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Epoxidation-Hydroxylation-Esterification
Processes for Obtaining Improved Performance
of Biolube and Thickener Components for
Biogrease

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MODIFICATION OF PALM OIL AND OLEIC ACID VIA EPOXIDATION-HYDROXYLATION-ESTERIFICATION PROCESSES FOR OBTAINING IMPROVED PERFORMANCE OF BIOLUBE AND THICKENER COMPONENTS FOR BIOGREASE

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Abstract. In this research, palm oil is modified to enhance its viscosity and oxidation stability to become a better biobased oil via a series of processes. The first process is epoxidation by using H₂O₂ to convert the unsaturated (C=C) of oil into epoxides, the second process is hydroxylation by using methanol and isopropanol to open the epoxides ring into hydroxylated palm oil, and the third and final process is esterification by using various acids (oleic acid and oxalic acid) to convert hydroxylated palm oil into estolide. The promising product to be used as an oil base for grease is Palm-ole estolide, where it gives viscosity 10cP@100°C (SAE-30) higher than that of palm oil 7.5cP@100°C (SAE-20). Its oxidation stability is then enhanced to that of mineral oil, with peroxide value 8 mg-eq/g (estolide) which was initially 16mg-eq/g (palm oil). Then this Palm-ole estolide is used as a base oil for making Calcium complex biogrease, using hydroxylated oleic acid as a thickener component. The hydroxylated oleic acid was prepared via epoxidation-hydroxylation of oleic acid (initially 4.3 mg KOH/g), and able to increase hydroxy value 133.0 mg KOH/g (hydroxylate oleic acid). The modified oleic acid could successfully work as a substitute of popular 12-HSA, since at composition ratio thickener to base oil 20:80, the obtained biogrease is soft, "fibrous", and mechanically stable, having a dropping point of 200°C.

Key word: Biogrease, Dropping point, Epoxidation, Esterification, Hydroxy value, Hydroxylation, Hydroxylated oleic acid Palm oil, Oleic acid, Palm-ole Estolide.

INTRODUCTION

Two main components for making a semi solid lubricating grease are base oil and thickener. Most of automotives and industrial's greases produced until now, are still dominated by the usage of mineral oil or petroleum oil as their base oil (Nelson Cheng, 2020). Mineral oil is a mixture of paraffinic, naphthenic, aromatic hydrocarbon which is not readily degraded by microorganism when entering environment due to leaking or disposing into earth's water or land. This mineral based grease's negative impact to

environment have been inspiring researcher to improve environmental accepted lubricant using renewable vegetable oil. Some of popular vegetable oil are palm oil, soybean oil, sunflower oil, coconut oil (Ebenezer et al., 2023; Singh et al., 2017).

In addition to its biodegradability and low toxicity, vegetable oil has also been known to have many lubrication advantages over mineral oil, such as better lubricity, higher viscosity index, lower volatility etc. (Woma et al., 2019). Those lubrication superiority are due to the oil's

triglycerides which contains ester. The polar end of the ester molecule can adhere to metal surfaces stronger than the non-polar mineral oil. However, many of vegetable oil show low oxidation stability. Two critical points are poly-unsaturated (multiple carbon double bond (C=C) of the fatty acid section, and secondary carbon (attached by OH in its glycerol section). Therefore, one challenging problem when using vegetable for lubricant is how to enhance their oxidation stability (Dandan et al., 2018).

Many efforts have been attempted to enhanced oxidation stability of vegetable oil by conducting structure modification of triglyceride. One example is the synthesis of polyol ester lubricant, where the triglyceride is trans esterified into more stable ester. For example, trimethylolpropane (TMP) ester is synthesized via transesterification of triglyceride and TMP. The TMP ester is popular as superior lubricant for extreme temperature application such as aeroplane lubricant (Owuna et al., 2020).

Another method of oil enhancement is by reducing the number of unsaturated C=C of oil. The less the number of unsaturated fatty acid in a vegetable oil, the more the oxidation stability of the vegetable. However, too much saturated fatty acid in oil, may cause undesirable high pour point of oil. Therefore, the partial hydrogenation to convert poly-unsaturated into monosaturated is consider the optimum way to get better oxidation stability and still has acceptable pour point (Hattimattur et al., 2018).

To reduce C=C can also be conducted via epoxidation by using H₂O₂ to converts the C=C into epoxides palm oil (Balde et al., 2022). The ring structure of epoxide has

unique reactivity since it can react with either electrophile or nucleophile. The epoxidation can be followed by esterification by addition carboxylic acid or hydroxylation by addition alcohol to gain higher viscosity and higher oxidation stability as well (Bockisch, 2015)

Viscosity of a base oil used in a grease formulation is relatively high because the grease usually used under condition of relatively low speed and high load. The higher the load to be carried by bearing/gear's grease the higher viscosity of base oil of grease needed. Viscosity of palm oil is relatively low, that is about 7.5 @100°C (SAE-20).

In this research, Palm oil (RBDPO) is modified to enhanced its viscosity and oxidation stability, via epoxidation-hydroxylation-esterification processes.

Thickener for grease is usually made by saponification metal alkali LiOH or Ca(OH)₂ with 12-hydroxystearic acid (12-HSA). Unfortunately, the in the country like Indonesia the availability of 12-HAS relatively rare. In other hand, oleic acid which has similar structure is widely available in national market. This research, attempt to use hydroxylated oleic acid (Musik et al., 2021) as a substitute of 12-HSA for thickener component of grease.

MATERIALS AND METHODS

The main material were Palm oil (RBPO) and Oleic acid. The supporting reactants were oxalic acid, methanol, isopropyl alcohol, H₂O₂, with H₂SO₄ and formic acid as catalysts (Hoang et al., 2015).

Epoxidation of palm oil was conducted by using H₂O₂ with mol ratio oil to oxidator (mol ratio 1:3) to converts the unsaturated (C=C) of oil into epoxide using 5% formic

acid as catalyst, at temperature 40°C. The Hydroxylation was conducted by using methanol and isopropanol (mol ratio 1:1) to open the epoxides ring into hydroxylated palm oil at 50°C. Esterification of the hydroxylated palm oil with oleic acid or oxalic acid with mol ratio 1:1 was conducted using catalyst H₂SO₄ at 110°C to produce estolides palm oil (Bonetti et al., 2019). All the processes were conducted using reactor glass under atmospheric pressure. The process is applied for Oleic acid. The intermediate product and the characterization of the products includes functional group identification by FTIR spectroscopy, measurement of iodine value and hydroxy value viscosity, oxidation stability by peroxide value measurement (Attila & Zhang, 2021). Grease was made using palm-ole estolide as the base oil and the epoxidized oleic acid as the thickener component. Grease characterization include NGLI grade by penetration measurement and dropping point measurement.

RESULT AND DISCUSSION

Change of functional group, iodine value and hydroxy value during process.

The changes of functional group in the palm oil, intermediates and final products during modification via epoxidation-hydroxylation-esterification processes are shown in FTIR's spectrum Figure 1, together with the measurement results of iodide value and hydroxy value as shown in Table 1.

After epoxidation, the palm oil changes into Epoxidized palm oil, which is indicated by the appearance of new peak at 800–950 cm⁻¹ (stretching vibration of C-O-C bond of the epoxide), as shown in FTIR spectrum Figure 1.b. This peak is

considered as epoxide ring which is formed from C=C after have been attacked by H₂O₂ (Meadows, 2018; Shauqi, 2024)

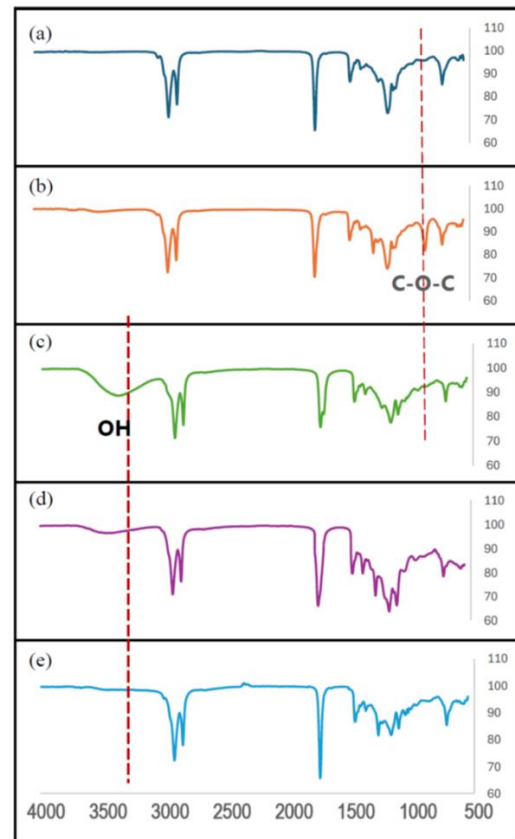


Fig. 1. FTIR spectrum of palm oil during transformation

The reduction of C=C due to the conversion is confirmed by the decrease of the iodide value, which reduces from 51.33 mgKOH/g (palm oil) to 24.12 mgOH/g (epoxidized palm oil), or equal about 50% reduction, as shown in Table1.

The next step is hydroxylation of the epoxidized oil to form a hydroxylated oil. This process is indicated by the disappearance of the epoxide's peak, and followed the appearance of new peak at 3000 cm⁻¹ (-OH stretching), as shown in the FTIR spectrum Figure1.c. During hydroxylation, the epoxides ring is opened by methanol/isopropanol, and hydroxyl

carbon and carbon alkoxy carbon are formed (Musik, 2021; Intan et al., 2023). This conversion is confirmed by the evidence, that its hydroxy value increases from 14 mgKOH/g (epoxide palm oil) to 142 mgKOH/g (hydroxylated palm oil) as shown in Table 1.

The third process is esterification, where the hydroxy peak disappears, as shown in the FTIR spectrum Figure 1.d or Figure 1.e.

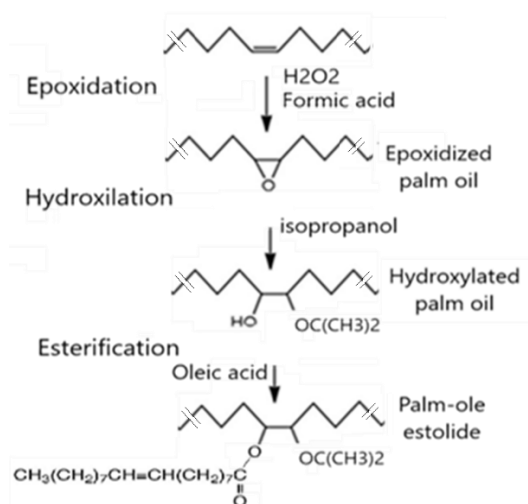


Fig.2 Palm oil's unsaturated conversion during modification

During esterification, hydroxyl OH is attacked a carboxylic acid (oleic acid or oxalic acid) to produce an oligomeric ester or Palm-ole estolide or Palm-oxal estolide. From this estolide, a new ester peak is expected to appear at 1714 cm^{-1} (Nandiyanto et al., 2019). Unfortunately, it cannot be identified due to the glyceride's peak existed there. Therefore, the change of viscosity and the change of density are used to proof that the molecular weight increase due to esterification has already happened. All the structural changes or modifications of the palm oil's unsaturated into palm-ole estolide as shown in Figure 2.

Visual appearance and lubrication characteristics of Estolide

The final products of Palm oil modification are Palm-ole estolide and Palm-oxal estolide, and their colour is light yellow, without much change from the initial colour of the palm oil.

Table 1. Iodine value and hydroxyl value of Palm oil intermediates

	Functional group	Iodine value (mg KOH/g)	Hydroxyl value (mg KOH/g)
Palm oil	unsaturated	51.33	-
Epoxidized	oxirane, unsaturated, hydroxyl	24.12	14.51
Hydroxylated	hydroxyl	-	142.98
Palm-oxal Estol	hydroxyl, ester	-	-
Palm-ole Estol	hydroxyl, ester	-	-

During transformation from palm oil to Palm-ole estolide, it gains molecular weight and changes functional group, due to attachment of the oleic acid. The increase in molecular weight would cause the increase in the viscosity and the density. As shown in Figure 3, the viscosity of Palm-ole is successfully increased to 8.5cP @100°C (close to SAE-30), which is higher than that of palm 3.7cP@100°C (SAE-20).

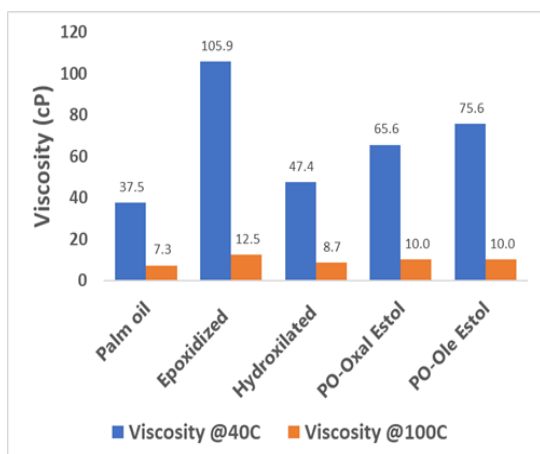


Fig.3 Viscosity of intermediates and products

The process of oleic acid modification was also conducted by using the same procedure. The change of functional group from Oleic acid to Ole-ole estolide during the process can be follow by their FTIR spectrum shown in Figure 4.

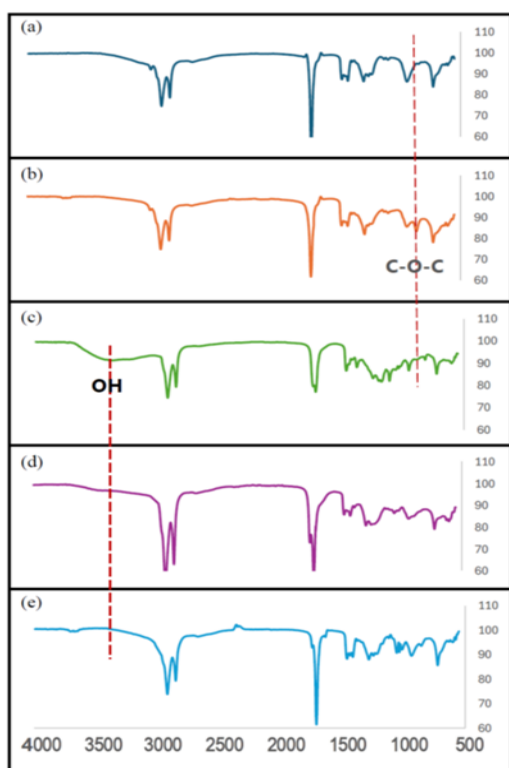


Fig.4. FTIR spectrum of oleic acid during transformation

Table 2. Iodine value and hydroxyl value of oleic acid intermediates

	Functional group	Iodine value (mg KOH/g)	Hydroxyl value (mg KOH/g)
Oleic acid	unsaturated	50.79	-
Epoxidized	oxirane, unsaturated, hydroxyl	36.39	4.33
Hydroxylated	hydroxyl	-	133.09
Ole-oxal estol	hydroxyl, ester	-	-
Ole-ole estol	hydroxyl, ester	-	-

Iodide value and hydroxy value of oleic acid and it intermediate are shown in Table 2. The final products of oleic acid modification are Ole-ole estolide and Ole-oxal estolide, where both the products are colourless.

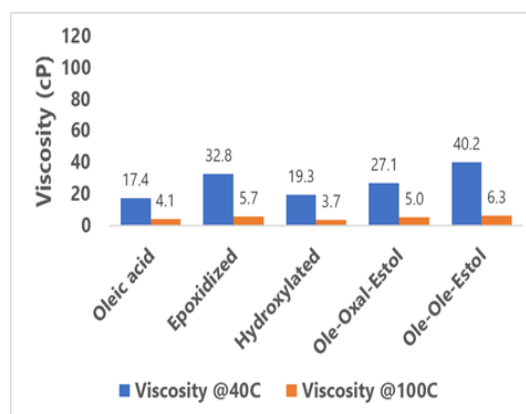


Fig.5 Viscosity of oleic acid derivatives

The change of viscosity during modification are shown in Figure 5. It seems that the increase of viscosity to follow the size or the molecular weight, therefore Ole-ole estolide get the highest viscosity.

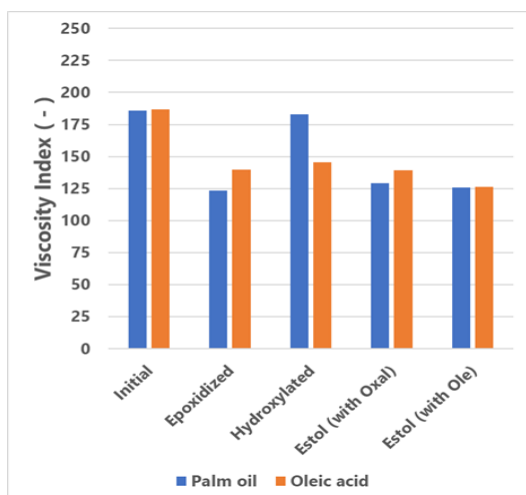


Fig.6 Viscosity index of palm oil and oleic acid derivatives

Polarity may also have strong influence in viscosity, as shown by the intermediate epoxidized products. Polarity of oxirane is thought to be able to explain the distinguish viscosity of the epoxidized product.

Figure 6 show the viscosity index of reactant, intermediate and final product during modification process. Due to the ester, all vegetable has relatively higher viscosity index than mineral oil. During the process modification the viscosity index is decreasing, but still higher.

The change of as shown in Figure 7, density during process seem to behave similar pattern to the change of viscosity. Both viscosity and density are determined by molecular weight and functional group. For epoxidized palm oil the influence of functional group seem more dominance than molecular weight.

Oxidation stability assessment of intermediate product and final during modification process of palm oil was conducted via measuring of the peroxide value (Zhang et al., 2021). The results of the peroxide value measurement of sample

after heating (2 hours, 4 hours, 6 hours) are shown

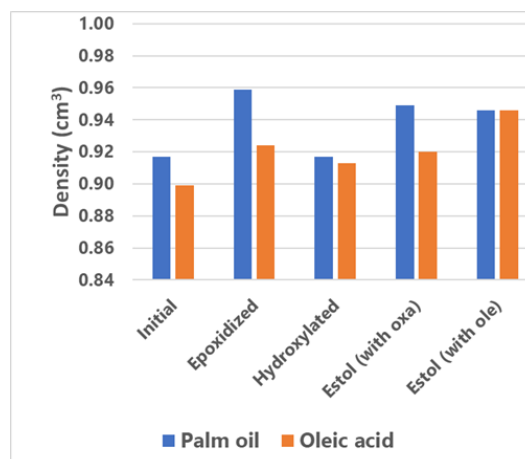


Fig.7 Density intermediate and products

Figure 8 and Figure 9. It indicates that each step of the process (epoxidation-hydroxylation-esterification) has contributed to reduce peroxide value or to increase oxidation stability.

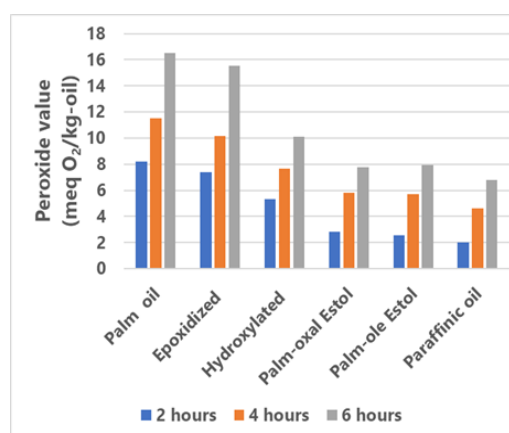


Fig.8. Peroxides number of palm oil derivatives

The palm-ole estolide as the final product, has higher oxidation stability (lower peroxide value). Both Palm-ole estolide and palm-oxal estolide show approximately similar level of oxidation stability. This modification is successfully able to enhanced oxidation stability of Palm oil. The improvement of stability is about 50%, from initial peroxide 16 mg-eq/g

(palm oil) to become peroxide value 8 mg-eq/g (estolide). This level of oxidation stability is comparable to that of mineral oil, as shown in Figure 8 and Figure 9.

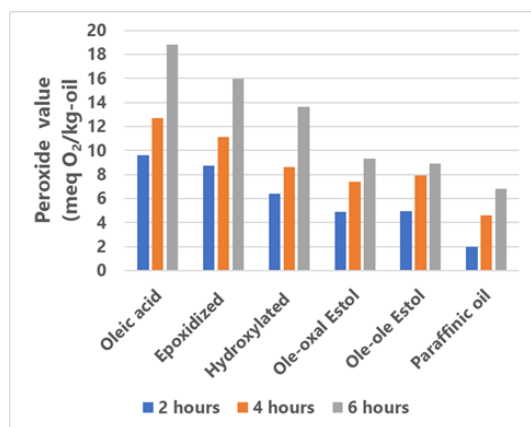


Fig.9. Peroxides number of oleic acid derivatives

Thus, based on the above data analysis and measurement, the palm-ole estolide is considered as the best product with enhanced viscosity and oxidation stability as well (Mannekote, 2012).

Hydroxylated oleic as substitute for 12HSA

Hydroxylated oleic acid, as shown in Figure 10, is intermediate product obtained by epoxidation followed by hydroxylation of oleic acid. The intermediate Hydroxylated oleic acid is rich of OH since it enhanced hydroxyl value 133 mgOH/g from initial hydroxyl value acid 4 mgOH/g (oleic acid), as shown in Table 2. With this enhanced number of OH and size and with 18 carbon chain of carboxylic acid structure, it indicates that the hydroxylated oleic acid has very close structure to that of 12-HSA.

As mentioned in the above introduction, 12-hydroxy stearic acid is the popular ingredient thickener component of grease. The reason is due to the ability of

12-HSA to form greatly stable structure of soap (in reaction with LiOH or Ca(OH)₂) or thickener of grease. This ability is due to the existence of -OH in the structure of 12-HSA and its ability to interact (hydrogen bond) among the molecule.

The usage of the hydroxylated oleic acid and the epoxidized oleic acid as thickener component for making biogrease grease had been trial. The base oil was palm-ole estolide SAE-30. Figure 11 show the visual appearance of the calcium complex biogrease NLGI2 which was made with mass ratio thickener to base oil 20:80.



Fig.10
Hydroxylated oleic acid



Fig.11 Calcium oleate complex grease

With appropriate mixing during saponification step, a homogenous, soft and "fibrous" grease could be obtained, approximately similar to biogrease that is produced in previous study and when using 12-HSA (Razak, 2021). This trial product, calcium oleate complex biogrease NLGI2 is found to have dropping point 200°C.

CONCLUSION

The effort of using palm oil and oleic acid as a main component of manufacturing biogrease has been attempted. To obtain a better quality of biogrease, especially in its load carrying capacity and oxidation stability, the palm oil's lubrication properties is enhanced. The palm oil is also modified to be able to

substitute 12-HSA. The efforts above are summarized in the following conclusion:

1. Great improvement on both viscosity and oxidation stability was obtained in modified palm oil via epoxidation-hydroxylation-esterification processes. The product which is called palm-ole estolide has higher viscosity 10cP @100°C, initially 7.5cP @40°C (palm oil), and better oxidation stability with peroxide value 8 mg-eq/g initially 16 mg-eq/g (palm oil).
2. Hydroxylated Oleic acid which was obtained from oleic acid via epoxidation-hydroxylation, contains hydroxyl value 133.0 mgKOH/g, and it is appropriate to be used as a substitute for 12-HSA as a thickener component for grease.

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