

## CHAPTER IV

### RESULTS AND DISCUSSION

This chapter is divided into 5 parts discussing the results of studies on the effects of: (1) heating rate, (2) oxides, (3) catalyst-to-tire ratio, (4) ITQ-loaded catalysts, and (5) loaded germanium, on pyrolysis products and product distribution. The results and discussion are presented in this chapter.

#### **4.1 Effect of Heating Rate on Pyrolysis Products and Product Distribution**

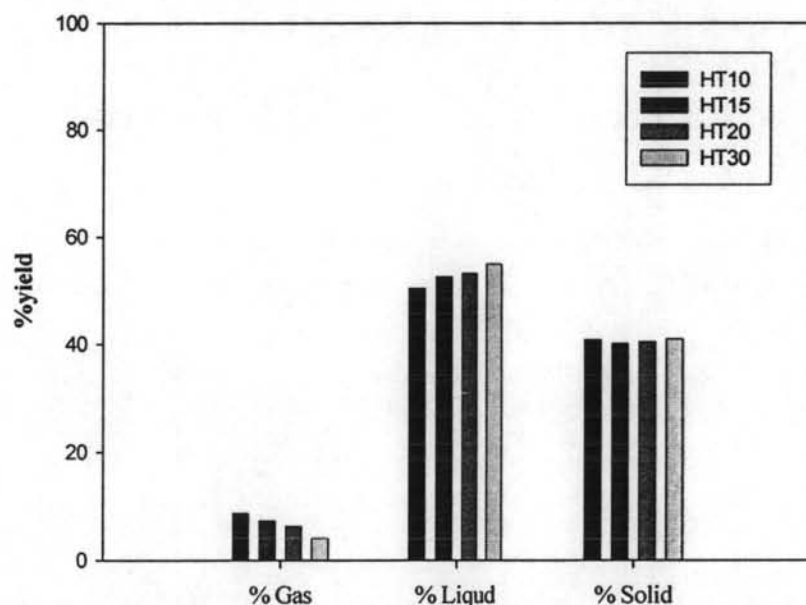
##### 4.1.1 Product Distribution

The liquid product had a brownish-yellow color, and the color was more brownish for higher heating rates. The effect of heating rate on gas, oil, and solid residue yield is shown in Figure 4.1. The gas yield ranges from 4 to 9%, the liquid yield varies between 50 and 55%, and the solid residue ranges between 40 and 41%. The obtained solid pyrolysis residue was a piece of equal dimensions and shape as in the original tire portion. The gas yield decreased along with the increase in heating rate while the liquid yield increased. This is because heating rate increases the production rate of free radicals, then the active free radicals can reaccumulate to larger hydrocarbon molecules leading to higher liquid yield. The gas phase presented the highest percentage when the heating rate was 10°C/min, while the liquid phase presented the highest percentage when the heating rate was 30°C/min. Moreover, the heating rate had no significant effect on the solid yield, therefore, the obtained solid residue was mainly carbon black.

##### 4.1.2 Components in Gas Product

A gas sample from each experiment was collected in one Tedlar bag during the reaction, and was analyzed by a gas chromatography. The components of the gas product from the pyrolysis of tires at various heating rates (10, 15, and 30°C/min) are shown in Figure 4.2. The pyrolysis gas was composed of methane, ethylene, ethane, propylene, propane, C<sub>4</sub>-, C<sub>5</sub>-, C<sub>6</sub>-, C<sub>7</sub>-, and C<sub>8</sub>- hydrocarbons. Methane was produced in the highest amount. High amounts of ethane, C<sub>4</sub>, and C<sub>5</sub>

were also produced, but not as much as that of methane. Methane can be generated by both direct breakdown of the polymer, and secondary reactions including char reduction, tar cracking, shift reaction, etc. The volume fractions of C<sub>4</sub> and C<sub>5</sub> were comparable. Only a trace amount of C<sub>7</sub> and C<sub>8</sub> was produced. The amounts of C<sub>4</sub> and C<sub>4</sub><sup>+</sup> may be produced from the depolymerization of styrene-butadiene rubber, which normally is the main component of automotive tires (Laresgoiti *et al.*, 2000). No significant differences in propylene, propane, and C<sub>6</sub>-C<sub>8</sub> were observed for waste tire pyrolysis at various heating rates. On the other hand, methane increases with increasing heating rate. Moreover, heavy hydrocarbons were produced in higher amounts with higher heating rates.



**Figure 4.1** Effect of heating rate on gas, oil, and solid residue yield.

#### 4.1.3 Carbon Number Range in Liquid Products

The evolved effluents from the pyrolysis experiments were condensed in a series of ice-NaCl condensers before being analyzed by a SIMDIST gas chromatograph. The carbon number range of the pyrolyzed liquid is shown in Figure 4.3. For thermal degradation, the liquid products are distributed over a wide range of carbon numbers (C<sub>6</sub> to C<sub>49</sub>) equivalent to the boiling point range of 68 to

560°C. When the heating rate was higher, the liquid was produced in narrower carbon distribution numbers and, the peak tended to have a slight shift toward the higher carbon numbers.

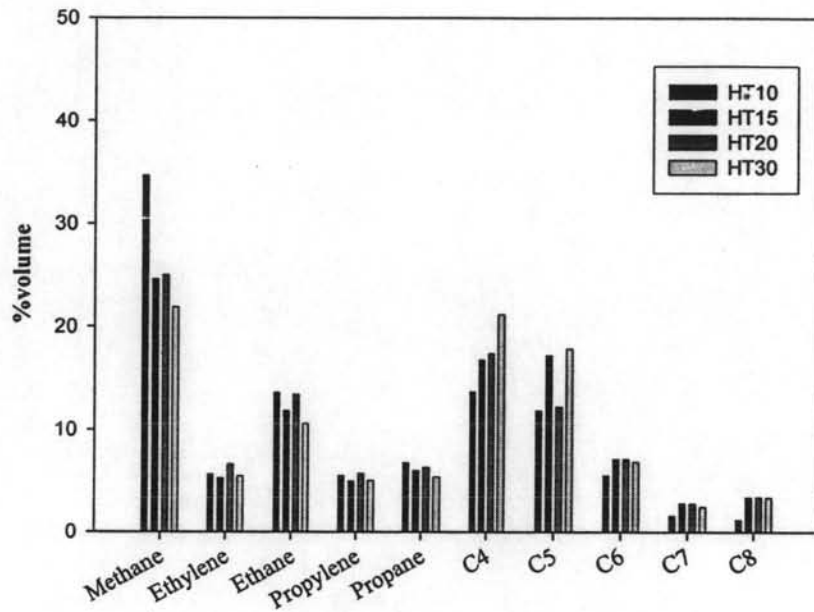


Figure 4.2 Effect of heating rate on gas composition.

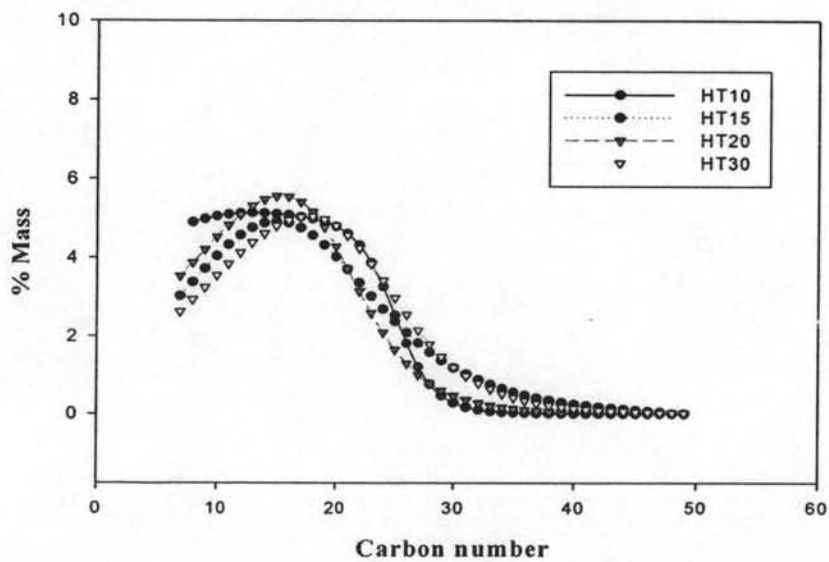
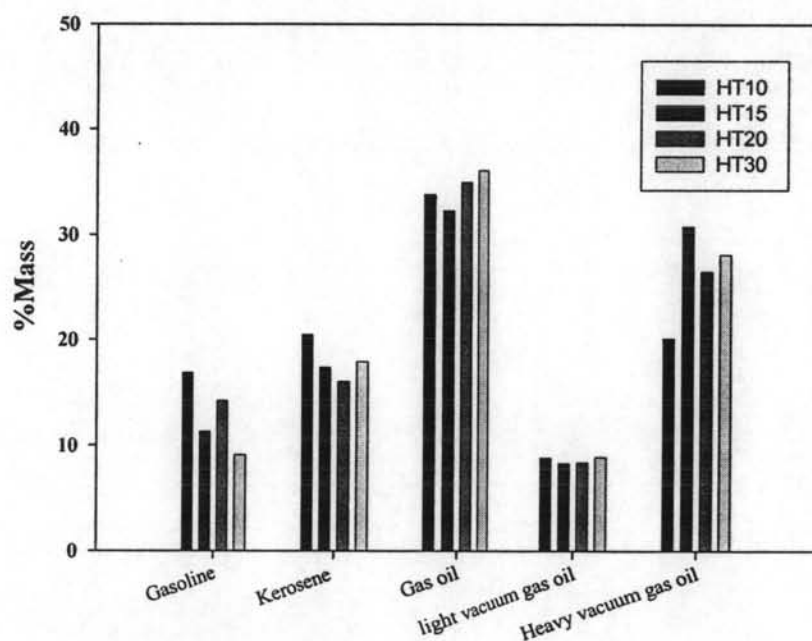


Figure 4.3 Effect of heating rate on carbon number distribution in oil products.

#### 4.1.4 Oil Fractions in Liquid Product

The oil fractions from simulated distillation GC are shown in Figure 4.4. Each fraction was classified according to its boiling point range. They are gasoline (<149°C), kerosene (149-232°C), gas oil or diesel (232-343°C), light vacuum gas oil (343-371°C), and heavy vacuum gas oil (>371°C). The amounts of gasoline and kerosene decrease with increasing heating rate. On the other hand, the amount of gas oil and heavy vacuum gas oil tend to increase with increasing heating rate. No significant difference in amount of light vacuum gas oil were observed for waste tire pyrolysis at various heating rates. Moreover, the amount of heavy vacuum gas oil increases with increasing the heating rate. This is because heavy vacuum gas oil was not cracked to gasoline and kerosene when the heating rate increased.



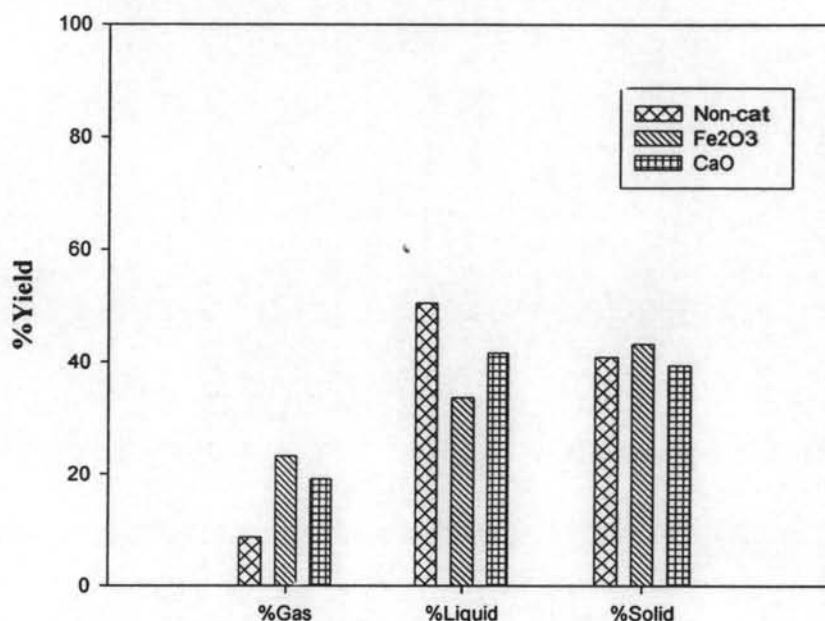
**Figure 4.4** Effect of heating rate on oil fractions.

## 4.2 Effect of Oxides on Pyrolysis Products and Product Distribution

### 4.2.1 Product Distribution

The effects of two oxides on gas, oil, and solid residue yield are shown in Figure 4.5. The gas yield ranges from 19 to 23%, the liquid yield varies

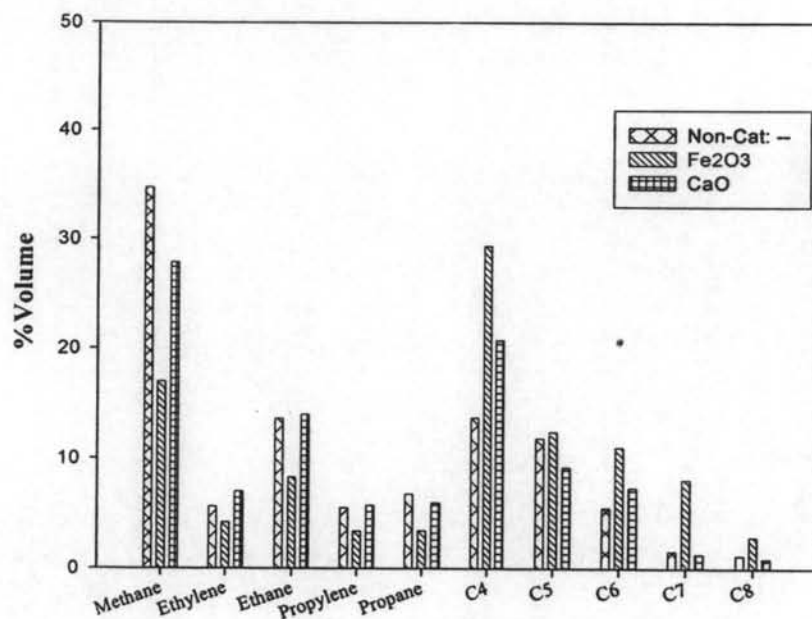
between 30 and 42%, and solid residue ranges between 39 and 44%. Both of oxide catalysts, iron oxide and calcium oxide provided the higher gas yield while lower liquid yield as compared to the non-catalytic case. No significant difference in the solid yield was observed with loading both of oxide catalysts.



**Figure 4.5** Effect of oxides on gas, oil, and solid residue yield.

#### 4.2.2 Components in Gas Product

The components of the gas product from the pyrolysis of tires using metal oxides, Fe<sub>2</sub>O<sub>3</sub> and CaO, are shown in Figure 4.6. High amounts of methane and C<sub>4</sub> are produced. The Fe<sub>2</sub>O<sub>3</sub> catalyst decreases the amounts of methane, ethylene, propylene, and propane while heavy hydrocarbons increase. Moreover, CaO catalyst provided the lower amount of methane, however the higher amount of ethylene, ethane, propane, and C<sub>4</sub> as compared to the non-catalytic case. There is no significant difference in the amount of propylene, C<sub>7</sub>, and C<sub>8</sub> obtained from using CaO and from the non-catalytic case.



**Figure 4.6** Effect of oxides on gas composition.

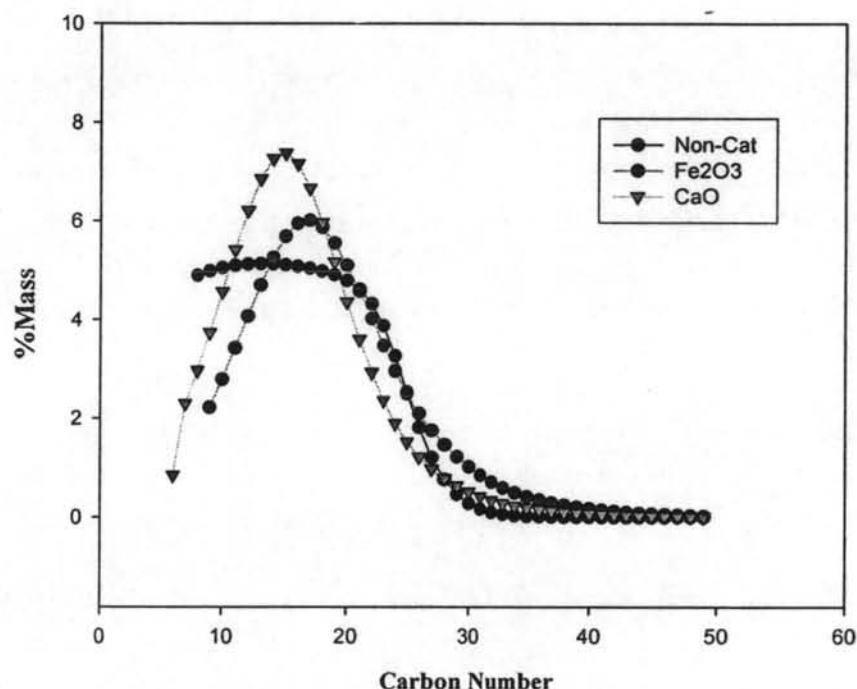
#### 4.2.3 Carbon Number Range in Liquid Products

The carbon number distribution of pyrolysis liquids is shown in Figure 4.7. It can be seen that both oxides as potential impurities in many catalysts have a positive influence on product distribution in which both give narrower carbon number distribution in the range of gasoline to gas oil. CaO gave the narrowest carbon number distribution, therefore, it seems to have more impact and more cracking activity than Fe<sub>2</sub>O<sub>3</sub>.

#### 4.2.4 Oil Fractions in Liquid Product

The oil fractions from simulated distillation are composed of gasoline (<149°C), kerosene (149-232°C), gas oil or diesel (232-343°C), heavy vacuum gas oil (343-371°C), and heavy vacuum gas oil (>371°C), and are shown in Figure 4.8. Each fraction was classified according to its boiling point range. In the presence of oxides, Fe<sub>2</sub>O<sub>3</sub> tends to decrease the amount of gasoline and kerosene, but increase the amount of gas oil, light vacuum gas oil, and heavy vacuum gas oil as compared to those obtained from non-catalytic case. The lower amounts of gasoline and kerosene

were obtained from  $\text{Fe}_2\text{O}_3$  because  $\text{Fe}_2\text{O}_3$  provided lower cracking activity, so the amount of gas oil and heavy vacuum gas oil cannot be cracked to gasoline and kerosene. On the other hand,  $\text{CaO}$  gave lower amount of heavy vacuum gas oil and the higher amount of kerosene and gas oil. The higher amounts of kerosene and gas oil were obtained from  $\text{CaO}$  because they were potential products, which can be formed from cracking of heavy vacuum gas oil. The major fraction is gas oil (22-43%volume).

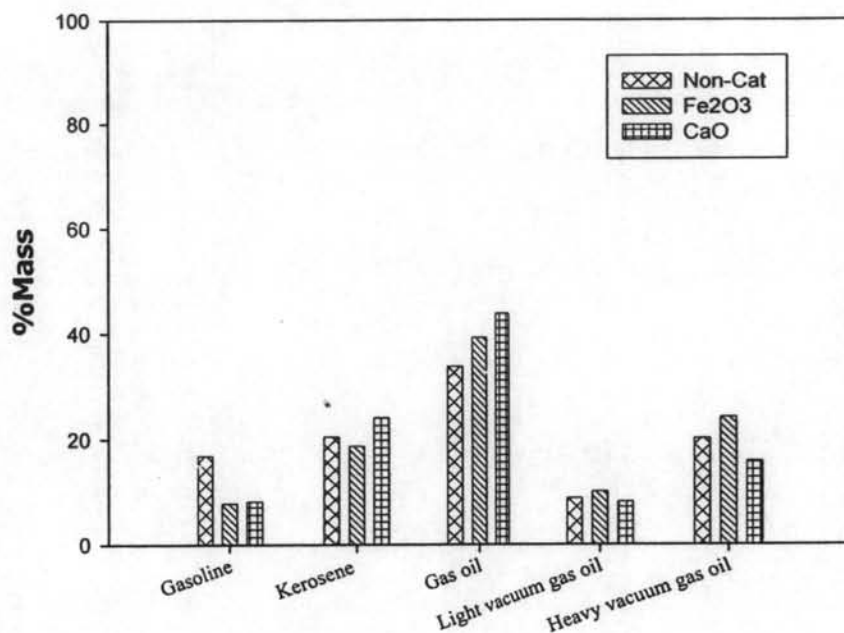


**Figure 4.7** Effect of oxides on carbon number distribution.

### 4.3 Effect of Catalysts on Pyrolysis Products and Product Distribution

#### 4.3.1 Zeolite Synthesis

A zeolite can be synthesized via sol-gel process. Microwave and hydrothermal techniques were used for this process. The synthesized ITQ zeolites were characterized by X-ray diffraction, TEM, and SEM.



**Figure 4.8** Effect of oxides on oil fractions.

#### 4.3.1.1 X-ray Diffraction Patterns

In ITQ-21 synthesis, many parameters were studied : heating method; hydrolyzing time; aging time; and, crystallization time. The suitable conditions can be summarized in the following table.

**Table 4.1** Conditions for successful synthesis of ITQ-21 catalyst

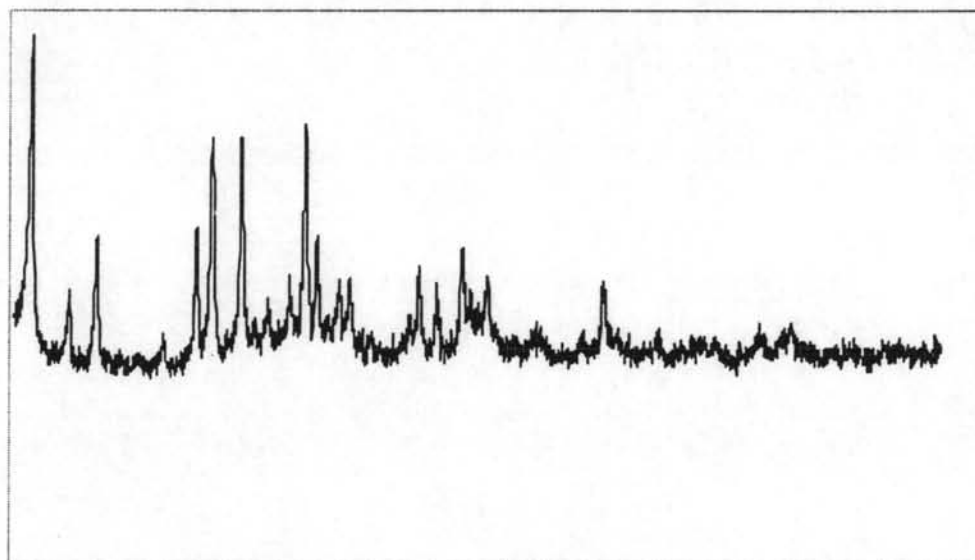
Hydrolyzing time	Aging time	Heating method	Crystallization time
3 days	1 day	hydrothermal	3 days

From varying the conditions of ITQ-21 synthesis, it can be stated that the most important factor was the hydrolyzing time of the precursors. A shorter period might not be enough for the diffusion and formation of a germanium atom in the framework of zeolite.



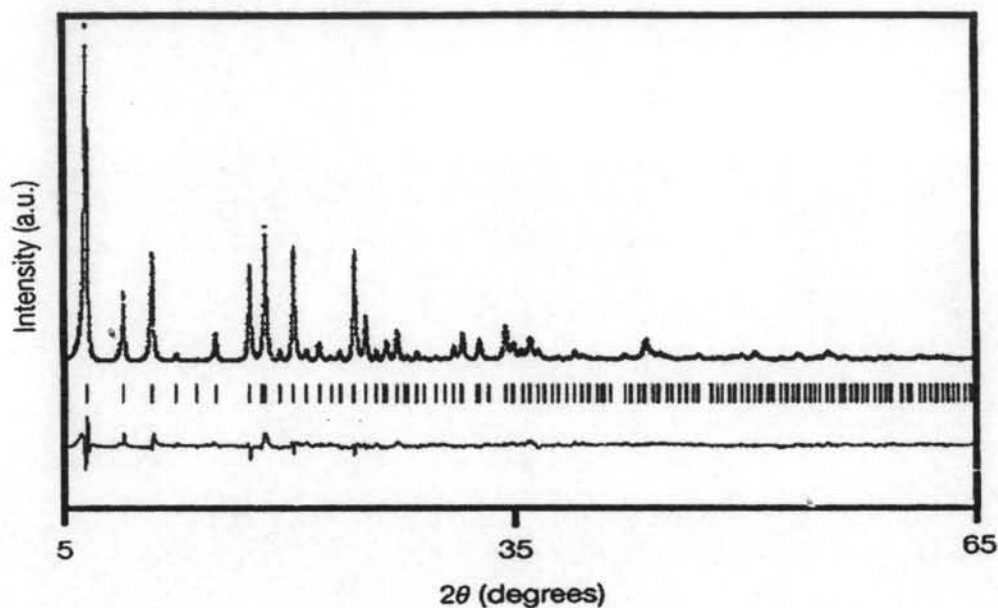
The samples can be identified by XRD. The diffraction data, which were collected at 0.02 ( $2\theta$ )/step in the  $2\theta$  range of 5.00 to 70.00 with a scan speed of 2 s/step, are shown in Figure 4.9. The XRD pattern of ITQ-21 from the literature (Corma *et al.*, 2002) is shown in Figure 4.10.

In the synthesis of ITQ-24 zeolite, hexamethonium dihydroxide was used as an organic structure-directing agent in combination with germanium. The gel mixture was aged for 3 and 5 days before undergoing hydrothermal treatment at 175°C in a microwave for 5 days. Then, the samples were washed with distilled water, dried at 100°C, and finally calcined to 540°C at a ramping rate of 1°C/min, and then held at the final temperature for 3 hours.



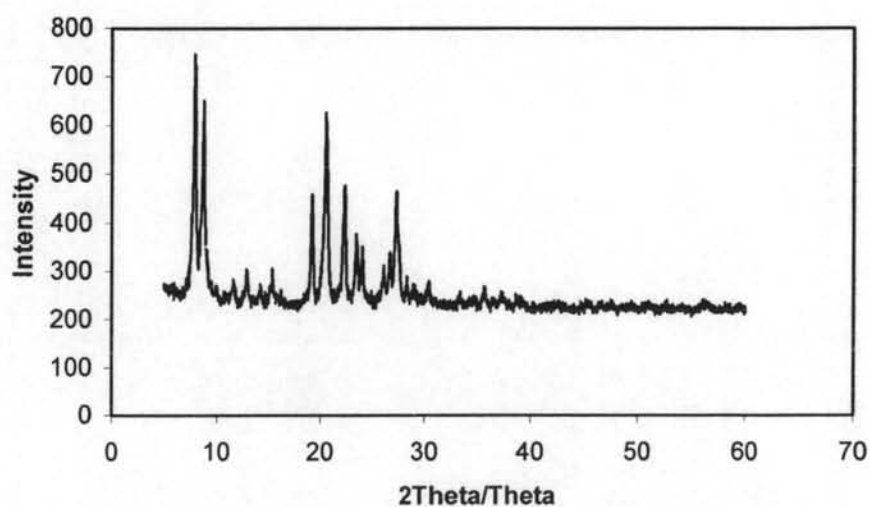
2 theta (degree)

**Figure 4.9** XRD patterns of ITQ-21 from the synthesis.



**Figure 4.10** XRD patterns of ITQ-21 (Corma *et al.*, 2002).

The XRD patterns of the synthesized ITQ-24 zeolite obtained from crystallization in microwave at 175°C for 5 days are shown in Figure 4.11, and the XRD pattern of ITQ-24 from the literature (Corma *et al.*, 2002) is shown in Figure 4.12.



**Figure 4.11** The XRD pattern of synthesized ITQ-24.

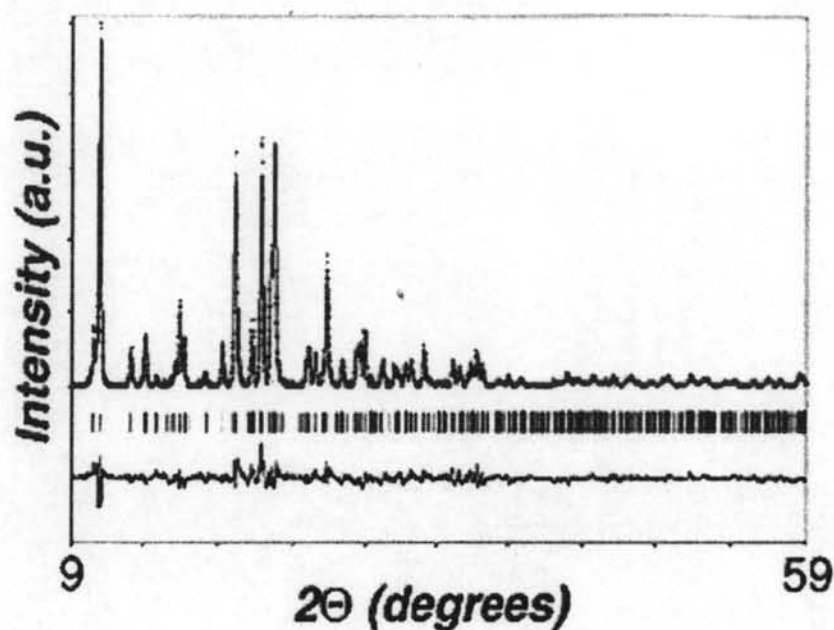


Figure 4.12 XRD spectra of ITQ-24 (Corma *et al.*, 2002).

#### 4.3.1.2 Scanning Electron Micrograph

The SEM micrographs were employed in order to observe the morphology in microscale of the prepared catalysts. The SEM image of the synthesized ITQ-21 zeolite using the hydrothermal method is shown in Figure 4.13, and the SEM images of synthesized ITQ-24 zeolite and commercial mordenite are shown in Figures 4.14 and 4.15, respectively.

#### 4.3.1.3 Transmission Electron Micrograph

The ITQ-21 zeolite catalyst can be clearly observed in TEM micrograph as shown in Figure 4.16. The result can be confirmed that the ITQ-21 catalyst was formed with very small crystals in nano-scales.

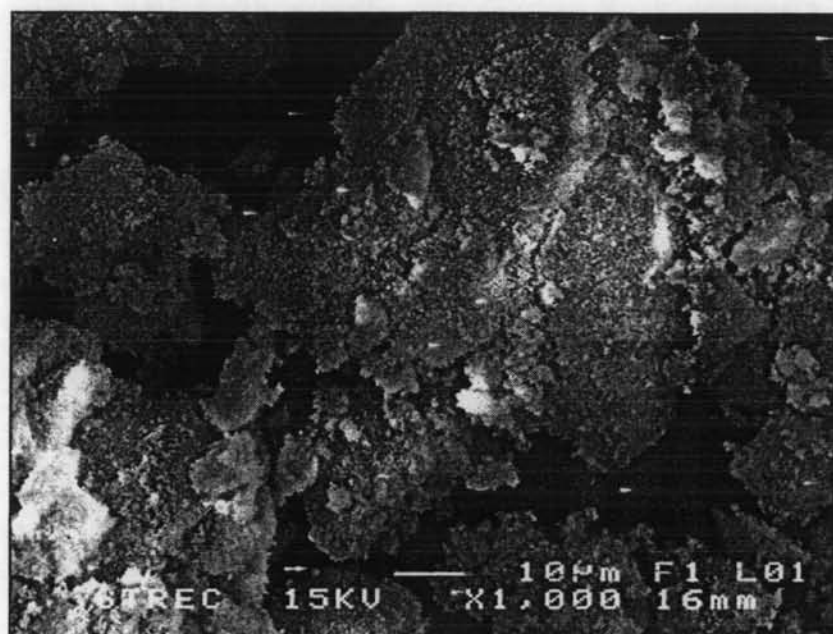


Figure 4.13 SEM image of ITQ-21 from hydrothermal synthesis.

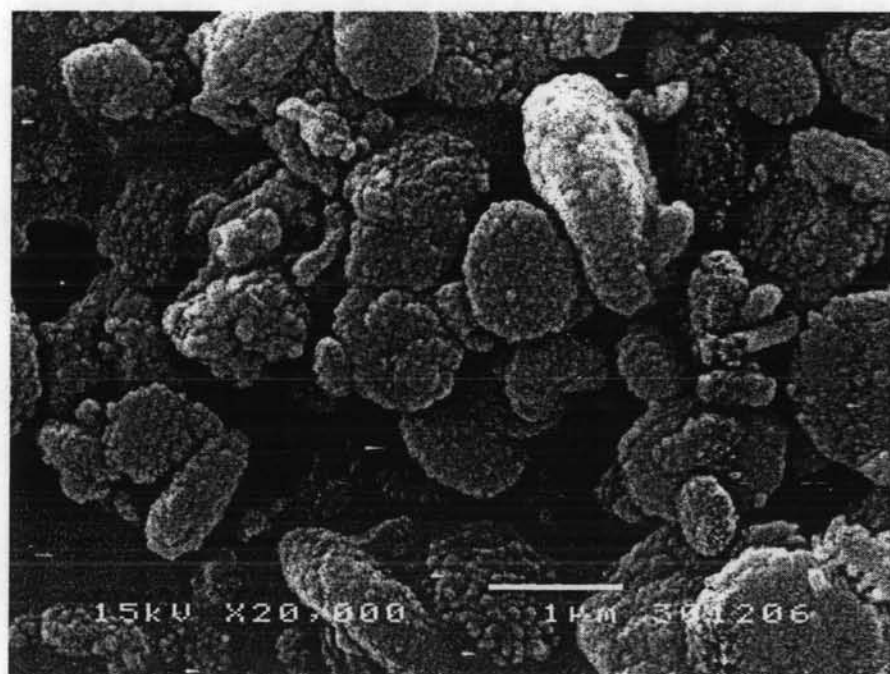


Figure 4.14 SEM image of ITQ-24 zeolite.

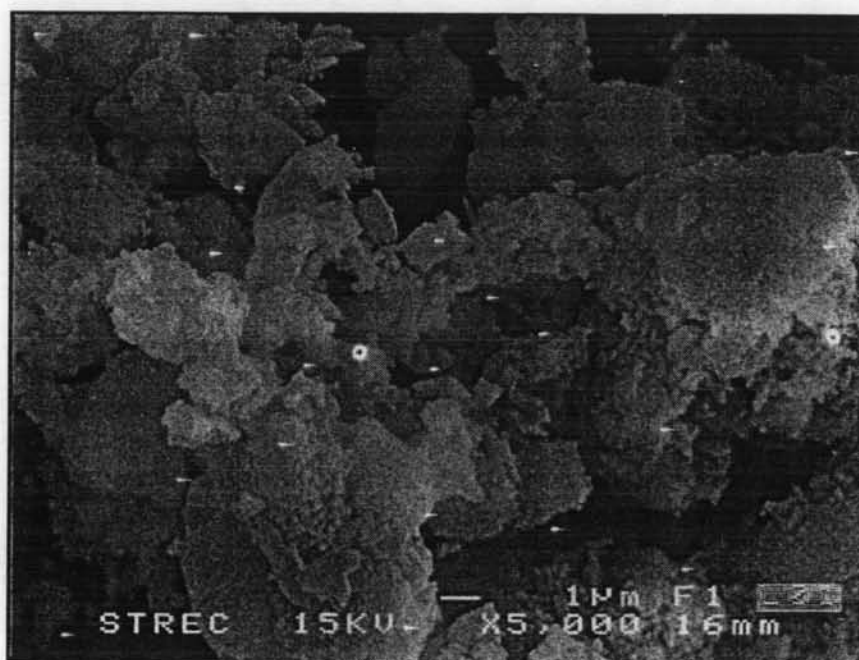


Figure 4.15 SEM image of commercial mordenite zeolite.

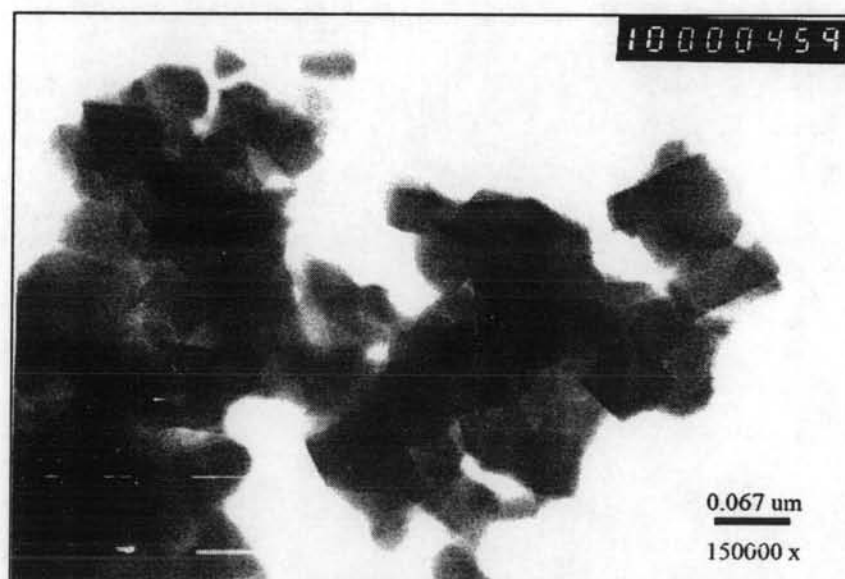


Figure 4.16 TEM image of synthesized ITQ-21.

#### 4.3.1.4 Specific Surface Area

The surface area of catalysts was measured by using BET technique. The synthesized ITQ-24 zeolite has a surface area more than the synthesized ITQ-21 zeolite in as shown in Table 4.2. On the other hand, the pore size diameter of ITQ-24 was smaller than ITQ-21. The BET surface area and pore volume decrease with increasing percentage of germanium loaded on mordenite while increases the pore size in Table 4.3. However, when the percentage of germanium is increased to 5%, the surface area, pore volume, and pore size are increased.

**Table 4.2** BET surface area of ITQ zeolites

Catalyst	Surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Pore size (Å)
ITQ-21	76.77	1.81x10 <sup>-2</sup>	6.304
ITQ-24	310.17	2.79x10 <sup>-1</sup>	5.673

**Table 4.3** BET surface areas of Ge-loaded mordenite zeolites with various percentages of Ge

Catalyst	%Ge	Surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Pore size (Å)
Mordenite	0	429.60	3.17x10 <sup>-1</sup>	7.611
	0.5	404.74	3.05x10 <sup>-1</sup>	6.263
	1	400.56	2.98x10 <sup>-1</sup>	6.485
	3	396.21	2.93x10 <sup>-1</sup>	6.793
	5	470.53	3.28x10 <sup>-1</sup>	8.259

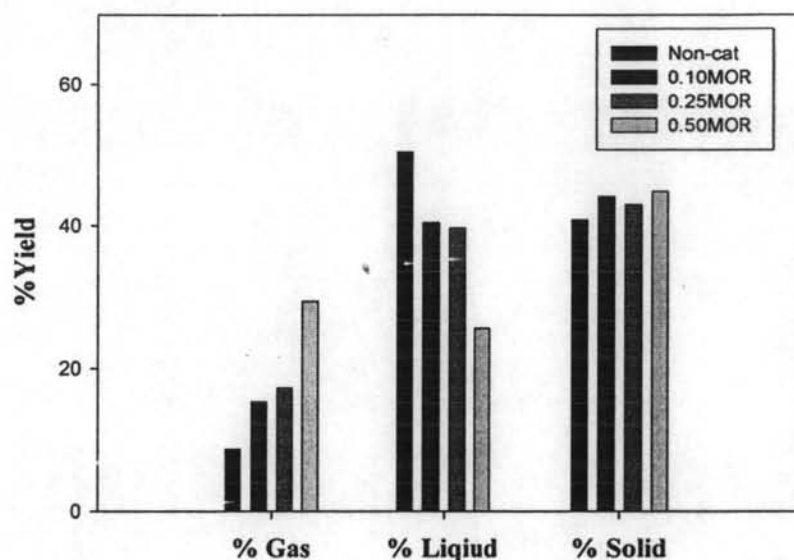
### 4.3.2 Effect of Catalyst-to-tire Ratio on Pyrolysis Products

#### 4.3.2.1 *Product Distribution*

In this experiment, the influence of catalyst-to-tire ratio was examined. Mordenite was inspected using the catalyst-to-tire ratio of 0.10, 0.25, and 0.50. The catalyst was calcined at 500°C with a ramping rate 10°C/min and, then, held for 3 hours. The total weight of the sample was fixed at 1.00 gram. The results show that the influence of the amount of catalysts was to increase in the gas yield with a consequent reduction of the yield of liquid. The yields of products from the pyrolysis of tire at various catalyst-to-tire ratios are shown in Figure 4.17. The yields of oil decrease from 50-25 %. There is a corresponding increase in the yield of gas from 8-30%. However, the amount of the catalyst-to-tire ratio has no significant effect on the solid yield. The obtained solid residue was mainly carbon black.

#### 4.3.2.2 *Components of the Gas Products*

Figure 4.18 shows the components of gas produced from catalytic degradation with various ratios of catalyst-to-tire from 0.10, 0.25, and 0.50. The individual gases showed somewhat different trends in relation to increasing catalyst-to-tire ratio. Methane, ethane, and C<sub>5</sub> showed a steady decrease with increasing ratio while ethylene, propylene, propane, and C<sub>6</sub> increase. For all catalyst-to-tire ratio no significant difference in C<sub>7</sub> and C<sub>8</sub> was observed with increasing the catalyst-to-tire ratio. C<sub>7</sub> and C<sub>8</sub> are exhibited as a trace. Minor amount of C<sub>7</sub> and C<sub>8</sub> in the gas composition were limited via the thermodynamics and the equilibrium of liquid-vapor system. Normally, C<sub>7</sub> and C<sub>8</sub> must be present in liquid phase under room temperature. However, C<sub>7</sub> and C<sub>8</sub> have a low vapor pressure, resulting in the partial presence in gas phase.



**Figure 4.17** Effect of catalyst-to-tire ratio on gas, oil, and solid yield.

#### 4.3.2.3 Carbon Number Range in Liquid Products

Carbon number ranges of tire pyrolysis oil obtained at various catalyst-to-tire ratios are illustrated in Figure 4.19. The carbon number range of oil from thermal pyrolysis is shown to have a wider distribution while, with the addition of catalysts, the range of carbon number shifts to become narrower. The peak of the distribution curves shifts from the right to the left until the catalyst-to-tire ratio changes to 0.50, indicating that higher a amount of lighter hydrocarbons are produced.

#### 4.3.2.4 Oil Fractions in Liquid Products

Figure 4.20 shows the influence of catalyst-to-tire ratio. The catalyst-to-tire ratios have an impact on every fraction. Indeed, the major fraction is gas oil, which slightly decreases with increasing amounts of catalysts. The amounts of gasoline and kerosene are not significantly different using between 0.10 and 0.25 of catalyst-to-tire ratio. However, the amounts of gasoline and kerosene increase with the ratio increase to 0.50. This is because the amounts of gasoline and kerosene would be obtained from catalytic cracking of heavy vacuum gas oil. The higher amount of catalyst, the higher acid sites were provided, resulting in the higher cracking activity.



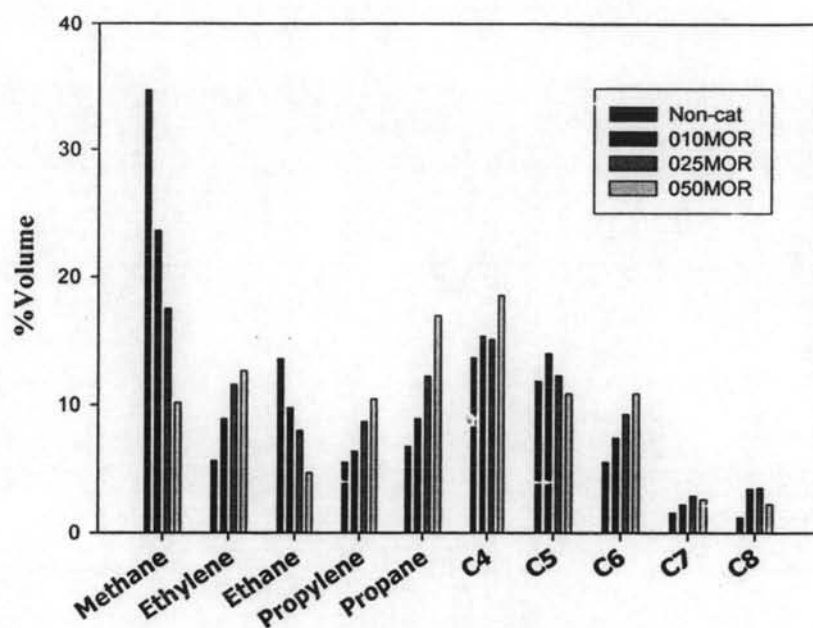


Figure 4.18 Effect of catalyst-to-tire ratio on gas composition of pyrolysis gas.

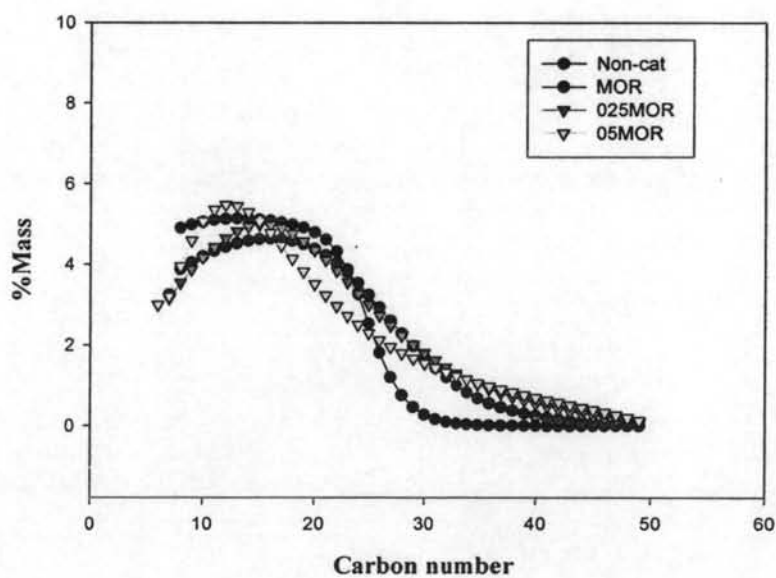
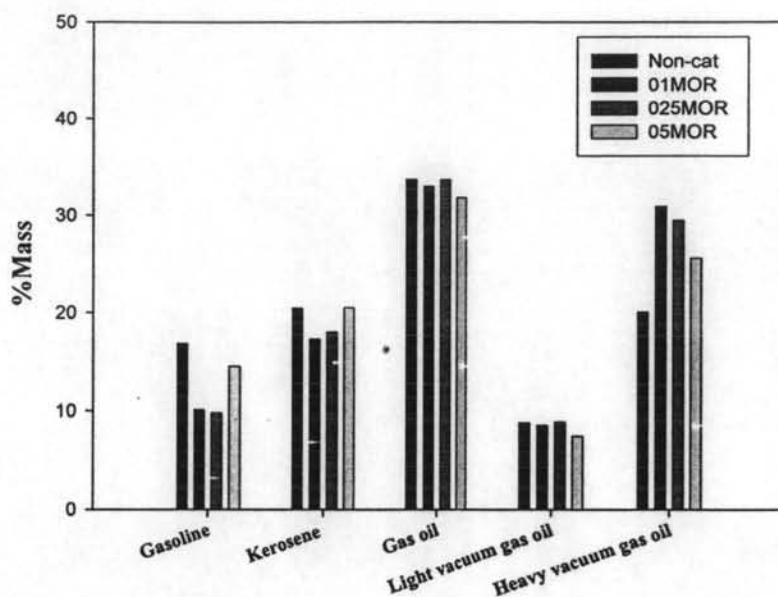


Figure 4.19 Effect of catalyst-to-tire ratio on carbon number distribution in oil products.

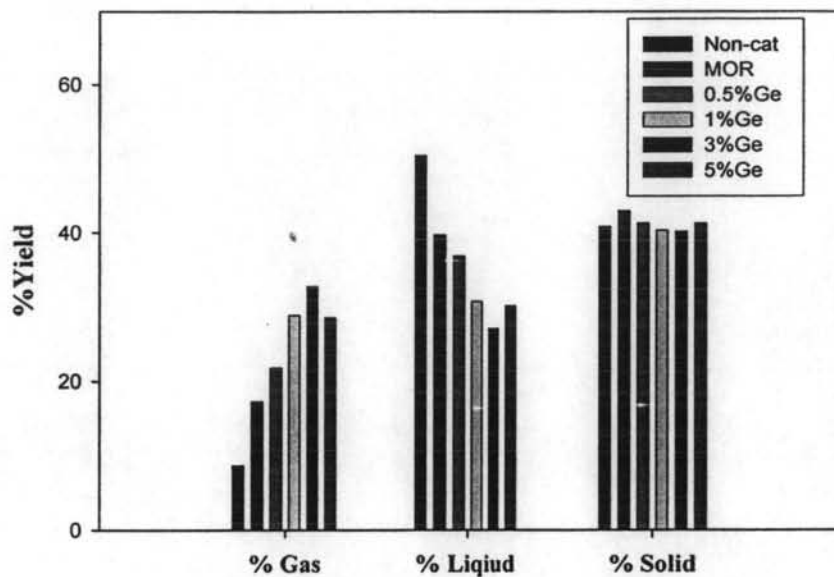


**Figure 4.20** Effect of catalyst-to-tire ratio on oil fractions.

### 4.3.3 Effect of Ge on Pyrolysis Products

#### 4.3.3.1 *Product Distribution*

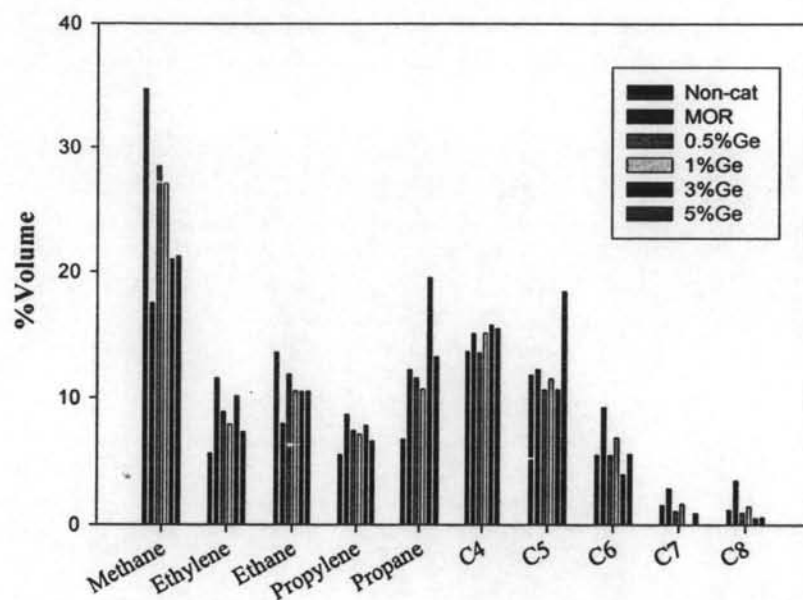
A catalyst-to-tire ratio of 0.25 was selected for studying the effect of loaded germanium on waste tire pyrolysis in the contact mode. The total weight of sample was 1.00 gram. The obtained conversion in the catalytic pyrolysis of waste tires can be considered complete. The liquid obtained in tire-catalytic pyrolysis is usually termed as oil. It was a dark-brown colored product which resembled petroleum fractions. The obtained solids from pyrolysis were pieces of equal dimensions and shape as those of the original tire portion. The color of the catalysts after pyrolysis was a dark gray color, as demonstrated by Sassi *et al.* 1999. The product yields from the pyrolysis of tire with various percentages of germanium are shown in Figure 4.21. The gas yield increases with an increase in the percentage of germanium up to 3%Ge, and then it markedly decreases. On the other hand, the liquid yield decreases and after that slightly increases.



**Figure 4.21** Effect of percentage of germanium loaded onto H-mordenite on gas, oil, and solid yield.

#### 4.3.3.2 Components of the Gas Product

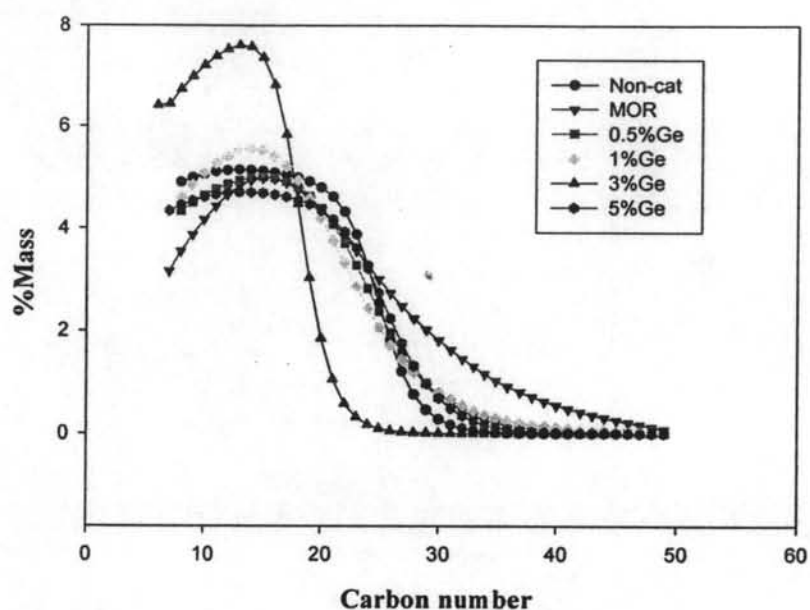
The gaseous products obtained from the pyrolysis of the waste tire using a mordenite catalyst at various percentages of germanium are shown in Figure 4.22. When the amount of loaded germanium was increased, the subsequent decrease in lighter hydrocarbons (methane to propane) and the increase in the heavier hydrocarbons (propane to  $C_8$ ) were observed. At 3% Ge, where the maximum gas yield and the maximum liquid yield occurred, propane and  $C_5$  hydrocarbons were produced in markedly high amounts as compared with other percentages.



**Figure 4.22** Effect of percentage of germanium loaded onto H-mordenite on gas composition.

#### 4.3.3.3 Carbon Number Range in Liquid Products

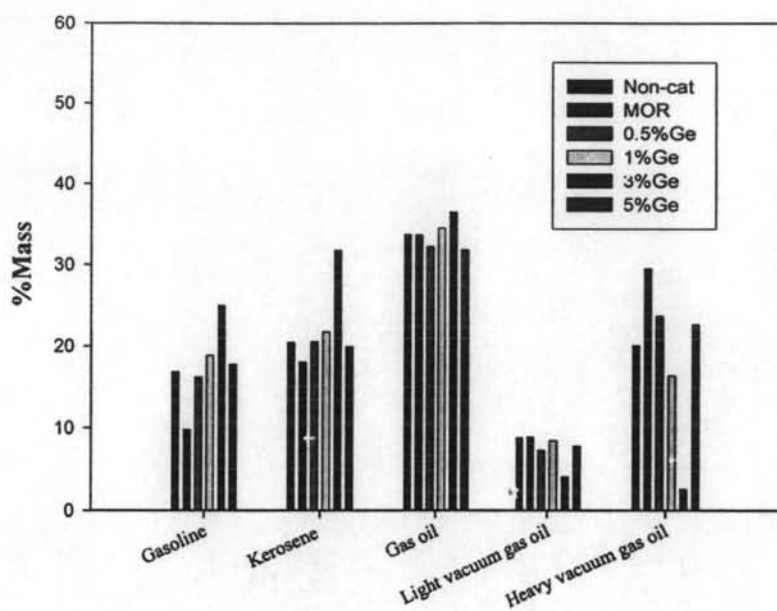
The liquid products from the pyrolysis of the tire obtained from using a mordenite catalyst with various percentages of loaded germanium as catalysts are shown in Figure 4.23. The distribution of carbon number shifts to the lighter hydrocarbons, and the change tends to increase with the increasing percentage of germanium. The peaks of distribution curves shift from the right to the left until the percentage of germanium reaches 3%Ge, indicating that the highest amount of lighter hydrocarbons are produced with the percentage of germanium increasing to 3%Ge. However, when the percentage of germanium is higher than 3%Ge, the curve shifts backward to higher carbon numbers, meaning that heavier hydrocarbons are reproduced. Hence, the optimum percentage of germanium to produce the highest amount of valuable lighter products is 3%Ge.



**Figure 4.23** Effect of percentage of germanium loaded onto mordenite on carbon number distribution in oil products.

#### 4.3.3.4 Oil Fractions in Liquid Products

Figure 4.24 shows the distribution of liquid products from pyrolysis of waste tire at various percentages of germanium. The major fraction is the gas oil (35-40%). Gasoline and kerosene increase with an increasing percentage of germanium. However, when the percentage of germanium is higher than 3%Ge, gasoline and kerosene start to decrease. The amount of gasoline and kerosene increase with the increasing amount of Ge because the non-framework Ge possibly acts as metal sites enhancing the dehydrogenation reaction, resulting in lighter hydrocarbon products. Therefore, alkanes could be converted to alkenes by dehydrogenation reactions. Alkenes are easier to form carbenium ions on acid sites, and then the carbenium ions are cracked by  $\beta$ -scission to produce lighter hydrocarbon products leading to the higher amounts of gasoline and kerosene.

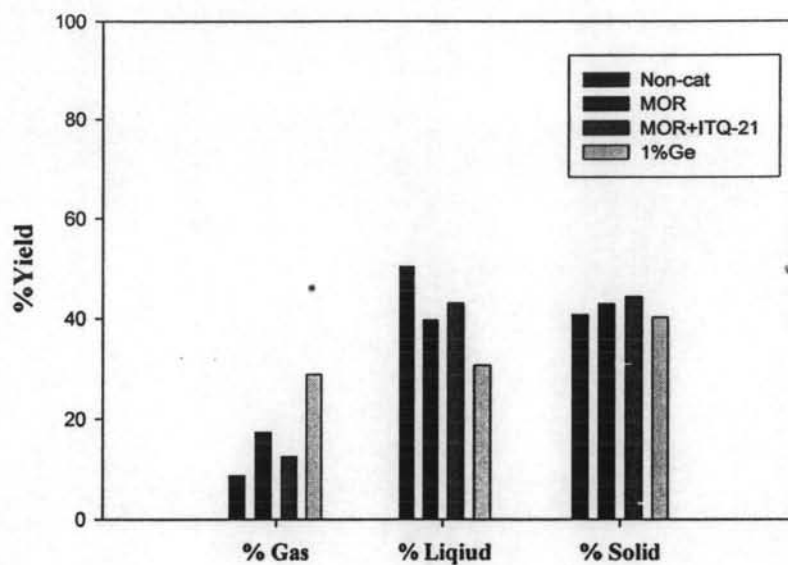


**Figure 4.24** Effect of percentage of germanium loaded onto H-mordenite on oil fractions.

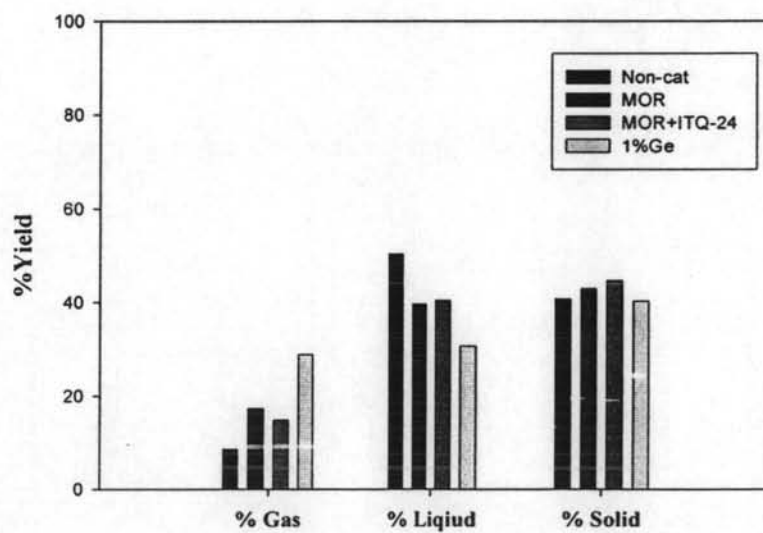
#### 4.3.4 Effect of ITQ-loaded Catalysts on Pyrolysis Products

##### 4.3.4.1 Product Distribution

A catalyst-to-tire ratio of 0.25 was selected for studying the effect of ITQ loading on pyrolysis products in the contact mode. The total weight of sample was 1.00 gram. The presence of catalysts served to reduce the oil yield and increase the gas yield. Figure 4.25 shows the comparison of three catalysts on product yield. The ITQ-21 loaded mordenite provided lower gas yield and higher liquid yield as compared to mordenite. The effect of ITQ-24 loaded mordenite on product yields is shown in Figure 4.26. The ITQ-24 loaded mordenite gave lower gas yield and higher liquid yields compared to mordenite. Moreover, when Ge inside and outside framework are compared, the results showed that non-framework Ge gave higher gas yield but lower liquid yield than Ge in the framework. This is because non-framework Ge might act as metal sites enhancing dehydrogenation reactions.



**Figure 4.25** Effect of ITQ-21 and 1%Ge loaded into H-mordenite on gas, oil, and solid yield.



**Figure 4.26** Effect of ITQ-24 and 1%Ge loaded into H-mordenite on gas, oil, and solid yield.

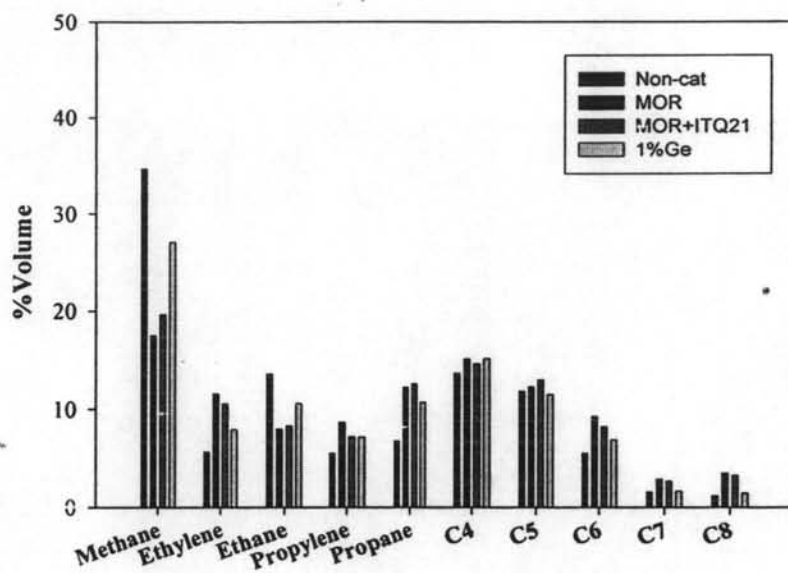
#### 4.3.4.2 Components of the Gas Product

The gas composition of the derived gases from the catalytic pyrolysis of tire and in relation to the type of catalysts are showed in the Figures 4.27 to 4.28. The gas compositions, when the catalyst was loaded, showed that the main gases from pyrolysis were methane, propane, C<sub>4</sub>, and C<sub>5</sub>. Other gases present were ethylene, ethane, propylene, C<sub>6</sub>, C<sub>7</sub>, and C<sub>8</sub>. The individual gases gave somewhat different trends in relation to type of catalyst. The mordenite loaded with ITQ-21 catalyst showed some similarities with mordenite catalyst in that the same yield of ethylene, ethane, propane, C<sub>4</sub>, C<sub>5</sub>, C<sub>6</sub>, C<sub>7</sub>, and C<sub>8</sub>. The yield of methane was much higher when using mordenite loaded with 1%Ge. Ethylene and propane production of 1%Ge were significantly more whilst ethane yield was significantly less than ITQ-21 loaded mordenite. For the ITQ-24 loaded mordenite catalyst are shown in Figure 4.28. The yields of C<sub>4</sub>-C<sub>8</sub> had no significant different trends in three catalysts. Ethane production of 1%Ge was more whilst ethylene and propylene yields were less than ITQ-24 loaded mordenite catalyst. Propane yield was much higher when using mordenite loaded with ITQ-24 as opposed to the mordenite loaded with 1%Ge catalyst. Propane yield was nearly 4% more than the yield of mordenite loaded with 1%Ge.

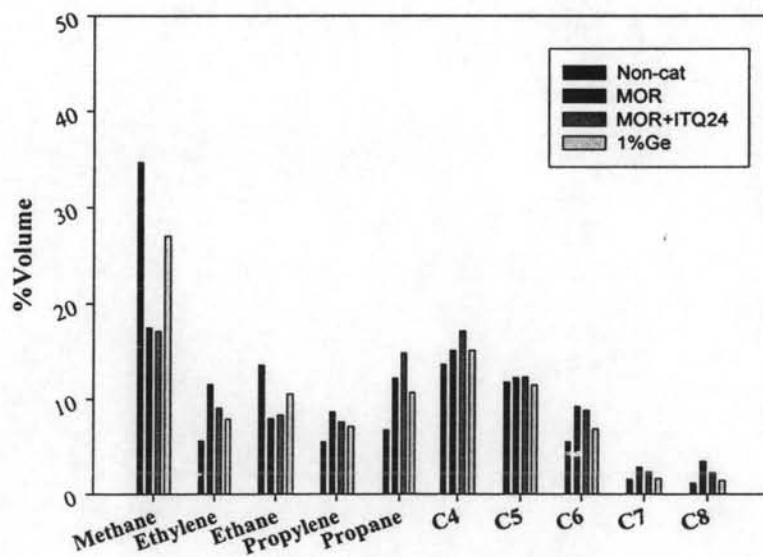
#### 4.3.4.3 Carbon Number Range in Liquid Products

The liquid products from the pyrolysis of the tire by using H-MOR, ITQ-loaded, and 1%Ge-loaded catalysts are shown in Figures 4.29 and 4.30. The distribution of carbon numbers shifts to the lighter hydrocarbons when using 1%Ge-loading. ITQ-24-loaded catalyst produced higher carbon number more than H-MOR and 1%Ge-loaded. The ITQ-24-loaded catalyst produced higher hydrocarbons as similar to H-MOR. On the other hand, the ITQ-24-loaded catalyst produced the lowest lighter carbon number products.

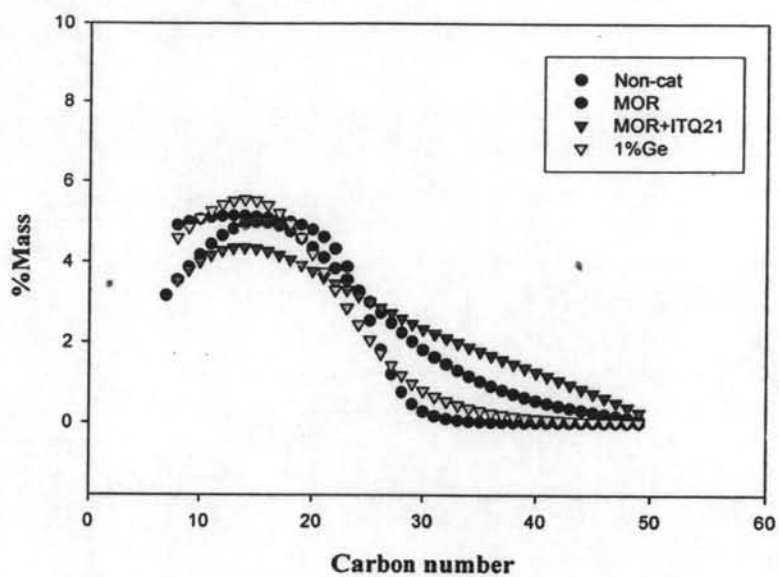




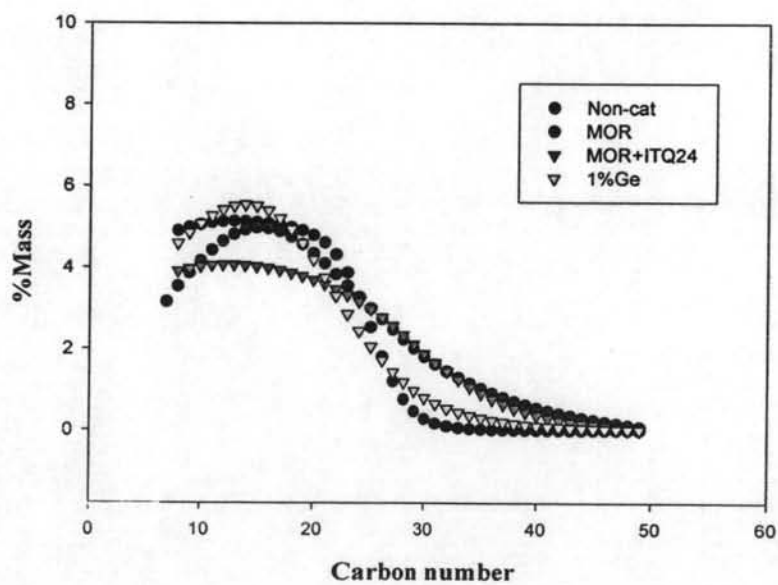
**Figure 4.27** Effect of ITQ-21 and 1%Ge loaded into H-mordenite on gas composition.



**Figure 4.28** Effect of ITQ-24 and 1%Ge loaded into H-mordenite on gas composition.



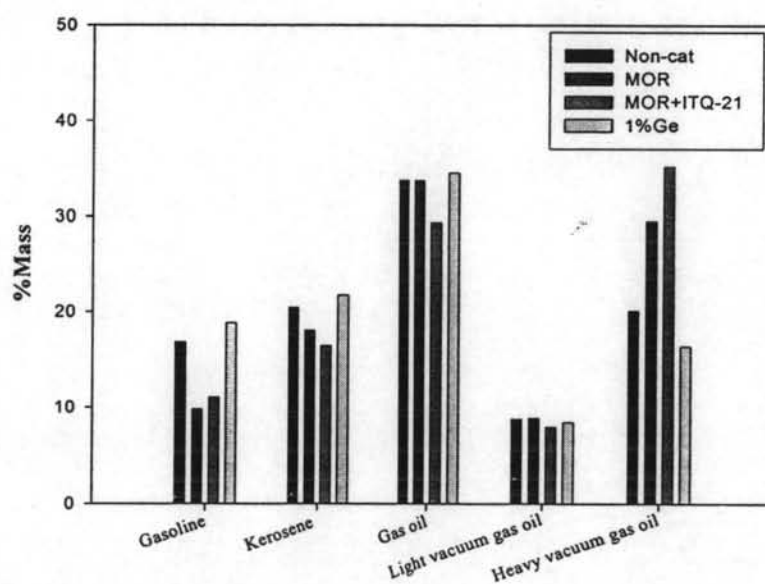
**Figure 4.29** Effect of ITQ-21 and 1%Ge loaded into H-mordenite on carbon number distribution in oil products.



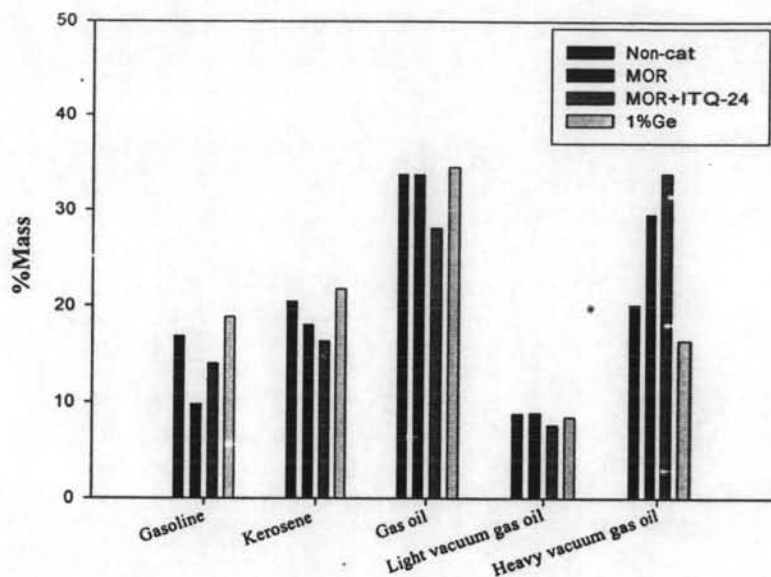
**Figure 4.30** Effect of ITQ-24 and 1%Ge loaded into H-mordenite on carbon number distribution in oil products.

#### 4.3.4.4 Oil Fractions in Liquid Products

The oil derived from tire pyrolysis with and without catalysts gave the results shown in Figures 4.31 and 4.32. Gasoline yield for ITQ-21 loaded mordenite is present in higher amount than those from pure mordenite because ITQ-21 has the higher acidity than mordenite catalysts. An increase in acidity also enhances cracking activity and increases the amount of gasoline fraction. ITQ-24 also has higher acid density than mordenite catalyst. Therefore, the higher amount of gasoline was obtained. Moreover, the lower yield of gasoline and kerosene were produced using by ITQ-loaded mordenite catalysts as compared to 1%Ge loaded mordenite catalyst.



**Figure 4.31** Effect of ITQ-21 and 1%Ge loaded into H-mordenite on oil fractions.

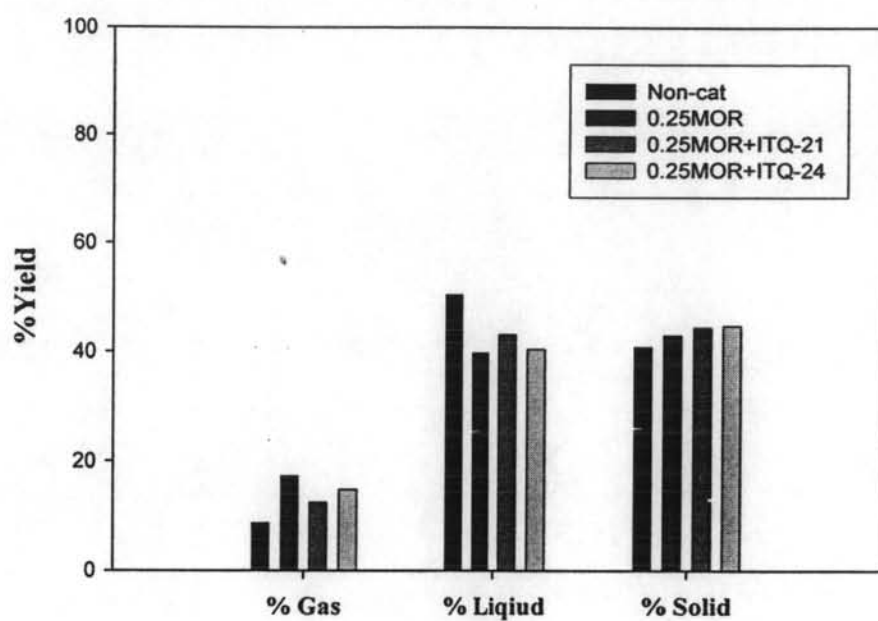


**Figure 4.32** Effect of ITQ-21 and 1%Ge loaded into H-mordenite on oil fractions.

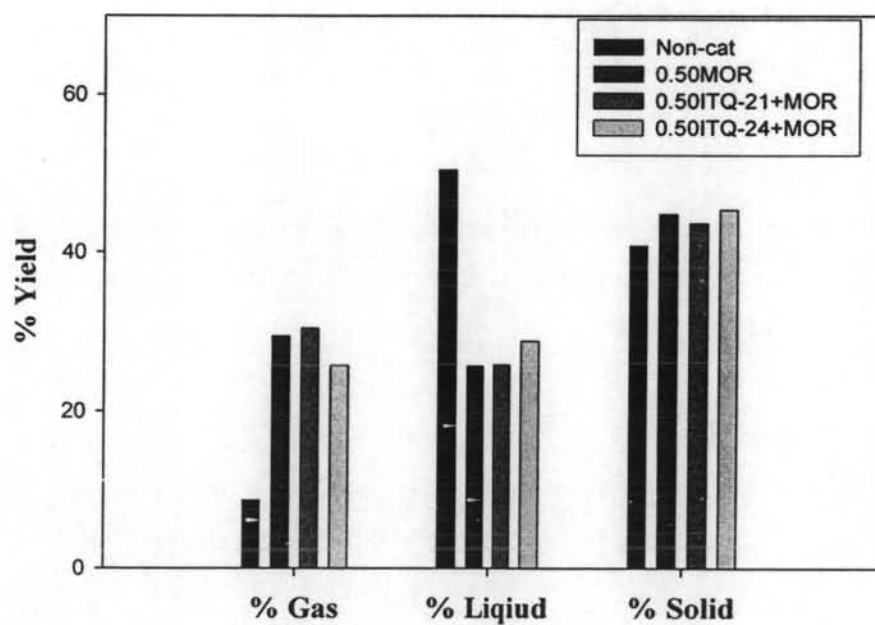
#### 4.3.5 Comparison between ITQ Catalysts

##### 4.3.5.1 Product Distribution

The catalyst-to-tire ratio applied to the experiments in this section was 0.25 and 0.50. A total 1.00 gram of tire and catalyst were mixed and loaded into the reactor. The percentage of ITQ-21 and ITQ-24 on the commercial mordenite was 10%. The product yields after pyrolysis are shown in Figure 4.33. The liquid fraction was higher than the gas fraction in the 0.25 catalyst-to-tire ratio. On the other hand, the gas fraction was approximately in equal amount to liquid fraction when changing to a 0.50 catalyst-to-tire ratio. Moreover, the ITQ-24 loaded mordenite gave higher gas yield but lower liquid yield than ITQ-21 loaded mordenite. This is because ITQ-21 had higher acid strength than ITQ-24, with increasing acid strength, they will further go alkylation and generate larger hydrocarbon molecule.



(a)

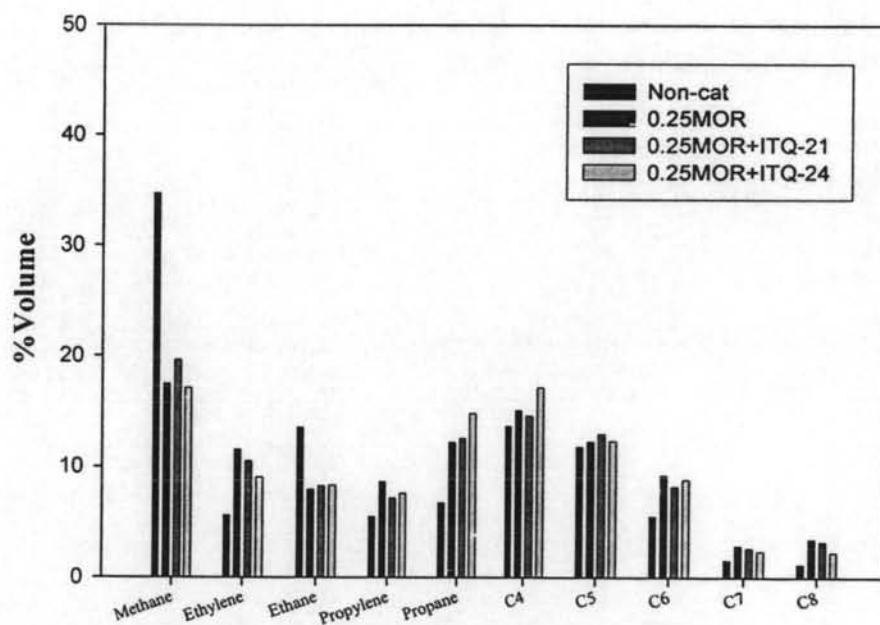


(b)

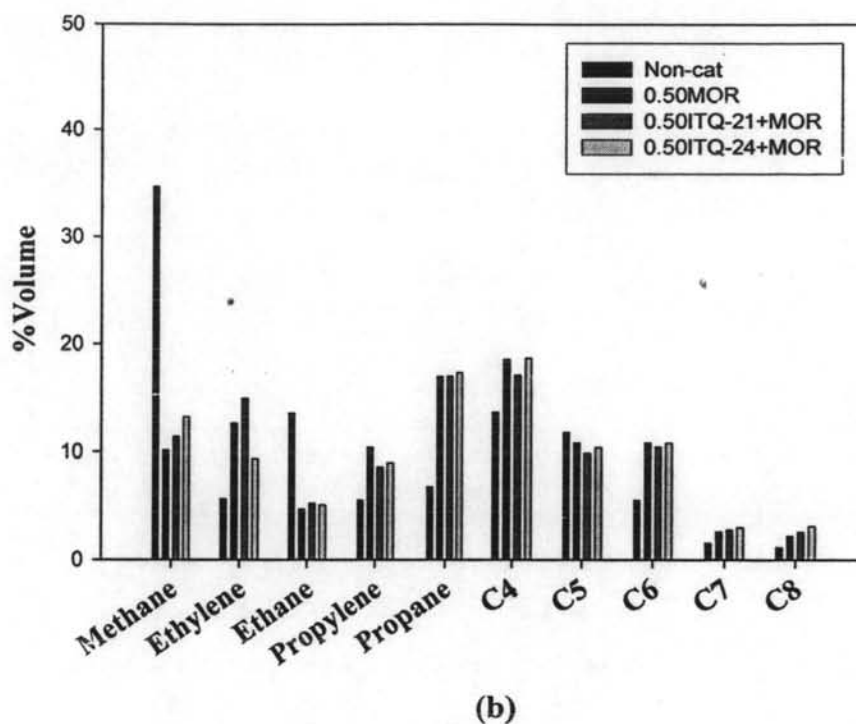
**Figure 4.33** Comparison between ITQ catalysts at the catalyst-to-tire ratios of: (a) 0.25 and (b) 0.50, in terms of gas, oil, and solid residue yield.

#### 4.3.5.2 Components of the Gas Products

The gas compositions of the tire pyrolysis with 0.25 and 0.50 catalyst-to-tire ratios at various types of 10%ITQ-loaded on mordenite are shown in Figure 4.34. The amount of methane was higher when using ITQ-21 at 0.25 catalyst-to-tire ratio while the amount of propane and C<sub>4</sub> were higher when using ITQ-24. Moreover, ITQ-21 and ITQ-24 gave more propane with increasing the catalyst-to-tire ratio. On the other hand, ITQ-24 gave higher amount of methane than ITQ-21 when increasing the catalyst-to-tire ratio. In the case of 0.50 catalyst-to-tire ratio, the amount of ethylene increases with using ITQ-21. For both catalyst-to-tire ratio, no significant difference of ethane and C<sub>5</sub>-C<sub>8</sub> was observed using the ITQ-loaded catalysts.



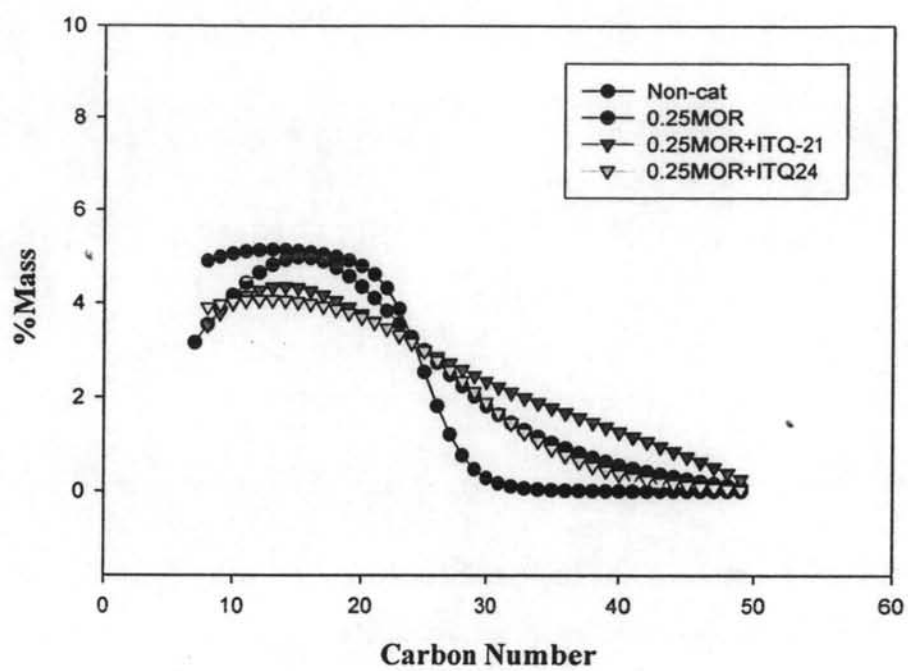
(a)



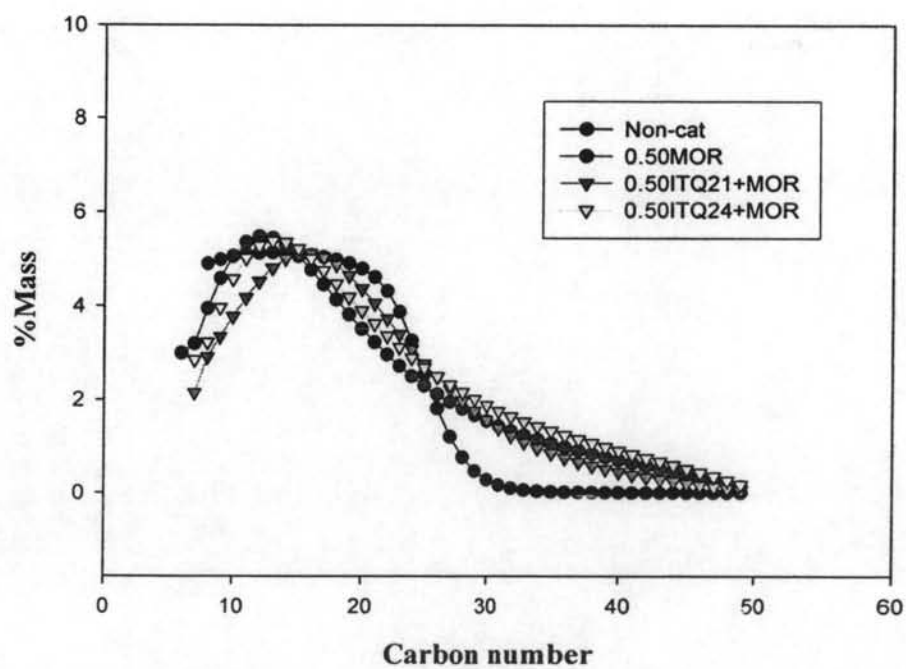
**Figure 4.34** Comparison between ITQ catalysts at the catalyst-to-tire ratios of (a) 0.25 and (b) 0.50 in terms of gas composition.

#### 4.3.5.3 Carbon Number Range in Liquid Products

The carbon number ranges of tire pyrolysis oils obtained at various catalyst-to-tire ratios are illustrated in Figure 4.35. It can be seen that, as expected, pyrolysis oils derived from tires are a very complex mixture containing a wide variety of organic compounds of 8-49 carbons. The carbon number range of oil from thermal pyrolysis is presented in wider distribution. With the increasing catalyst to-tire-ratio, the range of carbon number shifts to the smaller carbon number range. The ratio of 0.50 shows more cracking activity of the catalyst than ratio 0.25, and the carbon number distribution of ratio 0.50 is narrower than the ratio of 0.25 as observed from the shape of peak.



(a)



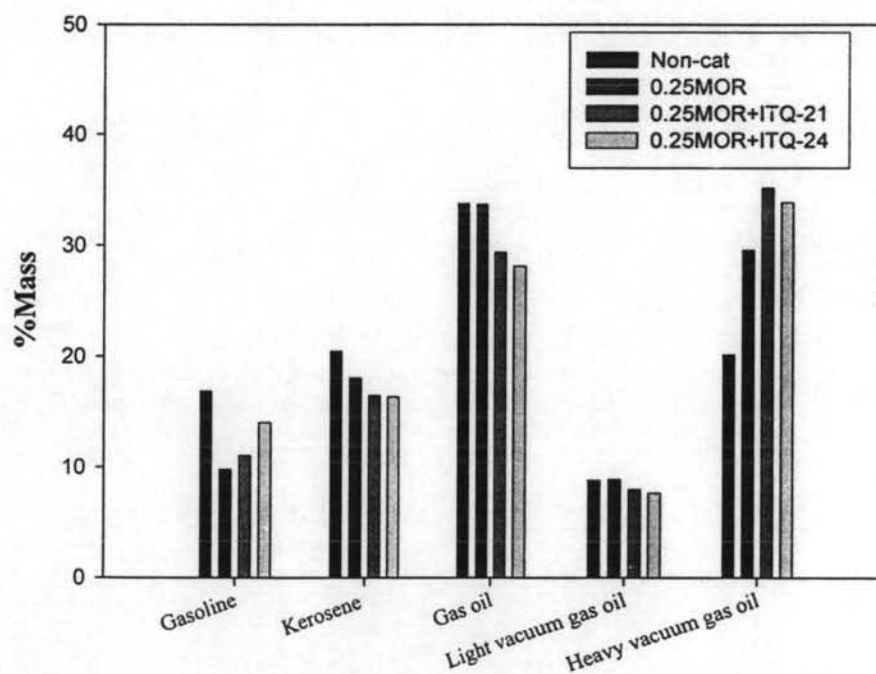
(b)

**Figure 4.35** Comparison between ITQ catalysts at the catalyst-to-tire ratios of (a) 0.25 and (b) 0.50 in terms of carbon number distribution.

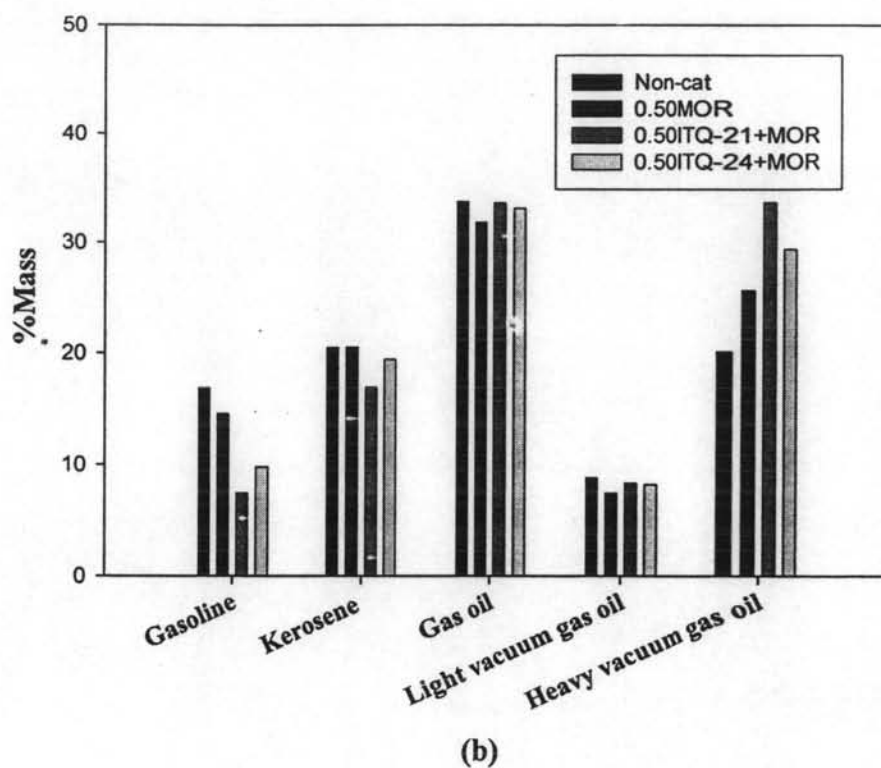


#### 4.3.5.4 Oil Fractions in Liquid Products

Figure 4.36 shows the distribution of the liquid products from the pyrolysis of tire with 0.25 and 0.50 catalyst-to-tire ratios at various types of 10%ITQ loaded on mordenite catalysts. At catalyst-to-tire ratio equal 0.25, gasoline was produced in higher amount when using the ITQ-24 loaded mordenite as compared to the ITQ-21 loaded mordenite. The same trends of gasoline and kerosene are observed at 0.50 catalyst-to-tire ratio. Because ITQ-24 has higher amount of Ge than ITQ-21. The Lewis acid sites can be created by adding Ge, so the acid density increases with increasing amount of Ge, leading to higher cracking activity. However, no significant difference in light vacuum gas oil was observed with increasing catalyst-to-tire ratio and various types of catalysts.



(a)



**Figure 4.36** Comparison between ITQ catalysts at the catalyst-to-tire ratio of (a) 0.25 and (b) 0.50 in terms of oil fractions.