The Effect of Temperature on MDAG Purification Using Creaming Demulsification Technique

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Abstract. Mono and di-Acyl Glycerol (MDAG) are emulsifiers needed for the fat-based food industry. Glycerolysis method is the most inexpensive and widely used to synthesize MDAG. In order to serve MDAG to be an emulsifier, glycerol residues in it must be removed. Creaming demulsification technique (CDT) is a MDAG purification method that is proven to produce MDAG free of glycerol. CDT working principle based on the destruction of W/O emulsion system (glycerol/MDAG) physically. CDT makes the emulsion to be instable through the application of temperature, stirring, and the addition of an electrolyte solution. The objective of the research was to determine the effect of CDT operating temperature on purifying MDAG. Four levels of temperature (50, 60, 70 and 80 °C) were applied on CDT. The result showed that the higher temperature being caused (glycerol/MDAG) emulsion system easier to be demulsified. CDT application at 50°C could remove glycerol for 75.81% (from 12.69% to 3.07%). The temperature increased to 60°C had improved the amount of glycerol which could be separated into 95.43% (from 12.69% to 0.58%). At 70°C and 80°C, almost all glycerol had been separated from MDAG. CDT temperature of 70°C was the most effective to produce high quality MDAG.

1. Introduction
MDAG is classified as emulsifier with GRAS status in the United States with regulatory number 21 CFR 184.1505 and is permitted to be used in food products in Europe. MDAG has no restrictions on the value of the acceptable daily intake (ADI) [1]. MDAG is widely used in processing margarine, peanut butter, whitener, pudding, bread, biscuits, and other fatty pastries [2].

The cheapest and easiest way to synthesize MDAG is through the glycerolysis process. Glycerolysis is a reaction between oil and glycerol at a certain temperature and time with or without the addition of a catalyst [3], [4]. The MDAG produced from this process still contains high glycerol residues, therefore purification is needed to obtain a high quality MDAG. This glycerol residue is difficult to separate because it is strongly bound to one of the hydrophilic sides of MDAG in the form of an emulsion. Creaming demulsification technique (CDT) has been proven to remove glycerol residues and purify MDAG to more than 99.5% purity [5], [6], [7]. The destruction of the emulsion system occurs physically driven by the application of temperature, stirring and addition of electrolyte solutions.

The effect of temperature on MDAG purification is estimated to be very significant. At high temperature it is expected to be more effective because in this state the emulsion system is very unstable kinetically, so it will be easier to be demulsified (damage). This study aims to determine the effect of the operating temperature of the CDT on purifying MDAG.
2. Methods
In this study, the electrolyte solution used was CaCl$_2$ 5%, stirring was carried out with a stirrer at 300 rpm, and the MDAG raw material was obtained from the SEAFAST Center LPPM IPB.

The initial process of removing glycerol residue was heating MDAG to 80 °C in a beaker and adding 500 mL of MDAG at 50, 60, 70 and 80°C (according to treatment) into a 1 L reactor. Electrolyte solution (at the temperature of 10°C above the temperature of MDAG) was mixed while stirring for 15 minutes using an agitator at a speed of 300 rpm. The ratio of MDAG to the electrolyte solution was 1:1. The mixture was then left for 15 minutes until the skim and cream fraction was separated. The skim fraction was discarded and the cream fraction was washed using hot water with a temperature of 10°C higher than the cream temperature while stirring at 300 rpm using agitator for 15 minutes. The ratio of MDAG to hot water for washing was 1:1. After washing, the mixture is centrifuged at 2000 rpm for 5 minutes to separate the remaining skim fraction. MDAG products obtained from washing were ready for analysis [5].

The application of CDT operational temperature levels were arranged in a complete randomized design with 3 replications. The parameters observed in this study were the composition of MDAG using Gas Chromatography (Shimadzu GC-9AM, Japan, with an FID detector) and free fatty acid content [8].

3. Results and Discussions
MDAG purification with the CDT method was found to be more effective at high temperatures in removing glycerol residues from (Table 1).

| Parameters          | Raw Material | Purified MDAG at different CDT temperature (°C) |
|---------------------|--------------|-----------------------------------------------|
|                     |              | 50    | 60    | 70    | 80    |
| Total Glycerol (%)  | 12.69        | 3.07  | 0.58  | 0.00  | 0.00  |
| Free fatty acid (%) | 5.05         | 4.95  | 4.78  | 4.76  | 4.45  |
| MAG (%)             | 31.92        | 36.47 | 34.96 | 40.69 | 41.94 |
| DAG (%)             | 20.68        | 25.74 | 24.84 | 27.70 | 28.38 |
| TAG (%)             | 29.66        | 29.78 | 34.84 | 26.85 | 25.23 |

Table 1 showed that temperature had a significant effect on the removal of MDAG glycerol residues. CDT carried out at 50°C was not enough to damage the stability of glycerol-in-MDAG emulsion and separate all glycerol from the system. However, the amount of glycerol that can be separated from MDAG at 50°C was quite large, i.e. 75.81% (from 12.69% to 3.07%), which met the maximum value of quality standards of WHO (7%) [1].

The increase in temperature to 60°C improved the amount of glycerol separated from MDAG to 95.43% (from 12.69% to 0.58%). At 70°C and 80°C, almost all glycerol were separated from MDAG. The chromatogram results from GC analysis for the effect of CDT temperature on the amount of glycerol separated from MDAG are presented in Figure 1. This data proved that the application of the CDT method in removing glycerol residues from MDAG was very effective at temperatures above 60°C. At temperatures above 60°C, this method could eliminate glycerol residues, which was as effective as the use of molecular distillation (above 99%) [9], [10].
Before purification

Purification at 50°C

Purification at 60°C

Purification at 70°C

Figure 1. MDAG chromatogram before and after purification at various CDT temperatures

Figure 1 showed that glycerol residues in MDAG before purification that appears at a retention time of 3.302 minute has a high peak (concentration of 12.69%). CDT at 50, 60 and 70°C had relatively the same retention time but with lower peaks (concentration of glycerol residue of 3.07, 0.58, and 0.00%, respectively).

The CDT method is selective in its working system. This method only removes glycerol residues and other polar components, but not free fatty acids and / or other compounds. It can be seen that the free fatty acid content in pure MDAG products obtained tends to be constant with slight increase. The increase in free fatty acids in MDAG products after being purified by the CDT method at the appropriate temperature did not indicate an increase in the content during the purification process, but due to the decrease of other component concentrations in the whole composition of purified MDAG.

Among the four temperature levels studied in CDT for removing glycerol residues from MDAG, the temperature of 70°C was the most effective one. At this temperature, the qualities of MDAG products were not too different from those produced from 80°C. The temperature treatment of 70°C was considered more effective than the temperature of 80°C because of economical reasons. The temperature difference of 10°C in industrial applications was very significant in order to save energy and reduce production costs.

4. Conclusions and recommendations

In order to remove glycerol residues from MDAG, the CDT must be applied at a certain temperature sufficient to physically damage the W/O (glycerol/MDAG) emulsion system. CDT application at 50°C removed glycerol 75.81% (from 12.69% to 3.07%). Application at 60°C improved the removal of
glycerol (95.43%) or from 12.69% to 0.58%. At 70°C and 80°C, almost all glycerol separated from MDAG. CDT temperature of 70°C was the most effective to produce high quality MDAG.

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