



Conversion of Waste Oil into Fuel Oil : Effect of Catalyst Ratio

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ABSTRACTS

Research has been conducted to convert waste lubrication oil into fuel oil. This work is the second part of a bigger work entitled "Conversion of Waste Oil into Fuel Oil". The first part dealing with the production of catalyst and the effect of temperature, whilst this part studying the effect of catalyst ratio. This work was done with procedure similar with the first part of the work. Conversion of waste lubrication oil into fuel oil was done using hydrocracking process with catalyst of combination of chromium and activated natural zeolith (Cr/ZAA). Controlled variables used for this researh were the type of waste oil (lubrication oil), feed volume (40 ml), temperature (500°C), and hydrogen gas rate (20 ml/sec).

The weight ratio of the catalyst and waste oil feed was varied at 1/8, 1/4, 1/3, 1/2, and 2/3. The parameters used to analyse the results were the amount of hydrocracking product, percentage of cracking fraction (gasoline, kerosene and solar) in the product and the heating value of the product. Analytic works were carried out with GC for cracking fraction and bomb calorimeter for heating value of the produced fuel oil.

Results showed that the amount of hydrocracking product decreases with the increase of catalyst ratio. Increasing catalyst ratio increases gasoline fraction lineary, decreases kerosene and solar fractions. The heating value of the product lineary increases with catalyst ratio. Best catalyst ratio for this work was 1/8 to get maximum amount of product (13.16 ml for 40 ml feed), and 2/3 to get maximum gasoline fraction (56.70%), and highest heating value (44.92 kJ/gr).

Keywords : hydrocracking, catalyst ratio, waste lubrication oil, fuel oil

I. INTRODUCTION

1.1. Background

Lubrication oil of different types, basically have same function, as lubricant to reduce wearing and heat produced by friction of two contacted metal surfaces when they were moving relatively one another. By the present of lubrication oil, wearing and heat produced due to friction can be reduced. It can be said that all vehicles, having moving parts, need lubrication oil in different amount of volume when they were operated. For instance, a motorcycle needs 800 ml, whilst a car needs 4 liters of lubrication oil (Wijaya,A. & Dhimas,W.P., 2008). After being used for a certain time, this lubrication oil will have a change in its chemical composition, and its physical and mechanical properties (Sani, 2010), making it can not function as lubrication oil anymore.

Normally, used lubrication oil will be discharged as waste. Direct discharge of this used lubrication oil as waste may pollute the

environment. The more vehicles were used, the more waste lubrication oil produced, the more they polluted the environment. Conversion of this waste oil into a more valuable kind of energy may reduce the pollution.

Government of Indonesia has regulation of PP. No.9 issued at 1999 about waste and waste treatment, concerning the usage of waste and the treatment of waste to be converted into more valuable things. One example is the treatment of waste oil into fuel oil (Wijaya,A & Dhimas,W.P., 2008). Referring to PP. No.18/1999, process for treatment of waste oil should not danger the environment (Metalia, 2012).

A method can be adopted to treat and use waste oil without endanger the environment, in accordance with government regulations, PP. No. 9/1999 and PP. No. 18/1999, is via hydrocracking process by the help of catalyst Cr/ZAA, since hydrocracking is a process capable of converting long chain hydrocarbon into short chain with the help of catalyst and hydrogen gas.



1.2. Aim of the Research

The main aim of this research is application of hydrocracking to convert waste lubrication oil into fuel oil using Cr/ZAA as catalyst.

Special aim :

1. To study the effect of catalyst ratio on hydrocracking (the amount of the product)
2. To determine the percent fraction of gasoline, kerosene and solar as the product of hydrocracking
3. To determine the heating values (combustion calor) of hydrocracking product.

II. RESEARCH METHOD

The method of this research is similar with our research method used in the previous research reported in the paper entitled "CONVERSION OF WASTE OIL INTO FUEL OIL, EFFECT OF TEMPERATURE".

2.1. Synthesis of Catalyst Cr/Activated Natural Zeolith (Cr/ZAA)

This synthesis contains 4 steps : production of H-zeolith, catalyst impregnation, catalyst oxydation, and catalyst reduction.

2.1.1. Production of H-zeolith

Natural zeolith was ground to 200 mesh, then refluxed in 1N H₂SO₄ for 6 hours. This zeolith was filtered and washed with aquadest until its filtrate has pH of normal. The zeolith was dried and again grounded to 200 mesh, and dried with microwave for 25 minutes. This process gives result of zeolith containing Bronsted acid situs (H-zeolith).

2.1.2. Catalyst Impregnation

Amount of 30 grams of zeolith was added to 76 grams of Cr(NO₃)₃.9H₂O (the percentage of metal in zeolith is 25%). This mixture was stirred with 500 ml aquadest for 24 hours. In the first 4 hours, NH₄OH was added drop by drop. After stirring process, Cr/zeolith was dried at 130°C for 3 hours into paste, and then calcined at 550°C for 1 hour.

2.1.3. Catalyst Oxydation

Oxydation is to convert metal ion into metal oxyde. This is done to help eliminating H₂O ligand in metal complex ion, which still strong enough to stack in catalyst pore.

Oxydation of zeolith after impregnated with Chromium metal is carried out by flowing O₂ gas with flow rate of 1ml/second. Impregnated zeolith is put in the reactor with glasswool in its base. Oxygen gas is flown through, and the reactor is put inside furnace. When the temperature has reached 400°C (thermocouple), the time is started to be

counted and the temperature held at 400°C for 2 hours.

2.1.4. Catalyst Reduction

After oxydation, the CR/zeolith was reduced with hydrogen gas at temperature of 400°C for 2 hours with hydrogen flow rate of 1ml/second. Reduction has been done to convert metal ion into metal atom (with neutral charge/null).

2.2. Waste Oil Hydrocracking

Hydrocracking catalytic process at gas phase was carried out by taking certain amount of catalyst and putting it into the reactor containing glasswool in its base. The amount of catalyst were varied at weight ratio of catalyst and waste lubrication oil feed of 1/8, 1/4, 1/3, 1/2 and 2/3. Hydrogen gas was flown through as hydrogenation reactant and as reactant carrier with flow rate of 20 ml/sec. This hydrogenation was conducted by heating to temperature of 500°C.

When the temperature has reached 500°C, 40 ml of waste oil started to be fed via burette into the reactor with the catalyst in it. Gas product leaving the catalyst was condensed in the condensor, and the liquid product going out from the reactor furnace were collected in vial bottle of known weight.

Hydrocracking was considered to be completed when there was no more liquid product comes out from the reactor furnace. This product was cooled, collected and weighted.

2.3. Product Analysis

The products from hydrocracking process were analysed their amount for one hour operation. The percentage of gasoline, kerosene and solar fractions in the hydrocracking products were analysed using Gas Chromatography (GC) apparatus. The heating value (gross heating value) of the product was analysed with bomb calorimeter.

III. RESULT AND DISCUSSION

3.1. Effect of Catalyst Ratio to the Amount of Hydrocracking Product.

The effect of catalyst ratio to the amount of hydrocracking product can be seen in Table 1 and Figure 1. It can be seen from Table 1 that the amount of product decreases with the increase of catalyst ratio. This is more obvious from Figure 1. This phenomenon is due to the amount of feed and heat used in the process were constant, whilst the amount of the catalyst was increased by the increase of the weight ratio of catalyst to feed at constant amount of feed. This gives effect that the heat were more used by the catalyst than by feed.



Table 1. Effect of Catalyst Ratio to the Amount of Hydrocracking Product (40 ml waste lubrication oil feed, 20 ml/sec hydrogen velocity, 500°C, 1 hour operation)

Ratio of catalyst to feed (gr/gr)	Amount of product (ml)
1/8	13,16
1/4	11,70
1/3	4,11
1/2	0,96
2/3	0.65

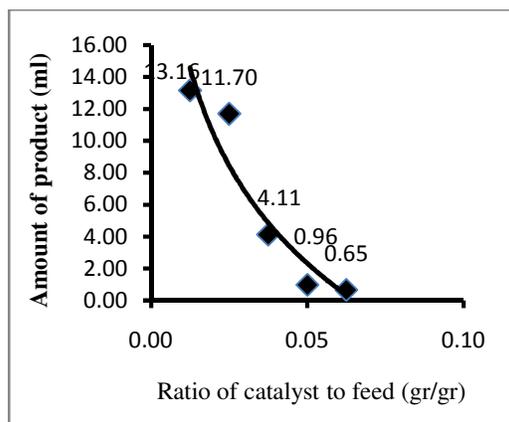


Figure 1. Effect of Catalyst Ratio to the Amount of Hydrocracking Product (40 ml waste lubrication oil feed, 20 ml/sec hydrogen velocity, 500°C, 1 hour operation)

The heat were used by the catalyst to activate its situs for reaction. When the catalyst ratio was increased, and thus the heat available to heat the feed was decreased, the amount of feed evaporated for conversion to product become less at the controlled operating conditions. Or, in other words, if the catalyst ratio is less, the feed evaporated for product will be more at certain operating condition. Highest amount of product was found at catalyst ratio of $1/8 = 0.125$, which was amounted to 13.16 ml for waste oil feed of 40 ml.

3.2. Effect of Catalyst Ratio to the Percentage of Gasoline, Kerosene, and Solar Fraction in the Hydrocracking Product

The percentage of each fraction in the hydrocracking product have been determined using Gas Chromatography (GC) analyser. The results were presented in Table 2 and Figures 2, 3, and 4. Table 2 shows the effect of catalyst ratio to the

percentage of gasoline, kerosene, and solar fraction in the product, whilst Figures 2, 3 and 4 show the effect of catalyst ratio to the products of hydrocracking, which were gasoline, kerosene and solar.

Table 2. The Effect of Catalyst Ratio to the Fraction of Gasoline, Kerosene, and Solar in the Hydrocracking Product (40 ml of waste lubrication oil, 20 ml/sec hydrogen velocity, 500 °C, 1 hour operation).

Ratio of catalyst to feed (gr/gr)	Fraction (%)		
	Gasoline	Kerosene	Solar
1/8	44,93	47,70	7,36
1/4	50,24	34,38	15,37
1/3	48,38	40,86	11,42
1/2	53,91	35,97	10,21
2/3	56,70	34,59	8,70

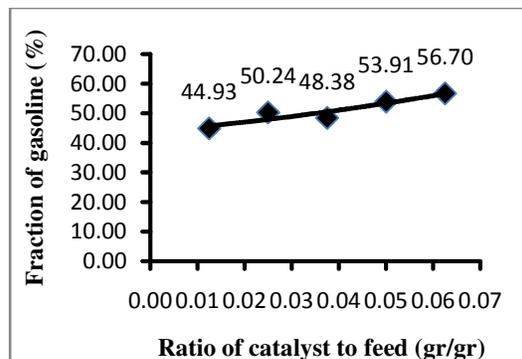
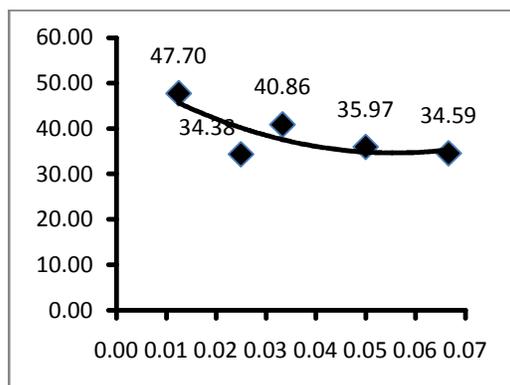


Figure 2. Effect of Catalyst Ratio to the Percentage of Gasoline in the Hydrocracking Product (40 ml of waste lubrication oil, 20 ml/sec hydrogen velocity, 500 C and one hour operation)

It is obvious from Figure 2 that the higher the ratio of catalyst to feed, the more the amount of gasoline fraction in the product. This is because the higher the ratio of catalyst to the feed, the more the surface area of the catalyst during the cracking process. This result was in accordance with the results of research conducted by Fanani (2010), stating that the surface area of the catalyst were increased with the increase of the amount of catalyst used.

Increasing surface area of the catalyst will increase active situs of the catalyst, so that the amount of collision frequency between active situs of the catalyst with the feed during cracking

process will increase, and thus the amount of waste oil cracked into short chain hydrocarbon will also increase. The highest percentage of gasoline fraction was produced by the highest ratio of the catalyst used in this research.



Ratio of catalyst to feed (gr/gr)

Figure 3. Effect of Catalyst Ratio to the Percentage of Kerosene in the Hydrocracking Product (40 ml of waste lubrication oil, 20 ml/sec hydrogen velocity, 500 °C, 1 hour operation).

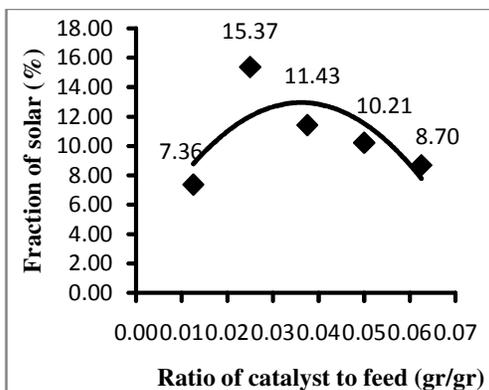


Figure 4. Effect of Catalyst Ratio to the Percentage of Solar in the Hydrocracking Product (40 ml of waste lubrication oil, 20 ml/sec hydrogen velocity, 500 °C, 1 hour operation).

It can be seen from Figures 2 and 3 that the higher the number of catalyst ratio to the feed, the less the percent fraction of kerosene and solar in the product. This is because the higher the ratio of the catalyst, the cracking of long chain hydrocarbon in the waste lubrication oil into kerosene and solar fraction become less effective. Less catalyst ratio used will produce kerosene and solar fraction more effective. This is because the

lower the ratio of catalyst to feed, the less the surface area and the chance of contact between waste oil feed with the catalyst used. As a result, it is more dominant to produce hydrocarbon with longer chain during cracking process. The amount of percent kerosene and solar in the hydrocracking product were at the most when the use of catalyst ratio to feed was at its least amount. Highest percentage of gasoline fraction is found at catalyst ratio of $2/3 = 0.67$, which was amounted to 56.70%.

3.3. Effect of Catalyst Ratio to the Heating Value of Hydrocracking Product

The heating value (the value of combustion calor) of the product of hydrocracking was determined from the amount of energy produced on combustion per unit mass of the product using bomb calorimeter. The results of analysis of the value of combustion calor of the product of hydrocracking is presented in Table 3.

Based on the result of analysis of the value of combustion calor at Table 3 above, it can be seen that the ratio of catalyst to feed affects the value of combustion calor of the product of hydrocracking. This is can be clearly seen from Figure 5.

Figure 5 shows that increasing the ratio of catalyst to feed, increases the value of combustion calor. This is because the higher the ratio of the catalyst, the more the amount of feed being cracked into short chain hydrocarbon (gasoline fraction), and so the higher the value of combustion calor of hydrocracking product.

Table 3. Effect of Catalyst Ratio to the Heating Value (Combustion Calor) of the Product of Hydrocracking (40 ml of waste lubrication oil, 20 ml/sec hydrogen velocity, 500 °C, 1 hour operation).

Ratio of catalyst to feed (gr/gr)	Combustion Calor (kJ/gr)
1/8	40.61
1/4	43.14
1/3	42.65
1/2	44.30
2/3	44.92

This finding is in accordance with the fact that the amount of short chain hydrocarbon (gasoline fraction) is proportional with the value of combustion calor, which increase with the increase of catalyst ratio. Highest value of combustion calor

of 44.92 kJ/gr was found at catalyst ratio of $2/3 = 0.67$.

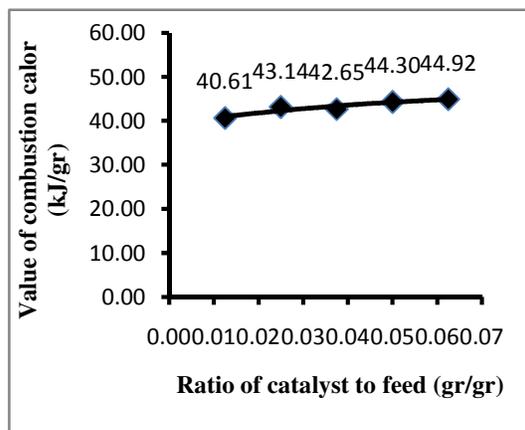


Figure 5. Effect of Catalyst Ratio to the Value of Combustion Calor of Hydrocracking Product (40 ml of waste lubrication oil, 20 ml/sec hydrogen velocity, 500 °C, 1 hour operation).

IV. CONCLUSION

1. The higher the ratio of catalyst used, the lower the amount of hydrocracking product.
2. Higher ratio of catalyst, increases the percentage of gasoline fraction, and decreases the percentage of kerosene and solar fractions in the product.
3. The more the ratio of catalyst used, the higher the heating value (combustion calor) of the product.
4. Within the range of variables used in this work, highest amount of the product is found at catalyst ratio of $1/8 = 0.125$, amounted to 13.16 ml for 40 ml of feed, whilst highest percentage of gasoline fraction is found at catalyst ratio of $2/3 = 0.67$, amounted to 56.70%, and highest heating value (combustion calor) of 44.92 kJ/gr is found at catalyst ratio of $2/3 = 0.67$.

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