

CHAPTER IV

RESULTS AND DISCUSSION

The study of catalytic cracking of waste lubricating oil over Fe/AC, CoMo/Al₂O₃ and HZSM-5 catalysts were investigated in three parts as followed:

Part I : Experimental design – 2³ factorial design was used to determine the factors that affected on liquid yield. Three factors consisted of temperature, initial pressure of hydrogen and amount of catalyst. Reaction time was fixed at 60 minutes. Each factor was presented in two levels.

Part II: Univariate experiment – the main factors were varied for studying the influence on products yield and composition in liquid product. An optimum condition of cracking waste lubricating oil over various catalysts was found in this part.

Part III: Kinetic study – kinetic parameters: order of reaction, rate constant, and activation energy, were studied

4.1 Experimental design and analysis [32]

The 2^k design is particularly useful in the early stages of experimental work. By this technique provide the smallest number of runs, k is the factors of the study.

In case of three factors, A, B, and C, at two levels, the design is called 2³ factorial design. Using the “+ and –” notation to represent the low and high levels of the factors, we may list the eight runs in 2³ design as shown in Table 4.1. This is

sometimes called the design matrix. We wrote the treatment combinations in standard order as (1), a, b, ab, c, ac, bc and abc.

In this study, three factors, temperature (A), initial pressure of hydrogen(B) and amount of catalyst (base on weight of feed) (C) were chosen because it is well known that these variables are the most significant controlling factors influencing oil yields in the catalytic cracking process. The reaction time was fixed at 60 minutes. Table 4.2 and 4.3 showed factors, coded factors, and factor levels of each experiment.

Table 4.1 The design matrix and labels of treatment combinations.

Run	A	B	C	Labels
1	-	-	-	(1)
2	+	-	-	a
3	-	+	-	b
4	+	+	-	ab
5	-	-	+	c
6	+	-	+	ac
7	-	+	+	bc
8	+	+	+	abc

Table 4.2 Factors, coded factors and factor levels for catalytic cracking waste lubricating oil over Fe/AC and CoMo/Al₂O₃ catalyst experiment.

Factor	Coded factor	Factor levels	
		Low (-)	High (+)
Temperature (°C)	A	375	425
Initial pressure of hydrogen (bar)	B	5	10
Amount of catalyst (wt%)	C	1	5

Table 4.3 Factors, coded factors and factor levels for catalytic cracking waste lubricating oil over HZSM-5 catalyst experiment.

Factor	Coded factor	Factor levels	
		Low (-)	High (+)
Temperature (°C)	A	375	425
Initial pressure of hydrogen (bar)	B	5	10
Amount of catalyst (wt%)	C	0.1	1.0

The table of plus and minus signs for the contrast constants and the liquid yield from cracking of waste lubricating oil over three types of catalyst was shown in Table 4.4. From these contrasts, we may estimate the 7 factorial effects and the sum of squares of liquid yield obtained from Fe/AC cracking shown in Table 4.5.

The normal probability plot of these effects is shown in Figure 4.1. All of the effects that lie along the straight line were negligible, whereas the large effects were

far from the line. The important effects that emerge from this analysis were the main effect of A, and C and the BC interaction.

The analysis of variance (ANOVA) and F-test at 95% confidence were used to confirm the magnitude of main effects as shown in Table 4.6. Statistical F-tests was used to determine the significance of effects. The sum of squares of the effects and that of the error were calculated, then the resulting F-values (F_{exp}) were calculated. For any factors to be statistically significant, the absolute value of F_{exp} should be greater than the F-value (F_{tab}) obtained from the standard F-distribution with a 95% confidence.

Table 4.4 Contrast constant for 2^3 factorial design experiment from catalytic cracking of waste lubricating oil over Fe/AC, CoMo/Al₂O₃ and HZSM-5.

	A	B	AB	C	AC	BC	ABC	Liquid yield (%)		
								Fe/AC	CoMo/ Al ₂ O ₃	HZSM-5
(1)	-	-	+	-	+	+	-	83.69	89.70	89.19
a	+	-	-	-	-	+	+	69.12	63.48	73.83
b	-	+	+	-	+	-	+	80.82	87.16	86.43
ab	+	+	-	-	-	-	-	63.36	60.21	70.58
c	-	-	+	+	-	-	+	70.81	76.18	81.08
ac	+	-	-	+	+	-	-	58.32	60.11	62.59
bc	-	+	+	+	-	+	-	80.89	79.33	85.24
abc	+	+	-	+	+	+	+	58.88	55.10	58.67

Table 4.5 Factor effect estimates and sum of square for the catalytic cracking of waste lubricating oil over Fe/AC.

Factor	Contrast	Effect estimate	Sum of square	%Contribution
A	-66.53	-16.6325	553.28	76.38
B	2.01	0.5025	0.50	0.07
AB	-12.41	-3.1025	19.25	2.66
C	-28.09	-7.0225	98.63	13.62
AC	-2.47	-0.6175	0.76	0.11
BC	19.27	4.8175	46.42	6.41
ABC	-6.63	-1.6575	5.4946	0.76

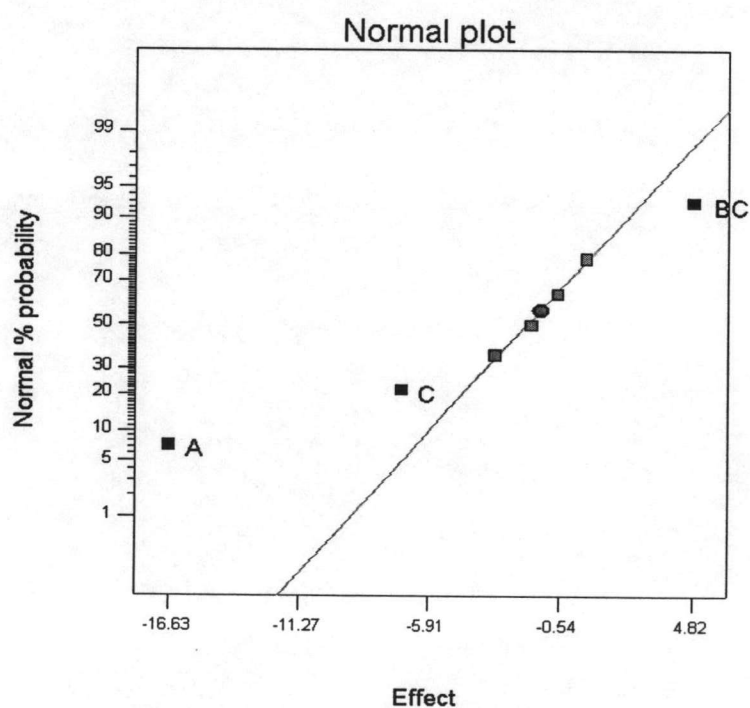


Figure 4.1 Normal probability plot of the effects for the 2^3 factorial of catalytic cracking of waste lubricating oil over Fe/AC.

Table 4.6 Analysis of variance from catalytic cracking of waste lubricating oil over Fe/AC.

Source of variation	Sum of squares	Degrees of Freedom	Mean square	F_{exp}	F_{tab}
A	553.28	1	553.28	85.09	> 7.71
C	98.63	1	98.63	15.17	> 7.71
BC	46.42	1	46.42	7.14	< 7.71
Error	26.01	4	6.50		
Total	724.34				

From analysis of variance in Table 4.6, F_{exp} of the main effects A and C were greater than the F_{tab} . It can be concluded that A (temperature) and C (amount of catalyst) were significantly affected on liquid yield, whereas BC was insignificantly affected on liquid yield from catalytic cracking of waste lubricating oil over the Fe/AC catalyst.

In the same way, contrast constant, factor effect estimate and analysis of variance were illustrated in Table 4.7 to Table 4.10 and Figure 4.2 and 4.3 for catalytic cracking of waste lubricating oil over CoMo/Al₂O₃ and HZSM-5 catalyst.

Table 4.7 Factor effect estimates and sum of square for the catalytic cracking of waste lubricating oil over CoMo/Al₂O₃.

Factor	Contrast	Effect estimate	Sum of square	%Contribution
A	-93.47	-23.37	1092.08	87.36
B	-7.67	-1.92	7.35	0.59
AB	-8.89	-2.22	9.88	0.79
C	-29.83	-7.46	111.23	8.90
AC	12.87	3.22	20.70	1.65
BC	3.95	0.99	1.95	0.15
ABC	-7.43	-1.86	6.90	0.55

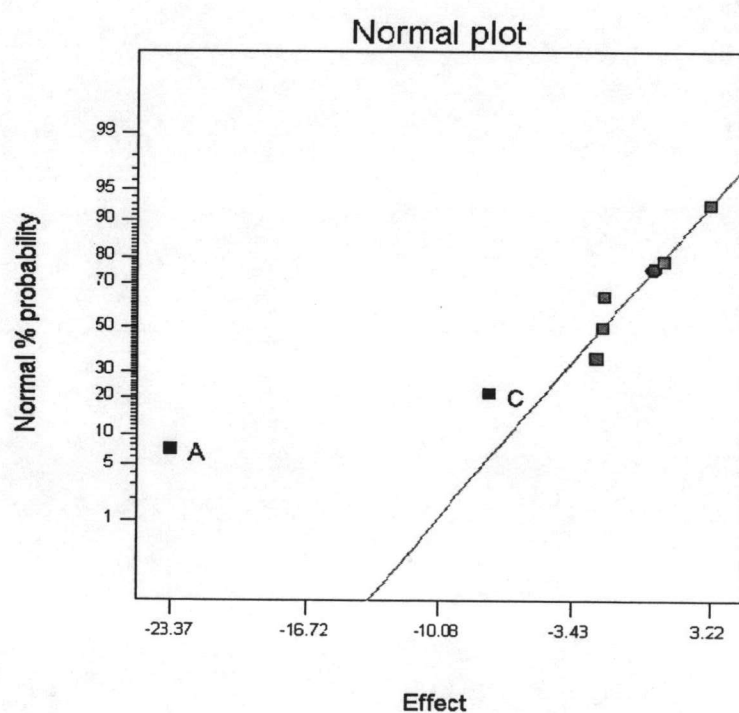


Figure 4.2 Normal probability plot of the effects for the 2³ factorial of catalytic cracking of waste lubricating oil over CoMo/Al₂O₃.

Table 4.8 Analysis of variance from catalytic cracking of waste lubricating oil over CoMo/Al₂O₃.

Source of variation	Sum of squares	Degrees of Freedom	Mean square	F _{exp}	F _{tab}
A	1092.08	1	1092.08	116.70	> 7.71
C	111.23	1	111.23	11.89	> 7.71
Error	46.79				
Total	1250.10	5	9.36		

Table 4.9 Factor effect estimates and sum of square for the catalytic cracking of waste lubricating oil over HZSM-5

Factor	Contrast	Effect estimate	Sum of square	%Contribution
A	-76.27	-19.07	727.14	80.07
B	-5.77	-1.44	4.16	0.46
AB	-8.57	-2.14	9.18	1.01
C	-32.45	-8.11	131.62	14.49
AC	-13.85	-3.46	26.98	2.64
BC	6.25	1.56	4.88	0.54
ABC	-7.59	-1.90	7.20	0.79

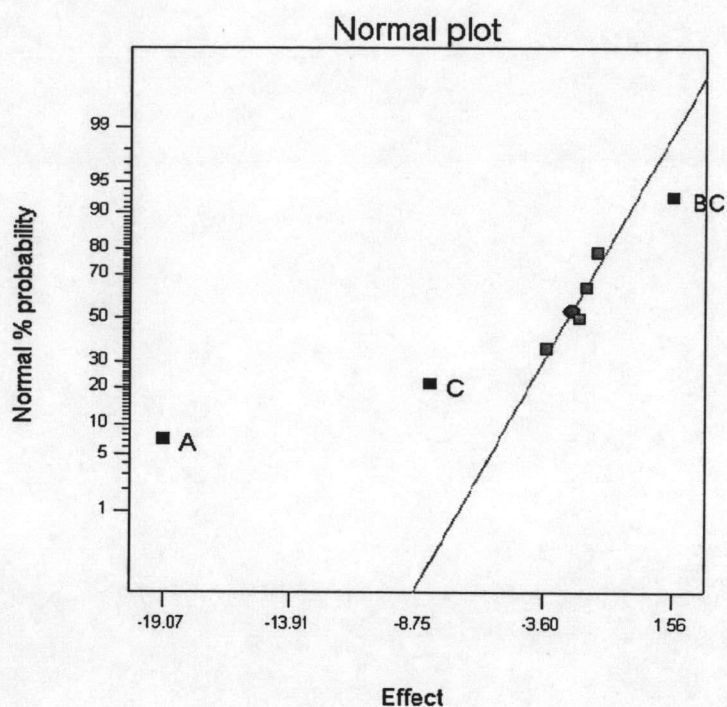


Figure 4.3 Normal probability plot of the effects for the 2^3 factorial of catalytic cracking of waste lubricating oil over HZSM-5.

Table 4.10 Analysis of variance from catalytic cracking of waste lubricating oil over HZSM-5.

Source of variation	Sum of squares	Degrees of Freedom	Mean square	F_{exp}	F_{tab}
A	727.14	1	727.14	65.33	> 7.71
C	131.62	1	131.62	11.83	> 7.71
BC	4.88	1	4.88	0.44	< 7.71
Error	44.52	4	11.13		
Total	908.17				

From analysis of variance as shown in Table 4.8 and 4.10, the main effects that influence liquid yield obtained from cracking of waste lubricating oil by using CoMo/Al₂O₃ and HZSM-5 were temperature (A) and amount of catalyst (C). These results were similar to that of cracking by Fe/AC.

The cracking of waste lubricating oil was performed at various temperature; 375, 390, 410 and 425 °C. The amount of Fe/AC and CoMo/Al₂O₃ was 1, 3 and 5 wt% based on weight of waste lubricating oil, while the amount of HZSM-5 was 0.1, 0.5 and 1 wt%. The initial pressure of hydrogen was not significant parameter on liquid yields, therefore the initial pressure of hydrogen was chosen at 5 bar for the univariate experiment.

4.2 Univariate Experiment

As shown in the 2^3 factorial experiment, temperature and amount of catalyst were main parameter effect on liquid yield. This experiment aimed to investigate the influence of main effect on product yield from catalytic cracking and composition in the liquid product. The reaction time at a suitable temperature and amount of catalyst was also studied.

4.2.1 Cracking of waste lubricating oil over Fe/AC

The cracking of waste lubricating oil over Fe/AC catalyst was performed at various reaction temperatures; 375, 390, 410 and 425 °C with a fixed amount of Fe/AC at 1, 3 and 5 wt% under an initial hydrogen pressure of 5 bar and a reaction time of 60 minutes.

4.2.1.1 Effect of reaction temperature on product yield and composition of liquid product

Gas yield, solid yield and the composition of products as a function of temperature at different amount of catalyst are presented in Figure 4.4 to Figure 4.6.

From the experimental results (Figure 4.4 to Figure 4.6), it was demonstrated that when temperature increased from 375 to 410°C, yield of gas, gasoline, kerosene and light gas oil slightly increased while gas oil and long residue slightly decreased.

When the reaction was heated up to 410 °C, percent yield of all compositions were largely changed, especially amount of gasoline.

It can be concluded that low reaction temperature (375-390 °C) was not suitable condition for cracking because the amount of all compositions in liquid product were insignificantly changed. At high temperature (425 °C), light hydrocarbon such as gasoline and kerosene were largely increased because the large amount of energy was supplied to break down molecules of heavy into smaller molecule. In the same way, energy input to the reaction was used to overcome the activation energy. Higher energy supplied to the reaction caused reactant molecules had higher kinetic energy, then, the collision of their molecules were increased. Therefore, a lot of light hydrocarbon molecules were produced.

Kerosene and light gas oil were also important liquid fuel like gasoline. Then we should determined the optimum temperature by considering liquid yield, gasoline yield and sum of three composition including gasoline, kerosene and light gas oil. It was found that optimum temperature for cracking waste lubricating oil over Fe/AC was 425 °C at any amount of Fe/AC. It can be explained that at this temperature, the gasoline yield and sum of gasoline, kerosene and light gas oil were higher than that at low temperature.

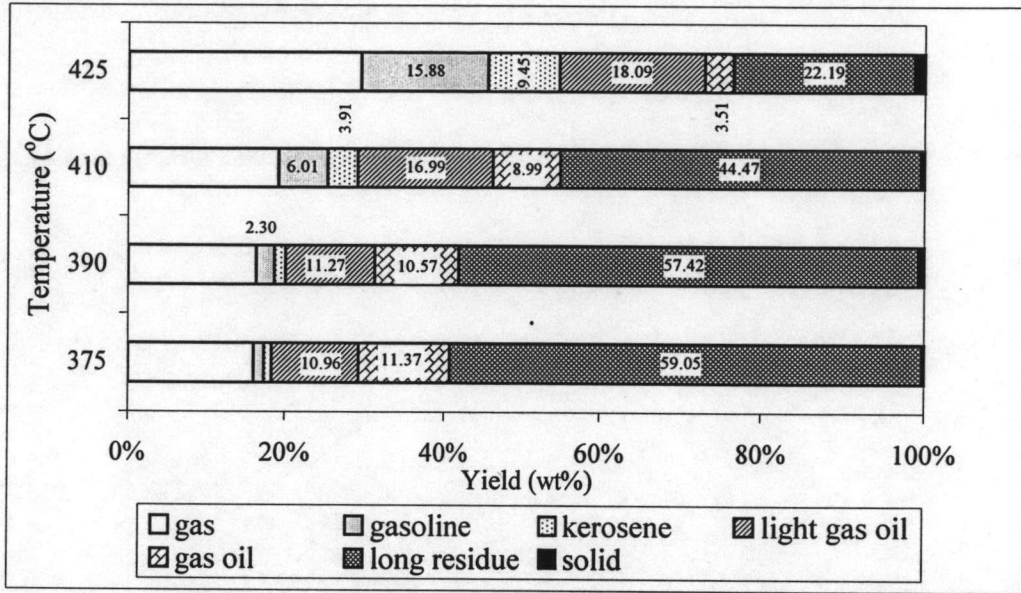


Figure 4.4 Product yield and composition of liquid product as a function of reaction temperature over Fe/AC (Pressure 5 bar, reaction time 60 minutes and 1 wt% Fe/AC).

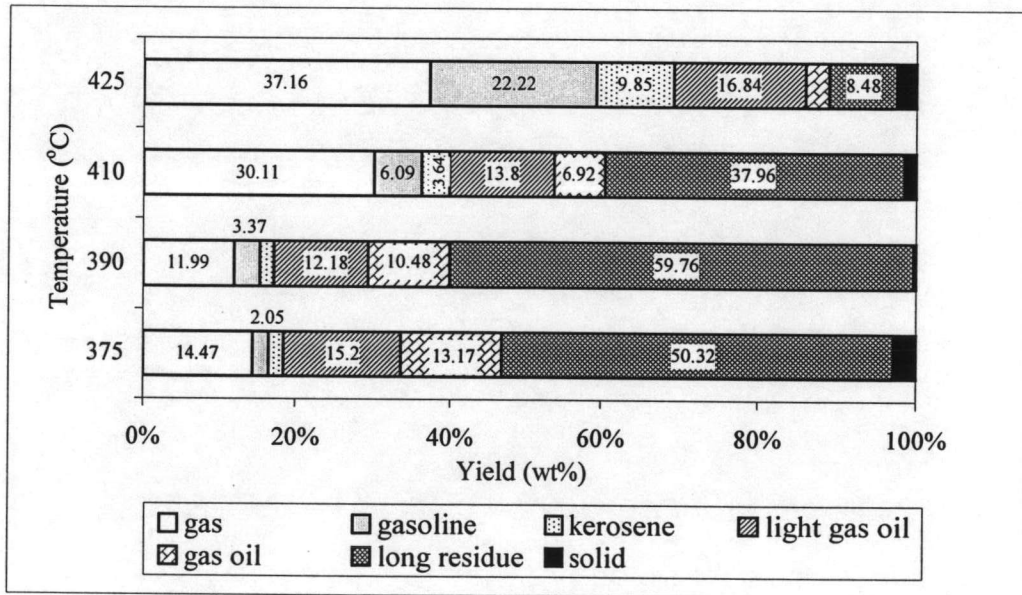


Figure 4.5 Product yield and composition of liquid product as a function of reaction temperature over Fe/AC (Pressure 5 bar, reaction time 60 minutes and 3 wt% Fe/AC).

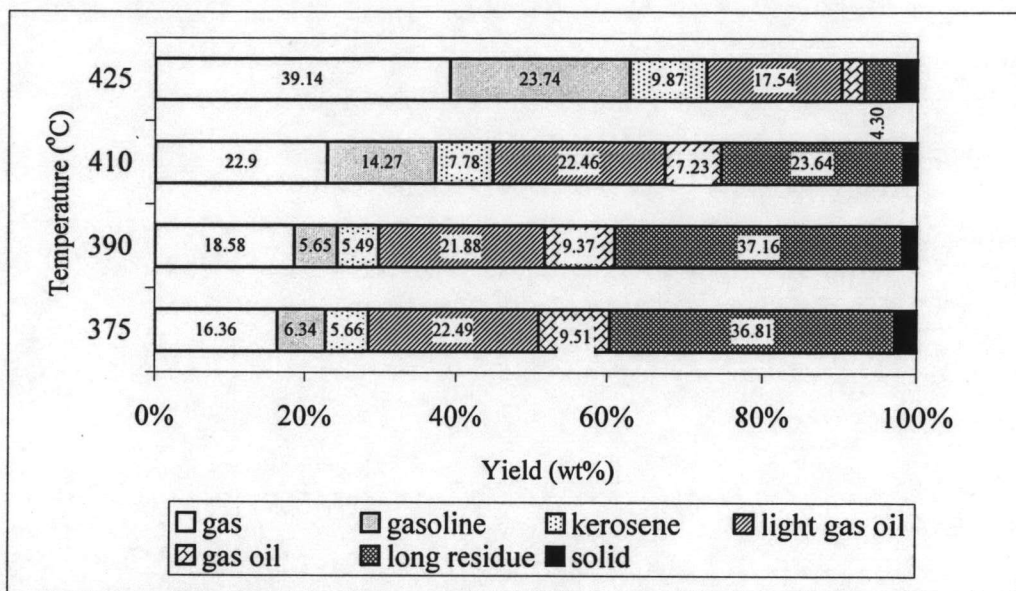


Figure 4.6 Product yield and composition of liquid product as a function of reaction temperature over Fe/AC (Pressure 5 bar, reaction time 60 minutes and 5 wt% Fe/AC).

4.3.1.2 Effect of the amount of catalyst on product yield and composition of liquid product

Gas yield, solid yield and composition of liquid product from cracking of waste lubricating oil over Fe/AC as a function of amount of catalyst at temperature of 425 °C is shown in Figure 4.7. In the range of 1 to 5 wt% of Fe/AC and reaction time of 60 minutes, gasoline significantly increased from 15.88% to 23.74%. The sum of gasoline, kerosene and light gas oil increased from 43.42% to 51.15%. It could be suggested that the high amount of catalyst increased the cracking reaction because it has more contacting the surface area and active site of catalyst. Hence, it caused the long chain hydrocarbon to break down a small hydrocarbon molecule.

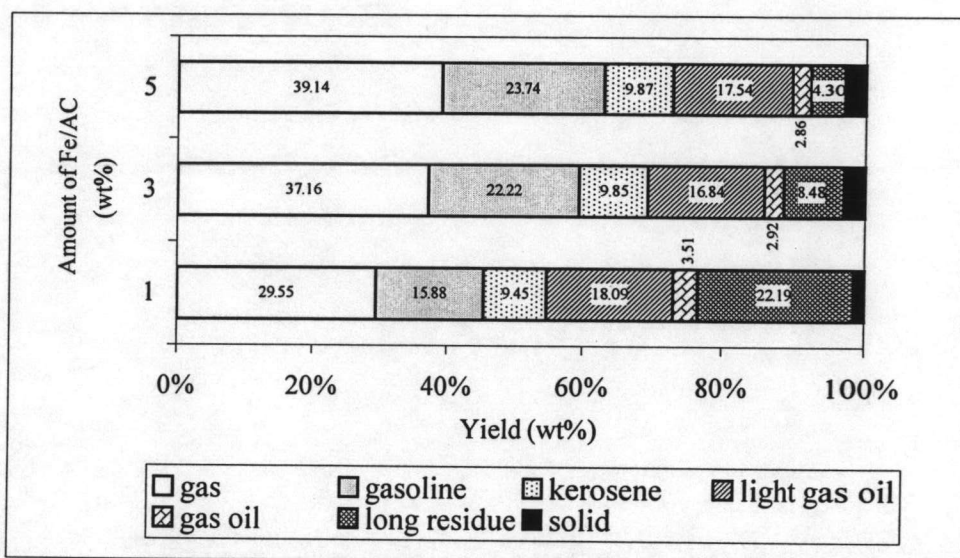


Figure 4.7 Product yield and composition of liquid product as a function of amount of Fe/AC (Pressure 5 bar, reaction time 60 minutes and temperature of 425 °C).

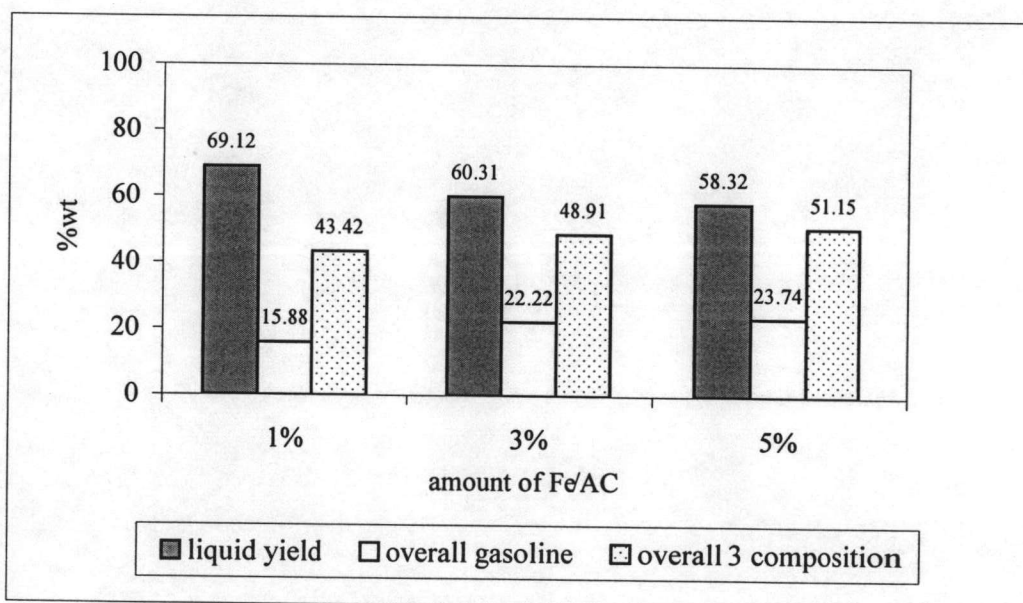


Figure 4.8 Liquid yield, gasoline and sum of 3 compositions as a function of amount of Fe/AC (Pressure 5 bar, reaction time 60 minutes and reaction temperature of 425 °C).

Figure 4.8 confirmed that cracking by using 5wt% of Fe/AC gave gasoline yield and the sum of gasoline, kerosene and light gas oil higher than that of 1 and 3 wt% of Fe/AC. We determine the optimum amount of Fe/AC was 5 wt%.

4.2.1.3 Effect of reaction time on product yield and composition of liquid product

The cracking of waste lubricating oil over Fe/AC were performed at optimum temperature of 425 °C with amount of Fe/AC of 5 wt% under initial hydrogen pressure of 5 bar and reaction time varied from 10 to 90 minutes. Product yield, composition of liquid product and sum of three compositions are shown in Figure 4.9 and Figure 4.10.

From the experimental results (Figure 4.9 and Figure 4.10), it was found that when reaction time increase from 10 to 90 minutes, liquid yield was decreased from 87.43% to 52.69%, in the mean time gas yield was increased from 11.55% to 45.54%. From Figure 4.10, at reaction time 60 minutes showed the quantities of gasoline, kerosene and light gas oil were higher than that of 90 minutes, on the other hand, long residue decreased in the same direction.

The yield of gasoline and sum of the three compositions increased with reaction time from 10 to 60 minutes, and after that they slightly decreased with reaction time from 60 to 90 minutes as shown in Figure 4.10. It can be explained that longer reaction time allowed the longer contact time between reactant molecules and catalyst. Hence, cracking of long chain hydrocarbon, i.e., long residue and gas oil to lighter molecule, i.e., light gas oil, kerosene, gasoline and gas was increased. Nevertheless, solid residue yield increasing with increase reaction time, it was implied

that the surface of catalyst was contaminated with coking or poisoning from heavy metal present in the waste lubricating oil [27]. For this reason, the activity of the catalyst was lost and decreasing of gasoline yield and sum of three compositions at higher reaction time may have occurred.

It can be concluded that the reaction time of 60 minutes was the optimum condition for cracking of waste lubricating oil over Fe/AC was 60 minutes.

In summary, the optimum condition for cracking reaction of waste lubricating oil over Fe/AC was a temperature of 425 °C, initial hydrogen pressure of 5 bar, the amount of Fe/AC 5 wt% with a reaction time of 60 minutes.

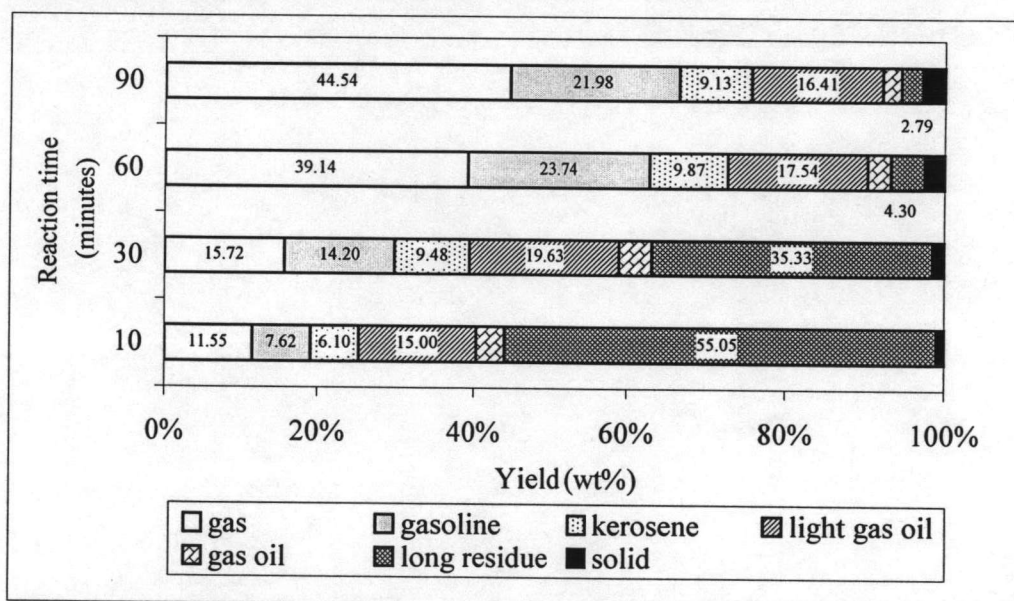


Figure 4.9 Product yield and composition of liquid product as a function of reaction time (Pressure 5 bar, temperature of 425 °C and amount of Fe/AC 5 wt%).

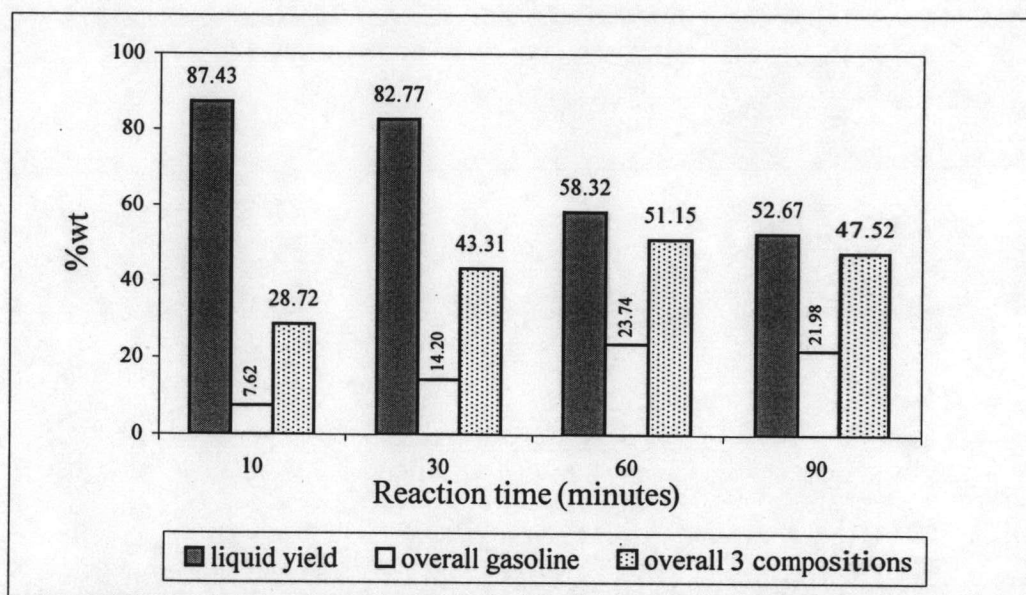


Figure 4.10 Liquid yield, gasoline and sum of 3 compositions as a function of reaction time (Pressure 5 bar, reaction temperature of 425 °C and amount of Fe/AC 5 wt%).

4.2.2 Cracking of waste lubricating oil over CoMo/Al₂O₃

The cracking of waste lubricating oil with a CoMo/Al₂O₃ catalyst was operated at various different reaction temperatures (375, 390, 410 and 425 °C) with CoMo/Al₂O₃ different amount (1, 3 and 5 wt% based on weight of waste oil) under an initial hydrogen pressure of 5 bar and reaction time of 60 minutes.

4.2.2.1 *Effect of reaction temperature on product yield and composition of liquid product*

Figure 4.11 to Figure 4.13 represent the effect of reaction temperature on product yield and composition of liquid product at 1, 3 and 5 wt% of CoMo/Al₂O₃,

respectively. The result showed that gas, gasoline and kerosene continuously increased with increasing temperature in the range of 375 to 425 °C. Gas oil and long residue continuously decreased with reaction temperatures. At 425 °C, overall yield of gasoline, kerosene and light gas oil was higher than that of lower temperature. It can be concluded that the optimum temperature for cracking of waste lubricating oil using a CoMo/Al₂O₃ catalyst was 425 °C.

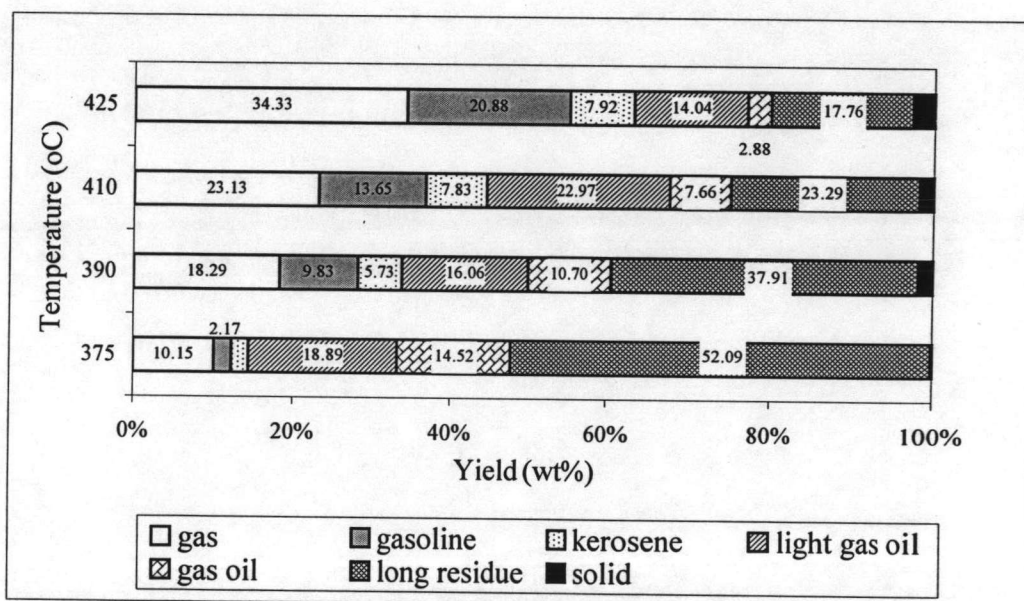


Figure 4.11 Product yield and composition of liquid product as a function of reaction temperature over CoMo/Al₂O₃ (Pressure 5 bar, reaction time 60 minutes and 1 wt% CoMo/Al₂O₃).

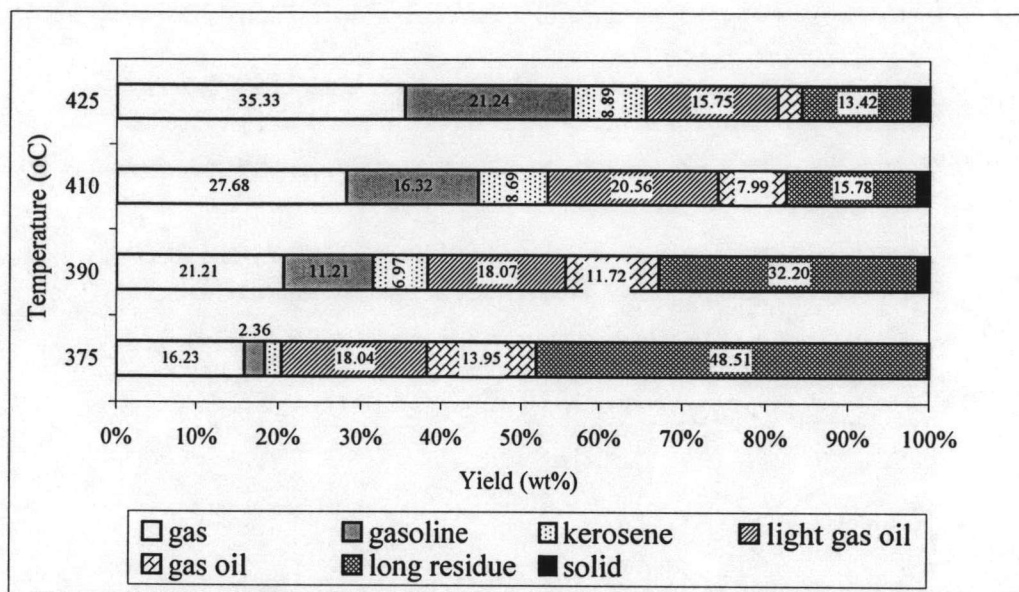


Figure 4.12 Product yield and composition of liquid product as a function of reaction temperature over CoMo/Al₂O₃ (Pressure 5 bar, reaction time 60 minutes and 3 wt% CoMo/Al₂O₃).

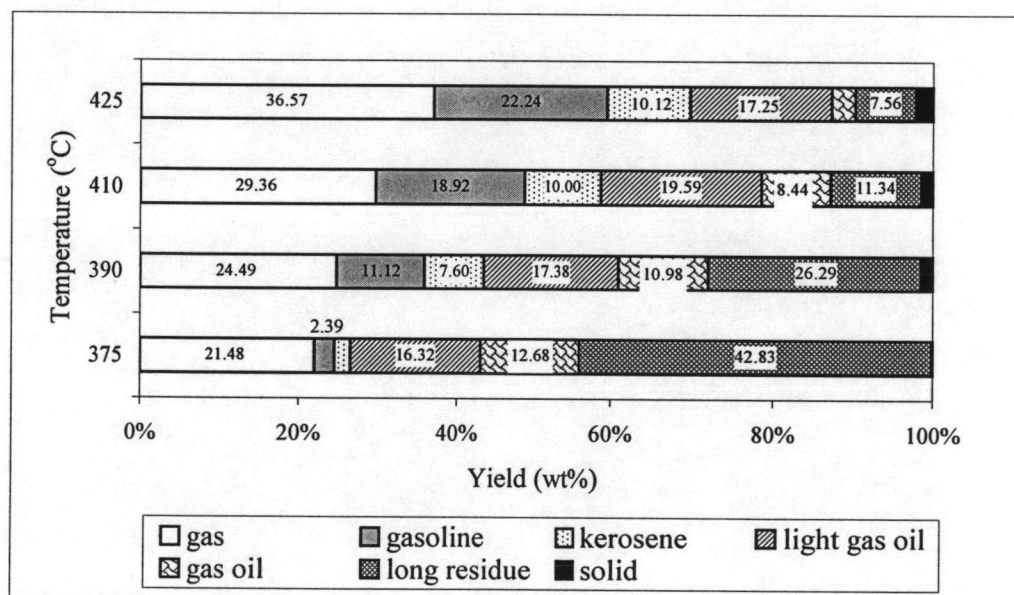


Figure 4.13 Product yield and composition of liquid product as a function of reaction temperature over CoMo/Al₂O₃ (Pressure 5 bar, reaction time 60 minutes and 5 wt% CoMo/Al₂O₃).

4.2.2.2 Effect of the amount of catalyst on product yield and composition of liquid product

The product yield and the composition of liquid product at 425 °C and amount of CoMo/Al₂O₃ of 1, 3 and 5 wt% was shown in Figure 4.14. It can be noticed that gas, solid, gasoline, kerosene and light gas oil slightly increased, gas oil remained constant and the long residue decreased with increasing temperature. In the range of catalyst content of 1 to 3 wt%, yield of gasoline changed from 20.88 % to 22.24%, and the sum of gasoline, kerosene and light gas oil increased from 42.84% to 49.61% as shown in Figure 4.15. It can be concluded that 5 wt% of CoMo/Al₂O₃ was the optimum catalyst content because this condition gave the highest gasoline content and sum of three composition.

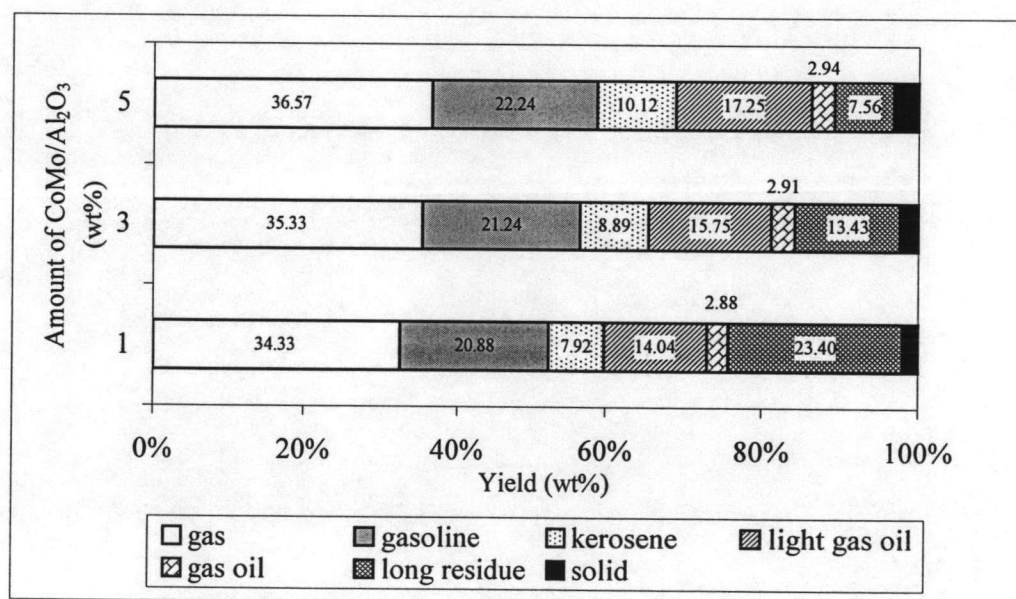


Figure 4.14 Product yield and composition of liquid product as a function of amount of CoMo/Al₂O₃ (Pressure 5 bar, reaction time 60 minutes and temperature of 425 °C).

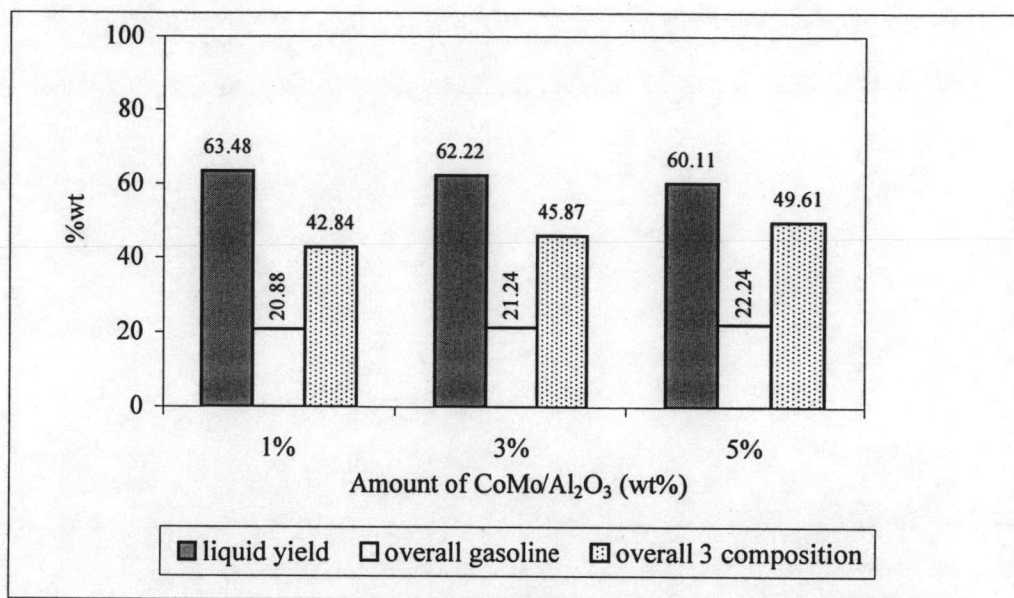


Figure 4.15 Liquid yield, gasoline and sum of 3 compositions as a function of amount of CoMo/Al₂O₃ (Pressure 5 bar, reaction time 60 minutes and reaction temperature of 425 °C).

4.2.2.3 Effect of reaction time on product yield and composition of liquid product

The cracking of waste lubricating oil with CoMo/Al₂O₃ was carried at optimum condition of 425 °C and amount of CoMo/Al₂O₃ of 5 wt% with an initial hydrogen pressure of 5 bar and reaction time of 10, 30, 60 and 90 minutes to investigate the influence of reaction time on product yield and composition of the liquid product.

Figure 4.16 showed the product yield and composition of the liquid product as a function of reaction time. It can be seen that yield of gasoline, kerosene and light gas oil increased with a reaction time from 10 and 60 minutes. When reaction time

increased from 60 to 90 minutes, they slightly increased. On the other hand, gas oil and long residue decreased with reaction time from 10 to 90 minutes.

The relation of yield of gasoline and sum of three compositions with reaction time is demonstrated in Figure 4.17. It is observed that at 60 minutes, yield of gasoline and sum of three compositions is not difference from that at 90 minutes.

Therefore, the optimum reaction time was chosen at 60 minutes.

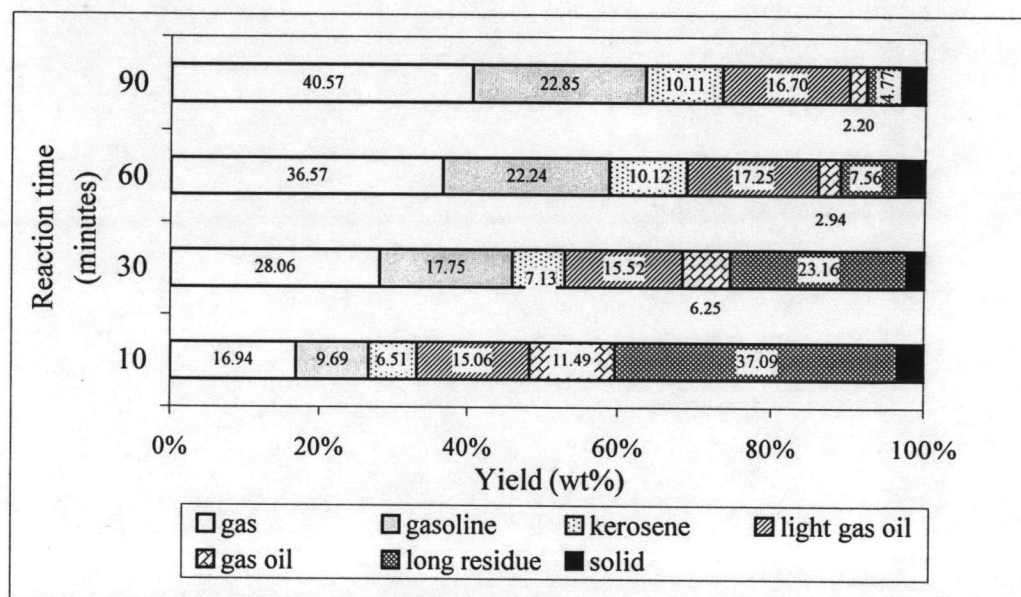


Figure 4.16 Product yield and composition of liquid product as a function of reaction time (Pressure 5 bar, temperature of 425 °C and amount of CoMo/Al₂O₃ 5 wt%).

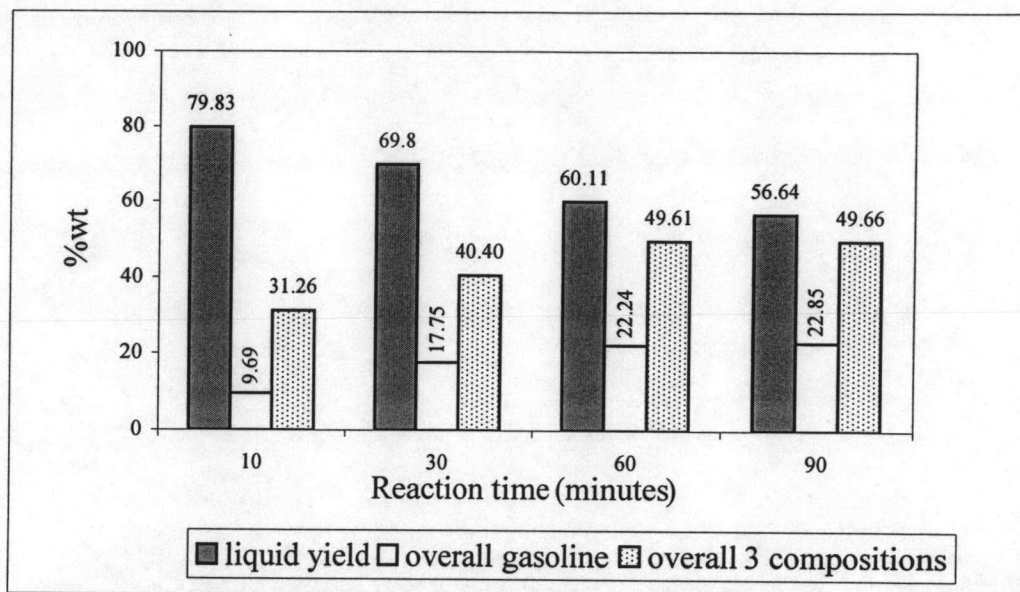


Figure 4.17 Liquid yield, gasoline and sum of 3 compositions as a function of reaction time (Pressure 5 bar, reaction temperature of 425 °C and amount of CoMo/Al₂O₃ 5 wt%).

4.2.3 Cracking of waste lubricating oil over HZSM-5

The cracking of waste lubricating oil with HZSM-5 catalyst was studied at temperatures of 375, 390, 410 and 425 °C with the amount of HZSM-5 of 0.1, 0.5 and 1.0 wt% based on the weight of waste oil. Initial hydrogen pressure and reaction time were kept at 5 bar and 60 minutes, respectively.

4.2.3.1 *Effect of reaction temperature on product yield and composition of liquid product*

The effects of reaction temperature on product yield and composition in liquid products at different amount of HZSM-5 are shown in Figure 4.18 to Figure 4.20. It can be seen from Figure 4.18 to Figure 4.20 that the yield of gas, gasoline, kerosene

and light gas oil increased with increasing temperature, whereas gas oil and long residue decreased. Moreover, the sum of three composition also increased with reaction temperature. Consequently, we found the suitable temperature for cracking waste lubricating oil by using HZSM-5 was 425 °C because this temperature gave a higher amount of gasoline, kerosene, and light gas oil, than that of temperatures below 425 °C.

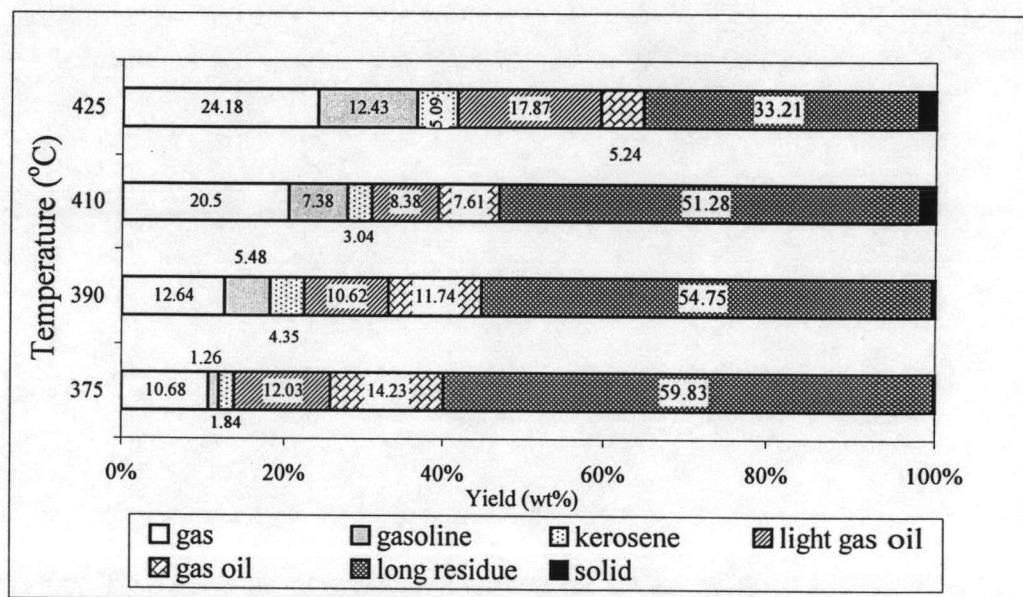


Figure 4.18 Product yield and composition of liquid product as a function of reaction temperature over HZSM-5 (Pressure 5 bar, reaction time 60 minutes and 0.1 wt% HZSM-5).

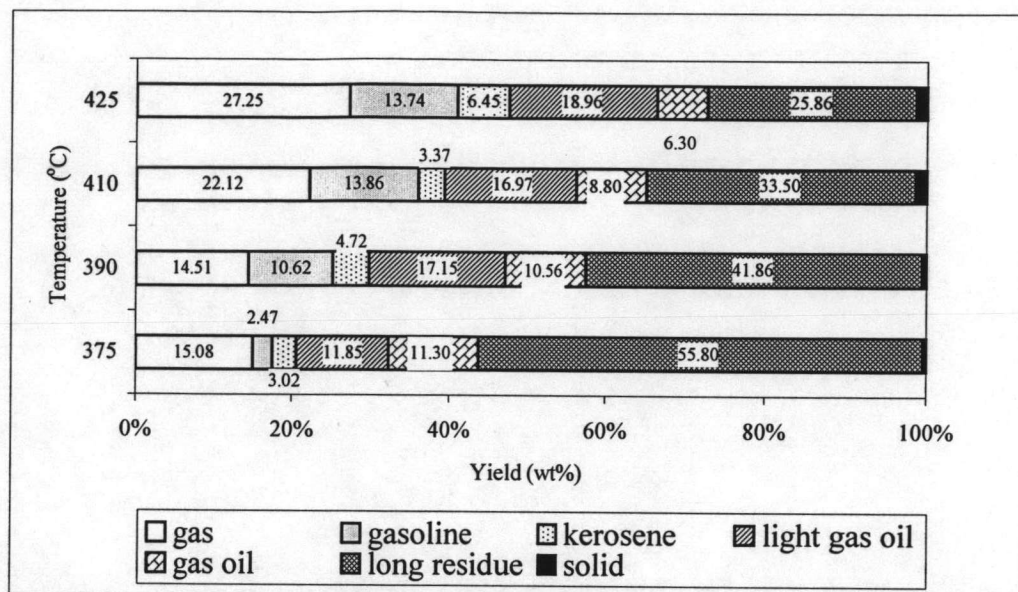


Figure 4.19 Product yield and composition of liquid product as a function of reaction temperature over HZSM-5 (Pressure 5 bar, reaction time 60 minutes and 0.5 wt% HZSM-5).

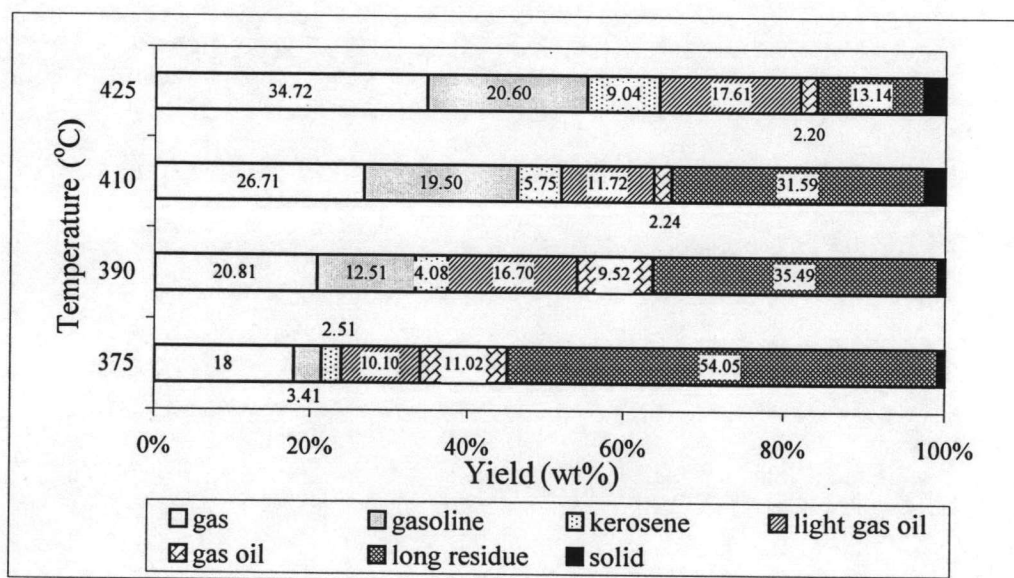


Figure 4.20 Product yield and composition of liquid product as a function of reaction temperature over HZSM-5 (Pressure 5 bar, reaction time 60 minutes and 1 wt% HZSM-5).

4.2.3.2 Effect of the amount of catalyst on product yield and composition of liquid product

As shown in 4.2.3.1, the optimum temperature was 425 °C. This study aimed to investigate the effect of the amount of HZSM-5 on product yield and composition of the liquid product at optimum temperature. Figure 4.21 presented product yield and composition in the liquid product as a function of amount of HZSM-5. It was found that in the range of 0.1 to 1 wt% of HZSM-5, gasoline, kerosene, light gas oil, gas and solid yield increased. For determining the optimum amount of HZSM-5, yield of gasoline and sum of three composition are shown in Figure 4.22. We found that from the range of HZSM-5 0.1 to 1wt%, gasoline increased from 12.43% to 20.60%, and the sum of three composition increased from 35.38% to 47.25% From this result, we determined the optimum amount of HZSM-5 was 1 wt%.

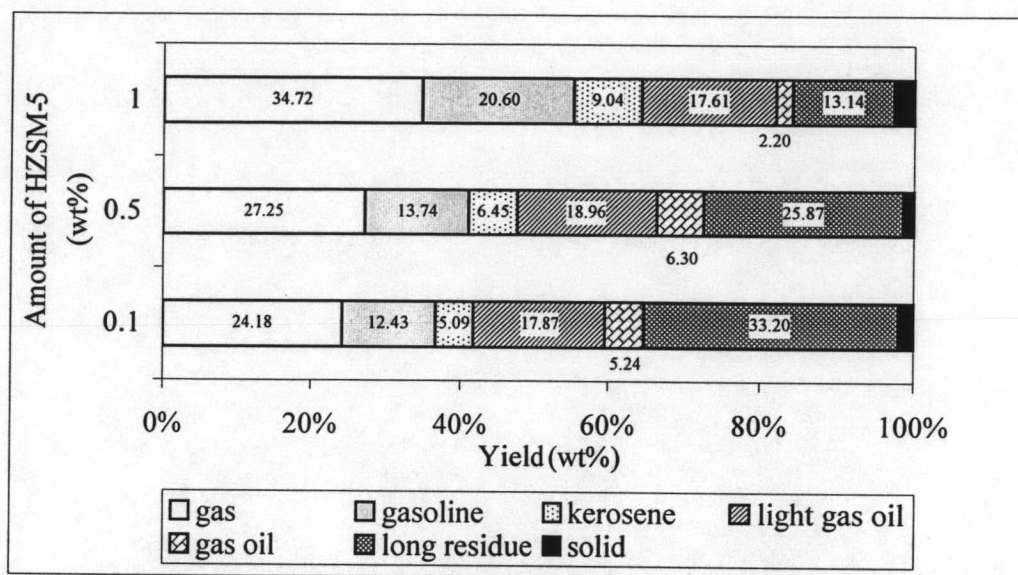


Figure 4.21 Product yield and composition of liquid product as a function of amount of HZSM-5 (Pressure 5 bar, reaction time 60 minutes and temperature of 425 °C).

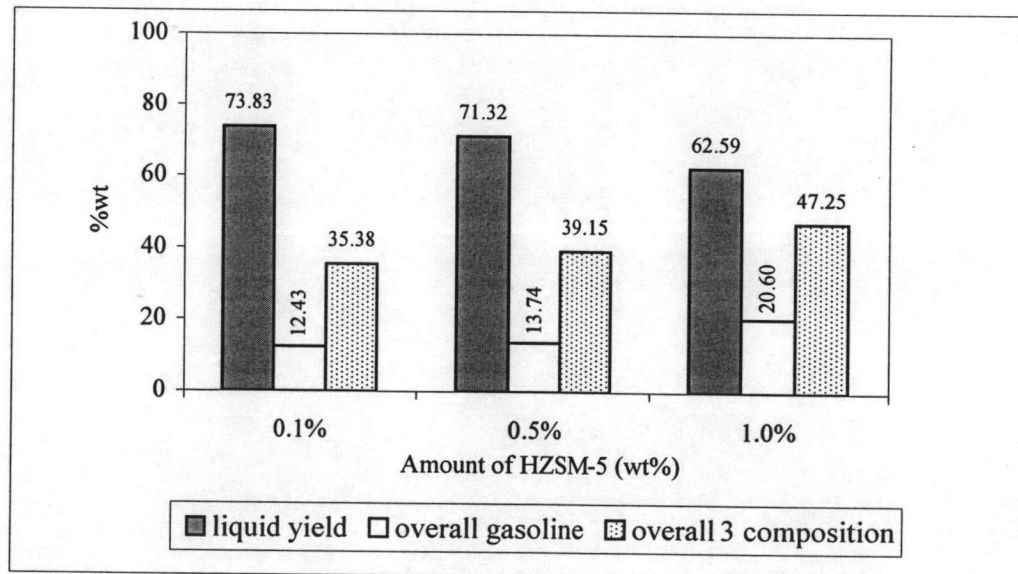


Figure 4.22 Liquid yield, gasoline and sum of 3 compositions as a function of amount of HZSM-5 (Pressure 5 bar, reaction time 60 minutes and reaction temperature of 425 °C).

4.2.3.3 Effect of reaction time on product yield and composition of liquid product

The experiment for studying the effect of reaction time was performed at optimum temperature and amount of HZSM-5 of 425 °C and 1 wt%, respectively, and under initial an hydrogen pressure of 5 bar and reaction time of 10, 30, 60 and 90 minutes. The effect of reaction time on product yield and the composition of liquid product are shown in Figure 4.23

As shown in Figure 4.23, in the range of reaction time between 10 and 60 minutes, the increasing of gasoline, kerosene and light gas oil was more than that of range between 60 and 90 minutes, on the other hand, the long residue decreased in the same direction.

Yield of gasoline and sum of three composition (gasoline, kerosene and light gas oil) increased with reaction time from 10 to 60 minutes. After that gasoline slightly decreased but the sum of three composition increased with reaction time from 60 to 90 minutes as shown in Figure 4.24. It can be concluded that the optimum reaction time for cracking of waste lubricating oil over HZSM-5 was 60 minutes because this time gave the largest yield of gasoline, although sum of gasoline, kerosene and light gas oil was slightly less than the sum of three composition at 90 minutes.

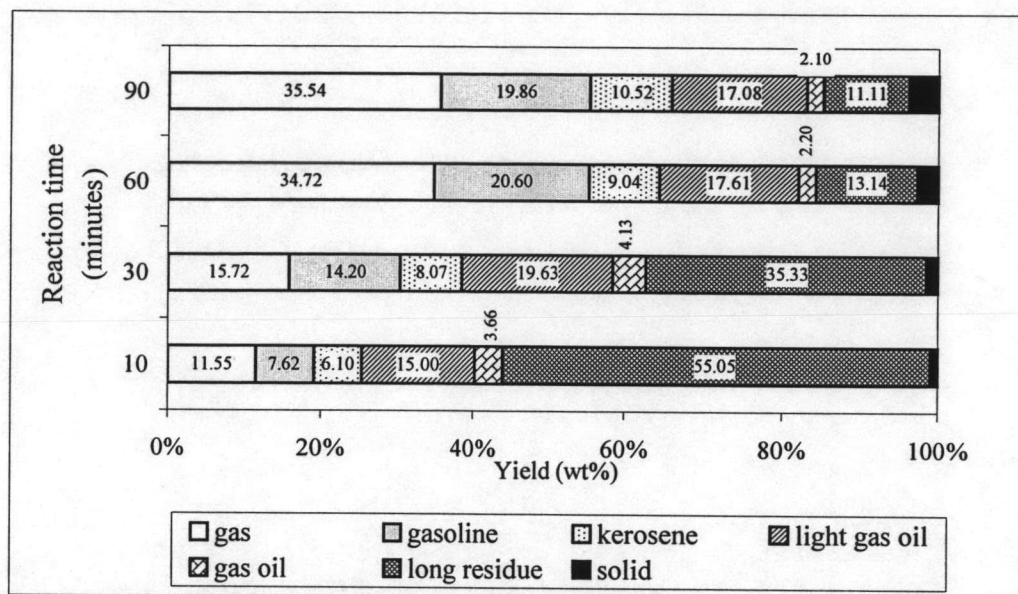


Figure 4.23 Product yield and composition of liquid product as a function of reaction time (Pressure 5 bar, temperature of 425 °C and amount of HZSM-5 1 wt%).

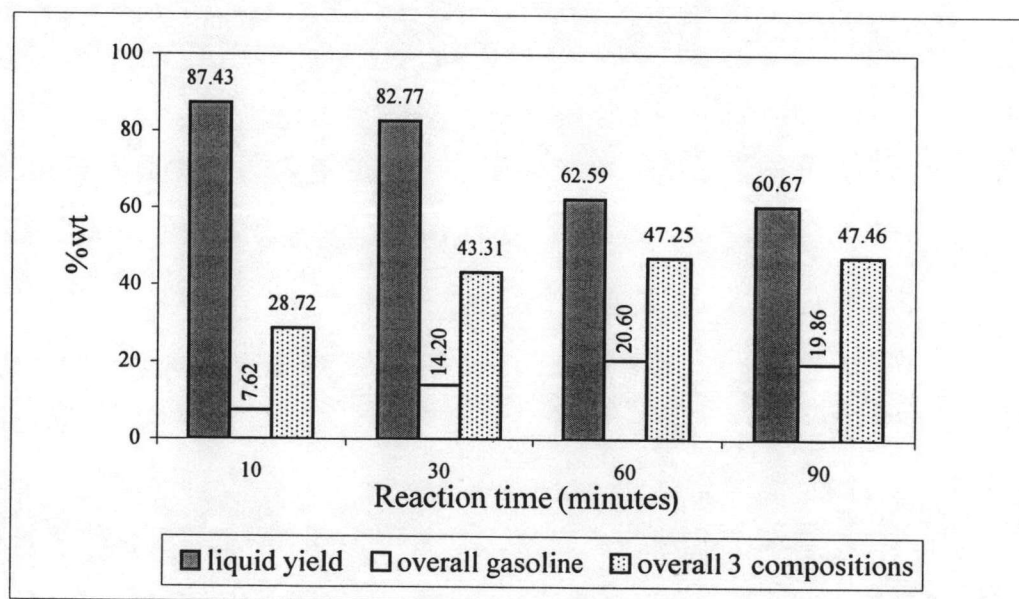


Figure 4.24 Liquid yield, gasoline and sum of 3 compositions as a function of reaction time (Pressure 5 bar, reaction temperature of 425 °C and amount of HZSM-5 1 wt%).

4.2.4 Comparison of performance of three types of catalyst

From the experimental results in section 4.2.1 to 4.2.3, optimum condition and product yields from catalytic cracking reaction of waste lubricating oil by three types of catalyst were summarized in Table 4.11

Among the three catalysts, Fe/AC gave the highest gasoline yield of 23.74%, while lowest yield of long residue of 4.30%. Kerosene, light gas oil and gas oil consisted in oil product from cracking by three catalysts were shortly different yield.

Based on the optimum yields (whole oil basis) obtained with each catalysts, the relative performance of the catalysts for the production of liquid fuels can be generally represented by the following orders:

1. Yield of gasoline : Fe/AC > CoMo/Al₂O₃ > HZSM-5
2. Overall yield of gasoline, kerosene and light gas oil : Fe/AC > CoMo/Al₂O₃ > HZSM-5
3. Conversion of long residue : Fe/AC > CoMo/Al₂O₃ > HZSM-5

These results showed that Fe/AC was the best catalyst for the production of liquid hydrocarbon (typically gasoline, kerosene and light gas oil).

Table 4.11 Comparison of optimum condition and product yields among Fe/AC, CoMo/Al₂O₃, and HZSM-5 catalysts.

Description	Types of catalyst		
	Fe/AC	CoMo/Al ₂ O ₃	HZSM-5
<u>Optimum condition</u>			
Reaction temperature (°C)	425	425	425
Initial hydrogen pressure (bar)	5	5	5
Reaction time (minutes)	60	60	60
Amount of catalyst (wt%)	5	5	1
<u>Product yields</u>			
Oil product (wt%)	58.32	60.11	62.59
Gasoline	23.74	22.24	20.60
Kerosene	9.87	10.12	9.04
Light gas oil	17.54	17.25	17.61
Gas oil	2.86	2.94	2.20
Long residue	4.30	7.56	13.14
Sum of gasoline, kerosene and light gas oil	51.15	49.61	47.25
Gas product (wt%)	39.14	36.57	34.72
Solid product (wt%)	2.54	3.32	3.79

It may be explained that Fe/AC was the bifunctional catalyst that consisted of metallic and acidic component. The metallic portion of Fe/AC catalyst was iron.

Generally, iron can be adsorb both hydrogen and the hydrocarbon molecule [24]. Activated carbon was the acidic component of Fe/AC catalyst. Acidic functional groups, e.g., -OH or -COOH, distributed on the surface of activated carbon, these functional group were a good proton donor, that is, a strong Bronsted acid [33]. Then, generation of carbocation (or carbenium ion) from alkenes and cracking were occurred on Bronsted acid site.

The cracking of waste lubricating oil begins with adsorption of long chain paraffins onto metal surface and dehydrogenation to olefins, followed by protonation on acidic surface to carbocation and undergo cracking by β -scission. In turn, the new olefin products will contact with metal site after migration from acidic support, where hydrogenation tends to occur, releasing new alkane species.

Fe/AC catalyst had a highest surface area of 654 m²/g and percent of Fe distribution on support surface of 9.25%, it was implied that Fe/AC had higher site for hydrogenation, dehydrogenation and cracking. From this reason, long chains hydrocarbon was highly possible converted to lighter molecule, i.e., gasoline.

CoMo/Al₂O₃ gave gasoline yield and sum of gasoline, kerosene and light gas oil 22.24% and 49.62%, respectively, these yields lower than that of Fe/AC but higher than that of HZSM-5. It can be described that CoMo/Al₂O₃ was the bifunctional catalyst same as Fe/AC. Molybdenum (Mo) was used as active component and Cobalt (Co) was promoters to improve catalyst activities [34]. Both Co and Mo can be adsorb hydrogen and hydrocarbon molecule as well as Fe [21]. Alumina (Al₂O₃) was used as acidic support which show Bronsted and Lewis acid properties [24]. Bronsted acid

was a good proton donor, while Lewis acid can be abstract hydride ion in heterolytic bond, so carbocation from alkane was generated.

Mechanism of catalytic cracking of waste lubricating oil over $\text{CoMo/Al}_2\text{O}_3$ was similar to that of Fe/AC . Olefins were generated from dehydrogenation of alkane at metallic site, then olefins product was diffused and adsorbed on acid surface (Bronsted acid site), followed by protonation, cracking and hydrogenation on metal surface. Furthermore, hydrogen of alkane molecules was abstracted by acidic surface (Lewis acid site) and became to carbocation. Although, $\text{CoMo/Al}_2\text{O}_3$ catalyst had both Bronsted and Lewis acid site and the distribution of Co and Mo on catalyst surface in the ratio of 6:1, but surface area of $\text{CoMo/Al}_2\text{O}_3$ ($374 \text{ m}^2/\text{g}$) was less than surface area of Fe/AC . Then, amount of cracking products, especially gasoline, were less than that of Fe/AC .

HZSM-5 gave the lowest gasoline yield and sum of gasoline, kerosene and light gas oil relative with Fe/AC and $\text{CoMo/Al}_2\text{O}_3$ catalyst. It can be explained that the catalytic properties of HZSM-5 were attributed to both its strong acid sites and the three-dimensional system of intersecting channels which was made up of elliptical straight channels ($0.51 \times 0.55 \text{ nm.}$) and near circular zig-zag channels ($0.54 \times 0.5 \text{ nm.}$) [35]. HZSM-5 possess both Bronsted and Lewis acid site which generate its catalytic activity. Then, cracking of waste lubricating oil was occurred at Bronsted and Lewis acid site. It is generally assumed that the reactions predominantly occur within the internal pore structure of the zeolite catalyst. Hydrocarbon molecule can penetrated into the zeolite pores by assuming a slender configuration alignment. However, geometric limitations have to be considered while making such assumptions because

of the possible incompatibility of the diameter of the reactant molecules and the pore opening of the HZSM-5 catalyst [36].

The average channel sizes of some of these zeolites were summarized in Figure 4.25 [23], along with the sizes of cavities and the critical molecular dimensions of a number of hydrocarbons that are potential reactants in zeolite-catalyzed reactions. From Figure 4.25, illustrated some hydrocarbon molecule which had critical molecular dimension less than 5.6 nm, for example, linear paraffin, benzene and iso-paraffin, can entered the pores of HZSM-5, whereas higher aromatic and naphthalene cannot. Waste lubricating oil feed consisted of linear paraffin ($C_{10}-C_{44}$) and high molecular weight aromatic such as naphthalene, fluorine, phenanthrene and anthracene [37]. Large molecules cannot penetrate into pore of catalyst and cracking of these compound in internal pore was not proceed. However, it was postulated that the initial fragmentation can occur on the external surface of the catalyst followed by their diffusion into the pores. Moreover, the activity of HZSM-5 was reduced by coking that deposited on pores of zeolite. From this reason, less amount of gasoline compare with two types of catalyst were generated by HZSM-5

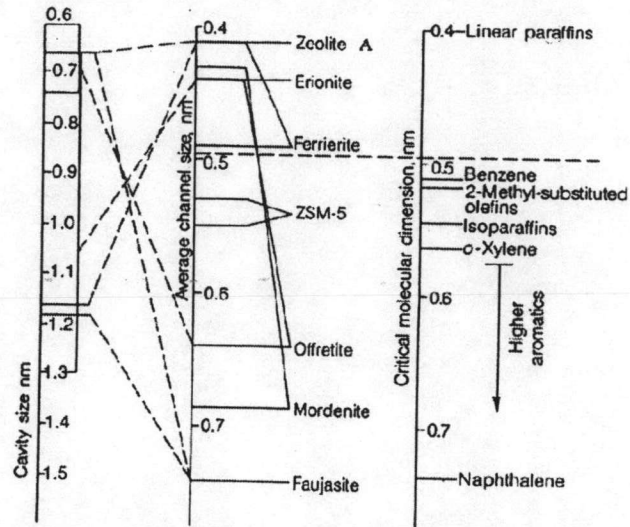


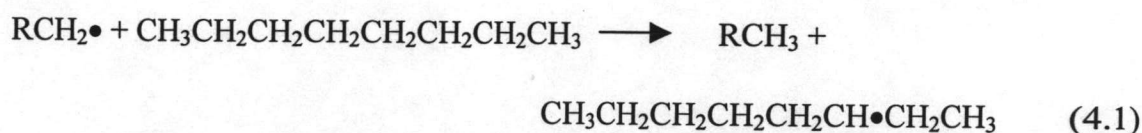
Figure 4.25 Pore dimensions of zeolites and critical dimensions of some hydrocarbon [23].

4.2.5 Comparison of product distribution between catalytic and thermal cracking

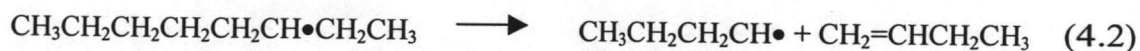
Product yield and composition of liquid product from catalytic cracking reaction at optimum condition was compared with thermal cracking at temperature of 425 °C, reaction time of 60 minutes and initial hydrogen pressure of 5 bar as shown in Figure 4.26 and 4.27.

Thermal cracking process gave the lowest liquid yield and highest gas yield when compare with catalytic cracking reaction by three types of catalyst (Figure 4.26). Moreover, production of gasoline, kerosene and light gas oil by thermal cracking was less than that of catalytic cracking process (Figure 4.27). It can be explained that thermal cracking reactions proceed very much in manner of the free radical cracking processes [24]. This process required higher temperature for generating free radical. The initial reaction was the hemolytic cleavage of a C-C bond

to form two free radicals. One of radicals produces in the initiating reaction attacks a second molecule of alkane, abstracting a hydrogen. Because a 2nd radical was more stable than a 1st radical, the hydrogen was removed from one of the interior carbon atoms:

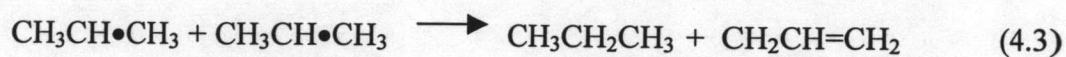


The products were a new, smaller alkane and a 2nd radical. The 2nd radical then undergoes a β -bond scission reaction production the expected 1-alkene and a 1st radical.

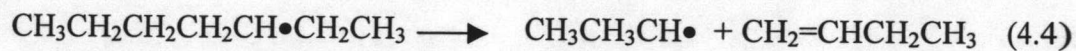


The small 1st radical can continue to undergo β -bond scission until ethylene was produced. Thus ethylene, sometimes in large amount, was produced as a by product from thermal cracking reaction.

The thermal cracking process, like thermal cracking in nature, begins with C-C bond cleavage more or less randomly along the carbon chain. Thus it is entirely possible for some large alkanes to cleave near the end of the chain, producing appreciable quantities of products less than five carbon atoms (that is, too light to be in the gasoline range). In addition, alkenes can be formed via disproportionation reactions or β -bond scission reactions:



or



The formation of alkenes is not necessarily an undesirable event. Then, it can conclude that thermal cracking reaction was the unsuitable reaction for converting waste lubricating oil to liquid fuels because this reaction gave the high amount of gas and low quantity of oil product.

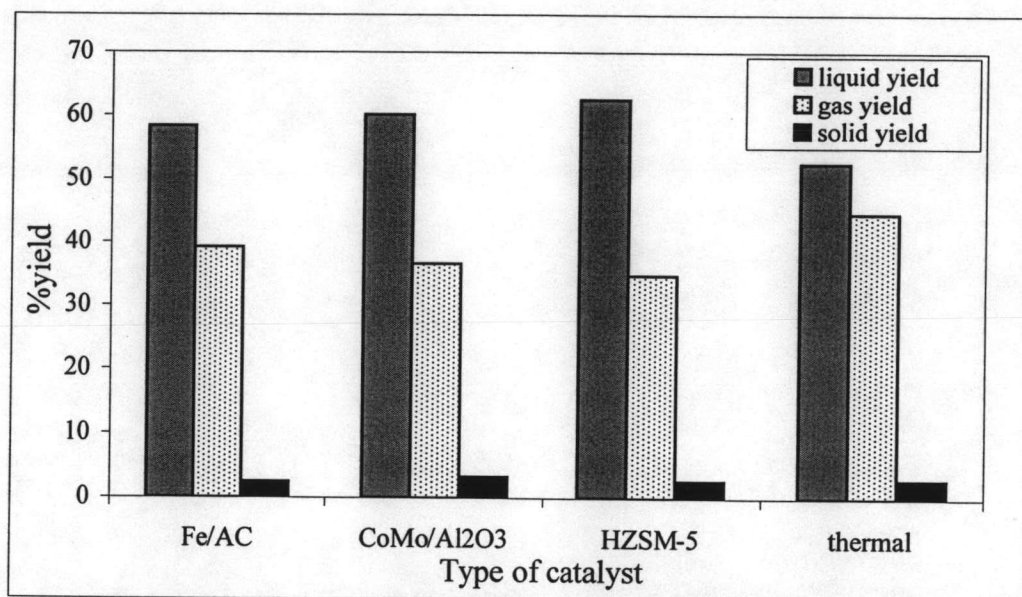


Figure 4.26 Comparison of yield between catalytic cracking at optimum condition and thermal cracking at temperature of 425 °C, reaction time of 60 minutes under initial hydrogen pressure of 5 bar.

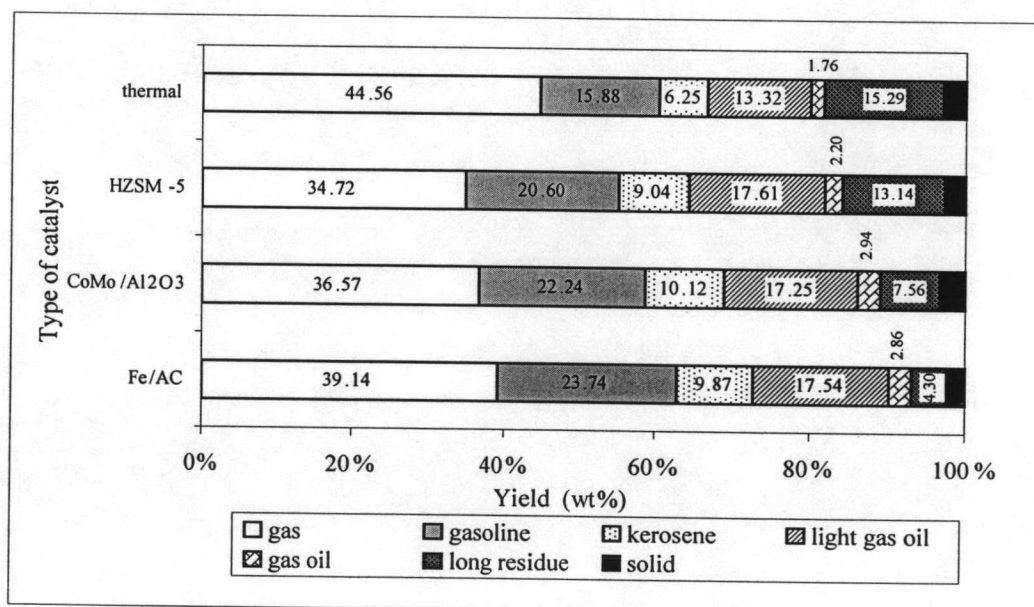


Figure 4.27 Comparison of product distribution between catalytic cracking at optimum condition and thermal cracking at temperature of 425 °C, reaction time of 60 minutes under initial hydrogen pressure of 5 bar.

4.3 Product analysis by GC-MS

Waste lubricating oil feed and liquid products from the cracking of waste lubricating oil at optimum condition of each catalysts were determined the chemical components by GC-MS. Table 4.12 showed the classification of hydrocarbon compounds consisted in feed and liquid products.

Table 4.12 Class of hydrocarbon and number of carbon atom consisted in waste lubricating oil feed and liquid product.

Classification	Number of carbon atom			
	Waste oil feed	Fe/AC	CoMo/Al ₂ O ₃	HZSM-5
n-Paraffin	C ₁₆ -C ₃₄	C ₇ -C ₁₅	C ₈ -C ₂₁	C ₈ -C ₁₈
Branch chain-Paraffin	C ₁₀ -C ₁₃	C ₇ -C ₉	C ₈ -C ₉	C ₈ -C ₉
Aromatics				
1-ring ^a	-	C ₇ -C ₁₁	C ₈ -C ₁₀ , C ₁₈	C ₇ -C ₁₂
2-rings ^b	C ₁₀ -C ₁₂	C ₁₀ -C ₁₁	C ₁₁ -C ₁₂	C ₁₀ -C ₁₁
3-rings ^c	C ₁₃ -C ₁₄	-	-	-

^a1-ring aromatic = alkyl benzene

^b2-rings aromatic = naphthalene, indene

^c3-rings aromatic = fluorine, phenanthrene and anthracene

As shown in Table 4.16, compounds were identified in waste lubricating oil composed of n-paraffin, branch chain-paraffin, olefin and aromatics (2- and 3-rings).

Product oil from the cracking of waste lubricating oil by three types of catalyst mainly composed of n-paraffin, branch chain-paraffin and aromatics (1-ring and 2-rings), none of 3-rings aromatic. It can be observed that n-paraffin in liquid product from catalytic cracking have carbon atom in the range from gasoline to light gas oil, namely 7 to 20 atoms.

It was also worthwhile to note the differences in paraffinic products results from the three types of catalysts. When waste lubricating oil feed was cracked on Fe/AC catalyst, the range of carbon atom of alkane products from C₇-C₁₅ was narrow than that of CoMo/Al₂O₃ (C₈-C₂₁) and HZSM-5 (C₈-C₁₈). This observation can be used to explain that higher surface area of Fe/AC was affected on cracking long hydrocarbon molecule to lower molecule, especially gasoline.

When three types of catalyst were used, the liquid products consisted of 1-ring aromatic compounds. It was interesting to note that 1-ring aromatic compounds were not presented in waste lubricating oil feed. The 1-ring aromatic hydrocarbons may have been formed first by thermal cracking or catalytic cracking of the waste lubricating oil feed followed by aromatization of some of the cracked molecules (mainly olefins) via cyclization and hydride transfer reactions. The major compounds were toluene, ethyl benzene, o-xylene, and substituted benzene.

3-rings aromatic compounds were not contained in oil product from cracking waste lubricating oil with three types of catalyst. It was possible that 3-rings aromatics were not cracked but also deposited on surface of catalyst in coke form.

4.4 Proposed reaction pathways

4.4.1 Reaction pathway for HZSM-5 catalyst

There is only limited information in the literature on the reaction pathways for cracking of waste lubricating oil with the catalysts used in this work. The only work reported by Prasad et al.[38] for the HZSM-5 conversion of canola oil. Thus, in this section, an attempt has been made to propose most likely reaction pathways for waste lubricating oil conversion over the HZSM-5 catalyst.

This pathway is shown in Figure 4.28. It was proposed that the conversion of waste lubricating molecules proceeds by two group of reactions occurring co-currently. In one route, thermal and catalytic cracking taken place at the surface of catalyst to produce small molecular size components comprising alkenes (step1). It is further proposed that the olefins produced from step 1 undergo secondary cracking reactions to produce a mixture light olefins and paraffins (step 2). Some of the olefins and paraffins-produce the hydrocarbon gases and the remaining undergo a number of aromatization reactions to produce the aromatic hydrocarbons. These reactions comprise of cyclization, H-transfer and isomerization (step 3) which occur through carbocation mechanism.

The other route proposed for the conversion of waste lubricating oil is direct polycondensation (step 5) of some of the aromatic hydrocarbons contributes to the coke formation.

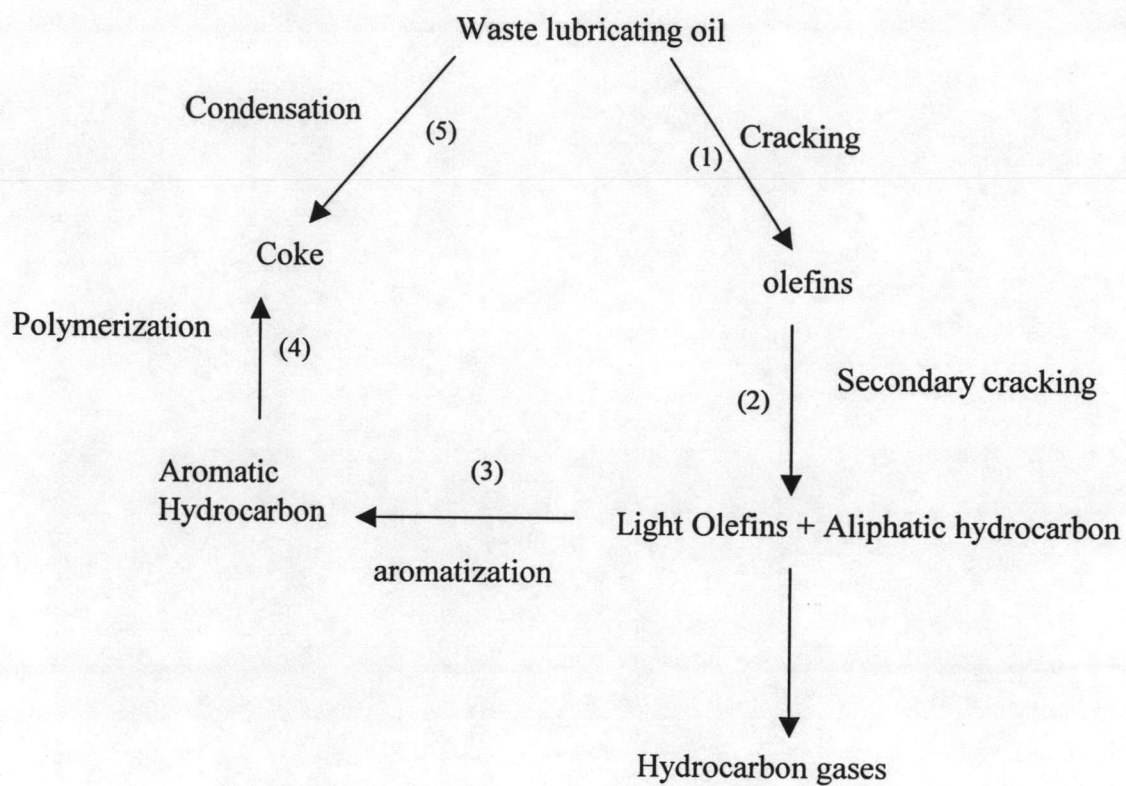
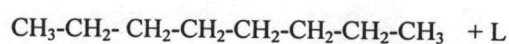
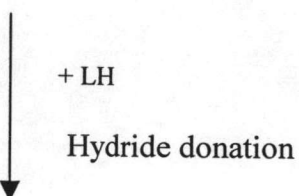
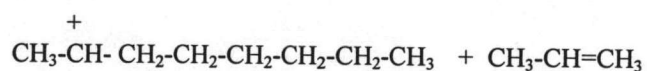
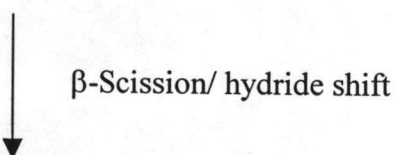
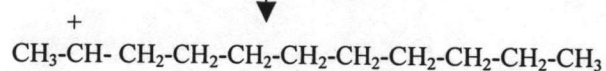
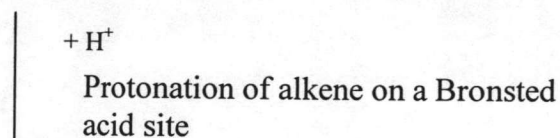
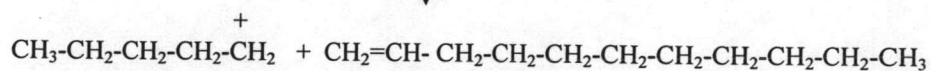
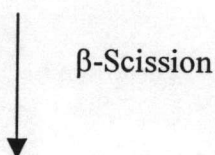
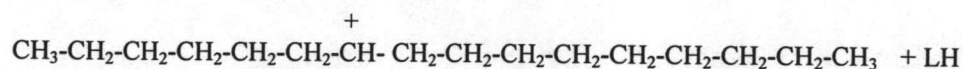
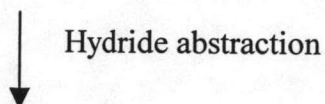
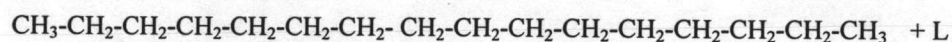


Figure 4.28 Proposed reaction pathway for the conversion of waste lubricating oil over HZSM-5 catalyst.

Mechanism of catalytic cracking of paraffins on HZSM-5

For example : cracking of hexadecane ($C_{16}H_{34}$) to octane (C_8H_{18}) by HZSM-5



n-Octane

L = Lewis acid site

4.2.2 Reaction pathway for bifunctional catalyst (Fe/AC and CoMo/Al₂O₃)

This pathway is shown in Figure 4.29. It was proposed that the dehydrogenation of n-paraffin take place on the metallic surface to produce n-olefin (step 1). The n-olefin produced from step 1 undergoes protonation reaction at acidic site to produce carbocation (step 2). It is further proposed that the carbocation produced from step 2 undergoes β -scission to generate light olefin and new carbocation (step 3). Light olefin will contact with metallic site, which hydrogenation tends to occur, releasing alkane product (step 4). The isomerization of new carbocation from step 3 take place to produced isomerized olefin that are rapidly hydrogenated (step 5).

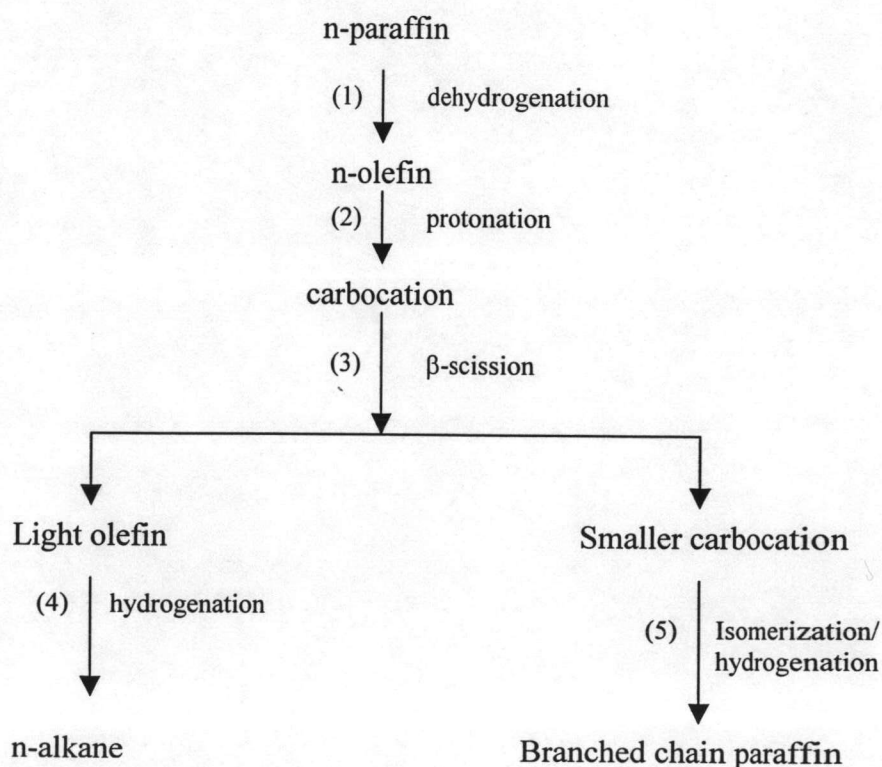
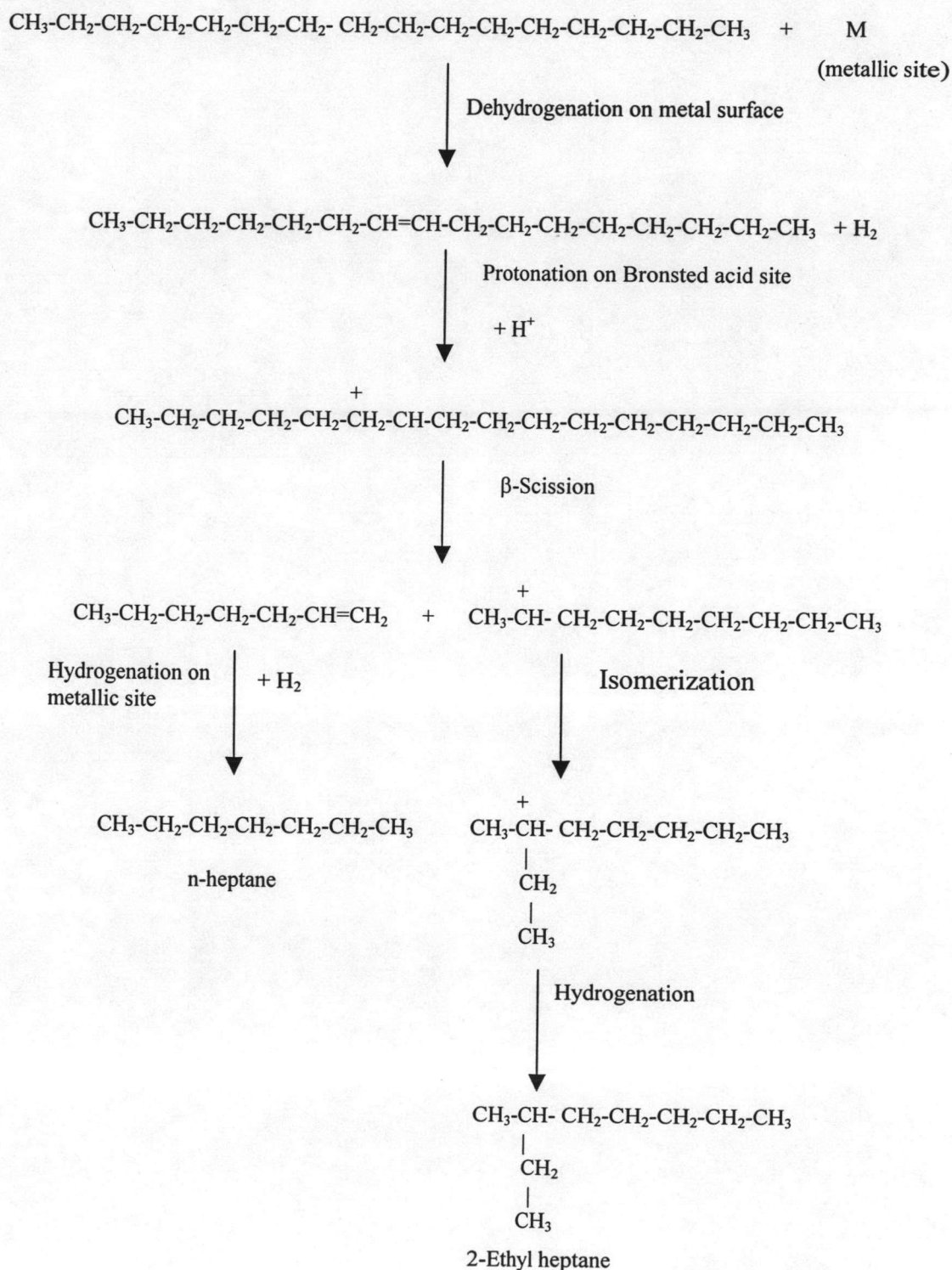


Figure 4.29 Proposed reaction pathway for the conversion of waste lubricating oil over bifunctional catalyst.

Mechanism of catalytic cracking of paraffins on bifunctional catalyst

For example : cracking of hexadecane ($C_{16}H_{34}$) to heptane (C_7H_{16}) and 2-ethyl heptane (C_9H_{20}) by Fe/AC



4.5 Kinetic Study

This experiment aimed to investigate the kinetic of catalytic cracking reaction of waste lubricating oil over three types of catalyst. Order of reaction, rate constant and activation energy were determined from this study.

Determination of reaction order was obtained from relationship between the reaction rate ($-r_A$) and the concentration of long residue consisting in the liquid product (C_A) as followed equation (4.5);

$$-r_A = -\frac{dC_A}{dt} = k_n C_A^n \quad (4.5)$$

In case of first order ($n = 1$), equation (4.5) was;

$$-\frac{dC_A}{dt} = k_1 C_A \quad (4.6)$$

which $C_A = C_{AO}(1 - X)$

$$X = \frac{(\% \text{long residue at } t=0) - (\% \text{long residue at any time})}{(\% \text{long residue at } t=0)}$$

Integration of equation (4.6) between $t = 0$ and $t = t$, relation between conversion term and time was obtained in equation (4.7);

$$\ln\left(\frac{1}{1-X}\right) = k_1 t \quad (4.7)$$

rate constant (k_1) was obtained from the slope of plotting $\ln\left(\frac{1}{1-X}\right)$ vs. time.

In case of second order ($n = 2$), equation (4.5) was;

$$-\frac{dC_A}{dt} = k_2 C_A^2 = k_2 C_{A0}^2 (1-X_A)^2 \quad (4.8)$$

Integration of equation (4.8) and rearrange, relation between conversion term and time was obtained in equation (4.9);

$$\frac{X_A}{(1-X_A)} = k_2 C_{A0} t \quad (4.9)$$

Plotting between $\frac{X_A}{(1-X_A)}$ and time, k_2 was obtained from slope.

The order of reaction was determined by plotting the conversion term and time between two relations in equation (4.7) and equation (4.9). Then, comparing the linear regression correlation coefficient (R^2) between two relations. The order of reaction was gained from the relation which had R^2 value most near by 1 than other relation.

Activation energy was calculated by Arrhenius's equation as shown in equation (4.10).

$$k = A \exp(-E/RT) \quad (4.10)$$

Plotting between $\ln(k)$ and $1/T$, activation energy (E) and frequency factor (A) was obtained from slope and intercept, respectively. Kinetic data including conversion of the three type of catalyst listed in Table 4.13.

Kinetic experiments were carried out at reaction times of 10-90 minutes and reaction temperature of 390, 410 and 425 °C under initial hydrogen pressure of 5 bar with 5 wt% of Fe/AC and CoMo/Al₂O₃ catalyst. HZSM-5 was used 1 wt% based on waste oil weight.

For kinetic study of catalytic cracking reaction over Fe/AC catalyst. R^2 for $\ln[1/(1-X)]$ versus reaction time was found to between 0.95 and 0.97, while R^2 for $\ln[X/(1-X)]$ plot were 0.85 and 0.91. So, the linear regression correlation coefficient of $\ln[1/(1-X)]$ versus time plot shown as Figure 4.30 indicate a good fitting of the experimental data to the first order kinetics. Plotting between $\ln[1/(1-X)]$ versus reaction time for catalytic cracking reaction over CoMo/Al₂O₃ and HZSM-5 catalyst shown as Figure 4.31 and Figure 4.32, respectively. The order of catalytic cracking reaction over CoMo/Al₂O₃ and HZSM-5 catalyst were first order as well as Fe/AC catalyst.

The rate constants for overall composition of long residues were determined from $\ln[1/(1-X)]$ versus residence time plots. Activation energies and frequency factors of three catalysts were also calculated from Arrhenius curves as shown in Figure 4.33 to Figure 4.35. All these calculated parameters have been mentioned in Table 4.14.

Table 4.13 Kinetic data of catalytic cracking of waste lubricating oil over Fe/AC, CoMo/Al₂O₃ and HZSM-5.

Temperature (°C)	Reaction time (minute)	Conversion (X) (base on long residue)		
		Fe/AC	CoMo/Al ₂ O ₃	HZSM-5
390	10	0.14	0.31	0.14
	20	0.21	0.34	0.17
	30	0.27	0.36	0.23
	40	0.34	0.38	0.29
	50	0.42	0.51	0.35
	60	0.57	0.59	0.48
	90	0.70	0.60	0.53
410	10	0.30	0.39	0.17
	20	0.34	0.43	0.21
	30	0.38	0.48	0.27
	40	0.47	0.54	0.29
	50	0.57	0.61	0.37
	60	0.73	0.81	0.49
	90	0.81	0.85	0.57
425	10	0.37	0.47	0.28
	20	0.52	0.50	0.42
	30	0.60	0.62	0.51
	40	0.77	0.64	0.56
	50	0.87	0.66	0.61
	60	0.95	0.86	0.69
	90	0.97	0.90	0.82

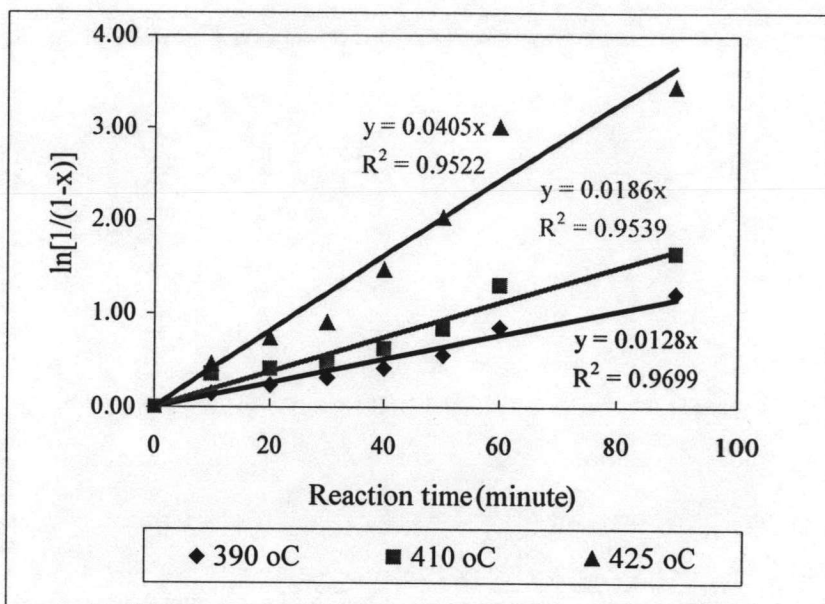


Figure 4.30 Relationship between $\ln[1/(1-x)]$ and time for catalytic cracking of waste lubricating oil over Fe/AC.

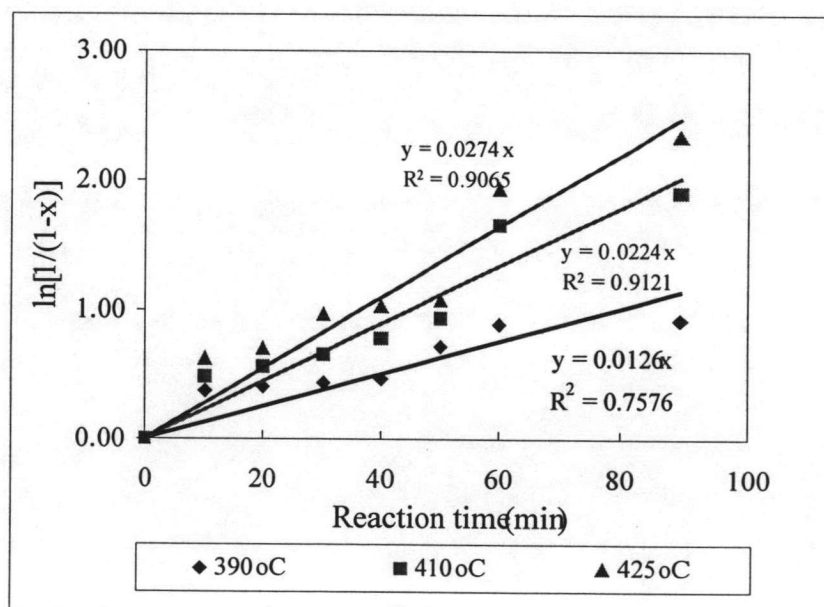


Figure 4.31 Relationship between $\ln[1/(1-x)]$ and time for catalytic cracking of waste lubricating oil over CoMo/Al₂O₃.

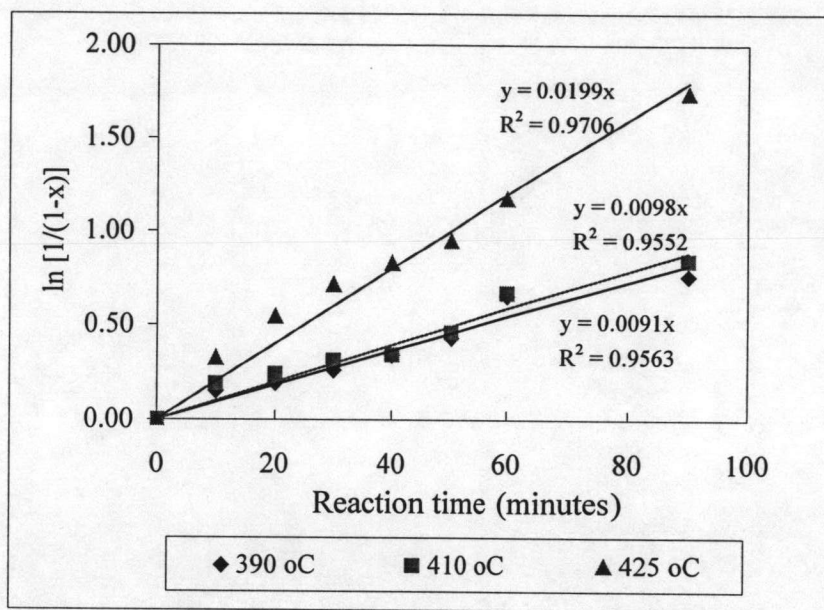


Figure 4.32 Relationship between $\ln[1/(1-X)]$ and time for catalytic cracking of waste lubricating oil over HZSM-5

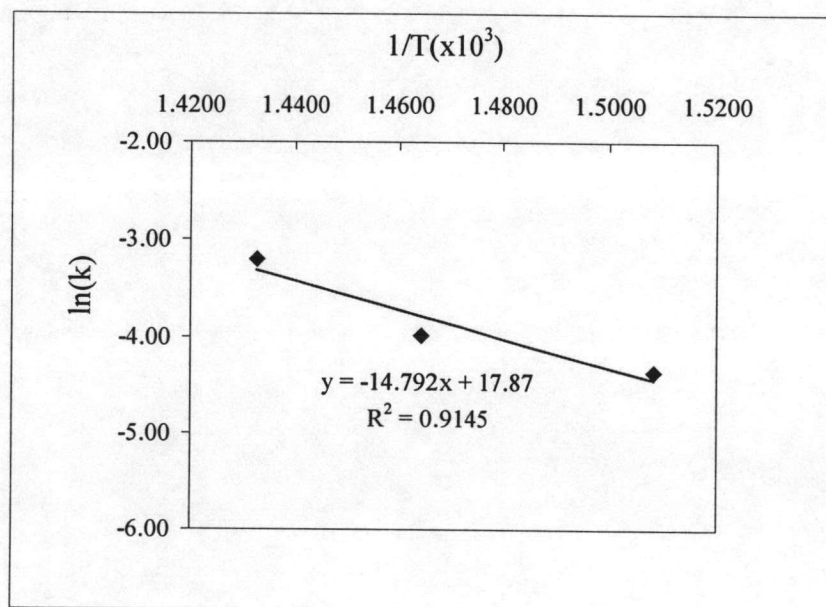


Figure 4.33 Relationship between $\ln(k)$ and $1/T$ for determined activation energy of catalytic cracking reaction over Fe/AC.

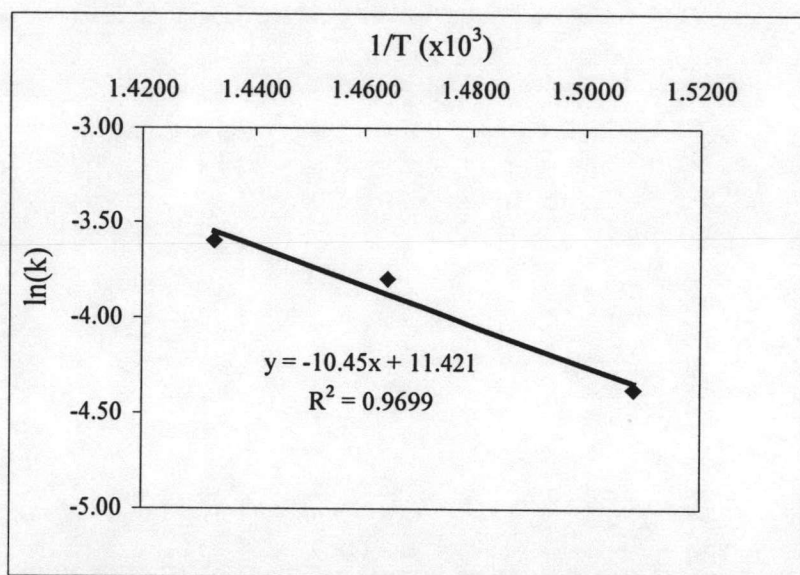


Figure 4.34 Relationship between $\ln(k)$ and $1/T$ for determined activation energy of catalytic cracking reaction over $\text{CoMo}/\text{Al}_2\text{O}_3$.

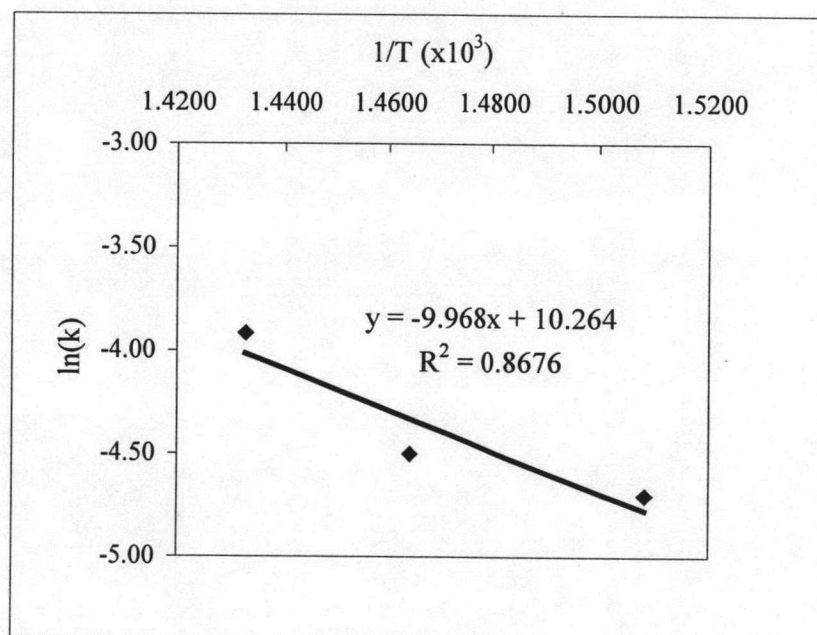


Figure 4.35 Relationship between $\ln(k)$ and $1/T$ for determined activation energy of catalytic cracking reaction over HZSM-5.

Table 4.14 Rate constants, activation energies and frequency factors for different catalysts.

Catalyst	Temperature (°C)	Rate constant (min ⁻¹)	Activation energy (kJ/mol)	Frequency factor (min ⁻¹)
Fe/AC	390	0.0128	122.98	5.765E+07
	410	0.0186		
	425	0.0405		
CoMo/Al ₂ O ₃	390	0.0126	86.88	9.122E+04
	410	0.0224		
	425	0.0274		
HZSM-5	390	0.0091	82.87	2.868E+04
	410	0.0098		
	425	0.0199		

As shown in Table 4.14, activation energies of three catalysts were found to be between 82.87-122.98 kJ/mol. Fe/AC has a highest activation energy of 122.98 kJ/mol. CoMo/Al₂O₃ and HZSM-5 have activation energies of 86.88 and 82.87 kJ/mol, respectively.

Singh J.et.al [38] studied thermal cracking of residual feedstock in the temperature range of 410-430 °C. The activation energy of this study was 206 kJ/mol. The activation energies of catalytic cracking reaction were less than that of thermal cracking. It can be concluded that catalytic cracking reaction was suitable process for converting waste lubricating oil to liquid fuels when compared with thermal cracking.