Effect of the addition of \( \text{H}_2\text{SO}_4 \) on the synthesis of sulfated oil from palm oil (\textit{Elaeis guinensis} JACQ) on the chemical properties of sulfated oil

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Abstract. This research aimed to determine the effect of adding sulfuric acid to the synthesis of sulfated oil from palm oil to the chemical properties of the resulting sulfated oil. The research method is the synthesis of sulfated oil from bulk palm oil, with a 98% \( \text{H}_2\text{SO}_4 \) emulsifier technically. The addition of \( \text{H}_2\text{SO}_4 \) varied with successive number of 10; 12.5; 15; 17.5; 20; 22.5 and 25% with sulphation time for 3 (three) hours. The resulting sulfated oil was chemically tested including water content, oil content, total alkalinity, saponification number, ash content, and \( \text{SO}_3 \) levels are bound. The results showed that there was an effect of adding \( \text{H}_2\text{SO}_4 \) to the synthesis of oil sulfated. The addition of 25% \( \text{H}_2\text{SO}_4 \) is the best compared to other samples. Sulfated oil obtained by its solubility in water is more stable than other samples. The chemical properties of the sulfur oil produced have a water content of 6.47%; oil content of 81.28%; total alkalinity of 0.25%; and ash content of 2.77%; meet the requirements IS: 6357-1971, specifications of sulfated oil for leather.

1. Introduction
The Chemically vegetable oils such as animal oil and fish oil contain triglycerides [1] which are esters of glycerol with three fatty acid molecules [2]. Palm oil has specific characteristics compared to other vegetable oils, consisting of various triglycerides with different fatty acid chains. The melting point depends on the triglyceride level, the chain length of 14-20 carbon atoms, with an unsaturated fatty acid content of 50.2% [3]. Palm oil consists of unsaturated fatty acids (linoleic and oleic acids) whose amounts are comparable to saturated fatty acids which contain a lot of palmitic acids[4][5]. According to [5], characterization of palm oil has iodine number 49.95 mg I\(_2\)/oil; free fatty acid 0.05%; water content 0.18%; peroxide number 16.23 mg/kg; acid number 0.19 mg KOH/g. Palm oil including palm oil is vegetable oil which has a high economic value and fatty acid components from palm oil have been proven suitable to be used as raw material for fatliquoring agents [6][4].

Sulfated oil is obtained by reacting animal or vegetable oils with sulfuric acid or \( \text{SO}_3 \) gas at low temperatures. To be able to convert the oil to the emulsion, it is necessary to add certain chemicals such as bisulfite and sulfuric acid. Through this reaction, the group of polar compounds which are hydrophilic is incorporated into the structure of the oil material, so that an oil emulsion is formed in water[7], the process is known as sulfation. The sulfation is the process of treating oil with concentrated sulfuric acid to get oil that can be emulsified in water. The sulfation of oil produces is
called sulfated oil. The purpose of sulphation is to enter a polar (hydrophilic) group so that the oil is emulsified with water. Unsaturated fats will react with sulfuric acid to form C-O-S bonds where carbon from oil will attack the sulfate group (-OSO$_3$H). In the reaction of sulfated oil, sulfuric acid enters into double bonds of unsaturated fatty acids such as addition reactions, so that the oil becomes polar. The sulfation group (-OSO$_2$OH) binds to C atoms in double bonds and H atoms bind to other C atoms [8]. In the sulphonation reaction of oil, the sulfuric acid compounds are separated into sulphonate (-SO$_2$OH) and hydroxyl (-OH) groups. The sulphonate group will bind to C atoms of saturated fatty acids replacing H atoms or it can be called a substitution reaction, while the hydroxyl groups will join with the loose H atoms and form H$_2$O compounds. 

Generally, sulfated oil is made by adding sulfuric acid by monitoring the temperature and time of stirring, followed by washing the acid with a salt solution to remove excess acid and neutralizing using sodium, potassium hydroxide to the desired pH[9][10]. The greater the amount of sulfuric acid and the duration of stirring, allowing sulfuric acid molecules to react with the double bond of fatty acids making up the oil, so that the double bond is formed by sulfuric acid which causes the number of iod numbers to decrease, saponification and SO$_3$ levels are bound higher[11]. The reaction of unsaturated fatty acids with sulfuric acid is exothermic, therefore the addition of sulfuric acid must be very slow using constant stirring to avoid rising temperatures [12]. The increase in temperature that occurs is not only due to sulphation reactions but because of secondary reactions that occur, especially in fatty acids that contain unsaturated bonds [13]. Through sulphation reaction, a group of hydrophilic polar compounds is inserted into the structure of the oil material, so that an oil emulsion is formed in water. This study focused on the effect of adding sulfuric acid to the synthesis of sulfated oil from bulk palm oil (without brands). Research related to sulphation of palm oil has been done previously by Shabrina [8], which is about the effect of sulfuric acid concentrations on sulphation of branded palm oil. The purpose of this study was to determine the effect of adding sulfuric acid to the synthesis of sulfated oil from palm oil to the chemical properties of sulfated oil.

2. Experimental

2.1 Materials and equipment

The material used in this study were bulk palm oil obtained from Yogyakarta bulk oil distributor, and sulfate oil of patent (control) from Yogyakarta. Other ingredients are 98% technical H$_2$SO$_4$, 10% technical NaCl, NaOH, ice cube, and ice gel. The equipment used included scales, drop pipettes, beaker glass, thermometer, glass stirrer, measuring glass, separation funnel, stativess and clamp, stainless steel container, overhead stirrer brand IKA Germany, LED digital hotplate magnetic serial stirrer No. MR 174A10002660, and FT-IR Thermo Scientific Nicolet iS 10 Spectrophotometer.

2.2 Synthesis of fatliquor from palm oil

One hundred grams of bulk palm oil in a beaker glass was put into a stainless steel bowl containing ice cubes, stirred with a mixer with a fixed speed of 300 rpm, added sulphating agent (H$_2$SO$_4$ with variation 10.0; 12.5; 15.0; 17.5; 20.0; 22.5; and 25.0% of the weight of oil) slowly, the temperature was maintained no more than 20ºC. The sulfating process runs slowly for 3 hours. Sulfated oil was washed with saturated salt solution (10% NaCl) at 35ºC three times. Sulfate oil was neutralized with a 50% NaOH solution to pH 6.5-7 [5].

2.3 Chemical analysis

The chemical analysis of oil includes water content, oil content, total alkalinity, saponification number, ash content, and SO$_3$ levels are bound were investigated. To determine the characterization of oil sulfated emulsion in water analysis was the stability of emulsion and broken temperature of emulsion.

The method of emulsion stability [9]:

1. Prepare the test tube clean and dry
2. Enter 5 ml of distilled water into the test tube then add 5 drops of sulfated oil into the water
3. Beat for 5 minutes until the oil is mixed with water, observe what happens for 15 minutes, 1 hour, 5 hours and 24 hours.
   Observation results: 1 = Translucent; 2 = partially translucent; 3 = milky; 4 = creamy; 5 = oil separation

Broken temperature of emulsion test [14]:
1. Prepared the beaker in a clean and dry
2. Added 40 ml of distilled water into the cup and then add 5 ml of sulfate oil
3. Stirred for 5 minutes
4. Heated in an electric stove
5. Noted the temperature at which the oil has broken or the liquid starts to clear

3. Results and discussion

3.1 Chemical analysis
The average chemical test results of sulfated oil (water content, oil content, total alkalinity, saponification number, ash content, and SO3 level are bound) presented in figure 1.

![Chemical analysis results](image)
Figure 1. (a) Water content (b) oil content (c) total alkalinity (d) ash content (e) saponification number (f) SO$_3$ levels are bound

The results of chemical analysis of sulfate oil from the research results are shown in Figure 1. shows that the water content, oil content, total alkalinity and ash content of sulfate oil from this research meet the requirements of IS: 6357-1971, sulfated oil specifications for leather. The maximum water content of 35%; minimum oil content of 60%, maximum total alkalinity of 3% and maximum ash content of 3%. Figure 1 shows that the more the amount of H$_2$SO$_4$ is added, the lower the water content, oil content, and total alkalinity. Conversely, the more amount of H$_2$SO$_4$ added, saponification number, ash content and SO$_3$ levels are bound to increase. This is in accordance with the opinion of [11], that the greater the amount of sulfuric acid, allows sulfuric acid molecules to react with double bonds of fatty acids making up the oil so that the double bond is formed by sulfuric acid which causes higher saponification and SO$_3$ levels. The more sulfuric acid added to palm oil, the greater the chance of sulfuric acid to add to the double bond. It is proven that the saponification number of 192.74% and SO$_3$ levels are bound of 7.68% in the 25% H$_2$SO$_4$ sample is the highest among the other samples.

The analysis of saponification number on sulfated oil aims to determine the number of sulfated groups bound to oil including the carboxylic group of the oil. While the analysis of SO$_3$ levels is bound is intended to determine the amount of sulfuric acid that contains double bonds after the sulphation reaction[11] or to know how much SO$_3$ content is in the sulfated oil [14]. The more SO$_3$ content that is bound to the sulfated oil, it is feared that if applied to the skin, SO$_3$ will bind to H$_2$O so that it can form H$_2$SO$_4$ which will damage the tanned skin. The good SO$_3$ levels are bond content for sulfated oil is 3 - 7% [14].

3.2 Emulsion stability
The results of the emulsion stability test can be seen in figure 2 and table 1. Figure 2 shows that sulphation of palm oil with 25% H$_2$SO$_4$ (left most test tube) is the best compared to control sulfated oil (far right) because the sulfated oil does not have oil and water separation. While other samples (11; 12.5; 15; 17.5; 20; 22.5%) after mixing with water, the separation between oil and water has been seen.
Table 1 shows that palm oil with 25% H₂SO₄ was stable for 1 hour, visually looks like milk (milky), while other samples have oil separation (value 5 = oil separation). Therefore, sulphation of palm oil with 25% H₂SO₄ is the best.

| Concentration of H₂SO₄ (%) | 15 minute | 1 hour | 5 hours | 24 hours |
|---------------------------|-----------|--------|---------|----------|
| 10,0                      | 5         | 5      | 5       | 5        |
| 12,5                      | 5         | 5      | 5       | 5        |
| 15,0                      | 5         | 5      | 5       | 5        |
| 17,5                      | 5         | 5      | 5       | 5        |
| 20,0                      | 5         | 5      | 5       | 5        |
| 22,5                      | 5         | 5      | 5       | 5        |
| 25,0                      | 3         | 3      | 5       | 5        |
| Control                   | 3         | 3      | 3       | 3        |

3.3 Emulsion stability

Results of broken temperature test of oil emulsion observed in table 2.

| Concentration of H₂SO₄ (%) | Temperature (°C) |
|---------------------------|------------------|
| 10.0                      | 75               |
| 12.5                      | 70               |
| 15.0                      | 70               |
| 17.5                      | 70               |
| 20.0                      | 70               |
| 22.5                      | 65               |
| 25.0                      | 55               |
| Control                   | 50               |
Table 2 shows that sulphation of palm oil with 25% H₂SO₄ is the best emulsion broken temperature at 55°C. According to Covington [15], ideally the dissolution of oil in water temperature is the same as the water temperature and the temperature limit is 60 °C. This is to avoid damage to the skin tanned with vegetable ingredients, although for chrome tanning resistant to high temperatures.

4. Conclusions
There is the effect of adding H₂SO₄ 10; 12.5; 15; 17.5; 20; 22.5; and 25% in the synthesis of sulfated oil against the chemical properties of the sulfated oil produced. The results showed that the addition of 25% H₂SO₄ was the best compared to other samples. Sulfated oil obtained by its solubility in water is more stable than other samples, the solution looks like milk (3 = milky) and the broken temperature of oil emulsion, at a temperature of 55°C. The chemical properties of the sulfated oil have a water content of 6.47%; oil content of 81.28%; total alkalinity of 0.25%; and ash content of 2.77%; meet the requirements of sulfated oil IS: 6357-1971, specifications of sulfated oil for leather.

5. References
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