Synthesis of Diethanolamide Surfactant from Palm Oil by Esterification and Amidation Processes

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Abstract. Coconut oil as a surfactant can be derived from renewable, cleaner, and purer resources than petrochemical-based raw materials. Therefore, this study was conducted to obtain the required criteria for forming a surfactant such as diethanolamide. During the analysis, diethanolamide surfactant was produced, with the procedure separated into transesterification and amidation. The transesterification process was carried out by reacting palm oil and methanol with sulfuric acid to form a methyl ester. The amidation process follows this process by reacting the methyl ester and diethanolamine with a NaOH catalyst to form a diethanolamide surfactant. Furthermore, the best conditions in the amidation process were obtained when the mole ratio of methyl esters to diethanolamine was 1 to 5, and the NaOH content of 5% was converted to 68.95%, with the qualification of surfactant diethanolamide and CMC values at 5 g/mL. The HLB value of 5.940 means that this surfactant can be applied to W/O or Water in Oil emulsifiers.

Keywords: Surfactant · methyl ester · amidation · diethanolamide

1 Introduction

A condition for accepting surfactant in developed countries is that new products should not be destructive to the environment or undergo any steps contributing to environmental degradation. Modern advancements in Indonesia include the explosive expansion of the country's cosmetics, detergent, personal care, and pesticide sectors. The increasing development of the industry has resulted in the need for active ingredients such as surfactants (Adisalamun et al. 2012, Adiputra and Rian 2020).

In general, surfactants from petroleum and natural gas derivatives can leave waste that is difficult to degrade so that it can cause environmental pollution. Furthermore, the petroleum used is a non- renewable source, and this problem has caused many parties to determine alternative surfactants from renewable raw materials (El-Sukkary et al. 2008, Cheah, et al. 2016).

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1.1 Types of Surfactants

Classification of surfactants based on the charge is divided into four types, namely:

1. **Anionic surfactants** are polar groups with a negative charge.The hydraulic properties come from the ionic head, which is a sulfate or sulfonate group. In this case, the hydrophobic group is attached to the hydrophilic moiety by a labile C-O-S bond, easily hydrolyzed. Some examples of anionic surfactants are linear alkylbenzene sulfonate (LAS), alcohol sulfate (AS), alpha olefin sulfonate (AOS), and paraffin or secondary alkane sulfonate (SAS), sodium dodecyl sulfonate: C12H23CH2SO3-Na^+, and sodium dodecyl benzenesulfonate: C12H25ArSO3-Na^+.
2. **Cationic surfactants** are positively charged polar groups, including alkyl trimethyl ammonium salts, dialkyl-dimethyl ammonium salts, and alkyl dimethyl benzyl ammonium salts (Duman, et al. 2020).
3. **Nonionic surfactants** are polar groups with no charge. These surfactants do not dissociate in water but depend on the structure to alter the hydrophilicity, making them water-soluble. Nonionic surfactants are used with anionic surfactants. These types are derivatives of polyglycols, alkylamides, or esters of polyhydroxy alcohols, including fatty acid glycerin esters, fatty acid sorbitan esters, fatty acid sucrose esters, polyethylene alkyl amines, glucamine, alkyl polyglucosides, etc.
4. **Amphoteric surfactants** are polar groups with positive and negative charges, containing betaine, phosphobetain, and amino acid. Surfactants are synthesized from petroleum derivatives, such as linear alkylbenzene sulfonate (LAS), alkyl sulfonate (AS), alkyl ethoxylate (AE), and alkyl ethoxylate sulfate (AES) (Holmberg et al. 2003).

A nonionic surfactant that does not ionize all the ions in the solution will be made. The oxygen- containing group forms hydrophilic, soluble, in the presence of hydrogen bonds with water (Paria et al. 2015). One example of a nonionic surfactant commercialized is diethanolamide (DEA), and the production process using fatty acids from palm kernel oil is conducted through an amidation reaction.

The mole ratio between lauric acid and diethanolamine is 1:1, and the amidation reaction conditions used a heating temperature of 140–160 °C, a stirring speed of 150–200 rpm, and a reaction time of 3–4 h. The reaction uses sodium methylate as a catalyst with a concentration of 0.3–0.5%. The characteristics of the DEA surfactant are free fatty acid content of 0.38–0.51%, and pH 9.28–9.87, as well as the ability to lower the surface tension of water, reduce interface tension, increase emulsion stability by 51.5–60.6%, 88.3–99.3%, and 78.61–76.83% (Suryani, et al. 2020).

DEA (Diethanolamide)/Alkanolamide (EthanolN-alkylamides) is a nonionic surfactant processed by the amidation method, which results from the reaction between alkanolamine and fatty acid vegetable oil/methyl ester. Furthermore, amidasia is a reaction to the formation of amide compounds. Alkanolamide surfactants have been widely developed in the surfactant manufacturing industry because amide bonds are chemically stable in alkaline media. DEA can be used for formulas in food products, cosmetics, and medicines (Zhang et al. 2016). As a nonionic surfactant, it can be non-toxic, non- irritating, and friendly to the environment. World demand for DEA is quite high, as indicated by the number of imports of nonionic surfactants in 2009, reaching 18.176 million tons, and the demand growth on an average of 3% per year (Almeida et al. 2022).

DEA is used to produce skin-beneficial transparent soap (Hambali et al. 2012). The formation is in the mechanism of the amidation reaction of methyl esters with diethanolamide using NaOH catalyst.

$$RCOOCH_3 + NaOH \rightarrow RCOONa + CH_3OH \tag{1}$$

$$RCOONa + NH(C_2H_4OH)_2 \rightarrow RCON(C_2H_4OH)_2 + NaOH \tag{2}$$

$$RCOOCH_3 + NH(C_2H_4OH)_2 \rightarrow RCON(C_2H_4OH)_2 + CH_3OH \tag{3}$$

(methylester) (diethanolamine) (diethanolamide) (methanol)

Palm and kernel oils are found in the fleshy part of the fruit and the seeds with different fatty acid compositions. Palm oil contains 50% saturated and 50% unsaturated fat with 44%, 5%, 39%, and 10% palmitic, stearic, oleic, and linoleic acid. The content of myristic and lauric acid is negligible (Saxena. et al. 2017, Nor et al. 2022, Oliveira et al. 2017).

Methyl esters are made by transesterifying fatty acids with methanol. There are four type of manufacturing procedures, namely mixing and direct use, microemulsion, pyrolysis, and transesterification. In this study, the manufacture of methyl esters uses a transesterification reaction between triglycerides with methanol to produce methyl esters and glycerol. Methyl ester is a raw material for manufacturing surfactants, biodiesel, and emollen in cosmetic products. Meanwhile, glycerol can be used in various industrial applications such as cosmetics, soaps, and pharmaceuticals. (Makalalag and Ardi, 2018, Tongnuanchan, et al. 2016).

1.2 Diethanolamide Surfactant Formation Process

Transesterification is the conversion stage of triglycerides (vegetable/animal oils) into alkylesters through an alcohol reaction to produce glycerol. Among the monohydric alcohols that are candidate sources/suppliers of alkyl groups, methanol is the most commonly used because it is cheap and has the highest reactivity. Transesterification also uses a catalyst in the reaction, and without a catalyst, the resulting conversion is maximum, but the reaction runs slowly. (Makalalag and Ardi 2018, Saxena et al. 2017).

The transesterification reaction between triglycerides and methanol into methyl ester in Fig. 1.

Amidation is a reaction to form a compound from fatty acid or methyl ester with an amine compound. One of the processes used to produce surfactants is the amidation process of reacting a fatty acid (fatty acid) or methyl ester with diethanolamine. The use of a catalyst serves to speed up the reaction time. With the same temperature, the reaction can take place more quickly.

Catalysts play an important role in increasing the efficiency of the process and the resulting product, such as NaOH, KOH, and NaOCH3 (Hasibuan et al. 2009, Fernanda et al. 2022). In this study, the amidation process used a NaOH catalyst, and the previous study used sodium methylate.

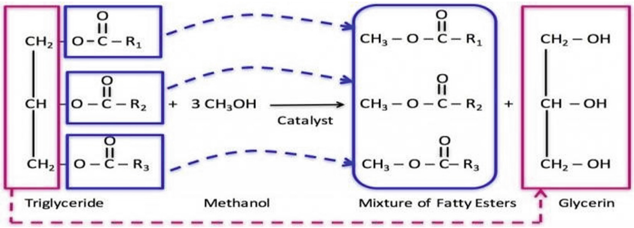

Fig. 1. The transesterification reaction between triglycerides and methanol into methyl ester

2 Methodology

2.1 Methyl Esters Preparation (Transesterification Process)

The palm oil of 200 ml was taken, then 100 ml of methanol was mixed with H_2SO_4 in a batch reactor (three-neck flask equipped with a stirrer with a stirring speed of 150 rpm and a water bath). The temperature was maintained at 60 °C for 2 h. After the transesterification process is complete, the methyl ester is separated from the glycerol using a separating funnel. The methyl ester is neutralized by adding NaOH and adding warm water to the methyl ester. Therefore, the remaining methanol, glycerol, and other impurities are separated from the methyl. Anhydrous H_2SO_4 is added to the methyl ester to absorb the remaining water before separating H_2SO_4.

2.2 Process of Diethanolamide Surfactant Preparation (Amidation)

The methyl ester was reacted with diethanolamine, and the mole ratio on the amount of reactant was varied. The reaction took place in a three-neck flask equipped with a water bath. Methyl ester and diethanolamine (1:5) were reacted with varying concentrations of NaOH catalysts. The temperature was maintained at 160 °C for 3 h, and the mixture was stirred with a magnetic stirrer at a speed of 150 rpm.

2.3 Diethanolamide Surfactant Test

FTIR Test. In Fourier Transformer Infrared Spectroscopy (FTIR), IR (Infra Red) radiation passes through the sample, which absorbs the radiation energy captured by the detector. Furthermore, each sample has a different absorption value, and FTIR is a measurement technique for collecting infrared spectrum. The energy absorbed by the sample at various infrared light frequencies is recorded and transmitted to the interferometer. The sample measurement beam is converted into an interferogram. The mathematical calculation for the signal will produce an identical spectrum in infrared spectroscopy. FTIR analysis on the methyl ester was conducted to determine the groups in the resulting surfactant (Griffin 1949, Gradzielski 2022).

Surface Tension Test. An imbalance of forces occurs when the two phases of gas-liquid, gas-solid, liquid-solid, and liquid- liquid, are in contact, leading to an accumulation of free energy at the interface. The interfacial excess or surface-free energy can

Table 1. Surfactant Specifications Based on HLB Value

HLB Value	Application
3–6	W/O Emulsif ier
7–9	Wetting agent
8–14	O/W Emulsifier
9–13	Detergent
10–13	Solubilizer
12–14	Dispersants

Source: Holmberg et al (2003)

be calculated by measuring the energy ratio divided by the surface area to increase the number of units. Furthermore, excess energy is present at all types of interfaces, and for the gas phase of the liquid, the measurement is referred to as surface tension. It is known as interfacial tension when the surface is the interface of two immiscible liquids (Griffin 1949).

HLB Test. A stable microemulsion system requires a surfactant with an appropriate hydrophilic-lipophilic balance (HLB) value. HLB surfactant is an empirical scale based on the relative percentages of hydrophilic and lipophilic functional groups, ranging from 1 to 20, where a lower and higher number indicates solubility in oil (lipophilic) and water (hydrophilic). The combination of several surfactants will add to the perfection of the physical and chemical properties of the emulsion. Besides having polar and non- polar groups in one molecule, it can reduce interfacial and surface tension (Griffin 1949). The HLB value can determine the application of the surfactant, and the Table 1 shows the application.

3 Results and Discussion

3.1 Effect of Variation in Mole Comparison of Reactants on Conversion in the Amidation Process

The amidation process of diethanolamine and methyl ester reactants was conducted using different mole ratios and NaOH catalysts at 160 °C for 3 h. Based on the research conducted, the results of the amidation process are shown in Table 2.

From Table 2, the moles of diethanolamine are directly proportional to the conversion. This is because more diethanolamine moles will affect the reaction product shift. The reaction shifts to the right, increasing conversion due to excess mole. After a 1:5 ratio, the conversion will tend to be constant because the equilibrium price of the reaction constant (C) will decrease. Therefore, the reaction will shift to the left, decreasing the product and the conversion.

Table 2. Results of the Amidation Process with 5% NaOH Catalyst

Methyl ester: diethanolamine mole ratio	Amidation Results (mole)	Conversion (%)
1:1	0.125	50.40
1:2	0.145	58.46
1:3	0.158	63.70
1:4	0.168	67.74
1:5	0.171	68.95
1:6	0.170	68.54

Table 3. Effect of NaOH concentration on the conversion

Variation of NaOH catalyst concentration (%)	Amidation result (mole)	Conversion (%)
1	0.138	55.69
2	0.144	58.06
3	0.164	66.12
4	0.169	68.14
5	0.171	68.95
6	0.170	68.54

The relationship between the concentration of NaOH catalyst and the conversion of surfactant can be seen in Table 3. Table 3 shows that from a concentration of 1% to 5%, the percentage of catalyst is directly proportional to the conversion. In addition, a high catalyst concentration can easily break the bond of methyl ester to form. Since NaOH is a strong base and is rapidly ionized, increasing the amount of catalyst used causes the conversion to decrease beyond 5%. The amidation of methyl esters with diethanolamine catalyst is as follows:

$$RCOOCH_3 + NaOH \rightarrow RCOONa + CH_3OH \quad (4)$$

$$(1) RCOONa + NH(C_2H_4OH)_2 \rightarrow RCON(C_2H_4OH)_2 + NaOH \quad (5)$$

$$(2) RCOOCH_3 + NH(C_2H_4OH)_2 \rightarrow RCON(C_2H_4OH)_2 + CH_3OH \quad (6)$$

(methylester) (diethanolamine) (diethanolamide) (methanol)

In the first step, the ionized NaOH catalyst breaks the methyl ester bond. The Na^+ and OH^- ions will bind to the ester and methyl group to form RCOONa and methanol.

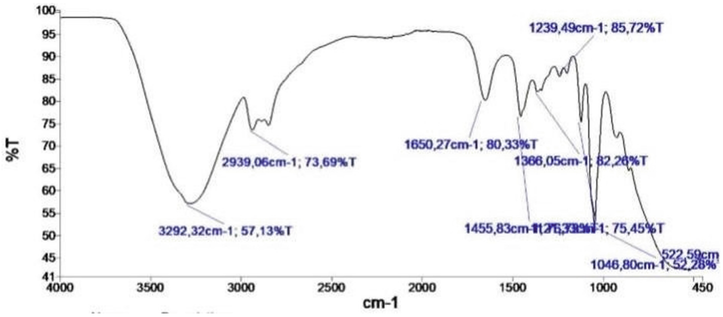

Fig. 2. Graph of FTIR Test Results on Diethanolamide

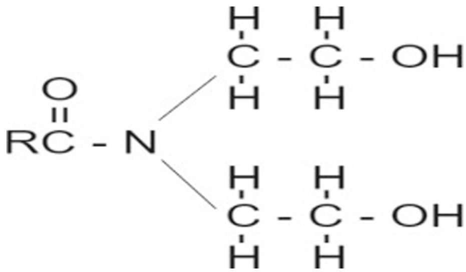

Fig. 3. Diethanolamide Structural Formula

The diethanolamide formation occurs in the second reaction, where the RCO^+ ion reacts with the $N(C2H4OH)2^-$ ion to form diethanolamide.

$$RCO^+ + N(C_2H_4OH)^{2-} \rightarrow RCON(C_2H_4OH)^2 \quad (7)$$

This RCO^+ is the result of breaking the methyl ester bond by the NaOH catalyst. The function of the NaOH catalyst is to break the bond in the methyl ester to facilitate the reaction. The resulting diethanolamide is also more than the reaction process without a catalyst. The possibility of the reaction proceeding is also slower because the ability to break the bonds in the methyl ester to react with diethanolamine is also reduced.

3.2 Functional Group Analysis Using FTIR Test

FTIR analysis indicated the presence of C-N, C=O, C-O, O-H, and C-H chain bonds formed in the product. The results on the surfactant products are shown in Table 4 with the C-N, C=O, C-O, O-H, and C-H chain bond groups, as shown in Fig. 1 (Figs. 2 and 3).

Based on the FTIR test above, the functional group spectrum readings are presented in Table 4.

Based on the reading of the functional group spectrum, the results of the FTIR test of the diethanolamide surfactant formed contain C-N, C=O, C-O-H, and C-H groups, which indicate the presence of esters and amides in the product. Therefore, the amidation process has formed surfactants in the presence of these functional groups.

Table 4. Reading of FTIR Test Results on Diethanolamide

No	Bond	Frequency area (cm^{-1}) (source: *Principle of Instrumental Analysis, Skoog, Holler, Nieman, 1998)*	Frequency area of FTIR test results on Diethanolamide (cm^{-1})
1	O-H	3200–3600	3292.32
2	C-H	2850–2970 1340–1470	2939.06 1455.83 1366.05
3	C=O (ester)	1650–1760	1650.27
4	C-N (amide)	1180–1360	1239.49
5	C-O	1050–1300	1121.33

Table 5. Surfactant Surface Tension Test Results Data

Concentration (%)	Value (N/m)
1	54.7
2	54.3
3	51.6
4	51.3
5	51
6	51

3.3 Surface Tension Test Analysis

Surface tension is a force that exists along the surface of a liquid. Surfactants have the function of lowering the interfacial tension between two different liquids. Based on the study, the results of the surface tension test are shown in Table 5.

Based on the results of the surface tension analysis in Table 5, the relationship between the concentration of diethanolamide surfactant and the surface tension value (N/m) can be illustrated in Table 5. The greater the surfactant concentration, the lower the face tension value until the CMC point is obtained. This shows that the resulting surfactant has the property of lowering the surface tension of a fluid.

3.4 HLB Analysis

HLB shows the balance scale of hydrophobic and hydrophilic groups of a surfactant to determine the application. The calculation is conducted with the CMC value in the face stress test, and the graph shows that the surfactant is 5 g/ml. Therefore, HLB can be calculated using the following formula:

$$HLB = 7 - 0.36 \frac{\ln 100 - CMC}{CMC} \quad (8)$$

The HLB is 5.940, and the emulsifier ranges from 1–20. The increased value indicates that the surfactant has hydrophilic properties and belongs to the W/O or Water in Oil emulsifier. W/O (water in oil) emulsion is conducted with water and oil as the dispersed and dispersing phase (Winarno 1997, Fernandes et al. 2013).

4 Conclusion

A nonionic surfactant, diethanolamide, can be made from methyl esters. The best effect of the mole ratio variable is methyl ester: diethanolamine at 1:5. The catalyst concentration variable is directly proportional to the conversion. The best conversion is at 5% NaOH catalyst concentration from the reaction of diethanolamide formation involving RCO+ ions. In the FTIR test, there are C=C and C=O bond groups with a spectrum value of 1644.97 and a C-O single bond at 1120.50. Therefore, the amidation process formed surfactants in the presence of these functional groups. Based on the surface tension test, the CMC and HLB values were obtained at a concentration of 5 g/mL and 5.940, which could be applied to W/O or Water in Oil emulsifiers.

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