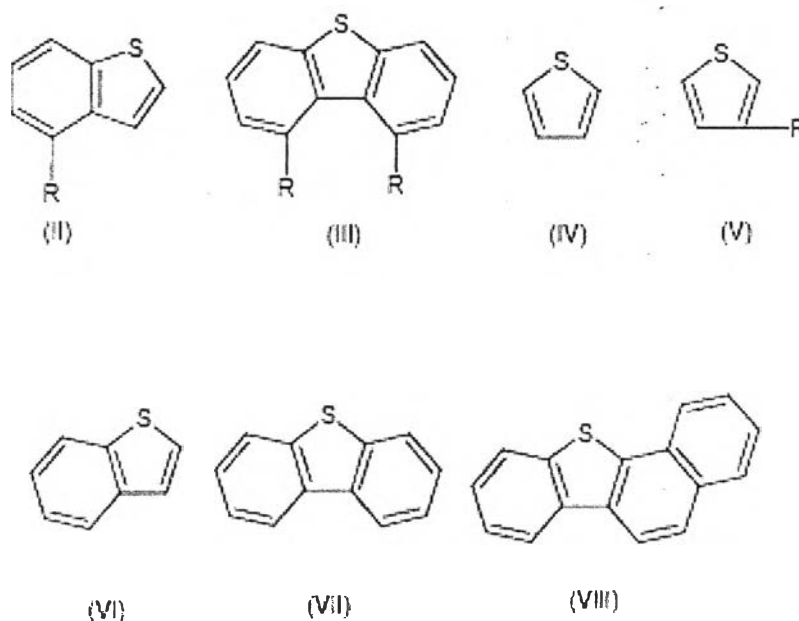


Figure 4.7 Polar-aromatics in pyrolytic oils (Pakdel *et al.*, 2001; Rodriguez *et al.*, 2001; Laresgoiti *et al.*, 2004; and Unapumnuk, 2008).

Figure 4.8 shows the amount of sulfur in pyrolytic oils obtained from waste tire pyrolysis. The result shows that the use of 1%Ag/Y as a catalyst can decrease the amount of sulfur containing in oil products. It can reduce concentration of sulfur in oil by approximately 36% as compared to the non-catalytic case.

1%Ag/Y slightly decreases sulfur in oils from 0.984% to 0.929% corresponding to the increased amount of sulfur deposit on the spent catalyst as compared to pure Y zeolite. Yang *et al.* (2003) reported that Ag-modified Y zeolite can adsorb sulfur compounds from commercial fuels. The selectivity for sulfur compound is resulted from the π -complexation of thiophene with Ag. Due to the fact that the 2%Ag/Y gives a high concentration of polar-aromatics (see Figure 4.4), it gives low sulfur removal capacity. The sulfur removal capacity in oils is an evidence of some competitive adsorption from olefins and aromatic molecules in polar-aromatic compounds (Gong *et al.*, 2009). In the case of increasing the amount of Ag loading, the desulfurization activity is lower than that obtained from using 1%Ag/Y.

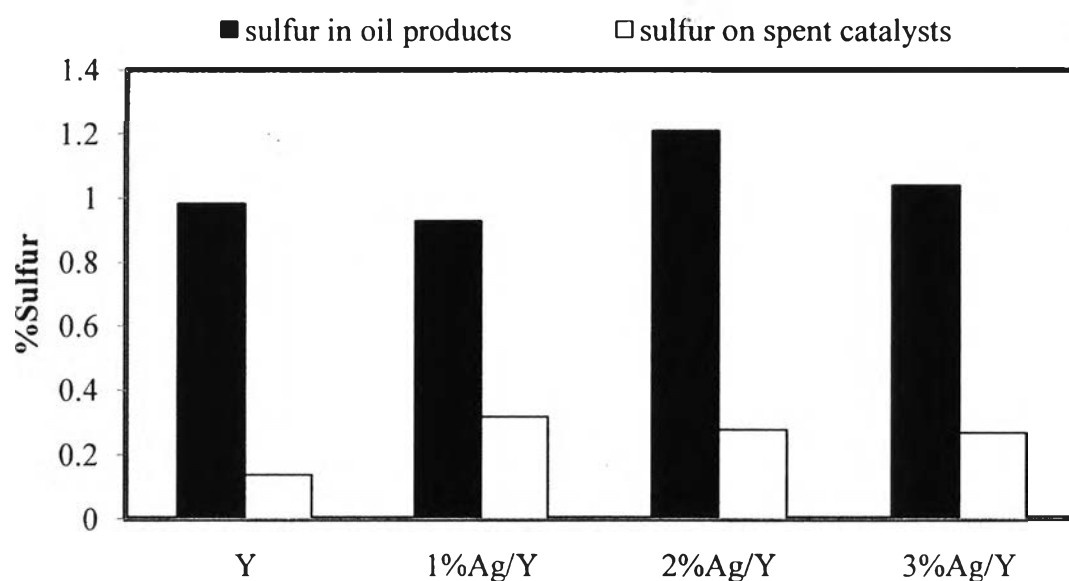


Figure 4.8 Effect of the amount of Ag loaded onto Y zeolite on sulfur content in the oil products.

The carbon number distribution of polar-aromatics is shown in Figure 4.9. From the figure, it can be seen that the use of catalysts decreases the amount of polar-aromatics in all ranges, especially the ranges of gasoline and kerosene as compared to that of the non-catalytic case. Moreover, the average carbon number shifts from light fractions (in the gasoline and kerosene ranges) to heavy fractions (gas oil or heavier). The use of Y zeolite as a catalyst shows a wide distribution of

carbon number in all ranges. And, the average carbon number also shifts from light fractions to heavy fractions as compared to the non-catalyst case. All of Ag loading on Y zeolite catalysts gives the similar carbon number distribution of polar-aromatics. 1% and 3% of Ag loading decrease the amount of polar-aromatics in the ranges of gasoline and kerosene. So, gasoline and kerosene obtained from using these catalysts contain a lower amount of sulfur compounds than those obtained from Y zeolite. In contrast, 2%Ag/Y gives the carbon number distribution and the amount of polar-aromatics similar to those obtained from using Y only.

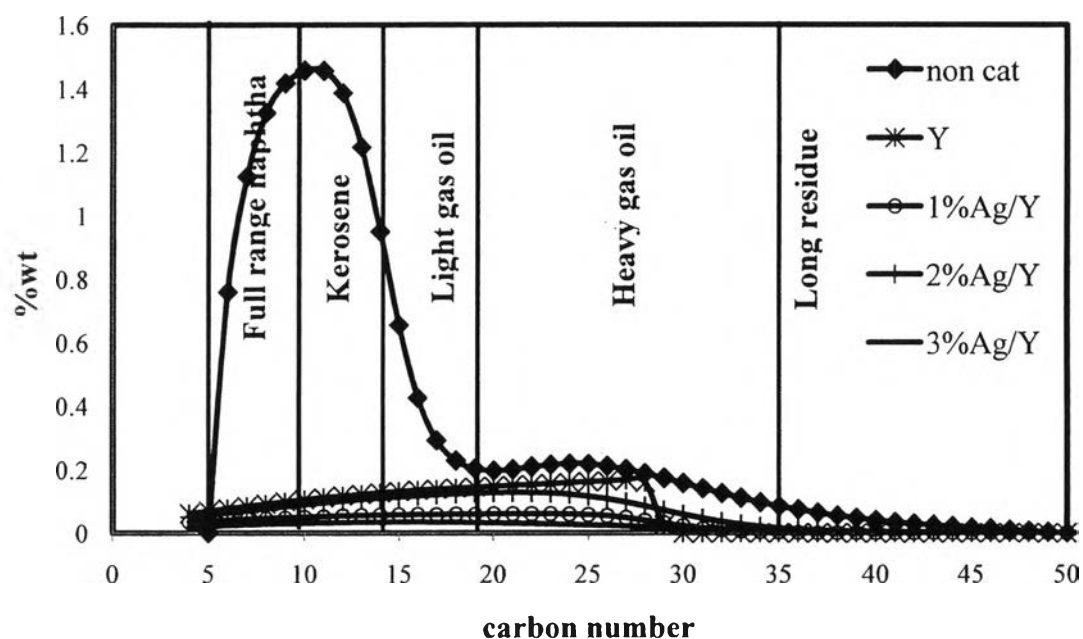
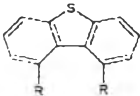
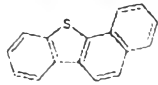
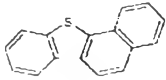
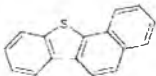
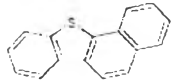


Figure 4.9 Effect of the amount of Ag loaded onto Y zeolite on carbon number distribution of polar-aromatics.

The average of carbon number using Ag/Y catalysts is shown in Table 4.3. All of catalysts give a larger size of polar-aromatics than that obtained from the non-catalytic case. It is due to the pore structure of Y zeolite. Y zeolite has 3D pore structure, which has the pore volume of $0.5763 \text{ cm}^3/\text{g}$. The high pore volume and acid property of Y zeolite enhance the pathways to produce large molecules of aromatics inside the pore of catalyst.

In summary, the amount of Ag loaded on Y zeolite has the influence on pyrolysis products. 1%Ag/Y zeolite gives the highest cooking gas production. Approximately 2.9 times higher cooking gas are obtained as compared to that from the non-catalytic pyrolysis. And, it also gives the highest gas production and mono-aromatics contents in oil products. 2% and 3%Ag/Y give a high long residue fraction in oil products (indicating the negative effect on the oil products). The increase of silver loading can decrease kerosene fraction whereas gasoil fraction increases. 2% and 3%wt of silver loading give a higher residue fraction and a lower naphtha fraction than those obtained from 1%Ag/Y. For the effect on desulfurization, increasing the amount of Ag onto Y zeolite decreases desulfurization activity.

Table 4.3 The average carbon number of polar-aromatics in oils obtained from using Ag/Y catalysts

Samples	Carbon number average of polar aromatics	Example of sulfur compounds
non cat	14.4	
Y	17.8	
1%Ag/Y	17.5	
2%Ag/Y	18.8	
3%Ag/Y	19.3	

4.2 Effect of Different Zeolites Loaded with 1%Ag

4.2.1 Properties of Studied Zeolites

Bifunctional catalysts consisting of metal and acid-basic properties of catalysts have been studied in many applications. The acid-basic properties can significantly affect the catalyst selectivity. In this section, four commercial zeolites namely BETA, HMOR, Y, and KL zeolite were studied. They have the differences in pore dimension and acid-basic properties. Arribas *et al.* (2002) reported that the moderate acidity of Y, BETA and HMOR can prevent the secondary reactions of the primary products. For basic catalysts such as KL, it is expected to improve the octane number of gasoline fraction due to its aromatization ability (Becue *et al.*, 1999). Table 4.4 concludes the properties and characteristics of the four commercial zeolites.

Table 4.4 Properties and characteristics of support zeolites (Tosoh Company)

Zeolites	Dimension	SiO ₂ /Al ₂ O ₃ (mol/mol)	Cations types	Surface area (m ² /g)	Pore size (Å)
Y	3D	15	H (acid catalyst)	~ 600	7.4
BETA	3D	27	H (acid catalyst)	~ 630	6.4 x 7.6
HMOR	1D	19	H (acid catalyst)	~ 380	6.5 x 7
KL	1D	6	K (basic catalyst)	~ 280	7.1

4.2.2 Product Distribution

The product yield of catalytic pyrolysis with the different zeolites is shown in Figure 4.10. The use of pure zeolites as catalysts can increase the gas product whereas the liquid product decreases as compared to the non-catalytic case. Compared among the pure zeolites, the 3D zeolites (Y and BETA) give a higher gas production than that obtained from the 1D zeolites (HMOR and KL). It might be caused by the 3D structures of zeolites that have high pore volume and active surface

area as shown in Table 4.5. Due to the high pores volume and active surface area of zeolites, the 3D zeolites have high cracking activity to crack heavy products (liquid product) to light products (gas product). For the cases of using Ag loaded on all zeolites, all catalysts further decrease the liquid fraction, and consequently the gas fraction increases as compared to using the corresponding pure zeolite. It can be explained that the presence of Ag metal on zeolites promotes cracking reaction. The fragments evolved from the cracking of the rubber chains of waste tire are further cracked to even lighter products (condensable products to non-condensable products). In the case of solid fraction, it remains constant (see Appendix B). It means that the rubber content in the tire sample is completely decomposed to lower molecular weight products (Miguel *et al.*, 2006).

Table 4.5 Physical properties of different zeolites loaded with 1%Ag

Catalysts	Pore structure	Specific surface area (m ² /g)	Total pore volume (cm ³ /g)	Spent catalysts	
				Sulfur (%)	Coke formation (g/g catalyst)
BETA	3D	455.4	0.391	0.176	0.228
Y	3D	590.4	0.576	0.137	0.171
KL	1D	297.8	0.392	0.203	0.163
HMOR	1D	462.5	0.359	0.148	0.148
1%Ag/BETA	3D	406.2	0.244	0.377	0.207
1%Ag/Y	3D	579.2	0.380	0.317	0.185
1%Ag/KL	1D	279.1	0.327	0.418	0.160
1%Ag/HMOR	1D	407.1	0.315	0.435	0.147

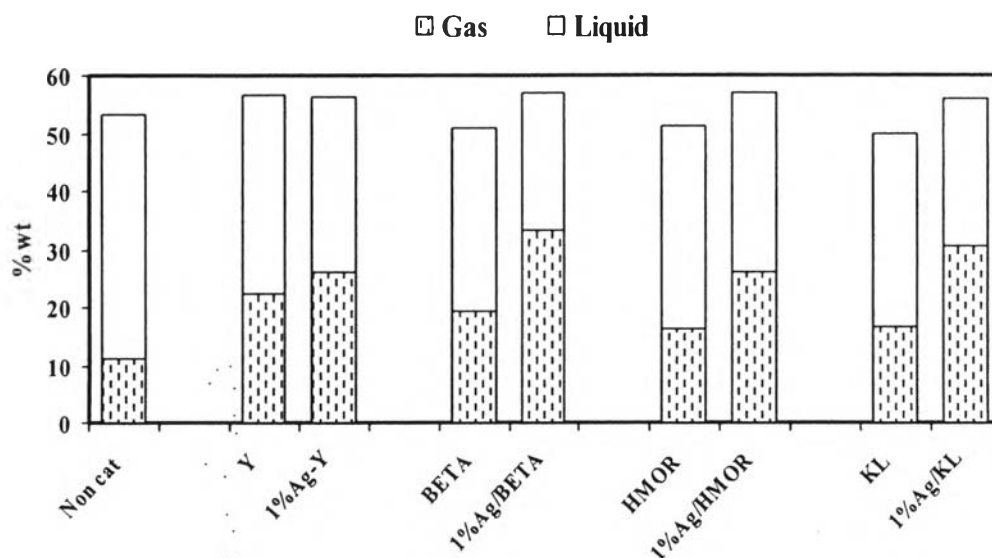


Figure 4.10 Product distributions obtained from using Ag supported on different zeolites.

4.2.3 Gaseous Products

Due to the activity, the use of catalysts can increase gaseous products. They have major influence on light olefins and cooking gas production. The gaseous products were analyzed in terms of valuable components such light olefins and cooking as shown in Figure 4.11. The unloaded zeolites slightly increase both light olefins and cooking gas production as compared to the non-catalytic case. Y zeolite gives the highest light olefins production. It is possibly caused from Y zeolite has the highest pore volume ($0.5763 \text{ cm}^3/\text{g}$) which heavy primary products can be cracked to light olefins inside the pore. BETA zeolite gives the highest amount of cooking gas among the other zeolites. For 1D zeolites (HMOR and KL), these two zeolites have the same pore structure, but HMOR is an acid zeolite which it gives a higher cooking gas production than that obtained from using KL zeolite. Ag loaded on all tested zeolites further increases both light olefins and cooking gas productions as compared to the pure zeolite cases. 1%Ag/BETA increases about 2.3 times higher light olefins production than BETA zeolite alone. The result also shows that 1%Ag has the influence on light olefins production. It increases light olefins production from 4.1 wt% to 6.1 wt% as compared to the case of using pure KL. For cooking gas

production, 1%Ag/HMOR catalyst shows the highest performance, because it gives the highest amount of cooking gas. In other words, 1%Ag/HMOR zeolite is a selective catalyst to produce an apparently-high amount of propane with a considerable amount of C4 hydrocarbons. Approximately 3.5 and 2 times higher of cooking are obtained as compared to those from the non-catalytic pyrolysis and from using only HMOR zeolite, respectively.

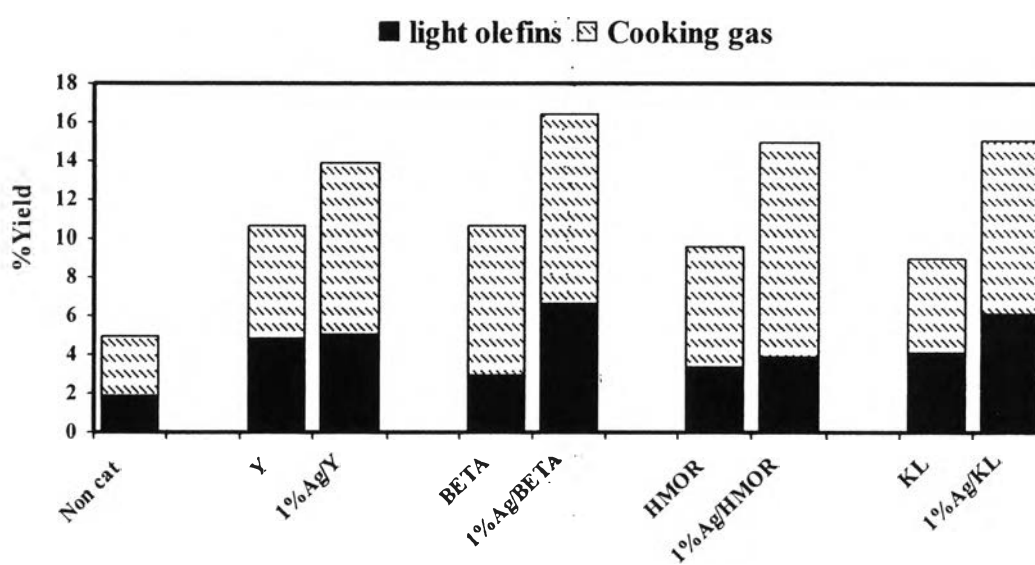


Figure 4.11 Effect of different zeolites loaded with 1%Ag on light olefins and cooking gas production.

4.2.4 Oil Products

4.2.4.1 Liquid Compositions

After the liquid products had been obtained from pyrolysis, they were fractionated using liquid chromatography for their compositions. The liquid compositions are classified into five fractions including saturated hydrocarbons, mono-aromatics, di-aromatics, poly-aromatics, and polar-aromatics. Figure 4.12 shows chemical composition in the oil products. BETA zeolite gives the highest amount of saturated hydrocarbons and the lowest amount of total aromatics as compared to the other unloaded zeolites. It is possibly caused by the highest acid strength (the highest $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio) of BETA zeolite, and resulted in high cracking activity. Although, BETA and Y zeolite have the same dimensional

structure (3D), BETA has the higher acid strength as indicated in Table 4.4. Therefore, BETA has the higher ability protonating some aromatic molecules to carbenium ions that can lead to many reactions such as hydrogenation and cracking. HMOR, Y, and KL zeolites give almost the same amount of saturated hydrocarbons. In the case of Ag loaded on zeolites, 1%Ag/BETA increases total aromatic compositions whereas saturated hydrocarbons are decreased. It is possibly caused from 1%Ag/BETA has strong interaction between the metal and the support (see Figure 4.13) resulting in low hydrogenation and cracking activity. Furthermore, BETA zeolite is a three-dimensional structure, and has high acid strength, promoting large molecules to enter the zeolite pores, and then favoring pathways to form aromatics compounds. Additionally, 1%Ag/HMOR increases saturated hydrocarbons, and decreases total aromatics. It is possible that 1%Ag/HMOR has weak interaction between the metal and the support (Figure 4.13) promoting hydrogenation reaction of unsaturated hydrocarbons to saturated hydrocarbons. The use of 1%Ag/KL as a catalyst increases total aromatics concentration whereas saturated hydrocarbons are slightly decreased. It is possibly due to aromatization ability of KL support behaving as a basic catalyst (Becue *et al.*, 1999).

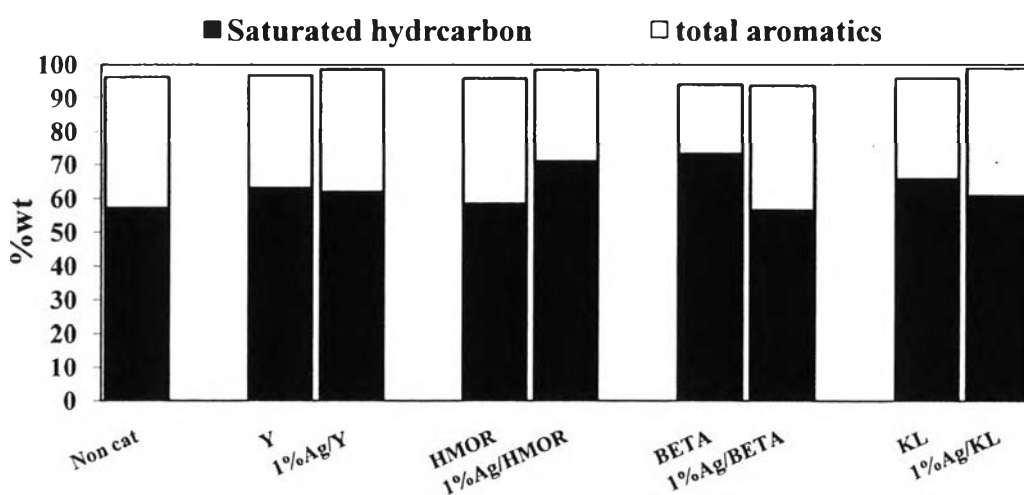


Figure 4.12 Effect of different zeolites loaded with 1%Ag on liquid compositions in the oil products.

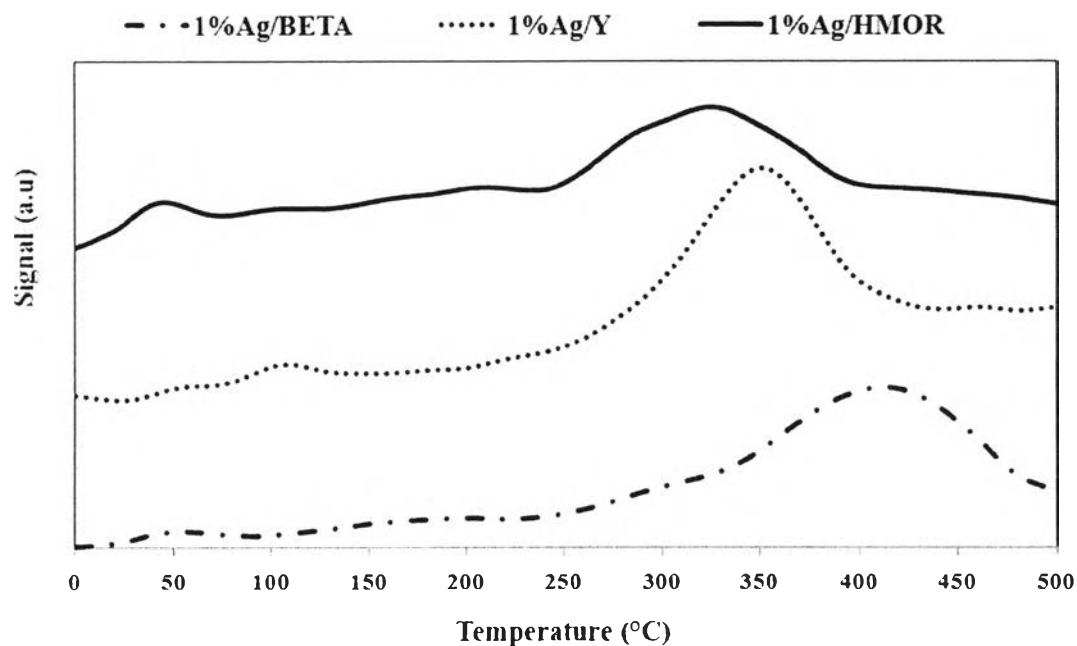


Figure 4.13 TPR profiles of Ag-loaded catalysts.

Table 4.6 shows the polar-aromatics content in the liquid products. Y zeolite decreases polar-aromatics as compared to the non-catalytic case. BETA and HMOR give the high amount of polar-aromatics than that obtained from the non-catalytic case. It might be caused from the high acid strength of BETA and HMOR zeolites which generates pathways to produce aromatic compounds. For KL zeolite, it also gives the higher amount of polar-aromatics as compared to thermal pyrolysis. It is possibly due to its basic property governing aromatization ability of KL (Becue *et al.*, 1999). In the cases of Ag loaded on zeolites, 1%Ag/KL, 1%Ag/HMOR, and 1%Ag/Y tremendously decrease polar-aromatics concentration in maltene as compared to the unloaded zeolites. 1%Ag/BETA gives the highest amount of polar-aromatics. BETA has high cracking ability to generate carbocations which create pathways to form aromatic compounds in maltenes.

Table 4.6 Polar-aromatics production

Samples	Polar-aromatic in oils (%)
Non catalyst	3.65
Y	3.21
BETA	5.95
HMOR	4.10
KL	4.17
1%Ag/Y	1.42
1%Ag/BETA	6.31
1%Ag/HMOR	1.54
1%Ag/KL	1.06

4.2.4.2 Petroleum Fractions

The quality of oil products is indicated by a simulated true boiling point curve, which can be obtained from a SIMDIST GC. It was next cut 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) (Chaiyavech and Grisadanurak, 2000).

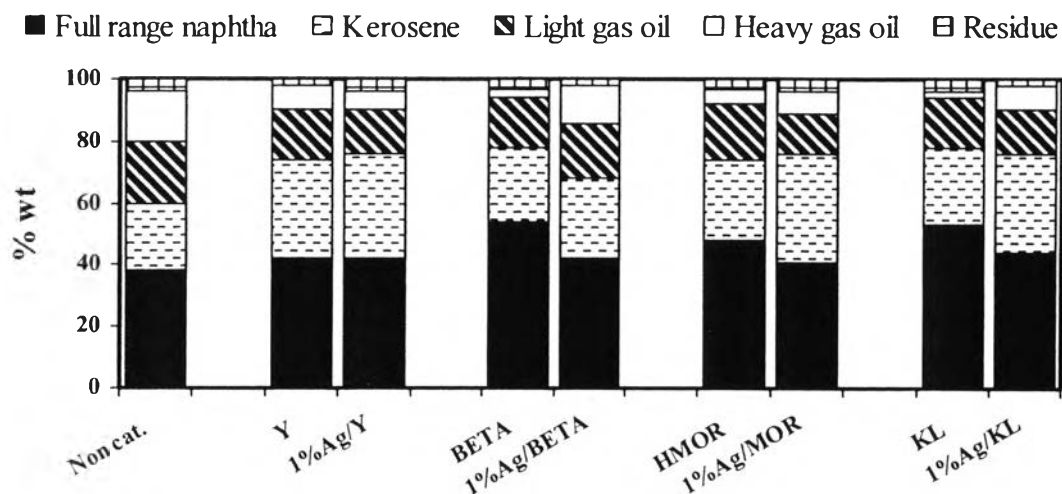


Figure 4.14 Effect of different zeolites loaded with 1%Ag on liquid petroleum fractions.

Figure 4.14 shows petroleum fractions obtained from using different zeolites. The result shows that BETA zeolite gives the highest full range naphtha production among all of unloaded zeolites. It can be explained by a high acid strength of BETA zeolite resulting in high cracking ability to crack heavy fractions to light fractions. Y and HMOR zeolite slightly increase full range naphtha as compared to the non-catalytic case. All of Ag-loaded catalysts decrease the light petroleum fractions (full range naphtha) whereas the heavy petroleum fractions (kerosene, gas oil, and residue) are increased. Ag-loaded basic zeolite (KL) increases kerosene and gas oil fraction whereas full range naphtha also decreases. Moreover, Ag-loaded acid zeolites (Y, BETA, and HMOR) give a high amount of gas oil and long residue.

4.2.5 Effect of Zeolites on Sulfur Removal

The sulfur content in the oil product is determined by CHNOS elemental analysis technique. The low amount of sulfur content in an oil product indicates that the oil has high quality. Figure 4.15 shows the quantity of sulfur content in the oil products. The use of catalysts gives a lower quantity of sulfur in the oil than that obtained from the non-catalytic case. Pyrolytic oil obtained from using no catalyst contains about 1.38% of sulfur. The use of pure zeolites dramatically decreases the amount of sulfur in the oil products as compared to the non-catalytic case. All of unloaded zeolites decrease sulfur concentration from 1.38% to 0.95%.

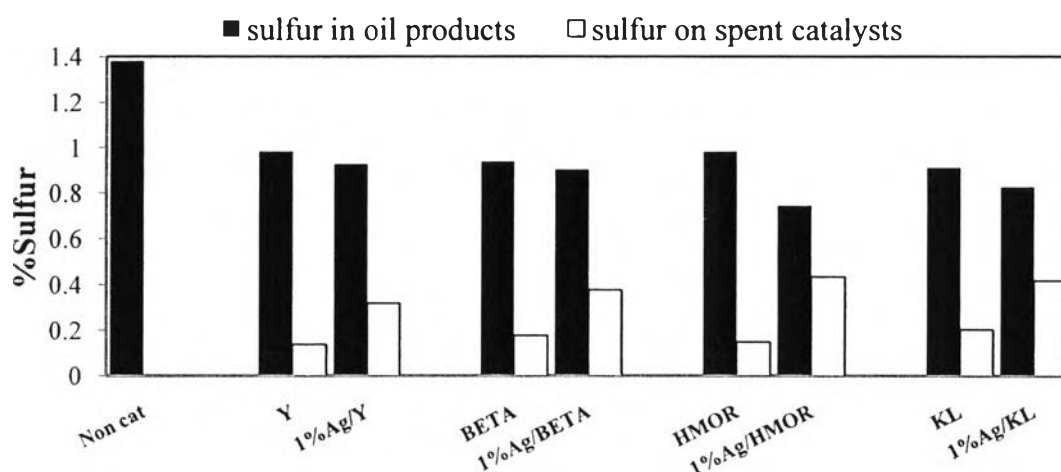


Figure 4.15 Effect of different zeolites loaded with 1%Ag on sulfur content in the oil product.

(average number from four zeolites). All 1%Ag-loaded zeolites slightly decrease sulfur in the oil. 1%Ag/HMOR catalyst shows a high performance in sulfur removal capacity. It gives the lowest concentration of sulfur in the oil product as compared to the other catalysts. It can decrease from 1.38 wt% to 0.75 wt% of sulfur as compared to the non-catalytic case. Compared with using pure HMOR, 1%Ag/HMOR decreases the amount of sulfur in the oil product from 0.98 wt% to 0.75 wt%. The presence of Ag on HMOR zeolite helps promote desulfurization reaction resulting in the decrease of sulfur concentration in the oil product. It can be suggested that the Ag metal has hydrogenolysis activity since it enhances C-S-C bond breaking.

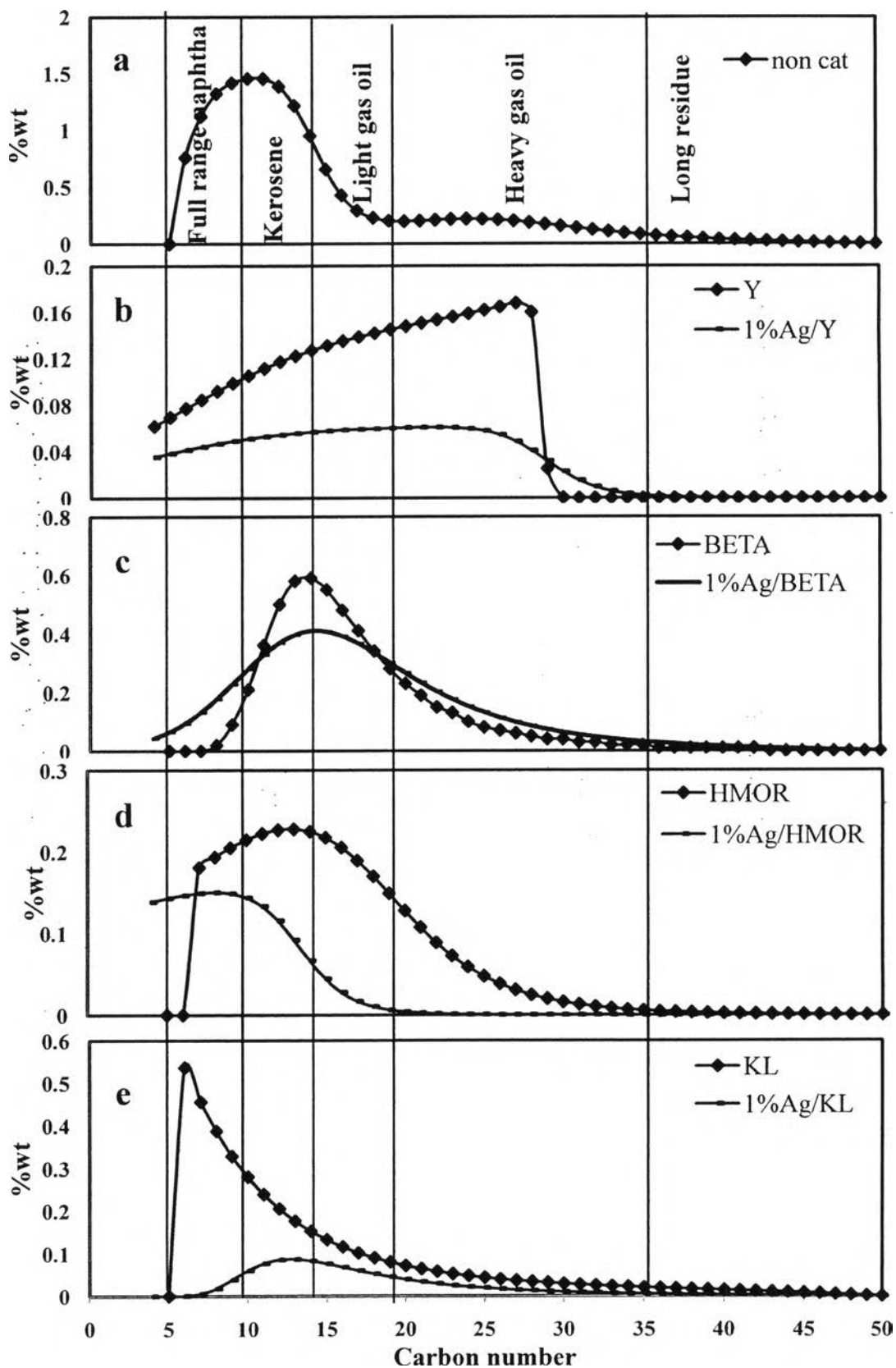
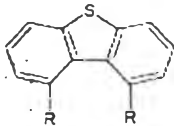
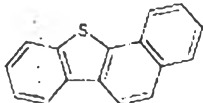
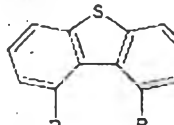
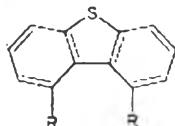
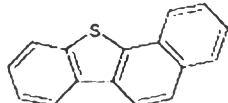


Figure 4.16 Effect of different zeolites loaded with 1%Ag on carbon number distribution of polar-aromatics

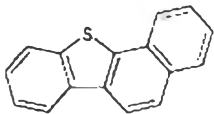
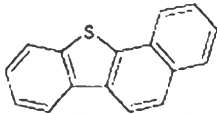
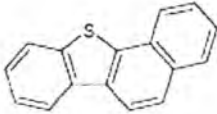
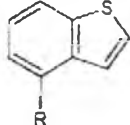
Figure 4.16 shows the carbon number distribution of polar-aromatics. Pyrolysis without a catalyst gives the carbon number distribution in the range of kerosene, which has the average carbon number around C14 (from Table 4.7). The use of catalysts differently shifts carbon number distribution from the non-catalytic case. For the unloaded catalysts, the zeolites which have 3D structure (Y and BETA) give the carbon number distribution in the range of gas oil (the average carbon number equal to C17 for BETA and C18 for Y). Moreover, the zeolites with 1D structure (HMOR and KL) give the carbon number distribution in the range of kerosene (the average carbon number equal to C15 for HMOR and C14 for KL). It can be implied that pore size of zeolites has the influence on carbon number distribution of polar-aromatics. The one-dimensional structure of zeolites has ability of selectively produce a lighter fraction (such as kerosene fraction) than three-dimensional structure. The carbon number in the cases of HMOR and Y zeolites widely distributes in all fractions. In the cases of Ag loading on zeolites, Ag loaded on BETA and Y zeolites decreases the amount of polar-aromatics in the same range as using pure BETA and Y zeolites, confirming that Ag loading help promote sulfur removal from the products. 1%Ag/HMOR shifts the carbon distribution curve from heavy fraction (kerosene) to lighter fraction (naphtha).

Table 4.7 The average carbon number of polar-aromatics obtained from using different zeolites

Samples	Carbon number average of polar aromatics	Example of sulfur compounds
non cat	14.4	
BETA	16.8	
KL	13.8	
HMOR	15.2	
Y	17.8	

The average of carbon number obtained from using different zeolites loaded with 1%Ag is shown in Tables 4.7 and 4.8. BETA and Y zeolites give the average carbon numbers of polar-aromatics lower than that obtained from HMOR and KL zeolites. It might be caused from pore structure. BETA and Y zeolites have three-dimensional structure having large pore sizes. The large pore size of BETA and Y zeolites supports large molecules of polar-aromatics formation. 1%Ag/BETA and 1%Ag/Y give the same average of carbon numbers as the unloaded cases. 1%Ag/HMOR gives the average carbon number lower than that obtained from using pure HMOR.

Table 4.8 The average carbon number of polar-aromatics obtained from using different zeolites loaded with 1%Ag

Samples	Carbon number average of polar aromatics	Example of sulfur compounds
1%Ag/Y	17.5	
1%Ag/BETA	17.3	
1%Ag/KL	17.4	
1%Ag/HMOR	9.1	

4.3 Effect of Pd-Ag/HMOR Bimetallic Catalysts

This section discusses the effect of addition of second metal (Pd) onto Ag-modified HMOR zeolite. The effect of bimetallic catalysts was studied on the qualities and quantities of the pyrolytic products. The metal ratio was defined in the terms of α_{metal} as shown in Equations 1 and 2. The appropriate metal ratio for the production of the high quality products is determined in this section.

$$\alpha_{Pd} = \frac{wt_{Pd}}{wt_{Pd} + wt_{Ag}} \quad \text{-----} \quad (1)$$

$$\alpha_{Ag} = 1 - \alpha_{Pd} \quad \text{-----} \quad (2)$$

4.3.1 Product Distribution

The product distribution of using the bimetallic catalysts is shown in Figure 4.17. The solid fraction remains constant (see Appendix B8) because all tire samples are completely cracked to pyrolysis products at the same conditions in the pyrolysis zone for each experiment. From the figure, the result shows that the use of bimetallic catalysts, except at $\alpha_{Pd} = 0.2$, give almost the same amount of liquid product as compared to monometallic catalysts. The bimetallic catalyst at $\alpha_{Pd} = 0.2$ gives the highest amount of liquid product (36.2%wt).

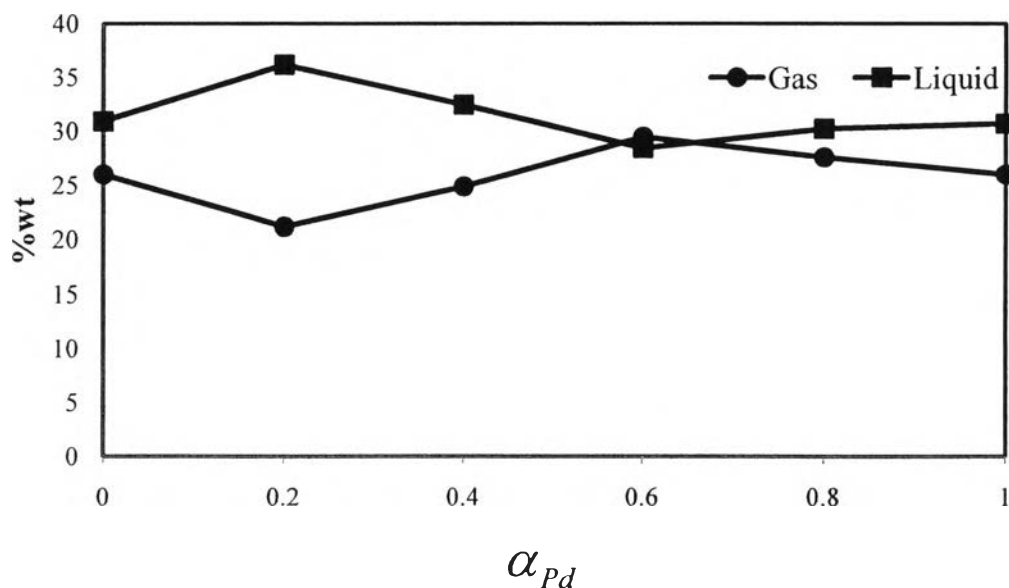


Figure 4.17 Product distributions obtained from using the bimetallic catalysts.

4.3.2 Gaseous Products

The compositions of gaseous product are shown in Figure 4.18. The addition of second metal (Pd) decreases light olefins (ethylene and propylene), and mixed C4s while methane is increased as compared to using 1%Ag/HMOR. Especially, the addition of second metal (Pd) dramatically decreases propane composition, and consequently extremely increases mixed C5s composition. The bimetallic catalysts give a higher amount of methane than that obtained from using the monometallic catalysts.

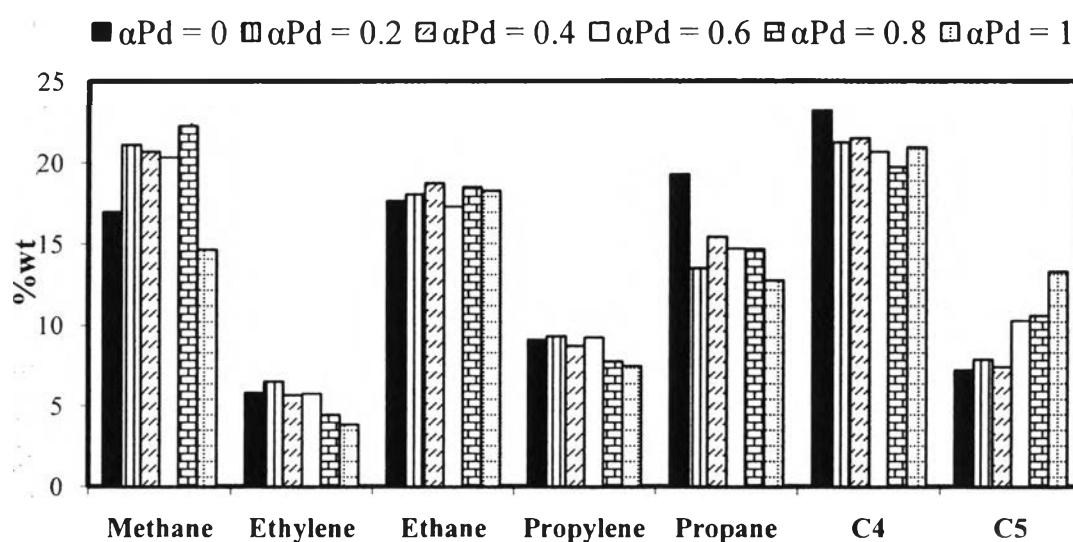


Figure 4.18 Gas compositions obtained from using the bimetallic catalysts.

From the gas composition in Figure 4.18, light olefin and cooking gas yields are separately plotted as shown in Figure 4.19. 1%Ag/HMOR gives both higher light olefin and cooking gas productions than those obtained from using 1%Pd/HMOR. The bimetallic catalysts give a lower cooking gas production than that obtained from using the monometallic catalyst (1%Ag/HMOR). Among the bimetallic catalysts, the one at $\alpha_{Pd} = 0.6$ gives the highest cooking gas production. It also gives a high amount of light olefins, which is slightly higher than that from 1%Ag/HMOR. Synergistic effect between Pd and Ag is not likely to exist on the production of gases.

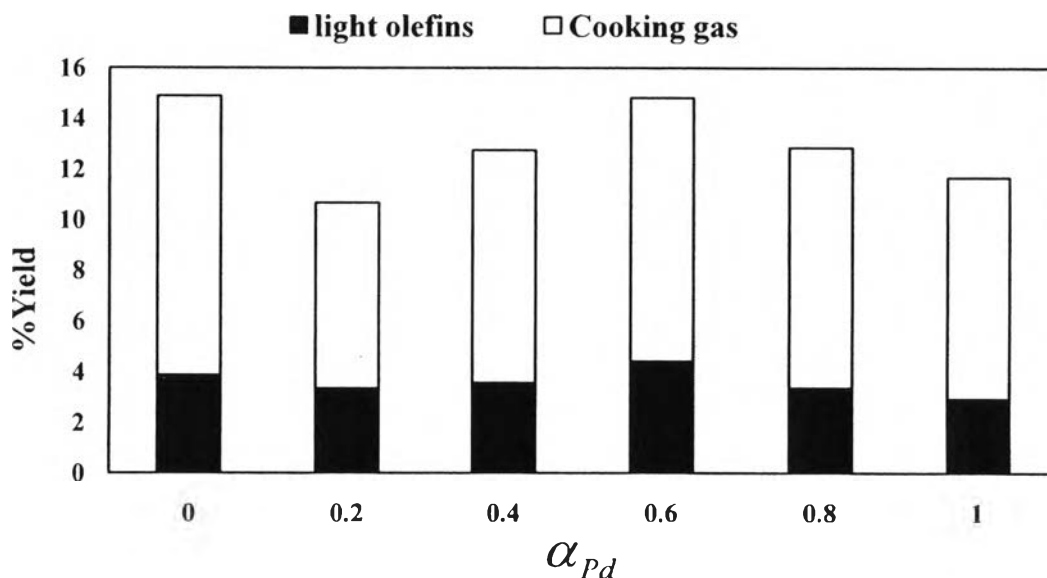


Figure 4.19 Cooking gas and light olefin productions obtained from using the bimetallic catalysts.

4.3.3 Oil Products

4.3.3.1 Liquid Compositions

Figure 4.20 shows chemical compositions in the oils obtained from using the bimetallic catalysts. The bimetallic catalysts give a lower and a higher saturated hydrocarbon production than that obtained from using 1%Ag/HMOR and 1%Pd/HMOR, respectively, whereas the increased amount of Pd loading increases total-aromatics production from what is produced by 1%Ag/HMOR. The polar-aromatic yield of 1%Ag/HMOR is lower than that obtained from 1%Pd/HMOR. The bimetallic catalysts, at $\alpha_{Pd} = 0.2$ and $\alpha_{Pd} = 0.4$, give a higher amount of polar-aromatics than using 1%Ag/HMOR as a catalyst. The bimetallic catalyst at $\alpha_{Pd} = 0.2$ gives the highest amount of polar-aromatics among all tested catalysts. It can be suggested that the co-loading of Pd-Ag suppresses C-S-C bond breaking activity. 1%Ag/HMOR gives the lowest amount of polar-aromatics among all tested catalysts.

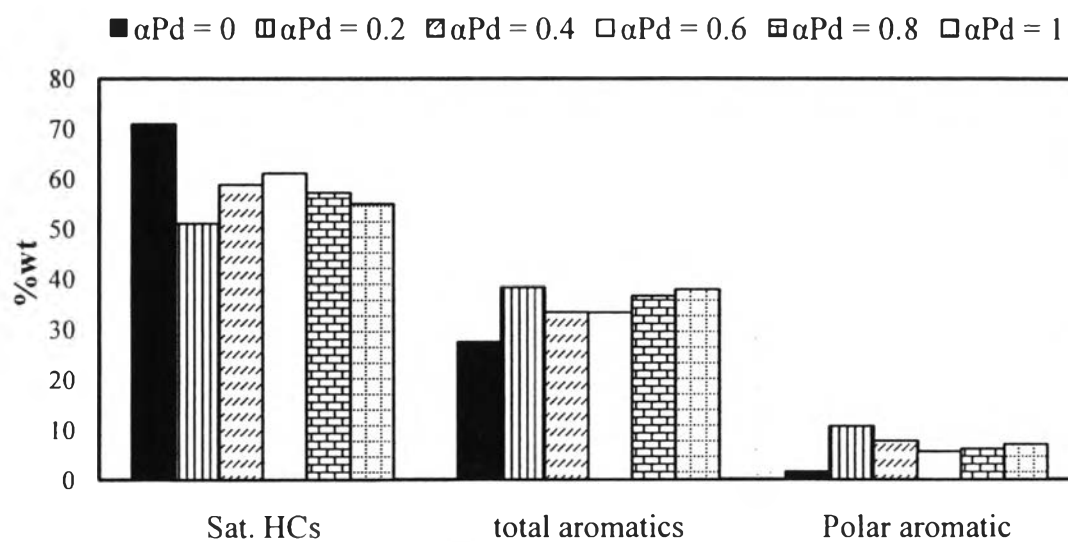


Figure 4.20 Chemical compositions in oils obtained from using the bimetallic catalysts.

Table 4.9 shows coke and sulfur formation on the spent catalysts. From the table, both amounts of sulfur and coke on the spent 1%Ag/HMOR are lower than most of bimetallic catalysts and 1%Pd/HMOR. Sulfur and coke formation on catalysts decrease the cracking activity of catalysts, and result in catalyst deactivation. From the result, co-loading Pd with Ag synergistically increases the coke formation.

Table 4.9 Coke and sulfur formation on spent catalysts

Catalysts	Coke on spent catalysts (%)	Sulfur on spent catalysts (%)	Sulfur in oils (%)
1%Ag/HMOR ($\alpha_{Pd} = 0$)	0.147	0.435	0.746
0.8Ag0.2Pd/HMOR ($\alpha_{Pd} = 0.2$)	0.092	0.565	1.021
0.6Ag0.4Pd/HMOR ($\alpha_{Pd} = 0.4$)	0.508	0.697	0.972
0.4Ag0.6Pd/HMOR ($\alpha_{Pd} = 0.6$)	0.494	0.644	0.897
0.2Ag0.8Pd/HMOR ($\alpha_{Pd} = 0.8$)	0.348	0.455	0.916
1%Pd/HMOR ($\alpha_{Pd} = 1$)	0.1477	0.525	

The carbon number distribution of polar-aromatics is shown in Figure 4.21. 1%Pd/HMOR gives the carbon number distribution in the range of full range naphtha whereas 1%Ag/HMOR gives a very low concentration of polar-aromatics widely distributed in all ranges. Polar-aromatics obtained from using bimetallic catalysts are highly distributed in the range of kerosene and light gas oil. They also apparently distribute in a heavier fraction than those obtained from using monometallic catalysts. It is suggested that the bimetallic catalysts from co-loading Pd with Ag catalyze reaction pathways that from larger polar-aromatic compounds (S-containing molecules).

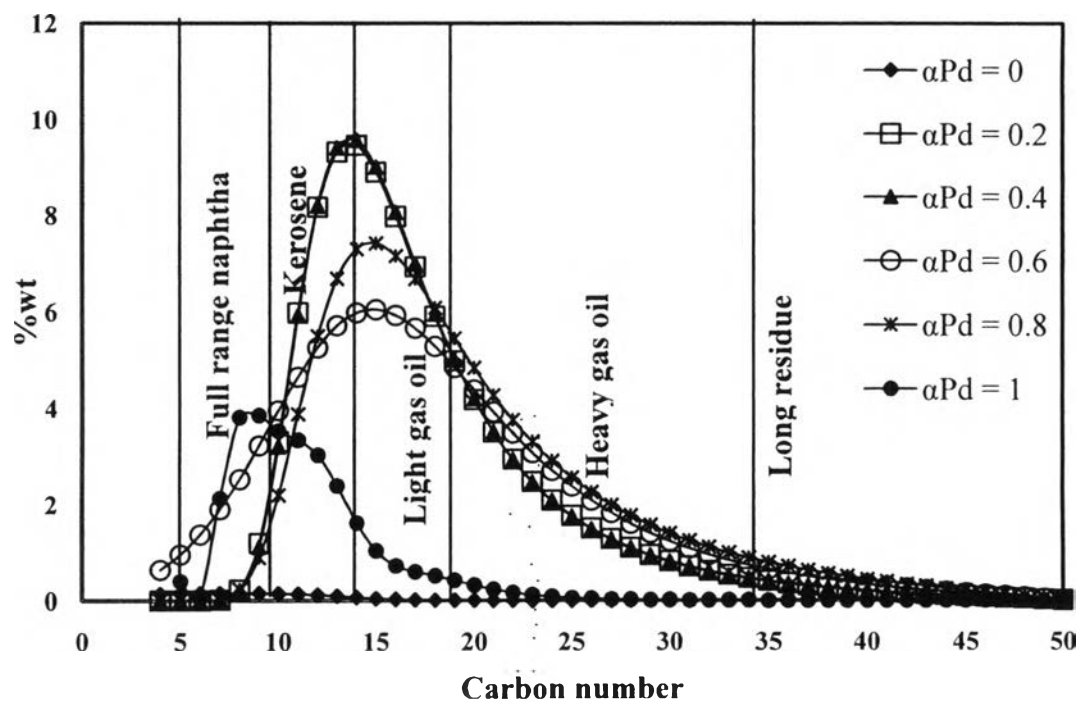
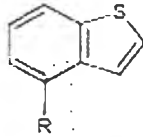
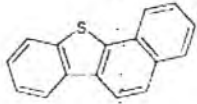
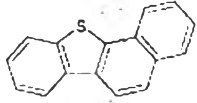
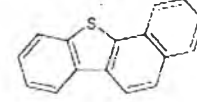
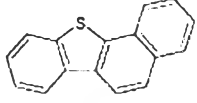
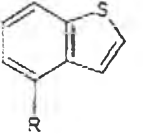


Figure 4.21 Carbon number distributions of polar-aromatics in oils obtained from using the bimetallic catalysts.

The examples of sulfur compounds in polar-aromatics are shown in Table 4.10. The use of bimetallic as catalysts gives larger average sizes of sulfur compounds than those obtained from the monometallic catalysts. The average of carbon number obtained from using bimetallic catalysts is C17-C20, which is in the range of light gas oil, while the monometallic catalysts give the average of carbon number at C9-C11, which is in the range of full range naphtha. So, the use of monometallic catalysts gives lighter polar-aromatics than the bimetallic catalysts.

Table 4.10 The average carbon number of polar-aromatics obtained from using the bimetallic catalysts

Samples	Carbon number average of polar aromatics	Example of sulfur compounds
1%Ag/HMOR	9.2	
0.8Ag0.2Pd/HMOR	17.5	
0.6Ag0.4Pd/HMOR	17.5	
0.4Ag0.6Pd/HMOR	18.1	
0.2Ag0.8Pd/HMOR	19.7	
1%Pd/HMOR	11.3	

4.3.3.2 Petroleum Fractions

Figure 4.22 shows petroleum fractions obtained from using the bimetallic catalysts. The result shows that 1%Pd/HMOR gives the highest amount of full range naphtha fraction. The bimetallic catalysts give lower full range naphtha and higher light gas oil than those both monometallic catalysts (1%Ag/HMOR and 1%Pd/HMOR). The use of bimetallic catalysts, therefore, has the negative effect on

full range naphtha production. Monometallic catalysts can produce lighter products than the bimetallic catalysts in general.

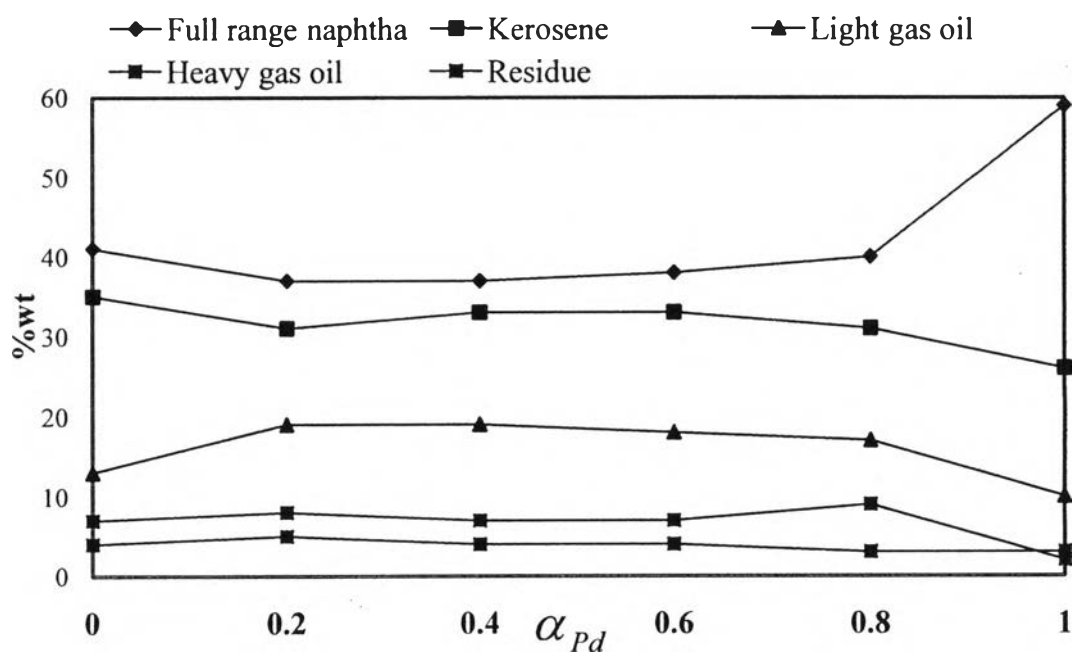


Figure 4.22 Petroleum fractions obtained from using the bimetallic catalysts.