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EFFECT OF LINEAR ALKYLBENZENE SULPHONATE ON OXIRANE OXYGEN OF EPOXIDIZED RICE BRAN OIL METHYL ESTERS

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Abstract

An increasing demand for lubricants and the awareness of environmental preservation lead the production of lubricant base oils and degradable additives. The widely used corrosion inhibitors are alkaline metal and alkaline earth metal salts of sulphonic acids. One of their weakness is that the metal substance is non degradable. Therefore studies of the production of vegetable oil-based inhibitors containing sulphonic acid are needed. Epoxidized methyl esters that contain sulphonates behave as corrosion inhibitor. The purpose of this research is to analyze the reaction between Epoxidized rice bran oil methyl ester (ERME) and Linear alkylbenzene sulphonic acid (LABSA). The method used was mixing ERME with LABSA for 4 hours, then heating the mixture up to 40°C. The process variable is weight ratio of ERME : LABSA = 1 : 1.1 ; 1 : 1.2 ; 1 : 1.3 and the response variable was oxirane oxygen. The identification was conducted using FTIR (Fourier Transform Infra Red). The equation obtained is $y = -43200x + 31,147$ with $R^2 = 0,9868$, where x is weight ratio of ERME : LABSA and y is oxirane oxygen. The result of this research shows that the best weight ratio of ERME : LABSA 1:1,3 with oxirane oxygen of 0,5%. FTIR test result indicates the presence of hydroxyl groups and sulphonic acids.

***Keywords**: epoxidized, linear alkylbenzene sulphonic acid, methyl ester, oxirane, rice bran oil*

INTRODUCTION

The chemical modification product of vegetable oils can be used as the raw material of various chemicals. Polyhydroxy triglycerides are compounds made from oil or fat with more than 2 hydroxyl groups. Polyhydroxy triglycerides compound are widely used as the material for polyurethane, additives for plastics, lubricants, surfactants, and others, resulting in the high demand for this compound. Polyhydroxy triglycerides is produced through hydroxylation reactions. The reaction involves two reaction steps, including the reaction of epoxidation and oxirane ring opening.

Some researches on the chemical modification of vegetable oils have been widely carried out to improve their performance as base oils. These chemical modifications involve epoxidation, hydroxylation, acetylation on Jatropha curcas, L. (Nugrahani., 2007). Purwanto, 2010 examined the process of creating polyols by epoxidation and hydroxylation from rice bran oil separately. In 2014, Borugadda synthesized Castor Oil Epoxidation Methyl Ester using alkaline catalyst ion exchanger as a base oil with oxidation stability. Rape oil epoxy methyl ester could be reacted with sulphonic acids to

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form a compound which could be used as a corrosion inhibitor for vegetable oils into base oil (Patent US5368776 A). Soybean oil epoxy methyl ester could be used to improve the rheological behavior of base oils (Sahoo *et.al*, 2015). The research conducted by Holser in 2008 stated that the Epoxy methyl ester could be used as surfactants, additives and base oil of various industrial products. They were manufactured by transesterification reaction of Soybean Oil Epoxy without reducing the epoxide. Base oil modification of vegetable oils was performed to improve oxidation stability. The widely used corrosion inhibitors are alkaline metal and alkaline earth metal salts of sulphonic acids. One of their weakness is that the metal substances are non degradable. Therefore studies on the production of vegetable oil-based inhibitors containing sulphonic acid are needed. The purposes of this research were to study the effect of weight ratio on ring opening of epoxide from epoxidized rice bran oil methyl ester by linear alkylbenzene sulphonic acid and to get an ester from vegetable oil that contain sulphonic acid.

MATERIALS AND METHODS

Materials and methods used in this research are as below

Materials

The materials used are Epoxidized rice bran oil methyl ester (ERME); Linear alkylbenzene sulphonic acid (LABSA), and aquadest.

Reaction of ERME with LABSA and Product Identification

Epoxy groups were reacted with another compound (sulfonate groups such as Linear alkylbenzene sulfonate (LAS) or LABSA to improve the oxidation stability and the ability to prevent corrosion. Epoxy group in the epoxy methyl ester (4-8%) was reacted with Sulphonic acid by 10-60% of the weight at 20-120^oC, preferrably 30-60^oC. The mole ratio of sulphonic acid to epoxy was = 1: 1.1 – 1 : 1.3 (Patent US5368776 A). The reaction between LABSA and ERME for 4 hours at 40°C will produce hydroxy sulphonic acid ester (HSAE) and / or ring opening of ERME by sulphonic acids. Prior to reaction, LABSA was analyzed for acid value. The product of reaction was tested by FTIR.

Oxirane Oxygen test

Oxirane oxygen of the product of reaction was analyzed. Titration was carried out to determine epoxy groups. Weighed 0.4 g sample of epoxy. Added 15 mL of glacial acetic acid and 2-3 drops of 1% crystal violet indicator . Titrated with 0.1 N HBr to achieve the end point, until blue – green.

Flow diagram of reaction between epoxidized rice bran oil methyl ester with linear alkylbenzene sulfonic acid can be seen in Figure 1.

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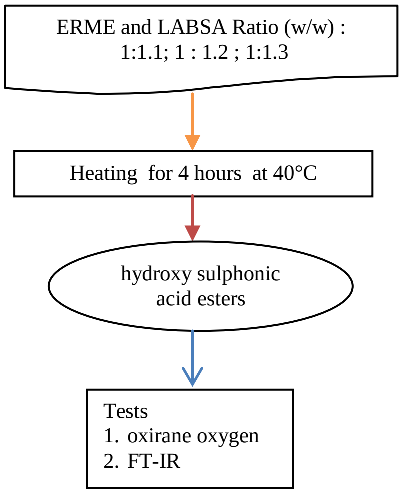

Figure 1. Reaction between epoxidized rice bran oil methyl ester with linear alkylbenzene sulfonic acid

RESULTS AND DISCUSSION

The Effect of weight ratio of ERME : LABSA (w/w) on oxirane oxygen

The purpose of this research was to study the effect of weight ratio (w/w) on epoxidized rice bran oil methyl ester (ERME) with linear alkylbenzene sulphonic Acid (LABSA) to oxirane oxygen change. ERME was reacted with LABSA for 60 minutes at 40°C. Weight ratio used were 1 : 1.1; 1: 1.2; and 1 : 1.3 (w/w). Samples were taken every 60 minutes for 4 hours and the oxirane oxygen was analyzed. Identification of the products was done by using FTIR (Fourier Transform Infra-Red). The following, Table 1 shows the effect of weight ratio (w/w) on the change in oxirane oxygen of ERME.

Table 1 The Effect of weight ratio of ERME : LABSA (w/w) on oxirane oxygen (initial oxirane oxygen was 3.37 (w%))

ERME : LABSA Ratio (w/w)	*Oxirane Oxygen (w%)*
1 : 1,1	*0,6*
1 : 1,2	*0,54*
1 : 1,3	*0,5*

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Table 1 shows that the increasing of feeding ratio of reaction from 1 : 1.1; 1 : 1.2; 1 : 1.3, resulting in a degradation of the ERME oxirane oxygen from 3.37%. The decrease in oxirane oxygen occurs because the epoxides from ERME undergo oxirane ring opening, caused by a reaction with LABSA. The higher of weight ratio, the more oxirane group experience ring opening causing the decrease in oxirane oxygen. The effect of weight ratio on the decline of oxirane numbers can be described in a curve and is correlated with the use of relational equation between the oxirane oxygen (y) and feeding ratio (x) as seen in Figure 2.

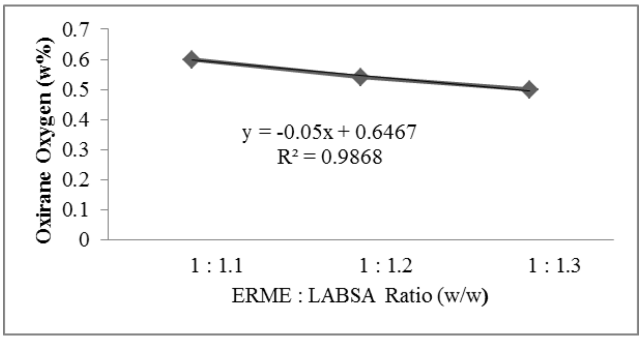

Figure 2. The effect of weight ratios of ERME : LABSA on 40°C to oxirane oxygen (w%)

Figure 2 shows the linear equation that correlate between weight ratios of reactant as x and oxirane oxygen (w%) as y. The oxirane oxygen will decrease with increasing feeding ratio, y = -0,05x + 0,6467 and R^2 = 0,98682, this value shows a strong correlation between changes in weight ratios and oxirane oxygen. The epoxide groups will clevage for reacting with LABSA. Epoxide was reactive and will be opened because of equaeous acid. The ring opening of epoxide decreased oxirane oxygen dan formed a compound that containg sulphonic acid. The highest decrease in oxirane oxygen occurs at 1 : 1.3 ERME : LABSA weight ratios. The change of oxirane oxygen was from 3.27 to 0.5, indicating that the reaction is incomplete. Zhang et. al., 2015 reported that epoxide ring opening is used to synthesize vegetable oil polyols from The polyols were prepared by the ring-opening reaction between epoxidized soybean oil and castor oil diol.

The Result of FTIR Analysis

Before of the reaction with LABSA, the spectrum of ERME (with 3.37% oxirane oxygen) was identified by FTIR. Figure 3 shows FTIR spectrum for ERME.

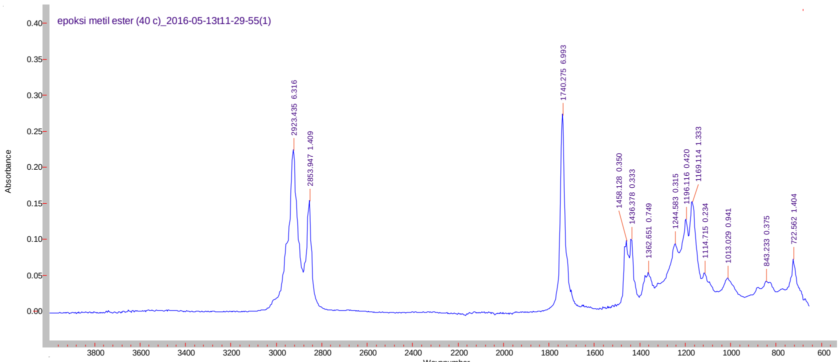

Figure 3 FT-IR spectrum of epoxidized rice bran oil methyl ester

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Figure 3 indicates the presence of the FTIR spectrum of epoxy group from ERME at 843.233 cm^{-1}. For comparison, the FTIR analysis of ESO (epoxidized soybean oil) showed a peak in the spectrum 826.4 cm-1 (Saremi *et. al.*, 2012). After a reaction between ERME dan LABSA, the peak of spectrum changes. It shows on Figure 4.

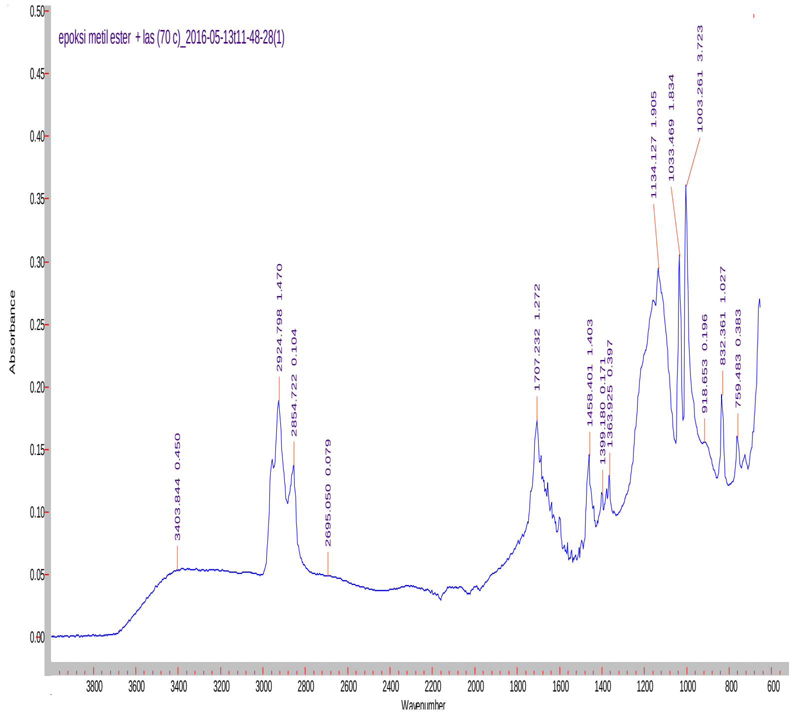

Figure 4 FT-IR spectrum of the product of reaction between ERME and LABSA

Figure 4 shows the indication of epoxy groups in the absorbance of 832.361 cm^{-1} and indicates that the reaction is incomplete. Reaction between ERME and LABSA causes the ring opening of epoxy groups. It forms hydroxyl groups, that indicated by -OH group at spectrum of 3403.844 cm^{-1} and sulfonate ester group or SO_2-O-) at a wavelength of 1335 to 1410 cm^{-1}, as well Sabagh, 2011. Reaction between ESBO and COD (Castor Oil-Based Fatty Diol) oxirane causes ring-opening of ESBO. Epoxide at 823 cm^{-1} disappears after 1 hour and 3392 cm^{-1} indicates hydroxyl groups or polyol based ESBO and COD (Zhang et al, 2015). Patent US5368776 A stated that the reaction between epoxide group and sulphonic group obtained a product as follow on Figure 5 and 6.

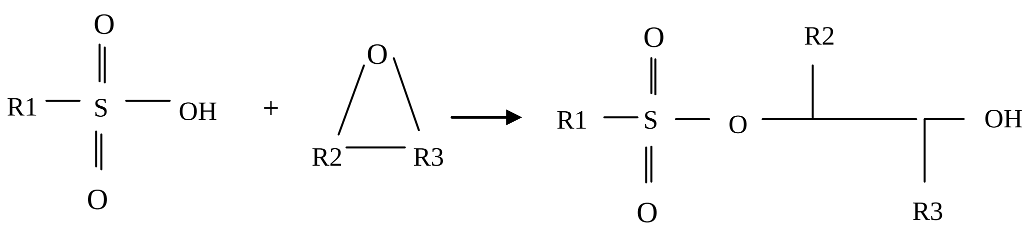

Figure 5. Reaction between sulphonic group and Epoxide

The ring opening of epoxide by LABSA with the molecular formula is R-C6H4SO3H is as below

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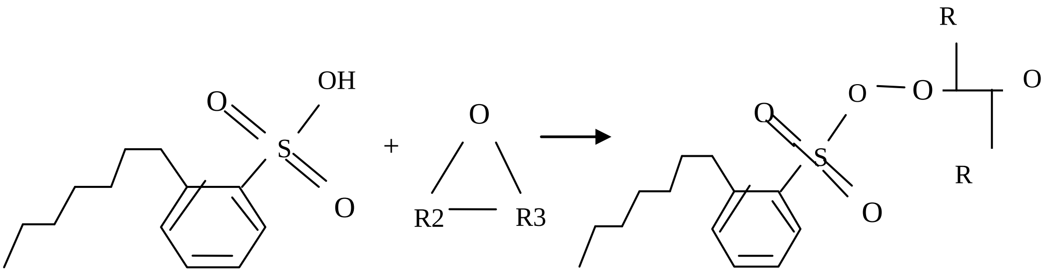

Figure 6. Reaction between LABSA and ERME

CONCLUSIONS

Research on the effect of weight ratios on the reaction between Epoxidized rice bran oil methyl ester (ERME) with Linear alkylbenzene sulphonic acid (LABSA) obtained result as the following conclusion: The weight ratio of ERME : LABSA (1 : 1.3) at 40 °C provides the lowest oxirane oxygen at 0.5%(wt). Epoxy groups are found in the absorbance of 832.361 cm^{-1} with a partially open epoxy group forms hydroxyl groups characterized by -OH group at wavelength of 3403.844 cm^{-1}. The reaction product of ERME and LABSA forms SO_2–O– at a wavelength of 1335-1410 cm^{-1}.

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