Synthesis of potassium methyl ester as foaming agent

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Abstract. Forest and land fires in Indonesia have been historically causing extensive damages and losses on economies, ecosystems, and environment, and affects all life in the region. Forest fire management in Indonesia still relies on water that is less effective than foaming agents i.e., extinguishers. Chemicals used in conventional extinguishers are expensive. Foaming agents based on palm oil can be used as an alternative for the extinguishers. The foaming agent synthesized in this study was potassium methyl ester, made from palm oil methyl ester (ME), with saponification by adding potassium hydroxide (KOH). The forming performance tests (foam stability and forming ability) and form related physicochemical analyses (surface economies, interface surface tension, density, and contact angle) of potassium methyl ester were conducted with ME:KOH molar ratio of 1:1; 1:1.25; and 1:1.5 and the saponification duration of 1.5, 2 and 2.5 hours. The molar ratio had significant effects on foam stability, interface surface tension, density, and contact angle. The duration of the saponification had a significant effect on density. There was no significant effect of the interaction between the molar ratio and saponification duration. The best foaming agent selected by the ranking method (composite performance index) of foam stability, foaming ability, and surface tension were one with ME:KOH molar ratio of 1:1 and 1.5 hours saponification.

Keywords: palm oil, potassium methyl ester, foaming agent, extinguishers for forest and land fires

1. Introduction

NASA Active Fire Data in 2015 reported that forest and land fires in Indonesia were estimated at over 2 million hectares. The number of losses and damages by those fires was estimated as much as 15 billion USD. Those losses were in the form of ecological, social, health, and economic losses such as loss of biodiversity, ecosystem changes, environmental damages, decreased tourism revenues, health disorders of fauna and human, and so on. The use of water to extinguish fires which have been the major practice to control fires is not optimal compared to the addition of foaming agents, as foaming agents can inhibit the entry of oxygen into the fire point, so more effective. The use of foaming agents for fire extinguishers costs because foaming agents for the forest and land fires are imported to the country at relatively high prices and are generally not environmentally friendly. The use of natural-based foaming agents such as palm oil is better for fresh and seawater biota compared to conventional extinguishers [1].
Extinguishing forest and land fires by water cannot be worked out effectively as water is not able to cover the surface and penetrate into the burning objects. This is due to the high surface tension of the water. By reducing the surface tension of water so that it easily covers the surface and penetrates into the inside of burning objects, stopping oxygen supply as well as decreasing immediate surface temperature eventually facilitates fire suppression [2].

The ability of surfactants to reduce surface tension is brought by the amphipathic structure of molecules, i.e., a molecular structure consisting of hydrophilic and hydrophobic groups to bind those components together [3]. The interaction of the hydrophilic and hydrophobic groups of surfactants can reduce the surface tension of water by the following phases: surfactants break the hydrogen bonds on the surface. The hydrophilic portion of the surfactant will stretch away from the surface of the water then micelles are formed. The hydrophilic portion of the surfactant dissolves in water while the hydrophobic part of the hydrocarbon is soluble in non-polar substances. As a result, a surfactant molecule is not completely soluble in water but suspended in water. Surfactant solutions in water show sudden changes in physical properties in a certain concentration range. This sudden change is caused by aggregate formation or clumping of several surfactant molecules into one, i.e., at the critical micelle concentration (CMC) [4].

Fires can be classified into classes of A, B, C, and D. Every type of fire requires a specific foam to be extinguished. Forest fires are class A, i.e., fires caused by flammable materials, such as wood, paper, cloth, and other fibrous materials. This type of fire can be extinguished using sand, extinguishing powder, foam, and water. Type A foaming agent was synthesized by Rivai et al. [5], using palm oil-based materials. The treatment given in the study was the mol ratio of reactants (1:0.5; 1:0.75; and 1:1). The best result in the study was a foaming agent with a mol ratio of 1:1. In this study, the analysis of foaming agent palm oil-based methyl ester with KOH was conducted at the ME mol ratios: KOH of 1:1, 1:1.25 and 1:1.5 and the saponification durations of 1.5, 2 and 2.5 hours.

Foam stability is the ability of the foam to maintain parameters such as bubble size, fluid content, and total foam volume at a certain time. Foam lifetime is the simplest measure to show foam stability [8]. Foam stability and foaming ability are of the most important to suppress the fire, as stable foam can maintain parameters, i.e., bubble size, fluid content, and total volume, to prevent the supply of oxygen into the fire point in a long time to facilitate fire suppression. Surface tension is closely related to foam stability. The addition of foaming agents was carried out to reduce surface tension to produce penetration properties and to increase the cooling effect.

Interfacial tension and contact angle are also essential factors in determining the best foaming agent. The addition of foaming agents aims to reduce the interfacial free energy or interfacial tension. Therefore, it can facilitate mixing between two phases, i.e., foaming agents and fire sources so that the fire is easily extinguished because there is no space at the interfacial boundary.

2. Materials and Methods

2.1. Materials

The main materials used in this study were Methyl Ester olein, KOH, water, and other chemicals for physicochemical analysis.

2.2. Methyl Esters Analysis (SNI 7182-2015)

The analysis was carried out to determine the physicochemical properties of methyl esters which include ester number, acid number, saponification number, total glycerol, density, and viscosity.
2.3. Synthesis of Potassium Methyl Esters (modified “Rivai et al. [5]”)

The synthesis of potassium methyl esters (Figure 1) was carried out using a saponification reactor with a control variable temperature of 75°C, stirring speed of 13 rpm, direct mixing method, independent variable mole reactant ratio (1:1, 1:1.25 and 1:1.5) and at saponification durations (1.5, 2 and 2.5 hours).

![Flowchart of potassium methyl ester saponification](image)

Figure 1. Flowchart of potassium methyl ester saponification

2.4. Form Performance Analysis of Potassium Methyl Ester (modified “Denkov et al. [9]”)

The foam performance test was carried out using the hand-shakes (Bartsch Method) using a 100 mL covered measuring cup. Foam analysis was carried out to see the foam height decrease for 3 hours. The foam stability value was obtained by the difference in foam heights between 0 hour and 3 hours. The foam stability test was conducted by diluting the foaming agent into a 1% (w/w) concentration solution of 30 mL then the solution was put into a 100 ml measuring cup, shaken 20 times. The foam height was measured exactly when the foam became stable every following hour. The foam percentage was calculated against the foam height when the foam was formed. This is a modification of the foam testing method of Denkov et al. [9], where foam height was measured once a day for three days. The foam produced by the foaming agent in this study did not last more than a day, so measurements were taken every hour.

\[
\text{Foaming Ability} = \frac{H_0}{H_w} \times 100\% \\
\text{Note}: \quad H_0 = \text{Initial form height} \\
\text{H}_w = \text{Water height}
\]

\[
\text{Foam stability} = \frac{H_n}{H_0} \times 100\% \\
\text{Note}: \quad H_n = \text{Foam height at three hours} \\
H_0 = \text{Initial form height}
\]
2.5. Analysis of the Physicochemical Properties of Potassium Methyl Esters ([10])

The analysis was carried out on potassium methyl esters which had been dissolved using water to obtain a solution concentration of 1% (w/w). The solution was made by stirring using a stirrer until a homogeneous solution was obtained. The stirring speed was set to the limit before the foam formation. The analysis performed includes surface tension, interfacial tension, density, and contact angle.

2.6. Analysis of Acid Number and Free Alkali (SNI 01-3555-1998)

The analysis was conducted to examine the remaining acid and free alkali formed from the saponification [11].

2.7. Experimental design

This study used a completely randomized design with 2 factors of the reactant mole ratio and the saponification durations with the treatment codes as shown in Table 1.

| Codes | Treatment                                      |
|-------|-----------------------------------------------|
| A1    | Mole Ratio ME:KOH = 1:1                       |
| A2    | Mole Ratio ME:KOH = 1:1.25                   |
| A3    | Mole Ratio ME:KOH = 1:1.5                    |
| B1    | Saponification duration of 1.5 h             |
| B2    | Saponification duration of 2 h               |
| B3    | Saponification duration of 2.5 h             |

The mathematical model in the experiment is as follows [12].
\[ Y_{ijk} = \mu + A_i + B_j + AB_{ij} + \varepsilon_{ijk} \]

Note:
- \( Y_{ijk} \) = response variable / result of observation because of the influence of factor A level i, factor B level j, replication k
- \( \mu \) = actual average influence (general average)
- \( A_i \) = the influence of the reactant mole ratio factor at the level i (i=1:1, 1:1.25, 1:1.5)
- \( B_j \) = the influence of the saponification duration factor at the level j (j=1.5, 2, 2.5 h)
- \( AB_{ij} \) = the interaction effect of mole reactant ratio (A) level i and duration of saponification (B) level j
- \( \varepsilon_{ijk} \) = the effect of errors of level i, level j, and replication k

2.8. Data Analysis

The analysis was conducted to determine the best foaming agent based on the ratings given to the foaming agent treatment. Decision making was done by the composite performance index (CPI) method. This method can be used to rank various alternatives based on several criteria [13].

3. Results and Discussions

3.1. Methyl Ester Physicochemical Properties

Raw materials of methyl ester olein were used. Methyl esters are derivatives of oil or fat triglycerides which can be produced from the esterification and transesterification. Analysis of methyl ester was based on SNI 7182-2015 [14], i.e., acid number, saponification number, total glycerol, ester number, density, and viscosity. The test results are shown in Table 2.
Table 2. Physicochemical properties of methyl ester olein

| Test Parameter     | Unit             | Analytical Result |
|-------------------|------------------|-------------------|
| Acid number       | mg KOH/g material | 0.22              |
| Saponification number | mg KOH/g material | 168.86          |
| Total glycerol    | %-mass           | 0.188             |
| Ester number      | %-mass           | 97.81             |
| Density           | kg/m³            | 881.35            |
| Viscosity         | mm²/s (cSt)      | 47.09             |

3.2. Foam Stability

The foam stability of foaming agents ranged from 15.50-78.50%. The highest foam stability was 78.50%, with a foaming agent to mole ratio ME:KOH 1:1 and the saponification duration of 2 hours. The lowest foam stability was 15.50%, with a foaming agent of mol ratio ME: KOH 1:1.5 and 2 our saponification duration (Figure 2).

![Figure 2. Effect of reactant mole ratio and duration of saponification duration on foam stability of potassium methyl ester](image)

3.3. Foaming Ability

The foaming agent with a mole ratio of ME:KOH 1:1 and the 2 hours saponification showed 267.5% forming stability. While the lowest foaming ability of 186.5% with the mole ratio of ME:KOH 1:1.5 and 2 hours saponification (Figure 6). Saponification had no significant effect on the foaming ability of the foaming agent.
Figure 3. Effect of reactant mole ratio and duration of saponification on foaming ability of potassium methyl ester

3.4. Surface Tension

Surface tension ranged in 25.03-27.80 mN/m (Figure 4). The lowest surface tension was obtained with mole ratio ME:KOH 1:1 and the 2.5 hours saponification, while the highest was with the mole ratio of ME: KOH 1:1.5 and the 1.5 hours saponification. The addition of KOH was linearly correlated to the increase in surfactant surface tension, the higher mole ratio of reactants, the higher surface tension. The analysis of variance indicated that the mole ratio and the saponification duration did not significantly affect the surface tension of the foaming agent.

Figure 4. Effect of reactant mole ratio and saponification duration on the surface tension of potassium methyl ester

3.5. Interfacial Tension

The lowest interfacial tension of 0.82 mN/m was observed with the mole ratio of ME:KOH 1:1 and the 1.5 hours saponification, while the highest interfacial tension of 1.62 mN/m with ME: KOH 1:1.5 mol ratio and 2 and 2.5 hours saponification (Figure 5). Analysis of variance showed that the mole ratio had a significant effect (α = 0.05), while the saponification duration had no significant effect on the interface voltage of the foaming agent.
The surfactant can reduce surface tension and interfacial tension, increase the stability of the dispersed particles and can control the type of formulation in either oil in water (o/w) or water in oil (w/o) [3]. Surfactants in low concentrations have the properties to be adsorbed on the surface and interface of a system and are able to reduce surface free energy and interfacial free energy. Interfacial free energy or interfacial tension is the minimum amount of energy needed to make the system remain in two non-intermixed phases so that the interfacial boundary is formed between the two phases [15]. The interfacial tension had a correlation with the reactant mole ratio. It might have been higher interfacial tension if the higher KOH mole ratio was endorsed.

3.6. Density

The density of the resulting foaming agent ranged from 0.99615 to 0.99679 g/cm³ (Figure 6). The lowest density was obtained with mole ratio ME:KOH 1:1.5 and 1.5 hours saponification, and the highest density of 0.99679 g/cm³ with mole ratio ME: KOH 1:1.5 and 2.5 hours saponification. The higher the ratio of the reactant mole ratio, the higher the density. This is in accordance with Rivai et al. [5], where density was inversely proportional to foaming ability. The lowest mole ratio of reactants produced the lowest density. The analysis of variance showed that the mole ratio and the saponification duration had a significant effect ($\alpha = 0.05$) on the interfacial tension of the foaming agent. However, the interaction of those two factors did not have a significant effect on the density tension of the foaming agent.
3.7. Contact Angle

The contact angle ranged from 38.73° to 48.58° at 0 minute then decreased to 22.41° and 27.40° at 10 minutes. The decrease in contact angle ranged between 23.09° and 26.92° (Figure 7). The highest decrease in contact angle was 26.92° with ME:KOH 1:1 mole ratio and 1.5 hours saponification, while the smallest is 23.09° with a mole ratio of 1:1.5 and saponification of 1.5 hours. The decreasing contact angle showed that the produced soap was hydrophilic and easier to glue to the surface [16]. This property is important in extinguishing forest and land fires as foaming agents and sprayed water will be easier to glue to the burning objects and reduce the surface temperature, so that the fire immediately extinguished. The analysis of variance showed that the mole ratio had a significant effect (α = 0.05), while the duration of the saponification had no significant effect on the contact angle of the foaming agent.

![Figure 7. Effect of reactant mole ratio and saponification duration on the decrease in the contact angle of potassium methyl ester](image)

3.8. Acid Number and Free Alkali

If it is excess alkali, a mixture of soap, glycerol, residual alkali and water is produced. Under less alkali, a mixture of soap, glycerol, and fatty acids is produced from alkaline hydrolyzed fatty acids [17]. The acid number and free alkali are shown in Table 3, the treatments of A1B1, A1B2, and A1B3 had acid numbers, whereas A2B1, A2B2, A2B3, A3B1, A3B2, and A3B3 had free alkali values. Formula with mole ratio ME:KOH 1:1.25 and 1:1.5 had excess alkali, those with a 1:1 mole ratio was less alkaline and contained fatty acids derived from alkaline hydrolysis.

| Treatment | Acid number | Free alkali (%) |
|-----------|-------------|-----------------|
|           | Replication | Mean            | Replication | Mean            |
|           | 1           | 2               |            | 1              | 2              |
| A1B1      | 2.81        | 3.37            | 3.09±0.28  | -              | -              |
| A1B2      | 0.56        | 0.70            | 0.63±0.07  | -              | -              |
| A1B3      | 0.51        | 0.56            | 0.53±0.03  | -              | -              |
| A2B1      | -           | -               | -          | 0.10           | 0.11           | 0.11±0.01     |
| A2B2      | -           | -               | -          | 0.15           | 0.14           | 0.15±0.01     |
| A2B3      | -           | -               | -          | 0.13           | 0.12           | 0.13±0.01     |
| A3B1      | -           | -               | -          | 0.25           | 0.22           | 0.24±0.02     |
| A3B2      | -           | -               | -          | 0.29           | 0.28           | 0.29±0.01     |
| A3B3      | -           | -               | -          | 0.24           | 0.23           | 0.24±0.01     |
Determination of the Best Foaming Agent

The determination of the best potassium methyl ester foaming agent was carried out by weighting each test parameter. The important factors in determination were foam stability, foaming ability, and surface tension. Foam stability, foaming ability, and surface tension parameters were given a weight of 20%. Interfacial tension and contact angle were given a weight of 15%. The density value in this study was given a weight of 10%. Weighting results using the composite performance index (CPI) method are shown in Table 4.

Table 4. Determination of the best foaming agent using the CPI method

| Treatment | FS (20%) | FA (20%) | ST (20%) | IT (15%) | D (10%) | CA (15%) | AV | R |
|-----------|----------|----------|----------|----------|---------|----------|----|---|
| A1B1      | 94.27    | 92.71    | 111.07   | 197.56   | 100.05  | 98.25    | 114| 1 |
| A1B2      | 100.00   | 100.00   | 109.75   | 174.19   | 100.05  | 99.74    | 113| 2 |
| A1B3      | 96.82    | 95.51    | 108.51   | 155.77   | 100.04  | 100.00   | 109| 3 |
| A2B1      | 44.59    | 77.57    | 105.99   | 126.56   | 100.03  | 89.34    | 88 | 5 |
| A2B2      | 77.71    | 81.12    | 105.18   | 123.66   | 100.03  | 93.08    | 95 | 4 |
| A2B3      | 76.43    | 86.36    | 104.32   | 113.29   | 100.01  | 94.74    | 95 | 4 |
| A3B1      | 22.93    | 72.71    | 102.63   | 106.58   | 100.01  | 84.25    | 78 | 7 |
| A3B2      | 19.75    | 69.62    | 101.35   | 100.00   | 100.01  | 89.65    | 77 | 8 |
| A3B3      | 22.95    | 77.57    | 100.00   | 100.00   | 100.00  | 93.91    | 79 | 6 |

Note:
FS = Foam stability
FA = Foaming ability
ST = Surface tension
IT = Interfacial tension
D = Density
CA = Decreased contact angle at 10th minute
AV = Alternative value
R = Rank

The highest records of those six parameters were indexed as 100.00. For those parameters of which forming encouraged, the indexes were scored proportionally. The others of which forming discouraged, reverse proportionally.

The foaming agent with mole ratio ME:KOH 1:1 and 1.5 hours saponification was ranked as the first. The mole ratio 1:1 seemed the best mole ratio. The addition of excessive KOH might have produced excess KOH and affected the performance of the foam. The most optimal saponification
duration seemed 1.5 hours, but the analysis of variance did not show that the saponification duration had significant effects on parameters except for the density.

4. Conclusions

The mole ratios of potassium methyl ester foaming agents affected foam stability, formability, interfacial tension, density, and contact angle. The saponification affected the density. The best foaming agent was with a 1:1 mole ratio and 1.5 hours saponification with characteristics of 74% foam stability, foaming ability 268%, surface tension 25.03 mN/m, interfacial tension 0.82 mN/m, density 0.99615 g/cm³ and decreased contact angle 26.92º.

Synthesized foaming agents had relatively high foaming ability compared to other palm oil-based foaming agents in Rivai et al. [5], but had very low foam stability, which did not stay more than 24 hours. Further research on foaming agent formulations should be carried out using other palm oil-based materials such as lauric acid and palmitic acid. Synthesis with the addition of emulsions or other additives might have improved foam stability. The saponification duration might have had significant effects on form parameters in variations of solution concentration such as 3% or 5% (w/w).

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