Synthesis Cocamide DEA as Green Surfactant from Virgin Coconut Oil

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Abstract. Petroleum-based surfactants are not biodegradable. In this study, a surfactant made from natural ingredients, namely cocamide DEA. Di-ethanolamine (DEA) is one of the surfactants from non-ionic natural ingredients which has the advantage of being nontoxic, biodegradable, and environmentally friendly. Cocamide DEA is used for the synthesis of a wide variety of heterocyclic compounds and has a wide application in the pharmaceutical, surfactant, polisher and cosmetic industries. Cocamide DEA is obtained from Virgin Coconut Oil (VCO) which contains fatty acids. Manufacture of Cocamide DEA surfactants by the Transesterification-amidase process. Transesterification is the process of chemical transformation of fatty acids reacted with methanol and a catalyst that produces methyl esters. Amidation is the reaction of the formation of amide compounds between di-ethanolamine and methyl esters (ME). Preparation of surfactant Cocamide DEA from VCO by esterification-amidase process with a ratio of ME:DEA (1:1, 1:1,25, 1:1,75 1:2) w/w, variations NaOH catalyst (0.25%, 0.5%, 0.75%, 1%, 2% and 3%) and operating temperatures (150°C, 160°C, 170°C, 180°C). The study was conducted on the optimization of Transesterification-Amidation process, and to analyze the cocamide DEA functional groups with FTIR. The optimization of Transesterification-Amidation process about ME:DEA ratio, catalyst concentration, and temperature of conversion. The result show that the transesterification-amidase process of cocamide DEA obtained optimum conditions at the ratio MEDEA = 1:2 w/w, 3% NaOH catalyst concentration on 180°C.

1. Introduction
Surfactants (surface active agents) are substances added to liquids to increase their dispersion properties by reducing the surface tension of the liquid. The ability of surfactants to reduce stress is because the surfactants have an amphiphatic molecular structure, which is a molecular structure consisting of a hydrophilic group and a hydrophobic group [1]. These surfactants are widely applied in terms of washing and cleaning (clean and washing products).

Surfactants from petroleum which are commonly used so far have the disadvantages of being non-renewable, non-biodegradable so they are not environmentally friendly [2] [3] [4] [5]. Meanwhile, surfactants from vegetable oils such as virgin coconut oil (VCO) have the advantage of being renewable, cleaner and purer [6]. Surfactants are divided into 4 groups based on hydrophilic groups including anionic, cationic, amphoteric and nonionic [7] [8]. Anionic and nonionic surfactants are the most widely used [9]. One of the nonionic surfactants that can be synthesized from vegetable oil is di-ethanolamine (DEA).
Availability of coconut oil in Indonesia is abundant. Indonesia virgin coconut oil are cooperating with many coconut farmers from Sumatra, Sulawesi and Java. Cocamide DEA is produced from virgin coconut oil (VCO) which contains fatty acids and is present in large quantities in nature, reaching 44 million tons [10]. Cocamide DEA surfactant can be obtained from VCO by transesterification-amidation process. The transesterification process is the chemical transformation process of fatty acids which are reacted with alcohol (methanol) with the help of a catalyst (base) which produces smaller molecules and a straight chain, namely (methyl ester) [11] [12]. While Amidase is a reaction between alkanolamine and vegetable fatty acids (methyl esters) to form amide compounds [13].

The study was conducted on the optimization of Transesterification-Amidation proces, and to analyze the cocamide DEA functional groups with FTIR. The optimization of Transesterification-Amidation proceses about ME:DEA ratio, catalyt concentration, and temperature of conversion. In addition, this study to synthesis green surfactant with low prices and sustainable raw material can be a novelty in the field of surfactants, especially the use of concept of eco-friendly chemistry in producing sustainable surfactant [14].

2. Material and methods

This study was designed to obtain the surfactant cocamide DEA from VCO with amidase process and saponin extract from lerak (Sapindus rarak) with high purity.

2.1. Materials

The tools used are a three-neck flask, reverse cooler, thermometer, magnetic stirrer (scilogex), magnetic stirrer bar, water bath, stative clamp and Fourier-transform Infrared Spectroscopy (FTIR), burette. the ingredients used include analytical grade of diethanolamine (C4H11NO), coconut oil used as commercial oil that is Braco®, Methanol (CH 32OH), sulfuric acid (H2SO4) 4% w solution, sodium hydroxide (NaOH) 1% w solution, Aquadest, Na2SO4 anhydrous. All chemicals were analytical grade and from Merck (Darmstadt, Germany).

2.2. Methods

Virgin Coconut oil (VCO Brand Barco) as much as 200 ml, reacted with 100 ml methanol which has been mixed with H2SO4 catalyst (4% by weight of solution) inside reactor (three neck flask) equipped with a waterbath. The mixture is stirred with a magnetic stirrer at 60ºC for 2 hours to form methyl ester. Separate the methyl esters from glycerol using separating funnel. Methyl ester which has separated from glycerol with a separating funnel, neutralized the pH with NaOH. Warm aquadest is added to the methyl ester to make the remaining methanol, glycerol and other impurities apart from methyl esters. Add anhydrous Na2SO4 to the inside separate methyl esters from Na2SO4 anhydrous and analysis of initial esters. The research was conducted in duplicate.

Conversion of the cocamide DEA obtained in the amidation process. First, the methyl ester is reacted with DEA with a weight ratio reacting ME: DEA varied (1: 1, 1: 12,5, 1: 1,5, 1: 1,75 1:20) w/w) and the addition of NaOH catalyst with varied NaOH catalyst concentrations (0.25%, 0.5%, 0.75%, 1%, 2% and 3%). Then, the reaction was carried out at 160° C for 3 hours, the catalyst used is NaOH, the reaction takes place in a three-neck flask equipped with a waterbath, the mixture is stirred with a magnetic stirrer with a stirring scale on the magnetic stirrer. Diethanolamide formed is analyzed remaining ester number and analyzed for functional groups by FTIR.

3. Result and discussion

3.1. Analysis of Transesterification Results of Cocamide DEA

Based on figures 1 - 3, it is known that the conversion value of cocamide DEA the highest obtained through experiment was 82.37%, namely at a ratio of 1:2 methyl esters: di-ethanolamine, 3% NaOH concentration and 180° C operating temperature.
3.1.1. Effect of ME:DEA ratio to cocamide DEA conversion. Observation of the effect of methyl ester is reacted with DEA with a weight ratio reacting ME:DEA is shown in Figure 1. In the substrate weight ratio varied (1: 1, 1: 1.25, 1: 1.5, 1: 1.75, 1: 2) v/v) with NaOH 3% and 180° C it appears that the conversion of methyl esters to cocamide DEA tends to increase along with the increase in the substrate mole ratio to certain limits. The conversion in the mole ratio of methyl ester and dietanolamine 1: 1 is 78.64% then the conversion increases at a mole ratio of 1: 1.25 by 80.33%. For a mole ratio of 1: 1.5 the conversion is 81.01% whereas the mole ratio of 1: 1.75 the conversion is 82.37%. The best cocamide DEA conversion was obtained at 1:2 weight ratio reacting ME:DEA with NaOH 3% and 180° C of 82.37%. This is due to the mole ratio of the reagent will affect the shift of the reaction yield on balance. If the mole of one of the reactants is made excess, it reacts the balance will shift to the right so that dietanolamine is produced increase. The reaction mechanism of methyl ester and DEA with NaOH catalyst can be describe as follows:

\[
\text{RCOOCH}_3 + \text{NaOH} \rightarrow \text{RCOONa} + \text{CH}_3\text{OH} \quad \text{(1)}
\]

\[
\text{RCOONa} + \text{NH(C}_2\text{H}_4\text{OH)}_2 \rightarrow \text{RCON(C}_2\text{H}_4\text{OH)}_2 + \text{NaOH} \quad \text{(2)}
\]

\[
\text{RCOOCH}_3 + \text{NaOH} + \text{NH(C}_2\text{H}_4\text{OH)}_2 \rightarrow \text{RCON(C}_2\text{H}_4\text{OH)}_2 + \text{CH}_3\text{OH} + \text{NaOH}
\]

The second reaction is the reaction between RCOONa and di-ethanolamine (NH(C2H4OH)2) which forms di-ethanolamine. Ionized di-ethanolamine react with RCOONa. The reaction mechanism:

\[
\text{RCOONa} \rightarrow \text{RCO}^+ + \text{NaO}^-
\]

\[
\text{NH(C}_2\text{H}_4\text{OH)}_2 \rightarrow \text{N(C}_2\text{H}_4\text{OH)}_2^- + \text{H}^+
\]

\[
\text{RCO}^+ + \text{N(C}_2\text{H}_4\text{OH)}_2^- \rightarrow \text{RCON(C}_2\text{H}_4\text{OH)}_2
\]

\[
\text{NaO}^+ + \text{H}^+ \rightarrow \text{NaOH}
\]

\[
\text{RCOONa} + \text{NH(C}_2\text{H}_4\text{OH)}_2 \rightarrow \text{RCON(C}_2\text{H}_4\text{OH)}_2 + \text{NaOH}
\]

In the second reaction, excess DEA will be used di-ethanolamine. The reaction that plays a role in the formation of di-ethanolamine is

\[
\text{RCO}^+ + \text{N(C}_2\text{H}_4\text{OH)}_2^- \rightarrow \text{RCON(C}_2\text{H}_4\text{OH)}_2
\]

Ion \(\text{N(C}_2\text{H}_4\text{OH)}_2^-\) is the ionization of di-ethanolamine releasing \(\text{H}^+\). On in this reaction the presence of the \(\text{N(C}_2\text{H}_4\text{OH)}_2^-\) influential in formation di-ethanolamine.

**Figure 1.** The effect of ME:DEA ratio to cocamide DEA conversion at NaOH 3% and 180° C

3.1.2. Effect of NaOH Concentration on Transesterification-Amidation Conversion. In Figure 2. the greater the percent by weight of the catalyst, so the greater the conversion. The conversion reaches a maximum at 3% catalyst weight by conversion amounted to 82.37%. However, at 0.5% catalyst
weight the conversion decreased by about 1% due to the ability of the catalyst to break the bonds on
the forming methyl esters reduced diethanolamine. The function of the NaOH catalyst is to break the
bond on methyl ester in order to facilitate the reaction and the formation of more diethanolamide than
without a catalyst. *Mechanism of methyl ester amidase reaction with DEA and the help of NaOH
catalyst:*

\[
\text{RCOOCH}_3 + \text{NaOH} \rightarrow \text{RCOONa} + \text{CH}_3\text{OH} \quad \ldots \quad (3)
\]

\[
\text{RCOONa} + \text{NH(C}_2\text{H}_4\text{OH})_2 \rightarrow \text{RCON(C}_2\text{H}_4\text{OH})_2 + \text{NaOH} \quad \ldots \quad (4)
\]

\[
\text{RCOOCH}_3 + \text{NaOH} + \text{NH(C}_2\text{H}_4\text{OH})_2 \rightarrow \text{RCON(C}_2\text{H}_4\text{OH})_2 + \text{CH}_3\text{OH} + \text{NaOH}
\]

The NaOH catalyst breaks the methyl ester bonds in the first stage of the reaction, the catalyst Ionized
NaOH breaks methyl ester bonds. Ion Na\(^+\) binds to the ester group being the OH ion\(^-\) with a methyl
group to form methanol. First reaction mechanism:

\[
\text{RCOOCH}_3 \rightarrow \text{RCOO}^- + \text{CH}_3
\]

\[
\text{NaOH} \rightarrow \text{Na}^+ + \text{OH}^-
\]

\[
\text{RCOO}^- + \text{Na}^+ \rightarrow \text{RCOONa}
\]

\[
\text{CH}_3^+ + \text{OH}^- \rightarrow \text{CH}_3\text{OH}
\]

\[
\text{RCOOCH}_3 + \text{NaOH} \rightarrow \text{RCOONa} + \text{CH}_3\text{OH}
\]

NaOH catalyst is strong alkaline and easy to ionize, Na ion will bind ester ions to RCOONa which
reacts to form diethanolamine. The reaction to form diethanolamide occurs in the second reaction in
which the RCO ion reacts with N ions (C\(_2\)H\(_4\)OH\(^-\)) form diethanolamide. The greater it is the
concentration of the methyl ester catalyst bond is more easily broken so RCO the easier it is formed
and the greater the resulting diethanolamide. Ion OH\(^-\) forming methanol, while NaOH is formed again
at the end of the reaction.

**Figure 2.** Effect of NaOH Concentration on Transesterification-Amidation conversion
at 180° C and 1:2 ratio

3.1.3. *Effect of Temperature on the Transesterification-Amidation conversion.* In Figure 3. the
influence of temperature on the conversion of reactions, almost all the reaction becomes faster when
the temperature is raised, because of the heat that is given off increase the kinetic energy of the
reacting particles. Consequently, amount and energy the impact got bigger.
3.2. Identification of Cocamide DEA

In Cocamide DEA the main absorbance peak seen in the FTIR results Figure 4. in the range 1400-1800 cm\(^{-1}\) where the peaks show bonding C-H which forms the CH\(_3\) (methyl) group. This methyl group will increase during the transesterification process takes place. Meanwhile, the C = O bond is in the 1600-1800 range cm\(^{-1}\) there was a change in absorbance before and after the reaction, which was during the transesterification process takes place a change in the functional group.

In the FTIR spectrum results in the range 1000-1190 cm\(^{-1}\) show bond O-CH\(_3\) on the diethanolamide ion. Meanwhile, the peak of 2800-3000 cm\(^{-1}\) has occurred the change in the decrease in absorbance in the C = C bond, indicated by the formation of a fairly high C = C group. Can be seen in the image below.

According to Silverstein et al., (2005) stated that at the peak absorption in the asymmetric and symmetrical wave area of 2925 cm\(^{-1}\) and 2855 cm\(^{-1}\) indicates the presence of a methylene compound group [15]. From the FTIR spectrum test results sample in Figure 4., this shows the peak of absorption in the area of 2922.60 cm\(^{-1}\) and 2851.15 cm\(^{-1}\) indicates the presence of a methylene group. Vibration C = O for unsaturated esters at wave number 1800-1700cm\(^{-1}\), vibration -CH\(_3\) on wave number 1446 cm\(^{-1}\) and O-CH\(_3\) vibrations which denotes a cluster biodiesel in the wave figure 1196 cm\(^{-1}\). The C-O vibration for the saturated ester is on wave number 1030.98 cm\(^{-1}\) - 1240.08 cm\(^{-1}\). From the results of the FTIR sample spectrum test, showing the absorption peak in the 1740.97cm wave area indicates the presence of groups C = O and 1113.49 cm\(^{-1}\), 1167.76 cm\(^{-1}\), 1196.23 cm\(^{-1}\) indicates the presence of the CO group in this wave number region which indicates the sample contains both saturated and unsaturated ester groups, absorption peak 1436 cm\(^{-1}\) for the -CH\(_3\) group, and 1196.23 cm\(^{-1}\) for Groups O-CH\(_3\). Next, the ester group will be converted to the inner amide. More research on the manufacture of cocamide diethanolamine.

![Figure 4. FTIR spectrum for cocamide DEA](image-url)
4. Conclusions

Based optimization of amidification of ME from virgin coconut oil with DEA using NaOH catalyst were successfully performed. The result show that the transesterification process-amidase cocamide DEA obtained optimum conditions at the ratio Methyl Ester:Diethanolamine = 1:2 w/w, 3% NaOH catalyst concentration and 180°C.

In Cocamide DEA the main absorbance peak seen in the FTIR results in the range 1400-1800 cm⁻¹ where the peaks show bonding C-H which forms the CH₃ (methyl) group. This methyl group will increase during the transesterification process takes place. Meanwhile, the C = O bond is in the 1600-1800 range cm⁻¹ there was a change in absorbance before and after the reaction, which was during the transesterification process takes place a change in the functional group.

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