# Chapter 4

RESULTS AND DISCUSSION

The results and discussion of our experiments are focused on the preparation of mixed catalytic cracking zeolite catalysts. The evaluation of catalytic performance was performed using the Microactivity Unit using n-octane as the feedstock. The evaluation conditions have been designed according to the ASTM D-3907 method.

1. NaY zeolite

The NaY zeolite was prepared from a silica source (sodium silicate), alumina source (sodium aluminate and aluminium sulfate) and NaY seeds consisting of amorphous sodium aluminosilicate. The resulting molar composition ratios of sodium aluminosilicate gel obtained from experiment was

$$4.76 \ Na_2O: Al_2O_3: 9.55 \ SiO_2: 190 \ H_2O.$$
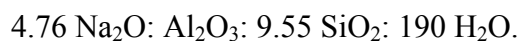
The physical and chemical properties of synthesized NaY zeolite are shown in Table 4-1 (the percent crystallinity of reference standard NaY is 100).

Table 4-1 Physical and chemical properties of synthesized NaY zeolite.

Zeolite	% Crystallinity	UCS (Å)	Thermal stability (^{o}C)	Surface area (m^2/g)	Na_2O (%wt.)	SiO_2/Al_2O_3 (mole ratio)
NaY[1]	97.54	24.83	926.67	664	10.98	3.22
NaY[2]	102.2	24.72	937.18	653	8.97	4.32
NaY[3]	96.3	24.70	-	-	8.70	4.55
NaY[4]	98.0	24.70	939.19	652	-	-
NaY[5]	88.32	24.66	-	-	12	5.11

1 = NaY prepared from this work
2 = NaY prepared by Prasit Songtuan
3 = NaY prepared by Kritsana Kritsanaphak
4 = NaY prepared by Jukkrit Tuntragul
5 = NaY prepared by RIPP

2. Preparation of USY, REY and ZSM-5 zeolites

2.1 Preparation of USY zeolite

In this experiment, the sodium ion was exchanged with ammonium chloride, since direct exchange with an acid destroys the crystallinity framework of the zeolite. Once the ammonium ions were placed inside the cages, the sodium ions were removed. The zeolites were calcined at a high temperature to decompose the ammonium ions, drive off ammonia and leave protons in the place of the original sodium ions. The level of sodium content was to be less than 0.1 %wt.

The hydrothermal approach to dealumination involved treating the zeolite with steam temperature at 600°C. Aluminium-oxygen bonds were broken by the steam and the aluminium atom was expelled from the zeolite framework.

The fully exchanged Y zeolite contained 0.74 %wt. of sodium oxide and the other properties are shown in Table 4-2.

Table 4-2 Physical and chemical properties of prepared USY zeolite.

Zeolite	% Crystallinity	UCS (Å)	Thermal stability (°C)	Surface area (m^2/g)	Na_2O (%wt)
USY[1]	62.5	24.36	1009.32	454	0.74
USY[2]	63.7	24.37	1011.52	480	0.73
USY[3]	65.5	24.37	1015.20	462	0.90

1 = USY prepared from this work
2 = USY prepared by Prasit Songtuan
3 = USY prepared by Wachira Ritthichai

2.2 Preparation of REY zeolite

Generally, the level of RE_2O_3 content in REY zeolite, which has been fully exchanged is about 16 %wt. or higher. The ion exchange process must be carried out at least twice to get a desired level of rare earth and to decrease the level of sodium content lower than 1 %wt. The fully rare earth exchanged Y zeolite contained 20.84 %wt. of rare earth oxide and 0.53 %wt. of sodium oxide. The other properties are shown in Table 4-3.

Table 4-3 Physical and chemical properties of prepared REY zeolite.

Zeolite	% Crystallinity	UCS (Å)	Thermal stability (°C)	Surface area (m^2/g)	Na_2O (%wt.)	RE_2O_3 (%wt.)
REY[1]	29.5	24.75	943.44	526	0.53	20.84
REY[2]	29.3	24.68	998.38	575	0.60	23.81
REY[3]	33.4	-	1001.32	-	0.63	22.41
REY[4]	48.2	24.67	-	-	0.38	22.31
REY[5]	43.8	24.66	-	-	1.30	20.20

1 = REY prepared from this work
2 = REY prepared by Prasit Songtuan
3 = REY prepared by Sutha Onkham
4 = REY prepared by Kritsana Kritsanaphak
5 = REY prepared by RIPP

2.3 Preparation of ZSM-5

For the preparation of ZSM-5 zeolite, the sodium ion was exchange with ammonium sulfate. A starting NaZSM-5 zeolite contained 12.73 %wt. of sodium oxide, and the first ion exchanged ZSM-5 zeolite contained 1.52 %wt. of sodium oxide. Therefore, the ZSM-5 zeolite was carried out for the second exchange. The fully exchange ZSM-5 zeolite contained 0.90 %wt. of sodium oxide. The other properties are shown in the Table 4-4.

Table 4-4 Physical and chemical properties of prepared ZSM-5 zeolite.

Zeolite	Thermal stability (°C)	Surface area (m^2/g)	Na_2O (%wt.)
ZSM-5	685.97	357.06	0.90

3. Catalyst Preparation

The modern catalyst technology is very complex and there are wide varieties of catalyst on the market. Catalyst formulations and performance can be adjusted by changing the amount and type of zeolite used, as well as by varying the composition of the nonzeolite matrix. Further modifications can be made base on the type of

treatment used on both the zeolite and the finished catalyst (Wilson, 1997). The most frequently used additive consists of ZSM-5 zeolite embedded in a matrix and is commonly used as a distinct physical particle in conjunction with an FCC catalyst. The additive represents only a small percentage (usually 1 to 3 percent) of the catalyst inventory in the unit and increases both RON and MON at low concentrations (Magee, 1993).

In this work the results of the laboratory evaluation and characterization of mixed zeolite catalysts are presented, with focus on the catalytic cracking of n-octane.

4. Evaluation of the Catalysts Performance

Microactivity test condition of this work was performed at standard conditions, as can be seen in section 7.1.1, page 61.

Definition

1. % Conversion = $100 - \left[(100-A) \times \dfrac{C}{B} \right]$

Where: A = Percent light hydrocarbon from GC analysis

B = Weight of feed (n-octane or n-hexadecane), g

C = Liquid in the receiver, g

2. % Liquid yield = $\dfrac{C \times A}{B}$

3. % Coke yield = $\dfrac{D \times \dfrac{\Delta Y}{1 - \left(\dfrac{\Delta Y}{100} \right)}}{B}$

Where: D = Weight of fresh catalyst used in MAT unit, g

ΔY = Percentage of coke on spent catalyst, %wt.

4. % Gas yield = $\dfrac{B-C-\left(\% \text{ Coke yield} \times \dfrac{B}{100}\right)}{B} \times 100$

5. % Gas & Coke yield = $\dfrac{(B-C) \times 100}{B}$

6. Liquid selectivity = $\dfrac{C \times A}{B \times \% \text{ Conversion}} \times 100$

7. Gas & Coke selectivity = 100-Liquid selectivity

8. % Paraffins = Percent paraffins, analyzed by GC, %wt.

9. % Olefins = Percent olefins, analyzed by GC, %wt.

10. % Aromatics = Percent aromatics, analyzed by GC, %wt.

11. Paraffins/Olefins ratio = $\dfrac{\% \text{ Paraffins}}{\% \text{ Oleffins}}$

12. Paraffins/Aromatics ratio = $\dfrac{\% \text{ Paraffins}}{\% \text{ Aromatics}}$

13. Research Octane Number = Calculated from hydrocarbon groups according to the model of Anderson et al., (1972). (see Appendix F)

5. Catalytic cracking of n-octane on REY and USY zeolite

5.1 N-octane catalytic cracking on REY zeolite
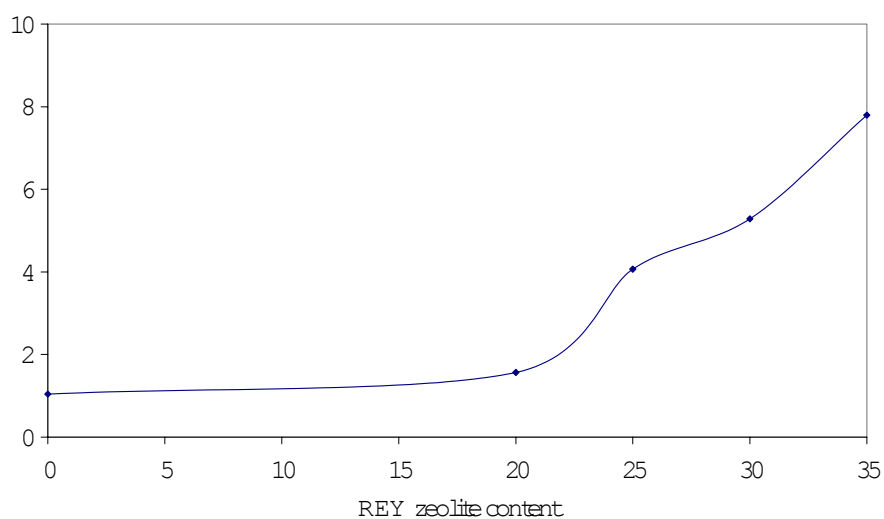
Figure 4-1 Effect of REY zeolite content on % Conversion.

Figure 4-1 shows the percent conversion of n-octane cracking on REY catalyst. The percent conversion increases with an increase in REY zeolite content. The improved activity is due to the higher number of Bronsted acid sites resulting from the partial hydrolysis of hydrated rare earth ions: $RE(OH_2)^{3+} \rightarrow REOH^{2+} + H^+$.
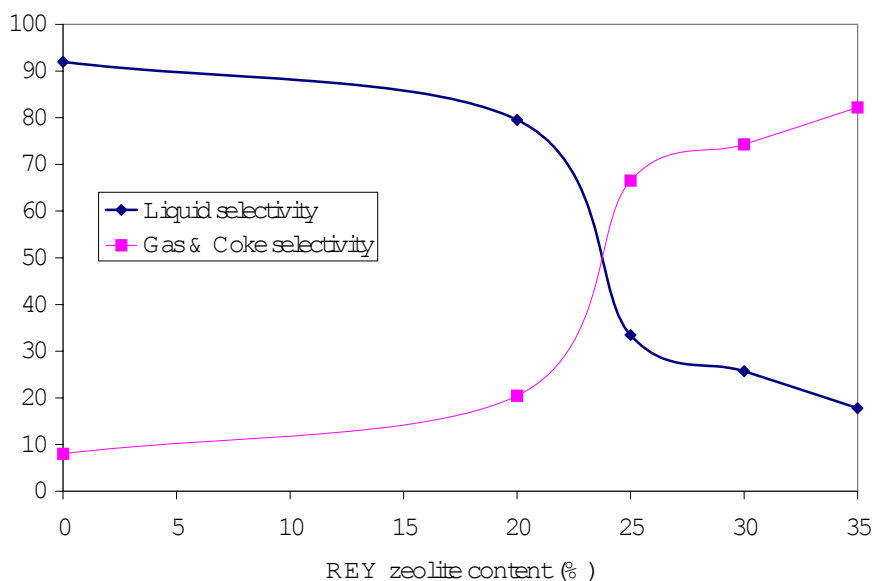
Figure 4-2 Effect of REY zeolite content on Liquid selectivity and
Gas & Coke selectivity.
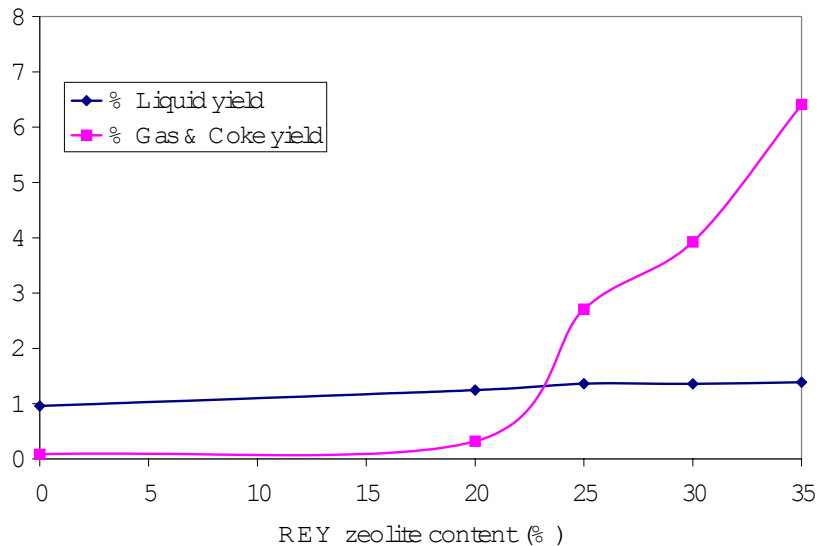
Figure 4-3 Effect of REY zeolite content on % Liquid yield and
% Gas & Coke yield.

Figures 4-2 and 4-3 liquid selectivity decreased, while gas selectivity, the percent liquid yield and gas & coke yield, increased with increasing REY content. Because higher REY zeolite content has higher number of acid sites, more secondary

reactions can take place which leads to the high gas and coke yield. But the liquid yield only increases slightly with increasing REY zeolite content.
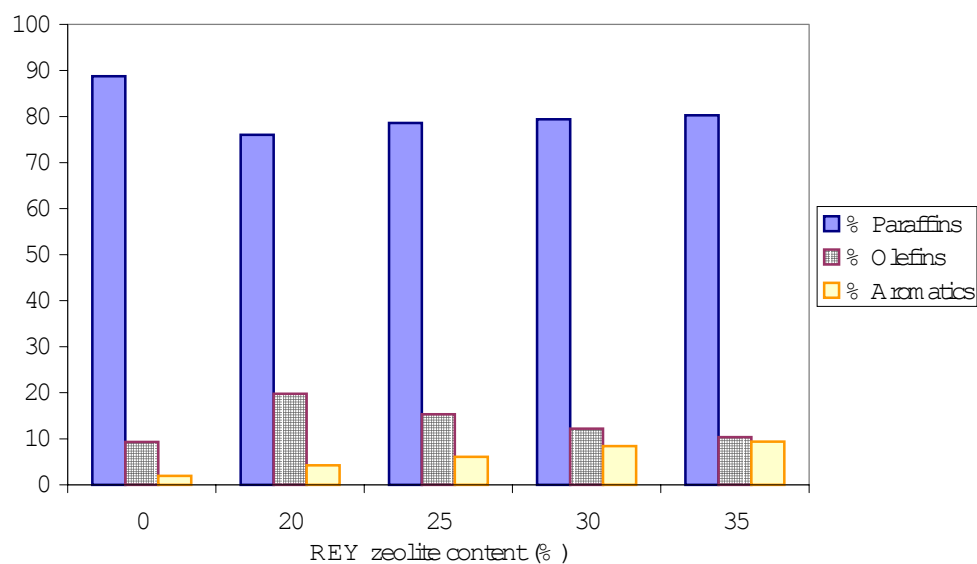
Figure 4-4 Effect of REY zeolite content on % Paraffins, % Olefins and
% Aromatics in liquid product.
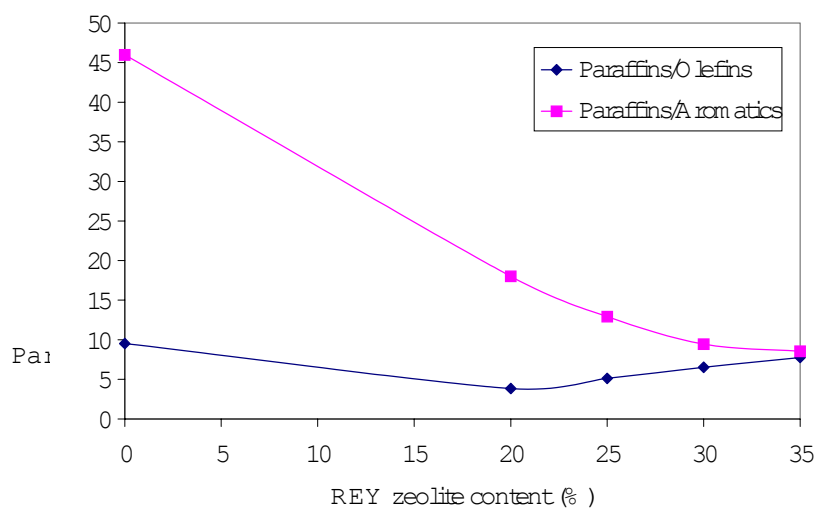
Figure 4-5 Effect of REY zeolite content on the ratios of Paraffins/Olefins and
Paraffins/Aromatics in liquid product.
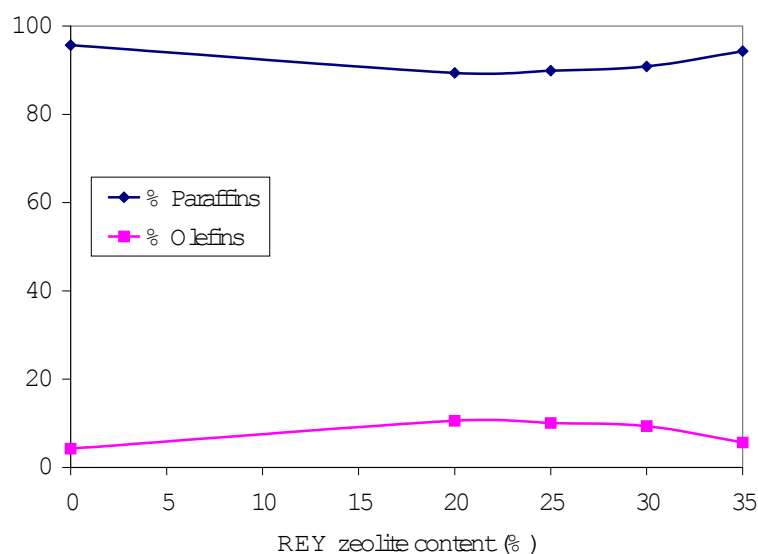
Figure 4-6 Effect of REY zeolite content on % Paraffins and % Olefins in
gas product.

Figure 4-4 shows the percent paraffins, olefins (such as butene, propene) and aromatics (such as benzene, toluene, xylene) in liquid products obtained from various REY zeolite content catalysts. As the REY zeolite content increases, the percent of paraffins and aromatics increases while the percent of olefins decreases.

The ratios of paraffins to olefins and aromatics as liquid products of REY catalysts are shown in Figure 4-5. The ratio of paraffins/olefins increases with increasing REY content, while that of paraffins/aromatics decreases. Gas products contain only paraffins and olefins (such as ethene, butene, propene) but no aromatics with the most being paraffins (Figure 4-6). An increasing of REY zeolite content leads to an increased percent of paraffins, while percent olefins is decreased similar to the liquid products. However, the olefins content is even higher than the one which contains no REY zeolite.
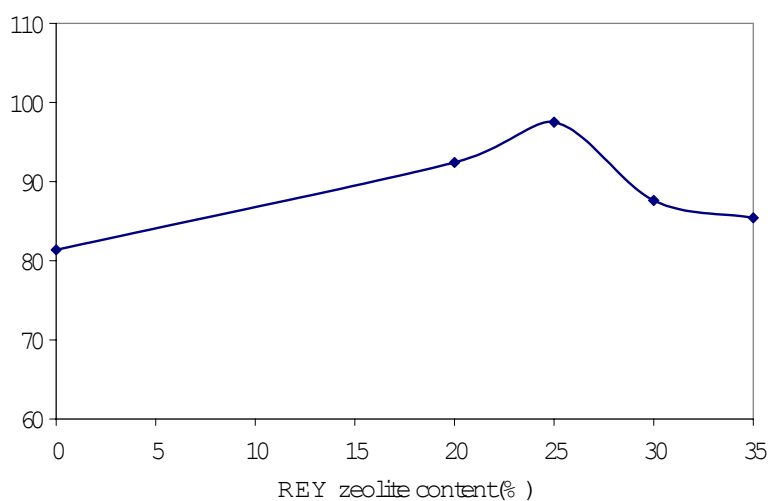
Figure 4-7 Effect of REY zeolite content on Research Octane Number.

One of the important properties of gasoline is the Research Octane Number (RON). Figure 4-7 shows the Research Octane Number of liquids cracking from the various REY zeolite content catalysts. The model of Anderson et al., (1972) was used for the calculation of RON. It should be noted that the objective of this octane correlation is to predict the relative octane potential of gasoline from wide variety of catalyst and feedstock types, rather than to give an engine test accuracy (Nalbandian, 1993). At 25%, REY zeolite has the highest RON and at 0%, REY has the lowest RON. The exchanged rare earth in zeolite increases the active sites per weight of zeolite and increases the rate of hydrogen transfer mechanism. The concentration, strength and distribution of acid sites in the zeolite play a key role in determining its activity and selectivity. Although the reactions that take place during catalytic cracking of gas oil are rather complex and many of the primary products undergo secondary reaction, most of these reactions involve carbocations as intermediates. The initial carbocations can arise either at Bronsted or Lewis acid sites on the zeolite (Scherzer, 1993). While cracking reactions of high input of zeolite contributes to high acid concentration, some primary products are converted to undesired product (e.g. gas and coke) by secondary reactions such as isomerization, cyclization, and intermolecular hydrogen transfer taking place at weaker acid sites. Hydrogen transfer

plays an important role in the gas oil cracking process. It reduces the amount of olefins in the product through bimolecular hydrogen transfer, whereby reactive olefins and naphthenes are converted to more stable paraffins and aromatics. Further hydrogen transfer from aromatics, coupled with condensation and polymerization, can lead to the formation of coke. The resulting loss in octane and olefinicity caused by the rare earth stabilization of unit cell size (Magee and Mitchell, 1993). Hence, the optimum REY zeolite content has been considered. The 25% REY represents the highest RON and 35% REY represents the lowest RON for the REY catalyst. Therefore, for the mixed ZSM-5 zeolite additive catalysts, we chose both the 25% and 35% REY zeolite content catalysts to investigate the influence of ZSM-5 zeolite additive.

5.2 N-octane catalytic cracking on USY zeolite
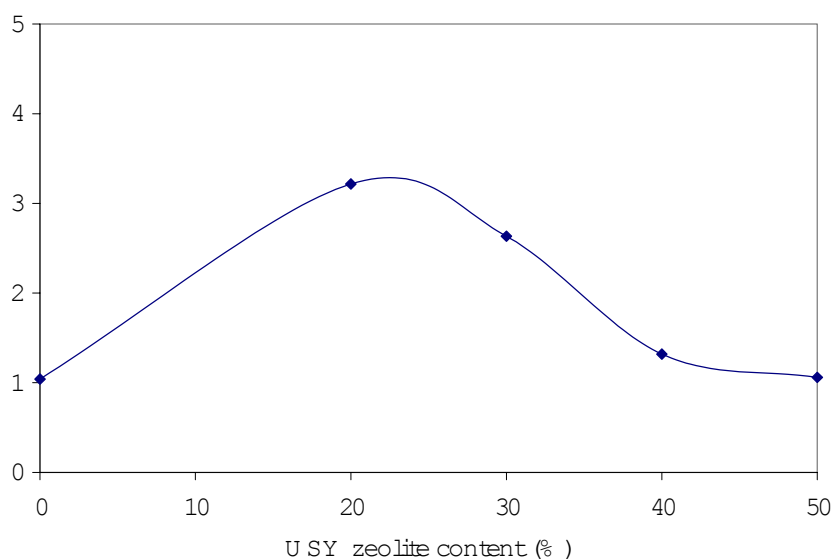
Figure 4-8 Effect of USY zeolite content on % Conversion.
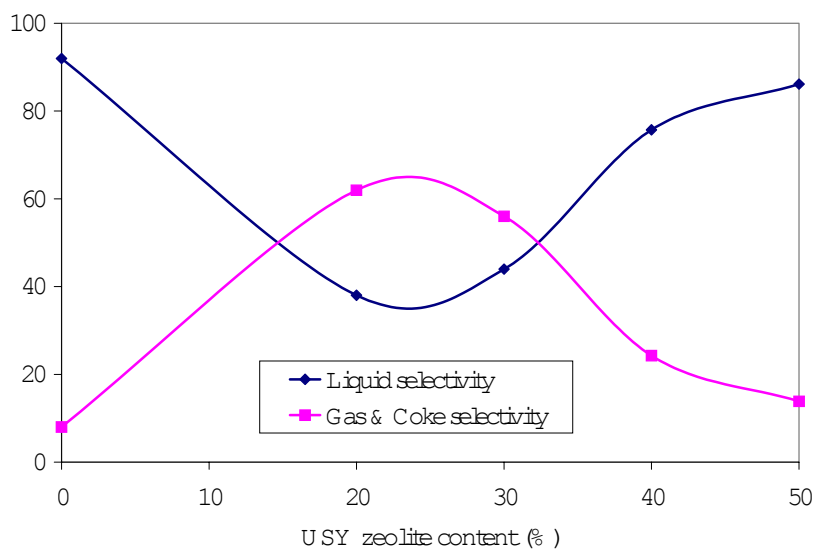
Figure 4-9 Effect of USY zeolite content on Liquid selectivity and
Gas & Coke selectivity.
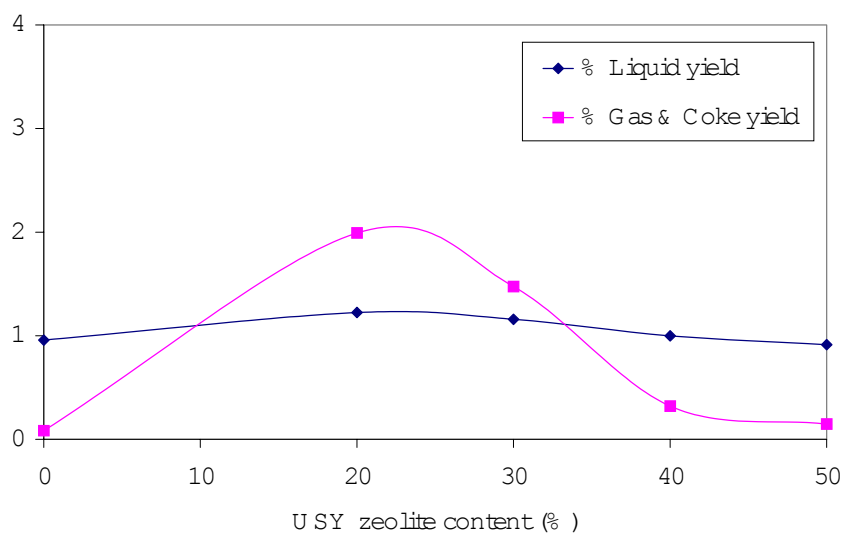
Figure 4-10 Effect of USY zeolite content on % Liquid yield and
% Gas & Coke yield.

Figure 4-8 shows the percent conversion of n-octane cracking on USY catalyst. From 20-50% USY zeolite content, the conversion tends to decrease with an increase in the USY zeolite content. Figure 4-9 shows that liquid selectivity trend to increase with increasing USY zeolite content. Conversly, gas & coke selectivity trend to decrease.

The percent liquid yield does not change so much as an increase in USY content but the % gas & coke yield sharply decreases from 20 to 40% of USY content (Figure 4-10).
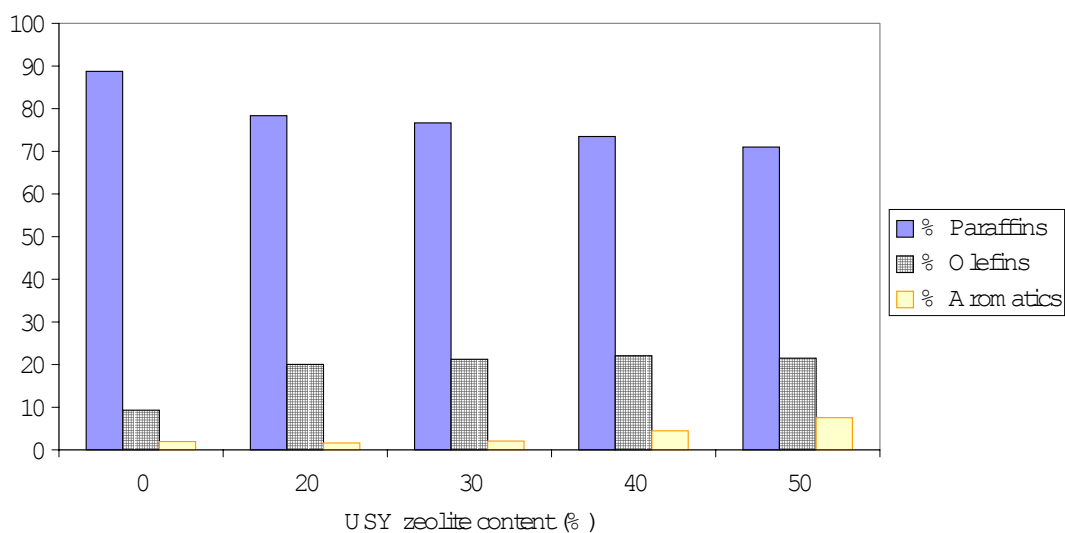
Figure 4-11 Effect of USY zeolite content on % Paraffins, % Olefins and
% Aromatics in liquid product.
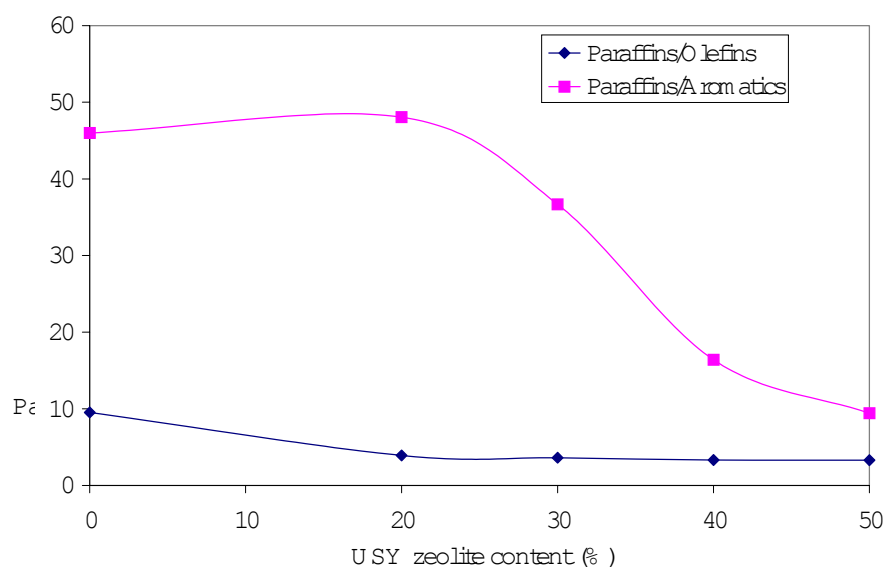
Figure 4-12 Effect of USY zeolite content on the ratios of Paraffins/Olefins and
Paraffins/Aromatics in liquid product.
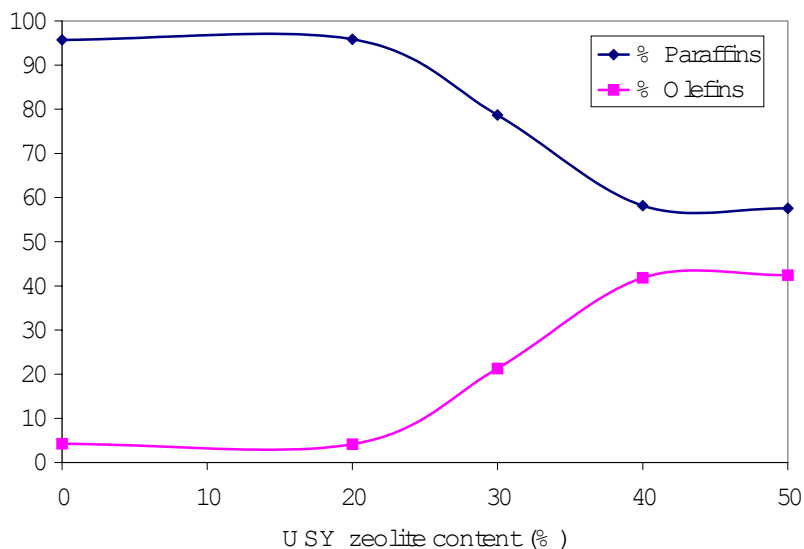
Figure 4-13 Effect of USY zeolite content on % Paraffins and % Olefins
in gas product.

Figure 4-11 shows the percent paraffins, olefins and aromatics in liquid product obtained from the n-octane cracking of USY catalysts. The percent of paraffins decreases with increasing USY zeolite content, while those of olefins and aromatics increase. Consequently, the ratio of paraffins to olefins and aromatics decreases (Figure 4-12). The composition of gas product is identified as paraffins and olefins in which the olefins increases rapidly from 20 to 40% of USY content (Figure 4-13). Apparently, they indicated that the USY zeolite has lower unit cell size than REY zeolite. At lower unit cell size the activity of zeolite is very low due to the low concentrations of active sites. At higher unit cell size, hydrogen transfer reactions will be favored due to the rapid increase in the number of pair Al atoms (Magee and Mitchell, 1993). In addition, the USY zeolite has a lower concentration of acid sites than REY zeolite. The lower acidity makes them catalytically less active.
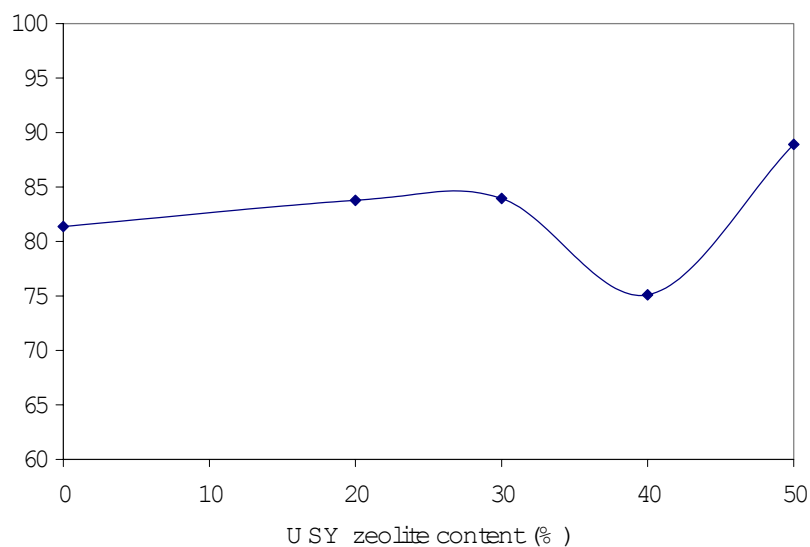
Figure 4-14 Effect of USY zeolite content on Research Octane Number.

According to the Figure 4-14 the RON of liquid product has no exact trend on the change of USY zeolite content. Theoretically, the rate of hydrogen transfer reaction also decreases with unit cell, the USY zeolite favors less hydrogen transfer reaction. Therefore, the increase USY zeolite favors the formation of compounds with high RON.

6. Catalytic cracking of n-octane on mixed zeolite catalyst

6.1 N-octane catalytic cracking on ZSM-5 and 35% REY zeolite
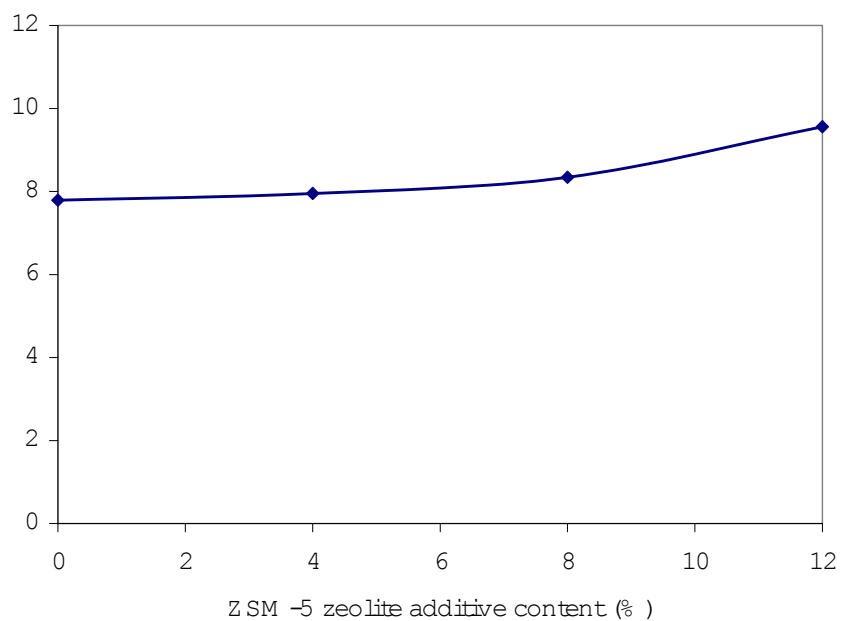
Figure 4-15 Effect of additive ZSM-5 zeolite content in 35% REY on % Conversion.
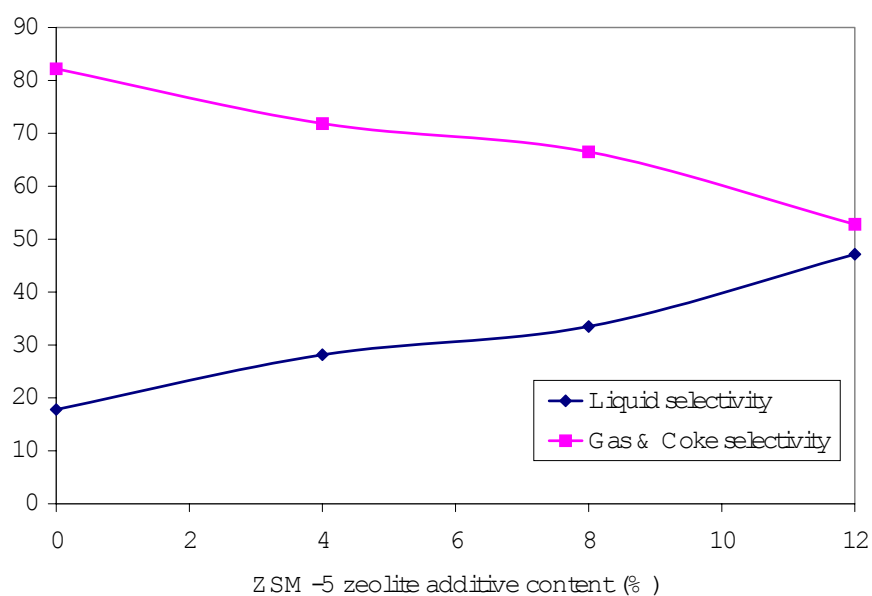
Figure 4-16 Effect of additive ZSM-5 zeolite content in 35% REY on Liquid
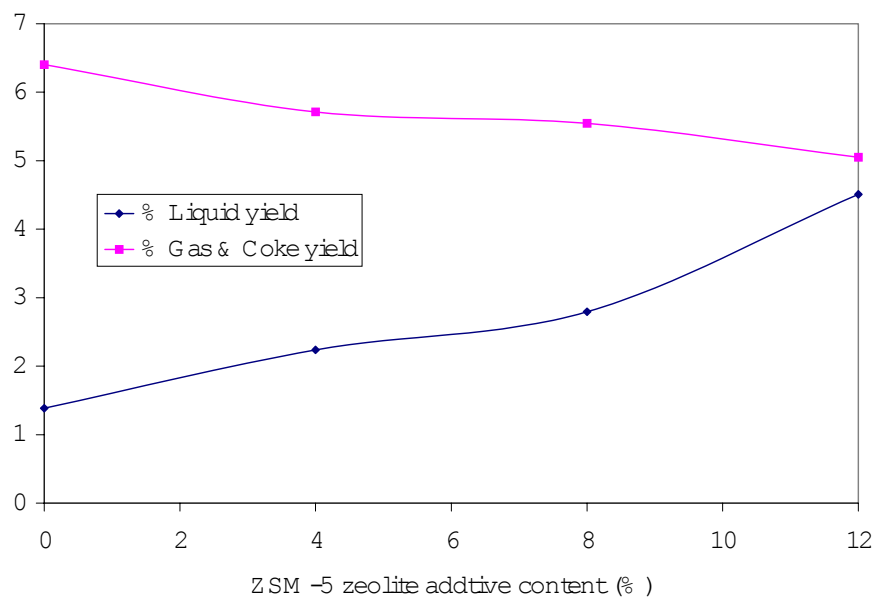selectivity and Gas & Coke selectivity.

Figure 4-17 Effect of additive ZSM-5 zeolite content in 35% REY on % Liquid yield
and % Gas & Coke yield.

Figure 4-15 shows the percent conversion of n-octane cracking from 35%
REY mixed ZSM-5 zeolite. The percent conversion gradually increases with
increasing ZSM-5 zeolite content. Figures 4-16 and 4-17 show that the liquid
selectivity and liquid yield increased, while the gas & coke selectivity and gas & coke
yield decreased. This behavior is explained by the increase in the secondary reaction
rate (gasoline overcracking into coke and gases) leading to a decrease in gasoline
yield and an increase in coke and gas yields by Y-zeolite (Al-Khattaf, 2002). At high
ZSM-5 zeolite additive content, with very little acidity and narrow pores, the
occurrence of reaction leading to coke formation is limited. Therefore, the coking
tendency of ZSM-5 is very low. ZSM-5 coke formation is a shape-selective reaction
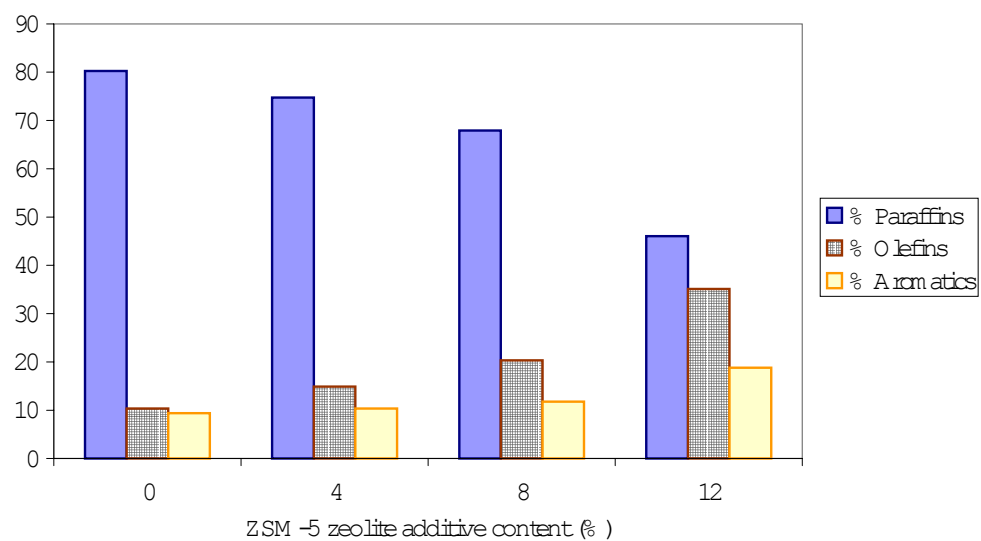(Scherzer, 1990).

Figure 4-18 Effect of additive ZSM-5 zeolite content in 35% REY on % Paraffins,
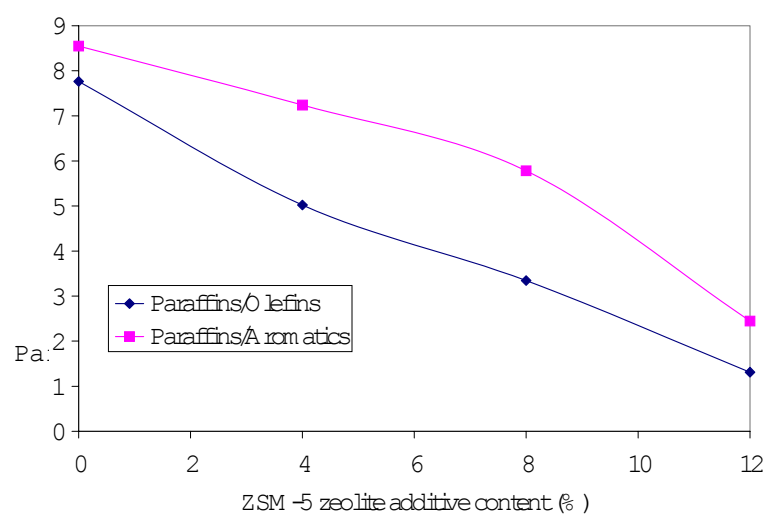% Olefins and % Aromatics in liquid product.

Figure 4-19 Effect of additive ZSM-5 zeolite content in 35% REY on the ratios of
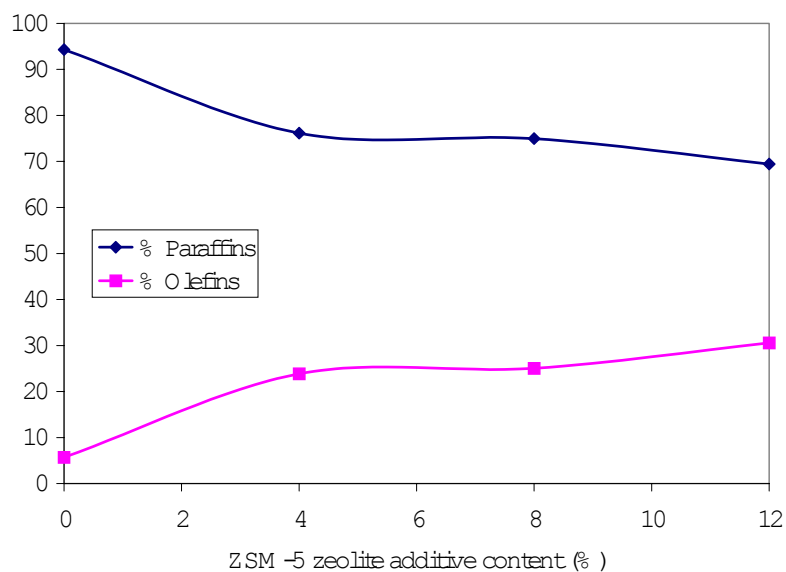Paraffins/Olefins and Paraffins/Aromatics in liquid product.

Figure 4-20 Effect of additive ZSM-5 zeolite content in 35% REY on % Paraffins and % Olefins in gas product.

The correlation of the paraffins, olefins and aromatics in liquid product obtained from the n-octane cracking of 35% REY with varying ZSM-5 zeolite additive content are shown in Figures 4-18, 4-19 and 4-20. Increasing ZSM-5 zeolite additive content resulted in a decrease in the percent paraffins, while the percent olefins and aromatics increased. The ratios of paraffins/olefins and parffins/aromatics were heavily decreased. This is possible because the ZSM-5 zeolite might interfere with the reaction pathway by increasing the surface coverage of carbenium ions which resulted in an increase in olefins (Buchanan and Adewuyi, 1996). Thus, the ZSM-5 zeolite gives a lower concentration of n-paraffins and higher concentration of olefins and aromatics.
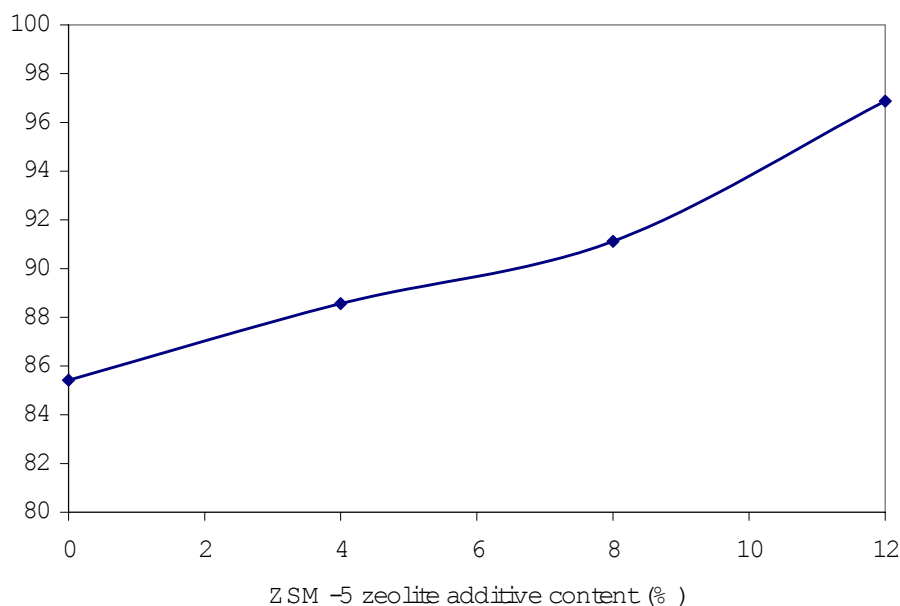
Figure 4-21 Effect of additive ZSM-5 zeolite content in 35% REY on Research
Octane Number.

Figure 4-21 shows the RON of liquids cracking from the n-octane cracking of mixed ZSM-5 and 35% REY catalysts. The RON sharply rises with increasing ZSM-5 zeolite additive content. The shape selectivity of ZSM-5 zeolite promoted an increase of olefins and aromatics which have higher RON. The most important change is the decrease of the alkanes, which are known to constitute the low-octane of gasoline (Nalbandian, 1993).

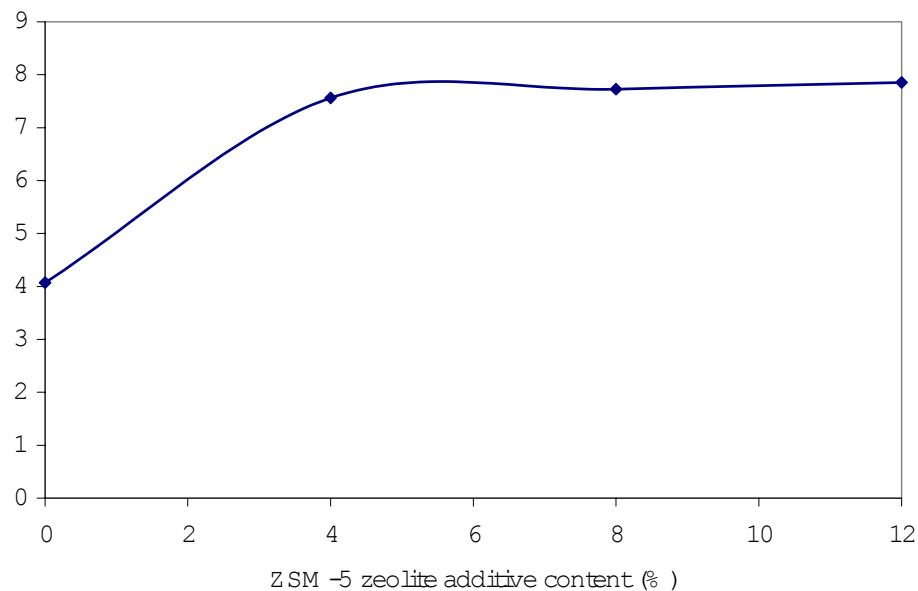**6.2 N-octane catalytic cracking on additive ZSM-5 content to 25% REY zeolite catalyst**

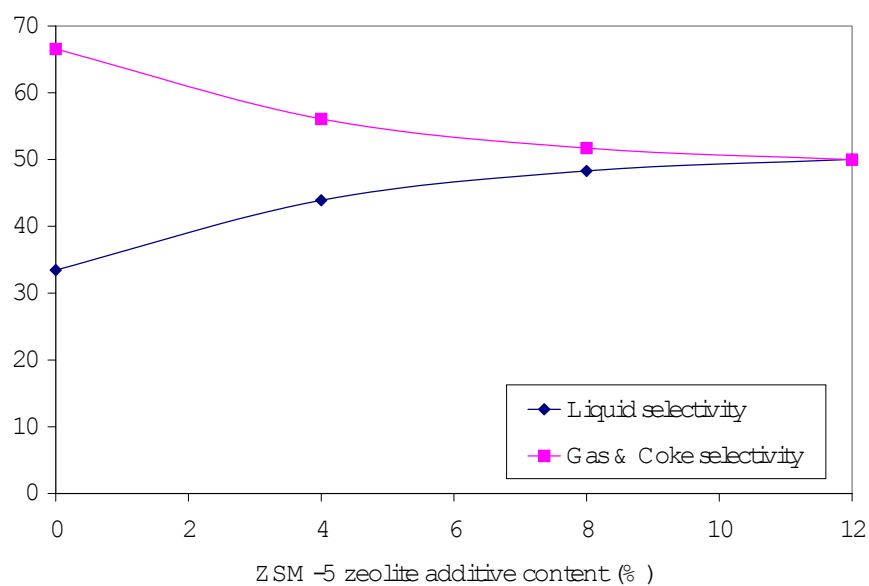**Figure 4-22** Effect of additive ZSM-5 zeolite content in 25% REY on % Conversion.

Figure 4-23 Effect of additive ZSM-5 zeolite content in 25% REY on Liquid selectivity and Gas & Coke selectivity.
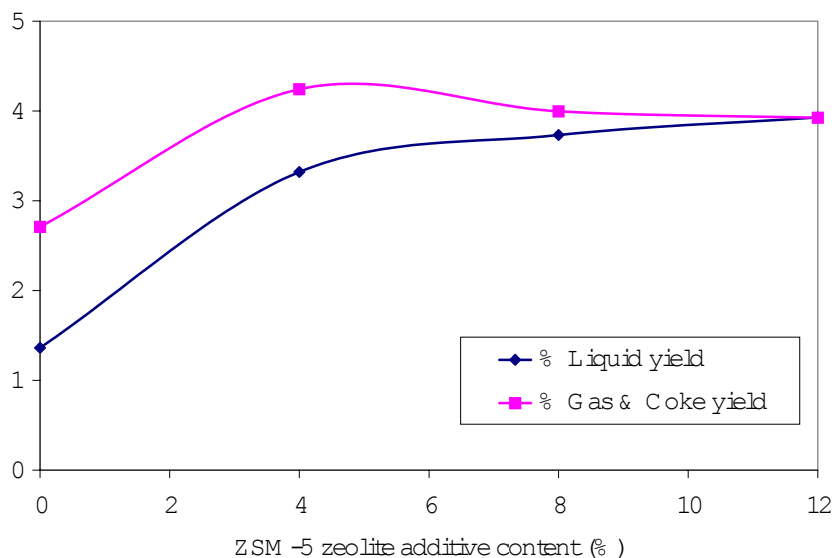
Figure 4-24 Effect of additive ZSM-5 zeolite content in 25% REY on % Liquid yield and % Gas & Coke yield.

Figure 4-22 shows the percent conversion of n-octane cracking on 25% REY with the variation of additive ZSM-5 zeolite of 0%, 4%, 8% and 12%. The percent conversion gradually increases with increasing ZSM-5 zeolite content. Figures 4-23 and 4-24 show an increase of liquid selectivity and liquid yield, while the gas & coke selectivity and gas & coke yield decrease.
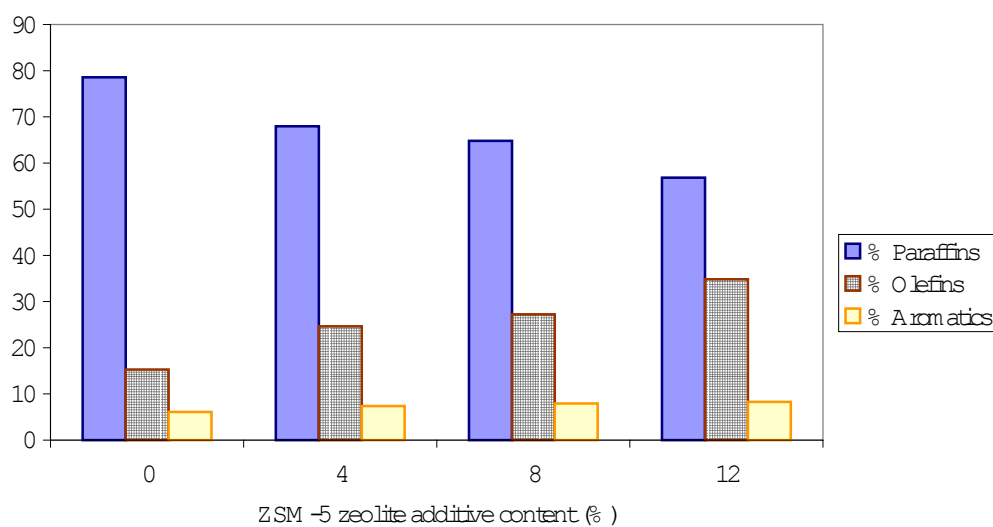

Figure 4-25 Effect of additive ZSM-5 zeolite content in 25% REY on % Paraffins, % Olefins and %Aromatics composition in liquid product.
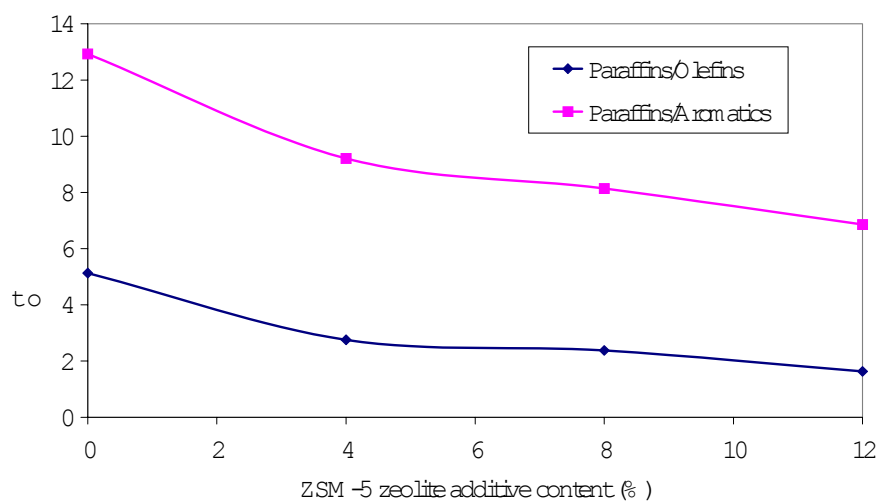
Figure 4-26 Effect of additive ZSM-5 zeolite content in 25% REY on the ratios of Paraffins/Olefins and Paraffins/Aromatics in liquid product.
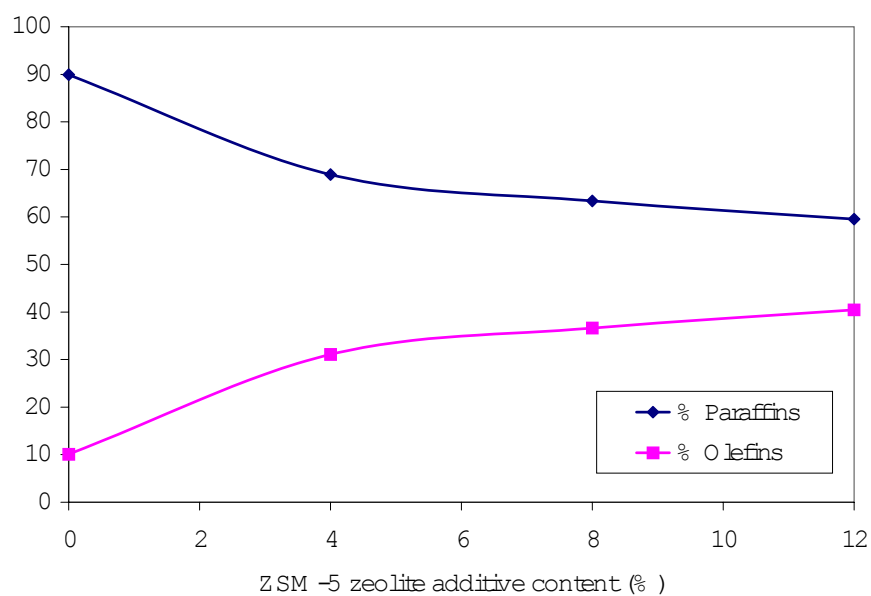

Figure 4-27 Effect of additive ZSM-5 zeolite content in 25% REY on % Paraffins and % Olefins composition in gas product.

Figures 4-25, 4-26 and 4-27 confirm the decreasing of paraffins and the increasing of olefins and aromatics with the higher ZSM-5 zeolite content as the same results as that of 35% REY zeolite. ZSM-5 zeolite has a lower hydrogen transfer

process and results in lower paraffins/olefins products ratio (Dzikh et. al., 1999). The main effects of adding ZSM-5 are to increase the gasoline octane rating. Figure 4-28 shows a simplified diagram of the main pathways for the formation of gasoline-range paraffins in the FCC unit, over the base catalyst. Some paraffins are formed by the cracking of higher paraffins. This cracking process also makes gasoline range olefins.
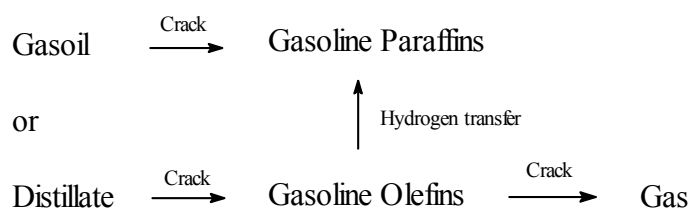
Gasoil $\xrightarrow{\text{Crack}}$ Gasoline Paraffins

or $\qquad\qquad\qquad\qquad\qquad$ $\uparrow$ Hydrogen transfer

Distillate $\xrightarrow{\text{Crack}}$ Gasoline Olefins $\xrightarrow{\text{Crack}}$ Gas

Figure 4-28 Dominant pathways for FCC paraffin production.
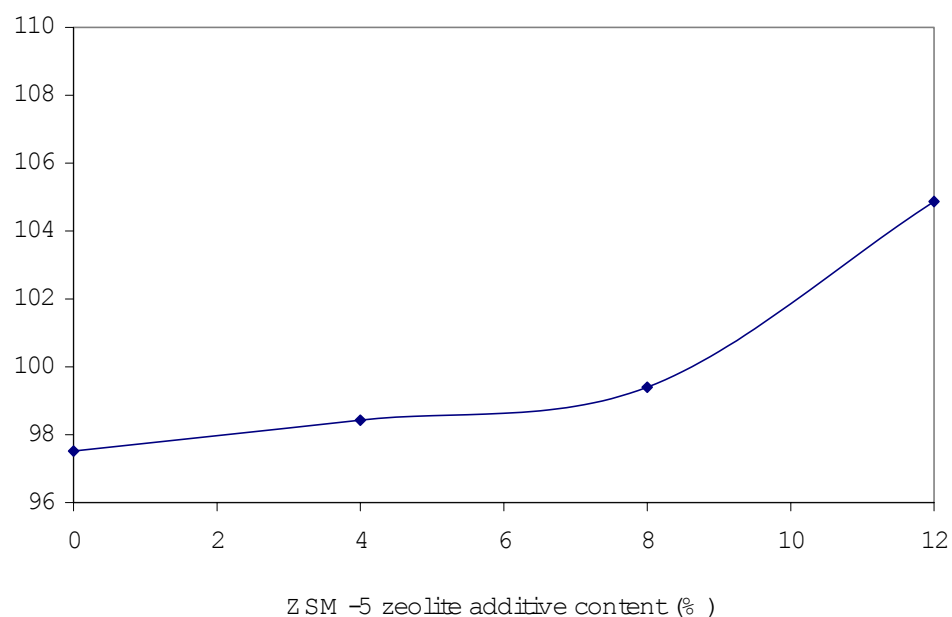Source: Buchanan, 2000: 209

Figure 4-29 Effect of additive ZSM-5 zeolite content in 25% REY on Research Octane Number.

Figure 4-29 shows the RON of liquid cracking from the 25% REY mixed ZSM-5 zeolite catalysts. The RON rises with increasing ZSM-5 zeolite content and the highest is at 12% ZSM-5 zeolite additive content. This explains that with the addition of cracking gasoline range paraffins, the presence of ZSM-5 zeolite inhibits certain secondary reactions, such as chain transfer or hydrogen transfer reactions that lead to the formation of gasoline range paraffins.

7. Catalytic cracking of n-hexadecane on mixed zeolite catalyst

In most micro-activity test laboratories, gas oil is used as the feedstock and many use modified feedstock to achieve the activity performance. This part was aimed to investigate the catalytic activity of mixed zeolite catalysts using a higher molecular weight feedstock with n-hexadecane having a higher molecular weight than n-octane. The n-hexadecane has 16 carbon atoms which is very well-known in catalytic cracking mechanism, so we have selected this substance as the feedstock in our investigation study. The properties of n-hexadecane are listed in Table 4-5.

Table 4-5 Properties of n-hexadecane.

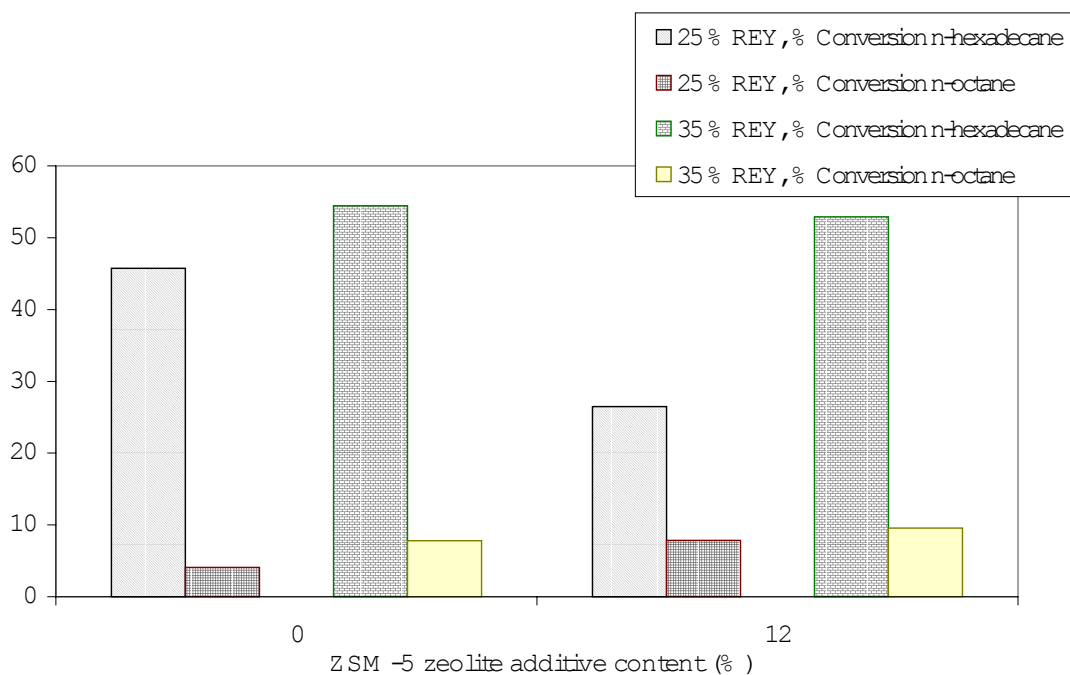| Properties	Values
Purity	98.0 %
Molecular weight	226.46
Boiling point	283-286 $^{\circ}$C
Density at 20 $^{\circ}$C	0.773 g/m^3

Figure 4-30 Effect of additive ZSM-5 zeolite content in REY catalyst on
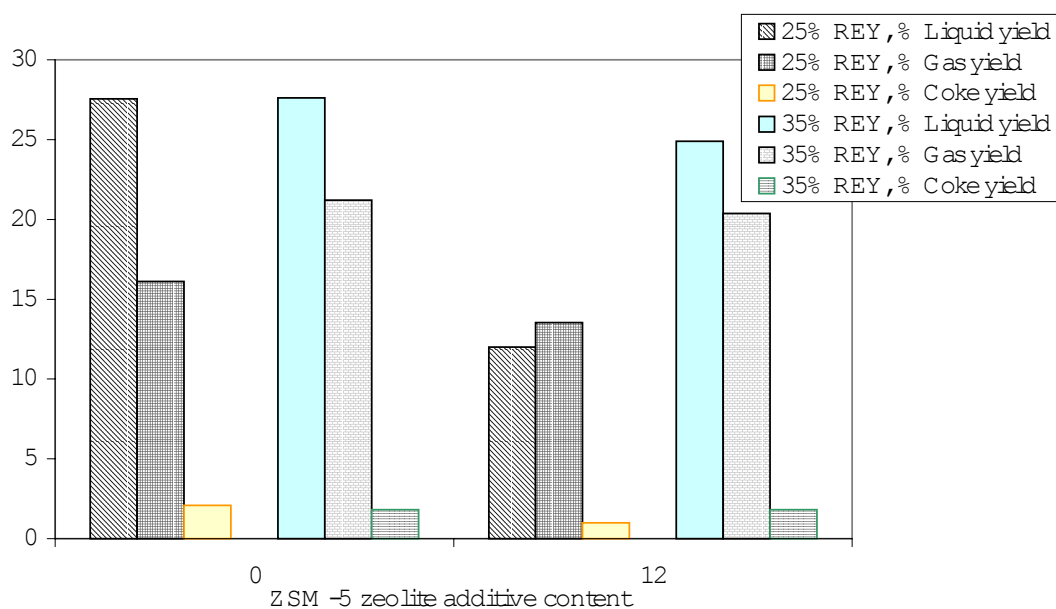% Conversion.

Figure 4-31 Effect of additive ZSM-5 zeolite content in REY catalyst on
% Liquid yield, % Gas yield and % Coke yield.

Figure 4-30 shows the percent conversion of n-hexadecane cracking on 25% and 35% REY catalyst and with 12% additive ZSM-5 zeolite. The % conversions of n-octane cracking on the same catalysts are also compared. The percent conversion of n-hexadecane decreases with increasing the ZSM-5 zeolite content and results in lower liquid yield, gas yield and coke yield in quite the same proportion (Figure 4-31). However, the percent conversions of n-hexadecane are 2 to 4 times higher than n-octane.
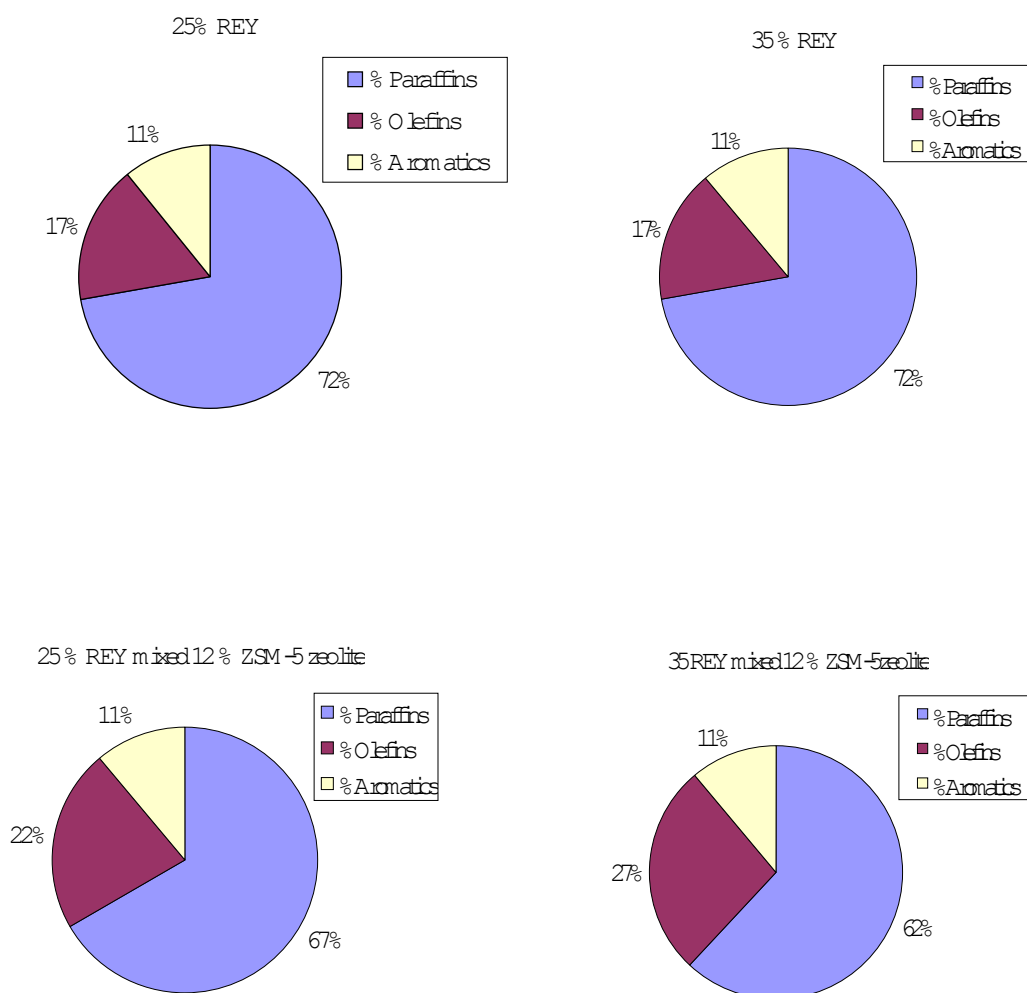

Figure 4-32 Effect of additive ZSM-5 zeolite content in REY catalyst on
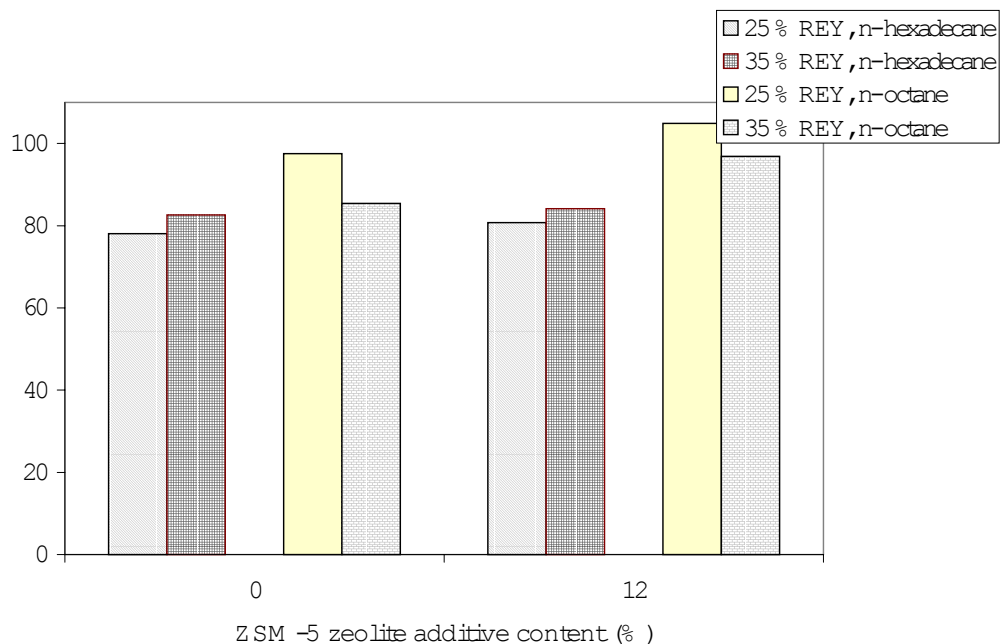% Paraffins, % Olefins and % Aromatics in liquid product.

Figure 4-33 Effect of additive ZSM-5 zeolite content in REY catalyst on Research
Octane Number.

The liquid products obtained from n-hexadecane cracking on mixed ZSM-5 catalysts have higher olefins composition than REY catalyst (Figure 4-32), while aromatics composition remains in the same level. So, the research octane number of gasoline obtained from mixed ZSM-5 and REY catalyst cracking is higher than the one obtained from only REY zeolite cracking (Figure 4-33). Gas composition obtained from mixed ZSM-5 catalyst cracking also shows the increasing of olefins content same behavior. So, from these results, we can conclude that ZSM-5 zeolite plays the important roles in lower catalytic activity and lower hydrogen transfer reaction which results in higher research octane number. Additive ZSM-5 zeolite enhances olefins composition in both n-octane and n-hexadecane cracking.
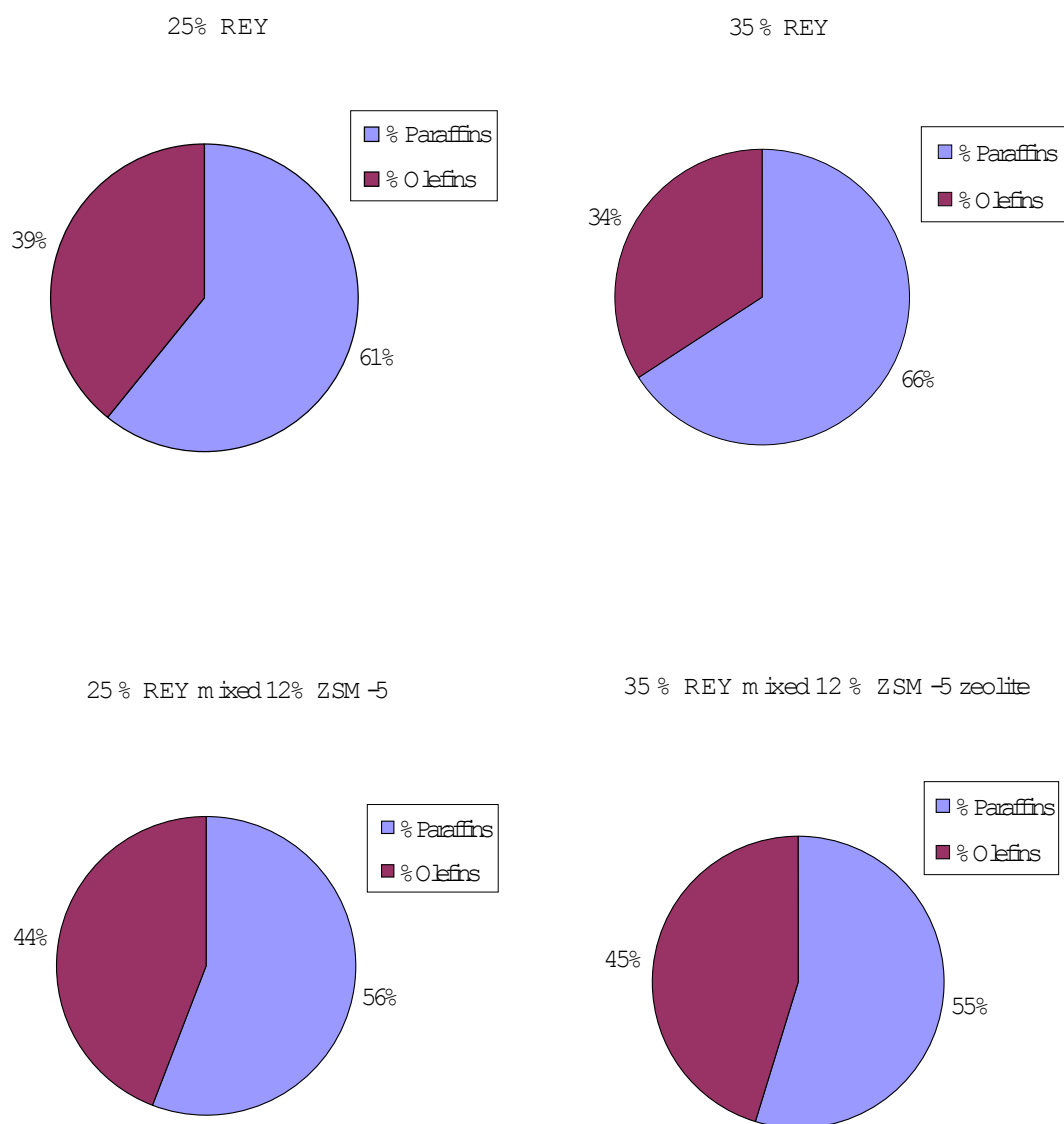
25% REY

35 % REY

25 % REY mixed 12% ZSM-5

35 % REY mixed 12 % ZSM –5 zeolite

Figure 4-34 Effect of additive ZSM-5 zeolite content in REY catalyst on gas

Composition.