

Conversion of Waste Lubricating Oil to Fuels via Catalytic Reaction

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Abstract

This research aimed to evaluate the effects of catalyst and temperature on the hydrocracking reaction of waste lubricant oil to produce fuel oils (gasoline, kerosene, diesel and heavier hydrocarbons). The hydrocracking reaction was studied in a 100 mL semi-batch reactor at atmospheric pressure and temperature of 513, 613 and 653 K. Three catalysts were used including Y-zeolite, Mordenite and Sulfated-alumina. Composition of fuel oils produced were analyzed using gas chromatography. Results showed the amount of products generated depend on the type of catalysts and the reaction temperature. An increase in the reaction temperature results in an increase in the amount of gasoline in the product. At 653 K, Y-zeolite had the high selectivity to gasoline of 37 wt.%. The mordenite catalyst gave the highest amount of diesel of 31 wt.%.

Keywords: Waste lubricating oil, Hydrocracking, Mordenite, Y-zeolite, Sulfated-alumina

1. Introduction

Crude oil shortage has caused the price of fuels and petrochemicals to increase dramatically over the last decade. One of the most demanded petrochemicals is lubricating oil, which is currently derived from atmospheric and vacuum distillation of crude oil. The main role of lubricating oil is to create a film barrier between dynamics parts of the internal combustion engine in order to reduce friction, heat and metal contamination. Typically, vehicle manufactures specify replacing lubricating oil in their engines every 5000 to 10,000 kilometres depending on operating conditions. It was estimated that approximately 230 million liters of lubricating oil is being disposed of every year from auto repair shops and factories [1]. If not treated properly, waste lubricating oil can contaminate the underground water source which can cause serious health problems for people in the area. Therefore, disposal of waste lubricating oil is an important issue that needs to be addressed as well. These two problems mentioned previously can be solved simultaneously by transforming waste lubricating oil to gasoline, jet and diesel fuel by a chemical reaction called hydrocracking.

Hydrocracking is a process in which large molecular weight hydrocarbons are converted to smaller hydrocarbons and alkene molecule over acid heterogeneous catalyst in a hydrogen gas atmosphere. The reaction is usually proceeded through a carbenium ion mechanism, where the reactant molecule is adsorbed on brönsted acid sites, then undergo isomerization

reaction and β -scissions [2, 3]. A variety of petrochemicals reactant have been transformed to higher value fuels via the hydrocracking reaction, such as the conversion of polystyrene [4], chicken fat [5], aromatic [6] and coal tar [7]. Among other catalysts, MoS₂ was found to give higher selectivity to product in the diesel range [8], while Lee et al. reported a fuel fraction yield of 51.9 wt.% from hydrocracking of vacuum residual over NiWS (Nickel-tungsten-sulfide) at 400°C and under 70 bar H₂ atmosphere [9].

Although heterogeneous catalysts are effective for hydrocracking reaction, one major drawback is the catalytic deactivation which proceeded through rapid polymerization of adsorbed reactant to form coke [10]. Incorporation of Mo and Co on beta zeolite was revealed to lower the catalyst deactivation rate during hydrocracking of pyrolysis fuel oil to BTX commodities [11]. The deactivation rate during hydrocracking reaction can be reduced by increasing the mesoporosity of the catalyst. In the case of zeolite catalyst, the ratio between mesopore and micropore can be increased through a process known as recrystallization which involved addition of alkaline and a hydrothermal treatment step during catalyst preparation [12]. Khawatimy et al. reported an increase in performance of Y-zeolite catalyst for hydrocracking of heavy molecular weight hydrocarbon after the catalyst blended with ZnO [13]. Cho et al. discussed the treatment of acidic resin with polyisobutenyl succinimide, which resulted in a reduction in coke formation during hydrocracking reaction [14]. Hierar-

chization of Pt/ZSM-11 through the demetallation was performed to enhance hydroisomerization reaction but reduce hydrocracking ability which was found to occur in both pore mouth and micropore of the catalyst [15]. Kinetic study of hydrocracking reaction over bifunctional silica-alumina revealed cleavage of carbon-carbon bond adjacent to the inner branches of the reactant molecule [16].

In this study, the efficiency of transformation of waste lubricating oil by using different acid heterogeneous catalyst, such as Y-zeolite, sulfated-alumina and mordenite were studied. Product obtained after the hydrocracking reaction included gasoline, jet fuel, diesel and heavier hydrocarbons. Additionally, the effect of reaction temperature on the hydrocracking activity will also be evaluated. The outcome of this research could be useful for conversion of waste lubricating oil to fuel on an industrial scale.

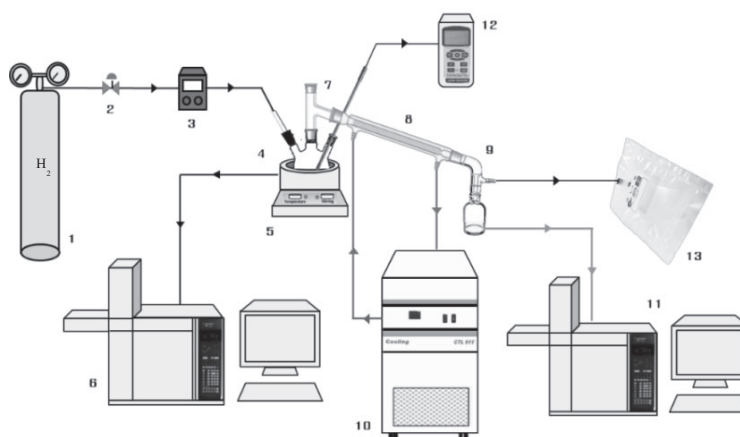


Figure 1 Schematic diagram of hydrocracking system for waste lubricating oil: (1) Hydrogen tank, (2) Flow controller, (3) Flow meter, (4) three neck flask, (5) stirring heating mantle, (6) Simulated distillation by Gas Chromatography, (7) Three-way adapter, (8) Liebig condenser, (9) Vacuum bent adapter, (10) cooling, (11) Gas chromatography, (12) Data logger, (13) Gas Sampling Bags

2. Experimental setup

2.1 Catalyst preparation

Sulfated-alumina was prepared by ion-exchange method between alumina (Sasol, 1 mm) and sulphuric acid solution (Carlo Erba, 98%). Alumina was dried in an oven overnight at 373 K and then stored in a desiccant. To begin the ion-exchange process, 10 g of dried alumina was obtained and put in a 250 mL beaker. Prepare sulphuric acid solution by diluting 98% sulphuric acid in 100 mL of DI water. The concentration of the sulphuric solution was 2.5 M. Pour the solution in the beaker containing alumina and stir vigorously for 1 h. Filter the treated alumina and dried in the oven at 383 K overnight and store in the desiccant until use. Before use, zeolites were calcined under air atmosphere at 723 K for 4 h.

2.2 Hydrocracking reaction

Waste lubricating oil collected from a local auto repair shop was initially filtered in a centrifuge at a rotational speed of 3,000 rpm for 30 minutes and then boiled at 393 K to remove moisture. A semi-batch set-up (Figure 1) was used for hydrocracking of the waste lubricating oil. The hydrocracking process was carried out over different catalysts (Sulfated-alumina, Mordenite, Y-Zeolite) having a ratio of catalyst to feed at 1:10 and hydrogen flow rate of 10 ml/min for 3 h. The reaction temperature range was from 573 to 653 K. A condenser was added at the top of the reactor to trap the liquid products, which will be referred to as upgraded liquid. The composition of upgraded liquid was analyzed by using gas chromatography (HP 5973) equipped with flame Ionized detector (GC-FID) and a DB-1 column (GC temperature program: starting

at 313 K increases to 583K at rate of 10 K/min). Gas product was collected using a 0.5L Tedlar bag and analyzed through a packed column in gas chromatography (GC temperature program: starting at 323 K and increases to 363 K at the rate of 10 K/min).

2.3 Catalyst characterization

Textural characterization of the catalyst samples were obtained by N₂ sorption technique using Quantachrome (Autosorb-1C) instrument at liquid nitrogen temperature. The sample catalyst was transferred to a cylindrical glass cell and degassed for 4 hours under vacuumed He atmosphere. Nitrogen sorption process was conducted under liquid nitrogen (90 K). The analysis revealed surface area, pore volume and pore size of the catalysts.

3. Results and discussion

3.1 Catalysts characterization

Hydrocracking of waste lubricating oil was performed over Y-zeolite (YZ), Mordenite (MOR) and Sulfated-alumina (Sulfated-ALU). The textural characteristics of the catalysts are shown in Table 1. The surface area of the zeolite catalysts is generally higher than sulfated alumina. On the other hand, pore size and pore volume of sulfated alumina is significantly larger than zeolite catalysts. The pore volume of Y-zeolite is higher than mordenite due to the cage-like structure of the Y-zeolite catalyst.

Table 1 Textural characteristic of the catalysts used for hydrocracking reaction

Catalysts	Framework	Surface area (m ² /g)	Pore size (mm)	Pore volume (mL/g)
Y-zeolite	Cage-like	746	3.1	0.59
Mordenite	Linear	511	2.4	0.16
Sulfated-alumina	Tetrahedral	236	12.8	0.45

3.2 Effect of catalysts

Hydrocracking reaction produces upgraded liquid and gas as presented in Figure 2 (mass balance). Residual waste lubricating oil is referred in this graph as Lube. The percentage of waste lubricating oil that is condensed and collected after the hydrocracking reaction is referred to as the upgraded liquid.

A fraction of the reactant waste lubricating oil is turned to gaseous phase due to high degree of hydrocracking activity. This graph shows that 55 wt% of the waste lubricating oil reacted over Y-zeolite (YZ) was transformed to gas product, mostly were small molecular hydrocarbons such as methane, ethane, etc. This reflected a high degree of hydrocracking over YZ due to the higher surface area relative to other catalysts. This result corresponded well with another experiment based on hydrocracking of hydrocarbon over metal loaded zeolite catalyst [17]. Gasoline formation from Y-zeolite was the highest among other catalysts due to the catalyst cage-like framework. Sulfated-alumina was

found to give the lowest conversion of waste lubricating oil. This might be because sulfated-alumina has the lowest surface area compared with the other two catalysts. It can be concluded that Mordenite gave the largest proportion of upgraded liquid of 31 wt%.

The composition of upgraded liquid is shown in Figure 3. Upgraded liquid, which is the condensed product generated from the hydrocracking reaction, consisted of gasoline, jet fuel, diesel and heavier hydrocarbons. At reaction temperature and time of 653 K and 180 min, Y-zeolite gave upgraded liquid containing 37 wt% gasoline, 8 wt% jet fuel, 15 wt.% diesel and 40 wt.% heavier hydrocarbons.

Mordenite produced upgraded liquid with the highest composition of diesel of 31 wt%. Sulfated-alumina was observed to give the highest amount of heavier hydrocarbons, which might be because of its large pore size allowing heavier hydrocarbons to diffuse.

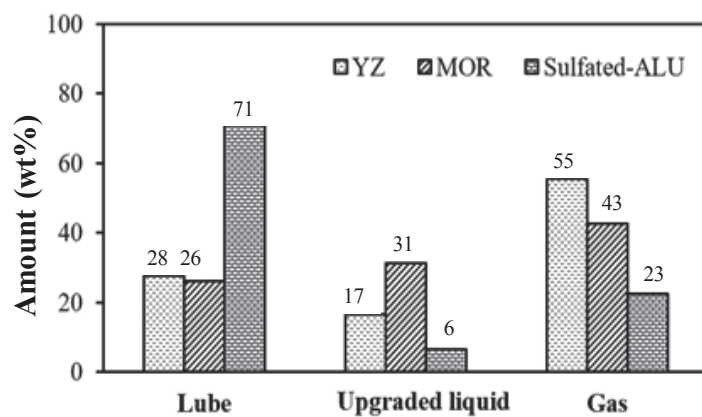


Figure 2 Hydrocracking of waste lubricating oil over three catalysts at 653 K, 180 mins, catalyst to feed ratio of 1:10, and under H₂ flow rate of 10 mL/min.

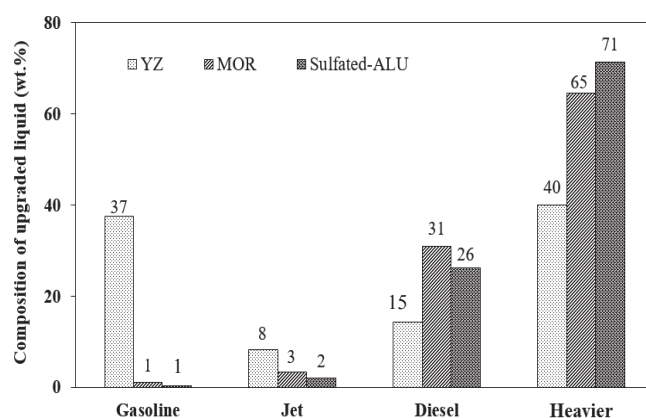


Figure 3 Composition of upgraded liquid from hydrocracking of waste lubricating oil over three catalysts at 653 K, 180 min., catalyst to feed ratio of 1:10 and under H₂ flow rate of 10 mL/min.

3.3 Effect of reaction temperature

The effects of the hydrocracking temperature was studied using Y-zeolite as a catalyst and shown in Figure 4. The Y-zeolite was chosen due to its high catalytic activity demonstrated in the previous section. The effect of temperature needs to be investigated in order to find the appropriate operating condition for hydrocracking reaction. Results showed that addition of Y-zeolite at 653 K generates both liquid and gas products. An increase in hydrocracking temperature was found to improve the activity of the reaction as demonstrated by a reduction in the amount of residual waste

lubricating oil after the reaction. The highest amount of upgraded liquid of 17 wt% was obtained from hydrocracking at 653 K. However, an increase in reaction temperature was also found to increase the formation of gas product, which reflected a high degree of hydrocracking activity at high temperature. Go et al. reported the same relationship between product formation and reaction temperature [18]. The magnitude of increase in reactant conversion was similar to that contained in a research on hydrocracking of *n*-decane over zeolite and SBA catalysts [19].

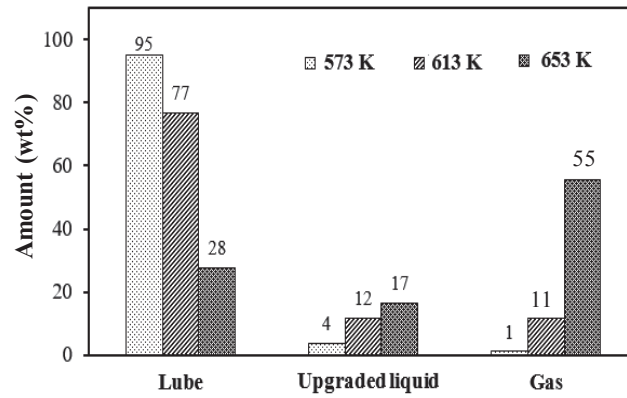


Figure 4 Hydrocracking of waste lubricating oil at difference temperature over Y-zeolite, 180 min, catalyst to feed ratio of 1:10, and under H₂ flow rate of 10 mL/min.

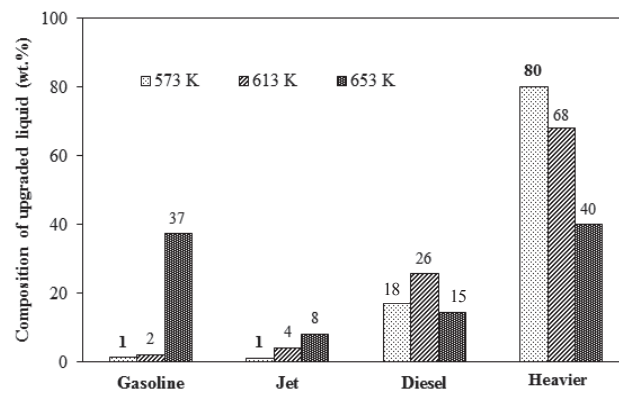


Figure 5 Composition of upgraded liquid from hydrocracking of waste lubricating oil at three different temperatures over Y-zeolite, 180 mins, catalyst to feed ratio of 1:10, and under H₂ flow rate of 10 mL/min.

The influence of reaction temperature on the composition of upgraded liquid is shown in Figure 5. It is observed that an increase in reaction temperature from 573 to 653 K resulted in a dramatic increase in the composition of gasoline from 1 to 37 wt%. The amount of jet fuel also increased with reaction temperature. The amount of diesel fuel peaked at 613 K (26 wt.%), but then decreased to 14 wt.% at 653 K.

4. Conclusion

Hydrocracking reaction of waste lubricating oil was performed in a batch reactor to generate fuel range products. Among the three catalysts Y-zeolite produced the most gas product. Mordenite catalyst gave the most upgraded liquid during the hydrocracking reaction, while sulfated-alumina gave very

small conversion of waste lubricating oil. The composition of upgraded liquid was analyzed further by gas chromatography. Upgraded liquid from Y-zeolite contained mostly gasoline, while mordenite gave a significant effect on the hydrocracking reaction. An increase in temperature was observed to promote formation of gas product. An increase in gasoline content was also associated with the raise in reaction temperature. The optimal amount of diesel fuel was produced at reaction temperature of 613 K.

5. Acknowledgement

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