The Study on Factors Affecting the Synthesis of Methyl Ester Sulfonate from Palm Oil using CaO Catalyst with Microwave-Assisted Heating Energy Source

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Abstract. Methyl ester sulfonate can be synthesized from palm oil using sodium bisulfite as a sulfonating agent with microwave-assistance as a heating energy source. The use of microwave as an energy source can reduce the reaction time and increase the product. Methyl ester sulfonate can be produced in several stages, that is transesterification, sulfonation, purification, and neutralization. The transesterification process was carried out by reacting palm oil and methanol with a mol ratio of 1:9 and 1%wt of KOH catalyst at a microwave power of 300 watts, and a temperature of 60°C for 10 minutes. Methyl ester was sulfonated using sodium bisulfite at a power of 300 watts for 40 minutes at a temperature of 80°C-100°C. This process also used a CaO catalyst of 1.5% and the mole ratio of methyl ester:NaHSO₃ is 1:2. The resulting methyl ester sulfonate was then purified by the addition of methanol and heated in a microwave power of 300 watts, at temperature 55°C for 10 minutes and then neutralized with NaOH. The resulting methyl ester sulfonate has a density of 0.8626 gr/ml, viscosity of 3.51 cSt, pH of 1.68, yield of 98.67%, and surface tension of 32.23 dyne/cm.

1. Introduction

Indonesia is one country that is very rich in natural potential. One of the many natural resources in Indonesia is oil palm. Indonesia is one of the countries that produces the largest palm oil in the world with a total production of palm oil reaching 46 million tons [1]. The total area of palm oil plantations in Indonesia in 2018 reached 12.76 million hectares and is expected to produce 36.59 million tons of palm oil [2]. Palm oil is a vegetable oil that is rich in fatty acids. One of the fatty acid contents in palm oil is palmitic acid and oleic acid with amounts of 45% and 40%, respectively [3]. Palm oil can be used in a variety of products, such as chocolate, soap, cosmetics, butter. Palm oil can also be converted into methyl esters which can be used as a raw material for making surfactants. The lack of use of palm oil is one of the factors that make palm oil very suitable for use as a raw material for making surfactants so that it can provide added value in the use of palm oil products. Besides, palm oil is a raw material that is renewable, environmentally friendly, in abundance, and has a low price.

The surfactant produced from palm oil is an anionic surfactant methyl ester sulfonate which is a derivative product of vegetable oil. Where this surfactant has advantages over surfactants produced from petroleum derivatives, because methyl ester sulfonate using materials that are renewable, environmentally friendly, and easy to decompose. Methyl ester sulfonate has several advantages including good dispersed properties, good detergency properties in water with high hardness levels and...
can be easily degraded. Methyl ester sulfonate is one of the surfactants that widely used in the industry because the excellent surface activity and self-assembly behavior [4].

Methyl ester sulfonate can be prepared using sulfonating agents such as gas SO$_3$, H$_2$SO$_4$, HSO$_3$Cl, and also NAHSO$_3$. The use of sodium bisulfite (NAHSO$_3$) as a sulfonating agent has several advantages including producing a methyl ester sulfonate with a brighter color, can be applied on a small scale, and can be used with a batch process [5]. The preparation of surfactants using sodium metabisulfite as a sulfonation has been carried out [6] using the raw material of palm oil methyl ester and CaO catalyst produces surface tension values of 32.6 - 33.6 dyne/cm with a temperature of 80°C and a sulfonation time of 4 - 6 hours. The research of surfactants using raw materials of Crude Palm Oil and sodium bisulfite as sulfonating agents resulting in a surface tension reduction value of 35.70 - 38.97 at a temperature of 100°C with a sulfonation time of 4.5 hours [7].

Methyl ester sulfonate is one of the renewable energy sources (new) so that in the manufacturing process it must consider and prioritize the effectiveness of energy use. Methyl ester sulfonate production generally only uses conventional heating methods that require long heating, long sulfonation times, are less effective, and can increase energy consumption. So the effective alternative heating methods can be used, one of which is by using a microwave. Methyl ester sulfonate can be made using heating from a microwave where the use of this microwave has advantages, including a short heating process, accelerates reaction time, uses relatively low energy consumption, is environmentally friendly, and can increase production yields and can improve product properties and quality [8].

Microwave technology use of electromagnetic waves which are formed by a combination of electric and magnetic fields. The microwave heats the material quickly because the heating process uses microwave radiation which directly heats the material itself so that it warms up faster and more evenly. Microwave radiation can be used to accelerate the reaction because the heat is directly transferred to the materials, therefore the heat transfer process is more effective when compared to conventional heating method and need a shorter time to complete the reaction [9].

The purpose of this research is to study the factors that affecting the synthesis of methyl ester sulfonate from palm oil using CaO Catalyst with microwave-assisted as a heat source and to study the characteristics of methyl ester sulfonate that affected by reactant ratio and temperature.

2. Material and Methods

2.1. Materials

The raw materials used in this study including palm oil, 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. Equipment

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

2.3. Transesterification

The transesterification process is carried out by reacting sawt oil with methanol with a ratio of 1:9 and a KOH catalyst as much as 1% wt. KOH catalyst and methanol are first mixed until homogeneous, and then palm oil is added to the methanol mixture. The mixture was then roasted using a microwave at 300 watts of power, at 60°C for 10 minutes with constant stirring. After the heating process is complete, the product is separated to separate the methyl ester and glycerol. The methyl ester which is in the top layer is then washed using warm distilled water to a neutral pH, and then the methyl ester is dried to evaporate the remaining water in it using an oven until no bubbles are formed.

2.4. Sulfonation

The sulfonation process is carried out by reacting the methyl ester with sodium bisulfite which has been dissolved in distilled water with a mole ratio of 1:2. The CaO catalyst used was 1.5% by weight of oil. Then the mixture was heated in a microwave with constant stirring at 300 watts of power, a
temperature of 100°C, for 40 minutes. The mixture is then separated to separate the methyl ester sulfonate with CaO catalyst and the remaining sodium bisulfite. The methyl ester sulfonate is then purified by adding methanol as much as 35% v / v and heated in a microwave with a microwave power of 300 watts, at a temperature of 55°C for 10 minutes. After that, evaporation is carried out to evaporate the methanol and the remaining water. The next step is the neutralization process which is carried out by adding 20% NaOH to the methyl ester sulfonate until the pH reaches 6-7.

2.5 Characteristics

Methyl esters are characterized by conducting density and viscosity analysis. The resulting methyl ester sulfonate was then analyzed for physical properties in the form of density analysis using a pycnometer, viscosity using an Ostwald viscometer, pH using a pH meter, yield, and surface tension using the capillary tube increase method. To determine the sulfonate groups formed, FTIR analysis was carried out.

3. Result and Discussion

3.1. Transesterification

Transesterification is the process of converting triglycerides contained in palm oil into methyl esters through a reaction with the addition of methanol. At this stage, palm oil is reacted with methanol with a mole ratio of 1: 9, as well as the addition of a KOH catalyst 1% by weight of the palm oil used. The resulting methyl ester was analyzed for its density and viscosity.

| Parameter                               | Palm Oil | Methyl Ester | SNI      |
|-----------------------------------------|----------|--------------|----------|
| Density at temperature of 40°C (gr/ml)  | 0.8958   | 0.8546       | 0.850 – 0.890 |
| Kinematic viscosity at temperature of 40°C (cSt) | 34.3176  | 3.1869       | 2.3 – 6   |

The transesterification process produces a yield of 98% of methyl ester. The resulting methyl ester has a density value of 0.8546 gr/ml and kinematic viscosity of 3.1869 cSt. The value obtained is in accordance with the SNI standard density and viscosity values.

3.2. Sulfonation

The Sulfonation process is a reaction to the formation of methyl ester sulfonate with the addition of a sulfonating agent with sodium bisulfite. The sulfonation process is carried out by reacting the methyl ester with NaHSO₃ using 1% w/w CaO catalyst. This reaction is carried out using a microwave at 300 watts of microwave power, with a 1:2 mole ratio of reactants and a temperature variation of 80-100°C.

3.3. Effect of Reactants Ratio on Density of Methyl Ester Sulfonate.

The density values obtained ranged from 0.8602 gr / ml - 0.8628 gr / ml. Figure 1 show the effect of reactant mole ratio on density of methyl ester sulfonate at various temperature.
Fig. 1. The effect of Reactant Ratio on Density of methyl ester sulfonate at Various Temperature

From Figure 1, it can be seen the relationship between the ratio of reactants at various temperatures on density. In the figure, it can be seen that the density value tends to increase with the increase of the reactant ratio and temperature. The highest average density value is at a temperature of 100oC and the lowest average density is at 80oC. The lowest density value is at a temperature of 80oC with a density value of 0.8602 gr/ml with a reactant mole ratio of 1:1. And the highest density value of 0.8628 gr/ml was obtained at a temperature of 100oC with a mole ratio of reactants of 1:3. This methyl ester sulfonate density value has increased compared to the density value of methyl ester, this indicates that there has been a reaction to the formation of methyl ester sulfonate where the bonding of the sulfonate group will increase the density value of the product.

3.4. Effect of Reactants Ratio on Viscosity of Methyl Ester Sulfonate

Viscosity measurement aims to see the thickness of the resulting surfactant methyl ester sulfonate. The bonding of the sulfonate group to the methyl ester causes the viscosity of the methyl ester sulfonate to be greater than the methyl ester used as raw material. The resulting viscosity ranges from 3.47 cSt – 3.53 cSt. Figure 2 shows the effect of reactant mole ratio on viscosity of methyl ester sulfonate at various temperature.

Fig. 2. The effect of Reactant Ratio on Viscosity of methyl ester sulfonate at Various Temperature
From Figure 2, it can be seen the relation between the ratio of reactants at various temperatures to viscosity. The result of the viscosity of the methyl ester sulfonate tends to increase along with the increase of the reactants ratio. The increase in sulfonation temperature used also affects the viscosity value of the resulting methyl ester sulfonate. Whereat 100oC has the highest average viscosity value when compared to the viscosity value at 80oC and 90oC with the highest viscosity value obtained at 3.53 cSt at 100oC with a reactant mole ratio of 1:3. The lowest viscosity obtained at 3.47 cSt at a temperature of 80oC with a reactant ratio of 1:1. Viscosity is related to density, where the greater the density value, the greater the viscosity value. The tendency of the increased viscosity value is due to the bonding of the SO3 sulfonate group to methyl ester component, making methyl ester sulfonate tend to have a larger molecular size, which causes a higher viscosity value.

3.5. Effect of Reactants Ratio on pH of Methyl Ester Sulfonate

PH analysis was carried out to determine the acidity of the methyl ester sulfonate produced in the sulfonation process. The pH analysis result ranged from 1.68 – 2.74. Figure 3 show the effect of reactant mole ratio on pH of methyl ester sulfonate at various temperature.

From Figure 3, it can be seen that with increasing the ratio of reactants used at ratio 1:2, the pH value tends to decrease, and from ratio 1:2 to reactant ratio 1:3 the pH is increase. The sulfonation temperature used also affects the pH value of the resulting methyl ester sulfonate that also can be seen in the figure 3 above, where the temperature of 80oC has an average pH value that is higher than the pH at 90oC and 100oC. And the lowest pH range is at a sulfonation temperature of 80oC. The lowest pH value is 1.68 which is obtained at temperature of 100oC with a reactant ratio of 1:3 and the highest pH is 2.74 which is obtained at 100oC with a reactant ratio of 1:1. pH conditions of methyl ester sulfonate after the sulfonation process before neutralizing with NaOH tend to be acidic. The decrease in pH is due to the reaction between methyl ester and sodium bisulfite which has acidic properties and the binding of the sulfonate group to the methyl ester.

3.6. Effect of Reactants Ratio on Yield of Methyl Ester Sulfonate

The Yield of methyl ester sulfonate product at various temperatures showed in Figure 4. The yield value of the methyl ester sulfonate obtained is ranging from 94.67% - 96.33%.
From figure 4, it can be seen that by increasing the ratio of the reactants used, the yield value of methyl ester sulfonate obtained tends to increase. The lowest yield value obtained was 94.67% at a temperature of 90°C with a mole ratio of reactants of 1:3. And the highest yield was 96.33% at a temperature of 100°C with a reactant ratio of 1:2. The average yield of methyl ester sulfonate obtained at 80°C was greater than the yield value of methyl ester sulfonate obtained at 90°C and 100°C.

3.7. Effect of Reactants Ratio on Density of Methyl Ester Sulfonate

The surface tension measurement of the methyl ester sulfonate surfactant was carried out using capillary rise methods. Figure 5 shows the effect of reactant ratio on methyl ester sulfonate surface tension at various temperature.

From figure 5, it can be seen that the value of the surface tension obtained tends to decrease with the increase of the reactants ratio used and the temperature used. The lowest surface tension value obtained was 32.22 dyne/cm which is at a temperature of 100°C with a mole ratio of reactants of 1:2. And the highest surface tension value obtained was 35.81 dyne/cm at a temperature of 80°C with a reactant ratio of 1:1.
3.8. FTIR Analysis.

To determine the structure of the methyl ester sulfonate formed, FTIR analysis was carried out. Figure 6 shows the FTIR results of methyl ester sulfonate.

![Fig. 6. FT-IR Spectrum of Methyl Ester Sulfonate](image)

Figure 6 showed the presence of typical absorption bands at certain wavenumbers. Based on the FTIR results, the sulfonate group is shown at the wave number 1361.07 to 1015.15 cm⁻¹, and for the S=O group at wave number 1117.70 cm⁻¹. The strong band at wavenumber 1741.01 cm⁻¹ is typical for C=O group. The absorption band at wave numbers 721.79-846.69 cm⁻¹ is typical for the S-O group. The broad vibration at 721.79 cm⁻¹ assigned for the alkene group (−CH = CH−) from unsaturated fatty acid chains. Peaks at 2920.54 cm⁻¹ and 2851.89 cm⁻¹ are absorptions for C-H of the fatty acid chain.

4. Conclusion

In this research of synthesis methyl ester sulfonate from palm oil, NaHSO₃ and CaO catalysts were used. Methyl ester sulfonate was analyzed for physical properties and identified the structure using FT-IR. The optimum conditions were obtained at a sulfonation temperature of 100°C with a mole ratio of methyl ester and NaHSO₃ of 1:2. With the resulting density of 0.8626 gr/ml, the viscosity of 3.51, pH of 1.68, the yield of 96.33%, and the surface tension of 32.23 dyne/cm.

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