Journal of Chemical Technology and Metallurgy, 52, 5, 2017, 797-802

SYNTHESIS OF COMPOUND-CONTAINING SULPHONIC ACID FROM EPOXIDIZED METHYL OLEIC OF RICE BRAN OIL AND LINEAR ALKYLBENZENE SULPHONIC ACID

Ratri Ariatmi Nugrahani , Athiek Sri Redjeki, Yunita Teresa, Nurul Hidayati

Department of Chemical Engineering
Muhammadiyah University of Jakarta
10510 Jakarta, Indonesia
E-mail: ratri.ariatmi@umj.ac.id

Received 05 October 2016
Accepted 19 May 2017

ABSTRACT

Epoxide is needed and used in the production of polyurethane, poly vinyl chloride, lubricants, and chemicals because of the high reactivity of the oxirane ring. Epoxidized methyl ester can be used to improve the rheology of base oils applied as surfactants and additives to numerous industrial products. Its reaction with a sulphonic acid group, such as the linear alkylbenzene sulphonate (LAS) or linear alkylbenzene sulphonic acid (LABSA) improves the oxidation stability and inhibits the corrosion caused by vegetable and mineral oils as base lubricants. The aim of this research is to study the effect of temperature on oxirane oxygen in the uncatalyzed reaction of epoxidized methyl oleic (EMO) of rice bran oil with LABSA and to identify the reaction product by using FTIR, NMR and GC-MS. The correlation between the temperature (y) and the oxirane oxygen (x) is $y = -0{,}0095x + 0{,}7914$ *with* $R^2 = 0{,}9452$ *at EMO : LABSA ratio (w/w) of 1:1,3. The presence of a peak in the product FTIR spectrum at 3403.844* cm^{-1} *is attributed to a hydroxyl (O-H) group, while that in the range of 1335* cm^{-1} *- 1410* cm^{-1} *– to a sulfonate ester (*SO_2*–O–) group. The NMR and GC-MS spectra indicate the presence of a hydroxy sulfonic acid ester. These results indicate that the epoxy group may be not completely opened by LABSA.*

Keywords: epoxidized, LABSA, methyl oleic, inhibitor, rice bran oil.

INTRODUCTION

Compounds containing polyhydroxy triglycerides are widely used in the production of polyurethane, additives for plastics, lubricants, surfactants, and others. This results in these compounds high demand. Polyhydroxy triglycerides compounds found in oil or fat have more than 2 hydroxyl groups. They may be obtained through hydroxylation reactions involving two reaction steps - the reaction of epoxidation and that of oxirane group ring opening.

Chemical modifications of vegetable oils have been extensively studied aiming to improve their performance as base oils. Some of these refer to epoxidation of jatropha curcas oils [1], polyols formation by epoxidation and hydroxylation on ximenia americana seed oil [2]. The epoxidation of methyl ester of castor oil has been recently carried out by using an ion exchanger as an alkaline catalyst. The product obtained is used as base oil characterized by oxidation stability [3]. Epoxidized methyl ester of rapeseed oil reacts with sulfonic acid to give a compound which can be used as an inhibitor for vegetable oils and mineral oil corrosion [4]. Epoxidized methyl ester of soybean oil can be used to improve the rheological behavior of base oils [5]. It can be obtained through transesterification reaction of epoxidized soybean oil without reducing the epoxide [6]. It can be further used as surfactant, additive and base oil for

various industrial products manufacture. Modification of vegetable oil to be used as base oil is performed to improve its oxidation stability. Epoxy methyl soyate used as bio-plasticizer is prepared by epoxidation to methyl oleate and distillation to obtain a higher oxyrane oxygen [7]. An additive to diesel fuel is made on the ground of olive oil. In fact the latter is subjected to epoxidation, cleavage of epoxide, and esterification [8]. Inhibitors of carbon steel corrosion are prepared [9] using linear alkyl benzene sulfonic acid and its three esters but the problem is that are nondegradable. An inhibitor from containing sulphonic acid but obtained on the ground of vegetable oil is required. The aim of this research is to sythesize a compound using epoxidized methyl oleic of rice bran oil and linear alkylbenzene sulphonic acid (LABSA), to identify the corresponding product and to study the effect of temperature on the oxirane oxygen in it.

EXPERIMENTAL

The ring opening was obtained through the reaction of epoxidized methyl ester in an amount of 4 % - 8 % and linear alkylbenzene sulphonic acid (LABSA) or dodecylbenzene sulphonic acid (Merck) quantity of 10% - 60 % (w/w) in the temperature range from 20^{o}C to 120^{o}C (the best temperature interval was that of 30 ^{o}C-60^{o}C). The mass ratio of sulphonic acid to epoxidized methyl ester was equal to 1 : 1.3. The reaction of 500 g of LABSA with 400 g of EMO for 4 h at 70°C gave hydroxy sulphonic acid ester (HSAE), which could be used as a corrosion inhibitor.

The oxirane oxygen test (AOCS Cd 9-57) was carried out. It required the introduction of 0.4 gram of epoxidized methyl oleic to an Erlenmeyer flask followed by the addition of 15 ml of glacial acetic acid. Then 2 - 3 drops of 1 % crystal violet indicator was added to the solution to turn its color to dark blue. Then titration with 0.1 N HBr solution was carried until reaching the end point when the solution became blue-green in color.

FTIR spectroscopy carried out with a spectrometer type Agilent technologies 630 was applied for qualitative and quantitative analysis of the inorganic and organic compounds used. The infra-red transmission of the latter observed at certain frequencies was compared to reference spectra.

NMR quantification was used to confirm the formation of hydroxy sulphonic acid ester.

GC-MS carried out on Agilent technologies 7890A spectrometer was applied to determine the product content.

RESULTS AND DISCUSSION

Rice bran oil EME reacted with LABSA at the mole ratio pointed above. The reaction temperature values were 30^{0}C, 40^{0}C, 50^{0}C, 60^{0}C, and 70^{0}C. Samples were taken every 60 min within 4 hours and the oxirane number was analyzed. The products obtained were identified by FTIR. The temperature effect observed is illustrated in Table 1.

Table 1 shows that the reaction temperature increase from 30°C to 70°C results in EMO oxirane oxygen decrease. This is due to oxirane ring opening taking place

Table 1. Temperature effect on oxirane oxygen (EMO: LABSA = 1:1.3 (w/w); initial oxirane oxygen of 4.06 mass%).

Temperature (°C)	Oxirane oxygen / mass %
30	0,48
40	0,45
50	0,342
60	0,176
70	0,144

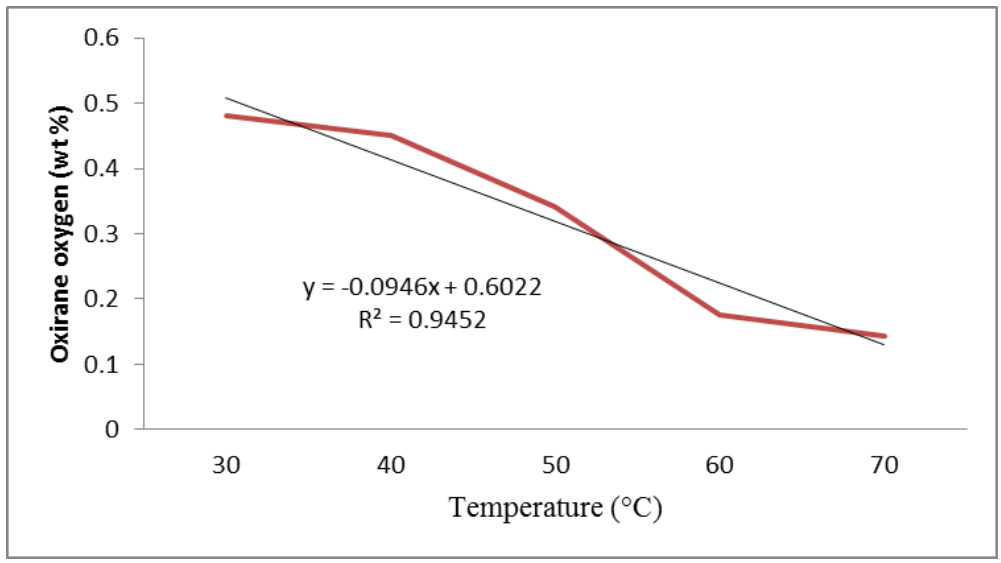


Fig. 1. Temperature effect on oxirane oxygen presence (%).

during the reaction of epoxides with LABSA. The higher the temperature reaction, the greater oxirane oxygen decrease is. The temperature effect on the oxirane numbers can be described by the dependence of the oxirane oxygen (x) and temperature (y) as seen in Fig. 1.

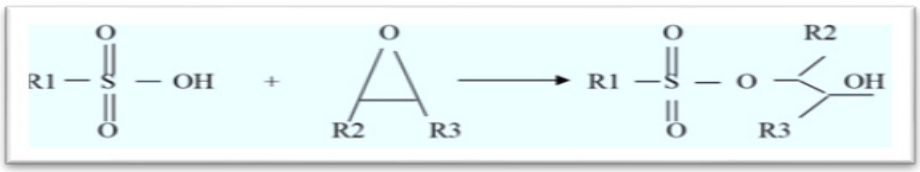
Fig. 1 shows that the dependence observed is in fact linear. It is described by the equation y = -0,0095x + 0,7914 (R^2 = 0,9452). It is worth adding that the reaction studied takes place in catalyst absence. The highest oxirane number decrease occurs at 70°C - varying from 4.06 to 0.144. This indicates that the reaction is not complete.

The reaction between EMO and LABSA is illustrated in Fig. 2. It shows that the reaction product is expected to contain sulphonic acid and a hydroxyl group. This is verified by the FTIR spectrum recorded. It is presented in Fig. 3.

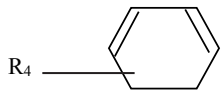
Fig. 3 shows the presence of epoxy groups at 832.361 cm^{-1} as their conversion is not complete. Hydroxyl groups formed on the ground of partially open epoxy groups are seen at 3403.844 cm^{-1}. The reaction of epoxy and LABSA results in oxirane opening, which in turn brings about sulfonic ester group or SO_2-O^- in the range from 1335 cm^{-1} to 1410 cm^{-1}. The reaction proceeding is presented on Fig. 2. It is also described in ref. [9 - 11].

The 1H NMR spectrum recorded verifies the presence of an ester. This illustrated in Fig. 4.

The reaction of EMO with LABSA gives HSAE as a product as indicated by the occurrence of a new signal in the HSAE spectrum. It is detected at 3.68 ppm which is located within the ester region. As shown in Fig. 4, the reaction of EMO with LABSA brings about groups alike the ester one at 3.68 ppm, $ROCCH_2CH_2CH_3$ at



where in R_1 is



R_2 = HOOC – (CH_2)n - R_3 = CH_3- (CH_2)m -

R_4 = C_8 – C_{30} alkyl,

Fig. 2. Presentation of the reaction between EMO and LABSA [4].

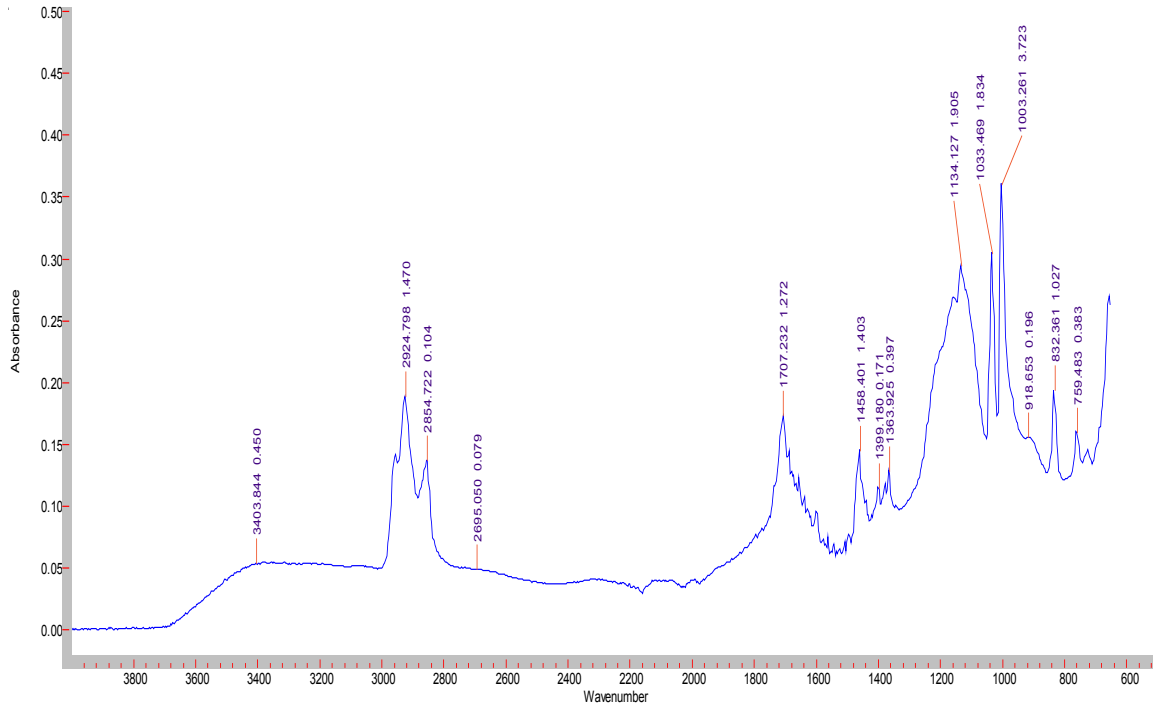


Fig. 3. FTIR spectrum of the product of a reaction between EMO and LABSA.

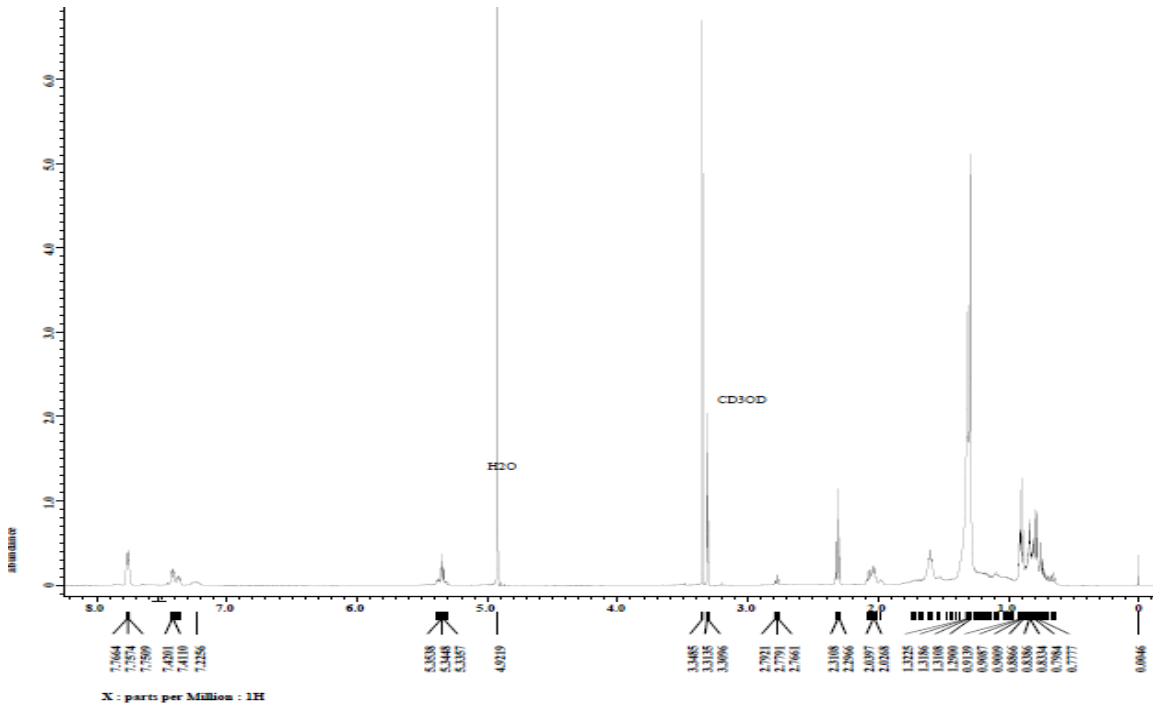


Fig. 4. ^{1}H NMR spectra of HSAE.

2.29 ppm - 2.31 ppm, $ROCCH_2CH_2CH_3$ at 1.59 ppm - 1.64 ppm, RCH_2CH_3 at 1.29 ppm - 1.33 ppm, RCH_3 at 0.89 ppm - 0.91 ppm, ROH at 4.06 ppm - 4.08 ppm, $-CH_2$-CHO-CH- at 2.2 ppm - 2.4 ppm and benzene at 7.0 ppm - 7.5 ppm. These data leads to the conclusion that the synthesis of the hydroxyl sulfonic acid ester through the reaction of EMO and LABSA is not complete. The band at 4.91 ppm shows the presence of H_2O. It is worth adding that reaction product is not purified [4].

The GC - MS data referring to the hydroxylation of EMO by LABSA is shown in Fig. 5.

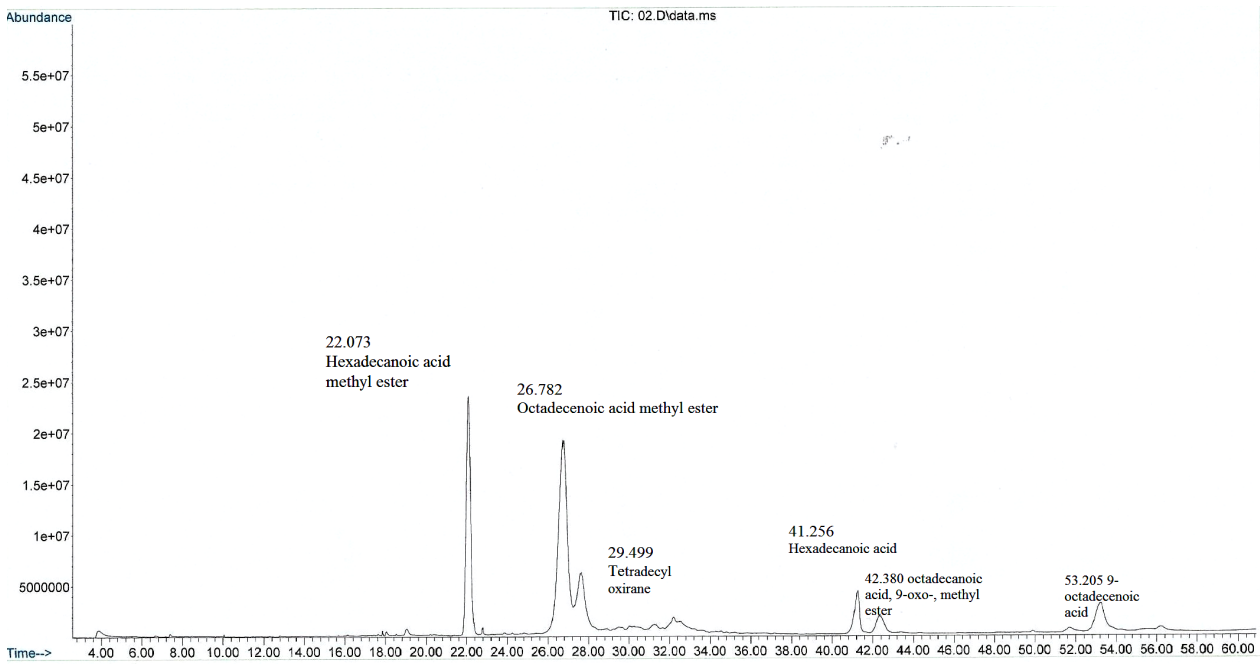


Fig. 5. GC chromatogram of HSAE derived from the uncatalyzed reaction between EMO and LABSA (EMO : LABSA = 1 : 1.3).

CONCLUSIONS

The increase of the temperature of the reaction between EME LABSA results in EME oxirane oxygen decrease because of epoxide ring opening. The reaction product contains hydroxyl and sulfonate ester groups identified by FTIR, NMR, and GC-MS.

Acknowledgements

The authors are very grateful to Departement of Chemical Engineering, Muhammadiyah University of Jakarta, Indonesia to all facilities, that provided during this research. The authors would like to thank to Indonesian General Directorate of Higher Education, Ministry of National Education for the research Grant No 772/ K3/KM/SPK.LT/2016, dated June 14, 2016.

REFERENCES

1. R.A. Nugrahani, D. Mangunwidjaja,, A. Suryani, Machfud, Sudradjat. Optimation Process and Kinetics of Epoxidation of Jatropha curcas L. Oil by Hydrogen Peroxide, J. Tek. Ind. Pert., 18, 2, 2008, 66-70.
2. M.H. Shagal, Synthesis of Polyol from Ximenia Americana Seed Oil, Research Journal in Engineering and Applied Sciences, 3, 4, 2014, 311-315.
3. V.B. Borugadda, Epoxidation of Castor Oil Fatty Acid Methyl Esters (COFAME) as a Lubricant base Stock Using Heterogeneous Ion-exchange Resin (IR-120) as a Catalyst, Energy Procedia, 01, 2014, 54, 75-84.
4. Patent US5368776 A.
5. S.K. Sahoo, S. Mohanty, S.K. Nayak, Toughened bio-based epoxy blend network modified with transesterified epoxidized soybean oil: synthesis and characterization, RSC Adv., 5, 2015, 13674-13691.
6. R.A. Holser, Transesterification of epoxidized soybean oil to prepare epoxy methyl esters, Industrial Crops and Products, 27, 1, 2008, 130-132.
7. F. Gallia, S. Nuccia, C. Piolaa, C.L. Bianchia, Epoxy Methyl Soyate as Bio-Plasticizer: Two Different Preparation Strategies, Chemical Engineering Transactions, 37, 2014, 601-606.
8. C. Sabina, P.Y. Bakoz, Z. Tinhinane, Synthesis of a biobased antioxidant additive for diesel fiel, American Journal of Applied Chemistry, 2, 1, 2014,10-14.
9. A.M. Sabagh, Abd-El-Bary, R.A. El-Ghazawy, M.R. Mishrif, B.M. Hussein, Corrosion inhibition efficiency of linear alkyl benzene derivatives for carbon steel

pipelines in 1M HCl. Egyptian Journal of Petroleum, 20, 2, 2011, 33-45.
10. R.N.M. Kamil, S. Yusup, L. Ismail, Application of Taguchi Method for Optimization of Polyol Ester Production by Esterification of Neopentyl Glycol with Hexanoic Acid, Asian Journal of Chemistry, 25, 15, 2013, 8256-8260.
11. R.A. Nugrahani, A.S. Redjeki, Y. Teresa, N. Hidayati, Effect of Linear Alkylbenzene Sulphonate on Oxirane Oxygen of Epoxidized Rice Bran Oil Methyl Ester, Proceeding The 2nd International Multidisciplinary Conference, pp.425-431.