Effect of Thickener's Percentage on the Characteristic of the Biogrease formulated with Combined Thickeners: Calcium Oleate Complex and Overbased Calcium Sulfonate Overbased

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Abstract. This research studied on the manufacturing of overbased Calcium OleSulfo biogrease NLGI 2, using a combination of 2 types of thickeners, Calcium complex soap (superior in thermal stability) and overbased calcium sulfonate soap (superior in antiwear performance), at various compositions. The Calcium complex soap was resulted via saponification of $Ca(OH)_2$, epoxidized oleic acid, and acetic acid, while the Calcium sulfonate soap was resulted via saponification of $Ca(OH)_2$, LABSA (Linear Alkyl Benzene Sulfonic Acid) and $CaCO_3$. The base oil was epoxidized RBDPO. The process of saponification was conducted in a reactor (laboratory scale) under ambient pressure. The characterization of the products includes penetration (consistency) test, elongation test, dropping point test, and antiwear performance test. The results show that the effect of Overbased calcium sulfonate to increase the antiwear performance is proportional to the percentage, and it is always followed by decrease of the dropping point. At composition up to 50%, the Calcium OleSulfo biogrease would give NLGI 2 with dropping point 220°C. However, if the percentage is above 50%, it will cause significant decrease in the product's consistency or in other words the grease will become too soft, (NLGI 1).

Key words: Antiwear, Calcium oleate complex grease, Consistency, Dropping point, NLGI 2, Overbased calcium sulfonate grease, 12-hydroxystearic acid, oleic acid.

INTRODUCTION

Thickener, both the type and the amount, are of the crucial factors of making grease, since they determine grease's ability to be in semi solid state under operation condition (Lugt, 2016). The most popular thickener for grease is lithium soap, which can be made via saponification reaction of LiOH and 12-hydroxystearic acid (12HSA).

Grease formulated with lithium soap account for about 70 percent of demand in automotives and the industry. The lithium soap has been widely used as grease thickener in automotives and industries for long time because it was greater mechanical stability, reliable, readily available and cost effective. But, two of those attributes are no longer as true. The rise of lithium batteries used in electric vehicles (EVs) has caused a sudden increase in lithium demand. It becomes less available (McGuire, 2020), which has greatly impacted the price of lithium oxide. Nowadays the usage of lithium hydroxide for grease must compete with car's batteries (Zafar, 2023; Ren, 2020).

Besides LiOH, the usage of $Ca(OH)_2$ as thickener component is also popular, since the soap made by $Ca(OH)_2$ and 12HSA also has many technical advantages. Moreover, calcium hydroxide is abundantly available in the earth. The usage of calcium hydroxide to replace lithium hydroxide as thickener component for making high quality grease became challenging research, because

$Ca(OH)_2$ is less soluble and less reactive than LiOH.

The Calcium stearate soap can be made via saponification $Ca(OH)_2$ and 12HSA under vigorous mixing. The Calcium 12HSA for grease has superior gelling ability, where at thickener composition about 15%w a semi solid grease NLGI 2 can be obtained (Fatma, 2015). Thermal stability of Calcium stearate can be enhanced by mixing it with complexing agent (acetic acid), to obtain Calcium complex grease (Razak & Ahmad, 2021). The coexistence of the two soaps (calcium stearate and calcium acetate) can create unique or complex interaction involving hydrogen bonding and also special arrangement, where the short molecules of Calcium acetate may fill the vacant space between the longer molecules Calcium stearate. Therefore, their molecular arrangement become more compact, and this gives the reason why Calcium complex grease can give higher dropping point than Calcium grease (single soap). Sukirno (2010) reported that Calcium complex grease NLGI 2, made by using $Ca(OH)_2$, 12HSA and acetic acid as the thickener components and palm oil as base oil, can give dropping point 300℃.

Another popular calcium grease is overbased calcium sulfonate grease where its thickener resulted via saponification reaction Alkyl Benzene Sulfonic Acid (LABSA) with $Ca(OH)_2$ excess and with addition of solid additive $CaCO_3$ powder of micro size. LABSA is a high molecular weight of long-chain structure hydrocarbon with polar end, usually used as component of detergent (Khayal et al., 2022). Calcium sulfonate thickeners provide the additional benefit by forming a thickening arrangement to improve wear resistance. This increased extreme pressure wear protection is especially beneficial in heavily loaded and slower moving bearings.

This grease type is popular as high duty grease with characteristic very elastic, sticky and provide superior antiwear performance (Brian, 2024).

However, the overbased calcium sulfonate has low gelling ability, which means that more amount of Calcium sulfonate is needed than that of Overbased calcium sulfonate for obtaining grease of the same consistency. Author found from previous work that for making overbased calcium sulfonate biogrease NLGI 2, the mass ratio the thickener to the base oil was 56: 44. The product has dropping point 217℃.

This research is intended to study manufacturing grease NLGI 2 using the combination of calcium complex and overbased calcium sulfonate, mention above. The purpose is to pursue the effect one soap to another, whether they can interact synergically or antagonistically to give positive or negative effect of interaction. In this research oleic acid is used instead 12HSA, and the effect of soap composition on the grease characteristic/performance were observed by comparing the product's elasticity, dropping point, antiwear performance.

MATERIALS AND METHOD

Process making of the Ca-OleSulfo using combined soaps are shown diagrammatically Figure 1. Thickener components of Calcium oleate complex biogrease consisted of epoxidized oleic acid, acetic acid and $Ca(OH)_2$. Preparations needed before making this grease were to do epoxidation of oleic acid to obtain epoxidized oleic acid. The thickener was called Ca-oleate complex soap. From previous, the mass ratio thickener to base oil was 20:80, to get grease consistency NLGI 2.

Meanwhile, thickener components of Overbased calcium sulfonate were LABSA,

$Ca(OH)_2$, $CaCO_3$ and the thickener was called Overbased Ca-sulfo soap. The biogrease that is produced by using these combined soaps was Ca-OleSulfo grease. From previous work the mass ratio thickener to base oil was 56:44, to get a biogrease with NLGI 2

Base oil for the grease is epoxidized palm oil The Epoxidation is conducted using H_2O_2 as reactant, formic acid as catalyst, at 40℃ in stirrer tank reactor, laboratory scale (Reeves et al., 2017).

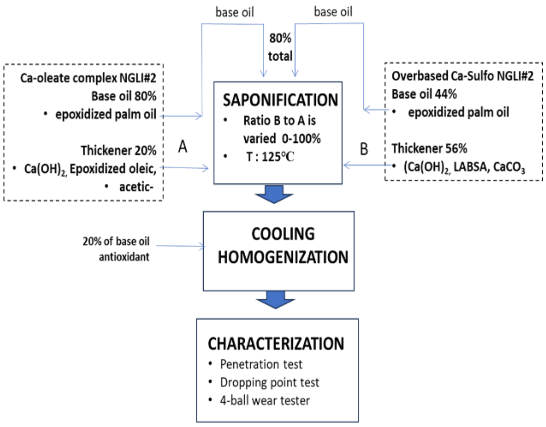

Fig.1 Block diagram of making grease

The processes making grease was started by heating mixture of base oil, LABSA, epoxidized oleic acid, acetic acid in stirrer tank, at 70°C. Then it was followed by adding little by little the $Ca(OH)_2$ and the $CaCO_3$ with increasing temperature up to 125℃ and speed of with mixing to appropriate speed (400 – 1500 rpm). Antioxidant and other additives were added during cooling and homogenizing step (Nelson, 2020).

The Ca-OleSulfo biogrease products were characterized by using penetration test for identifying NLGI number, elongation test for mechanical stability, dropping point test for thermal stability, 4-ball wear tests for antiwear performance (International, 2020). In this research, operation condition during the wear measurement were speed 1150 rpm, load 62 kg, duration 60 minutes.

RESULTS AND DISCUSSION

Visual appearances of products

The Calcium Oleate complex biogrease appearance is light brown, soft with "stickiness " represented by the length of the tail, as shown in Figure 2A. below.

Fig.2A Calcium Oleate complex biogrease

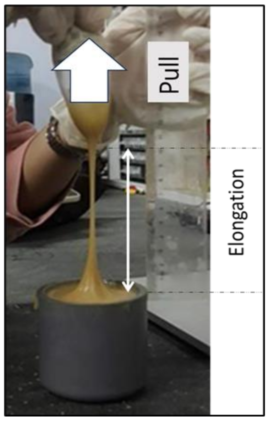

Fig.2B "Pulling test" to measure "elongation"

In the other hand, the Overbased calcium sulfonate biogrease is darker and stickier that of Calcium oleate complex. The "stickiness" assessment in this research was conducted by "pulling test" which is to dip a stick into the grease and then to pull it until breaking, as shown in Figure 2B.

Penetration tests and pulling tests of the grease

The results of penetration tests are shown as shown Figure 3. It shows that the Calcium OleSulfo biogrease can keep its solidity at consistency NLGI 2 when the percentage of Overbased calcium sulfonate is below 50%. Otherwise, the biogrease products would be too soft, the penetration become deeper than 29.5 mm, and it fall to group NLGI#1 since the penetration out of ranges 26.5-29.5 mm (NLGI 2).

The results of "pulling test" are shown in Figure . It is found that the "elongation" is agree with the penetration test. The longer the elongation the deeper the penetration, or become softer. And in this case, the longer the elongation, the more mechanically stable the grease is. Therefore elongation can represent mechanical stability of the grease. (Wang et al., 2014)

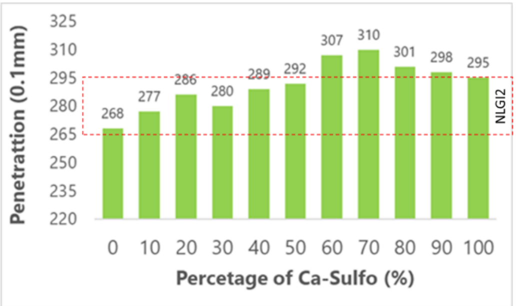

Fig.3 Effect of the Overbased calcium sulfonate percentage on consistency (NGLI grade) of biogrease

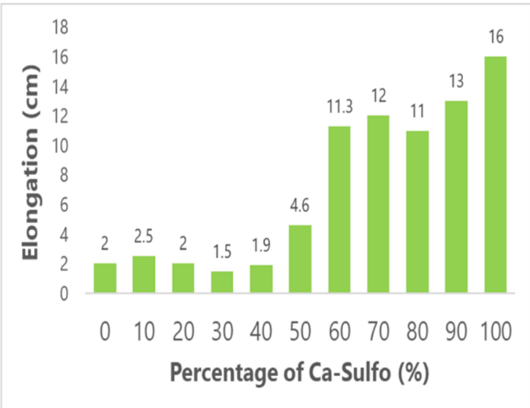

Fig.4 Results of "Pulling" test results

The higher the composition of the Overbased calcium sulfonate, the softer the product, and also the more stable (not to break) the products. These above results suggest that even though Overbased calcium sulfonate soap is more polar and stickier, but it does contribute much to the formation of "compact fiber structure" that is responsible for holding the base oil to keep it semi solid state. The reason is because the "active site" or polarity of Calcium sulfonate exists only at the end of molecule structure. In the other hand, Calcium oleate has both hydroxyl in the middle and carboxyl in the end of the molecule structure, as active site. The contribution of the hydroxyl in the middle of the oleate structure is thought to be the reason why calcium oleate has better gelling ability than calcium Sulfonate.

Chemical structure of the grease and their thickener components

Commercial greases mostly use 12-HSA as their thickener component, a very popular carboxylic acid with very strong gelling ability since it has hydroxyl in the middle its structure. In this research, epoxidized oleic acid is used, instead of 12HSA. It was prepared by epoxidation of oleic acid as shown in Figure 5. (Hambali et al., 2021), The epoxidized oleic acid and the 12HSA have similar structure and size, functional group, because the epoxide can easily change into hydroxy (Karmakar et al., 2017).

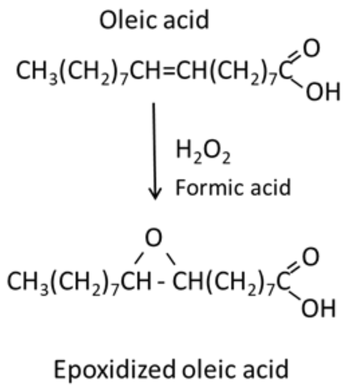

Fig.5 Epoxidized oleic acid with its oxirane group

The saponification reaction of the epoxidized oleic acid with $Ca(OH)_2$ to produced Calcium oleate soap, as shown in Figure 6. Calcium oleate is the main soap the Ca-oleate complex soap. The other soap is Calcium acetate soap, resulted by reaction of complexing agent acetic acid with $Ca(OH)_2$.

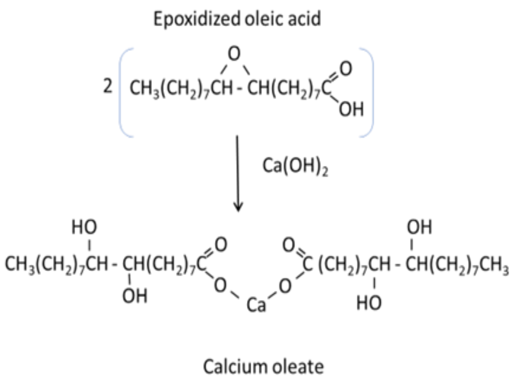

Fig.6 Saponification of Calcium oleate

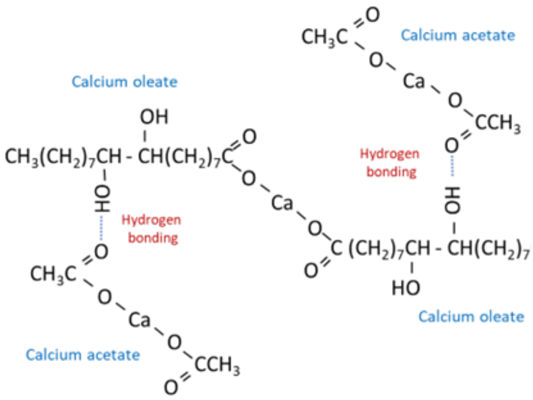

Fig.7 Interaction by hydrogen bonding in a calcium oleate complex

Complexing agent, acid acetate react with $Ca(OH)_2$ in the same way as the epoxidized does. The coexistence of 2 soaps, the calcium acetate (smaller size) and the calcium oleate in the mixture, causes unique and complex interaction due to difference size and hydrogen bond, as illustrated in Figure 7. This interaction causes the calcium Complex soap dan attain more compact structure. This 3-dimensional interaction among molecules of difference size gives the reason why calcium oleate complex grease gives higher dropping point (260℃), calcium oleate grease (single soap) does (140℃). In the previous research, Author found the optimum dropping point was reach at ratio mol Calcium stearate to Calcium acetate 1:5.

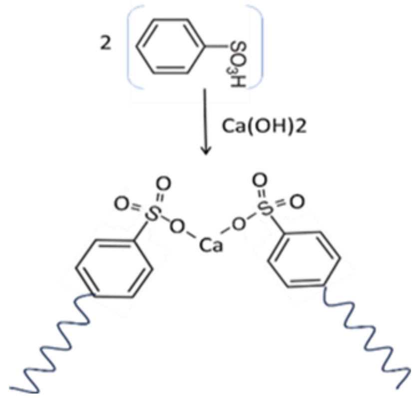

Fig.8 Saponification of Overbased calcium sulfonate

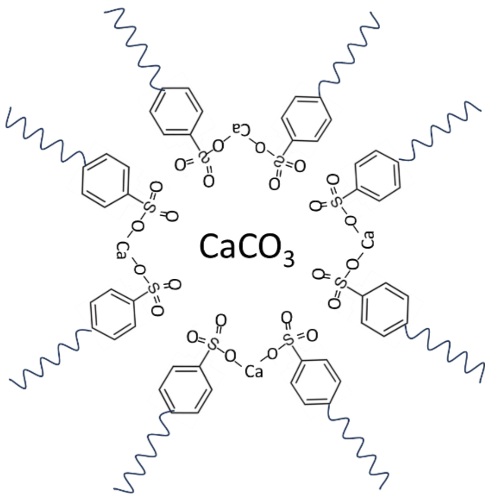

Fig.9 Adsorption of Overbased sulfonate on $CaCO_3$ particle to form "micelle"

Calcium sulfonate grease is made by saponification of LABSA with $Ca(OH)_2$ illustration is given in Figure 8. As shown, the existence of sulfur and more oxygen it has more polar end. Over based Calcium sulfonate is formulated with $CaCO_3$. The highly polar calcium sulfonate has ability to adsorb on the surface of CaCO3 particles to form a "micelle" which is considered solid-liquid configuration that can provide cushion to avoid metal direct contact (Bakuninn et al., 2022), as illustrated in Figure 9.

Dropping Point Test

Dropping point shows the maximum temperature at which the grease still able to keep its semisolid state before melting to become liquid state. The results of dropping point measurement of Calcium OleSulfo biogrease is shown in Figure 10, where the dropping point decreases as the percentage of Overbased calcium sulfonate increases. The Calcium oleate complex grease has dropping point 262℃, while the Overbased calcium sulfonate has dropping point 200℃. The Calcium OleSulfo grease has dropping point between the two, inversely proportional to the percentage of the overbased calcium soap. The higher the percentage of the Overbased calcium sulfonate the lower the dropping point. The overbased calcium sulfonate contribute less attractive force than the calcium oleate complex (Bosman & Lugt, 2018).

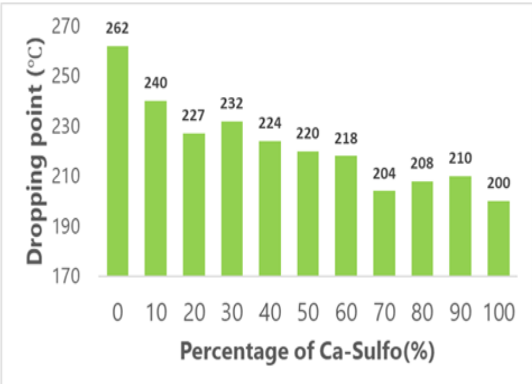

Fig.10 Effect of the Overbased calcium sulfonate percentage on the dropping point of biogrease

Performa antiwear of the Calcium OleSulfo biogrease

The amount of wear resulted during 4-ball wear test represents antiwear performance. As shown in Figure 11, the antiwear performance of the Overbased calcium sulfonate grease is much better than Calcium oleate complex, where the ration amount of wear is 1:12. Extreme pressure performance of the Overbased calcium sulfonate grease without additives to protect surface of metal was reported by Bosman (2018).

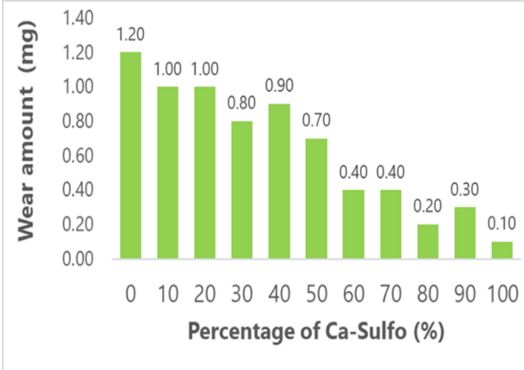

Fig.11 Effect of the Overbased calcium sulfonate percentage on antiwear performance of the biogrease

The reasons are explained as follows. First, the sulfonate group has very strong polar end which able to adsorb and protect the rubbed surface. Polarity may also be responsible for the grease's stickiness and elasticity which make it easier to be dragged by rotating ball surface to enter "contact zone" to form hydrodynamic layer to protect metal direct contact (Márquez et al., 2021). Second, the Overbased calcium sulfonate is formulated with CaCO3 solid particle which can form micelle in interaction with sulfonate. This micelle may able to act as cushion that prevent direct contact of metal surface (Wang et al., 2014).

The antiwear performance of the Calcium OleSulfo grease increases as the percentage of the Calcium sulfonate increases. When the composition of Overbased calcium sulfonate is 50%, it could reduce amount of wear to 0.7 mg from 1.2 mg (palm oil).

CONCLUSION

From the results discussed above, the study of manufacturing biogrease NLGI 2 by combined thickeners, the calcium oleate complex, and the Overbased calcium sulfonate can be summarized as follow:

1. In term of thermal stability, the calcium oleate complex grease is better than the

overbased calcium sulfonate grease. Their dropping point comparison is 260℃ and 200℃ respectively, however in terms of antiwear performance the former is worse than the latter whereas compared by the amount of wear is 1.2 mg and 0.7 mg.
2. When they are combined, the effect of overbased calcium sulfonate to increase the antiwear performance is proportional to the percentage, and it is always followed by the decrease of the dropping point.
3. At the percentage up to 50%, the Calcium OleSulfo biogrease would give NLGI 2 with dropping point 220°C. However, if the percentage is above 50%, it causes significant decrease in the product's consistency, or in other words, the grease becomes too soft (NLGI 1).

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