Application of Mono-Diacyl Glycerol from Palm Oil By Product as Emulsifier for Body scrub

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Abstract. Mono-diacyl glycerol (M-DAG) widely used as food emulsifier, where in this study was produced through esterification of palm fatty acid distillate (PFAD) and glycerol from biodiesel by product. This research aimed to found the best formulation of the purified M-DAG on body scrub and identify physical characteristics of the product. This study is divided into two stages. First, is the selection of the preferred body scrub formulation based on the color, homogeneity, impression in the skin, the ability to remove dead skin’s cells and viscosity through the hedonic test. The selected formula then treated by M-DAG concentration (4%, 4.5%, 5%) and the type of scrub (rice, oat, PE20) at the second stage. Different concentrations of M-DAG give significant influence on density of body scrub but not for pH. While different types of scrub give significant influence on pH and density. Different concentration of M-DAG affect the size of emulsion globula. When the higher concentration used, the smaller globulas are formed. Body scrub with MDAG addition is stable at -4°C and 45°C and no heavy metals (Hg, Pb, As) were detected in the product. Based on the hedonic test towards parameters of texture, viscosity, and the ability to remove dead skin cell, it is known that 5% MDAG + PE20 formula has the highest preference level from panelist.

1. Introduction
Body scrub is basically a cosmetic used to treat the skin especially for women. The use of body scrubs can remove dry, dull, and lifeless skin without causing side effects on the skin. this product is generally in the form of emulsion cream and emulsion paste [1].

Emulsion system provides an important role in determining body scrub texture. The emulsion is a heterogeneous system consisting of two non-mixed liquid phases but one fluid is well dispersed in the other liquid in granular form [2]. Emulsifiers are used to stabilize the emulsion and give specific characteristic to the final product. Common emulsifiers used in body scrub are Cetyl Alcohol and Cetyl Glucoside. Both emulsifiers are widely used because they have good qualities such as giving a soft texture when used and can maintain skin moisture by reducing water evaporation on the skin. In addition, both emulsifiers are in a wide range and are not sensitive to hydrolysis [3].

Mono-Diacyl Glycerol (M-DAG) is the most widely used synthetic emulsifier, about 70% in the food industry with GRAS status (generally recognized as safe) so it is safe for consumption [4]. Moreover, this emulsifier is used in cosmetic, pharmaceutical, and other industries [5]. M-DAG can be produced through three different processes, that is hydrolysis, glycerolysis, and esterification. Hydrolysis is the process of forming glycerol and free fatty acids through the breakdown of fat molecules and the
addition of water elements [6]. This procedure generally involves the activity of enzymes and microbes. While glycerolysis is the process of transesterification of oil (triglycerides) with glycerol, using the help of chemical or enzyme catalysts. This process using an inorganic alkali catalyst, takes place at high temperatures, between 220°C-250°C.

In this study, we examined the utilization of M-DAG in body scrub formulations. M-DAG was synthesized by esterification of glycerol with fatty acid from palm fatty acid distillate (PFAD), using a methyl ester sulphonate (MESA) catalyst. The preferred synthesis process was chosen because the reaction temperature is lower than glycerolysis, ie 110-130°C and shorter reaction time.

2. Materials and Method

2.1. Materials
The material used for M-DAG synthesis was glycerol from biodiesel by products and methyl ester sulfonic acid (MESA) catalyst from palm oil derivates which has been purified from Surfactant and Bioenergy Research Center (SBRC), Palm Fatty Acid Distillate (PFAD) from PT Asianagro Agungjaya and zeolite. For M-DAG purification we used sodium bicarbonate, hexane and alcohol 96%/v/v. Stearic acid, olive oil, tween 60, cethyl alcohol, lip luxe, methyl paraben, propyl paraben, BHT, TiO2, sorbitol, TEA, destilled water, PE20 scrub, rice, oats and essential oils are used for body scrub formulations.

2.2. Glycerol Purification
Purification of glycerol was done to separate the crude glycerol from biodiesel by-product with residual methanol, catalyst, and other materials to obtain high purity glycerol (>90%/b/b). As much as 20 liters of crude glycerol mixed with 1 liter of 85% phosphoric acid, stirred at 75 C with agitation of 6.7 Hz for 120 min. After precipitation for 24 hours, the pure glycerol layer then filtered by vacuum filtration to remove residual salts and free fatty acids. Furthermore, glycerol was evaporated to remove water and methanol [7,8]. Product characterizations includes glycerol content, ash, pH value, and color.

2.3. Synthesis of Crude and Purified Mono-Diacyl Glycerol (M-DAG)
The crude M-DAG preparation was carried out by reacting glycerol and PFAD at 25 L batch vacuum reactor, a molar ratio of glycerol and PFAD was 1:6 and 1.5% w/v MESA catalyst. It was performed at 120°C, vacuum pressure -2.5inHg, moderate agitation for 75 minutes. Characterizations of the crude M-DAG include free fatty acid content, melting point, ash, emulsion stability [9], pH, color, texture, and odor.

M-DAG Purification is done by extraction, saponification and crystallization at low temperature. The purification procedure was initiated by adding a mixture of hexane and ethanol to the crude MDAG with volume-weight ratio of 5:1. The ratio of solvents volume was 1:1. The mixture was then homogenized with addition of 15% sodium bicarbonate. The saponified sample is then allowed to stand for 10 minutes to remove residual alkali. The filtrate is then crystallized at a low temperature for 24 hours. The formed M-DAG crystals filtered and washed with 96% ethanol and cooled for 24 hours. Product characterization includes visual appearance (texture, odour, colour), yield, free fatty acid content, emulsion stability [9], pH, ash, and glycerol content.

2.4. Body Scrub Formulation
The body scrub formulation begins with the preparation of two phases of the solution, ie oil phase (stearic acid, olive oil, cethyl alcohol, methyl paraben, propyl paraben, BHT, and TiO2) and water phase (distilled water, TEA, and sorbitol) with formulations like bellow (Table 1). Both phases are heated in a separate container at a temperature of 70°C. After that, both solutions are mixed and
homogenized at 2 000 rpm for 10 minutes until emulsion system was formed. To the emulsion then added scrub (oat, rice, or PE20 synthetic scrub) and essential oil (green tea oil and lavender oil) to improve the scent of product. Body scrub characterization include density, pH, emulsion type, globular size, heavy metal content and organoleptic. Bayes test performed on hedonic test results to find out the best body scrub formulation based on consumer preferences.

### Table 1. Body scrub formulation

| Composition       | Formula 1 (%) | Formula 2 (%) | Formula 3 (%) |
|-------------------|---------------|---------------|---------------|
| Stearic acid      | 2.54          | 9.4           | 7.8           |
| Cethyl alcohol    | 4.07          | 3.8           | 3.3           |
| Lip luxe          | 1.83          | -             | -             |
| Tween 60          | -             | -             | 2.8           |
| Olive oil         | 1.73          | 6             | 13.6          |
| Methyl paraben    | 0.20          | 0.6           | 0.6           |
| Prophyl paraben   | 0.10          | 0.34          | 0.34          |
| TiO2              | 1.02          | 0.74          | 3             |
| BHT               | 0.01          | 0.04          | 0.04          |
| Sugar             | 4.88          | -             | -             |
| Sorbitol          | -             | 3.4           | 3.3           |
| Destillate water  | 81.38         | 69.6          | 59.02         |
| TEA               | 0.19          | 0.44          | 0.2           |
| Scrub PE20        | 2.05          | 5.64          | 6             |
| Essential oil     | q.s           | q.s           | q.s           |

### 3. Result and Discussion

#### 3.1. Glycerol Purification and Characterization

The biodiesel industry produce crude glycerol as by product, approximately 12% of the total product [10]. Crude glycerol has a dark brown colour and bad odour because it contains catalyst, methanol, dissolve soap and impurities derived from biodiesel feedstock. Therefore, it is necessary to separate glycerol from other compounds and obtain high purity glycerol. The glycerol purification can be done by acidification with 85% phosphoric acid by 5% (v/v) of the crude glycerol [7]. The addition of phosphoric acid aims to break the dissolve soap molecules into free fatty acids and salts and neutralize the KOH catalysts into salt and water, following equation (1) and (2). Glycerol characteristics before and after purification can be seen on Table 2.

\[
\text{RCOOK} + \text{H}_3\text{PO}_4 \rightarrow \text{RCOOK} + \text{K}_3\text{PO}_4 \quad (1)
\]

\[
\text{RCOOK} + 3\text{KOH} \rightarrow \text{K}_3\text{PO}_4 + \text{H}_2\text{O} \quad (2)
\]

### Table 2. Characteristics of crude and purified glycerol

| Parameter         | Crude Glycerol [8] | Purified Glycerol | SNI 06-1564-1995 |
|-------------------|--------------------|-------------------|------------------|
| Glycerol content (%) | 40                 | 91.68             | Min. 80          |
| Ash (%)           | 5.52               | 2.18              | Max.10           |
| pH                | 11                 | 6                 | -                |
| colour            | Dark brown         | Dark brown        | -                |
Glycerol content are important because it determines the level of purity of glycerol products. Glycerol levels increased after purification, from 40% to 91.68% due to the separation of free fatty acids and salts from glycerol. The content of glycerol complied with the Indonesian standard (SNI 06-1564-1995) where the minimum glycerol content of 80%. Ash content decreased from 5.52% to 2.18% due to the elimination of inorganic compounds such as potassium salts from purified glycerol. It was obtained from residual catalyst used in transesterification process of oil into biodiesel [11]. pH of purified glycerol has decreased from 11 to pH 6. Crude glycerol has an alkaline pH because of the presence of KOH and dissolve soap. When reacted with phosphoric acid, there is binding of potassium ions from KOH and soaps to form salts [12]. The pure glycerol has a dark brown colour instead of light brown. This can be caused by the use of a high evaporation temperature (130°C). Thus triggering a Maillard reaction which causes the color becomes dark.

3.2. Mono-Diacyl Glycerol Synthesis and Purification

Mono-diacyl glycerol (M-DAG) is a non-ionic surfactant consisting monoglyceride (MAG) and diglyceride (DAG). Monoglycerides have one fatty acyl chain, while the diglycerides have two fatty acyl chains that are esterified with glycerol molecules [13]. In this study, M-DAG was produced by a simple esterification process between free fatty acids and glycerol chemically with the help of MESA catalyst. The reaction produces MAG, DAG, triacylglycerol (TAG), free fatty acid (FFA) and water. Crude M-DAG has a pasta texture, brown colour and rancid odour with a high content of FFA. Therefore, the purification step is done to remove unwanted compounds. The chemical physico-chemical characteristics of crude and purified M-DAG can be seen in Table 3.

| Table 3. Properties of crude and purified mono-diacyl glycerol |
|---------------------------------------------------------------|
| Parameter | Unit     | Crude MDAG | Purified MDAG |
| Yield     | %        | -          | 6.64          |
| Ash       | %        | 0.047      | 1.91          |
| FFA       | %        | 36.19      | 15.94         |
| Emulsion Stability | % | 2.14 | 63.70 |
| pH        | -        | 6          | 8             |
| Colour    | -        | brown      | white         |
| Texture   | -        | pasta, oily| dry powder   |
| Odour     | -        | rancid     | odorless      |
| Glycerol Content |     |          |              |
| • Total Glycerol | % | 0.39 | 0.38         |
| • Free Glycerol | % | 0.03 | 0.03         |
| • Bounded Glycerol | % | 0.36 | 0.35         |

Purification of M-DAG begins by mixing a crude M-DAG with a solvent to dissolve TAG, then saponification of FFA by alkaline (NaCHO3) addition. M-DAG was separated from the solvent and TAG by crystallization at a low temperature (4°C) because MAG and DAG will crystallize first, while TAG will remain soluble in the hexane and dissolve soap soluble in methanol [14]. Thus the M-DAG crystals can be easily separated by a vacuum filtration procedure. Washing with alcohol was done to removed residual impurities such as ALB, TAG and NaCHO3.

Pure M-DAG yield is quite low, ie 6.64% predicted because most of the product dissolves in the solvent fraction. The pure M-DAG ash content is higher than crude M-DAG, that can be caused by the presence of NaCHO3 residue from the saponification process. In addition, the saponification process also causes an increase in the pH of the product. The selected purification technique effectively
reduced FFA from 36.19% to 15.94%, since most fatty acids are soluble in the hexane. The decrease in FFA correlates with increased on emulsion stability. The emulsion stability of pure M-DAG is 63.70%. Pure M-DAG has white colour, dry powder textured and odorless that resembles the visual characteristics of commercial products.

3.3. *Body Scrub Formulation*

![Figure 1](attachment:image.png)

**Figure 1.** Panelist preferences on colour (a), homogeneity (b), skin impression (c), ability to remove dead skin cells (d) and viscosity (e) of body scrub formula
All body scrub formulations were tested organoleptically using a hedonic test with a limited panelist (10 people). Parameters tested include color, homogeneity, impression on the skin, the ability to remove dead skin cells, and viscosity (Fig. 1). Color is a sensory attribute that first attaches to a product and becomes one of the valuation factors in product selection by consumers. Body scrub produced in this study are generally white in colour. The color difference is influenced by the concentration of TiO$_2$ which acts as a coloring agent and gives a glossy impression to the product. The impression when body scrub applied to the skin and homogeneity is influenced by the product composition and the emulsifier ability to form and maintain a stable emulsion system. From the organoleptic test, it is known that the highest consumer preference is obtained from formula 2 for the five observed parameters.

Bayes method is used to determine the best formula based on previous hedonic test results. Previously, all five observed parameters were ranked based on interest index, from the most important parameter to the least one (5-1). The interest index refers to the main body scrub function as exfoliative. The parameters considered most important in determining the body scrub formulation are the ability to remove dead skin cells, viscosity, skin impression, homogeneity and color. The results of the Bayes method analysis show that formula 2 is the best formula with a total value of 2.78 (Table 4). Thus, it can be concluded that formula 2 is used as a reference in the next formulation of body scrub. The selected formula then modified by substituting cetyl alcohol with M-DAG of 4%, 4.5%, and 5% w/w with the type of scrubs of PE20, rice and oats. The modified body scrub formulation follows the composition as described in Table 5. Product characterization includes physico-chemical and organoleptic properties described on the next point.

**Table 4.** Weight of organoleptic parameters by Bayes Method

| Parameter                    | Formula 1 | Formula 2 | Formula 3 | Weight Value |
|------------------------------|-----------|-----------|-----------|--------------|
| Colour                       | 1         | 3         | 2         | 0.44         |
| Homogeneity                  | 3         | 2         | 1         | 0.22         |
| Skin impression              | 2         | 3         | 1         | 0.15         |
| Remove dead skin cells       | 2         | 3         | 1         | 0.09         |
| Viscosity                    | 1         | 3         | 2         | 0.11         |
| Total value                  | 1.67      | 2.78      | 1.55      |              |
| Rank                         | 2         | 1         | 3         |              |

**Table 5.** Modified formula of body scrub

| Composition       | Formula 1 (%) | Formula 2 (%) | Formula 3 (%) |
|-------------------|---------------|---------------|---------------|
| Stearic acid      | 9.4           | 9.4           | 9.4           |
| M-DAG             | 4             | 4.5           | 5             |
| Olive oil         | 6             | 6             | 6             |
| Methyl paraben    | 0.6           | 0.6           | 0.6           |
| Propyl paraben    | 0.34          | 0.34          | 0.34          |
| TiO2              | 0.74          | 0.74          | 0.74          |
| BHT               | 0.04          | 0.04          | 0.04          |
| Sorbitol          | 3.4           | 3.4           | 3.4           |
| Destilled water   | 69.4          | 68.9          | 68.4          |
| TEA               | 0.44          | 0.44          | 0.44          |
| Scrub             | 5.64          | 5.64          | 5.64          |
| Essential oil     | q.s           | q.s           | q.s           |
3.4. Product Characterization
Identification of heavy metal content in body scrub is important because it is related to the skin health of consumers. Heavy metal identification was performed on three types of metals, i.e. arsenic (As), lead (Pb) and mercury (Hg). The results showed that pure MDAG and body scrub are free from heavy metals. Thus, both are safe to use (Table 6).

Table 6. Heavy metal identification of purified MDAG and body scrub

| Parameter | Unit | Result          | Limit of Contamination | Method |
|-----------|------|-----------------|------------------------|--------|
| Pb        | ppm  | Not identified  | 0.14                   | ICP    |
| Hg        | ppm  | Not identified  | 0.02                   |        |
| As        | ppm  | Not identified  | 0.008                  |        |

Globular size is one of the physical characteristics that can be used to determine the emulsion stability of a product. The appearance and distribution of emulsion globules of body scrub can be seen in Figure 2. Observations were made using a light microscope with magnification of 40x10. The results showed that the higher concentration of M-DAG used, the globular size of the emulsion becomes smaller. Thus, the emulsion globula is better distributed and the emulsion system becomes more stable.

Figure 2. Morphology and distribution of emulsion globula at magnification 40x10: (a) M-DAG 4% (b) M-DAG 4.5% (c) M-DAG 5% (d) Cethyl Alcohol

The increased concentration of M-DAG affects the increase in pH value. As well as product density. Different types of scrub applications also affect pH changes. The use of PE 20 has the highest pH value at various M-DAG concentrations, i.e. 7.90, 7.92, and 7.94 respectively (Fig 3). The emulsion stability test was carried out through a freeze and thaw test in which the sample was stored at -4°C for 24 hours and then fed into a 45°C oven. This procedure repeated until 6 cycles (12 days). The observation showed that all samples do not show any phase separation. Emulsions are a heterogeneous
system containing two fluid phases, one being dispersed as globules in a dispersing medium. A good emulsion does not form layers, no change in colour and consistent.

Figure 3. pH and density of body scrub formula

Hedonic test also performed to modified body scrub formulas, for texture attributes, viscosity, and the ability to remove dead skin cells. Body scrubs with 5% M-DAG+rice scrubs have the highest value texture attributes, 5% MDAG + PE50 for viscosity and 4% MDAG + PE 50 for the ability to remove dead skin cells (Fig. 4). Parameter ranking from the most important was the ability to remove dead skin cells, viscosity, and texture. Bayes calculations to determine the best body scrub formula can be seen in Table 7. It was known that the best formulation obtained from the use of M-DAG 5% and PE20 with value 8.4.
Figure 4. Panelist preference for texture (a), viscosity (b) and ability to remove dead skin cells attribute of body scrub products.
4. Conclusion
Mono-diacyl glycerol (M-DAG) is a food and non-food emulsifier type with GRAS status so it is safe to use. M-DAG synthesis through esterification of glycerol and fatty acids takes place at lower temperatures and shorter reaction times. Purification is required to produce high purity MDAG. Purification using extraction, saponification and crystallization is able to remove free fatty acids significantly and produce a pure MDAG resembling the characteristics of commercial products. M-DAG application in a body scrub formulation affects the density and size of the globules. The type of scrub also affects the level of consumer preference for body scrub products. Based on the hedonic test of texture, viscosity, and ability to remove dead skin cells, formula which have the highest level of consumer preference obtained from body scrub with M-DAG 5% + scrub PE20.

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Table 7. The Bayes method analysis for modified body scrub formulas

| Parameter | 4% PE20 | 4.5% PE20 | 5% rice | 4% rice | 4.5% Oat | 5% Oat | Weight value |
|-----------|---------|-----------|---------|---------|---------|--------|--------------|
| Texture   | 5       | 3         | 8       | 1       | 2       | 9      | 6            | 4            | 7            | 0.26        |
| Viscosity | 2       | 3         | 9       | 1       | 5       | 7      | 6            | 4            | 8            | 0.32        |
| Ability to remove dead skin cell | 9       | 7         | 8       | 3       | 5       | 4      | 2            | 1            | 6            | 0.43        |
| Total value | 5.81   | 4.75      | 8.4     | 1.87    | 2.12    | 6.3    | 4.34         | 2.75         | 6.96         |
| Rank      | 4       | 5         | 1       | 9       | 8       | 3      | 6            | 7            | 2            |
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