The Production of Surfactant Anionic Methyl Ester Sulfonate (MES) from Virgin Coconut Oil (VCO) with Ultrasound-Assisted

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Abstract. Virgin coconut oil (VCO) is a vegetable oil that has many ingredients that can be used, one of the highest ingredients is lauric acid about 41-51%. It can be used to synthesis of surfactants, which is the surfactant anionic methyl ester sulfonate (MES). However, time of transesterification and sulfonation needed is very long in the conventional process. Because of that, some researchers have proved that ultrasound-assisted can accelerate and increase the yield because ultrasound can directly cavitation that help the rupture mechanism of matrix cells. In the sulfonation process, methyl ester is reacted with sodium bisulfite (NaHSO₃) with several predetermined variables. After being reacted, the mixture of methyl ester and NaHSO₃ used a separating funnel and then purified using 50% of methanol, then evaporated and neutralized using 20% of NaOH. The measured quantities include yield, density, viscosity, surface tension, FT-IR analysis and Gas Chromatography-Mass Spectrometry (GC-MS) analysis. In transesterification, the optimum conditions were obtained in 1:6 of mole ratio in 3 minutes, the yield of 90%. In sulfonation, the optimum conditions were obtained in temperature at 65°C in 30 minutes. With the resulting viscosity of 4.04 cSt, the yield is 98%, and the surface tension is 32,028 dyne/cm.

Keywords: Virgin coconut oil, ultrasound-assisted, transesterification, sulfonation, methyl ester sulfonate (MES)

1. Introduction

Surfactants are surface active agents that are widely applied in the chemical industry because it can increase the stability of the emulsion between the oil phase and the water phase. The population growth resulted in an increase the requirement for chemical industry products such as detergents, pharmaceuticals, textiles, cosmetics, food and so on. The domestic surfactant production capacity is no longer able to meet the surfactant demand for industrial activities in Indonesia, so a large amount of surfactant imports must be carried out. Most of the surfactants produced from petroleum, that availability is decreasing because it cannot be renewed [1].

Therefore, the raw materials that can be renewed are needed, which is virgin coconut oil. Virgin coconut oil (VCO) is a vegetable oil that has many ingredients that can be used, most of which consists of saturated fatty acids, which is about 90% of the total composition. One of the ingredients is lauric acid at 41-51%. Where the content is considered as a surfactant [2]. The surfactants that are most widely used are surfactants anionic (~ 66%). Anionic surfactants have hydrophilic characteristics
due to the presence of sulfate or sulfonate ion groups. Methyl ester sulfonate (MES) surfactant is an anionic surfactant currently being developed. It can be produced using methyl ester as raw material from coconut oil. Surfactants of MES have the advantage of being environmentally friendly (biodegradable) and have good detergency properties [3].

The transesterification and sulfonation processes in this study used the batch method, because the batch method is easier to control the reaction and not require equipment when compared to the continuous method. Heating by ultrasound-assisted which have different characteristics from conventional heating. [4,5].

Using ultrasound-assisted, water can be converted into a medium as well as a very extreme reagent because of the very large local energy. At first the waves propagate through the water medium and cause nucleation (bubble growth) as well as gaps filled with gases trapped in a particulate. These small cavities experience growth from time to time, so there is a change in the size of the cavity which is getting bigger until an explosion occurs which is termed a collapsing bubble. This process is known as cavitation. During the cavitation process, a large amount of energy is generated. Thus, using ultrasound-assisted is better than the use of stirring because of the cavitation effect [6,7,8].

Surfactant synthesis from palm oil using a sulfonating agent alpha-sodium ethyl ester (α-SEE) for 30 minutes at 60 °C obtained a surface tension of $1.17 \times 10^{-2}$ mN /m [9]. The utilization of sodium metabisulfite as a sulfonate agent has been carried out by using palm oil methyl ester (POME) as raw material with CaO catalyst with a decrease in surface tension of 31.8-33 dyne/cm [10]. The manufacture of surfactants using palm oil and sodium bisulfite as a sulfonate agent with H$_2$SO$_4$ catalyst obtained a decrease in surface tension of 35.7-38.97 dyne/cm [11]. From some of the studies above, there are weaknesses such as it takes a long time to carry out the sulfonation process, so on this research, i tried to use ultrasound-assisted to synthesis surfactants, because it can shorten the transesterification and sulfonation processes.

2. Material And Methods

2.1. Material

The raw materials used in this study are Virgin coconut oil (VCO), methanol (CH$_3$OH), potassium hydroxide (KOH) catalyst, sodium bisulfite (NaHSO$_3$), potassium oxide (CaO) catalyst, and distilled water (H$_2$O) and sodium hydroxide (NaOH).

2.2. Equipments

The equipment used in this study included laboratory equipment consisting of a ultrasound, condenser, 2-neck flask and thermocouple.

2.3. Transesterification

The study was taken in the Technology Process laboratory of Chemical Engineering Department ITS. Transesterification and sulfonation process was done using ultrasonic cleaning bath used for this research is the KRISBOW model KW1801033, with voltage 240 V/50 Hz, Power 100 W, frequency 40 kHz, tank capacity 2.8 L. Transesterification is carried out with several variables, including: variable mole ratio 1: 6; 1: 9 and 1:12 and times variable 1; 2; 3; 4 and 5 minutes by mixing coconut oil and methanol with the ratio of each mole into a two-neck flask and 1% KOH catalyst. Next, adjust the predetermined time, temperature of 60 °C and frequency of the ultrasonic instrument is 40 kHz. Then the product obtained is separated in a separating funnel using warm aquaest with a controlled temperature of 40 °C. Furthermore, the density, yield and viscosity were tested and obtained the methyl ester which was included in the SNI range which would be analyzed by GC-MS and FT-IR to ensure that the methyl ester was formed.

2.4. Sulfonation

Methyl ester which is formed from transesterification, then sulfonated with sodium bisulfite (NaHSO$_3$) with a ratio of methyl ester and sodium bisulfite 1: 1% v / v with a temperature of 45 °C for 10 minutes with a frequency of 40 kHz. The catalyst used is CaO with a concentration of 1%. Then the result is purified with methanol 50% at 60 °C for 10 minutes. Then neutralized until it reaches a
neutral pH with 20% of NaOH. Repeat the same process for temperatures 55 °C and 65 °C. The time variables used were 10, 20, 30, 40, 50 and 60 minutes and the frequency used was 40 kHz. The product was analyzed by calculation of yield, viscosity, surface tension and FT-IR.

3. Results And Discussion

3.1. Transesterification Process by Ultrasound-Assisted

The transesterification process is the first step for making methyl esters, because it aims to convert triglycerides into methyl esters. In this study, there are two variables, which is the mole of ratio between virgin coconut oil and methanol and then the variables of time.

a) Effect of Time on Various Mole Ratios on Viscosity of Methyl Ester

Based on SNI 7182: 2015, the standard of viscosity of methyl ester is 2.3 to 6 cSt and the density of methyl ester is 0.85-0.89 gr/mL.

![Viscosity of Methyl Ester obtained vs. time of Transesterification at various Mole Ratios.](image)

From Figure 1, it can be concluded that the optimal ratio to obtain a viscosity in accordance with SNI of methyl ester is 1: 6 ratio, which is, all the result of viscosities based on SNI range of methyl ester. The optimum molar ratio between methanol and VCO is 6: 1 [12]. While the optimal time is found in the 3rd minute. The decrease of viscosity indicates that the component of coconut oil has been converted into methyl ester and is influenced by the application of ultrasonic wave frequency, because the greater of frequency will have a large thermal effect, marked by an increase in temperature very fast.

b) Effect of Time on Various Mole Ratios on Yield of Methyl Ester

The time is one of the factors that affects the transesterification reaction, the longer the reaction time, the greater the result. The yield obtained is based on the mole ratio and time variables.
Figure 2 showed that at 1: 6 and 1: 9 of ratio there is an increase of yield until the 3rd minute by 90%. However, at the 4th minute the ratio decreased and was constant until the 5th minute. It’s because there is an increase of % yield along with the time of reaction was getting longer due to the temperature generated by ultrasonic waves tends to be constant at 4th to 5th minutes. The increase of time in reaction causes an increase in temperature in the ultrasonic cleaning bath so that affects the yield produced in the transesterification process. The ultrasonic cleaning bath provides a large thermal effect, marked by an increase of temperature and an increase in the yield of the resulting methyl ester products. The results of this study are supported by previous research which states that the time variable affects the yield produced [5,6]. So, from Figure 2 it can be seen that the optimal time & mole ratio in producing high yields at the 3rd minute of 90%.

**Table 1. Characteristics of Virgin Coconut Oil Methyl Ester**

| Parameter                              | VCO  | Methyl Ester | SNI       |
|----------------------------------------|------|--------------|-----------|
| Density at temperature of 40°C (gr/ml) | 0.909| 0.864        | 0.850 – 0.890 |
| Kinematic viscosity at temperature of 40°C (cSt) | 28,825 | 3,718       | 2.3 – 6   |

The transesterification process produces a yield of 90% of methyl ester. The resulting methyl ester has a density value of 0.864 gr/ml and kinematic viscosity of 3,718 cSt. The value obtained is in accordance with the SNI standard density and viscosity values, with density of 0.850 - 0.890 gr/ml and kinematic viscosity of 2.3 - 6 cSt.

c) **Analysis component of Methyl Ester**

In this study, analysis of Gas Chromatography-Mass Spectrometry (GC-MS) and Fourier Transform Infra Red (FT-IR) was carried out on the resulting methyl ester to determine the methyl ester components present in the product and the functional groups in the product.
Fig. 3. Results of GC-MS Methyl Ester Analysis.

Based on the results of GC-MS analysis, it’s known that the methyl ester composition of virgin coconut oil is dominated by methyl lauric and methyl myristate, respectively 34.57% and 21.24%. The identification of the methyl ester by infrared spectrophotometer gave the spectrum as shown in Figure 4. The absorption bands at wave numbers, $\nu = 2922.12$ and 2852.80 cm$^{-1}$ originate from the C-H stretching vibration. The C-H bending vibration indicating the presence of an olefin / alkene group is shown on the absorption band, $\nu = 1459.18$ cm$^{-1}$. The typical absorption bands of an olefin / alkene are shown at $\nu = 879.04$ and 721.90 cm$^{-1}$. The sharp absorption band at, $\nu = 1740.83$ cm$^{-1}$ indicates a stretching vibration of C = O of an ester. The sharp absorption band at, $\nu = 1194.86$ cm$^{-1}$ shows the C-O stretching vibration, which is a typical absorption band from an ester. It can be concluded that the methyl ester has been formed at 3 minutes with 1: 6 of ratio.

Fig. 4. Methyl Ester Spectrum.

3.2. Sulfonation Process by Ultrasound-Assisted

The preparation of MES methyl ester sulfonate was carried out at variations of time 10; 20; 30; 40; 50 and 60 minutes of time. The ratio used 1: 1 with 1% of CaO catalyst with 45 °C, 55 °C and 65 °C of temperature variation. The reaction product for synthesis of MES was tested of viscosity, yield, surface tension and FTIR analysis.

a) Effect of Sulfonation Time at Various Temperatures on Viscosity of Surfactant

In this study, the aim of this research is to find the optimal conditions of the reaction, so the effect of the right time on the resulting methyl ester sulfonate is very important to know, because it’s also related to the economic value of a process.
Fig. 5. Viscosity of Surfactant vs. time of Sulfonation at various Temperatures.

Based on Figure 5, the highest viscosity at 65 °C in 40 minutes at 4.3058 cSt, while the lowest viscosity at 45 °C in 40 minutes at 3.8487 cSt. The increasing time in the process, it make increased the viscosity of surfactant. The viscosity of surfactant methyl ester sulfonate will increase with reaction time. This can be due to the relatively low temperature used during sulfonation, so that the reaction does not run optimally which causes the methyl ester not to be completely converted into methyl ester sulfonate [10]

b) Effect of Sulfonation Time at Various Temperatures on % Yield of Surfactant

In Figure 6 the effect of time and temperature on % yield of surfactants, it can be seen that the lowest % yield is each temperature in 40 to 60 minutes at 92%, while for the highest % yield is at 65 °C in 30 minutes at 98 %. It’s because the increasing temperature and time can be increase the % yield of the product, but there is a decrease after 30 minutes and the resulting of % yield tends to be constant. The increase in reaction time causes an increase in the temperature of the ultrasonic, so this affects of yield produced in the sulfonation process. So it can be concluded from Figure 6 that the optimal time and temperature to produce a high % yield are 30 minutes at 65 °C, respectively.

Fig. 6. Yield of Methyl Ester vs. time of Sulfonation at various Temperature.
c) Effect of Sulfonation Time at Various Temperatures on Surface Tension of Surfactant

The surface tension measurement of the methyl ester sulfonate surfactant was carried out using capillary rise methods. Figure 7 shows the effect of time ratio of methyl ester sulfonate on surface tension at various temperatures. Based on Figure 7, it can be seen that the surface tension value of the methyl ester sulfonate obtained tends to increase with the length of the reaction time used and tends to be unstable with increasing temperature. The lowest surface tension value obtained was 25.276 dyne/cm, at temperature of 45°C within 10 minutes. And the highest surface tension value obtained is 32.028 dyne/cm at 65°C within 30 minutes.

![Fig. 7. Surface Tension of Surfactant vs.time of Sulfonation at various Temperatures.](image)

3.3. FTIR analysis

To determine the structure of the methyl ester sulfonate formed, FTIR analysis was carried out. Figure 8 shows the FTIR results of methyl ester sulfonate.

![Fig. 8. FT-IR Spectrum of Methyl Ester Sulfonate.](image)

Figure 8 showed the presence of typical absorption bands at wavenumbers 2921.41 cm⁻¹ (CH₂ vibration), 1740.41 cm⁻¹ (bonds C = O), and 1167.14 cm⁻¹ (S = O bond). Based on the results of the FTIR test already performed, the sulfonate group is shown in the surrounding wave number 1361.64 to 1015.19 cm⁻¹, and the group S = O at wave number 1112.95 cm⁻¹. The strong band at 1740.41 cm⁻¹
is typical for carbonyl group C = O. The absorbing band resembling the S-O group is at the wavenumber between 721.80-879.03 cm⁻¹. The broad vibration at 721.80 cm⁻¹ assigned for the alkenic group (−CH = CH−) from unsaturated fatty acid chains. Peaks at 2921.41 cm⁻¹ and 2852.48 cm⁻¹ are absorptions for C-H of the fatty acid chain.

4. Conclusion
In this research of synthesis anionic surfactant methyl ester sulfonate from virgin coconut oil (VCO), NaHSO₃ and CaO catalysts were used. The resulting methyl ester sulfonate was analyzed for physical properties and identified the structure using Fourier Transform Infrared Spectroscopy (FT-IR). The optimum conditions were obtained at a sulfonation temperature of 65°C in 30 minutes. With the resulting viscosity of 4.04 cSt, the yield of 98%, and the surface tension of 32,028 dyne/cm.

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