Application of MAG (monoacyl glycerol) as emulsifier with red palm oil in body cream product

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Abstract. Palm Fatty Acid Destilate (PFAD) is one of the wastes from the palm oil processing. PFAD can be reacted with glycerol to form MAG (monoacyl glycerol). MAG is an emulgator that can be applied in a cosmetic product in the form of a red palm oil cream. Red palm oil is one of the products processed from palm oil that still has a lot of natural antioxidant content such as carotenoids and vitamin E. formulation of red palm oil cream is carried out by treating variations of stearic acid substitution with red palm oil 50%, 75% and 100% as the source of active ingredients and variations in the combination of MAG and tween 80 as emulsifiers with each weight ratio of 1:3; 2:2 and 3:1. Each formula is then characterized based on its physical properties such as type of emulsion, pH, and stability of the emulsion. Some formulas that have the best physical properties will be selected and continued with sensory and total carotene tests. The synthesize MAG used has the characteristics of water content, free fatty acids and free glycerol, each at 1.27%; 0% and 0.37%. with a pure MAG yield of 18.85%. The best formula for red palm oil cream is formula with variation of stearic acid substitution with red palm oil by 50% and a variation of the MAG: tween 80 combination of 2:2. The formula has a HLB emulgator value of 9.4 and contains active carotenoid of 311.82 ppm.

1. Introduction
There are so many kinds of skincare product in cosmetics industry, such as hand and body lotion, moisturizer, toner, milk cleanser, etc. When the cosmetic has an active ingredient that useful to human’s body it is called cosmesetical product. Cosmesetical has two kind of active agent based on the source. They are naturally and synthetic’s active agent. When the active ingredients are from part of the plant, it’s called naturally active agent. One plant in Indonesia, which contains many nutrients and active substances is red palm oil [1].

Red Palm Oil is one of the palm oil products which not have bleached process yet, so it has many active ingredients on there, and the active ingredients are from carotenoid and tocoferol. Carotenoids are a natural pigment that is reddish orange, orange to yellow. Carotenoids have a structure composed of 8 isoprene units and 4 methyl groups and conjugated double bonds between these methyl groups. The two methyl groups are located close to C-1 and C-6, while the methyl groups are located in positions C-1 and C-5. They called as active agents because they could be an antioxidant agent. Base
on clinical trials, it can eliminate black spots, wrinkles and moisturizer for human’s skin [2]. Carotenoids and vitamin E are a natural antioxidant that can counteract the reactive free radicals become inactive thereby protecting cells from oxidative damage to cells [3].

There are many ingredients in the cosmetic products and always includes some emulsifier. Emulsifier was very important because it can bond two compounds that have different polarity such as water and oil. Based on structure emulsifier have two main part of them, polar and non polar part. Polar parts, can bind with water and non polar parts can bind with oil compound, so the water can dissolve in oil or oil can dissolved in water, and the cosmetic products are always form by oil and water. At present, Cream is an emulsion type cosmetic product consisting of an oil phase and a water phase which is stabilized by an emulsifier and contains one or more active substances in it [4].

Palm fatty acid distillate (PFAD) is one of the wasted from palm oil production. PFAD has around 80% of fatty acid, and these fatty acids can be reacte with glycerol from esterification reaction to form monoacyl glycerol. MAG or monoacyl glycerol is one of many emulsifiers that we knew. It has two hydroxyl groups from glycerol and one of long carbon chain from fatty acid. Hydroxyl group as polar parts and the long carbon chain as non polar parts, so it must to be an emulsifier [5].

2. Materials and Methods

2.1. Materials
The material used for MAG synthesis was glycerol and para Toluene sulfonic acid (pTSA) catalyst, Palm Fatty Acid Destillate (PFAD) and zeolite were obtained from PT Asianagro Agungiayia. For MAG purification we used aquadesr, hexane and alcohol 96% v/v and for formulation we used red palm oil from ptpn viii PKS Cikasungka, stearic acid, sorbitol, methyl paraben, cetyl alcohol, tween 80 from PT Bratachelm Bogor and fragrance from PT Ogawa Indonesia.

2.2. Synthesis of Crude and Purified Monoacyl Glycerol (MAG)
The crude MAG preparation was carried out by reacting glycerol and PFAD at 25 L batch vacuum reactor, a molar rasio of PFAD and glycerol was 1:6 and 1.5% w/w pTSA catalyst. It was performed at 150 °C, vacuum pressure -2,5 inHg, moderate agitation for 60 min.

MAG Purification was performed by extraction and crystallization at low temperature. The purification procedure was initiated by adding a hexane to the crude MAG with volume weight ratio of 10:1. The mixture was then homogenized at a low temperature for 24 h. The filtrate was then crystallized with alcohol 96% at low temperature for 24 h. Product characterization included visual appearance (texture, odour, colour), yield, free fatty acid, glycerol content and water content.

2.3. Body Cream Formulation
The body cream formulation started with preparation of two phases of the solution. Oil phase (red palm oil, stearic acid, cetyl alcohol, MAG, methyl paraben) and water phase (destilled water, tween 80, and sorbitol) with formulation like bellowy (Table 1). Both phases were heated in a separated container at a temperature of 70 °C, after that, both solutions were mixed and homogenized at 600 rpm until emulsion system was formed. Fragrance was added to the emulsion. Body cream characterization included type of emulsion, pH, and stability of the emulsion. Some formulas that have the best physical properties were selected and continued with organoleptic and total carotene tests. Organoleptic test was performed to find out the best body cream formulation based on costumer preferences.

Formula was based on modified Young’s Formula, there were substitute of stearic acid with RPO in amount of 50 %, 75 % and 100 %. The more red palm oil are filled, the more active agent in the
The formula used MAG and Tween 80 as emulsifier which each variate had 6.6; 9.4; and 12.2 HLB values. MAG with 3.8 HLB value and Tween 80 with 15 HLB value can form emulsifier with HLB value between 3.8 and 15 HLB value.

### Table 1. Body cream formulation

| Composition     | F1 | F2 | F3 | F4 | F5 | F6 | F7 | F8 | F9 |
|-----------------|----|----|----|----|----|----|----|----|----|
| Red palm oil    | 6  | 6  | 6  | 9  | 9  | 9  | 12 | 12 | 12 |
| Stearic acid    | 6  | 6  | 6  | 3  | 3  | 3  | 0  | 0  | 0  |
| Cetyl alcohol   | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 1  |
| Sorbitol        | 5  | 5  | 5  | 5  | 5  | 5  | 5  | 5  | 5  |
| MAG             | 3  | 2  | 1  | 3  | 2  | 1  | 3  | 2  | 1  |
| Tween 80        | 1  | 2  | 3  | 1  | 2  | 3  | 1  | 2  | 3  |
| Methyl paraben  | 0.3| 0.3| 0.3| 0.3| 0.3| 0.3| 0.3| 0.3| 0.3|
| Aquades         | 100| 100| 100| 100| 100| 100| 100| 100| 100|

### Table 2. Properties of purified mono-diacyl glycerol

| Synthesis Result       | Weight (g) | Value (%) (w/w) | Yield (%) (w/w) |
|------------------------|------------|-----------------|-----------------|
| Crude MDAG             | 408.10     | -               | -               |
| Purified MDAG          | 85.50      | -               | 20.95           |
| MAG (90% MDAG)         | 7695       | 90              | 18.85           |
| DAG                    | 7.15       | 8.36            | 1.75            |
| Free Fatty Acid        | 0          | 0               | -               |
| Water Content          | 0.32       | 0.37            | -               |
| Free Glycerol          | 1.08       | 1.27            | -               |
Purification of crude MDAG begins by mixing a crude MDAG with hexane to dissolve TAG. MAG and DAG can be dissolved too in hexane, but their solubility decrease in low temperature. MAG and DAG (MDAG) was separated by vacuum filtration. Residue containing MDAG crystalized with alcohol 96% in low temperature for 24 h. Yield of MAG is very low, it can be cause of synthesis procedure, PFAD and glycerol molar ratio is 1:6, where the mole glycerol higher than PFAD, it aimed to increase the possibility of free fatty acids can react entirely with glycerol to form monoasil glycerol (MAG). Temperature conditions and optimum time was 150 °C for 60 min, if the temperature and time exceed the optimum conditions, the reaction will continue in the direction triasil glycerol (TAG), while the temperature and the time that is less than optimum conditions, will increase levels of free fatty acids.

3.2. Body Cream Characterization
Nine red palm oil cream formulas obtained, were selected again by testing the type of emulsion, emulsion stability and pH. The three tests refer to Wedana's (2016) research which is the most important physical test for cosmetic cream preparations. The formula that has the best physical test results was followed by a sensory preference test and a total carotene test.

Testing of emulsion type cream red palm oil for all formulas show the same results, namely the type of oil-in-water emulsion. Emulsion type o/w tends to be preferred because it is easily spread on the skin surface, easily removed with the washing as well as more acceptable because it is easy and convenient to be applied to the skin than the cream-type water in oil (w/o).

Glycerol monostearat or monooleate has 3.8 HLB value, and it works to make a water in oil emulsion, MAG could be combined with the other emulsifier which have higher HLB value to increase the HLB value. MAG with 3.8 HLB value and Tween 80 with 15 HLB value can form emulsifier with HLB value between 3.8 and 15 HLB value, if the HLB value increase, oil in water emulsion can form.

| Formula | Solubility in water | Methylene blue dispers | Type of emulsion |
|---------|---------------------|------------------------|------------------|
|         | Yes                 | No                     |                  |
| F1      | √                   | -                      | o/w              |
| F2      | √                   | -                      | o/w              |
| F3      | √                   | -                      | o/w              |
| F4      | √                   | -                      | o/w              |
| F5      | √                   | -                      | o/w              |
| F6      | √                   | -                      | o/w              |
| F7      | √                   | -                      | o/w              |
| F8      | √                   | -                      | o/w              |
| F9      | √                   | -                      | o/w              |
The test results showed that all formulas pH into the skin pH range. The pH value for each formula shows a number around 5. The pH value should not be too acidic because it can cause irritation to the skin, if the pH is too alkaline it can cause scaly skin, therefore the pH for cosmetic creams should be attempted into the physiological pH range according to SNI 16-4399-1996 of 4.5-8.

**Table 4. pH value**

| Formula | Ratio (w/w) of Red palm oil : stearic acid | MAG : Tween 80 | pH value (X ± SD) |
|---------|------------------------------------------|----------------|------------------|
| F1      | 6 : 6                                    |                | 5.26 ± 0.09      |
| F2      | 3 : 1                                    |                | 5.21 ± 0.01      |
| F3      | 2 : 2                                    |                | 5.56 ± 0.11      |
| F4      | 3 : 1                                    |                | 5.85 ± 0.01      |
| F5      | 9 : 3                                    | 2 : 2          | 5.45 ± 0.01      |
| F6      | 1 : 3                                    | 1 : 3          | 5.31 ± 0.01      |
| F7      | 3 : 1                                    |                | 5.55 ± 0.06      |
| F8      | 12 : 0                                   | 3 : 1          | 5.32 ± 0.02      |
| F9      | 1 : 3                                    |                | 5.69 ± 0.02      |

Emulsion stability test was carried out by centrifugation method, using Eppendorf tube and speed of 10,000 rpm at room temperature. This method is equivalent to one year of stability testing [7]. In this study, the emulsifier combination used was MAG and Tween 80. MAG based on the literature for glycerol monosterate and monooleats had HLB values of 3.8 while tween 80 had HLB values of 15, by combining both at certain weight ratios, some formulas with HLB values were varied.

**Table 5. Stability of Emulsion**

| Formula | Ratio (w/w) of Red palm oil : stearic acid | MAG : Tween 80 | HLB     | Stability |
|---------|------------------------------------------|----------------|--------|-----------|
| F1      | 3 : 1                                    |                | 6.6    | Stable    |
| F2      | 6 : 6                                    | 2 : 2          | 9.4    | Stable    |
| F3      | 1 : 3                                    | 1 : 3          | 12.2   | Less stable |
| F4      | 3 : 1                                    |                | 6.6    | Stable    |
| F5      | 9 : 3                                    | 2 : 2          | 9.4    | Less stable |
| F6      | 1 : 3                                    | 1 : 3          | 12.2   | Unstable  |
| F7      | 3 : 1                                    |                | 6.6    | Less stable |
| F8      | 12 : 0                                   | 2 : 2          | 9.4    | Unstable  |
| F9      | 1 : 3                                    |                | 12.2   | Unstable  |
The stability level of the red palm oil cream formula can be seen from the results of the centrifugation (Figure 1). Formula 1, 2, and 4 are said to be stable because there is no phase separation, where the oil phase does not separate at the top of the cream, while formulas 3, 5, and 7 are said to be less stable because the oil phase is slightly separated from the cream, finally for formulas 6, 8, and 9 are said to be unstable because many oil phases are separated from the cream. Based on the results of physical tests that have been carried out, it can be concluded that from the nine samples of red palm oil cream tested, formulas 1, 2 and 4 are the best formulas. The three formulas were further tested by sensory testing including the test of preference and total carotene test. Sensory tests and active ingredient levels are a further test of some of the best formulas physically red palm oil cream, this aims to ensure that the cream that has been made, is physically preferred and contains the desired active ingredients.

(Figure 1. Stability of Cream Emulsion)

(Formula one through nine from left to right) substitution red palm oil 50% (F1-F3); 75 % (F4-F6); 100% (F7-F9) and ratio MAG : tween 80 3:1 (F1, F4, and F6); 2:2 (F2, F5, and F7); 1:3 (F3, F7, and F9)

The sensory test conducted was the hedonic liking test, which aims to find out the preference or preference values of some individuals on the 3 physically best formulas of red palm oil cream. The assessment criteria used include assessment of aroma, color, thickness, impression of moisture and absorption. The panelists used were 30 untrained panelists, using a range of 1-5 assessment scores, the results of the assessment were then statistically tested to find out if there were any real differences from the panelists' preference for the treatment of the 3 formulas tested.

| Criteria       | F Result Sample | F Result Panelists | F table 5% | F table 1% |
|----------------|-----------------|--------------------|------------|------------|
| Aroma          | 0.57            | 1.03               |            |            |
| Color          | 3.11            | 0.32               | 3.17       | 5.00       |
| Thickness      | 0.18            | 0.66               |            |            |
| Impression of moisture | 2.64 | 1.67               |            |            |
| Absorption     | 0.23            | 1.97               |            |            |

Based on the ANOVA table, it can be seen that the F count for each parameter is smaller than the F table at the 5% and 1% levels, so it can be concluded that the three formulas are not significantly different in terms of aroma, color, viscosity, moisture impression and power absorbency. The panelists' preference level for the three samples can be sorted by their average points.

Organoleptic test results showed the best overall level of assessment of all parameters was formula 2 with a variation of substitution of red palm oil against stearic acid by 50% and variation in addition of MAG: tween 80 by 2: 2. The aroma parameter with the highest organoleptic test score was formula 1, however, this value is not significantly different from formula 2 at the levels of 5% and 1% (Table 9), therefore, formula 2 was chosen with a variation of substitution of red palm oil against stearic acid by 50% and variations in the addition of MAG: Tween 80 as much 2:2. The preferred level of the aroma
parameters of the chosen formula 2 is between the neutral and liking levels. The assessment can be improved by regulating the addition of fragrance in red palm oil cream. The characteristics of the second formula are thick enough texture, fresh light yellow, not oily, not sticky, sweet-scented and leaves a moist impression on the skin.

The active ingredients contained in red palm oil are Vitamin E and carotenoids. Both are types of vitamins that can ward off free radicals and clinically can inhibit cell damage from cell oxidation. Vitamin E is stable under acidic conditions and high temperatures, but its stability will decrease at alkaline pH. The level of stability of carotenoid compounds is greater than vitamin E, so in this study the active substance tested was total carotene.

Viewed from its structure, carotenoid compounds can be identified spectrophotometrically with wavelengths in visible light, this is evidenced by PORIM [8] who tested carotenoid compounds in palm dissolved in hexane resulting in maximum absorption values at wavelength of 446 nm. This result was also reinforced by De Man [9] who stated that the colors in carotenoids were formed due to conjugated bonds. The more bonds are conjugated in a molecule, the absorption band will shift to a higher wavelength region, so the color becomes redder.

The absorbance samples were measured with a spectrophotometer at a wavelength of 423 nm and obtained six points of the calibration curve with a straight line equation $y = 0.0164x + 0.0019$ and $R^2$ of 0.9996. The results of total carotene measurements in the steaming acid substitution formula cream samples with red palm oil 75% (Formula 4) and 50% (Formula 1 and 2) are 467.73 ppm and 311.82 ppm, respectively.

Vitamin E and carotenoids are antioxidants in cells that can prevent lipid peroxidation in the plasma membrane. Lipids in the plasma membrane contain abundant PU Unsaturated Fatty Acids which make them the main target of ROS because lipids have a carbon double bond. Carotenoids can protect PUFAs on membranes so that lipid peroxidation can be prevented. Lipid oxidation to membranes can cause damage to membrane structures that affect function and permeability resulting in cell damage and death, besides lipid peroxidation can damage enzyme activity on membranes and ion channels, resulting in the mechanism of the proliferation process is inhibited.

The mechanism of inhibition of lipid peroxidation by carotenoids begins when a lipid (LH) loses one hydrogen and becomes a radical product (L *) that reacts with free oxygen to produce peroxyl radicals (LOO *). Peroxil radical reaction will then be followed by a chain reaction that can disrupt the membrane structure. Carotenoids in the form of β-carotene can stop the chain reaction by interactions with peroxyl lipids to form β carotenyl radicals (β-Car *) so that they become stable.

4. Conclusion
MAG (monoacetyl glycerol) which is an emulsifier synthesized between glycerol and PFAD palm oil processing waste can be applied in a cosmetic product in the form of a red palm oil cream. The synthesized MAG used has the characteristics of water content, free fatty acids and free glycerol, each at 1.27%; 0% and 0.37%. The synthesized MAG has a 90% purity level with a pure MAG yield of 18.85%. The best red palm oil cream formula is formula 2, i.e., in the variation of stearic acid substitution with red palm oil by 50% and a variation of the MAG:Tween 80 combination of 2:2. The formula has a HLB emulsifier value of 9.4 and contains active carotenoid ingredients as an antioxidant of 311.82 ppm.
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