Synthesis of Cocoamide Dea Surfactant from Virgin Coconut Oil (VCO) Through Ester Aminolysis Using Microwave

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***Abstract*—** this research aims to find the optimum operating conditions in the aminolysis process of methyl ester into surfactant with variable of microwave power, heating time, and reactant weight ratio. Transesterification is a reaction that removes alcohol and forms esters and other forms of alcohol. In the transesterification, VCO was mixed with methanol mol ratio of 1:6 and NaOH catalyst as much as 0.6% by weight of oil was added. The reaction was carried out for 3 minutes and the microwave power was 450 W while stirring with a magnetic stirrer. After that, the ester aminolysis step was carried out by mixing the methyl ester from the transesterification step with diethanolamine in the microwave power range of 150-750 W, reaction time range of 0-30 minutes, and reactant weights ratio range of 1-2. Cocoamide DEA will be analyzed using FT-IR spectrophotometry, acid number, saponification number, ester number, and also HLB. The highest yield of Cocoamide DEA and surfactant conversion were 87.47% and 0.83 at reaction time of 20 minutes, microwave power of 600 W, and ratio of weight of methyl reactant 1:2. Cocoamide DEA compounds have been formed with the emergence of amide groups, namely C=O with a wavenumber of 1619.75 cm-1. The surfactant value of HLB is 6-8 which corresponds to its function as a water in oil emulsifier. These findings demonstrate that microwave-assisted synthesis of DEA surfactant from VCO not only improves reaction efficiency but also yields a product suitable for potential applications in detergent and cosmetic formulations.

***Keywords*—** Cocoamide DEA, Detergent, Microwave, Surfactant, VCO

INTRODUCTION

Detergent is a cleaning agent that is commonly used by the wider public, both by households, industry, hotels, restaurants, and also hospitals. The continuous use of detergents every day causes the amount of detergent that enters the waters to increase, so that it can be found in river water, sediment, soil, and even drinking water [1]. High levels of detergent in waters can be toxic to aquatic organisms so that they can cause disturbances to aquatic ecosystems and will indirectly have an impact on human life [1].

Surfactant is an abbreviation of Surface-Active Agent which usually refers to amphiphilic organic compounds. That means the surfactant has a hydrophobic group and a hydrophilic group in its chemical structure so that the depiction of the surfactant structure is modeled on the head (hydrophilic) and tail (hydrophobic). Such a surfactant structure causes the surfactant to be able to increase the solubility of the solution and reduce the surface tension in the solution. [2]

Detergents circulating in the market are generally detergents with the active ingredient of LAS (Linear Alkylbenzene Sulfonate III) surfactant derived from petroleum (petroleum). In a large number of tests carried out on the level of toxicity, it was found that LAS can cause acute and chronic toxicity in aquatic organisms. LAS with a concentration of 20-30% solution can cause tissue damage in mice after skin contact for more than 15 days. At a concentration of 25 mg/L of LAS, fish reacted with a pattern of increased activity, inactivation and immobilization, and if not removed from the system it would cause death. Minimal effects associated with biochemical and histopathological changes in the liver have been reported in sub chronic toxicity tests on rats treated with LAS concentrations of 120 mg/kg body weight per day in food or drinking water [3].

Indonesia as a producer of surfactants which are synthesized by coconut oil fatty acids is very large, considering that Indonesia's coconut oil production has increased from year to year. Indonesia is the largest coconut producing country in the world, worth around 18.3 million tons per year. The main competitor producing countries are the Philippines and India. Other countries are only able to produce coconuts under 3 million tons per year. Indonesia has a large export power in terms of production volume so that it is also able to offer more competitive prices. Therefore, research is needed regarding the utilization of VCO into surfactant products.

One type of surfactant that is widely used in industry is Cocoamide DEA. Cocoamide DEA or commonly called Cocoamide Diethanolamine is a non-ionic surfactant belonging to the alkanolamide group. Alkanolamides are commonly used to enhance the properties of other surfactants in cleaning and cosmetic products.

Although several studies have reported the synthesis of cocoamide DEA surfactants from coconut oil using conventional heating methods [3], there is still a lack of research addressing the use of microwave-assisted ester aminolysis of VCO as a more sustainable and energy-efficient route. This gap is particularly relevant given the increasing global demand for green surfactants derived from renewable natural resources such as coconut oil, which is abundant in Indonesia [4]. Therefore, this study aims to determine the optimum operating conditions for the microwave-assisted synthesis of cocoamide DEA surfactant from VCO, with emphasis on the effects of microwave power, reaction time, and reactant ratio, in order to improve process efficiency and support the development of sustainable surfactant alternatives.

Several previous studies have been conducted for the manufacture of Cocoamide DEA including the manufacture of surfactants from Pure Coconut Oil (VCO) through the amidation process with a NaOH catalyst with a conversion result of 70.9% used the number of catalysts 1% wt, reaction time of 3 hours, the ratio of moles of DEA to Methyl Ester is 1.25:1. [4] Research on the synthesis of DEA cocoamide as a green surfactant from (VCO) with a NaOH catalyst. With optimal operating parameters at 180oC, catalyst volume 3% wt, DEA Ratio: Methyl Ester 2:1; Duration 3 hours; Checking the results with FT-IR analysis, it was found that Cocamide DEA was successfully formed[5]. Research on the Making of Cocamide Diethanolamine from coconut oil with CaO catalysts. In the study, a 97% conversion at a temperature of 70^{o}C and a catalyst of 1% wt.

In this study, the experimental procedure was carried out in two main steps. First, virgin coconut oil (VCO) was transesterified with methanol in the presence of a NaOH catalyst under microwave irradiation to obtain methyl esters. Second, the resulting methyl esters underwent ester aminolysis with diethanolamine (DEA) under microwave heating at various power levels, reaction times, and reactant ratios to synthesize Cocoamide DEA. The surfactant products were then characterized using GC-MS, FT-IR, acid value, saponification value, and HLB number to evaluate their structural and functional properties. [6,7]

Compared to conventional heating, microwave-assisted synthesis offers rapid and uniform heating, reduced reaction times, and improved product selectivity, making it a promising green technology for surfactant production.[6]

The second stage is the methyl ester aminolysis stage, Mix methyl ester and DEA with a mole ratio of 1:1 on the neck pumpkin 3 and then add a 1% wt NaOH catalyst. The mixture is placed in the microwave and the reaction is carried out at 600 W microwave power and a time of 20 minutes.

METHOD

Materials

The research materials used are Virgin Coconut Oil/VCO by CV. Botanica Asri, NaOH, 99% Diethanolamine/DEA by CV. Chemicalindo, 0.5 N ethanolic Potassium Hydroxide, 99% Methanol, and 1 N Hydrochloric Acid/HCl by CV. Chemical Indonesia Multi Sentosa.

Equipment

The tools used include the microwave used is a microwave oven (SHARP 23 L R-21 DO(S)). The microwave is equipped with a Pyrex branded 3-neck flask which functions as a reactor. The reactor is equipped with a magnetic stirrer. The microwave provides variable power from 150 W, 300 W, 450 W, up to 750 W.

Transesterification Step

This research begins with mixing the reactants, namely 400 grams of VCO and 80 grams of methanol in a neck flask 3. The mole ratio between the selected VCO and methanol is 1:6. Furthermore, NaOH catalyst as much as 0.6% by weight of oil i.e., 2.4 grams was put into a three-neck flask. After all the reactants and catalysts had been added, the three-neck flask would be assembled in the microwave. After that, the microwave is run on variable power from 150 W, 300 W, 450 W to 750 W and reaction time of 0 - 30 minutes. After the reaction is complete, the methyl ester and glycerol will be separated by a separatory funnel where the mixture will be allowed to stand for 12 - 24 hours to form 2 layers. The length of time for separation depends on the condition of the product. Methyl ester products will be at the top. Therefore, in the separation process, the top layer will be taken. The methyl ester obtained will be washed using hot water to dissolve the NaOH catalyst. Furthermore, the methanol and water in the biodiesel will be removed by evaporation at a temperature of ±100°C. The methyl ester obtained will be tested with GC-MS to determine the purity of the methyl ester produced and then also tested for the acid number and saponification as a parameter for checking the reaction conversion and ester number.

Ester Aminolysis Step

The methyl ester from the transesterification step that has been analyzed will be converted to Cocoamide DEA through an aminolysis reaction. 10 grams of methyl ester will be mixed with 10 grams of DEA as well. This is in accordance with the use of a 1:1 reactant weight ratio variable. Furthermore, NaOH catalyst as much as 1% by weight of the solution i.e., 0.2 grams was added to the mixture. Then the microwave is turned on with a variable power of 600 W with a variable time of 20 minutes. After the reaction is complete, the methanol which is a by-product of the reaction will be separated by evaporation at a temperature of 90°C. After that, Cocoamide DEA will be analyzed for its acid number, saponification number, HLB number, and FT-IR spectrum.

GC-MS is an instrument capable of analyzing compounds based on a method that separates volatile substances, allowing for the identification and quantification of each individual compound. This test aims to determine the purity level of the methyl ester content formed in the transesterification reaction.

Acid value analysis is used to decide the level of oil or fat degradation. Oils and fats can undergo hydrolysis or oxidation to form free fatty acids. The higher the acid value, the greater the free fatty acid content, which shows a decline in quality.

Analysis the saponification value indicates the amount of alkali required to saponify a certain amount of fat or oil, providing insight into the composition and quality of the sample. The saponification value analysis aims to determine the fatty acid chain length in a fat or oil. Fats containing short-chain fatty acids will have a higher saponification value, as more molecules can be saponified per gram. Conversely, fats with long-chain fatty acids have a lower saponification value. In addition, the saponification value analysis is used to assess the purity and type of oil or fat, as well as to identify any contamination or adulteration."

FTIR spectroscopy is an excellent analytical technique for identifying the molecular structure of a compound. Through this analysis, the identification of the Cocamide DEA compound can be clearly observed

Hydrophilic-Lipophilic Balance (HLB) is a measure of the balance between the hydrophilic (water-loving) and lipophilic (oil-loving) parts of a surfactant molecule. The HLB value helps determine:

The type of surfactant (whether it is more soluble in water or oil), O/W (Oil in Water) emulsifier: High HLB (typically 8–18), or W/O (Water in Oil) emulsifier: Low HLB (typically 3–6)

An experimental method to determine the HLB value is the water-solubility method (ICI Americas, Inc., 1984). This method is carried out by mixing a certain amount of surfactant into distilled water (aquadest). The mixture is then stirred and observed for its behavior.[13]

In addition to the above analysis, tests were also conducted to decide physical properties such as boiling point, melting point, density, solubility in water, shape, and color, in order to compare them with standard conditions. The physical properties of the synthesized DEA surfactant, including density, melting point, boiling point, solubility, color, and odor, were also determined. Density was measured at 25 °C using a pycnometer, while melting and boiling points were measured with a melting point apparatus (Electrothermal, UK) and a digital thermometer, respectively. Solubility was tested by dissolving 1 g of sample in 100 mL of distilled water at room temperature. Color and odor were recorded by visual and sensory observation. All measurements were performed in triplicate, and the average values were reported. [7]

RESULTS AND DISCUSSION

GC-MS Analysis in Transesterification Steps

The experiment was divided into several stages, including the manufacture of methyl esters from Virgin Coconut Oil and the manufacture of the surfactant Cocoamide DEA.

In the manufacture of methyl esters and surfactants using a microwave with NaOH base catalyst. The analysis was carried out at both stages where at the stage of making the methyl ester, the composition of the compound was analyzed using the GC-MS method.

In the second stage, namely the manufacture of the surfactant Cocoamide DEA, several analyzes were carried out, namely the analysis of the effect of heating time on the conversion of methyl esters before and after the reaction, analysis of the use of microwave power on the conversion of methyl esters before and after the reaction, analysis of the amount of reactant Diethanolmina on the conversion of methyl esters before and after reaction, as well as FT-IR Analysis

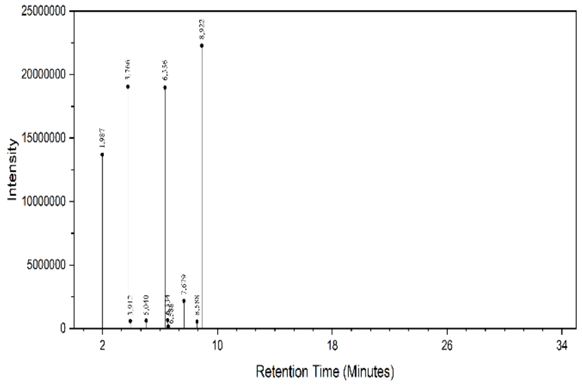

Fig 1. Chromatogram of GC-MS

Analysis of fatty acid composition in biodiesel samples was carried out using the GC-MS method. **Figure 1** shows the 10 peaks detected. However, among the 10 peaks, it is divided into 2 types of peaks, namely 4 fairly high peaks and 2 moderate peaks. The 4 peaks detected were quite high, namely at peak 1,2,5 and peak 10, the abundance of which was quite high as seen from the peak with a retention time of 1.987; 3.766; 6.356; and 8.922 minutes. From Fig. 1, it can be determined what compounds are contained in the transesterification reaction of virgin coconut oil with methanol.

Table 1. Compound Composition of Methyl Ester Solution

No	Compound	Peak	Retention Time (Minutes)	Area (%)
1	Methyl Hexanoate	1	1.987	25.61
2	Methyl dodecanoate (Laurate)	10	8.922	24.72
3	Methyl decanoate	5	6.356	19.17
4	Methyl Octanoate	2	3.766	17.58
5	Methyl Undecanoate	8	7.679	5.61
6	2-EthylHexyl Octanoate	9	8.588	4.75
7	Methyl Nonanoate	4	6.588	1.2

Based on **Table 1**, the composition of the compound in the methyl ester consists of various chains and is dominated by methyl hexanoate and methyl laurate. This is in accordance with the VCO content which consists of a fairly high content of lauric acid. In the content of each methyl ester, it will be followed by an aminolysis reaction to form a surfactant.

Functional Group Analysis on Cocoamide DEA

Identification of surfactant synthesis by FTIR was used to determine the groups contained from the synthesis of alkanolamide which can be seen in **Fig 2**.

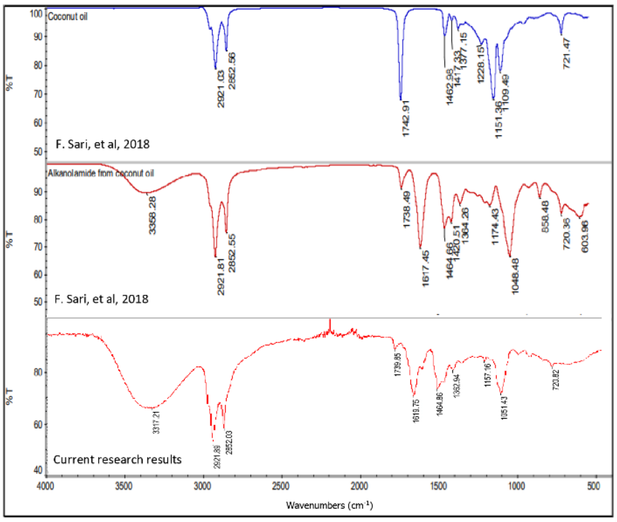

Fig 2. Comparation of Surfactant FT-IR Graph with Other Research

The FTIR spectrum of the product showed a strong absorption band at 1619.75 cm^{-1}, corresponding to the vibration of the amide group, which confirms the formation of Cocoamide DEA. Similar absorption bands were also reported by Ginting et al. for coconut oil-based surfactants, indicating consistent structural characteristics across different synthesis methods.[7] Compared with the findings of Aryanti et al., who reported Cocamide DEA formation through conventional amidation of VCO at 180

°C for 3 hour [5], the present microwave-assisted method achieved comparable spectral features within only 20 minutes, highlighting the advantage of microwave heating as a green and energy-efficient technology [6].

Effect of Heating Time on Conversion of Methyl

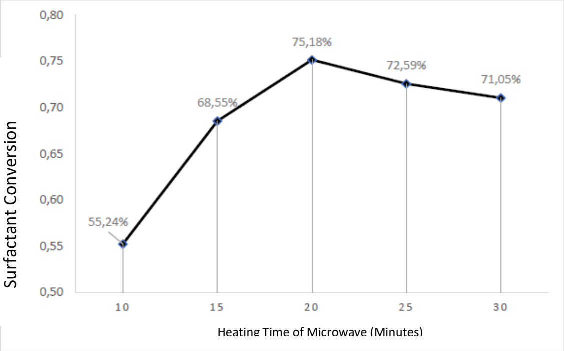

Fig 3. The Effect of Microwave Heating Time with Surfactant Conversion

To determine the effect of heating time on the conversion of methyl esters in surfactants, the same power was used, namely 600 W and the ratio of reactant weight to methyl ester 1:1 as a control variable to see the effect of heating time on the solution. The power of 600 W is used so that the reaction runs faster compared to lower power. Higher power provides higher heat. For most chemical reactions, the reaction rate increases at higher temperatures.[9]

There is an increase in the conversion of methyl ester into surfactant along with the increase in heating time used. This can be seen in **Fig.3**. At the heating time of 10 minutes, the conversion result was 55.24%, at the heating time of 15 minutes the conversion yield increased by 68.55%, at the heating time of 20 minutes the results were quite optimal, which was 75.18%. The longer heating time of 25 and 30 minutes showed results that were not too different from the 20 minutes variable. This indicates that the reaction has reached equilibrium. The longer the reaction time is given, the more the conversion results will increase[10]

The Effect of Microwave Power on the Conversion of Methyl Esters to Surfactants

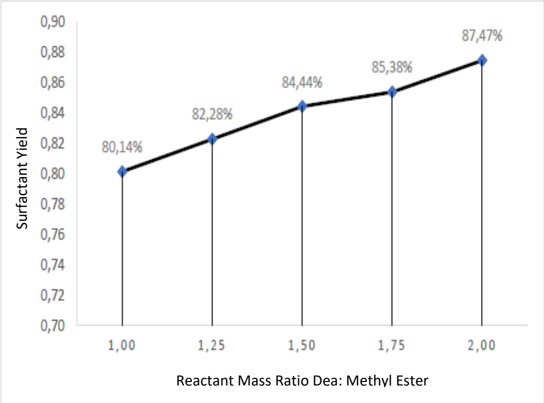

Fig 4. Effect of Microwave Power on Surfactant Conversion

Fig 4 shows that there is an increase in the conversion of methyl esters into surfactants along with the increase in the amount of power used. At 300 W the conversion result is 63.65%, at 450 W the conversion result is increased by 70.34%, at 600 W the result is quite optimal, which is 75.18%. At a large power of 750 W, the conversion results fell to 68.09%. This decrease in yield indicates an anomaly in conversion results. Chemical reactions have faster reaction rates at higher temperatures, but some literature mentions "limits" regarding the temperature that must be reached in a reaction.[11]

The observed absorption bands are consistent with previous studies on VCO-based surfactants [8], confirming the formation of DEA surfactant.

In general, the reaction rate refers to Le Chatelier's law where the higher the reaction temperature, the equilibrium shifts in the endothermic direction. Aminolysis reaction is a nucleophilic addition-elimination reaction which requires heat energy so that it is classified as an endothermic reaction. This equilibrium shifts towards the product due to an increase in temperature will cause a decrease in the required activation energy, but in this research, it is stated that there is a possibility of a minus activation energy due to the reaction has crossed the limit in general.[11]

Effect of Reactant Weight Ratio on Conversion of Methyl Esters

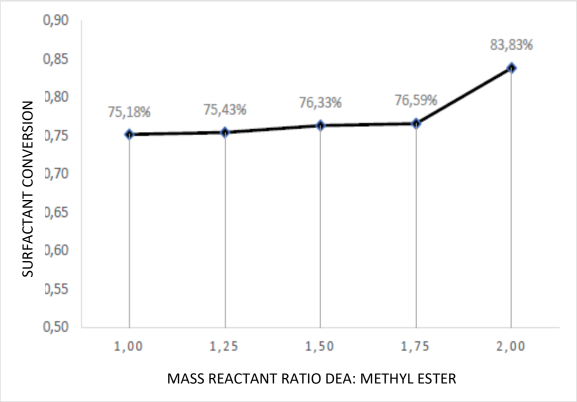

Fig 5. Effect of Reactant Weight Ratio of DEA: Methyl Ester on Reaction Conversion

Based on **Fig 5**, it can be seen that the higher the mole ratio of the reactants, the higher the conversion. Conversion at a weight ratio of 1:1 methyl ester and diethanolamine was 75.18% then the conversion increased at a weight ratio of 1:1.25 by 75.43%. For a weight ratio of 1:1.5 the conversion is 76.33%, while the mole ratio of methyl ester: diethanolamine is 1:1.75 the conversion is 76.59%. The maximum conversion of 87.47% was achieved at a DEA: methyl ester ratio of 2:1 under 600 W microwave power and 20 minutes of reaction time. This yield is higher than that reported by Probowati et al. who obtained 70.9% conversion under conventional heating with NaOH catalyst.[4] These results reinforce previous claims that microwave irradiation can shorten reaction times while maintaining or even improving product yield.[6] This is because the mole ratio of the reactants will affect the shift in the reaction products when viewed from a balance point of view. The use of excess moles of one reactant will cause the reaction to shift to the right so that the diethanolamide produced also increases.[12]

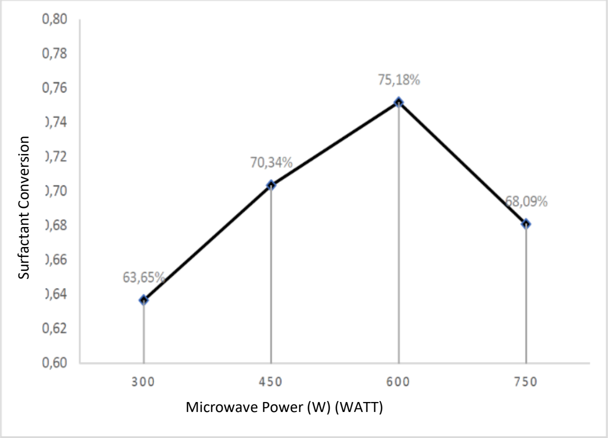

Figure 6. The Effect of The Weight Ratio of DEA: Methyl Eester on The Yield of Surfactants

Furthermore, in addition to analysing the effect of the weight ratio of the reactants on the conversion, the yield of each product is also calculated. This is because the results of the conversion of the mass ratio of the reactants show significant results. Yield is calculated by weighing the mass before the reaction and the mass after the reaction. The result of the effect of the reactant weight ratio on the surfactant yield is shown in **Fig 6**.

Cocamide Diethanolamine Surfactant HLB Number Analysis

This method is done by mixing a number of surfactants into aquades. Then the mixture will be stirred, and the condition will be seen. The conditions that occur show the HLB value of the surfactant as shown in **Fig. 7**

One way to decide the HLB value qualitatively is by experimental means by measuring water solubility. The method is to mix a number of surfactants into distilled water. Then the resulting mixture will be stirred and seen its condition. The condition that occurs shows the HLB number of the surfactant as shown in **Fig 7**. Where the solution shows a cloudy color when given strong stirring.

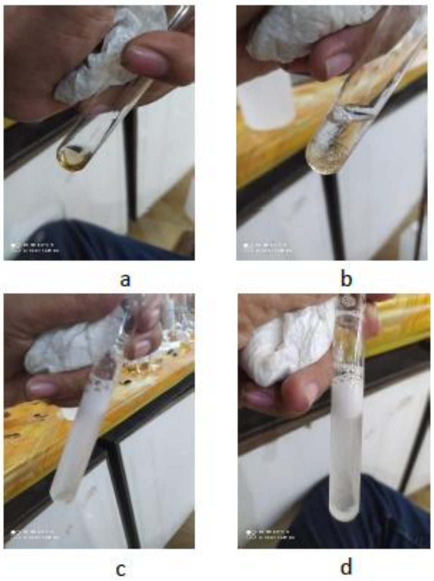

Fig 7. Results of HLB Analysis (a) Surfactant Sample (b) Surfactant Sample + Water (c) Surfactant Sample + water after shaking (d) Surfactant Sample + water after being allowed to stand for a while

The HLB of the surfactant product formed corresponds to the characteristics of the emulsifier with an HLB value of 6 - 8. The obtained HLB value of 6–8 indicates that the synthesized surfactant functions as a W/O emulsifier. This is consistent with the report of Ginting et al. (2020), who noted that coconut oil-based surfactants exhibit similar HLB values suitable for cosmetic formulations [7]. Hence, the product synthesized in this study has comparable application potential to established VCO-derived surfactants in commercial formulations. This emulsifier serves to disperse water into oil in a system commonly used in the cosmetic industry.

Physical Properties of Cocoamide Diethanolamine Surfactant Products

The physical properties of the product are measured to determine the surfactant quality standard. The things that are measured are boiling point, melting point, density, solubility in water, shape and color. In the measurement and observation of surfactants, data was obtained in the form of a clear yellow liquid, with a characteristic coconut smell with a melting point of about 20 - 25°C, boiling point of 170°C, soluble in water and having a density of 1.02 g/cm^3. Based on IARC standards, the products produced are in accordance with quality standards.

CONCLUSION

The highest of yield and surfactant conversion were 87.47% and 0.83 at heating time of 20 minutes, microwave power of 600 W, and ratio of weight of methyl reactant 1:2. Cocoamide DEA compounds have been formed with the emergence of amide groups, namely C=O with a wavenumber of 1619.75 cm-1. The surfactant value of HLB is 6-8 which corresponds to its function as a water in oil emulsifier. Physical properties of the surfactant Cocoamide DEA produced has the appearance of a clear yellow liquid with a characteristic coconut odor, a melting point of 20 - 25°C, a boiling point of 170°C, and a density of 1.02 g/cm^3. The physical properties of the surfactants obtained are similar to the physical properties of surfactants based on the IARC standards.

ACKNOLEDGEMENTS

Thank you to the chemical engineering department for providing financial support and facilities.

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