

CHAPTER IV

RESULTS AND DISCUSSION

The main products from pyrolysis waste tire are gas, liquid, and char. Especially, the light olefins are one of components in the gas product, which can be used as petrochemical feedstock and low heating value fuels. In this work, the Ru/HMOR and Ru/MCM-48-based catalysts, which consist of an active component, a matrix, and a binder, were developed for the industrial production of light olefins. The appropriate composition of catalysts and the appropriate type of matrix were investigated.

4.1 Effect of Each Component on Pyrolysis Products

MCM-48 is the cubic mesoporous hydroxylated silicate material, whereas HMOR is an acidic zeolite. Sritana's work (2010) studied the appropriate composition of industrial Ru/HMOR-based catalysts, and she found that the composition of 20% Ru/HMOR, 70% matrix, and 10% binder was the most appropriate ratio for using catalytic pyrolysis. However, the composition of below 20% Ru/HMOR has not been investigated; therefore, this work continues from Sritana's work. The composition of the cracking catalysts was varied in the range 5-20% of either 0.7%Ru/MCM-48 or 0.7%Ru/HMOR, 70-85% kaolin, and 10% α -alumina. Then, the cracking catalysts of all compositions were extruded to the cylindrical extrudate form with 2 mm diameter.

4.1.1 Characterization of Components

The physical properties of kaolin, α -alumina, MCM-48, 0.7% Ru/MCM-48, HMOR, and 0.7% Ru/HMOR catalysts are shown in Table 4.1. The surface area and pore volume were determined by the BET method and the B.J.H. method, respectively. Namely, the pore size of each component can be separated to two ranges, which are meso-pore and micro-pore size. The meso-pore diameter was determined by the B.J.H. method whereas the micro-pore one was determined by using the Horvath-Kawazoe method. As a result, MCM-48 has the highest surface

area ($\sim 1,400 \text{ m}^2/\text{g}$) and pore volume ($\sim 0.87 \text{ cm}^3/\text{g}$) among all materials. HMOR has the surface area and the pore volume of ~ 370 and ~ 0.63 , respectively. The MCM-48 (mesoporous material) and HMOR (zeolite) have both micro-pores and meso-pores. In particular, they are 8.46 \AA (micro-pore) and 35.87 \AA (meso-pore) for MCM-48, and 7.2 \AA (micro-pore) and 38.0 \AA (meso-pore) for HMOR. Ru metal supported on MCM-48 can significantly reduce the surface area of MCM-48 from $1,400$ to $915 \text{ m}^2/\text{g}$, and reduce the pore volume from 0.87 to $0.63 \text{ cm}^3/\text{g}$. Ru supported HMOR slightly decreases the surface area of HMOR from 370 to $330 \text{ m}^2/\text{g}$, and reduce the pore volume from 0.23 to $0.19 \text{ cm}^3/\text{g}$. Kaolin, which is a mesoporous clay, has low a surface area and pore volume. In contrast, it has the large pore size about 420 \AA . Alumina has a low surface area, and medium pore size which are about 44 \AA .

According to Figure 4.1, it presents the pore distribution of each material obtained from the BET method. Ru/MCM-48 has a uni-modal pore distribution, which is in the range of mesopore. Ru/HMOR has also a uni-modal pore size distribution as Ru/MCM-48 does. However, the pore size of Ru/HMOR cannot be obtained by using the BET method because it is below 10 \AA . Alumina has a bi-modal distribution of pore diameters whereas kaolin has a uni-modal distribution with the average diameter of around 418 \AA .

Table 4.1 Physical properties of individual catalyst

| | Surface area (m ² /g)* | Pore volume (cm ³ /g)** | Pore diameter (Å) |
|-------------------|--------------------------------------|---------------------------------------|-------------------------|
| MCM-48 | 1,405 | 0.87 | 8.46***, 35.87** |
| 0.7% Ru/MCM-48 | 915.7 | 0.63 | 7.00***, 32.94** |
| HMOR | 372.5 | 0.23 | 7.2***, 38.00** |
| 0.7% Ru/HMOR | 332.6 | 0.191 | 7.05***, 37.35** |
| Kaolin | 32.87 | 0.16 | 418.8** |
| α -alumina | 73.34 | 0.48 | 44.18** |

*BET method **B.J.H. method *** Horvath-Kawazoe method

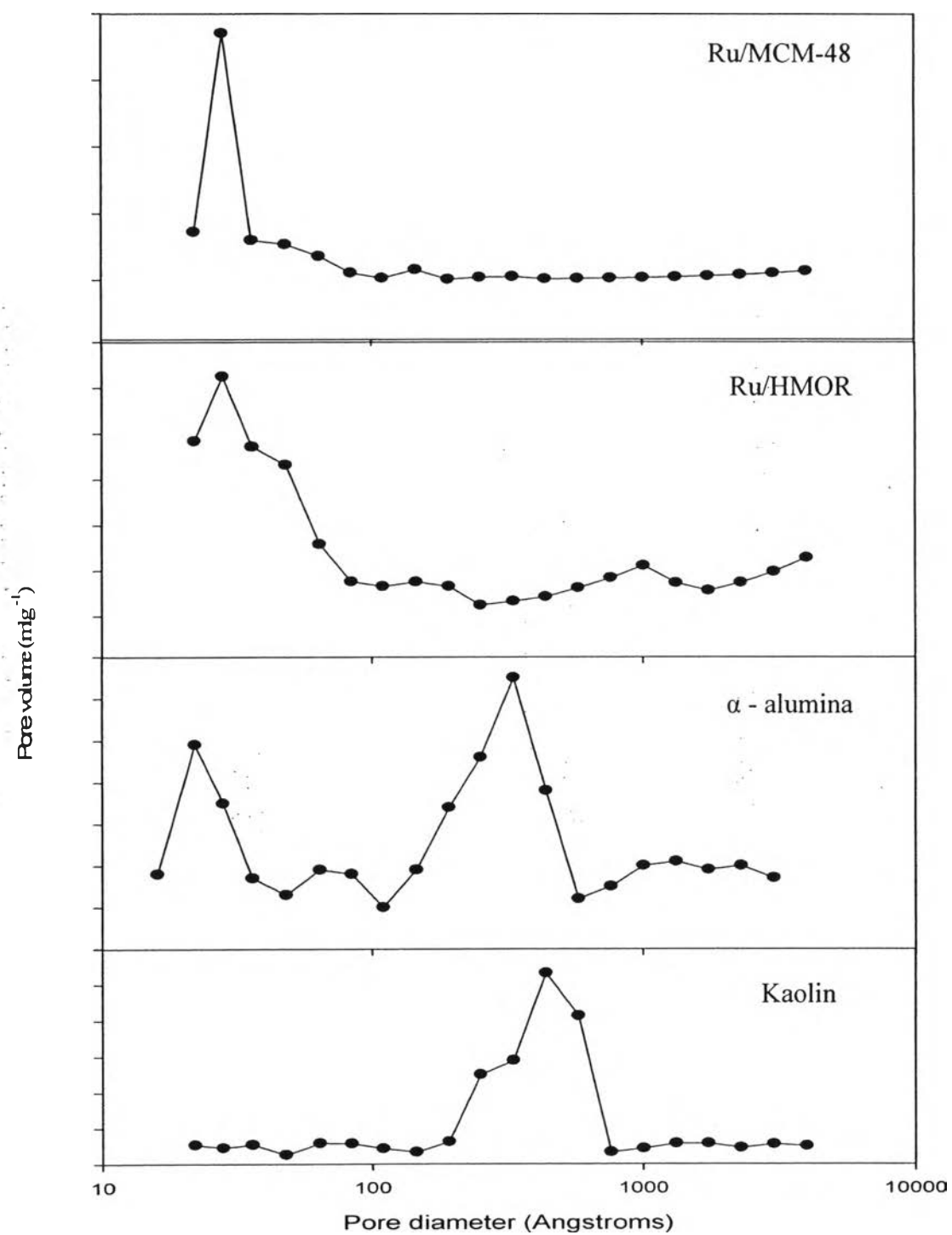


Figure 4.1 Variation of the pore size distribution of the individual catalysts.

Figure 4.2 shows the diffraction patterns of HMOR zeolite and mesoporous material MCM-48. The XRD peaks of HMOR appear at 2θ of 10° , 13° , 15° , 20° , 22° , 26° , 27° , and 31° . However, from a literature (Fan *et al.*, 2004), the unique peak of HMOR is 25.78° . The peak of MCM-48 is detected at $2\theta = 2.2^\circ$, which is the unique peak. The peaks corresponding to Ru metal are generally obtained at 38° , 42° , 44° , and 58° (Perring *et al.*, 1998). However, they are rarely detected because of the low loading amount. Moreover, Ru metal loaded on both supports does not lead to crystalline destruction.

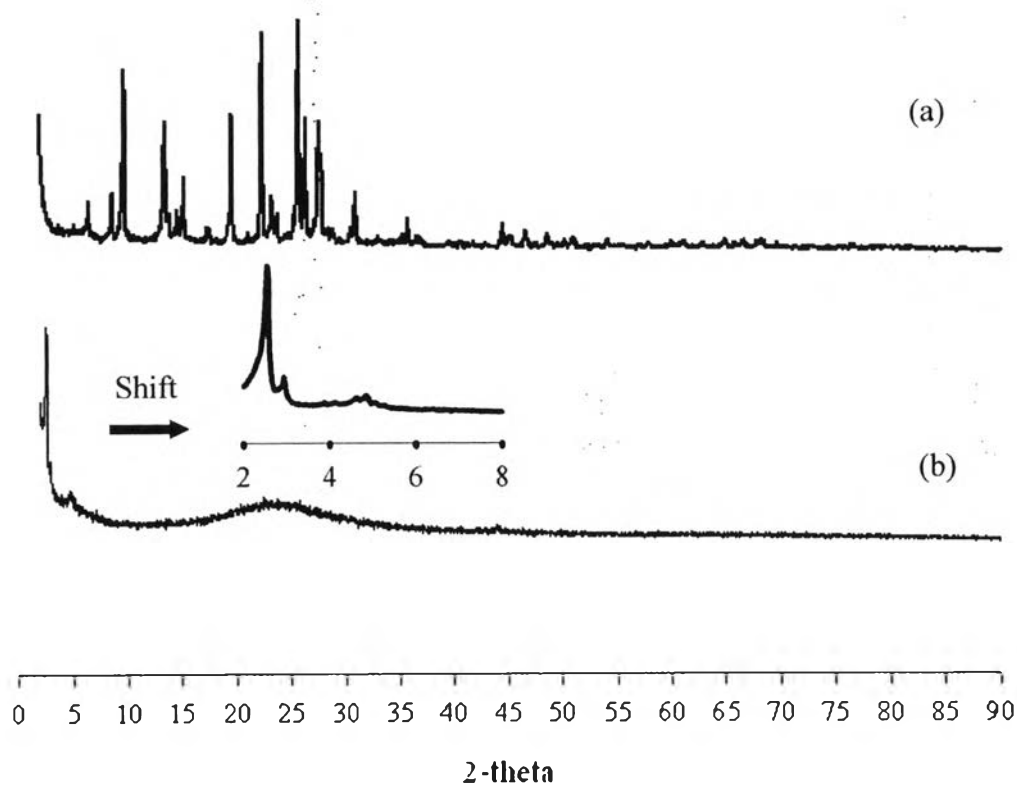


Figure 4.2 XRD patterns of (a) HMOR zeolite, and (b) MCM-48 mesoporous material.

4.1.2 Pyrolysis Results

First, and foremost, in order to understand the behavior and be able to make a reasonable explanation on the effect of the different compounded extrudates

compositions later in this chapter, it is important to first investigate the effect of each of the pure components to be composed in the extrudates on both the quality and quantity of the products. In general, the pyrolytic products can be classified into gas, oil, and solid char. The distribution of the pyrolytic products from non-catalytic pyrolysis is 14%wt, 39%wt, and 48%wt of gas, oil, and solid char, respectively. According to the fact that each of the pure components used can have a unique effect on the product obtained from the pyrolysis; therefore, the results are first reported separately for pure component used, which are illustrated as follows:

(a) *Kaolin*

Kaolin is one of the important catalyst compositions, which is used as a catalyst matrix for the production of extrudated catalyst. It is found that the matrix (Kaolin) itself has some influences on the products from pyrolysis. As compared to the non-catalytic case, Figure 4.3 shows that the use of kaolin can slightly increase the gas production, which is found to increase approximately to 16.5%. For the gas product composition (Figure 4.4), the use of kaolin slightly decreases ethylene, propylene, and heavy gases (above C₄s) in accordance with increasing methane, ethane, propane, and C₄-hydrocarbons as compared with the non-catalytic case. The light olefins yield of each pure component is demonstrated in Figure 4.5. Compared to the thermal pyrolysis, kaolin can produce slightly higher light olefins, which the yield is found at about 2.9 % (g/100g tire). Regarding the oil product, the quantity of the oil product produced is slightly decreased (dropped to 35%wt) compared to the non-catalytic case (Figure 4.3). For the chemical composition in the oil product, it is found that the concentration of saturated hydrocarbons is slightly decreased in accordance with an increase in the total aromatic compounds (Figure 4.6). Moreover, the relative selectivity of mono-aromatic is also increased (Figure 4.7). The other important property of oil is the petroleum fraction. It is found that the use of kaolin can drastically increase both naphtha and kerosene to 34 %wt in accordance with the decrease in light and heavy gas oil (Figure 4.8). Finally, the asphaltene content in the oil product is dramatically decreased as compared to the non-catalytic case (Figure 4.9).

(b) α -Alumina

α -Alumina is used as the binder in the extruded catalysts. As observed from the results, the use of alumina shows a similar effect to kaolin in increasing the gas production (Figure 4.3). However, unlike kaolin, it is found that it gives no significant difference in the gas compositions as compared to the non-catalytic case (Figure 4.4). It is found that the light olefins yield of alumina is slightly increased as compared to the non-catalytic case (Figure 4.5). In particular, it can produce light olefins yield at about 3.1 g/100 g tire. The oil production from using alumina is decreased in accordance with the increase in the gas products. The use of α -alumina can produce the total oil yield at about 32.5 %wt, which is less than the one obtained from the non-catalytic case. The quality of the oil product can be roughly estimated by their chemical compositions and the petroleum fraction of the oil product. Owing to Figures 4.6 and 4.7, the presence of alumina slightly increases the concentration of saturated hydrocarbons, and the selectivity of mono-aromatic hydrocarbons also increases in relation to the decrease in aromatic compounds. In addition, from Figure 4.8, alumina can produce a significantly higher portion of naphtha range product than the non-catalytic case. The increase of naphtha happens in accordance with the decrease of light gas oil. Lastly, it is found that alumina can dramatically decrease asphaltene content in the pyrolytic oil, and the weight percentage of asphaltene is found to be below 0.1.

(c) HMOR and 0.7% Ru/HMOR

For the product distribution, it is found that HMOR alone can provide a higher gas production than the non-catalytic case (Figure 4.3). Moreover, with the loading of Ru metal on HMOR, the amount of gas produced is found to increase further to the 24% of the total products. For the gas product compositions, the HMOR zeolite alone is found to dramatically increase propane and slightly increases ethane with slight decreasing other gas compositions. Moreover, the case of 0.7%Ru/HMOR increases C4s in accordance with decreasing propane as compared to HMOR case. The light olefins yield of HMOR is found to be similar to that of the non-catalytic case whereas Ru/HMOR provides the higher yield of light olefins than non-catalytic, kaolin, and alumina cases. In contrast, the oil yield using HMOR (~34%wt) is lower than that obtained from thermal pyrolysis. Moreover, it is found

that HMOR can increase saturated hydrocarbons content with a decrease of total aromatic compounds in maltene. The ratio of saturated to total aromatic hydrocarbons can be seen in Figure 4.5. Furthermore, Ru metal loaded on the HMOR zeolite can slightly increase saturated hydrocarbons higher than using HMOR alone. Regarding to the mono-aromatic selectivity, HMOR alone cannot increase mono-aromatic selectivity (Figure 4.6) whereas the use of Ru/HMOR shows a slight increase in mono-aromatic selectivity compared to the non-catalytic case. For petroleum fraction (Figure 4.7), HMOR zeolite can improve not only naphtha 13% higher but also increase kerosene 5% higher than the non-catalytic case. However, when Ru metal is loaded on HMOR, a slightly increase in both naphtha and kerosene fractions is found in conjunction with the reduction in heavy fractions, such as light and heavy gas oil, as compared to the non-catalytic case. The Ru metal loading can provide higher naphtha yield than using HMOR zeolite alone, but the other fractions, which are heavier than naphtha, decrease in accordance with increasing naphtha. For asphaltene content in the oil product, with using HMOR and Ru/HMOR (Figure 4.9), the concentration of asphaltene in oils is dramatically decreased as compared to the non-catalytic case.

(d) MCM-48 and 0.7%Ru/MCM-48

MCM-48 is a mesoporous non-acidic material. According to Figure 4.3, the use of MCM-48 can produce a very high gas yield of about 23%wt, and its production is much higher than the non-catalytic case (~10%). Furthermore, Ru metal loading on MCM-48 further improves gas production (by~3%) from the MCM-48 case. The use of synthesized MCM-48 can drastically improve the concentration of methane, ethane, and especially C₄-, and C₅-hydrocarbons in the gas product (Figure 4.4). By considering the light olefins products, MCM-48 and Ru/MCM-48 show high activity on light olefins production, which is found to increase up to 1.5 times higher than that of the non-catalytic case (Figure 4.5). They can convert invaluable waste tire to valuable products at a high yield of light olefins. When Ru metal is loaded on MCM-48, the Ru/MCM-48 can improve the efficiency on light olefins selectivity. Concerning the oil product, it is found that the total amount of oil product produced from using the MCM-48 and Ru/MCM-48 catalysts are remarkably dropped (~10%) as compared to the non-catalytic case (Figure 4.3).

Figures 4.6 and 4.7 show that the use of MCM-48 alone strongly increases the total aromatic hydrocarbons in the oil product at the expense of the saturated hydrocarbons, and no significant difference in mono-aromatic hydrocarbons selectivity is found. On the other hand, with the loading of Ru metal on MCM-48, the result shows the dramatical increase in the saturated hydrocarbon content in the oil product. Moreover, the mono-aromatic selectivity is also found to increase when compared among all types of aromatic compounds. For naphtha and kerosene production (Figure 4.8), MCM-48 has no influence on naphtha production, but it can dramatically increase kerosene with decreasing other oil product compositions. However, the Ru metal loading on MCM-48 causes an increase in the naphtha in accordance with the decrease in all other fractions. Lastly, the amount of asphaltene from pyrolytic oil is decreased when MCM-48 and Ru/MCM-48 are used. However, the asphaltene content is still relatively higher than that of the others (Figure 4.9).

(e) Comparison of HMOR and MCM-48

The MCM-48 and HMOR are used as supports. According to Figure 4.3, MCM-48 can produce higher gas yield than HMOR. Moreover, the difference between MCM-48 and HMOR is also seen in the gas composition. MCM-48 can decrease methane in accordance with increasing C4s and heavy gas whereas HMOR mainly decreases ethylene, propylene, C4s, and heavy gas with increasing ethane and especially propane as compared to the non-catalytic case. MCM-48 produces higher light olefins than HMOR. In contrast, HMOR can produce higher oil yield than MCM-48 by about 4%wt. In the oil products, it is found that HMOR gives a higher selectivity toward saturated HCs than the MCM-48, while the selectivity of mono-aromatic HCs obtained from both HMOR and MCM-48 are alike. For the petroleum fractions, it is found that the influence of these two catalysts is different. HMOR illustrates the higher amount of naphtha in the oil than MCM-48, whereas MCM-48 provides the higher kerosene content than HMOR. The increase in the light oil fractions is found in accordance with the decrease in the heavy hydrocarbon fractions such as gas oil and long residue. Lastly, due to the higher cracking activity of HMOR than that of MCM-48, the asphaltene reduction for the case of HMOR is found to be greater than that of MCM-48 as well.

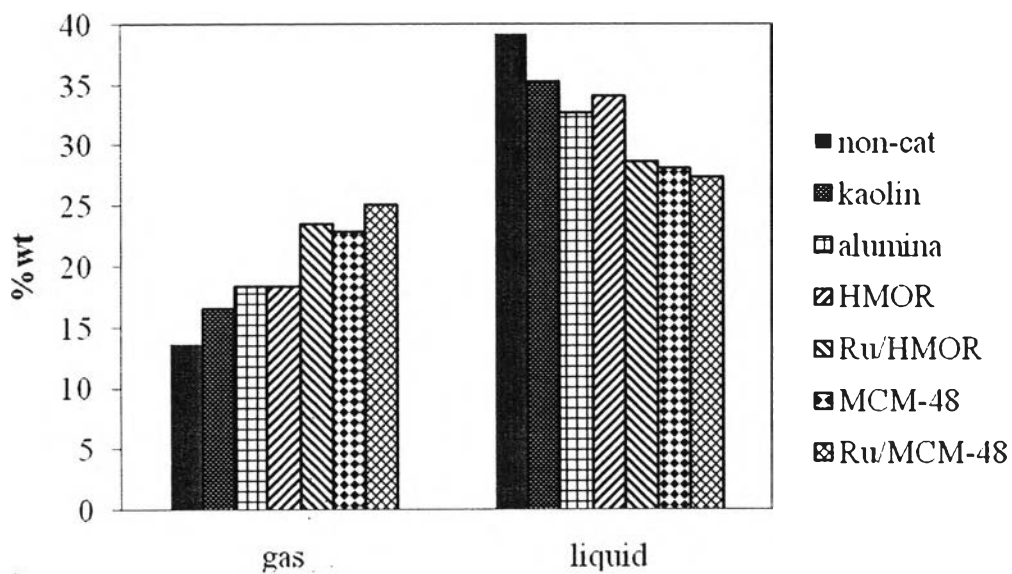


Figure 4.3 Gas and oil production from the catalytic pyrolysis of scrap tire using each component.

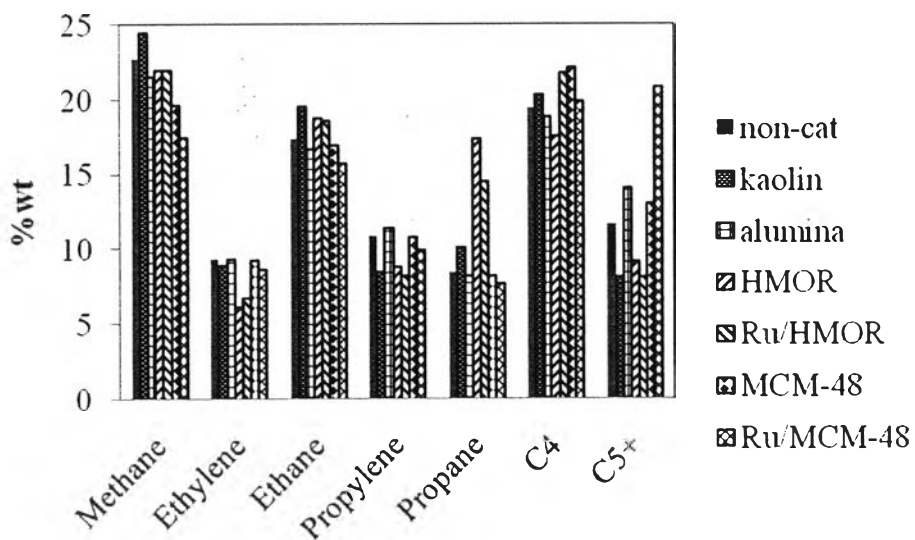


Figure 4.4 Gas compositions from the catalytic pyrolysis of scrap tire using each component.

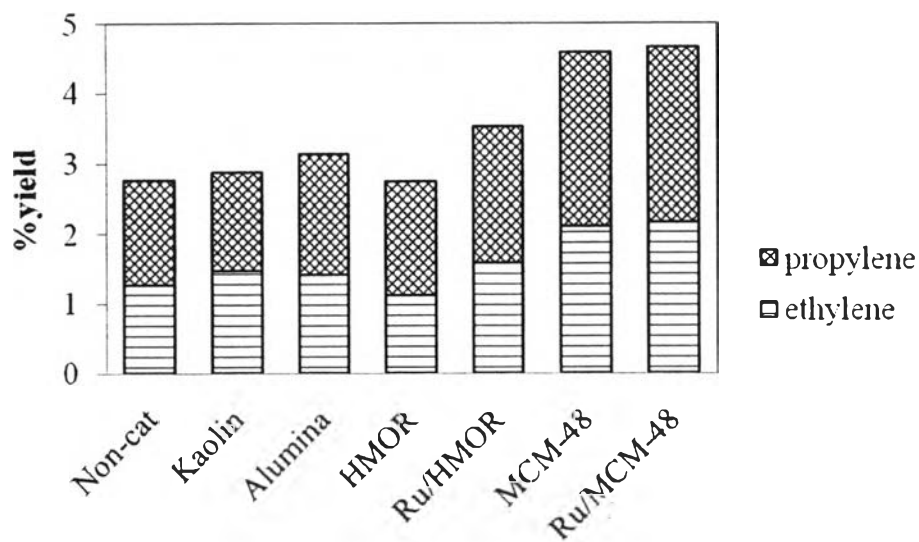


Figure 4.5 Light olefins yield in the gas products from using each component.

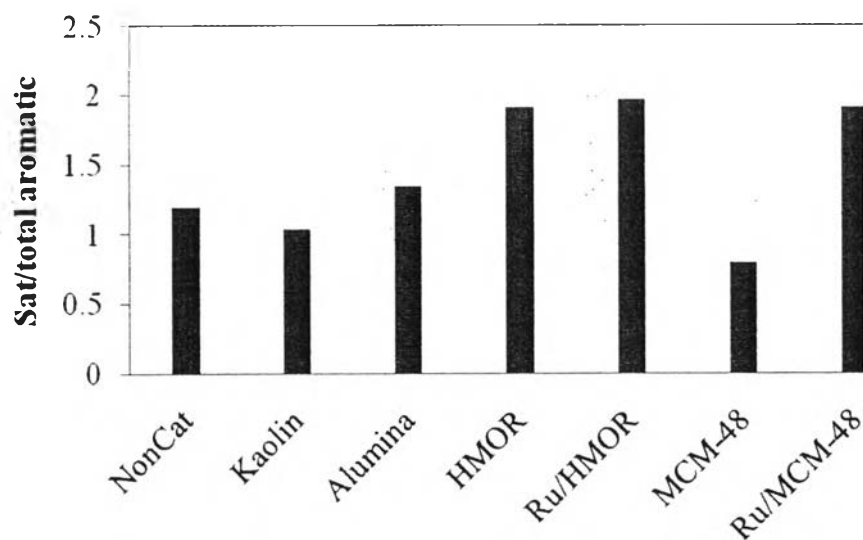


Figure 4.6 Ratio of saturated hydrocarbon to total aromatic compound of the oil from the catalytic pyrolysis of scrap tire using each component.

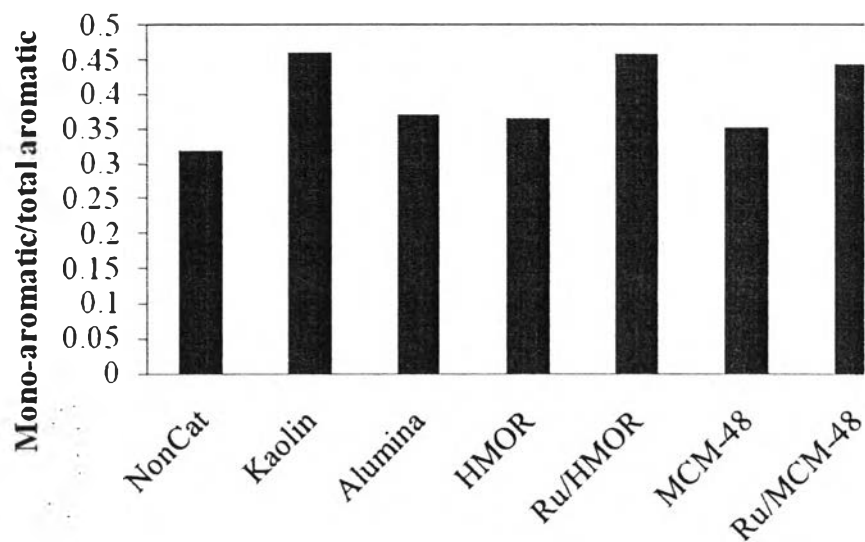


Figure 4.7 Ratio of mono-aromatic hydrocarbon to total aromatic compound in the oils from using each component.

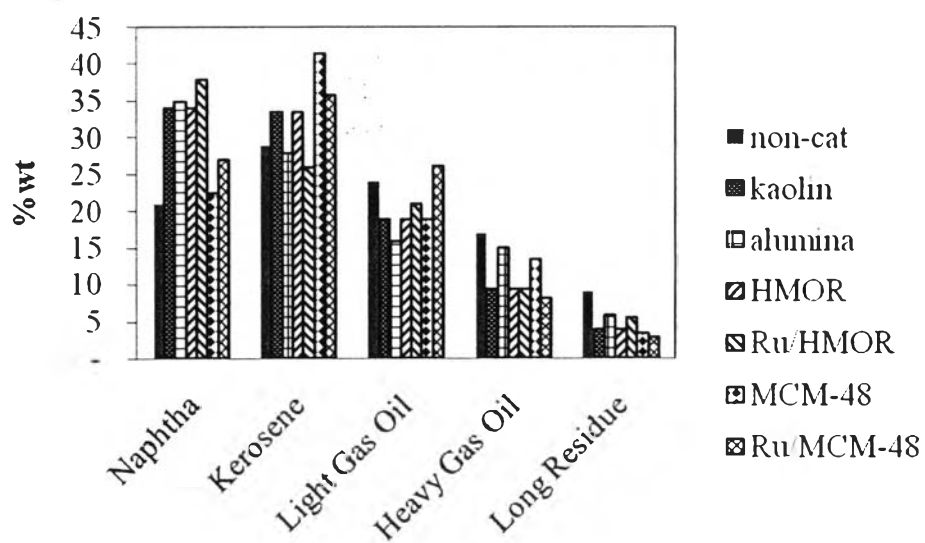


Figure 4.8 Petroleum fractions in the derived oils from each component.

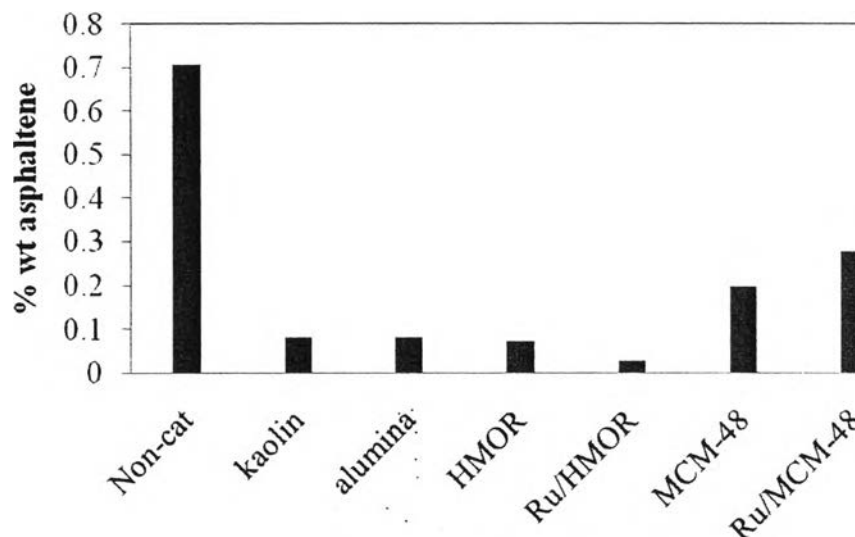


Figure 4.9 Asphaltene in the derived oils from using each component.

4.1.3 Discussion: Activity of each component

As mentioned above, each of the components has the different effects on the pyrolysis products. For the gas and oil production, kaolin and α -alumina slightly produce higher gas than the non-catalytic case. MCM-48 is the material which gives higher gas production than HMOR. Furthermore, Ru metal loading on both HMOR and MCM-48 can improve the gas yield as well. The gas fractions are composed of methane, ethylene, ethane, propylene, propane, C4-, C5-, C6-, C7-, and C8-hydrocarbons. It was found previously that the gas also consisted of 0.233% H₂, and 0.423% CO_x for the non-catalytic case (Berruenco *et al*, 2005) and H₂S about 0.4% (Laresgoti *et al*, 2000). Additionally, kaolin and alumina can slightly influence to increase light olefins content. HMOR can also somewhat increase the light olefins, but MCM-48 can significantly improve the light olefins yield. However, Ru metal loading on MCM-48 causes a slight increase of light olefins.

On the other hand, the oil production is reduced with using all catalysts and materials. Kaolin and alumina are not selective to saturated hydrocarbons because they can increase mono-aromatic hydrocarbons. The HMOR can dramatically increase saturated hydrocarbons, and Ru/HMOR can increase both the selectivity of saturated and mono-aromatic hydrocarbons. Nevertheless, MCM-48

has no effect on saturated and mono-aromatic hydrocarbons production, but Ru/MCM-48 can increase both fractions.

The effects of kaolin on the gas and oil might be caused by its pore size. The pore size of kaolin, which is a mesoporous material, can allow tire fractions to access, and then they are cracked. For the oil product, kaolin also cracks large molecules to small molecules, and the basic properties of kaolin might have some effect on increasing the mono-aromatic hydrocarbons in maltene. Alumina also has no effect on the type of molecules in oil. For the derived oil, alumina can increase naphtha in accordance with gas oil reduction since alumina has a mild acidity.

HMOR is an acid zeolite. The pore size and acidity of HMOR cause catalytic cracking, which produces a high amount of C3 and C4 (Choosuton, 2007). Furthermore, HMOR can crack heavy oil to light oil (Dũng, 2009). Saturated hydrocarbons can be slightly increased by using Ru/HMOR because Ru metal can hydrogenate poly- and polar-aromatic hydrocarbons and then cracked by HMOR to saturated and mono-aromatic hydrocarbons. For asphaltene production, both HMOR and Ru/HMOR can reduce asphaltene because their acidity causes the cracking of large molecules.

MCM-48 is synthesized by silatrane route; therefore, it is not an acidic material. However, the effect on gas production of synthesized MCM-48 is through the 3D pore structure (Viveka *et al*, 1997), which holds up the reactants inside its pore long enough that hydrocarbons have great mass transfer to undergo cracking reaction in the porous MCM-48. Moreover, the acidity of synthesized MCM-48 is extremely less than HMOR zeolites; therefore, it has the low amount of coke deposition. The activity of catalyst is then maintained because of the low amount of coke deposition (Lan-Lan *et al*, 2005). The Ru metal site promotes the hydrogenation reaction of aromatic hydrocarbons, which are subsequently cracked and undergo ring-opening reaction in the pore of MCM-48. For gas product, the C4- and C5-hydrocarbons productions are high yield in the gas because tires originally consisted of high butadiene and isoprene; hence, hydrocarbons chains tend to be cracked to the monomers. Moreover, the increment of C5-hydrocarbon might be resulted from the 3D pore structure of MCM-48, which maintains hydrocarbon molecules, and then gas molecules combine with them to larger gas molecules. Furthermore, the Ru

loading on the MCM-48 increases gas production. Ru metal, which is the metal sites, promotes the hydrogenation reaction of aromatic hydrocarbons, which are subsequently cracked and undergo ring-opening reaction in the pore of MCM-48. When MCM-48 is compared with HMOR, HMOR has more acidity than MCM-48 and can crack light olefins and other fractions. Due to the non-acidity of synthesized MCM-48, it can preserve light olefins molecules, and these molecules are not over-cracked to other HCs. In contrast, HMOR has high cracking activity; thereby, light olefins can be cracked. Although, Ru metal also converts heavy HCs to the gas product, ethylene and propylene are still slightly improved because of the higher gas yield. MCM-48 does not affect saturated and mono-aromatic hydrocarbons in maltene, but it can increase kerosene in accordance with the reduction of gas oil. For Ru loading, Ru/MCM-48 can improve saturated and mono-aromatic hydrocarbons in maltene oil because the hydrogenolysis activity of Ru metal makes poly- and polar-aromatic reduce. Moreover, Ru/MCM-48 can slightly increase naphtha and light gas oil with kerosene and heavy gas oil reduction. It might be noted that Ru metal can also crack large oil molecules to small molecules. Therefore, Ru/MCM-48 can slightly increase naphtha and light gas oil with kerosene and heavy gas oil reduction.

4.2 Ru/MCM-48-Based Extrudates

The extrudates used in this part are composed of 5-20 %wt Ru/MCM-48, 70-85 %wt kaolin and a fixed 10 %wt alumina. The compositions of the extrudates are presented in Table 4.2. The main objective was to determine the appropriate composition of Ru/MCM-48-based extrudates, which can preserve or improve light olefins production from waste tire pyrolysis.

Table 4.2 Nomenclatures of Ru/MCM-48-based extrudates

| Extrudate | Composition (%wt) | | |
|-----------|-------------------|--------|-------------------|
| | 0.7%Ru/MCM-48 | Kaolin | α -Alumina |
| 5-7RM48 | 5 | 85 | 10 |
| 10-7RM48 | 10 | 80 | 10 |
| 15-7RM48 | 15 | 75 | 10 |
| 20-7RM48 | 20 | 70 | 10 |
| 100-7RM48 | 100 | - | - |

4.2.1 Product Yield from Using Ru/MCM-48-based Extrudates

All Ru/MCM-48 extrudates can produce higher gas yield than the non-catalytic, kaolin, and alumina cases (Figure 4.10). Kaolin and alumina can produce the gas yield slightly higher than the non-catalytic case. The 100-7RM48 catalyst can produce the gas and oil yields at about 25 %wt and 27 %wt, respectively. The extrudates can produce the gas yield from 17-26 %wt. Only 5-7RM48 gives lower gas yield than alumina. The gas yield is increased with increasing 0.7%Ru/MCM-48 content up to 15 %wt whereas the gas yield is slightly decreased with increasing 0.7%Ru/MCM-48 content over 15 %wt. However, the 15-7RM48 and 20-7RM48 extrudates can produce higher gas yield than the pure Ru/MCM-48 catalyst (100-7RM48). Moreover, the 15-7RM48 extrudate gives the highest gas yield at about 27 %wt.

As shown in the Figure 4.1, it was found that the introduction of any kind of catalysts including the pure matrix and binder can help improve the gas yield as compared to the non-catalytic or the thermal pyrolysis case. The use of pure kaolin and alumina can slightly produce higher gas yield than the non-catalytic case. Concerning the compounded catalysts, it is found that the yield of gas product produce increases with an increasing active 0.7%Ru/MCM-48 composition. The highest gas yield is obtained from the case of 15 wt. % of 0.7%Ru/MCM-48, which hereby gave up to 27wt. % of the yield of gas product (higher than the case of pure 0.7%Ru/MCM-48).

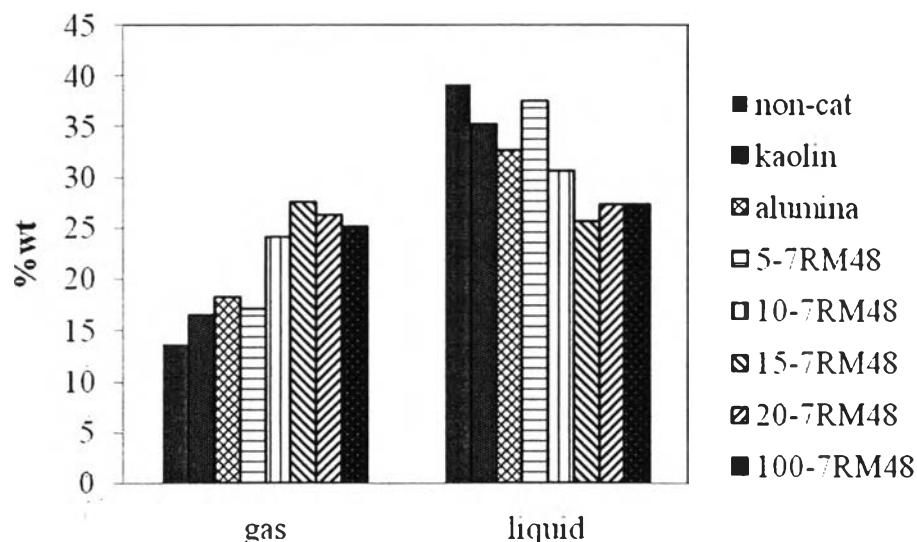


Figure 4.10 Product yields from using the Ru/MCM-48-based extrudates

4.2.2 Light Olefins Production from Using Ru/MCM-48-Based Extrudates

The ethylene and propylene production from the catalytic pyrolysis of scrap tire using the Ru/MCM-48-based extrudates are presented in Figure 4.11. Kaolin has no significant effect on light olefins production whereas the pure Ru/MCM-48 (100-7RM48) can produce higher light olefins yield of about 4.6 %. Most extrudates can produce higher light olefins yield than the non-catalytic, the pure binder, and matrix cases, except 5-7RM48 which produces less light olefins yield than alumina. In particular, the light olefin production is increased with increasing the composition of 0.7%Ru/MCM-48 in the extrudates. In addition, the case of 15-7RM48 and 20-7RM48 extrudates are found to give the maximum light olefins yield as compared to all the other cases including the pure Ru/MCM-48 itself. However, with concerning about less amount of Ru/MCM-48 used than 20-7RM48 the best extrudate composition is found to be the case of 15-7RM48.

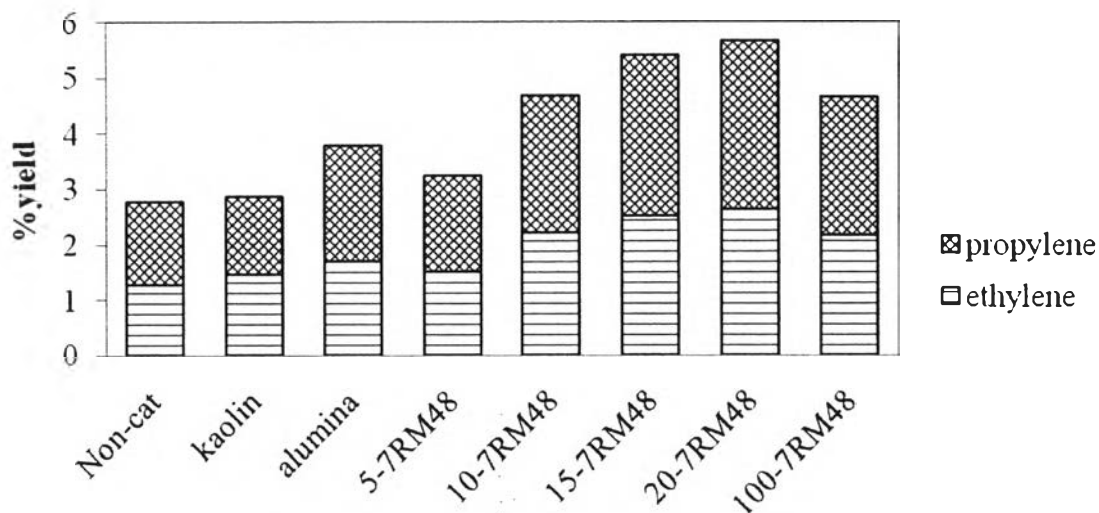


Figure 4.11 Light olefins production from using the Ru/MCM-48-based extrudates.

4.2.3 Molecular Compositions, Asphaltene, Sulfur in Pyrolytic Oil, and Coke and Sulfur Deposition on Spent Extrudates from Using Ru/MCM-48 Based Extrudates

The saturated and mono-aromatic hydrocarbons in maltenes were determined. From the previous part, kaolin can give lower saturated hydrocarbons but higher mono-aromatics than the non-catalytic case whereas alumina can produce both saturated and mono-aromatic HCs higher than the non catalytic case. However, using the Ru/MCM-48 based extrudates produces the saturated and mono-aromatic HCs contents that lie in between those of thermal pyrolysis and the Ru/MCM-48 catalyst (Table 4.3). It can be observed that saturated hydrocarbons increase with increasing the composition of 0.7%Ru/MCM-48 in the the extrudates whereas the mono-aromatic is insignificantly increased.

Table 4.3 Relative ratio of saturated and mono-aromatic hydrocarbons to total aromatics obtained from using the Ru/MCM-48-based extrudates

| Extrudate | Ratio | |
|-----------|--------------------------|------------------------------|
| | Saturated/total aromatic | Mono-aromatic/total aromatic |
| Non-Cat | 1.20 | 0.32 |
| Kaolin | 1.04 | 0.46 |
| Alumina | 1.35 | 0.37 |
| 5-7RM48 | 1.00 | 0.37 |
| 10-7RM48 | 1.17 | 0.42 |
| 15-7RM48 | 1.24 | 0.41 |
| 20-7RM48 | 1.30 | 0.43 |
| 100-7RM48 | 1.92 | 0.44 |

As shown in Table 4.4, the asphaltene in oils is decreased into 0.08%wt with using kaolin and alumina whereas it is 0.28% with using the 100-7RM48 catalyst. This suggests that kaolin and alumina have a higher ability for asphaltene reduction in oils than the pure Ru/MCM-48 catalyst. Ru/MCM-48 based extrudates have moderate ability for asphaltene reduction, and they can reduce the asphaltene in oils from what obtained from the non-catalytic case and the pure Ru/MCM-48 catalyst. Moreover, the 20-7RM48 extrudate seems to be the best extrudate composition for asphaltene reduction because it can reduce asphaltene to 0.08%wt as the same amount as kaolin and alumina can, although it contains only 70% kaolin.

For sulfur deposition on the spent catalysts, the amount of sulfur on the spent kaolin and alumina are about 0.25%wt and 0.14%wt, respectively. On the other hand, the sulfur on the spent 100-7RM48 is found to be higher (0.42%wt). Nonetheless, the sulfur deposition is dramatically decreased from 0.42% to 0.15% for all the Ru/MCM-48 based extrudates. It can be concluded that compounding the catalyst in the extrudate form can help reduce the sulfur deposition on the catalysts, especially at low percentages of active Ru/MCM-48.

In the case of coke deposition on the spent extrudates, the amounts of coke deposition are about 0.13 g/g kaolin, 0.07 g/g alumina, 0.07 g/g 5-7RM48,

0.08 g/g 10-7RM48, 0.13 g/g 15-7RM48, 0.12 g/g 20-7RM48, and 0.29 g/g 100-7RM48. The coke deposition of spent Ru/MCM-48 based extrudates is found to be decreased the same as sulfur deposition on the spent extrudates as shown in Table 4.4.

Table 4.4 Percentage of asphaltene, sulfur in oils, sulfur on spent extrudates and coke deposition from using Ru/MCM-48 based extrudates

| Extrudate | %asphaltene | %sulfur in oils | %sulfur on spent catalyst | Coke deposition (g/g cat) |
|-------------------|-------------|-----------------|---------------------------|---------------------------|
| Non-Cat | 0.71 | 0.73 | | |
| Kaolin | 0.08 | 0.66 | 0.25 | 0.13 |
| α -alumina | 0.08 | 0.76 | 0.14 | 0.07 |
| 5-7RM48 | 0.12 | 0.61 | 0.13 | 0.07 |
| 10-7RM48 | 0.17 | 0.64 | 0.14 | 0.08 |
| 15-7RM48 | 0.16 | 0.66 | 0.15 | 0.13 |
| 20-7RM48 | 0.08 | 0.74 | 0.20 | 0.12 |
| 100-7RM48 | 0.28 | 0.69 | 0.42 | 0.29 |

4.2.4 Petroleum Fractions from Using Ru/MCM-48 Based Extrudates

According to Figure 4.12, the petroleum fractions are altered by using different extrudates. Kaolin and alumina have the high ability in changing heavy oils to light oils such as naphtha when compared with the non-catalytic case. In previous study, Ru/MCM-48 is the best catalyst for kerosene production. The increase of 0.7%Ru/MCM-48 content in the extrudates can improve naphtha and kerosene production. Among the extrudate catalysts tested, 20-7RM48 is the composition for high naphtha production (33%wt). It can produce naphtha higher than Ru/MCM-48 itself but less than kaolin and alumina. However, 15- and 20-7RM48 can produce more kerosene than Ru/MCM-48, kaolin, and alumina itself. Especially, the 15-7RM48 extrudate can give the highest kerosene production (41%wt) among all extrudates.

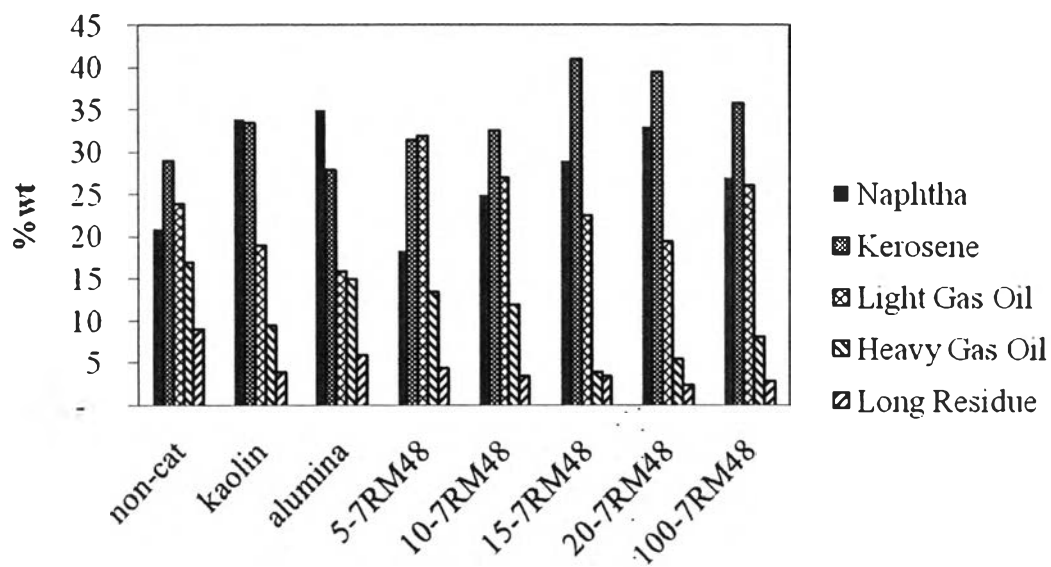


Figure 4.12 Petroleum fractions in the derived oils from using Ru/MCM-48 based extrudates.

4.2.5 Discussion: Ru/MCM-48 Based Extrudates

According to the product yields, the gas production can be obtained by using Ru/MCM-48 based extrudates. This suggests that Ru/MCM-48 based extrudates have a cracking activity. Furthermore, the light olefins yield is increased with increasing the Ru/MCM-48 component in the extrudates. Among the extrudates, 15-7RM48 and 20-7RM48 can produce light olefins yield higher than the Ru/MCM-48 itself. Therefore, 15-7RM48 is the appropriate composition of Ru/MCM-48 based extrudates for light olefin production. The Ru/MCM-48 based extrudates can increase mono-aromatic but decrease saturated hydrocarbons in oil. Moreover, it can potentially reduce high amount of asphaltene in oil and prevent sulfur deposition on the spent catalysts. Moreover, the uses of Ru/MCM-48 based extrudates have no effect on sulfur reduction in oil. For the oil cracking activity, the Ru/MCM-48 based extrudates can crack heavy fractions into lighter fractions such as kerosene. Especially, 15-7RM48 gives the highest of kerosene in the extrudates. However, Ru/MCM-48 based extrudates are not selective to naphtha production because it can produce less naphtha than kaolin and α -alumina.

In conclusion, 15-7RM48 is the appropriate composition of Ru/MCM-48 based extrudate for light olefins production. The matrix particles have some effect on light olefins production. According to the Sritana's work (2010), the catalytic cracking is mainly caused by carbenium ion-driven beta scission, which the overall reaction is an exothermic reaction. When the catalyst contains only the active Ru/MCM-48 component, the dissipation of heat is hardly possible. This is because the active component has a low thermal conductivity substance. If the particles of active component contact among others during cracking, a hotspot can occur. This hotspot can crack ethylene and propylene, which are intermediate products of cracking, into other molecules. The surrounding matrix helps to dissipate the heat from the active component, and then prevents over-cracking. Therefore, light olefins can be preserved by a matrix.

For the oil production, it can be explained that MCM-48 is a selective catalyst for kerosene production because of the appropriate pore size of MCM-48. Moreover, when the matrix is mixed in the catalyst, the mild acidity and basicity of matrix helps to crack large HCs molecules to smaller HCs molecules. Saturated HCs decrease with the decreasing amount of Ru/MCM-48 in the extrudate due to the hydrogenation reaction of Ru metal in catalyst. However, no reduction of sulfur in oil is found for all Ru/MCM-48 based extrudates. This may be because the amount of Ru/MCM-48 in the extrudates is not sufficient to break C-S bond resulting in a high sulfur content in the pyrolytic oils.

4.3 Ru/HMOR-Based Extrudates

For this part, the compositions of the Ru/HMOR-based extrudates are varied as shown in Table 4.5. The mixtures were mixed and extruded to the extrudate form. The goal of using Ru/HMOR extrudates is the preservation of light olefins production at the least amount of active Ru/HMOR catalyst. The nomenclature "7RMOR" is named after 0.7% of Ru/HMOR.

Table 4.5 Nomenclatures for Ru/HMOR-based extrudates

| Extrudate | Composition (%wt) | | |
|-----------|-------------------|--------|-------------------|
| | 0.7%Ru/HMOR | Kaolin | α -Alumina |
| 5-7RMOR | 5 | 85 | 10 |
| 10-7RMOR | 10 | 80 | 10 |
| 15-7RMOR | 15 | 75 | 10 |
| 20-7RMOR | 20 | 70 | 10 |
| 100-7RMOR | 100 | - | - |

4.3.1 Product Yields from Using Ru/HMOR-Based Extrudates

According to Figure 4.13, the gas production can be increased with using Ru/HMOR based extrudates as compared to the non-catalytic case. Moreover, the composition of Ru/HMOR component has the effect on gas production. The pure Ru/HMOR (100-RMOR) catalyst gives the highest gas yield about 24 %wt. The increase amount of Ru/HMOR component (7RMOR) from 5 to 20%wt increases gas production from 15 to 18%wt, respectively. In particular, the increment of active component from 5 to 10% can significantly increase the gas yield, while the increment of active component from 10 to 20% slightly decreases gas production. However, the gas production of all Ru/HMOR based extrudates is less than that of active catalyst. The oil production is decreased in accordance with the increasing gas production.

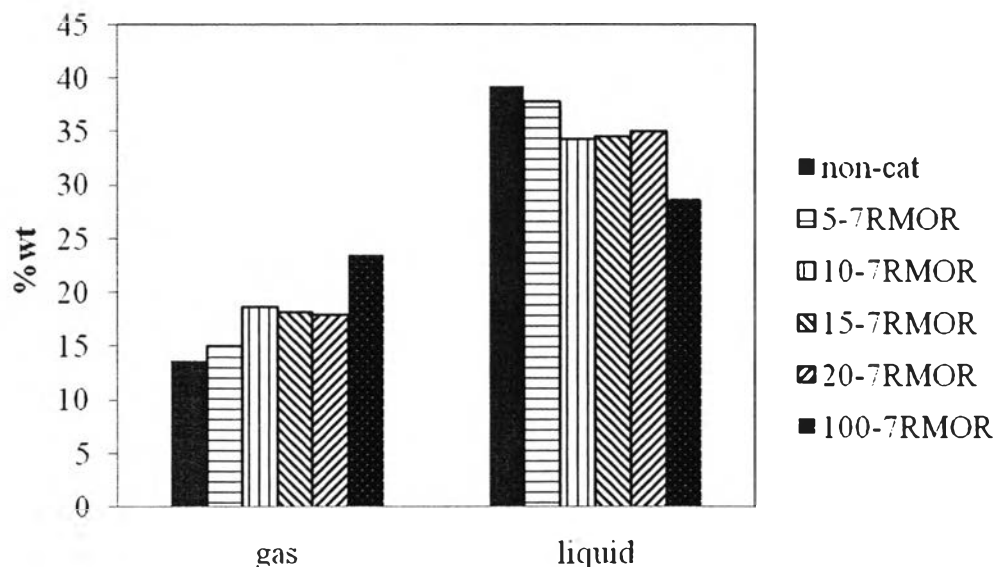


Figure 4.13 Product Yields from using the Ru/HMOR-based extrudates.

4.3.2 Light Olefins Production from Using Ru/HMOR-based Extrudates

Figure 4.14 indicates the light olefins production obtained from using Ru/HMOR based extrudates. The light olefins production is found in the same trend as the gas production shown in the previous figure. Kaolin and alumina has the impact on the light olefins production when compared to the non-catalytic case. The active Ru/HMOR catalyst provides the highest light olefins yield among all Ru/HMOR extrudates. The use of most Ru/HMOR based extrudates gives higher light olefins than that obtained from kaolin and alumina, except 5-7RMOR. The extrudates can produce light olefins at around 3-3.5 %yield. Moreover, the light olefins production is increased, when the active component in the extrudate is increased from 5 to 10%. Above 10%, light olefins remain constant. However, the 10-7RMOR extrudate can provide the same light olefins yield as the active Ru/HMOR catalyst. Consequently, the 10-7RMOR is the most appropriate composition among all Ru/HMOR based extrudates for light olefins production.

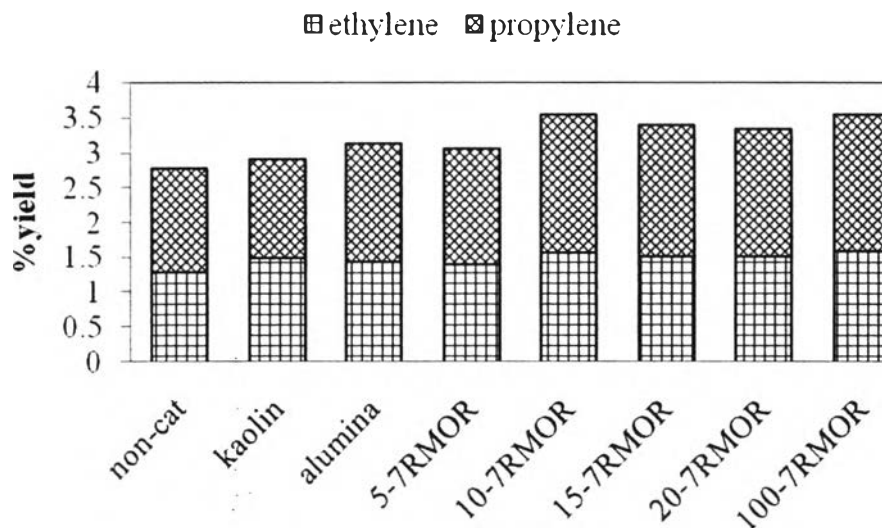


Figure 4.14 Light olefins production using the Ru/HMOR-based extrudates.

4.3.3 Pyrolytic Oils from Using Ru/HMOR Based Extrudates

Among Ru/HMOR extrudates, the pure Ru/HMOR catalyst has the highest performance to increase the concentration of saturated HCs. The saturated hydrocarbons from using Ru/HMOR based extrudates are higher than that obtained from the non-catalytic, kaolin, and α -alumina cases. Moreover, the increasing amount of active component in the extrudates can increase the amount of saturated hydrocarbons in maltene. However, the ratio obtained from all extrudates lies in between that of the non-catalytic case and the pure Ru/HMOR, suggesting that the dilution by the matrix plays the role on saturated HCs formation. For mono-aromatic production the Ru/HMOR based extrudates can produce higher mono-aromatic than the pure components (Ru/HMOR, kaolin, and α -alumina), indicating that the synergy between Ru/HMOR and kaolin occurs on the formation of mono-aromatics. 10-7RMOR gives the highest amount of mono-aromatic among of all tested catalysts.

Table 4.6 Relative ratio of saturated and mono-aromatic hydrocarbons to total aromatic from using the Ru/HMOR-based extrudates

| Extrudate | Ratio | |
|-----------|--------------------------|------------------------------|
| | Saturated/total aromatic | Mono-aromatic/total aromatic |
| Non-Cat | 1.20 | 0.32 |
| Kaolin | 1.04 | 0.46 |
| Alumina | 1.35 | 0.37 |
| 5-7RMOR | 1.50 | 0.57 |
| 10-7RMOR | 1.76 | 0.58 |
| 15-7RMOR | 1.79 | 0.56 |
| 20-7RMOR | 1.83 | 0.49 |
| 100-7RMOR | 1.97 | 0.46 |

Asphaltene are molecular substances that are found in crude oil and bitumen, along with aromatic hydrocarbons, and alkanes (saturated hydrocarbons). Hence, asphaltene is an invaluable fraction. According to Table 4.6, Ru/HMOR based extrudates can reduce the high amount of asphaltene in the pyrolytic oil as compared to the non-catalytic case. The synergistic effect on asphaltene, sulfur in oils, and sulfur deposition occurs with using two extrudates, 5-7RMOR and 10-7RMOR, which suggests that compounding in the extrudate forms is beneficial to the reduction of asphaltene and sulfur. According to Table 4.7, on the other hand, the coke reduction seems not be to the benefit from the compounded catalyst.

Table 4.7 Percentage of asphaltene, sulfur in oils, and sulfur and coke on spent extrudates from using Ru/HMOR based extrudates

| Extrudates | %asphaltene | %sulfur in oils | %sulfur on spent catalyst | Coke deposition (g/g cat) |
|------------|-------------|-----------------|---------------------------|---------------------------|
| Non-Cat | 0.71 | 0.73 | | |
| Kaolin | 0.08 | 0.66 | 0.25 | 0.13 |
| alumina | 0.08 | 0.76 | 0.14 | 0.07 |
| 5-7RMOR | 0.02 | 0.59 | 0.15 | 0.13 |
| 10-7RMOR | 0.04 | 0.69 | 0.16 | 0.21 |
| 15-7RMOR | 0.10 | 0.74 | 0.22 | 0.15 |
| 20-7RMOR | 0.10 | 0.76 | 0.22 | 0.15 |
| 100-7RM48 | 0.03 | 0.65 | 0.35 | 0.23 |

4.3.4 Petroleum Fractions From Using Ru/HMOR Based Extrudates

From Figure 4.14, naphtha fraction is the major fraction which can be produced by the Ru/HMOR based extrudates. The pure Ru/HMOR catalyst potentially increases naphtha production in accordance with heavy oils reduction. The use of Ru/HMOR based extrudates provides higher naphtha than that of the non-catalytic, kaolin, and alumina cases. Furthermore, the extrudates can preserve naphtha production with the maximum naphtha production of about 38%wt. Namely, the Ru/HMOR based extrudates give the same petroleum fractions as using the pure Ru/HMOR catalyst. Moreover, all Ru/HMOR extrudates give almost the same amount of kerosene.

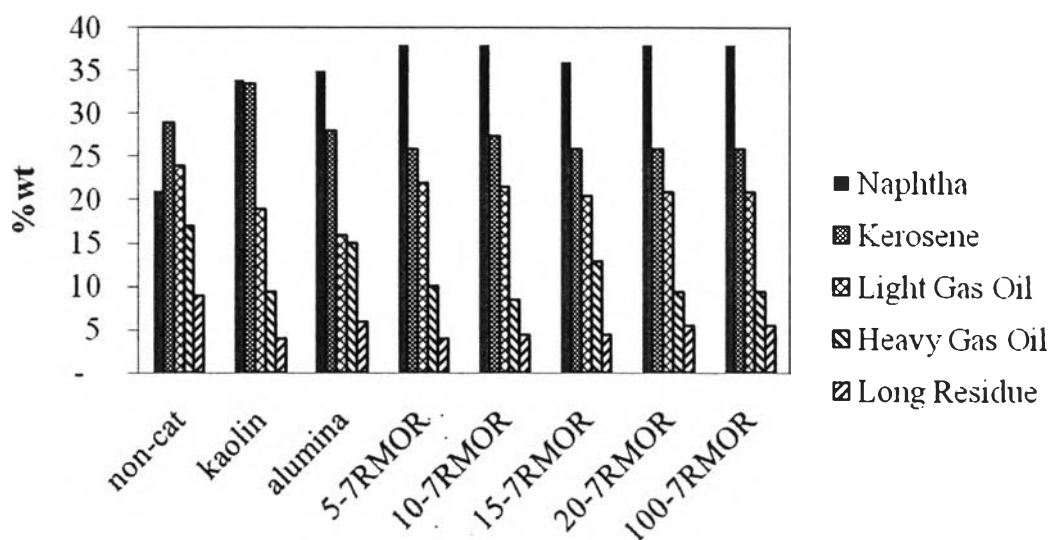


Figure 4.15 Petroleum fractions from using Ru/HMOR based extrudates.

4.3.5 Discussion: Ru/HMOR Based Extrudates

For the results, the matrix has some impact on the cracking activity of the Ru/HMOR based extrudates as same as Ru/MCM-48 extrudates. The heat generation from the active component particles needs to be dissipated by the matrix particles to prevent the over-cracking of ethylene and propylene. With the fact that, Ru/HMOR has higher acidity than Ru/MCM-48; therefore, Ru/HMOR might have higher activity on the over-cracking than Ru/MCM-48. It is the reason why Ru/HMOR needs higher matrix content in the extrudate than Ru/MCM-48. Moreover, the Ru/HMOR extrudates can improve mono-aromatic HCs because of consisting of the higher kaolin content in the extrudates. For naphtha production, it can be noted that matrix can pre-crack large hydrocarbons molecules prior to passing the cracked products to Ru/HMOR that then further cracks them again to even smaller hydrocarbons molecules.

For pyrolytic oils, the amount of asphaltene and sulfur in oil obtained from using Ru/HMOR extrudates is decreased to the same extent as the active Ru/HMOR catalyst. It is possible that kaolin has some impact on sulfur reduction in oil. Moreover, Ru/HMOR extrudates can reduce coke and sulfur deposition on the spent catalysts since the surface area and pore volume of extrudates are decreased

when Ru/HMOR is physically mixed with kaolin. Finally, 10-7RMOR (10% Ru/HMOR, 80% kaolin, and 10% α -alumina) is found to be the most appropriate composition of extrudate for waste tire pyrolysis because it is the best among of all tested catalysts to preserve the production of light olefins and naphtha.

4.4 Effect of Matrix Type

In this part, the influence of clay matrix type on the quantity and quality of the product from tire pyrolysis were focused. Five different types of clays, which are kaolin, bentonite, montmorillonite, and talc were selected as matrixes for the investigation. As shown in the Table 4.8, all the extrudates are composed of 5% active component, 85% matrix, and 10% alumina binder.

Table 4.8 Nomenclature of the extrudates compounded from various clay matrixes

| Extrudates | Composition (%wt) | | | | | |
|------------|-------------------|--------|-----------|--------|-----------------|-----------------------------|
| | Ru/HMOR | Kaolin | Bentonite | Talcum | Montmorillonite | Binder (α -alumina) |
| 5-7RM-kao | 5 | 85 | 0 | 0 | 0 | 10 |
| 5-7RM-ben | 5 | 0 | 85 | 0 | 0 | 10 |
| 5-7RM-tal | 5 | 0 | 0 | 85 | 0 | 10 |
| 5-7RM-mon | 5 | 0 | 0 | 0 | 85 | 10 |

4.4.1 Characterization of Matrixes

According to Table 4.9, the physical properties of various matrixes are exhibited. The surface area and pore volume are alike in most matrixes (about 10-50 m²/g, and 0.14-0.19 cm³/g, respectively) except montmorillonite, which has high surface area and pore volume of about 275.9 m²/g and 0.48 cm³/g, respectively. However, bentonite, talc, and alumina have special pore distribution, which are the bi-modal pore distribution having two average pore sizes. In particular, bentonite has the average pore sizes of 44.34 Å and 194.9 Å (mesopore), whereas talc has the

average pore sizes of 392.5 Å and 1,539 Å (macropore). The active component (0.7%Ru/HMOR) has the highest surface among all components, but it has the smallest pore size. The pore distribution can be observed in Figure 4.16, and the pore diameters are listed in Table 4.9.

Table 4.9 Physical properties of each component in the extrudated catalysts

| | Surface area (m ² /g)* | Pore volume B.J.H. (cm ³ /g)** | Pore diameter (Å) |
|-----------------|--------------------------------------|--|----------------------|
| α-alumina | 73.34 | 0.48 | 44.18 |
| Kaolin | 32.87 | 0.16 | 418.8 |
| Bentonite | 46.71 | 0.14 | 44.34,194.9 |
| Montmorillonite | 275.9 | 0.48 | 62.92 |
| Talc | 11.09 | 0.19 | 392.5,1,539 |
| 0.7% Ru/HMOR | 332.6 | 0.19 | 7.05, 37.35 |

* BET method, ** B.J.H. method

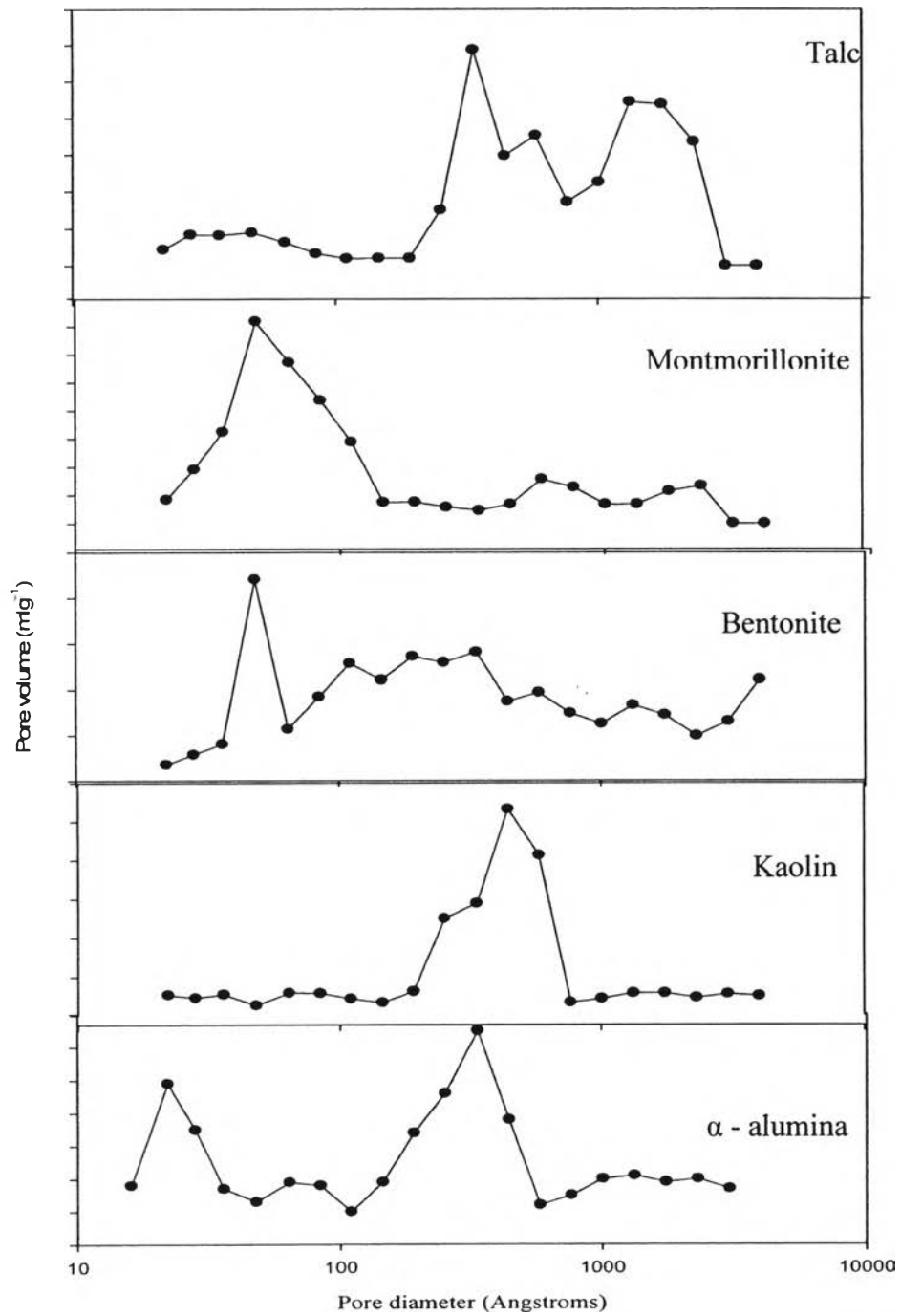


Figure 4.16 Variation of the pore sizes of the studied clays and α -alumina.

4.4.2 Product Yields from Using Various Different Matrixes in Extrudates

The product yields of Ru/HMOR based extrudates composed of different matrixes can be observed from Figure 4.16. Kaolin and montmorillonite produce less gas yield (~15 wt %) than bentonite, talc, and alumina (about 18%wt). The active Ru/HMOR catalyst itself can produce the highest gas yield of about 24 %wt among all the other cases. All extrudates, however, can produce higher gas yield than the non-catalytic case. The use of various matrixes in the extrudates gives less gas production than the active catalyst itself. Moreover, the oil yield decreases in accordance with the increase in the gas production. The product yield of all pure clays can be seen in Appendix B.

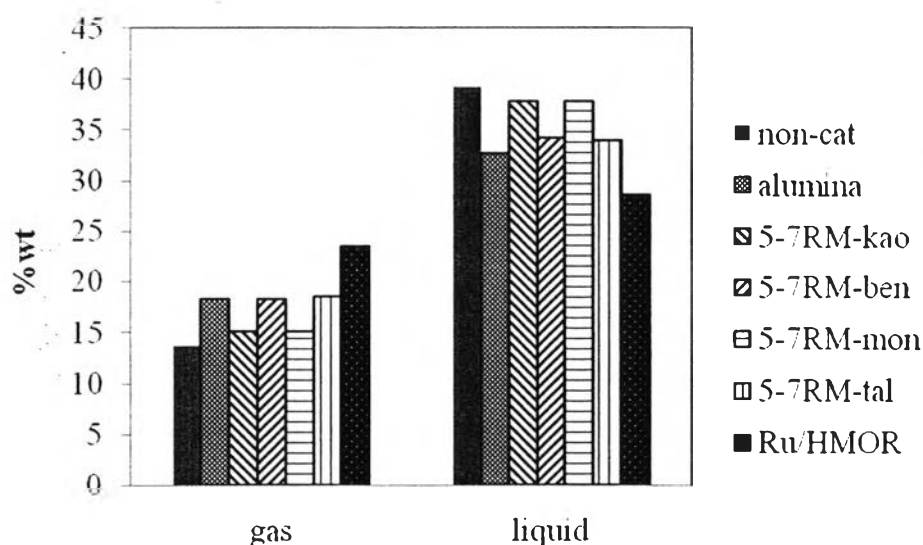


Figure 4.17 Gas and oil yields from using different matrixes in the extrudates.

4.4.3 Light Olefins from Using Different Matrixes in the Extrudates

From Figure 4.18, montmorillonite provides the least amount of light olefins production among all matrixes used in the extrudates. Kaolin can produce higher light olefins yield (~3 g) than montmorillonite. (~2.9 g). Nevertheless, both montmorillonite and kaolin provide less light olefins than alumina. On the other hand, bentonite and talc have the high potential light olefins preservation. In

particular, both can provide light olefins as the same yield as the active Ru/HMOR (about 3.5 g.).

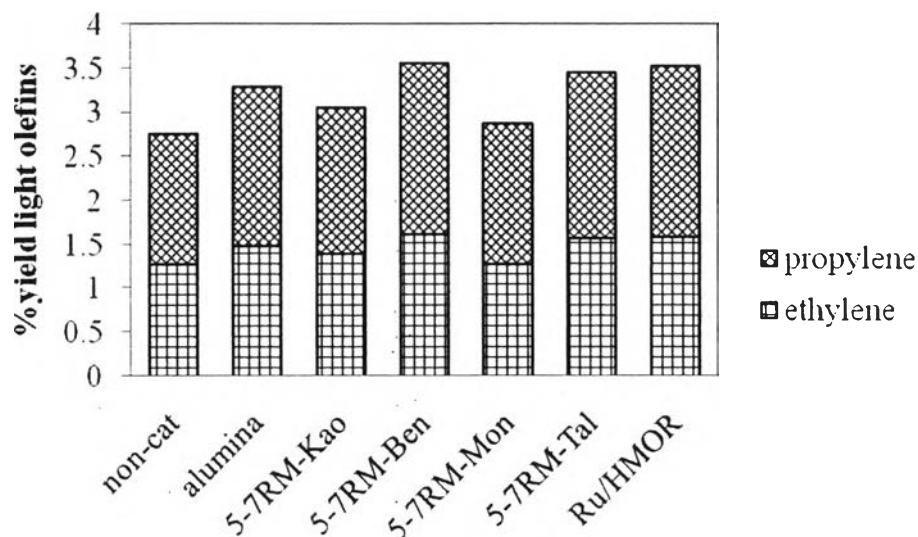


Figure 4.18 Light olefins production from using different matrixes in the extrudates.

4.4.4 Pyrolytic Oils from Using Different Matrixes in Extrudates

The ratios of saturated and mono-aromatic hydrocarbons to total aromatic hydrocarbons are exhibited in Table 4.10. Even if the extrudates with various matrixes can give a higher concentration of saturated hydrocarbons than the non-catalytic and alumina cases, they give less concentration of saturated HCs than the active Ru/HMOR catalyst, suggesting the dilution effect may cause this outcome. However, the extrudates composed of different matrixes can produce higher mono-aromatic hydrocarbons than the Ru/HMOR catalyst and the non-catalytic case. Pure clays such as kaolin prefer to produce mono-aromatic HCs, but do not prefer to provide saturated HCs. The details about pure matrixes can be seen in Appendix E. The results suggest that the higher production of mono-aromatic is contributed from the clays that are used as the matrixes.

Table 4.10 Relative ratio of saturated and mono-aromatic hydrocarbons to total aromatic from using the extrudates composed of different matrixes

| Extrudate | Ratio | |
|------------|--------------------------|------------------------------|
| | Saturated/total aromatic | Mono-aromatic/total aromatic |
| Non-Cat | 1.20 | 0.32 |
| Alumina | 1.35 | 0.37 |
| 5-7RM-kaol | 1.43 | 0.57 |
| 5-7RM-ben | 1.54 | 0.58 |
| 5-7RM-mon | 1.46 | 0.56 |
| 5-7RM-tal | 1.61 | 0.49 |
| Ru/HMOR | 1.97 | 0.46 |

Table 4.11 indicates the amount of asphaltene in oils, sulfur in oils, sulfur, and coke deposition on the spent catalysts. The various matrixes themselves can efficiently reduce the amount of asphaltene in the oil, especially kaolin. The matrixes charged in the extrudates have no significant impact on asphaltene reduction. However, bentonite mixed in the extrudate can provide the lowest amount of sulfur in oils at around 0.55%. The extrudate that is produced from kaolin gives sulfur in the oil of around 0.59% whereas the other extrudates show no impact on the reduction of sulfur in the oils. All extrudates do not have the impact on the reductions of sulfur and coke deposition since the reductions are contributed from the clays themselves that are used as the matrix. Furthermore, from the table, bentonite and talc show the highest effect on the reduction of coke and sulfur content among all matrixes.

Table 4.11 Percentage of asphaltene, sulfur in oils, and sulfur and coke on spent extrudates content from using matrixes extrudates composed of different matrixes

| Catalyst | %asphaltene | %sulfur in oils | %sulfur on spent catalyst | Coke deposition (g/g cat) |
|-------------------|-------------|-----------------|---------------------------|---------------------------|
| Non-Cat | 0.71 | 0.73 | | |
| α -alumina | 0.08 | 0.76 | 0.14 | 0.074 |
| kaolin | 0.08 | 0.66 | 0.25 | 0.13 |
| bentonite | 0.014 | 0.56 | 0.28 | 0.13 |
| montmorillonite | 0.01 | 0.61 | 0.42 | 0.22 |
| talc | 0.022 | 0.57 | 0.40 | 0.09 |
| 5-7RM-kaol | 0.02 | 0.59 | 0.16 | 0.13 |
| 5-7RM-ben | 0.04 | 0.55 | 0.16 | 0.1 |
| 5-7RM-mon | 0.03 | 0.73 | 0.26 | 0.17 |
| 5-7RM-tal | 0.06 | 0.65 | 0.17 | 0.09 |
| Ru/HMOR | 0.03 | 0.65 | 0.35 | 0.23 |

4.4.5 Petroleum Fractions from Using the Different Matrixes in Extrudates

Figure 4.20 shows the increase of naphtha production from the extrudates composed of different matrixes in conjunction with the decrease in all other heavier fractions. All extrudates can preserve naphtha production of the active Ru/HMOR catalyst, except the one composed of montmorillonite. The montmorillonite gives a negative impact on naphtha production. Since talc gives the highest naphtha production, even higher than the pure Ru/HMOR, it is the most suitable matrix for naphtha production. The petroleum fractions obtained from the pure clays are shown in Appendix I.

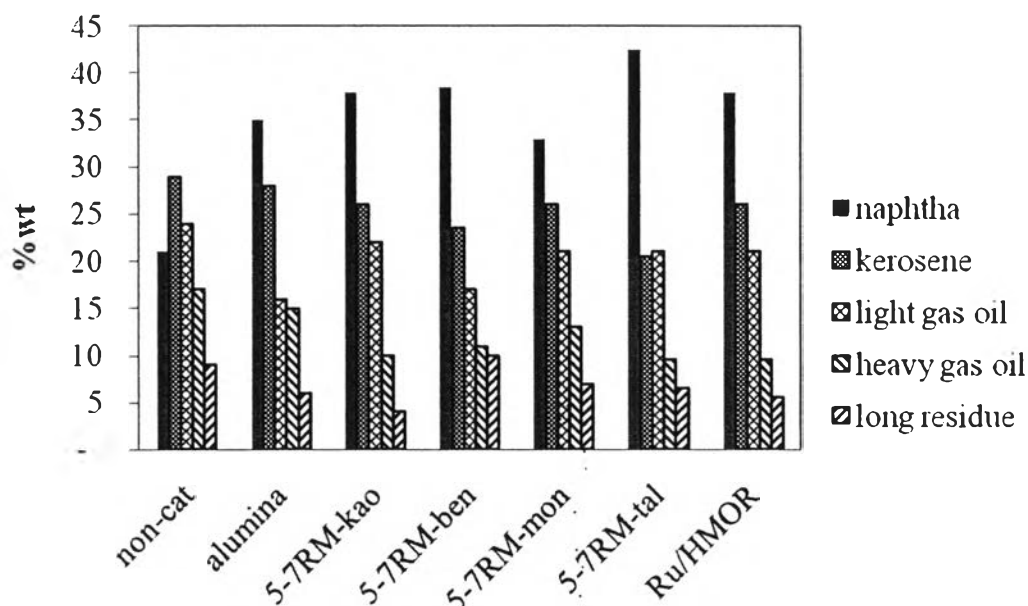


Figure 4.19 Petroleum fractions from using the extrudates composed of different matrixes.

4.4.6 Discussion: The Effect of Matrix Types

From the results, it is found that bentonite and talc can improve and preserve light olefins production of the Ru/HMOR catalyst, and all clays as matrixes can reduce the amount of asphaltene in the oils and sulfur deposition on the spent catalysts. All the matrixes have no influence on the selectivity of saturated hydrocarbons. Lastly, talc is the best matrix for production as it can improve the naphtha production of the active Ru/HMOR catalyst. The bentonite and kaolin can preserve the naphtha production whereas montmorillonite has the negative impact. Consequently, bentonite and talc are the appropriate candidates to be used as the matrixes for the light olefins and naphtha production. They may possibly be able to prevent hot spot as well as over-cracking. This phenomenon can be explained by using overall heat transfer equation. From Eq(1), the heat transfer rate is based on overall heat transfer coefficient (U), and heat transfer surface area (A), and log mean temperature difference (ΔT_{LM}). Therefore, ΔT_{LM} should be the same value for all extrudates.

$$q = UA\Delta T_{LM} \quad (1)$$

q = heat transfer rate (W)

U = overall heat transfer coefficient (W/(m²·K))

A = heat transfer surface area (m²)

ΔT_{LM} = log mean temperature difference (K)

Eq(2) indicates that overall heat transfer coefficient depends on two terms, which are heat transfer coefficient (h) and thermal resistance (R). However, heat transfer coefficient is the specific value for a fluid, which in this case is the same for all experiments.

$$\frac{1}{UA} = \sum \frac{1}{hA} + \sum R \quad (2)$$

R = Resistance(s) to heat flow (K/W)

h = Heat transfer coefficient (W/m²K)

Therefore, the heat transfer depends on only overall transfer coefficient, which is proportional to thermal resistance. Eq(3) demonstrates that thermal resistance relies on thermal conductivity (k).

$$R = \frac{x}{k \cdot A} \quad (3)$$

x = the wall thickness (m)

k = the thermal conductivity of the material (W/(m·K))

A = the total area of the heat exchanger (m²)

However, x and A values can be neglected because they should be the same for every extrudates at the same condition. Therefore, how well heat can be dissipated depends on the thermal resistance, which is inversely proportional to k . From the thermal conductivity in Table 4.12, bentonite and talc have the highest thermal conductivity among all matrixes. Consequently, the high thermal

conductivities of the two matrixes are the explanation of why they are the best matrixes for the production of light olefins and naphtha.

Table 4.12 Thermal conductivity of each component used in the extrudates

| | Ru/HMOR^a | α- alumina^b | Kaolin^c | Bentonite^d | Montmo- rillonite^f | Talc^g |
|------------------------------------|----------------------------|---|---------------------------|------------------------------|--|-------------------------|
| Thermal conductivity (w/m.K) | 0.16 | 3.1 | 1.40 | 2.00 | 0.046 | 1.90 |

^a From Jakubinek *et al.*, 2007, ^b From Perry and Green, 1997, ^c From Michot *et al.*, 2008, ^d From Tang *et al.*, 2007, ^f From Hoshi *et al.*, 1995 ^g From Gammow and Sigalas, 1988