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The Synthesis of Surfactant by Alcoholysis Between Glyceryl Trilaurate and n-Amyl Alcohol

Daniel [1,2 a)]

[1)]Department of Chemistry, Faculty of Mathematics and Natural Sciences, Mulawarman University, Samarinda 75123, East Kalimantan, Indonesia.
[2)]Organic Chemistry Laboratory, Faculty Matematika and Natural Science, Mulawarman University, Samarinda 75123, East Kalimantan, Indonesia.

[a)]Corresponding author: daniel_trg08@yahoo.com

Abstract. The alcoholysis reaction of triglycerides in producing fatty acid alkyl ester can be prepared by using short chain alcohol such as methanolysis or ethanolysis. Similarly, partial alcoholysis can be carried out to produce mono and diglyceride which act as surfactant agents. They can be obtained either by glicerolysis or long chain hidrocarbon alcoholysis of triglyceride. In this study, the synthesis of glyceryl trilaurate was conducted by esterification of lauric acid with glycerol and glyceryl trilaurate. Then it was followed by the alcoholysis reaction with n-amil alcohol in mol ratio 1:3 using $NaOCH_3$ as catalyst mixed at 3000 rpm rotation in order to produce a mixture of glyceryl mono. di and trilaurate as well as n-amil laurate. The next stage was separating n-amil laurate and glyceril trilaurate from the mixture of glyceryl mono and dilaurate in ethanol. The alhoholysis reaction produced glyceril trilaurate and n-amil alcohol at around 65.55%. After determined by iodometry titration, the mixture of glyceril mono and dilaurate produced glyceril monolaurate at percentage of 15.5% after. It was found that the HLB (Hidrophilic Lipophilic Balance) value was 4.84 and determined as anti-foam agent surfactant. FT-IR spectroscopy analysis was used to confirm the structure of reaction result.

INTRODUCTION

It has been known that glycerolysis reaction can be used in producing mono- and diglycerides from lipids and through this process, glycerides mixture was produced. The reaction is a random exchange between acyl and alkoxy groups. Thus, it would be necessary to reveal whether the reaction of monoalcohol with triglyceride will produce monoglycerides and diglycerides [1]. The main problem in the methanolysis reaction is the formation of fatty acid methyl esters consisting of glycerol without any formation of mono and diglycerides. However, if the extension of hydrocarbon chain from the alcohol used in the reaction exists. Then the mono and diglycerides could be possibly produced [2, 3].

This study attempts at extending the hydrocarbon chain by forming the reaction of n-amyl alcohol and glyceryl trilaurate. It is expected that the reaction will not only forming fatty acids n-amyl esters but also mono- and glycerides. FT-IR spectrum will be used in analyzing the results [4, 5]. It is used to check whether the hydroxyl group interacts through hydrogen bridge and therefore the wave number in the vibration region of the hydroxyl group becomes weak as shown by the FT-IR spectrum. To some extent, alcohol will be used to separate the esters. mono- and glycerides [6, 7]. Thus, the main aim of this study is extending the alcohol chain in order to provide detention for esters with alkoxy from alcohol and acyl from fatty acids.

The alcoholysis reaction of triglycerides by using methanol and ethanol will produce a high amount of reaction results of fatty acid methyl esters and fatty acid ethyl esters. In this reaction, it is important to note whether the additional length of the hydrocarbon chain from alcohol will give the expected reaction results. As it is assumed that the longer hydrocarbon chain, the more it becomes non-polar and it may reduce the chance of fatty acid alkyl esters formation [8]. Based on the above mentioned explanation, the questions that need to be addressed are whether an alcohol reaction between glyceryl trioleate and n-amyl alcohol will produce a mixture of mono- and glyceride, and how much is the amount obtained [9, 10].

From this study, it is expected that the increase of the length of the alcoholic hydrocarbon chain which has a single alcohol group will affect the alcoholysis reaction. Therefore, it will not only produce full alkyl ester but also mono- and glycerides. In addition, the amount of the reaction results will be monitored [11]. This research

is also expected to provide benefits in a form of suggestion to the oleochemical industry that the finest way to produce fatty acid alkyl ester is by using short chain hydrocarbons such as methyl and ethyl partially. While, in producing mono- and glycerides, medium chain hydrocarbons can be used [12, 13].

EXPERIMENTAL

This study was a laboratory experiment in which lauric acid (pellet), glycerol, n-amyl alcohol, sodium methoxide, n-hexane, ethanol and acetone were the products of E-Merck Germany with p.a. level. Lauric acid was esterified with glycerol by using sodium methoxide catalyst. Then, it was separated by chromatography with a mixture of eluent n-hexane and diethyl ether in a ratio of 9:1 (v/v) in order to obtain glyceryl trilaurate and the result was analyzed by FT-IR spectroscopy (Shimadzu). The next was the alcoholysis of Glyceryl trilaurate with n-amyl alcohol by using sodium methoxide as the catalyst in attempt to get glyceryl monolaurate and glyceryl dilaurate. It is then continued with determining the values of HLB. The amount of glyceryl monolaurate, acid values, and saponification values were determined[14, 15].

RESULTS AND DISCUSSION

The Synthesis of Glyceryl Trilaurate

The esterification reaction between glycerol and lauric acid by using $NaOCH_3$ as the catalyst produced the compounds of glyceryl trilaurate, glyceryl monolaurate and glyceryl dilaurate. Glyceryl trilaurate was extracted from the mixture of n-hexane solvent and purified by column chromatography by using mixture eluent of n-hexane: diethyl ether 9:1 (v/v) and produced glyceryl trilaurate at the amount of 54.8 g (61.9 %) in the form of clear yellow liquid [16]. The result from thin layer chromatography analysis with developer n-hexane:diethyl ether 9: 1 (v/v) is a single stain for triglycerides with the rf value of 0.67.

The result from FT-IR spectroscopy analysis of functional group for glyceryl trilaurate showed a spectrum with absorption peaks in the wave number of 2927.7 cm^{-1}, 2854.5 cm^{-1}, 1708.8 cm^{-1}, 1411 cm^{-1}, 1377.1 cm^{-1}, 1284.5 cm^{-1} and 725.2 cm^{-1}, respectively (Fig. 1).
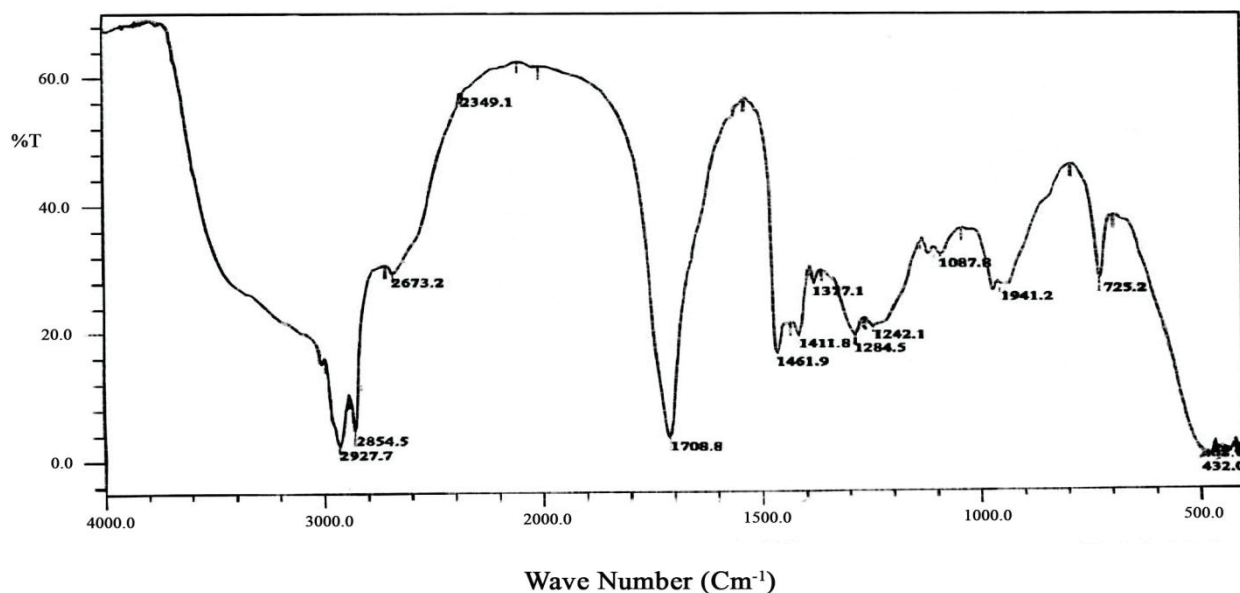

FIGURE 1. FT-IR Spectrum of Glyceryl Trilaurate Compounds

Glyceryl Trilaurate Alcoholysis with *n*-Amyl Alcohol

The alcoholysis of glyceryl trilaurate with n-amyl alcohol by using $NaOCH_3$ as the catalyst produced a compound of glyceryl monolaurate and glyceryl dilaurate in addition to amyl laurate compound. Glyceryl monolaurate and glyceryl dilaurate compounds were separated by the extraction process using ethanol solvent and the amount of the compound obtained was 61.23 g (60.38%). The result from thin layer chromatography analysis with the developer n-hexane: diethyl ether: 9:1 (v/v) produced two stains with Rf value of 0.11 and

0.27, respectively. The HLB value was 0.178. The amount of glyceryl monolaurate obtained from the titration process was 10.6%. The result from FT-IR spectroscopy analysis of functional group for the mixture compounds of glyceryl monolaurate and dilaurate showed a spectrum with the absorption peaks in the wave number of 3400 cm^{-1}, 3008.7 cm^{-1}, 2923.9 cm^{-1}, 2854.5 cm^{-1}, 1708.8 cm^{-1}, 1566.1 cm^{-1}, 1407.9 cm^{-1}, 1288.4 cm^{-1} and 721.3 cm^{-1}, respectively (Fig. 2).
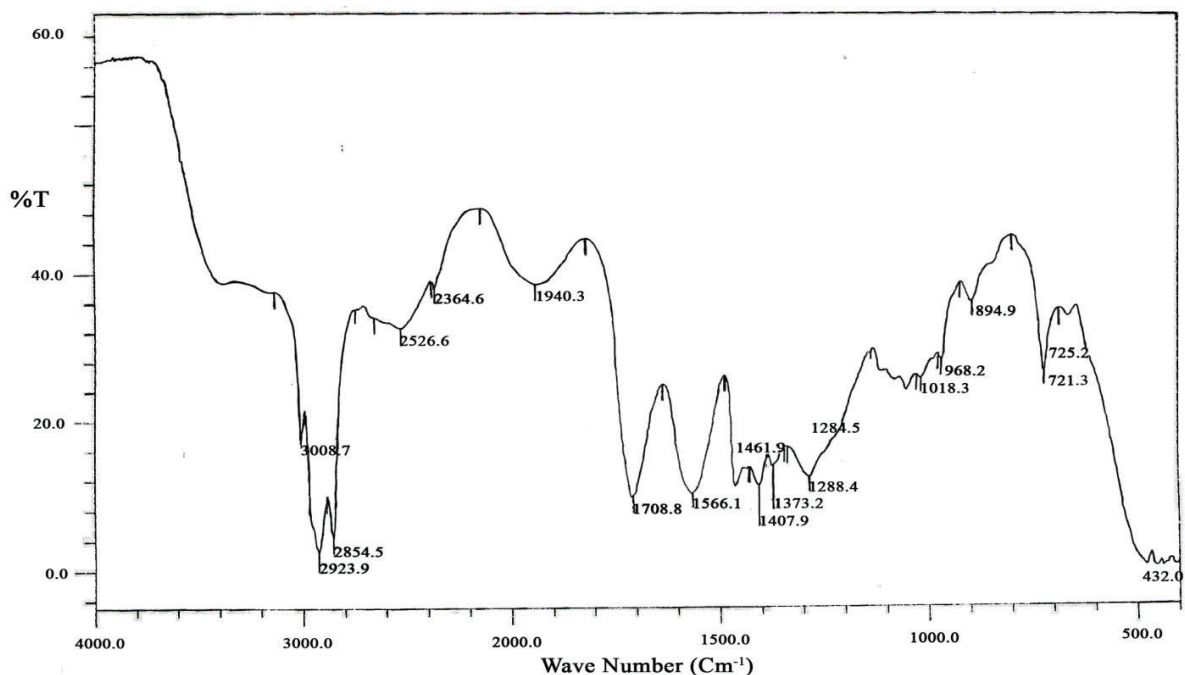

FIGURE 2. FT-IR spectrum of the glyceryl monolaurate and dilaurate compounds

Glyceryl monolaurate, glyceryl dilaurate and glyceryl trilaurate were produced from the esterification of lauric acid with glycerol by using NaOCH$_3$ as the catalyst and combined with the stirring process.
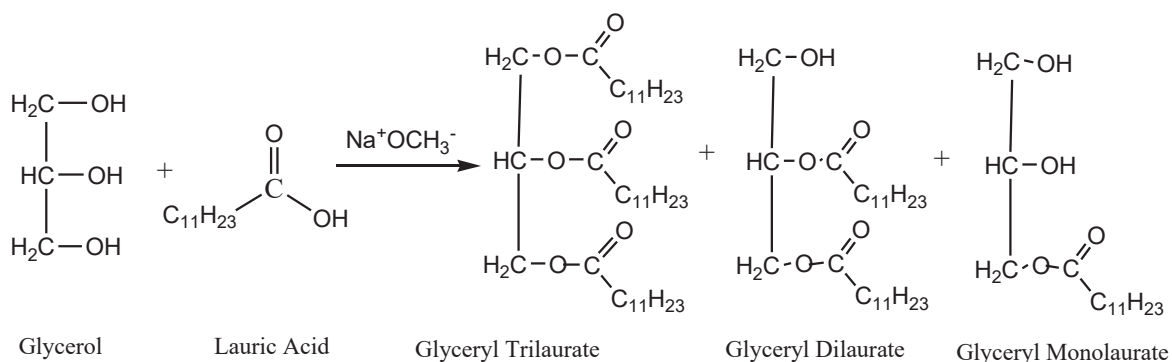

FIGURE 3. Esterification reaction of lauric acid with glycerol

The above results was based on the reaction principle of random exchange between lauric acid acyl and alkoxy glycerol groups which produced glycerolate compounds as shown in the reaction mechanism in Fig. 4. Glyceryl trilaurate was separated by extracting using non-polar n-hexane solvents as it was expected that the more polar compounds, glyceryl monolaurate and glyceryl dilaurate compounds would not be included. The result of extraction was purified by implementing column chromatography and produced glyceryl trilaurate [17, 18]

The formation of glyceryl trilaurate compound was supported by the FT-IR spectrum (Fig. 1) for analysis of functional group which showed a spectrum with absorption peaks at wave number of 1708.8 cm^{-1}. It indicated the presence of ester C = O groups and supported by the appearance of absorption peaks in wave number of 2927.7 cm^{-1} and 2854.5 cm^{-1}. It was CH-sp^3 stretching vibration and supported by an absorption peak in the

wave number of 1461 cm^{-1} which belong to the CH$_3$ metal group. The rocking vibration of - (CH$_2$)-n for n $\geq$ 4 was shown at the absorption peak of 725.2 cm^{-1}.
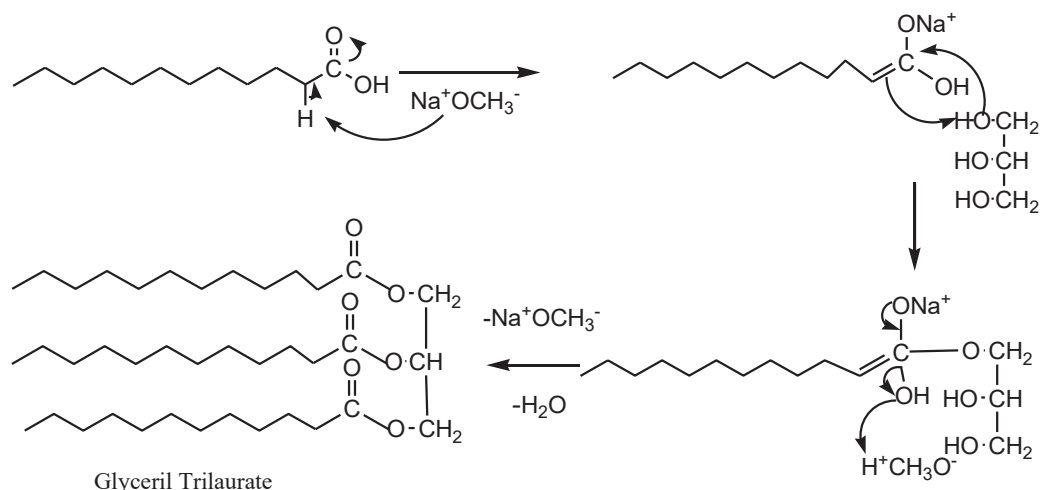

FIGURE 4. Reaction mecanism of acid laurate and glycerol with NaOCH$_3$ catalyst

Glyceryl Trilaurate Alcoholysis with n-Amyl Alcohol

The alcoholysis of glyceryl trilaurate by using NaOCH$_3$ as the catalyst with n-amyl alcohol produced a mixture compound of gryceryl monolaurate, glyceryl dilaurate and amyl oleate. It was predicted that by extending the alcohol hydrocarbon chain, the reactivity would also decrease. Thus, it would prevent the formation of esters from the original glyceryl trilaurate group with alkoxy n-amyl alcohol groups because of the decrease of nucleophilic characteristic of alkoxy groups and the extension of the hydrocarbon chain.
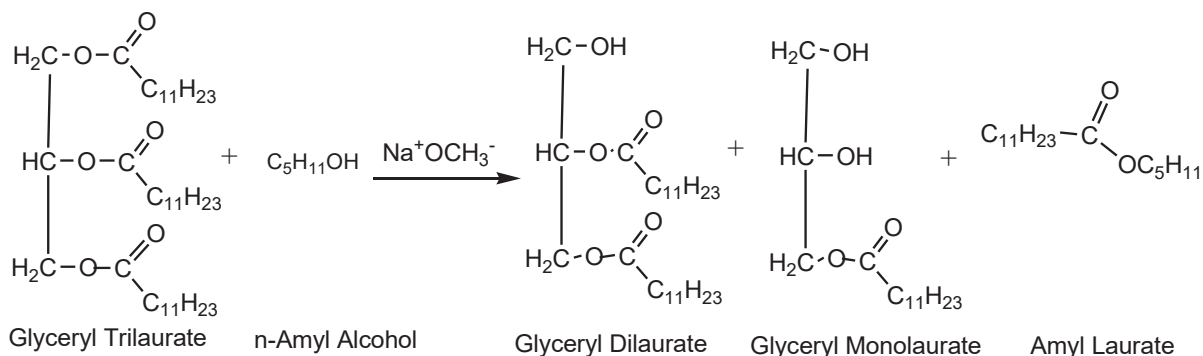

FIGURE 5. Glyceryl Trilaurate Alcoholysis with N-Amyl Alcohol

Glyceryl monolaurate and glyceryl dilaurate were extracted by using alcohol which was derived from mixture compounds of product as these two compounds were more polar than amyl laurate. The formation of glyceryl monooleate and glyceryl dioleate compounds were supported by FT-IR spectrum (Fig. 2) which showed the absorption peak at wave number of 1708.8 cm^{-1}. This result indicated the presence of ester C=O groups. It was supported by the appearance of the absorption peak at the wave number of 1288.4 cm^{-1} and it was a C-O-C vibration from ester. The absorption peak at wave numbers 2923.9 cm^{-1} and 2854.5 cm^{-1} were the stretching vibration of CH-sp^3 and it was supported by the absorption peaks at the wave number of 1461.9 cm^{-1} and 1407.9 cm^{-1}. These results showed an indication of methylene CH$_2$ group. At the absorption peak 721.3 cm^{-1}, it showed the rocking vibration of -(CH$_2$)-n for n $\geq$ 4. While the absorption peak at wave number of 3008.7 cm^{-1} was the absorption of olefin group. The absorption peak at 1566.1 cm^{-1} was the absorption of CH$_2$-O- group.

The absorption peak at the wave number of 3400 cm^{-1} was the vibration of the –OH group. This absorption peak was very weak. It was predicted that the structural shape of the gliceryl monolaurate compound allowed the formation of a hydrogen bridge between those hydroxyl groups through the structural confirmation in the form of chair or fork shape-like [17, 18].
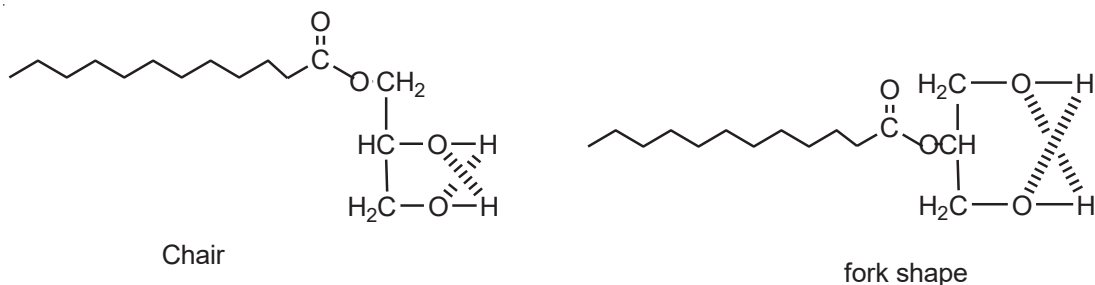
FIGURE 6. Stuctural confirmation of glyceryl manolaurate of chair and fork shape

In order to determine the amount of monogliceryd by using titration method with $Na_2S_2O_4$, a formula was applied as shown in equation 1.

$$\% \text{ Monoglycerides} = \frac{(V_{blanko} \times V_{sample\ of\ titration}) \times N_{Na-tiosulfat} \times AR}{Weight\ of\ Sample\ x\ 10} \tag{1}$$

Based on the formula above, the amount of glyceryl monolaurate was 15.5% while the amount glyceryl dilaurate was 85.5%. From Table 2, it can be seen that the value of Critical Micelle Concentration (CMC) from glyceryl mono and dilaurate is 0.0004%. The value of CMC can reduce the surface tension of water at around 57.03 dyne/cm, while the surface tension of water itself is 71.06 dyne/cm at the degree of 30 °C. From the value of CMC combined with Du Nuoy tensiometer, the value of HLB will be computed, where:

$$\text{Correction factor} = \frac{\gamma\ water\ based\ on\ the\ reference}{\gamma\ water\ at\ the\ measuring\ time} \tag{2}$$

Where: γ water based on the reference at 30 °C = 71.06 dyne/cm
        γ water at measuring time at 30 °C = 81.6 dyne/cm

$$\text{Correction factor} = \frac{71.06}{81.6} = 0.87 \tag{3}$$

Based on the results presented in Table 2, the value of CMC is 0.0004%. Therefore the value of HLB can be calculated by using the following formula:

$$\text{HLB} = 7 - 0.36\ln(Co/Cw) \tag{4}$$

Where: Cw = CMC value = 0.0005%
        Co = 100 - Cw = 99.9996

Based on the computation above, the value of HLB is 4.84. It means that the glyceryl mono and dilaurate compounds are surfactants that can be used as anti-foam substance.

The following results prove that the glyceryl mono and dilaurate compounds are surfactant based on the measurement of surface tension by using Du Nuoy ring tensiometer: from the graph of surface tension-Vs-log C (Table 1) it can be seen that the surface tension decreases while the glyceryl mono and dilaurate concentration in water increase. In the final stage, it became constant even though the glyceryl mono and dilaurate concentration increased which was caused by micelle formation of dilauroyl maltosa. This result showed that dilauroyl maltosa is a surfactant in which its hydrophilic groups are hydroxyl and ester groups. Meanwhile, the hydrocarbons belong to lipophilic groups [14].

TABLE 1. Data of the Surface Tension Measurement (γ) Glyceril mono and dilaurate

No.	The concentration of surfactant on the water (%)	Log. C	Identified surface tension (γ) (dyne/cm)				γ after correction
			γ_1	γ_2	γ_3	γ	
1	0.000001	-6.00	72.3	72.2	72.4	72.3	71.43
2	0.000005	-5.30	69.6	69.6	69.6	69.6	68.73
3	0.000010	-5.00	67.2	67.2	67.3	67.2	66.33
4	0.000030	-4.52	65.6	65.5	65.4	65.5	64.63
5	0.000050	-4.30	64.5	64.5	64.4	64.5	63.63
6	0.000080	-4.09	63.2	63.2	63.3	63.2	62.33
7	0.000100	-4.00	61.8	61.7	61.8	61.8	60.93
8	0.000200	-3.69	60.8	60.7	60.9	60.8	59.93
9	0.000300	-3.52	59.1	59.1	59.1	59.1	58.23
10	0.000400	-3.39	57.9	57.9	57.9	57.9	57.03
11	0.000600	-3.22	57.8	57.7	57.10	57.9	57.03
12	0.001000	-3.00	57.8	57.9	57.9	57.9	57.03
13	0.002000	-2.69	57.8	57.8	57.10	57.9	57.03
14	0.003000	-2.52	57.8	57.9	57.9	57.9	57.03
15	0.005000	-2.30	57.8	57.9	57.9	57.9	57.03
16	0.010000	-2.00	57.8	57.9	57.9	57.9	57.03
17	0.050000	-1.30	57.9	57.8	57.9	57.9	57.03
18	0.100000	-1.00	57.7	57.7	57.7	57.7	56.96

CONCLUSION

The esterification between Lauric acid and glycerol by using $NaOCH_3$ as the catalyst produced glyceryl trioleate at the amount of 61.9%. The alcoholysis of Glyceryl trilaurate and n-amyl alcohol by using $NaOCH_3$ as the catalyst produced 60.38% of glyceryl mono- and di-laurate in addition to amyl laurate at the amount of 15.5% and 85.5%, respectively. The mixture compound of glyceryl mono- and di-laurate has 4.84 HLB value which can be used as an anti-foam substance.

ACKNOWLEDGMENTS

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