

Purification engineering of mono-diacylglycerol using creaming demulsification technique in 20 kg-scale

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Abstract

Glycerolysis is the easiest, cheapest, and most widely used method for producing mono-diacylglycerol (MDAG). The crude MDAG resulting from chemical glycerolysis still contains a glycerol residue of more than 7.5% so it needs to be purified. Purification with a simple method using a creaming demulsification technique (CDT) on a laboratory scale has been proven to produce MDAG with a glycerol content of less than 1%. This study was aimed to apply CDT on a scale of 20 kg and determine the process conditions that need to be adjusted so that the results are not different from the laboratory scale. Through trial and error method, the process condition adjustment was done iteratively to produce MDAG glycerol content after purification of less than 1.5%. The initial content of crude MDAG was 12.48%, application of CDT on a scale of 20 kg produces pure MDAG with a glycerol residue content of 3.07% (without adjusting the process conditions) and was 1.15% (with adjusting the process conditions). The adjustments meant include: increasing the operating temperature from 65 to 70°C, changing the type of stirrer from a propeller into a 2-level impeller, applying the nozzle for electrolyte mixing, providing longer skim and cream separation opportunities (applying repeated settling), using 1.5 times more hot water for washing, the washing technique was set twice, the first washing using nozzle without stirring and the second using nozzle with stirring. The adjustments were able to increase the purity of the MDAG produced and has met the European Union and FAO/WHO standards.

1. Introduction

Glycerolysis is the easiest, cheapest, and most widely used method for producing mono-diacylglycerol (MDAG) (Cheng *et al.*, 2005; Chetpattananondh and Tongurai, 2008; Galucio *et al.*, 2011). MDAG produced from the glycerolysis still contains quite high glycerol residues, between 16.61–19.04% (Rachmawati, 2017) and 7.26–12.29% (Agustina, 2019). The presence of glycerol in MDAG reduces MAG levels, causes off color, decreases the melting point (Laksana, 2016), and reduces the ability of the product as an emulsifier (Moonen and Bas, 2015). According to European Union regulations (EEC-E471), the maximum limit of glycerol content in MDAG is 7% (Hasenhuettl, 2008). Therefore, purification is needed to separate the glycerol residue from the crude MDAG. MDAG purification could be carried out by Short Path Distillation (SPD) (Rossi *et al.*, 2012; Zhang *et al.*, 2014), solvent extraction (Rumondang *et al.*, 2016; Sanchez *et al.*, 2018), solvent extraction and molecular distillation (Mardaweni *et al.*,

2017), solvent saponification and extraction (Setyaningsih *et al.*, 2016) and creaming demulsification technique (CDT) (Mursalin, Lavlinesia and Yernisa, 2017; Mursalin, Sahrial and Wulandari, 2017).

Purifying MDAG using molecular distillation requires a large cost and special expertise to operate it, this method is difficult to apply widely (Sanchez *et al.*, 2018). Purification by solvent extraction also has disadvantages because of the possibility of the remaining solvent in the final product. In addition, time-consuming and decreasing yield are other disadvantages of this method (Sanchez *et al.*, 2018). Thus, CDT becomes a new method of purifying MDAG which is more efficient than molecular distillation and solvent extraction, especially in separating glycerol residues.

The principle of CDT in purifying MDAG is by destroying the stability of the emulsion system where glycerol is dispersed. Demulsification occurs due to the change in the emulsion system w/o to o/w (due to the

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addition of aqueous electrolyte solution), heating, stirring, and separation of creams and skim (Mursalin, Lavlinesia and Yernisa (2017)). Three types of electrolyte solutions that have been analyzed for their effects in removing glycerol from MDAG produced by glycerolysis are NaCl, CaCl₂, and Ca(NO₃)₂·4 H₂O. MDAG purification process with 5% NaCl solution can reduce glycerol from 14.99% to 1.64%, while with 5% CaCl₂ solution can reduce glycerol from 14.99% to 0.70% (Mursalin, Lavlinesia and Yernisa (2017)). The 5% Ca(NO₃)₂·4H₂O solution can reduce glycerol levels from 11.69±0.88% to 0.57±0.07% (Putri *et al.*, 2019). The optimum operating temperature is 60-70°C, stirring at 400 rpm, and separation of the skim by sinking and by centrifugation (Mursalin, Lavlinesia and Yernisa (2017)).

MDAG purification with CDT on a laboratory scale developed by Mursalin, Lavlinesia and Yernisa (2017) was carried out with typical processing steps. The crude MDAG was preheated in a beaker until the temperature of 65°C was reached and all the crystals melt. 500 mL of liquid MDAG (M₁) at 65°C was put into the reactor, then 500 mL of electrolyte solution with a concentration of 5% (w/v) at 10°C above the temperature M₁ was also inserted into the reactor and stirring at 500 rpm for 40 mins. After that, the mixture was deposited for 10 mins (separation I) and then the skim fraction was separated and cream I (M₂) were collected. Then, M₂ was then washed by adding 1:1 (v/v) hot water at a temperature of 10°C above the temperature of M₂. During the washing process, the mixture was stirred 500 rpm for 10 mins at 65°C. After that, the mixture was re-deposited for 10 mins (separation II). This deposition will produce 3 layers in the form of cream II, intermediate, and skim II. Then, cream II was centrifuged 2000 rpm for 5 mins, to produce pure MDAG (M₃) with glycerol residue content of less than 1%.

For a scale of 20 kg, it is estimated that process engineering is needed in order to allow the purification method applied productively. The engineering includes operational temperature, type of stirrer, mixing method, amount of hot water, washing method, and sedimentation time. The purpose of this research was to apply CDT on a scale of 20 kg and determine the process conditions that need to be adjusted so that the results are not different from the laboratory scale.

2. Materials and methods

The main material used was MDAG from Fully Hydrogenated Palm Kernel Oil (FHPKO) produced by chemical glycerolysis, obtained from the SEAFast Center of IPB (Bogor, Indonesia). Other materials are Distillated Monoglyceride from Rikevita Malaysia Sdn.

Bhd. (Johor, Malaysia), rac-1-Lauroylglycerol from Sigma Aldrich (Germany), N-methyl-N-(trimethyl silyl)-trifluoro acetamide from Sigma Aldrich (St. Louis, MO), calcium nitrate tetrahydrate from PT. Setia Guna (Bogor, Indonesia), tetrahydrofuran (Merck), and heptane (Merck).

Process equipment used includes a set of reactors with a capacity of 20 L made of stainless steel which is equipped with agitators, heaters, tanks for electrolyte solutions, water pumps, and nozzle systems. Av20 kg scale purification reactors used in this study mimicked the purification reactors used on a laboratory scale.

Analysis of the composition of the acylglycerol fraction was using the Official Method Cd 11b-91 modification method (AOAC, 2003). Crude MDAG and pure MDAG were each analyzed using Gas Chromatography (GC) FID (Hewlett Packard series 6890 series DB5 HT column). The yield of pure MDAG was determined by comparing the volume of pure MDAG with the volume of crude MDAG multiplied by 100%. The engineering implementation of the MDAG purification process was carried out with trial and error which refer to the technique was developed by Mursalin, Lavlinesia and Yernisa (2017) in laboratory scale. The data obtained was an average of three replications ± standard deviations.

3. Results and discussion

3.1 Application of CDT on a scale of 20 kg without "scaling-up adjustment"

CDT is an MDAG purification method with a working principle based on the destruction of the emulsion system through the formation of creams and skims due to the application of temperature, stirring, and the addition of an appropriate electrolyte solution. At the laboratory scale, MDAG purification was carried out by mixing liquid MDAG and electrolyte solution with the same amount, at a temperature of electrolyte solution 10°C higher than MDAG's. During the purification process, the temperature and stirring were kept constant at 65°C and 400 rpm, respectively. The function of stirring is to facilitate the occurrence of oil droplets collision easily and intensely allows floc being formed quickly Mursalin, Lavlinesia and Yernisa (2017).

Crude MDAG containing glycerol as shown in Table 1, was quite high, which was 12.69%; after purification with a method similar to that done on a laboratory scale CDT, the glycerol content dropped to 3.07%. This shows that the application of CDT on a scale of 20 kg even without the scaling up adjustment, has been quite successful in reducing the glycerol content of MDAG. However, we are not yet satisfied with the pure MDAG

Table 1. Comparison of MDAG before and after purification

Parameters	MDAG's Characteristics	
	Before Purification	After Purification
Faction Composition		
• MAG (%)	29.93±1.89	33.76±1.19
• DAG (%)	28.63±2.87	31.61±1.05
• TAG (%)	27.72±2.74	29.78±1.07
Total Glycerol (%)	12.48±0.29	3.07±0.05
Acid Numbers (mg KOH/g)	6.56±0.31	6.67±0.27
Free Fatty Acids (%)	2.34±0.11	2.86±0.14
Water (%)	1.06±0.14	2.06±0.17
Iod Number (g / 100 g)	0.31±0.00	0.31±0.00
Slip Melting Point (°C)	39-41	40-42
Color	Brownish white	Brownish white

results, where the glycerol residual content was still more than 1.5%. Therefore engineering efforts in the form of adjusting the process conditions were carried out. MDAG chromatograms before and after purification were illustrated in Figure 1.

The MDAG glycerol content before purification on the chromatogram appeared at the 3.302 mins which was 12.69% (Figure 1A) and after purification, it appeared at the 2,451 and 3,225 mins which were 3.07% (Figure 1B). The 20 kg scale MDAG Purifier was illustrated in Figure 2 and the pure MDAG product in Figure 3.

3.2 Application of CDT on a scale of 20 kg with "scaling-up adjustment"

The experimental results of using a 20 kg scale MDAG purification reactor with adjustments to several indicators of the engineering process were proven to reduce the glycerol content in the final product to only 1.15%. The intended engineering included increasing the operating temperature from 65 to 70°C, changing the type of stirrer from a propeller into a 2-level impeller, applying the nozzle for electrolyte mixing, providing longer skim and cream separation opportunities (applying repeated settling), using 1.5 times more hot water for washing, the washing technique was set twice,

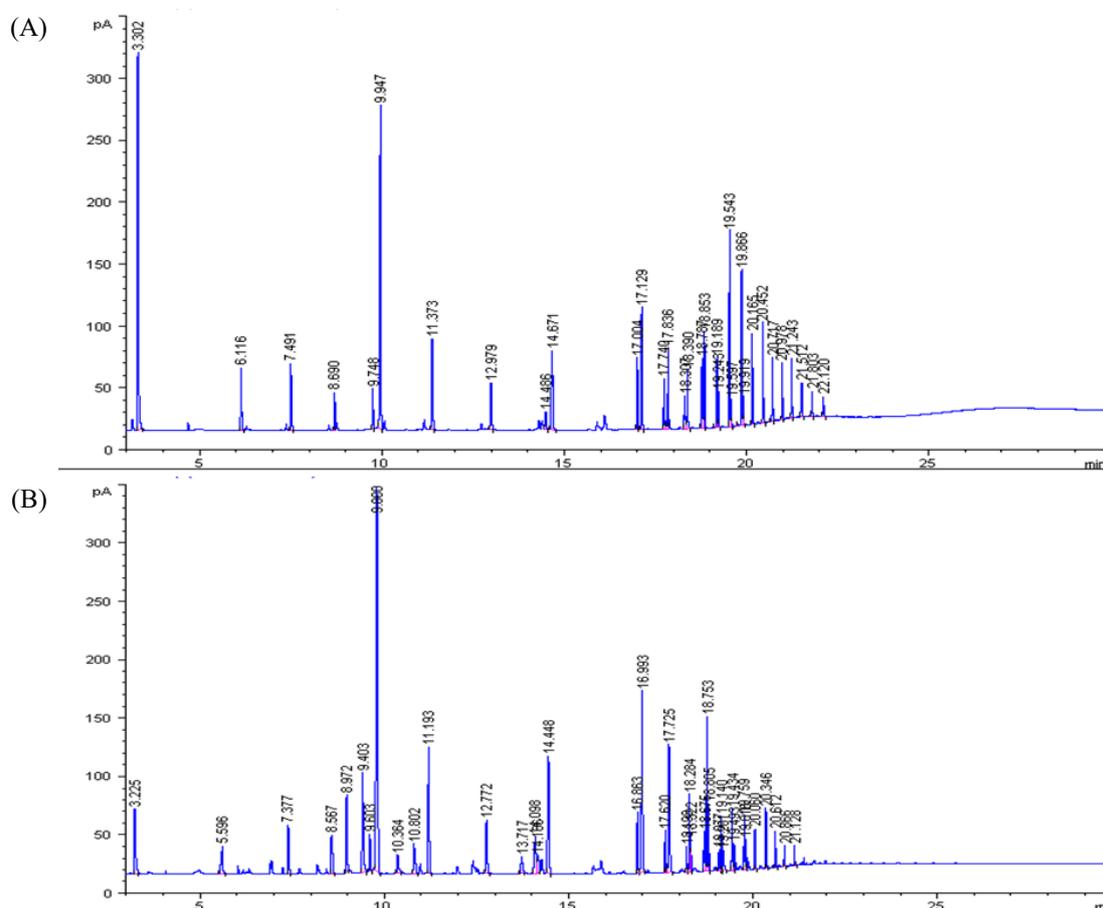


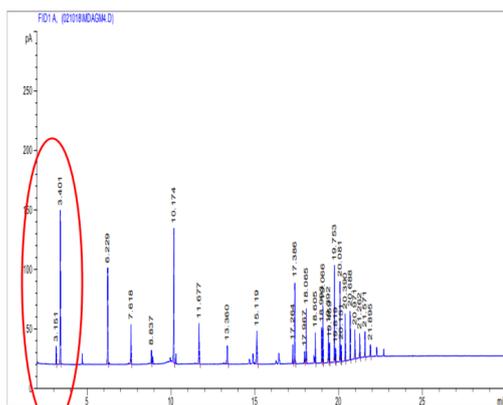
Figure 1. MDAG chromatogram before purification (A) and after purification (B) using the CDT method on a scale of 20 kg



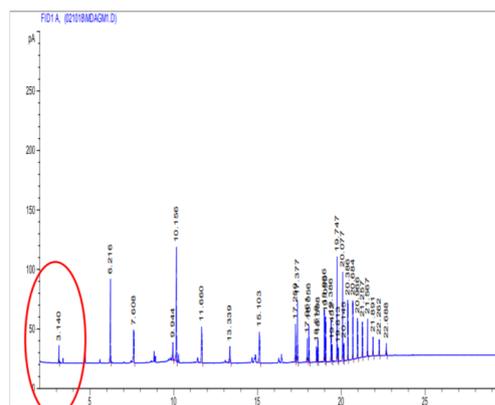
Figure 2. MDAG Purifier scale of 20 kg



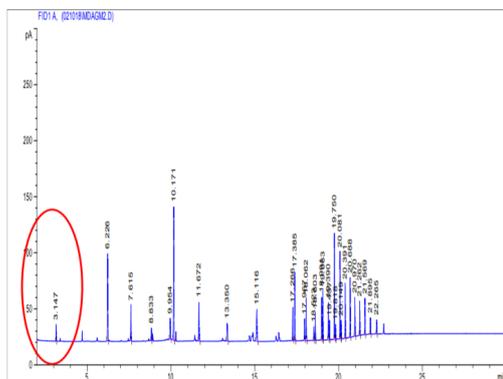
Figure 3. MDAG products purified from the 20 kg scale CDT method



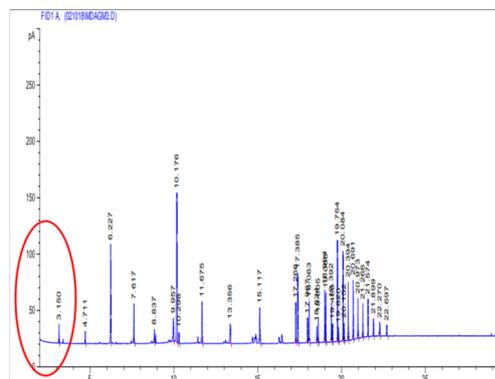
MDAG before purification



Adjustment of purification process indicators 1



Adjustment of purification process indicators 2



Adjustment of purification process indicators 3

Figure 4. MDAG chromatogram before purification and consistency 3 times the purification result by adjusting the process indicator, red circles indicate changes in the content of glycerol residues in the product

the first washing using nozzle without stirring and the second using nozzle with stirring.

The stages of applying CDT to purify MDAG on a scale of 20 kg become slightly different from the laboratory scale. The first stage, 20 kg of crude MDAG was put into the reactor tank and heated while stirring at 400 rpm until a temperature of 70°C (not 65°C) is reached. Meanwhile, 20 L of 5% calcium nitrate tetrahydrate electrolyte solution was also heated in another tank to a temperature of 80°C. Second stage, after the MDAG temperature had been reached 70°C, the heater was turned off but stirring continues. Five mins

later, the 80°C electrolyte solution was pumped and sprayed through eight nozzles found at the top of the tank. The pressure of the electrolyte solution produced from the nozzle was estimated to be quite strong and evenly distributed (hence there was no need to stir), as a result polar components dispersed as impurities (including glycerol) in MDAG would be carried to the bottom of the tank and separated as a skim. During this process, the temperature was maintained at 70°C, stirring was stop, and the settling was applied. This settling lasts for 15 mins or until the skim was separated from the cream phase (M_1). In the third stage, the stirrer was turned on again at 200 rpm for 5 mins. Settling for 15

Table 2. Characteristics of MDAG before and after purification

Parameters	MDAG's Characteristics		
	Before Purification	Purification without Adjustment	Purification with Adjustment
Faction Composition			
• MAG (%)	29.93±1.89	33.76±1.19	33.53±1.15
• DAG (%)	28.63±2.87	31.61±1.05	32.97±0.90
• TAG (%)	27.72±2.74	29.78±1.07	32.35±1.11
Total Glycerol (%)	12.48±0.29	3.07±0.05	1.15±0.03
Acid Numbers (mg KOH/g)	6.56±0.31	6.67±0.27	5.63±0.21
Free Fatty Acids (%)	2.34±0.11	2.86±0.14	2.78±0.13
Water (%)	1.06±0.14	2.06±0.17	3.19±0.16
Iod Number (g / 100 g)	0.31±0.00	0.31±0.00	0.31±0.00
Slip Melting Point (°C)	39-41	40-42	40-41
Color	Brownish white	Brownish white	Brownish white

mins after the process had obtained cream phase (M_2) and the second skim phase. Meanwhile, as much as 30 L of distilled water was heated to a temperature of 80°C. At the fourth stage, 15 L of 80°C distilled water was sprayed through the nozzle into the reactor containing M_2 , and allowed to mix without stirring. The temperature of the mixture was held constant at 70°C and the mixture of MDAG with aquadest was allowed to separate into cream (M_3) and skim phase, again. In the fifth stage, after all the skim had been removed, 15 L of distilled water at 80°C was re-sprayed through the nozzle into the reactor containing M_3 and allowed to mix without stirring and it took about 15 mins until the fourth cream and skim were separated. Finally, after all the skim from the forth phase had been removed, the cream from the forth phase (pure MDAG) was obtained.

The 20 kg scale MDAG refining technique succeeded in reducing the glycerol levels in MDAG from an initial concentration of 12.49±0.29% to 1.15±0.03% (Table 2). This showed that by adjusting several process conditions (temperature, type of stirrer, applying the nozzle, repeated settling, and increasing of hot water for washing), refining MDAG on a scale of 20 kg could be as effective as on a laboratory scale. MDAG chromatograms, before and after purification was illustrated in Figure 4.

The results of GC analysis (Figure 5), showed that MDAG before purification contained MAG, DAG, and TAG of 29.93±1.89%, 28.63±2.87%, and 27.72±2.74%, respectively. The raw material acylglycerol fraction in this study was different from that reported by Mursalin, Sahrial and Wulandari (2017) which was 32.27% (MAG), 11.84% (DAG), and 33.62% (TAG). This difference according to Triana (2014), occurred because during the process of chemical glycerolysis not all fatty acids could be released and react with glycerol.

Purification without adjustment produces MDAG with MAG, DAG, and TAG contents of 33.76±1.19%,

31.61±1.05%, and 29.78±1.07%, respectively. MDAG from the purification results with adjustments containing MAG, DAG, and TAG were respectively 33.53±1.15%, 32.97±0.90%, and 32.35±1.11% (Table 2). Mursalin, Sahrial and Wulandari (2017) reported that MDAG from Fully Hydrogenated Palm Kernel Oil (FHPKO) purified by CDT containing MAG, DAG, and TAG were 36.24%, 17.42%, and 37.67%, respectively. The percentage of MAG and TAG in this study was lower than the results of Mursalin, Sahrial and Wulandari (2017), but the percentage of DAG was much higher. It was due to differences in the composition of the acylglycerol fraction of the crude MDAG used.

Based on Figure 5, the MAG and DAG content of the product increased from the initial content in the raw material. Similar to what was reported by Mursalin, Sahrial and Wulandari (2017), MDAG purification increased the MAG, DAG, and TAG content due to decreased glycerol content. The percentage of pure MDAG yield resulting from purification without and with adjustments was 80.00±4.00% and 81.00±3.61%, respectively. These results are not much different from those produced by Moura *et al.* (2011a) and Moura *et al.* (2011b), who conducted research on refining MDAG from the same raw material, namely FHPKO, which was 76-95%.

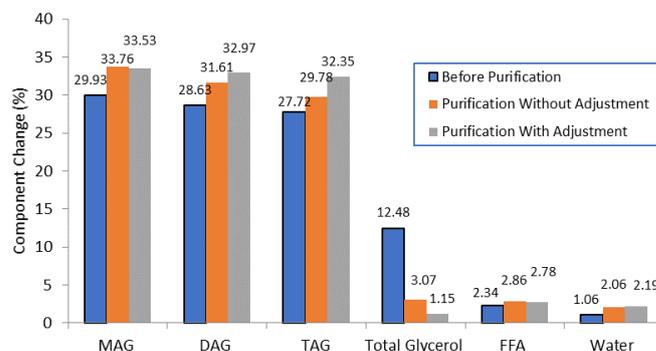


Figure 5. Changes in the MDAG acylglycerol fraction before purification, purification 1 (without adjustment of process parameters), and purification 2 (by adjusting process parameters)

4. Conclusion

MDAG purification at a scale of 20 kg will be as effective as a laboratory-scale if done by adjusting the following process conditions: increase the operating temperature from 65 to 70°C, changing the type of stirrer from a propeller into a 2-level impeller, applying the nozzle for electrolyte mixing, providing longer skim and cream separation opportunities (applying repeated settling), using 1.5 times more hot water for washing, and the washing technique was set twice. By this technique, the pure MDAG could be produced containing 1.15% glycerol residue, meet the European Union and FAO/WHO standards.

Conflict of Interest

The authors declare that there are no conflicts of interest.

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