Synthesis of palm oil fatty acid as foaming agent for firefighting application

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Abstract. Many factors including natural factor, human carelessness, new land clearance or agricultural burning/act of vandalism and ground fire are suspected as the causes of forest fire. Foam, which cools the fire down, covers the burning material/fuel, and avoids contact between burning materials with oxygen, is an effective material used to fight large-scale fires. For this purpose, surfactant which can facilitate foam formation and inhibit the spread of smoke is required. This study was aimed at producing prototype product of foaming agent from palm oil and its formulation as a fire fighting material. Before the formulation stage, the foaming agent was resulted from saponification process of oleic, lauric, and palmitic acids by using NaOH and KOH alkaline. Foam stability was used as the main indicator of foaming agent. Results showed that potassium palmitate had the highest foam stability of 82% until the 3rd day. The best potassium palmitate concentration was 7%.

1. Introduction
In 2015, land and forest fires in Indonesia were estimated to damage more than 2 million hectares of land consisting of about 600,000 hectares of peatland and 1.5 million hectares of non peatland. The loss caused by these fires were suffered not only in local but also national, regional, and even international levels. Several factors are indicated as the causes of forest fires including (a) natural factors including high temperature during dry season, lightning strike, and volcanic activity (volcanic mudflow or hot clouds), (b) human carelessness such as careless cigarette butt littering and fire left in camping ground, (c) land-clearing open burning and vandalism, and (d) ground fire which usually occurs beneath the ground in peatland and lit fire especially during dry season with high air temperature.

Surfactant is the main component of a foaming agent. The use of surfactant in foaming agent improves the effectiveness of water use and the performance of foaming agent in putting out the fire. Surfactant in a foaming agent functions as a surface tension reducer and foaming agent. Foam is used to cool the fire down, cover the burning fuel, and avoid recontact with oxygen that may lit the fire back. In the field of firefighting, many products are available for use in different needs and types of fire. With regard to its use in the field, a foaming agent to be used in firefighting should be environmentally friendly, biodegradable, and nontoxic. Therefore, a foaming agent made of natural
feedstock is preferable as it is not only renewable, but also environmentally friendly and not harmful. Palm oil is one of surfactant feedstock which is abundant in Indonesia. Based on the above notion, this study was aimed at producing a prototype product of foaming agent from palm oil fatty acid which could be used as a feedstock of firefighting agent and assessing the physicochemical properties of the produced foaming agent.

Soap is an alkaline carboxilate salt (RCOONa) with a hydrophobic (non polar) R group and hydrophilic (polar) COONa group. The head part of a soap molecule is a hydrophilic group and the tail part is a hydrophobic group. Soap is widely known as very important as a reducer of surface tension [1] and interfacial tension. Palm oil-based soap is easily degraded and safe for the environment so that it is used in this study as the biggest component in the production of foaming agent. Soap can be synthesized by reacting oil or fatty acid with caustic soda, soda ash, or potassium salt. Soap is resulted through a saponification process of oil/fat and fatty acid. Saponification process is a reaction between triglyceride and alkali resulting in glycerol as a by-product. Meanwhile, fatty acid saponification process which is also called a neutralization process is a reaction between free fatty acid and alkaline without producing glycerol as a by-product [2,3].

Fatty acids produced from the hydrolysis of oil/fat consist of saturated and unsaturated fatty acids. The difference between these fatty acids lies in the existence of double bonds in their hydrocarbon chains. The dominant fatty acids in palm oil are palmitic acid and oleic acid while lauric acid is found to be dominant in coconut oil and palm kernel oil [4]. Oleic acid is long chain unsaturated fatty acid having C18 chain length, one double bond, and a melting point 15.3°C. Lauric acid is a saturated fatty acid having C12 chain length and a melting point 43.2°C. Palmitic acid is a saturated fatty acid having C16 chain length and a high melting point 62.9°C. High content of palmitic acid make palm oil more resistant to oxidation (rancidity) than the other types of oil [5]. These three fatty acids have good solubility in water, good detergency property, and good performance in hard water. Saponification (neutralization) results in soap of sodium oleic, potassium lauric, and sodium palmitic types. Studies have been done on the utilization of plant oil derivatives as firefighting agents which are environmentally friendly. Mizuki et al. [6] formulated fire fighting agent by using long chain fatty acid (LCFA), biodegradable chelating agent, and additive to produce a firefighting agent which was also biodegradable. The concentration of firefighting agent was 1% and environmentally friendly firefighting agent was produced. However, the resulted foam had shorter lifetime than did synthetic firefighting agent. Kawahara et al. [7] formulated a firefighting agent by using a biodegradable chelating agent (MGDA) which was different from that used by Mizuki et al. [6] who produced a firefighting agent which was also biodegradable having an expansion ratio of 9.6 times higher than that of the commercial firefighting foam for structural fire.

2. Methods
Materials used in this study included oleic acid, lauric acid, palmitic acid, NaOH, KOH, commercial surfactant, and others. Equipment including saponification reactor, Anton Paar DMA 4500M densitometer for density test, Brookfield DV-III Ultra viscometer for viscosity test, Phoenix 300 contact angle analyzer for wettability test, homogenizer, spinning drop tensiometer TX500C for surface tension dan interfacial tension test, and other glass equipment.

2.1. Fatty acid analysis
Analysis of physicochemical properties of fatty acid was done to determine the properties of fatty acids used in this study. Acid number, iodine number, saponification number, viscosity, and density tests were conducted.
2.2. Synthesis and analysis of fatty acid sodium and potassium

Synthesis of fatty acid sodium and potassium was done by using three fatty acids including oleic acid, lauric acid, and palmitic acid. NaOH and KOH of 30% were used as alkaline reactants. The mole ratio of fatty acid and alkaline was 1:0.5 – 1:1. The process was done at 65°C for 90 minutes. Sodium and potassium analysis of the resulted fatty acid was done on foam stability, foaming ability, surface tension, and interfacial tension.

2.3. Selection of fatty acid sodium/potassium concentration

In this stage, selection was done to get the best sodium/potassium concentration of fatty acids produced in the previous stage. The concentration tested was 3, 5, and 7%. The analysis was done on surface tension, foaming ability, foam stability, viscosity, density, and contact angle tests.

3. Results

3.1. Fatty acid analysis

Three types of palm oil fatty acid feedstock, namely oleic acid, lauric acid, and palmitic acid were used in this study. Results of the analysis showed that these three fatty acids had acid value of 199.2 – 280.6 mg KOH/g, saponification number of 200.2 – 281.6 mg KOH/g, iodine number of 0.1 – 87.7 g/100 g Iodine, viscosity of 4.26 – 7.42 cP, and density of 0.85812 – 0.86650 g/cm³. These results are listed in Table 1.

| Parameter                  | Unit     | Oleic Acid | Lauric Acid | Palmitic Acid |
|----------------------------|----------|------------|-------------|---------------|
| Acid Number                | mg KOH/g | 199.2      | 280.6       | 218.5         |
| Saponification Number      | mg KOH/g | 200.2      | 281.6       | 219.4         |
| Iodine Number              | g/100 g  | 87.7       | 0.1         | 0.2           |
| Viscosity (70°C)           | cP       | 7.25       | 4.26        | 7.42          |
| Density (70°C)             | g/cm³    | 0.85812    | 0.86650     | 0.86233       |

3.2. Synthesis and analysis of fatty acid sodium and potassium

In this stage, saponification process of oleic acid, lauric acid, and palmitic acid by using a reactor of 2L/batch scale. Sodium and potassium of the resulted fatty acid was analyzed for its foam stability, foaming ability, surface tension, and interfacial tension. Results of the analysis are as follows.

3.2.1. Foam Stability

Foam can improve the efficiency of water as firefighting agent. Foam is defined as a dispersion system consisting of gas bubbles covered with a liquid layer. Significantly different density levels found in the bubble and liquid medium make the system quickly separate into two layers with the bubbles go up to the top. When gas bubbles are formed beneath the liquid surface, they will immediately break out as the liquid flow (drainage) occurs as a result of gravity or downward force. Therefore, pure liquid will not be foamy unless a surfactant is added.[8]. This added surfactant reduces interfacial tension of gas/liquid making the dispersion of gas in liquid easier to occur [9] which then leads to foam formation. The mechanism of foam formation starts when gas bubbles enter the surfactant solution. The surfactant will then be adsorbed in gas/liquid interface to form gas bubbles covered with a film layer. This covered bubble is called foam which trends to float upward to the surface because the specific gravity of gas is smaller than that of water. However, surfactant is also found on liquid surface on the border layer between water and air. This surfactant holds the floating foam on the border of liquid surface and avoids it from being released to the air. The accumulating foams on the surface will get closer, make contact one to another, or even resemble to create bigger foams [9].
Foam stability refers to the ability of the foam to maintain the main parameters (bubble size, liquid content, total foam volume) in a constant situation for a certain period of time. Foam analysis was done in order to assess the ability of foam to stay in its shape and without disappearing in a period of time. For foaming agent application, foam stability was measured for 3 days. The value of foam stability was obtained from the difference of foam height in minute 0 after the foam was vortexed/homogenized and the foam height in day 3. The foam stability was expressed in cm unit and percentage. Results of foam stability measurement showed that the stability of foam produced from sodium oleic, lauric, palmitic and potassium oleic, lauric, palmitic was about 2-3 days. The highest foam stability was shown by sodium palmitic and potassium palmitic. Sodium palmitic at a molar ratio of 1:0.75 had a foam percentage of 82.2% while potassium palmitic with a molar ratio of 1:1 had a foam percentage of 81.8%. The histogram of the analysis of foam stability of sodium oleic, lauric, palmitic and potassium oleic, lauric, palmitic is depicted in Figure 1.

![Foam Stability Histograms](image)

**Figure 1.** Histogram of the analysis of foam stability of sodium oleic, lauric, palmitic and potassium oleic, lauric, palmitic.

Higher molar ratio and longer testing time resulted in reduced foam stability. Yet, potassium palmitic and sodium palmitic had relatively higher foam stability as at testing day 3 their foam stability was about 80% while foam of other samples stayed for 2 days only and quickly collapsed. Foam collapse was caused by thinning in film layer and accumulation of foam to form a bigger foam (coalescent)[8]. Film layer thinning occurs because foam has a tendency to float upward while at the same time it is constantly pulled downward by liquid flow (drainage) occurring as a result of gravity force. Being pulled into two opposite directions, the film of foam gets thinner and easier to break up. Varied foam sizes also create gradient of gas pressure resulting in gas diffusion. This then leads to the accumulation of small foams to form bigger size foam (coalescent) which is easier to break out [10]. This foam break out can be avoided by slowing down the drainage through the improvement of liquid bulk viscosity. Adding materials such as glycerol, polymer, or stabilizer (CMC) increases viscosity...
and increased viscosity reduces the speed of drainage. Reduced drainage speed minimalizes thinning [8].

3.2.2. Foaming Ability

Foaming ability, which is expressed in % unit, refers to the ability of a liquid to form foam in 0 minute after the liquid is vortexed or homogenized. In this study, results showed that sodium oleic, lauric, and palmitic had foam height of about 19.51 to 170.73% and the two highest foam heights were found in sodium lauric at a molar ratio of 1:0.75 (170.73%) and at a molar ratio of 1:1 (165.85%). Meanwhile, potassium oleic, lauric, palmitic had foam height of about 8.54 to 170.73% and the highest foam heights were found in potassium lauric at a molar ratio of 1:1 (170.73%) and potassium palmitic at a molar ratio of 1:1 (162.2%). The histogram of the analysis of foaming ability of sodium oleic, lauric, palmitic and potassium oleic, lauric, palmitic is depicted in Figure 2. There was a tendency that wider molar ratio resulted in higher foaming ability.

![Foaming Ability](image)

**Figure 2.** Histogram of the analysis of foaming ability of sodium oleic, lauric, palmitic and potassium oleic, lauric, palmitic

3.2.3. Surface Tension

Surface tension of a liquid is a work done to widen the liquid surface expressed in a unit area. Surface tension occurs because there is an adhesive force between liquid and air. The surface of a liquid tends to get tensed making the surface look like a thin film. This is affected by a cohesive force between molecules of water. Surface tension works only on the surface area and it is evenly spread all over the points. The cohesive force between molecules in a liquid is equal in all directions, yet molecules on liquid surface are more forced downward into the liquid. In this study, it was found that surface tension of sodium oleic, lauric, palmitic was 11.08–30.60 dyne/cm and of potassium oleic, lauric,
palmitic was 11.91–39.30 dyne/cm. The histogram of the analysis of surface tension of sodium oleic, lauric, palmitic and potassium oleic, lauric, palmitic is depicted in Figure 3. There was a tendency that wider molar ratio resulted in lower surface tension. This tendency was in line with that of foam stability but inversely proportional to that of foaming ability.

![Figure 3](image-url)

**Figure 3.** Histogram of the analysis of surface tension of sodium oleic, lauric, palmitic and potassium oleic, lauric, palmitic

### 3.2.4. Interfacial Tension

Interfacial tension is a force per unit length which occurs at interfaces of two phases which are not immiscible. Interfacial tension is always lower than facial tension as the adhesive force between two liquids which are not immiscible is bigger that the adhesive force between liquid and air. Results in this study showed that the interfacial tension of sodium oleic, lauric, palmitic was 0.93–3.93 dyne/cm and of potassium oleic, lauric, palmitic was 1.32–9.85 dyne/cm. The histogram of the analysis of interfacial tension of sodium oleic, lauric, palmitic and potassium oleic, lauric, palmitic is depicted in Figure 4. There was a tendency that wider molar ratio resulted in lower interfacial tension.
Figure 4. Histogram of the analysis of interfacial tension of sodium oleic, lauric, palmitic and potassium oleic, lauric, palmitic.

It was shown that potassium palmitic had the best results as shown in its foam stability of 82% on day 3, foaming ability of 162.2%, surface tension of 19.79 dyne/cm, and interfacial tension of 1.32 dyne/cm. Compared to the other type of surfactant (commercial), the potassium palmitic foams were more stable. On the first day, the stability of commercial surfactant foams was found to drastically drop which continued to the second day when it was found to be below 40%. The comparison between the stability of potassium palmitic foams and that of commercial surfactant foams is shown in Figure 5.

Figure 5. Results of the stability test of potassium palmitic and commercial surfactant foams
3.3. Selection of Potassium Palmitic Concentration
In this stage, selection of 3, 5, and 7% concentration of potassium palmitic was done and analyzed. Measurements were taken on foam stability, foaming ability, surface tension, solution viscosity, solution density, and wettability (contact angle).

3.3.1. Foam Stability
It was found that the foam stability of potassium palmitic at 3, 5, 7% gave was 32.9 - 85% on day 3. The histogram of the analysis of foam stability of potassium palmitic is depicted in Figure 6. It was shown that higher concentration of potassium resulted in higher foam stability. Potassium palmitic of 7% gave the highest foam stability (85.2%) on day 3. This indicated that potassium palmitic at the concentration of 7% gave relatively longer foaming effect to be applied on firefighting.

3.3.2. Foaming Ability
It was found that foaming ability of potassium palmitic at the concentration of 3, 5, and 7% was 192.68 to 214.63%. The histogram of foaming ability is depicted in Figure 7. It was shown that higher concentration of potassium palmitic resulted in higher foaming ability. Potassium palmitic 7% had the highest foaming ability.

3.3.3. Surface Tension
The surface tension of potassium palmitic at the concentration of 3, 5, and 7% was 39.25 – 55.40 dyne/cm. The histogram of surface tension of potassium palmitic is depicted in Figure 8. Higher concentration of potassium palmitic was found to result in lower surface tension. Potassium palmitic 7% had the lowest surface tension. Low surface tension of soap indicates its better ability to dissolve air. In other words, it can be said that low surface tension made the emulsion of air and soap solution easier to occur which could lead more foam formation.

![Figure 6: Histogram of foam stability of potassium palmitic](image1)

![Figure 7: Histogram of foaming ability of potassium palmitic](image2)
3.3.4. **Viscosity**
The viscosity of potassium palmitic at the concentration of 3, 5, and 7% was 1.18–1.87 cP. The histogram of viscosity of potassium palmitic is depicted in Figure 9. Higher concentration of potassium palmitic was found to result in higher viscosity. Potassium palmitic 7% had the highest viscosity (1.87 cP).

![Figure 9. Histogram of viscosity level of potassium palmitic](attachment:image.png)

3.3.5. **Density**
The density levels of potassium palmitic at the concentration of 3, 5, and 7% was 0.99734 – 0.99863 g/cm³. The histogram of density level of potassium palmitic is depicted in Figure 10. Higher concentration of potassium palmitic was found to result in higher density. Potassium palmitic 7% had the highest density level (0.99863 g/cm³).

![Figure 10. Histogram of density level of potassium palmitic](attachment:image.png)

3.3.6. **Wettability (Contact Angle)**
Contact angle test was done at hydrophilic and hydrophobic solid surfaces. The contact angle of potassium palmitic at the concentration of 3, 5, and 7% at minute 0 was 60.31°–65.56° which reduced to 21.15°–33.64° at minute 10. The histogram of contact angles of potassium palmitic is depicted in Figure 11. It was shown that at minute 10, higher concentration of potassium palmitic resulted in
higher reduction of contact angles. Potassium palmitic 7% had the lowest contact angle and the highest contact angle reduction of up to 44.41°. Lower contact angle indicated that the resulted soap was hydrophilic and had higher surface energy so that its adhesive force to the surface was stronger.

![Contact Angle vs Concentration](image)

Figure 11. Histogram of contact angle

The selection process of potassium palmitic concentration showed that higher concentration of potassium palmitic increased foam stability, foaming ability, viscosity, and density and reduced surface tension and contact angle at minute 10. Potassium palmitic 7% had the highest foam stability (85.2%), foaming ability (214.63%), surface tension (43 dyne/cm), viscosity (1.87 cP), density (0.99863 g/cm³), and contact angle reduction (44.41°).

4. Conclusions
Sodium oleic, lauric, palmitic and potassium oleic, lauric, palmitic had foam stability of about 2-3 days. Potassium palmitic with a molar ratio of 1:1 was the best product with a foam stability on day 3 of up to 82%. The best potassium plamitic concentration was 7%. It was suggested that formulation of foaming agent for firefighting application be made by using potassium palmitic with a molar ratio of 1:1.

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