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

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Abstract. Palm Fatty Acid Distillate (PFAD) has a high potential to be used as raw material for oleochemical products, one of them is for grease. This is because the fatty acid composition contained in PFAD is not much different from the fatty acid composition contained in palm oil. The purpose of this research is to study the formulation grease from PFAD which has characteristic approaching grease SNI 06-7069-8-2005. The method used in the manufacture of grease consists of two steps. The first step is the process for preparing a mixture of metal soap (Na-Ca) with predetermined variations and analyzing metal alloy soaps. The second step is the manufacture of grease from a mixture of metal soaps (Na-Ca) and PFAD and analyzing the product. Based on the research the optimum solids obtained in accordance with the SNI standard is in composition A2: B1, A2 is the ratio of NaOH: Ca (OH)₂ = 80%: 20% and B1 is PFAD ratio: metal soap = 10%: 90% with density analysis 1.108 g/ml, melting point 1100C, titrant value 92 and NLGI 6 consistency.

1. Introduction

Utilization of palm oil in the manufacture of solid lubricants is a substitute for base oil and thickening components. Palm oil is one of alternatives, however, direct use of palm oil as a lubricant remain cause problems namely high density of palm oil leads to imperfect lubrication [1]. The need for lubricating oil made from synthetic materials derived from non-renewable energy sources is increasing, so we must immediately search for alternative ingredients as Lubricants[2]. The type of palm oil used is PFAD. PFAD is a by-product of the process of purifying crude palm oil. Until now the use of PFAD is limited, which is used as a raw material for making low-quality soap [3]. Palm Fatty Acid Distillate (PFAD) oil from vegetable oils family was compared with mineral oil with regard to tribological properties, such as anti-wear, anti-friction, viscosity index, and flash parameter point, using a four-ball tribotester under different temperatures [4]. One type of vegetable oil that has been assessed as a base for lubricants and lubricating oils is Castor oil. Castor oil has a low pour point, resistance to load (wear) and a better viscosity index compared to super-refined mineral oil (SRMO) which is a lubricant base material. This allows castor oil to be used as a variation of the lubricant base
material [5]. The characteristics of PFAD are influenced by three basic parameters namely boiling point, specific heat, and latent heat from fatty acids [6].

The solid lubricant is a solid or semi-solid mixture of lubricants with thickener which serves to reduce friction between two surfaces that intersect or rub against each other [7]. Good solid lubricating properties are reducing friction, preventing corrosion, as insulation from dirt or water, preventing leakage, consistency and unchanging structure, not hardening at low temperatures, properties suitable for elastomeric insulation, and having a certain level of pollutant tolerance. Based on previous research, the research team has made grease from Palm Fatty Acid Distillate (PFAD) using Na and Li metal soap. The optimum ratio obtained at the composition of 95:5 for sodium metal and 35:65 for lithium metal [8], but the results of penetration test and melting point are still not optimal if applied to vehicles or machines.

Additives are an additional ingredient that functions as a vitamin for solid lubricants whose uses include, as an anti-corrosion, as anti-wear, as an anti-oxidant, maintaining a thick lubricant viscosity (viscosity index improver). The solid lubricant is composed of several components [9], namely, basic oil (base oil), thickener, additives. According to the latest theory, base thickener and oil always exist together on the surface of the friction and do not justify popular theories that view thickener only as a sponge that releases base oil to the friction surface [10].

The grease is a material that serves to protect several functioning engine components, so that grease can have a positive effect on tools and machines, which can prevent wear due to friction between components with one other component. In addition, grease can also minimize maintenance and repair costs of tools and machinery. Increased development in the industrial and transportation sectors currently increases the use of grease significantly. This means a large amount of grease is needed to meet consumption needs in the industrial and transportation sectors. Generally, many greases found on the market are made from petroleum or petroleum base oil. With the depletion of petroleum reserves, fewer basic raw materials for grease can meet Indonesia's needs. This is predicted to lead to a shortage of grease in the market or more expensive grease due to imports from abroad.

Vegetable oil is one of the raw materials that can be used as basic material of making alternative lubricant for machine. The derivatives of palm oil, especially glycerol and oleic acid have the potential to be developed as a synthetic grease feedstock. In addition, grease can also be synthesized from fatty acid esters derived from vegetable oils. Generally, grease is synthesized from fatty acid esters with carbon chains in the above range, thus having the opportunity to be developed as raw materials for lubricating oils.

Oil development studies have not been conducted in Indonesia and information is still limited. Therefore, this study attempts to develop further the technology of manufacturing grease to assess the extent to which the potential of palm oil and its derivative products can be developed as grease. Palm oil derivative products namely Palm Fatty Acid Distillate (PFAD) is a by-product of cooking oil factory, where its utilization is still limited. In addition, PFAD is only used as a raw material of soap maker with low quality. Meanwhile, PFAD has a high potential for use as a raw material for oleochemical products, one of which is grease. This is because the fatty acid composition contained in PFAD is not much different from the fatty acid composition contained in palm oil. The utilization of byproducts from this cooking oil factory in the manufacture of greases done by processing technique that is mixing between mixed metal soap (sodium and calcium) with palm oil and its derivative is PFAD which is used as base oil.

2. Material and Methods

2.1 Materials

Sodium hydroxide, stearic acid, phenol, glycerol purchased from Bratachem and calcium hydroxide purchased from Rudang Jaya. All of the chemicals were technical grade and were used without any purification. The products were evaluated by the determination of free base content and unsaponifiable matter on metal soap. The result obtained is in the form of the density test, titrant, melting point, and National Lubricating Grease Institute (NLGI) number.
2.2. Variables and Process Conditions of Preparation of mixed metal soaps

The functions of mixed metal soap (Na-Ca) is as a thickener in the grease which is produced from the reaction between PFAD and the bases of NaOH and Ca(OH)$_2$. Made by heated up PFAD until melting at 70 °C then added NaOH and Ca(OH)$_2$ 4N solution and stirred at 650 rpm for 30 minutes. The ratio between NaOH 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. Preparation of Mixed sodium-calcium soaps

PFAD (100 g) is heated to a temperature of 70 °C, stirred continuously at a speed of 650 rpm for 30 minutes. To the PDAF solution was gradually stirred and added a mixture of 4N sodium and calcium solution according to variations in the manufacture of metal soaps, i.e. the ratio between NaOH and Ca(OH)$_2$ in mixed metals is 90:10 (A1) and 80:20 (A2).

2.4. Analysis of Free Base Content and unsaponifiable matter

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. Whereas the 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.

2.5. 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 20:20 (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 4 hours at a temperature of 120 °C until homogenous.

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.

2.6.1. 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.

2.6.2. 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 corks 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.
3. Results and Discussion

From the research, it was found that the free base rate for A1 metal soap type was 0.04% and the type of metal soap A2 was 0.03% or slightly above the neutral level (point 0). In addition to the free base content of metal, soaps have also analyzed the characteristics of unsaponifiable matter value, which in the type of metal A1 is 0.88% and metal soap A2 0.84%.

The focus of lubricant production generated in this research is to obtain a grease formula that approximates the characteristics of commercial grease based on ASTM quality standards (American Society for Testing and Materials International). In this research as for the raw materials used in the manufacture of solid grease is PFAD. The metal soaps used in grease formulations are obtained by process of Saponification using Sodium (NaOH) and Calcium (Ca(OH)₂) with PFAD raw materials.

| No | Composition (%) (Metal Soap : PFAD) | Density (gr/ml) | Titrant 25 °C ASTM D 217 | Dropping point ASTM D566 | NLGI Grade ASTM D217 |
|----|-----------------------------------|----------------|--------------------------|--------------------------|-----------------------|
| 1  | A1 : B1                           | 0.827          | 91                       | 106                      | 6                     |
| 2  | A1 : B2                           | 0.931          | 88                       | 100                      | 6                     |
| 3  | A1 : B3                           | 1.103          | 86                       | 96                       | 6                     |
| 4  | A2 : B1                           | 1.108          | 92                       | 110                      | 6                     |
| 5  | A2 : B2                           | 1.022          | 87                       | 92                       | 6                     |
| 6  | A2 : B3                           | 1.107          | 85                       | 85                       | 6                     |

Description: A = Ratio NaOH : Ca(OH)₂ (%); B = Ratio Metal Soap : PFAD (%); A1 : B1 = (90 : 10); A1 : B2 = (90 : 10); A1 : B3 = (90 : 10); A2 : B1 = (80 : 20); A2 : B2 = (80 : 20); A2 : B3 = (80 : 20).

3.1 Density Grease

The raw material consisting of base oil and mixed metal soap (Na-Ca) after being physically blended and has become grease and then analyzed its characteristics respectively using ASTM D-566 method for melting point test and ASTM D-217 method for determination titrant and NLGI conducted at LEMIGAS, Oil and Gas Technology Research and Development Centre (PPPTMGB) Laboratory, South Jakarta.

Figure 1 showed that the NaOH ratio with Ca(OH)₂ also affects the grease density. This density is affected by the density of each metal, where NaOH has a density of 1.0 g/ml and Ca(OH)₂ has a density of 2.2 g/ml [3]. This causes the density of grease with the type of metal soap A2 has a higher density than metal soap A1. Because the metal soap A2 has a composition of 20% Ca(OH)₂ compared to 10% metal A1 soap.

![Figure 1. Density grease versus composition of metal soap (%)](image)
The composition of A1: B2 obtained density of 0.931 g/ml of composition A1: B2 obtained density of 0.103 g/ml of composition A1: B3 obtained density of 1.103 g/ml, composition A2: B1 obtained density of 1.108 g/ml, composition A2: B2 obtained density of 1.022 g/ml, and composition A2: B3 obtained density of 1.107 g/ml. This increase in density is due to the decreasing of the metal soap composition and the increased composition of PFAD increasing the density of the grease.

3.2 Titrant

Titrant analysis is conducted with the aim to know the level of hardness or consistency level of the grease that has been made. The results of the analysis that has been done can be seen in Figure 2.

The results obtained indicate a decrease in titrant value. Where in composition A1: B1 obtained titrant of 91, composition A1: B2 obtained titrant equal to 88, and at composition A1: B3 titrant equal to 86. In composition A2: B1 obtained titrant equal to 92, composition A2: B2 obtained titrant equal to 87, and on the composition A2: B3 obtained titrant of 85.

Figure 2 showed that the decreasing of the metal soap composition and the increased composition of PFAD resulting in a decrease in the titrant value of the grease. This condition corresponds to the level of NLGI 6 violence.

Dropping point is a critical temperature where the gel structure in grease starts to undergo a phase change to liquid. The melting point represents the highest temperature at which the grease can maintain its structure. The stronger the structure of grease, the more difficult it is to change the phase.

3.3 Dropping point of Grease

![Figure 2](image2.png)

**Figure 2.** The relationship between % composition (metal soap: raw material) versus the titrant value

![Figure 3](image3.png)

**Figure 3.** Composition Relation (%) vs. Melting Point (°C)
Where the composition A1: B1 obtained a melting point of 106 °C, composition A1: B2 obtained melting point of 100, and the composition A1: B3 obtained melting point of 96. In composition A2: B1 obtained the melting point of 110, the composition A2: B2 obtained melting point of 92, and on composition A2: B3 obtained melting point of 85.

Figure 3 explained that because of the decreasing of metal soap composition and increasing the composition of PFAD resulting in a decrease in the melting point. This condition is in accordance with the theory that the minimum allowable melting point for solid lubricant is 80 °C where the higher melting point possessed by a solid lubricant the better its resistance in maintaining the solid condition of the solid lubricant, so that the solid lubricant having high melting point will not melt quickly and lifetime increases. This result is in accordance with the specification of solid lubricant performance characteristics and parameters for quality level of NLGI GA, SNI 06- 7069-8-2005.

4. Conclusion

PFAD can be used as raw material for the manufacture of grease based on environment-friendly palm oil and has the characteristic of commercial solid lubricant. Variations of mixed soap metal composition (thickening agent) and PFAD (base oil) in the manufacture of grease affect the results of density analysis, titrant, melting point, and NLGI. The best grease generated according to ASTM standard and SNI 06 - 7069 - 8 - 2005 included in Grade A is found in composition A2: B1, A2 is the ratio of NaOH : Ca(OH)$_2$ = 80%: 20% and B1 is PFAD ratio: metal soap = 10% : 90% with the following criteria: Density: 1.108 g/ml, Titrant: 92 (25 °C), Melting Point: 110 °C, NLGI: 6.

5. Acknowledgment

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