Optimization Ratio of Mixed Metal Soaps (Al-Ca) and Palm Fatty Acid Distillate (PFAD) on Making Grease

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Abstract. Palm Fatty Acid Destilate (PFAD) to be used as a raw material for making oleochemical products, solid lubricant. This is caused by the composition of fatty acids contained in PFAD not much different from the composition of fatty acids found in palm oil. This study aims to determine the formulation of solid lubricants (grease) from PFAD and compound metal soap (Al-Ca) as thickener which has characteristics close to SNI solid lubricants and know the quality of solid lubricants produced. The method used in the manufacture of solid grease (grease) consists of two stages. The first stage is the process of making mixed metal soap (Al-Ca) by mixing PFAD and Al(OH)\textsubscript{3}-Ca(OH)\textsubscript{2} and analyzing the mixed metal soap. The second stage is the manufacture of solid lubricants (grease) from mixed metal soap (Al-Ca) and PFAD as well as analyzing the resulting product.

Based on the research that has been done, the optimum solid lubricant obtained according to SNI standards is in the composition of A:B1, A1 is the ratio of Al(OH)\textsubscript{3}:Ca(OH)\textsubscript{2} = 90\%:10\% and B1 is the ratio of metal soap:PFAD =90 \%.10\%, so the density is 0.95gr/ml and the penetration value is 194 (25 °C).

1. Introduction

Increased development in the industrial and transportation sectors today significantly increases the use of lubricants. This means that a significant amount of lubrication is needed to meet consumption needs in the industrial and transportation sectors. Generally, lubricants that are often found on the market are made from petroleum or petroleum base oil. With the depletion of petroleum reserves, fewer and fewer basic raw materials for making lubricating oil can meet the needs in Indonesia. This is predicted to result in scarcity of lubricants in the market or increasingly expensive lubricants due to imports from abroad. This condition certainly provides inspiration for several countries including Indonesia to continue to increase efforts in finding alternative raw materials that can substitute petroleum. Vegetable oil is one of the raw materials that can be used as a base for making alternative lubricants for machines. Palm oil derivatives, especially glycerol and oleic acid, have the potential to be developed as raw materials for synthetic lubricants [1]. In addition, lubricating oils can also be synthesized from fatty acid esters derived from vegetable oils. Generally, the lubricating oil is synthesized from fatty acid esters with carbon chains in the range above, so that it has the opportunity to be developed as a raw material for lubricating oil [2]. Palm oil derivative products namely Palm
Fatty Acid Destilate (PFAD) are by-products of cooking oil factories, where their utilization is still limited. In addition, PFAD is only used as a raw material for making soap with low quality. Meanwhile, PFAD has high potential to be used as raw material for making oleochemical products, one of which is solid lubricant. This is caused by the composition of fatty acids contained in PFAD not much different from the composition of fatty acids found in palm oil. The utilization of cooking oil by-products in the manufacture of solid lubricants is carried out with a treatment technique that is the mixing of mixed metal soap (Na-Ca) with palm oil and its derivative namely PFAD which is used as a base oil.

Based on previous research, the research team has made a solid grease from Palm Fatty Acid Distillate (PFAD) using Na and Li metal soap. The optimum ratio obtained in the composition of 95: 5 for Na metal and 35: 65 for Li metal [3] [4], but the test results are still not optimal enough if applied to vehicles or machinery. And in 2016 the researchers continued the study using Li-Ca mixed metal soap to obtain the optimum A2 : B3 composition. A2 is a LiOH : Ca(OH)2 ratio of 80% : 20% and B3 which is a metal soap : PFAD ratio of 70% : 30%, a density of 0.953 gr/ml, a dropping point of 105°C, with a NLGI consistency value 6.

2. Material and Methods

2.1. Materials
Palm Fatty Acid Destillate (PFAD) as a material for making metal soap and raw material for making solid lubricants, mixed metals (Al and Ca) as a thickening agent in the manufacture of metal soap, glycerol as a substance to maintain the thickness of a solid lubricant, phenol as an antioxidant, and as anti-corrosion stearic purchased from Bratachem and Rudang Jaya.

2.2. Manufacture of Mixed Metal Soap
The functions of mixed metal soap (Al-Ca) is as a thickener in the grease which is produced from the reaction between PFAD and the bases of Al(OH)3 and Ca(OH)2. Made by heated up PFAD until melting at 70 °C then added Al(OH)3 and Ca(OH)2 4N solution and stirred at 650 rpm for 30 minutes. The ratio between Al(OH)3 and Ca(OH)2 in mixed metals is 90:10 (A1) and 80:20 (A2). The mixed metal soap was evaluated by free base content and non-soaped ingredients.

2.3. Analysis of Free Base Content
Analysis of the free base content was carried out by adding 100 ml of 95% alcohol into 5 grams of sample and heated for 30 minutes then titrated with 0.5N HCl and phenolphtalein indicator of 2-3 drops.

2.4. Analysis of unsaponifiable matter
Analysis of the non-soaped ingredients is carried out by putting in 50 ml of alcoholic KOH 0.5N into a free base analysis solution and heated for 1 hour, then titrated with 0.5N HCl with the Phenolphthalein indicator 2-3 drops. Then do the same thing with the blank.

2.5. Grease Production
Grease is made by heating PFAD up to 70 °C in the reactor then added mixed metal soap as thickener according to the predetermined variations. The ratio between PFAD and mixed metal soaps is 10:90 (B1) and 20:80 (B2). After that, 5 ml of stearic acid, glycerin and phenol were added to each variations solution and then stirred at a speed of 650 rpm for 240 minutes at a temperature of 120 °C until homogeneous. Obtain solid lubricant and analyze solid lubricant.

2.6. Analyzing of Grease
The resulting Grease products were analyzed of the density, melting point, penetration, and NLGI analysis parameters. The melting point and NLGI penetration analysis based on ASTM-D-566 and
ASTM-D-217, respectively. Conducted at the LEMIGAS Oil and Gas Technology Research and Development Laboratory Center in South Jakarta.

2.7. Procedure of ASTM D-217

The order is to determine the stiffness of a grease. The P0 or unworked and P60 or worked penetration tests followed the ASTM D-217 method for full scale. This is one of the four required tests performed on every single batch of grease at Nye prior to shipping. The penetration test begins with the grease at 25 degrees Celsius, plus or minus 1 degree Celsius, being leveled into a cup. The sample size and cone weight for this test is determined by your application needs. Using a penetrometer, it is dropped into the cup for 5 seconds, creating a hole in the grease. The technician records the depth of a millimeter of this hole. This value is known as the P0 or unworked penetration. The grease is then sheared (or worked) using a mechanically operated device through 60 double strokes, simulating the use of the grease. When this is completed, the technician repeats the P60 value, also known as a worked penetration. Nye technicians can also carry out P10,000 and P100,000 tests, depending on the application’s specifications.

The penetration values of P60 are rated using the NLGI grade chart from 000 to 6. These values determine the stiffness of the grease and how the grease will react over time to service and wear. The higher the penetration value, the softer the grease. The lower the penetration value, the stiffer the grease. Grease that is not too easy to pass from the area that needs to be lubricated. Grease that is too stiff may not effectively migrate to those areas that need to be lubricated.

2.7.1. ASTM-D-566

Fill a test cup with a sample by pressing the larger opening into the grease to be tested until the cup is filled. Place the cork on the thermometer depth gage position in the test tube. Replace the depth gage with the grease cup. Suspend the test tube in the oil bath to a depth corresponding to the 76 mm immersion mark on the thermometer. Suspend the second thermometer in the oil bath so that its bulb is at approximately the same level as the bulb of the test tube thermometer. Stir the oil bath and heat. Two determination can be made simultaneously in the same bath.

Analysis of Grease Density

Weigh of a clean and dry empty pycnometer then record the weight. Put aquadest into it and review again then record the results. Calculate the density of aquadest by using the formula: $\mu = \frac{(\text{Pycnometer weight contains aquadest}-\text{Empty pycnometer weight})}{(\text{Pycnometer volume})}$. $\mu = \text{grams} / \text{ml}$

Perform the same procedure for solid lubricants.

3. Results and Discussion

| No | Composition (%) (PFAD:Metal Soap) | Density (gram/ml) | Titrant 25$^\circ$C ASTM D 217 | Colour |
|----|----------------------------------|------------------|-------------------------------|--------|
| 1  | A1 : B1                          | 0.95             | 194                           | Brown  |
| 2  | A1 : B2                          | 0.91             | 140                           | Brown  |
| 3  | A1 : B3                          | 0.87             | 115                           | Brown  |
| 4  | A2 : B1                          | 0.96             | 34                            | Brown  |
| 5  | A2 : B2                          | 0.91             | 34                            | Brown  |
| 6  | A3 : B3                          | 0.87             | 50                            | Brown  |

Description: $A =$ Ratio $\text{Al(OH)}_3 : \text{Ca(OH)}_2$ (%);
$B =$ Ratio $\text{PFAD:Metal soap}$ (%)

A1 : B1 = (90 : 10) ; (10 : 90); A1 : B2 = (90 : 10) ; (20 : 80); A1 : B3 = (90:10) ; (30 : 70);
A2 : B1 = (80 : 20) ; (10 : 90); A2 : B2 = (80 : 20) ; (20 : 80); A2 : B3 = (80 : 20) ;(30:70)
From the graphic image of the relationship of composition (PFAD:Al-Ca metal soap) to the density showed a decrease, both for compositions 1, 2 and 3 (type of metal soap A1) and composition 4, 5, and 6 (type of metal soap A2). Where in the composition 1 (one) (A1: B1) obtained a density of 0.95 gr / ml; composition 2 (two) (A1: B2) obtained a density of 0.91 gr / ml, composition 3 (three) (A1: B3) obtained a density of 0.87 gr / ml; composition 4 (four) (A2: B1) obtained a density of 0.96 gr / ml; composition of 5 (five) (A2: B2) obtained a density of 0.91 g / ml; and the composition of 6 (six) (A2: B3) obtained a density of 0.87 gr / ml. This is due to the decreasing composition of metal soap and increasing composition of PFAD resulting in a decrease in lubricant density. This condition is slightly different from commercial solid lubricants which is 0.82 gr / ml.

The ratio of Al(OH)₃ to Ca(OH)₂ also affects the density of the solid lubricant. This density is influenced by the density of each metal, where Al(OH)₃ has a density of 2.4 gr / ml [5] and Ca (OH) 2 has a density of 2.2 gr / ml [5]. This causes the density of solid lubricants with A1 and A2 metal soap types to have a slight difference because the densities of the two types of metals are also not much different. From the results of tests conducted, it can be said that palm oil based solid lubricants that have been formulated have the same relative density as commercial lubricants, ranging from 0.827 gr / ml - 1,107 gr / ml.
3.1. Titrant

From the graphic image of the relationship of composition (PFAD:Al-Ca metal soap) to the penetration value, it shows a decrease and an increase in penetration value. Where in the composition of 1 (one) (A1: B1) a penetration of 194 mm / 10 was obtained; composition 2 (two) (A1: B2) obtained a penetration of 140 mm / 10; composition 3 (three) (A1: B3) obtained a penetration of 115 mm / 10; composition 4 (four) (A2: B1) obtained 34 mm / 10 penetration; composition 5 (five) (A2: B2) a penetration of 34 mm / 10 is obtained; and the composition of 6 (six) (A2: B3) is obtained a penetration of 50 mm / 10. From the above data, we can see the decreasing composition of PFAD and the increasing composition of metal soap resulting in a decrease in the value of lubricant penetration. The resulting solid lubricant has an NLGI value close to the hardness level of commercial solid lubricants according to NLGI, namely NLGI 2. Where in composition 1, with a penetration value of 194 mm / 10 included in NLGI 4, composition 2 with a penetration value of 140 mm / 10 included in NLGI 5, composition 3 with a penetration value of 115 mm / 10 included in NLGI 6, composition 4 with penetration value 34 mm / 10 included in NLGI> 6, composition 5 with penetration value 34 mm / 10 included in NLGI> 6, composition 6 with penetration value 50 mm / 10 included in NLGI> 6.

Based on the results of the study obtained the number of bases, which are in accordance with the quality standards set by the Ministry of Industry and Trade in accordance with SNI 06-2048-1990 regarding the quality standards of metal soap. From the results of the study the levels of free base obtained for the type of metal soap A1 is 0.05% and the type of metal soap A2 is 0.02% or slightly above the neutral level (point 0). In addition to the free base content in metal soap also analyzed the characteristics of non-soapy material numbers, where in the A1 metal type is 0.86% and A2 metal soap 0.84% the characteristics of commercial solid lubricants based on ASTM (American Society for Testing and Materials International) quality standards. In this research, the raw material used in the manufacture of solid lubricants is Palm Fatty Acid Distillate (PFAD) and metal soap. The metal soap used in the formulation of solid lubricants is obtained by saponification using aluminum (Al (OH)₃) and Calcium (Ca(OH)₂) with PFAD raw material.

The raw materials consisting of base oil are PFAD and Al-Ca alloy soap after being physically blended and have become solid lubricants then their characteristics are analyzed using the methods of ASTM D-217 for penetration and ASTM D-566 for point melting conducted at the Laboratory of Research and Development Center for Oil and Gas Technology "LEMIGAS" Jalan Ciledug Raya No 109, RT.07 / RW.05, Cipulir, Kebayoran Lama, South Jakarta City, Special Capital Region of Jakarta. Density testing was conducted at the Laboratory of Research in the Chemical Engineering ITM-Medan.
From Figure 2 it can be seen that the ratio of Al (OH)$_3$ to Ca (OH)$_2$ also influences the density of solid lubricants. This density is influenced by the density of each metal, where Al (OH)$_3$ has a density of 2.4 gr / ml [5] and Ca (OH)$_2$ has a density of 2.2 gr / ml [5]. This causes the density of solid lubricants with A1 and A2 metal soap types to have a slight difference because the densities of the two types of metals are also not much different. From Figure 2 above we can see the decreasing composition of PFAD and the increasing composition of metal soap resulting in a decrease in the value of lubricant penetration.

4. Conclusion
Palm Fatty Acid Distillate (PFAD) can be used as a raw material for making palm oil based grease which is environmentally friendly and has the characteristics of commercial solid lubricants. The variation of the composition of the mixture of metal soap (thickening agent) and PFAD (base oil) in the manufacture of solid lubricants affects the results of density analysis, penetration, melting point and NLGI. The best solid grease produced in accordance with ASTM standards and SNI 06-7069-8-2005 which is included in Grade A, is found in the ratio of metal soap to base oil, namely A1: B1. A1 is the ratio of Al (OH)$_3$ : Ca (OH)$_2$ = 90%: 10% and B1 which is the ratio of metal soap: PFAD = 90%: 10% with the following criteria: Density: 0.95 gr / ml, Penetration: 194 (25°C)

5. Acknowledgment
The authors are grateful to LLDIKTI for financial support.

6. References
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