

LOW DENSITY AND VISCOSITY OF USED LUBRICANT OIL CONVERSION OVER AlPO_4 CATALYST TOWARDS FUEL OIL

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Abstract. The conversion of used lubricating oil towards fuel oil by catalytic conversion is a suitable way to recycle waste oil. Catalyst has a key role in used lubricating oil conversion. Therefore this research was to study the catalytic cracking of used lubricating oil, and thus its properties as an alternative for fuel oil over aluminum fosfate. The experiments were carried out in a batch microreactor at a temperature of 350-400 °C, atmospheric initial air pressure, 5% w/w catalyst concentration, and reaction time of 5 min over aluminum fosfate catalyst. Aluminum fosfate catalyst produced low-density liquid product, and low viscosity of used lubricant oil conversion at any temperature of 350 – 400 °C, compared with those over alumina. Moreover, product converted at 400 °C is easy to flare. The credible reason for the low density and viscosity of AlPO_4 can be proposed by three potentials: this catalyst is an acid type, the acid type is Bronsted and Lewis and this catalyst has a resistance toward contaminant.

Keywords : aluminum fosfate, catalyst, fuel oil, nickel, used lubricant oil, low density, low viscosity.

1. INTRODUCTION

The demand for fuel oil is increasing as the need for transportation and electricity increases. One of the alternative resources is used lubricating oil. Essentially, it is a hydrocarbon consisting of 20 to 50 carbon atoms and categorized as petroleum-, and vegetable oil-based lubricating oil. This resource is generated, after use, in a large and increasing volume, as the usage of machines increases. However, this resource has some properties such as low API gravity, high viscosity, and low flammability. This is well known that the longer the hydrocarbon chains of oil, the viscosity is higher; and vice versa, as the hydrocarbon chain is shorter, the viscosity is lower. To meet fuel oil criteria, it needs viscosity reduction and applicable flammability. To achieve that, it might be upgraded through catalytic pyrolysis, thermal cracking, or catalytic cracking.[1] One of the most important processes in converting low-value hydrocarbons with higher viscous ones into various high-value marketable products with lower viscous ones is catalytic cracking. [2] This process involves pressure, temperature, time, and catalyst. The presence of catalysts accelerates the cracking reactions of long carbon chains under mild conditions processing among others temperature and pressure. Mostly, the range temperature is 390 – 470 °C, 0 – 6% w/w catalyst, initial hydrogen pressure 0 – 200 psi, reaction time 5 – 90 minutes [3], [4].

Many researchers reported catalysts for catalytic cracking of used lubricating oil. The catalysts included or exclude active metals. Some catalysts are based on zeolite, silica-alumina, gamma-alumina, and sulfated zirconia. Makvisai et al published $\text{Fe/Al}_2\text{O}_3$ catalyst for catalytic cracking of used lubricating oil. The product of this catalyst was composed of gas, liquid, and solid. They also reported that the oil and solid product of catalytic cracking is lower than a thermal cracking process of used lubricating oil, and gasses products were higher on catalytic cracking, compared with those on thermal cracking [4]. Gamma alumina is often used because it has an economical price, a stable structure, and a controllable pore size. This alumina is relatively stable at high temperatures and has a high specific area (160-300 m^2/g). Sulfated zirconia, an acidic material, was reported as a reactive cracking catalyst for long-chain hydrocarbons under mild conditions.[5], [6] It was converted from used

lubricating oil into naphtha, kerosene, and light gas oil [3]. Prasad et al. showed HZSM-5, a family of zeolite with a specific ratio of SiO_2 and Al_2O_3 and 5 nm pore in diameter, present to be most efficient in the oil cracking processes of aromatic hydrocarbons of canola oil towards organic fuel oil [7]

It is well known that aluminum phosphate (AlPO_4) is an inorganic material that is included in the metal phosphate category and has stability at high temperatures. This material is categorized as an acidic material, by fosfate structure. Aluminum fosfate has been used widely for many reactions, for instance, transesterification of soybean oil [8], dehydrogenation of cyclohexane [9], selective hydrogenolysis of glycerol to 1,3-propanediol in the vapor phase [10], alcohol conversion, and cumene cracking/dehydrogenation [11]. Thermodynamically, aluminum phosphate remains stable until it melts at a temperature of 2000 °C [12]. The stability of aluminum phosphate depends on the phase present, for example, berlinite is stable up to 700 °C, tridymite is stable up to 1050 °C and the highest is cristobalite [13]. This material also has good resistance to thermal shock, oxidation, and thermal insulation. Aluminum fosfate properties have been studied well. Based on the acid type, aluminum phosphate has Lewis and Bronsted acid, in contrast to alumina which has only Lewis acid sites [14].

Here, aluminum fosfate was applied to the catalytic cracking of used lubricating oil towards fuel oil, and the effects of temperature were investigated under initial atmospheric air pressure.

2. METHODS

Aluminum phosphate (AlPO_4) was prepared from a commercial hydrated aluminum sulfate (Indonesia Acid Industry), ammonia solution (Merck, 25% in wt.), phosphoric acid (food grade), and distilled water. All materials were used as received without further purification. A dropwise ammonia solution was added to aluminum sulfate and phosphoric acid solution until the pH of the supernatant reached 5. The resulting white gel was aged for 1 hour, then washed several times with distilled water, and dried in air at 110 °C. The solid product was calcined in air at 900 °C for 3 hours. Gamma-alumina ($\gamma\text{-Al}_2\text{O}_3$) was prepared by precipitation of aluminum sulfate solution. Ammonia solution was added dropwise until the pH of the supernatant reached 9. Then the supernatant was aged for 1 hour, washed, and dried at 110 °C. The solid obtained was calcined at 600 °C for 6 hours.

The catalytic activity test was carried out in a stainless-steel batch reactor. A total of 5% by weight of cylindrical catalyst (5 mm in diameter, and 3 mm in thickness) was placed in a stainless-steel basket and immersed in the used lubricating oil of the motorcycle with stirring. The initial pressure in the reactor is atmospheric air pressure, and the reaction time is 10 minutes.

Furthermore, the density, viscosity, and flammability tests of the product were carried out. The density test was measured by a pycnometer, the viscosity test was performed by a viscometer Ostwald, and the flammability test was performed by a fire near the liquid product.

3. RESULTS AND DISCUSSION

3.1 Effect Temperature on Density

Figure 1 shows the density of the product under a catalytic cracking process of used lubricating oil over catalysts as a function of temperature. The product was a liquid. The densities of product over AlPO_4 catalyst tend to decrease as temperature increases. Similar results were shown as a product over Al_2O_3 . For all of the temperatures, only at maximum temperature (400 °C) is the product density of both catalysts comparable. It shows a tendency as the reaction temperature increases, the density decreases. It is well known as temperature increases the cracking of carbon chain takes place rapidly. So that a shorter carbon chain is produced. The carbon chain contributed to its density by its low weight under the same volume. The shorter carbon chains, the smaller their density. Conversely, the longer the carbon chain, the higher its density.

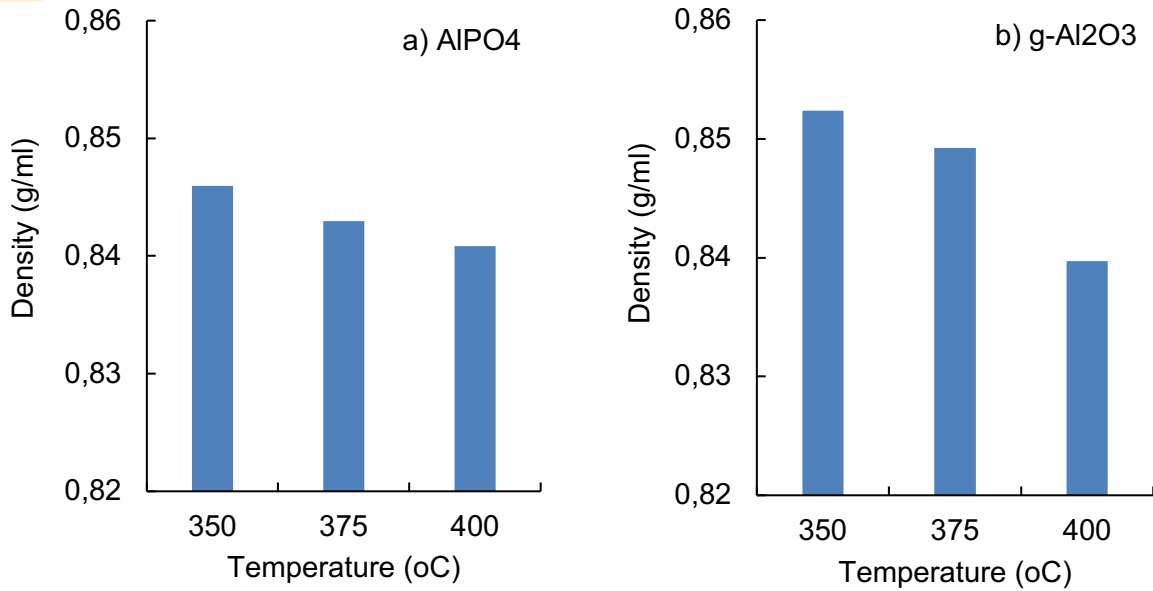


Figure 1. The density of product under catalytic cracking process a) AlPO₄, b) g-Al₂O₃. The initial air pressure was atmospheric, and the reaction time was 10 minutes under vigorous stirring.

Comparing the density of products over AlPO₄ and g-Al₂O₃, they show that the liquid density of those produced by AlPO₄ is lower than those over g-Al₂O₃. For instance, at a temperature of 350 °C, the density of those over AlPO₄ is around 0.8460 gram/ml, compared with those over g-Al₂O₃ i.e. 0.8520 gram/ml. It can be understood that the cracking of the carbon chain over AlPO₄ takes place intensively and the product is a shorter carbon chain compared with those over g-Al₂O₃.

3.2 Effect Temperature on Viscosity

Figure 2 shows the dynamic viscosity of the liquid product under the catalytic cracking process of RBD used lubricating oil over catalysts as a function of temperature. The dynamic viscosity of the product over the AlPO₄ catalyst tends to decrease as temperature increases. Similar results were shown by a product over g-Al₂O₃. At all temperatures, only at maximum temperature (400 °C) the product dynamic viscosity of both catalysts is comparable. It shows a tendency as the reaction temperature increases, the dynamic viscosity decreases. For a given sample, μ_{din} is dynamic viscosity (mPa.s), ρ is density (kg/cm³), and t is flowing time (s), the dynamic viscosity was correlated by a formula:

$$\mu_{din\ sample} = \frac{\rho_{sample} \times t_{sample}}{\rho_{water} \times t_{water}} \times \mu_{din\ water}$$

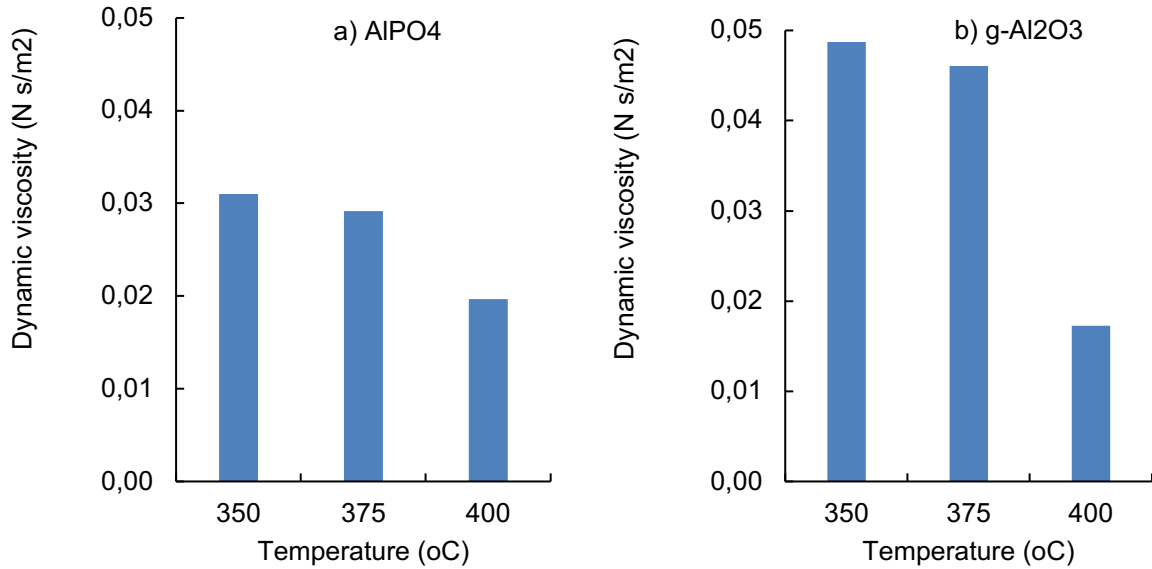


Figure 2. The viscosity of product under catalytic cracking process a) AlPO₄, b) g-Al₂O₃. The initial air pressure was atmospheric, and the reaction time was 10 minutes under vigorous stirring.

Based on the correlation, the dynamic viscosity is affected by the density and flowing time of samples, as the properties of water are constant. As density and/or flow time decrease, the dynamic viscosity decrease. Vice-versa, as density and/or flow time increase, the dynamic viscosity increase. It is well known that low-density liquid is commonly easy to flow so that the time flow is in low number.

Comparing the dynamic viscosity of the product over AlPO₄ and g-Al₂O₃, they show that the dynamic viscosity of liquid produced by AlPO₄ is lower than those of g-Al₂O₃. For instance, at temperature 350 °C, the density of those over AlPO₄ is around 0.0310 N s/m², compared with those over g-Al₂O₃ i.e. 0.0487 N s/m². It can be understood that the cracking of the carbon chain over AlPO₄ takes place intensively and the product is a shorter carbon chain compared with those over g-Al₂O₃.

3.3 Effect Temperature on Flammability

Table 1 shows the flammability test of the product. For both AlPO₄ and g-Al₂O₃ catalysts only at a temperature of 400 °C the products are easily burned/ignite. This showed that the conversion of used lubricating oil into fuel occurs at 400 °C under initial atmospheric air pressure.

Table 1. Flammability test of a product under catalytic cracking process. The initial air pressure was atmospheric, 5%w/w catalyst, and the reaction time was 10 minutes under vigorous stirring.

Catalyst	Temperature (°C)	Flammability test
AlPO ₄	350	Not easy to burn/ignite
AlPO ₄	375	Not easy to burn/ignite
AlPO ₄	400	Easily burn/ignite
g-Al ₂ O ₃	350	Not easy to burn/ignite
g-Al ₂ O ₃	375	Not easy to burn/ignite
g-Al ₂ O ₃	400	Easily burn/ignite

3.4 Possible reason

The present study demonstrates that AlPO₄ catalyst exhibits a lower density and viscosity liquid product. These phenomena can be associated with the following two features of metal fosfate. First, the catalytic performance might be affected by its acidity. It is well known that aluminum fosfate is an acidic material by its fosfate structure while g-Al₂O₃ tends to be basic material by its oxide. To estimate the acid strength, one of the methods is electronegativity. Electronegativity is a chemical property relating to the ability of an atom (or more precisely a functional group) to attract electrons (or electron density) towards itself in a covalent bond. A small number of

electronegativity means the material is a base, and a high number of electronegativity means the material is acidic. Based on Sanderson electronegativity, for a compound $X_xY_yZ_z$, the mean electronegativity (S) is the geometric mean of the electronegativities of each of the constituent atoms (S_X , S_Y , and S_Z) given by the equation:

$$S = [S_X^x \cdot S_Y^y \cdot S_Z^z]^{1/(x+y+z)}$$

Table 2. The geometric mean of the electronegativities is based on the Sanderson correlation.

Compound	The geometric mean of the electronegativities
AlPO ₄	2.81
g-Al ₂ O ₃	2.54

The obtained parameter has been successfully correlated with physicochemical properties such as the NO_x conversion efficiency, [15] the acidity of ZrO₂, and acidity of metal phosphates. The geometric mean of the electronegativities was shown in Table 2. Clearly, Table 2 shows that the geometric means of the electronegativities on AlPO₄ is higher than that on g-Al₂O₃. That means AlPO₄ has higher acidity than g-Al₂O₃. Second, this can be related to the acid-base properties of materials. Aluminum fosfate contains Lewis and Bronsted acid types, in contrast to g-Al₂O₃ which has Lewis acid type only. Moreover, AlPO₄ was dominated by acid type, rather than base type; in contrast to g-Al₂O₃ which was dominated by base type rather than acid type.[14] Third, note that the used lubricating oil contains contaminants. The contaminants reported include metal, water content, phosphorus, and sulfur.[16], [17] These contaminants affected the catalytic activities. For instance, the presence of phosphorus and sulfur was reported to decrease catalytic activities. [14] Aluminum fosfate was reported to have a resiliency toward phosphorus and sulfur poisoning, in contrast to g-Al₂O₃.

4. CONCLUSION

The conversion of used lubricating oil over AlPO₄ and g-Al₂O₃ was successfully achieved. Liquid density product over AlPO₄ catalysts shows a low number compared with those over g-Al₂O₃. In all of the temperatures, only at maximum temperature (400 °C) the product density of both catalysts is comparable. Aluminum fosfate resulted in a lower dynamic viscosity than g-Al₂O₃ at all temperatures, except at maximum temperature (400 °C). At 400 °C, the dynamic viscosity of both catalysts is equivalent. The flammability test shows only at 400 °C the liquid product is easily burned. The possible reason for the low density and viscosity of AlPO₄ can be suggested by three possibilities: this catalyst is an acid type, acid the type is Bronsted and Lewis, and this catalyst has a resilience toward contaminant.

5. ACKNOWLEDGEMENT

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