

## CATALYTIC CRACKING OF USED LUBRICATING OIL OVER Fe/Al<sub>2</sub>O<sub>3</sub> AND Fe/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>

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### Abstract

The main objective of this research was aimed to study the catalytic cracking of used lubricating oil with Fe/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, Fe/Al<sub>2</sub>O<sub>3</sub> and Ni/Al<sub>2</sub>O<sub>3</sub> catalysts. The catalytic reaction was carried out in 70 ml micro-reactor volume. The 0.5-5 wt.% of Fe on SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, 5 wt.% of Fe on Al<sub>2</sub>O<sub>3</sub> and 5 wt.% of nickel on Al<sub>2</sub>O<sub>3</sub> catalysts were prepared. The cracking process was performed at reaction temperature in the range of 390 to 470°C, reaction time range from 30 to 90 minutes, initial hydrogen pressure of 0 to 200 psi and mass of catalyst was varied between 0 to 6.0 %by wt. Simulated Distillation Gas Chromatography, (DGC) analyzes liquid products. The experimental result was found that 5% Fe/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> gave highest content of naphtha. The optimum condition of 5% Fe/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> was 450°C of reaction temperature, 75 minutes of reaction time, 6.8 bar of initial hydrogen pressure and 4.0% by wt. of Fe/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>. The liquid product yield in case of using 5% Fe/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> was 76.24%, the liquid composition were consist of 45.35% of naphtha, 15.71% of kerosene, 22.83% of light gas oil, 3.70% of heavy gas oil and 12.41% of long residue. The liquid product yield in case of using 5% Fe/Al<sub>2</sub>O<sub>3</sub> was 80.38%, the liquid composition were consist of 35.14% of naphtha, 14.47% of kerosene, 24.16% of light gas oil, 5.53% of heavy gas oil and 20.70% of long residue. The liquid product yield in case of using 5% Ni/Al<sub>2</sub>O<sub>3</sub> was 77.20%, the liquid composition were consist of 38.24% of naphtha, 15.67% of kerosene, 25.44% of light gas oil, 3.38% of heavy gas oil and 16.94% of heavy residue. The analysis of oil product by FT-IR showed strong presence of both aromatic and aliphatic hydrocarbon. Which was very strong peaks of the substituted aromatic hydrocarbon.

**Keywords:** Catalytic Cracking; Used Lubricating Oil; Fe/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>; Fe/Al<sub>2</sub>O<sub>3</sub>.

## 1. Introduction

One of the most important lubricants of today use is lubricating oil. It is used in industrial machines; automobiles and all mechanical equipments, in order to operate them for a longer period and be done efficiently and nowadays, Thailand used 3.8 million vehicles. Quality of used lubricating oil assumed to be at 45 million liters per year, excluding other engine. Although used lubricating oil must be wasted in enormous residue chemical waste, if it has not managed. So that idea to recycle the used lubricating oil by uses in heavy industrial such as fuel for smelt industry, cement industry. And reprocess for new grade lubricant return to industrial again. But recycle processes are little points of method to get rid of used lubricating oil waste [1-4]. High portion of lubricant waste must effect to environment. In order to perform properly, used lubricating oils were usually disposed in three ways: disposal as toxic/hazardous waste, re-refining to produce base oils and used as fuel [5]. The cracking process was selected to convert waste of use lubricating oil to the value chemical and fuel. Thermal cracking was used high temperature consequently high cost and energy. More researches have interested in catalytic

cracking reaction by using acid catalyst [6-7] due to high selectivity of products while low cost and temperature. Catalysts are more interesting to study such as acid catalysts and non-acid catalysts i.e. metal supported [8-10].

The objectives of this study is to investigate the effects of the variables on % yield and % composition of oil products and to determine the optimum conditions of catalytic conversion of used lubricating oil to light oil products.

## 2. Experimental and procedure

### 2.1. The cracking unit

The reaction of used lubricating oil with Fe/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, Fe/Al<sub>2</sub>O<sub>3</sub> and Ni/Al<sub>2</sub>O<sub>3</sub> were carried out by using apparatus (shown in figure 3.1). The micro-reactor is a stainless steel tube (SS.316) with an inner volume of 70 cm<sup>3</sup>, 30 mm inside diameter (shown in figure 3.2). It was heated by 450-watt electricity and temperature was measured by thermocouple type K having 1.6 mm diameter with and accuracy ±5°C by means of a programmable temperature controller. A speed motor was used to control the shaking rate of micro-reactor. The schematic and micro reactor is shown in fig.1.

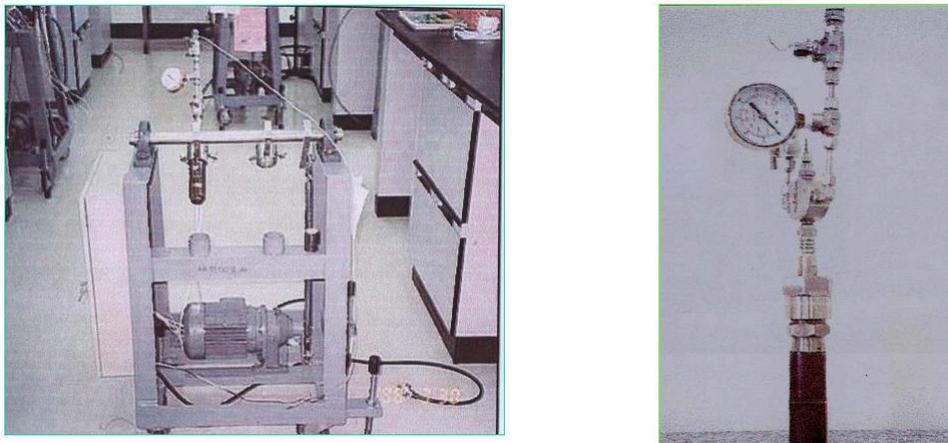


Figure.1 Apparatus for catalytic cracking and micro-reactor for reaction experimental

### 2.2. Catalyst preparation

A preparation of Fe on SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst (Fe/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>) has been done through impregnation method with different percentage of Fe at, 0.5, 1, 3 and 5%. A 100 g of each type of catalyst are prepared with the following steps: the 5% Fe supported on SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (5% Fe/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>) was prepared by wet impregnation method using excess water. Ferric nitrate nanohydrate (Fe(NO<sub>3</sub>)<sub>2</sub>·9H<sub>2</sub>O) was dissolved in deionized water to Fe concentration of 5% and then loaded on to SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> by wet impregnation under continuous agitation and heated at 80°C. This slurry was dried at 120°C for 24 hrs. and thermally treated at 600°C to remove the nitrate or ammonium group. Finally, the sample was reduced in hydrogen gas at 400°C for 2 hrs. and keeping it cool at room temperature, catalyst usable for the intended purposes will be given. Catalyst characterization was realized by SISONA 9410 X-ray fluorescence spectrometer, Micromeritics adsorptometer model ASAP 2020 in order to determine the % loading Fe and BET surface area respectively.

### 2.3. Catalytic cracking reaction procedure

Weighing 20 g of used lubricating oil and 0, 2.5, 4.0 and 6.0 wt. % of catalysts were fed in 70 ml micro-reactor under hydrogen pressure. Heating coil, insulator, and thermocouple were set up with reactor. The reactor was fixed with a shaker (Figure 1) at 120 rpm for desired reaction time. The parameters were reaction temperature, reaction time, initial hydrogen pressure and the mass of catalyst were investigated. The raw material was converted under the

following condition: reaction temperature range from 390 to 470°C, reaction time range from 45 to 90 minutes, initial hydrogen pressure range from 0 to 200 psi. and mass of Fe/ SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst range from 0.5 to 1.2 g. Simulated Distillation Gas Chromatography, following the ASTM D-2887 method, determined the oil products. The conversion of % naphtha in the oil products as a function of the above variables was allowed to determine the suitable conditions.

### 3. Results and discussion

#### 3.1. Properties of used lubricating oil

The composition of used lubricating oil was analyzed by DGC before cracking. It is found that the main composition of used lubricating oil is compound of 87.25% heavy residue, heavy gas oil 8.48% and light gas oil 3.72%.

#### 3.2. Properties of Fe/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst

##### 3.2.1. BET surface area

The BET surface area of catalysts of prepared 0.4, 1.0, 3.0, and 5% of Fe/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> were showed that the BET surface area of SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> was 602 m<sup>2</sup>/g while that other sample loaded Fe on SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> were decreased to 589, 526, 468 and 461 m<sup>2</sup>/g respectively. It is because of the deposition of Fe in the pores of SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>. However the surface area of 5% Fe/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> is 461m<sup>2</sup>/g, which is reduced 23% of SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>.

##### 3.2.2. Chemical analysis of impregnated Fe on SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>

The composition of 0.5, 1, 3 and 5% Fe/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> was determined by XRF. It showed that the Fe loading of Fe 0.436, 0.986, 2.942 and 5.006 respectively, which is close to the desired value. This can firm the prepared Fe loading catalysts. These catalysts could be used in the next experiments.

#### 3.3. Effect of percentage of Fe on SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> on distribution of oil product

The variation of percentage loading of Fe 0.5, 1, 3 and 5% on SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> using as catalyst at a fixed condition of 20g of used lubricating oil, with initial hydrogen pressure of 100 psi, reaction time of 60 min, temperature at 430°C and 4.0% by wt. Fe/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst and comparing with non using catalyst. The product distributions were shown in Figure 2.

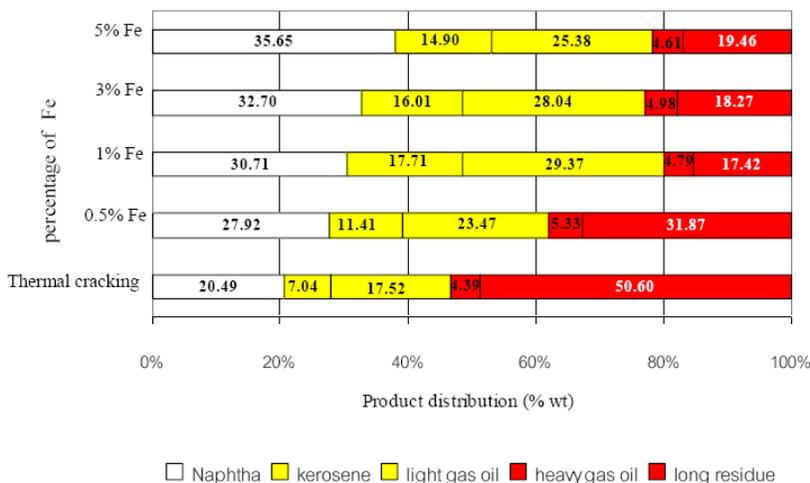


Figure 2. Effect % Fe on product distribution at 430°C of reaction temperature, 6.8 bar of initial hydrogen pressure, 60 minutes of reaction time and 4.0% by wt. Fe/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst.

The conversion of used lubricating oil in non using catalyst at 430°C, pressure of hydrogen gas of 6.8 bar, time of reaction of 60 minutes and 4.0% by wt. Fe/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> was roughly

80.42%, 8.05% and 11.53% in liquid product, gas product and solid, respectively. In addition, the liquid product gave the product distribution, which determined from simulated distillation gas chromatograph about 20.49% of naphtha, 7.05% of kerosene, 17.52% of light gas oil, 4.39% of heavy gas oil and 50.55% of long residue.

While the reaction was carried out without using catalyst, the percentage of oil composition was low quality from that using catalyst because only thermal cracking not enough because lubricating oil was complex structure and high molecular weight. The reaction of catalytic cracking over Fe/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, the liquid yield was decreased with increased of %Fe whereas the yield of naphtha fraction increased. Thermal cracking mechanism of long chain hydrocarbon from lubricating oil firstly was broken down to a middle hydrocarbon molecule such as kerosene and gas oil. Thereafter kerosene, light gas oil and heavy gas oil were catalytically cracked at the surface of Fe/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, converting them into naphtha and gaseous (normally C<sub>1</sub>-C<sub>4</sub>). Whereas, thermal cracking and catalytic cracking, as a result the distribution of hydrocarbon molecules simultaneously proceeded the catalyst system was obtained the higher naphtha and gases.

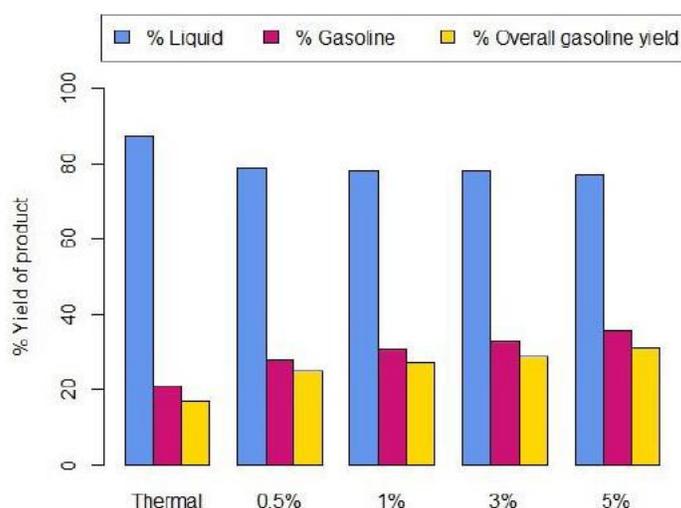


Figure 3. Effect of % Fe on product distribution at 430°C of reaction temperature, 6.8 bar of initial hydrogen pressure, 60 minutes of reaction time and 4.0% by wt. Fe/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst

When the percentage of Fe loading in catalysts increased to 5%, a large amount of gaseous products have been observed to increase substantially shown Fig. 3. It seemed that when higher percentage of Fe was used, light hydrocarbon could be cracked more. The result of this effect showed that 5% (Figure 2) of Fe loading in catalyst gave the appropriate fraction of naphtha; the liquid yield of 77.04% was obtained with the composition of naphtha 35.65%, kerosene 14.90%, light oil 25.38%, heavy gas oil 4.61% and long residue 19.46% whereas the gas by product of 17.82% and solid of 5.14% were obtained, it decided to choose 5% loading of Fe on SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> using as catalyst for studying others variables because 5% loading of Fe gave highest gasoline and overall gasoline.

### 3.4. Effect of reaction temperature on product distribution

The study of reaction temperature on the catalytic cracking of used lubricating with Fe/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst was performed by operating in various temperatures: 390, 410, 430, 450, 470°C. Mass of Fe/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst at 4.0% by wt., 6.8 bar of initial hydrogen pressure, reaction time 60 minutes. Generally, at reaction temperature lower 400°C the product was sticky like wax. At reaction temperature above 470°C, carbon was deposited on the surface of catalyst. Therefore, the experiment was carried out at temperature 390°C to 470°C only. The product distribution was shown in Figure 4.

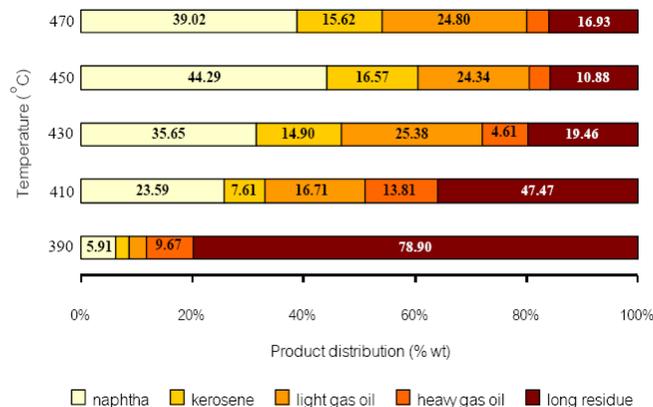


Figure 4. Effect of reaction temperature range of 390-470°C on product composition at 4.0% by wt. Fe/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst, 6.8 bar of initial hydrogen pressure, 60 minutes of reaction time.

From figure 4 shows the reaction of catalytic cracking over 5% Fe/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, the liquid yield was decreased with increased of temperature whereas the yield of naphtha fraction increased with increased temperature. A possible reason for this behavior is that the higher temperature accelerated the thermal cracking into a middle hydrocarbon molecule such as kerosene and gas oil fraction [5-6]. Thereafter kerosene, light gas oil and heavy gas oil were catalytically cracked at the surface of Fe/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, converting them into naphtha and gaseous (normally C<sub>1</sub>-C<sub>4</sub>). When the temperature was increased from 390°C to 450°C, % yield of naphtha increased from 5.91% to 44.29% because the high temperature (450°C) accelerating the thermal cracking which changed kerosene and gas oil. However, at temperature 470°C, it was that noticed the % yield of naphtha decreased from 44.29% to 39.02%, because catalytic cracking was dominated by thermal cracking. The gaseous product increased with increasing temperature which long chain hydrocarbon as broken into lower hydrocarbon (C<sub>1</sub>-C<sub>4</sub>). When the temperature reached 470°C, we observed the large decreasing of naphtha and kerosene from 44.29% to 39.02% and 16.57 to 15.62%, respectively. It seemed that when higher temperature was used, light hydrocarbon could be cracked more, as a result we found the % of gases increasing because thermal cracking was faster than catalytic cracking.

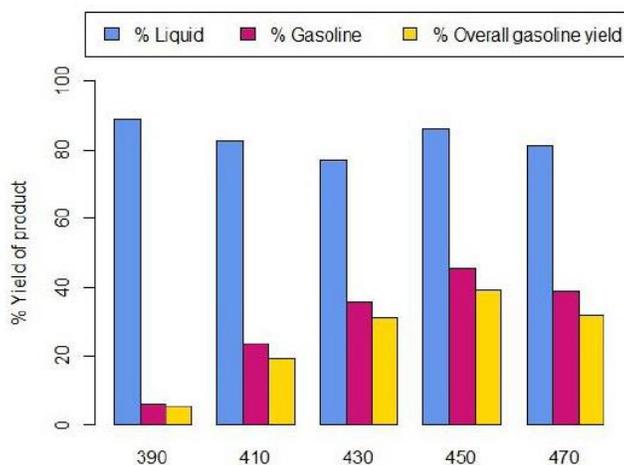


Figure 5. Effect of reaction temperature on product distribution 6.8 bar of initial hydrogen pressure, 60 minutes of reaction time and 4.0% by wt. Fe/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst

In conclusion, the optimum reaction temperature was 450°C because of highest % yield of liquid (Figure 5) and % overall gasoline. The conversion of used lubricating oil was about

75.79%, 18.60% and 5.61% in liquid product, gas product and solid, respectively. In addition, the liquid product gave the product distribution which determined from simulated distillation gas chromatograph about 44.29% of naphtha, 16.57% of kerosene, 24.34% of light gas oil, 3.92% of heavy gas oil, 10.88% long residue and 33.57% of % overall gasoline.

### 3.5. Effect of reaction time on product distribution

The study of the reaction time on the catalytic cracking of used lubricating oil with Fe/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst was performed by operating with various reaction times: 45, 60, 75 and 90 minutes by using mass of Fe/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst at 4.0% by wt., 6.8 bar of initial hydrogen pressure and reaction temperature at 450°C. The product distribution was shown in figure 6. The reaction time contributed mainly to the liquid yield and product distribution that the yield of liquid was increased with increasing reaction time from 45-75 minutes and decreased with increasing reaction time from 75-90 minutes. It seems that in the first of reaction, used lubricating oil begins crack and undergoes more cracking when the reaction time is continues, and hence, the light hydrocarbon molecules were produced in greater from the effect of the thermal cracking [7-8]. When the time of reaction is continued the liquid yield which consisted of the fraction of light hydrocarbon was continued cracking to the gaseous product. Hence, the gaseous product increased with increasing the time of reaction. The yield of liquid product was decreased from 86.00% to 74.53% in ranging of increased the reaction time of 45 to 90 minutes.

In conclusion, the optimum condition of reaction time was 75 minutes, reaction temperature 450°C and initial hydrogen pressure of 100 psi, the liquid yield of 76.24% was obtained with the composition of naphtha 45.35%, kerosene 15.71%, light gas oil 22.83%, heavy gas oil 3.70%, long chain hydrocarbon molecule 12.41% and 34.58% gasoline overall whereas the gaseous products of 18.94% and solid of 4.82% were obtained.

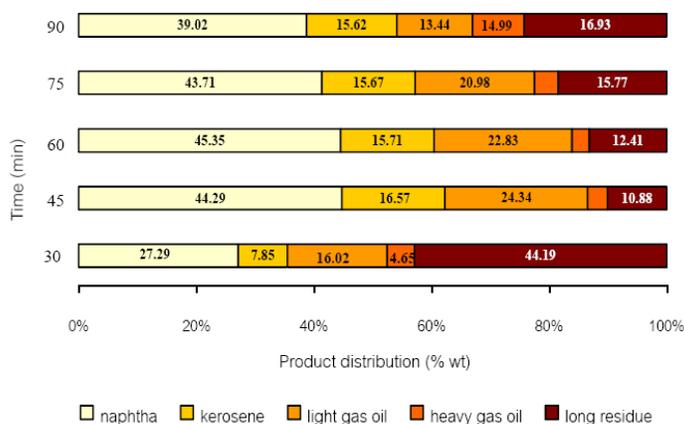


Figure 6 Effect of reaction time range of 45-90 minutes on product composition at 450°C of reaction temperature, 6.8 bar of initial hydrogen pressure and 4.0% by wt. Fe/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst.

### 3.6. Effect of mass of catalyst on liquid product distribution

The study of mass of catalyst on the catalytic cracking process of used lubricating oil with Fe/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst was performed by operating in various mass of catalyst: 0, 2.5, 4.0 and 6.0% by wt. Fe/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts were treated under 6.8 bar of initial hydrogen pressure at reaction time 75 minutes, reaction temperature 450°C and 5% Fe/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>. The product distribution was shown in Figure 7. The investigate of catalytic cracking of used lubricating oil in non using catalyst at 450°C, pressure of hydrogen gas at of 6.8 bar and time of reaction of 75 minutes was about 79.42%, 15.05% and 5.53% in liquid product, gas product and solid, respectively. It seems that the effect of temperature mainly cracked long chain hydrocarbon to the middle molecule and continuously cracked to light hydrocarbon. Whereas using variation

of the mass of Fe/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> shows the trend of gaseous yield increased with increasing the mass of ranging of 2.5-4.0 wt.%. Hence, the mass of Fe/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> in the catalytic cracking was significant on the yield of gases is due to the acid sites in the catalyst promotes the cracking reactions responsible for the formation of gaseous product. In addition, the light hydrocarbon molecules from thermal and catalytic cracking were converted to light gases. Therefore, the catalytic cracking of used lubricating oil at reaction temperature of 450°C, initial hydrogen pressure of 100 psi, time of reaction of 75 minutes over 4.0 wt.% of Fe/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> was gave the highest naphtha fraction amounting 45.35% while, kerosene 15.71%, light gas oil 22.83%, heavy gas oil 3.70% and heavy residue 12.41% were obtained.

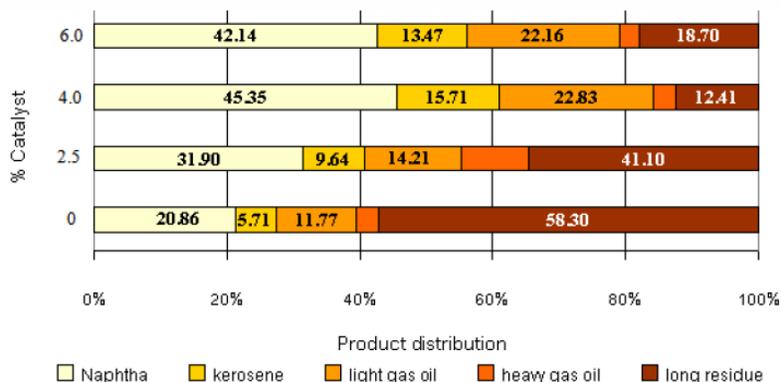


Figure 7 Effect of mass of Fe/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst on product composition at 450°C of reaction temperature, 6.8 bar of initial hydrogen pressure, 5% Fe/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst and 75 minutes of reaction time

### 3.7. Effect of initial hydrogen pressure on product distribution

The study of initial hydrogen pressure on the catalytic cracking process of used lubricating oil with Fe/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst was performed by operating in various initial hydrogen pressure; blank, 6.8, 10.2 and 13.6 bar, with 4.0% by wt. of catalyst, reaction time 75 minutes and reaction temperature 450°C.

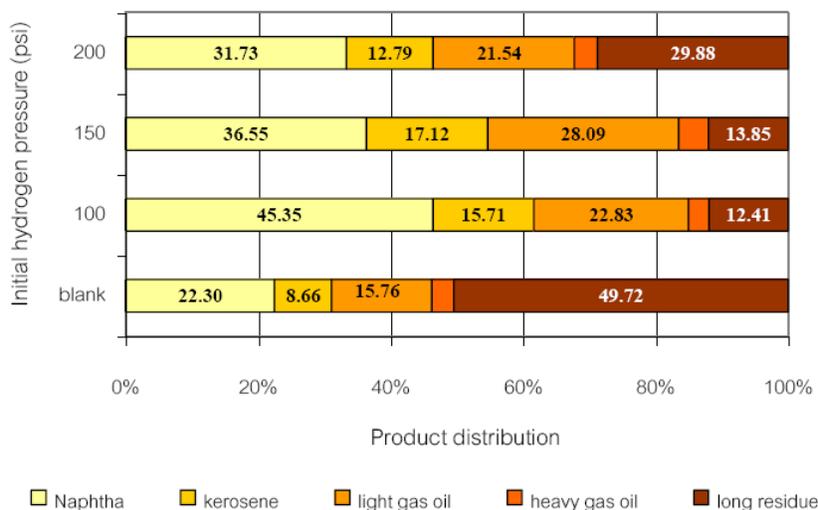


Figure 8 Effect of initial hydrogen pressure range of blank-16.8 bar on product distribution at 450°C of reaction temperature 4.0% by wt. of catalyst, 75 minutes of reaction time and 5% Fe/ SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst.

Effect of variation of initial hydrogen pressure show in Figure 8, when the initial hydrogen pressure was increased from 6.8 bar to 13.6 bar on the hydrocracking process of used

lubricating oil with 5%Fe/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst at reaction time 75 minutes, 4.0% by wt. of catalyst and reaction temperature at 450°C. It noticed that the pressure increased from 0 to 100 psi, the % of naphtha increased from 22.30% to 45.35%. It was observed the difference between using and without using initial hydrogen pressure. When hydrogen concentration increased, it would promote the catalytic reaction by increasing more hydrogen free radical. Thus catalytic cracking could be occurred than thermal cracking at 100 psi of initial hydrogen pressure as a result. When the initial hydrogen pressure increased from 6.8 to 13.6 bar, the % yield of liquid and % naphtha was decreased from 76.24% to 62.30% and 45.35% to 31.73%, respectively. But the gases and solids were slightly increased from 18.94% to 25.03% and 4.82% to 12.67%, respectively. It seemed that the pressure at 6.8 bar was the best condition.

In conclusion, the initial hydrogen pressure condition was 6.8 bar, this pressure gave the highest % yield of overall gasoline and % yield of kerosene were 34.58% and 15.71%, respectively. Thus, catalytic cracking could be occurred at 100 psi of initial hydrogen pressure as a result.

### 3.8. Comparison of type of catalyst on product distribution

The comparison of the selectivity of 3 types of catalyst of 5% Fe/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, 5% Fe/Al<sub>2</sub>O<sub>3</sub>, 5% Ni/Al<sub>2</sub>O<sub>3</sub> and thermal cracking reaction. The condition was fixed at 4.0% by wt. of each catalyst, reaction time 75 minutes, reaction temperature 450°C and 6.8 bar of initial hydrogen pressure. The product distributions were shown in Table 1.

From Table 1 showed that all of catalyst gives nearly % yield of oil product. The Fe/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> gave highest light oil *i.e.*, % naphtha, kerosene and light gas oil. The Fe/Al<sub>2</sub>O<sub>3</sub> gave the highest heavy hydrocarbon product while and low naphtha composition. It was obviously noticed that, the role of catalyst to convert of used lubricating oil was very important. Fe/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> gave high gaseous product more than other catalysts because of its acidic catalyst and high surface area. The mechanism was investigated *via* the carbonium ion consequence to crack the long chain hydrocarbon to short chain (C<sub>1</sub>-C<sub>5</sub>) while the other catalysts.

Table 1. Effect of type of catalyst on product composition at 450°C of reaction temperature, 4.0% by wt. of each catalyst, 6.8 bar of initial hydrogen pressure and 75 minutes of reaction time

Type of catalyst	Gas product (%yield)	Oil product (%yield)	Solid (%yield)	Oil product (% recovered)				
				naphtha	kerosene	Light gas oil	Heavy gas oil	Heavy residue
Thermal cracking	8.05	80.42	11.53	20.86	5.71	11.77	3.37	58.30
Fe/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	12.94	76.24	10.82	45.35	15.71	22.83	3.70	12.41
Fe/ Al <sub>2</sub> O <sub>3</sub>	11.62	80.38	8.00	35.14	14.47	24.16	5.53	20.70
Ni/Al <sub>2</sub> O <sub>3</sub>	12.00	77.20	10.80	38.24	15.67	25.44	3.38	16.94

In conclusion, to comparison of catalyst Fe/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, Fe/Al<sub>2</sub>O<sub>3</sub> and Ni/Al<sub>2</sub>O<sub>3</sub> using to convert used lubricating oil to light oil by hydrocracking process was found that Fe/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> shows better efficiency catalyst than Ni/Al<sub>2</sub>O<sub>3</sub> and Fe/Al<sub>2</sub>O<sub>3</sub>. When the catalyst was not used in the reaction, the thermal cracking reaction was developed. The long chain hydrocarbon of reactant was cracked into medium chain hydrocarbon (light gas oil and heavy gas oil). Whereas the long reaction time, the medium chain hydrocarbon was cracked continually into short chain hydrocarbon such as naphtha composition and gaseous product (C<sub>1</sub>-C<sub>4</sub>). On the contrast, the Fe/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst was used in the reaction. The long chain hydrocarbon was cracked into medium chain hydrocarbon (light gas oil and heavy gas oil) and then the catalyst produced hydrogen radical to develop catalytic cracking reaction. The medium chain hydrocarbon was cracked into short chain hydrocarbon such as naphtha more than without using catalyst. Thus, when the catalyst was used, it showed the good efficiency for produced naphtha more quantity than without using catalyst. That is the reason that when thermal cracking was carried out only, it gave less quantity of naphtha when compare with catalytic cracking. The model of the

thermal and catalytic reaction was shown in figure 9. The mechanism of Fe/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst was developed by free radical as shown in figure 10

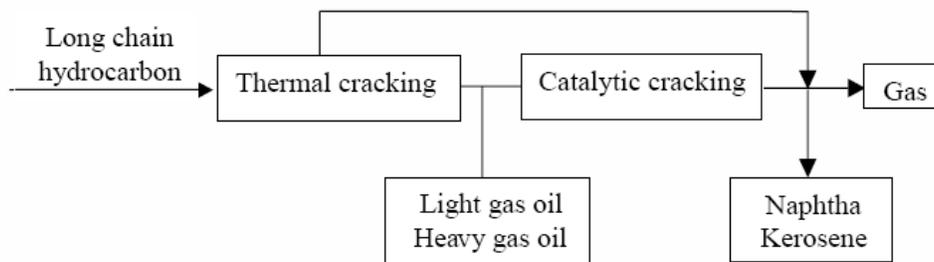


Figure 9. The model of the thermal and catalytic reaction

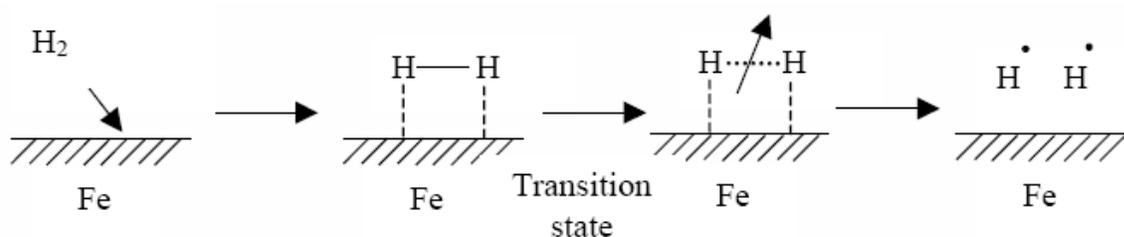
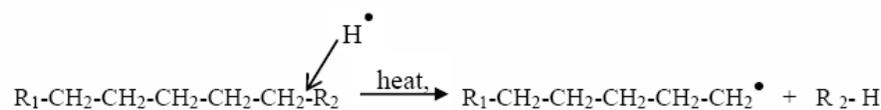


Figure 10. The mechanism on surface of Fe/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst

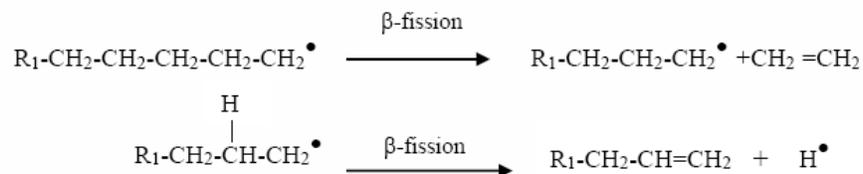
The hydrogen radical was produced and attacked the long chained hydrocarbon. The mechanism was shown in follow:

**1. Initial step**

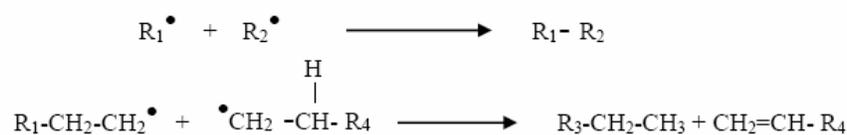


**2. Propagation Step**

**β-fission**



**3. Termination Step**



### 3.9. Characterization of functional groups of oil product by Fourier Transform Infrared Spectroscopy (FT-IR)

Figure 11 shows the functional group compositional analysis of the oil derived from catalytic reaction of 20 g of used lubricating oil, 450°C of reaction temperature, 5% Fe/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, 100 psi of hydrogen pressure, 75 minutes of reaction time and 4.0% by wt. of Fe/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst by Fourier transform infrared (FT-IR) spectrometry. The oil product showed a strong spectrum presence of both aromatic and aliphatic functional group. The strong peak at 1600 cm<sup>-1</sup>, 1495 cm<sup>-1</sup> and 1454 cm<sup>-1</sup> were indication of the presence of C=C stretching of aromatic. In addition, there are weak peak between 3000 and 3100 cm<sup>-1</sup> shows the presence of C-H stretching and the very strong peaks present at 700 cm<sup>-1</sup> indicated the substituted aromatic ring. Figure 12 shows the functional group of gasoline octane number 95 by Fourier transform infrared (FT-IR) spectrometry. It showed a strong spectrum of both aromatic and aliphatic functional group same functional group of oil product. Compared the functional groups of oil product with functional group of gasoline octane number 95 that the aromatic group presents show that some of the functional groups are similar which show that oil products obtained from hydrocracking process can be used as fuel oil effectively.

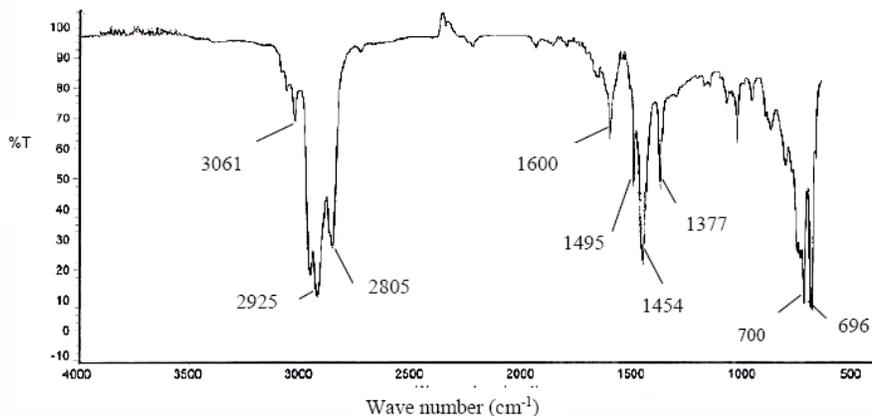


Figure 11 FT-IR spectrum of oil product derived from catalytic reaction of 20 g of used lubricating oil, 450°C of reaction temperature, 6.8 bar of initial hydrogen pressure, 5% Fe/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, 75 minutes of reaction time and 4.0% by wt. of catalyst.

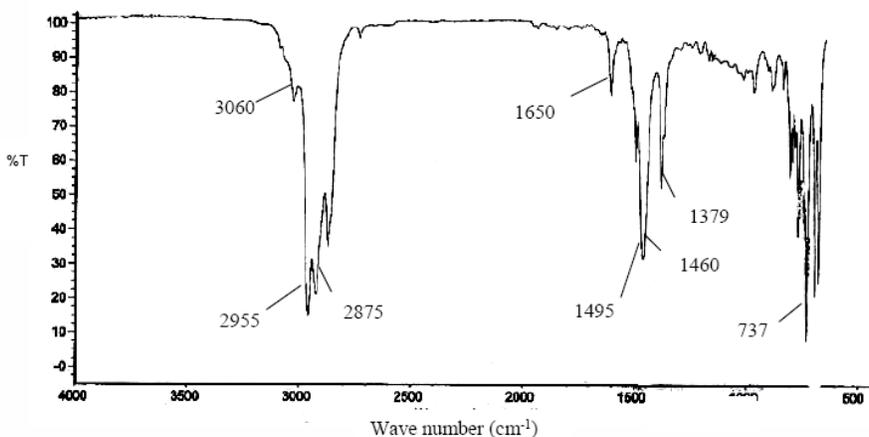


Figure 12 FT-IR spectrum of gasoline octane number 95

#### 4. Conclusions

In this research, the used lubricating oil was used to convert to light oil product by catalytic cracking with Fe/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst. To achieve this objective, the reaction conditions were varied in terms of percentage of Fe load on SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, reaction temperature, reaction time, initial hydrogen pressure and percentage of catalyst. The following conclusion from this study has been drawn: The 0.5, 1, 3 and 5% Fe/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts were prepared. The analysis of percentage of Fe was determined using XRF. The 0.5, 1, 3 and 5% Fe/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts were 0.44%, 0.10%, 2.94% and 5.01%, respectively and BET surface area of catalysts were performed using BET analyzer have 589, 526, 468 and 461 m<sup>2</sup>/g, respectively.

This work aims to study the catalytic cracking of used lubricating oil with Fe/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts in 70 ml micro-reactor, was used the percentage of Fe load on SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> from 0.5%-5%, 390-470°C of reaction temperature, 0-13.6 bar of initial hydrogen pressure, 45-90 minutes of reaction time and 0-6.0% by wt. of Fe/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst. Analysis of oil product was performed using DGC. It may be concluded that the optimum condition: 5% Fe/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, reaction temperature 450°C, initial hydrogen pressure 6.8 bar, 75 minutes of reaction time and 4.0% by wt. of Fe/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst. The products from the optimum condition were 18.94% of gas, 76.24% of oil and 10.82% of solid. The oil products distribution were 45.35% of naphtha, 15.71% of kerosene, 12.50% of light gas oil, 14.04 % of heavy gas oil, 12.41% of long residue and 34.58% overall gasoline.

To compare efficiency of Fe/Al<sub>2</sub>O<sub>3</sub>, Ni/Al<sub>2</sub>O<sub>3</sub> and thermal cracking were compared with Fe/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst. It was found that Fe/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst shows better efficiency than other catalysts, while used same reaction time and percentage of catalyst because it gave high % light oil especially highest % overall gasoline. From FT-IR, the oil product was showed strong presence of both aromatic and aliphatic hydrocarbon. There were very strong peaks of the substituted aromatic hydrocarbon and the present of C-H stretching of aromatic which same a position of spectrums of gasoline.

#### Acknowledgement

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