KnE Life Sciences

UASC Life Sciences 2016
The UGM Annual Scientific Conference Life Sciences 2016
Volume 2019

Conference Paper

Synthesis of Emulsifier from Refined Bleached Deodorized Palm Stearin by Chemical Glycerolysis in Stirred Tank Reactor

Ayu Puspita Arum, Chusnul Hidayat, and Supriyanto

Faculty of Agricultural Technology, Universitas Gadjah Mada, Jl. Flora, Bulaksumur, Yogyakarta 55281 Indonesia

Corresponding Author:
Chusnul Hidayat
chusnulhi@yahoo.com
chusnul@gadjahmada.edu

Received: 10 November 2018
Accepted: 6 January 2019
Published: 10 March 2019

Publishing services provided by Knowledge E

Selection and Peer-review under the responsibility of the UASC Life Sciences 2016 Conference Committee.

Abstract

Emulsifiers are widely used in the food and beverage industry, especially the mixture of mono- and diacylglycerol. They are produced from glycerolysis reaction using chemical catalysts because of fast reaction time, high conversion of reactants and low cost. Palm stearin is abundant and less utilized. Therefore, palm stearin is used as raw material for the synthesis of emulsifiers. The goal of this project was obtained emulsifier containing high concentrations of mono- and diacylglycerol. Synthesis of emulsifier was conducted with reaction time (1 h to 12 h), catalyst concentration (1 %, 2 %, 3 %, and 4 %) (w/w) and addition of molecular sieve (12 % (w/w) and without as control). Furthermore, products were fractionated at various temperatures (40 °C, 30 °C, 20 °C, and 10 °C). These results suggest that the best conditions for the synthesis of mono- and diacylglycerol from palm stearin using NaOH catalyst in Batch stirred Tank Reactor are NaOH concentration 3 % (w/w), reaction time 6 h, molecular sieves 12 % (w/w), reaction temperature 90 °C, addition of tert-butanol as solvent 2 $\mathrm{mL \cdot g^{-1}}$ of oil, palm stearin: glycerol molar ratio (1 : 5), the speed of the stirrer of 400 rpm. The fractionation temperature is 30 °C with product yield is 61.43 % which contains 91.00 % ± 2.50 % and 9.00 % ± 2.50 % of mono- and diacylglycerol, respectively. Characteristic of emulsifiers are emulsion capacity 95.55 % ± 0.71 %, emulsion stability 90.44 % ± 1.24 %, HLB value 10.25 ± 0.44, melting point 62.67 °C ± 2.52 °C to 70.33 °C ± 0.58 °C and type of emulsion is oil in water (o/w).

Keywords: Emulsifier, Glycerolysis, Mono- and diacylglycerol, NaOH, Palm stearin

1. Introduction

The need for emulsifier is increasing around 2.7×10^6 t in 2017, especially a mixture of mono- and diacylglycerol. It is most widely used in the food industry around 70 % of the total emulsifier using [1]. The mixture of emulsifier mono and diacylglycerol used in bakery, confectionary, dairy milk, and butter because the characteristic is a stabilizer,

How to cite this article: Ayu Puspita Arum, Chusnul Hidayat, and Supriyanto, (2019), "Synthesis of Emulsifier from Refined Bleached Deodorized Palm Stearin by Chemical Glycerolysis in Stirred Tank Reactor" in *The UGM Annual Scientific Conference Life Sciences 2016*, KnE Life Sciences, pages 130–148. DOI 10.18502/kls.v4i11.3859

emulsifier, and conditioner. Apart from that, mono- and diacylglycerol are used to cosmetic product and medicine industry. It usually improves the consistency of cream and lotion [2].

Mono- and diacylglycerol can be made from triglyceride and glycerol through glycerolysis reaction. One of triglyceride source in Indonesia is palm oil. Plantation area of palm more increase along with increasing crude palm oil production around 15×10^6 t in 2012 [3].

The increased production of palm oil, it is partially exported in crude palm oil. That has a low economy value from the derivative product. Apart from that, solid palm oil fraction or RBD palm stearin utilization is still low. Because of that, this study wants to make mono and diacylglycerol using refined, bleached, and deodorized palm stearin and glycerol through glycerolysis reaction.

Glycerolysis is an important reaction between glycerol and triglyceride to produce mono and diacylglycerol. The high conversion and fast reaction of glycerolysis need catalyst [4]. There is two catalyst type, that is chemistry catalyst (heterogeneous and homogenous) and enzymatic catalyst. From that catalyst, only chemistry catalyst is more efficient for the commercial level because of chemistry catalyst higher reactant conversion, faster reaction time and cheaper than enzymatic catalyst [5, 6].

However, the homogenous catalyst has many disadvantages; they are separation problem catalyst after the reaction, wastewater treatment, no recycle, saponification can shape stable emulsion, base catalyst sensitives free fatty acid and water, cost process is higher than cost process of using heterogenous catalyst [6]. Many studies have used NaOH catalyst to produce monoacylglycerol. Study of Harismawati, et al., is using NaOH 1 % (w/w), 80 °C, molar ratio oil:glycerol (1:4), co-solvent isopropanol $20\ \text{m} \cdot 10\ \text{g}^{-1}$ oil, stirring speed 400 rpm (1 rpm = 1/60 Hz) and reaction time 4 h produces reactant conversion of mono- and diacylglycerol 92.35 % [7].

While [6] explains that heterogenous catalyst has some advantages, they are environmentally friendly, no corrosive, recycle, no wastewater treatment, easy separation catalyst after reaction, heterogenous acid catalyst can use in esterification and interesterification, heterogenous catalyst acid is not sensitive free fatty acid and water and cost process is cheaper than homogenous catalyst. Macroporous resin Amberlyst-15 is a new solid acid catalyst, most widely used in catalytic of acid reaction condition. The reaction is catalyzed, it shows high catalytic efficiency, cheap cost process, and non-toxic, so it is used in general condition [8–10]. Apart from that, [11] explained Amberlyst-15 could give a high conversion of free fatty acid is around 60.2 % in esterification reaction free fatty acid of waste cooking oil. If it is compared with other heterogenous acid catalyst. They are Amberlyst-16 and Dowex HCR-W2 just giving free fatty acid conversion 49 %.

Because of that, this study wants to use heterogenous acid catalyst Amberlyst-15 to synthesis mono- and diacylglycerol from refined, bleached and deodorized palm stearin through glycerolysis reaction in Batch Stirrer Tank Reactor using comparative catalyst is homogenous base catalyst NaOH. Then, the second step study is getting the best reaction condition (time reaction, catalyst concentration and adding water adsorbent). The last step study is getting the pure product through the best fractionation temperature.

2. Materials and Methods

2.1. Materials

The main ingredient is used in this study is refined, bleached and deodorized palm stearin from PT. Sinar Mas Tbk., glycerol (Merck), t-butanol (Merck), Amberlyst-15 (Sigma-Aldrich), molecular sieve (Sigma-Aldrich) and NaOH (Sigma Aldrich).

The ingredient for analysis of thin layer chromatography is TLC plate (Silica Gel G60 F254 from Merck), hexane (Merck), diethyl ether (Merck), acetic acid (Merck), Coomassie blue (Sigma), methanol (Merck) and aquadest. This study is testing capacity and stability of the emulsion. The ingredient for that analysis is aquadest and edible oil (Rose Brand), emulsifier in ice cream “Cortina” is used to compare with the product in capacity and stability of emulsion testing. The ingredient of free fatty acid analysis is NaOH (Sigma-Aldrich), aquadest, neutral alcohol and phenothrin indicator (Chemix Pratama). The ingredient of hydrophilic and lipophilic balance value analysis is dimethylformamide (DMF) and benzene (Chemix Pratama).

2.2. Methods

2.2.1. Glycerolysis reaction

The method is based method of [12] with modification. The fixed variable is stirring speed 400 rpm, reaction temperature 90 °C, molar ratio palm stearin: glycerol (1 : 5) [5] and adding co-solvent tert-butanol 20 $mL \cdot 10\ g^{-1}$ oil. Dependent variable is catalyst type NaOH 1 % (w/w) [7] and Amberlyst-15 15 % (w/w) [13], reaction time (1 h to 12 h), catalyst concentration (1 %, 2 %, 3 %, and 4 %) (w/w) and adding molecular sieve 12 % (w/w) [14] and without molecular sieve 12 % (w/w).

2.2.2. Catalyst deactivation

The purpose of this step is stopping glycerolysis reaction. This study, deactivation catalyst is done with adding citric acid solution 20 % (w/v) in the reaction mixture after the temperature of reaction mixture 60 °C until PH of reaction mixture neutral. This step based on a study of [15].

2.2.3. Removal of catalyst and glycerol residue

The removal of catalyst and glycerol residue in this study is based on the method of [16] with modification. This method is based on the solubility of the product. The solution of the reaction mixture is dissolved in hexane (1 : 10) w/v. Then, the solution centrifuges 2 000 rpm for 10 min (1rpm = 1/60 Hz). So, it will shape two layers. The top layer color is transparent. It is a product, that soluble in hexane. The bottom layer color is turbid. It is a residue of glycerol, citric acid, and catalyst (NaOH). The bottom layer is discarded, then the top layer is evaporated using a rotary evaporator (40 °C, 335 mmHg) to evaporate hexane. The mixture of product (monoacylglycerol, diacylglycerol, free fatty acid, and triglyceride) free hexane is stored for quantitative and qualitative analysis of the content using Thin Layer Chromatography and fractionation process.

2.2.4. Product fractionation

Product fractionation method is based on a study of Mustafa [17] with modification. The method of fractionation is solvent fractionation. Triglyceride-rich of mono- and diacylglycerol is dissolved using hexane (1 : 10) w/v at 50 °C. Then it is refrigerated at a certain temperature. This study is done using a variation of fractionation temperature (40 °C, 30 °C, 20 °C, and 10 °C). Incubation at temperature 40 °C to 10 °C, 24 h will make crystallization of mono- and diacylglycerol component in triglyceride, but triglyceride and free fatty acid still dissolve in hexane. So, triglyceride and free fatty acid can be separated using vacuum filtration. Filtration paper is dried in room temperature in 12 h. Materials on filtration paper is suspected pure product of mono- and diacylglycerol.

3. Analysis

Analysis of raw materials (RBD Palm stearin and glycerol) are water content (Oven Method, SNI 01-0018-2006) and free fatty acid content in RBD palm stearin (SNI

01-0018-2006). Analysis of product mixture is free fatty acid content in RBD palm stearin (SNI 01-0018-2006) and analysis of concentration mono- and diacylglycerol using thin layer chromatography on plate G60 F254 with developers solution hexane:diethyl ether:acetic acid 80:20:2 (v/v/v). This method is based on Fransisco et al. [18].

Based on Lopez, et al., coloring of TLC plate is done using Coomassie blue 0.02 % (w/v), it has dissolved in acetic acid:methanol:aquadest 1:3:6 (v/v/v) [19]. Developers solution is saturated in TLC chamber for 1 h. Activating of TLC plate is heated in oven 100 °C for 30 min. After that, 1µL sample is applicated on the plate using micropipet. The distance of between spot is 15 mm. Then, Plate is incubated in TLC chamber until developer's solution up until line marking. After that, the plate is taken out from the chamber and dried in room temperature.

Moreover, then, coloring of TLC plate is done with swapping TLC plate in Coomassie blue solution 0.02 % for 1 min accompanied by shaken. Then, TLC plate is dried at temperature room.

After TLC plate is dried, TLC plate is taken in Camag Automatic TLC Scanner *III* "*dummy*" S/N (1 14 16) with *software Camag WinCATS planar chromatography*. Scanning is done at λ = 629 nm. The wide of peak area mono- and diacylglycerol in chromatogram described the concentration of mono and diacylglycerol.

Analysis of concentration mono- and diacylglycerol in fractionation product using thin layer chromatography method is based on [18]. Analysis of product from the best condition process is concentration mono- and diacylglycerol in fractionation product using thin layer chromatography method is based on [18]. The characteristic of product emulsification are capacity and stability of emulsion testing is based on [20], Hydrophilic and Lipophilic Balance value are based on [21] and melting point product using the method of AOAC 920 157.

4. Result and Discussion

4.1. Raw material analysis

Table 1: Raw material analysis.

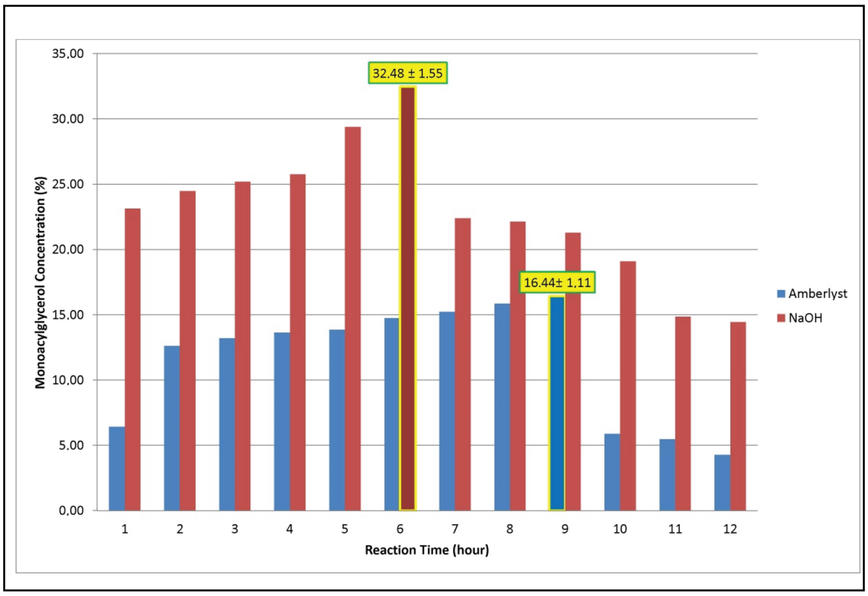
Analysis	**Reference**	**Analysis Result**
Water Content % (w/w)	Max.0.1 % * Max. 0.5 % **	RBD Palm Stearin: 2.98 % Glycerol: 2.27 %
Free fatty Acid Content % (w/w)	Max. 0.15 % *	RBD Palm Stearin: 0.30 %
*SNI 01-0021-1998		
** Product information of Merck Millipore		

Based on Table 1, the water content of raw materials is higher than the maximum water content from reference. Increasing of raw materials water content during storages is caused adsorption of water from the atmosphere to raw materials surface [22]. Increasing of raw materials water content especially RBD palm stearin will support hydrolysis of triglyceride produce free fatty acid. It is caused by free fatty acid content of RBD Palm stearin increases during storage [22]. It matches with the analysis result of free fatty acid content in RBD palm stearin from Table 1. The content of free fatty acid RBD palm stearin is higher than RBD palm stearin commercial from reference.

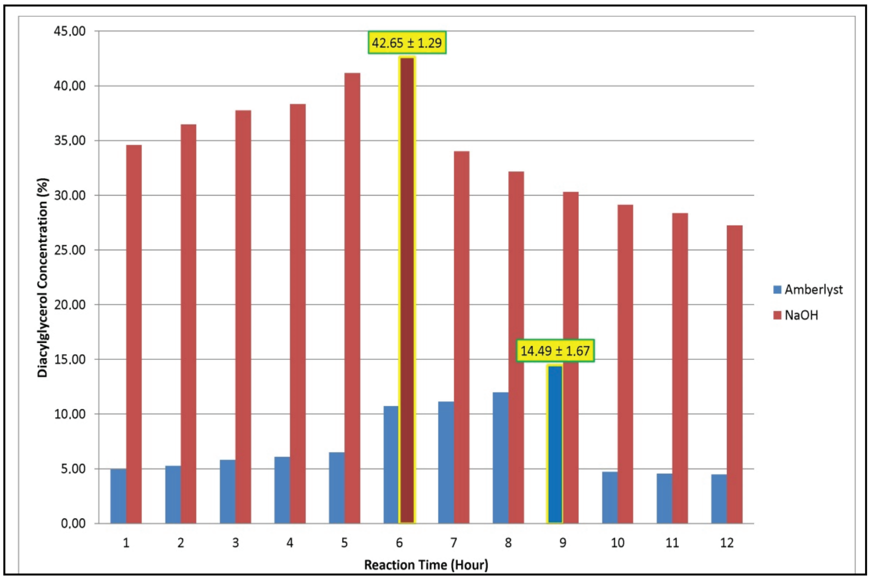
Based on Fig. 1, the highest concentration of mono and diacylglycerol for heterogenous acid catalyst Amberlyst-15 in glycerolysis reaction is 16.44 % ± 1.11 % and 14.49 % ± 1.67 % for 9 h. While The highest concentration of mono- and diacylglycerol for homogenous base catalyst NaOH in glycerolysis reaction is 32.48 % ± 1.55 % and 42.65 % ± 1.29 % for 6 h. NaOH catalyst produces concentration mono- and diacylglycerol is higher and faster than Amberlyst-15.

It matches from study of Harismawati, et al. that using NaOH catalyst 1 % (w/w), 80 °C, molar ratio palm stearin:glycerol (1:4), adding co-solvent isopropanol 20 mL · 10 g^{-1} oil, stirring speed 400 rpm and 4 h reaction time can produce reactant conversion of mono- and diacylglycerol 92.35 % [7]. While study result from Ulfa, using Amberlyst-15 15 % (w/w), 70 °C, molar ratio oil:glycerol (1:1), adding co-solvent tert-butanol 2 : 1 (v/w) to oil, stirring speed 400 rpm and 10 hours reaction time can produce concentration monoacylglycerol 9.87 % [13]. So, synthesis mono and diacylglycerol using heterogenous acid catalyst Amberlyst-15 in glycerolysis reaction are lower and slower than homogenous base catalyst NaOH.

It is caused homogenous catalyst (NaOH) have a similar phase with the reactant phase. So, it makes increasing contact between catalyst and reactant. So the catalytic activity increases. It makes an increasing product if it is compared with heterogenous catalyst Amberlyst-15. Heterogenous catalyst has a different phase between catalyst and reactant. So, it makes decreasing contact between catalyst and reactant. So, it makes decreasing product [23]. The key factor of catalytic activity of Amberlyst-15 are crosslinking bond level, swelling catalyst capacity, pore diameter, and surface area catalyst (BET) [11]. Based on that information, the next study will use homogenous catalyst NaOH.



(a)



(b)

Figure 1: The effect of catalyst type amberlyst-15 15 % (w/w) and NaOH 1 % (w/w) to concentration of monoacylglycerol (a) and diacylglycerol (b).

4.2. Determination of the best reaction time

Based on Fig. 2 showed reaction time influences of mono- and diacylglycerol concentration. Increasing reaction time will increase the concentration of mono- and diacylglycerol. Reaction time for 1 h until 6 h will increase concentration of mono and diacylglycerol 23.14 % ± 0.82 % and 34.61 % ± 0.67 % (1 h) increases become 32.48 % ± 1.55 % and 42.65 % ± 1.29 % (6 h). However, increasing glycerolysis reaction time. That is

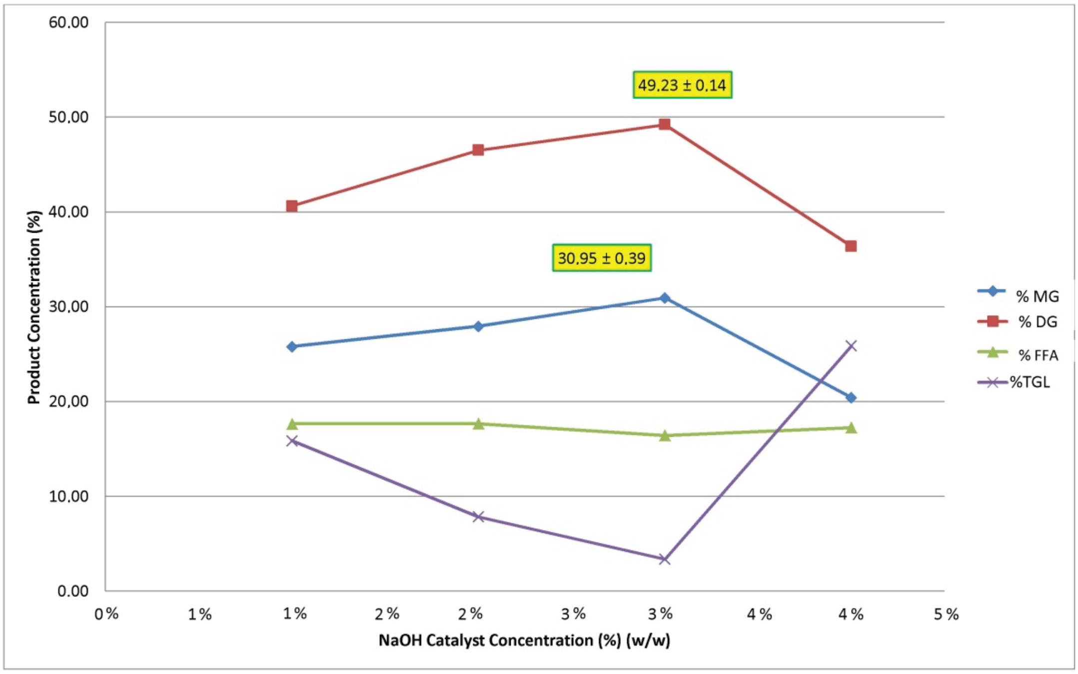


Figure 2: The effect of Reaction Time (1 h to 12) to Monoacylglycerol (% MG), Diacylglycerol (% DG), Free Fatty Acid (% FFA) and Triglyceride (% TGL) Concentration with NaOH Catalyst 1 % (w/w).

reaction time on 7 h until 12 h decreasing concentration of mono- and diacylglycerol 22.40 % ± 0.78 % and 34.04 % ± 1.12 % (7 h) decreases become 14.45 % ± 0,59 % and 27.26 % ± 2.32 % (12 h). It matches in study of Margareth [24], synthesis mono- and diacylglycerol from Refined Bleached Deodorized Palm Oil using CaO catalyst, 70 °C, molar ratio glycerol:oil (6:1) with adding co-solvent tert-butanol 3:1 (v/w) to oil, catalyst concentration CaO 2 % (w/w), 4 h reaction time decreases concentration of mono- and diacylglycerol from 40 % (reaction time on 3 h) become 15 %.

Glycerolysis reaction is a reversible reaction. The reaction time of glycerolysis is too long can make hydrolysis of mono and diacylglycerol [25]. So, the concentration of mono and diacylglycerol decreases. It is caused during glycerolysis reaction produces water. Water can hydrolysis of mono and diacylglycerol become free fatty acid and glycerol [26]. Furthermore, tert-butanol have vapor pressure 31 mmHg at 20 °C. So, the temperature at 90 °C (glycerolysis reaction), tert-butanol change vapor phase, as a result, the ability of tert-butanol as co-solvent decreases and makes the concentration of mono and diacylglycerol low [25]. Based on Fig. 2, the best reaction time is 6 h.

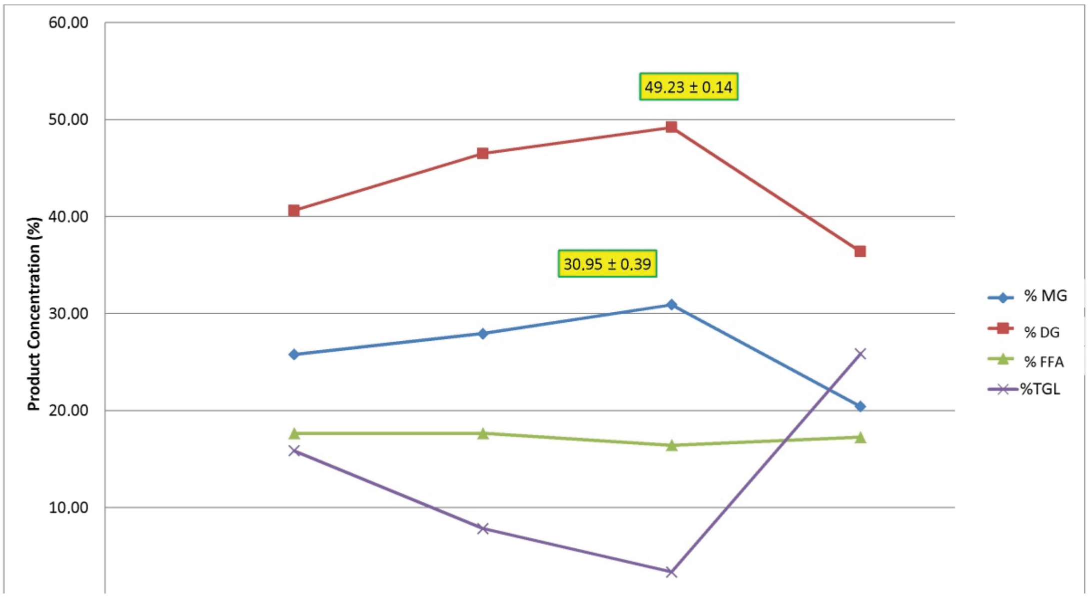


Figure 3: The Effect of Catalyst Concentration NaOH (1 %, 2 %, 3 %, and 4 %) (w/w) to Monoacylgylcerol (% MG), Diacylglycerol (% DG), Free Fatty Acid (% FFA) and Triglyceride (% TGL) Concentration.

4.3. Determination of the best catalyst concentration

Based on Fig. 3, catalyst concentration NaOH in glycerolysis reaction influences to mono- and diacylglycerol concentration. Increasing catalyst concentration makes increasing mono- and diacylglycerol concentration. Catalyst concentration NaOH 1 % (w/w) produces mono and diacylglycerol concentration 25.80 % ± 0.77 % and 40.65 % ± 0.47 % until catalyst concentration NaOH 3 % (w/w) produces mono and diacylglycerol concentration 30.95 % ± 0.39 % and 49.23 % ± 0.14 %. It is caused the function of the catalyst is decreasing activation energy. Increasing catalyst concentration in solution causes reaction activation energy decreases. So that can increase collision between the reactant molecule. It makes the product increase [27]. Increasing catalyst concentration NaOH will increase mono and diacylglycerol concentration.

On catalyst concentration NaOH 4 % (w/w), mono and diacylglycerol concentration decrease 20.44 % ± 0.88 % and 36.40 % ± 0.66 %. It matches with study of Harismawati et al., synthesis of mono and diacylglycerol pseudohomogen glycerolysis reaction from waste cooking oil with molar ratio oil : glycerol (1:4), 80 °C, stirring speed 400 rpm, adding co-solvent isopropanol to oil 2:1 (v/w), reaction time 4 h, catalyst concentration NaOH 3 % (w/w) produces 94.35 % mono- and diacylglycerol [7]. While catalyst concentration NaOH 4 % (w/w) decreases mono and diacylglycerol become 85.30 %. It is caused catalyst concentration too much will support saponification reaction [28–30].

Increasing triglyceride changes soap causes conversion of triglyceride decreases. It makes the concentration of mono and diacylglycerol low. Based on Fig. 3, the best catalyst concentration NaOH is 3 % (w/w).

4.4. Effect of water-absorbent (molecular sieve) to concentration of monoacylglycerol and diacylglycerol

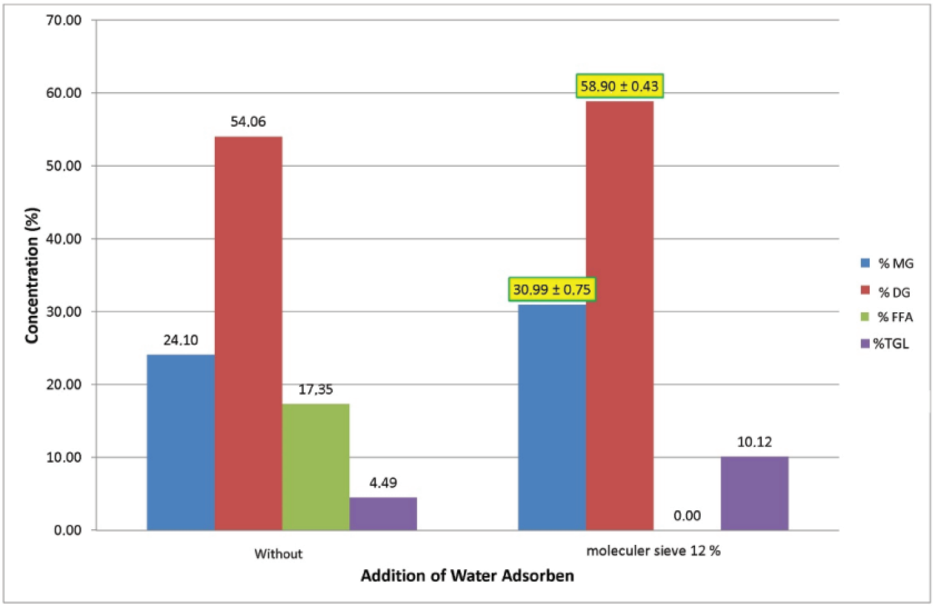


Figure 4: The Effect Of Using *Water Adsorbent* (*Molecular sieve* 12 % (b/b)) to Monoacylglycerol (% MG), Diacylglycerol (% DG), Free Fatty Acid (% FFA) and Triglyceride (% TGL) Concentration.

Based on Fig. 4, water adsorbent (molecular sieve 12 % (w/w)) in glycerolysis reaction influences to mono- and diacylglycerol concentration 30.99 % ± 0.75 % and 58.90 % ± 0.43 %. If it is compared without adding water adsorbent that is 24.10 % ± 0.29 % (monoacylglycerol concentration) and 54.06 % ± 0.80 % (diacylglycerol concentration). Molecular sieve is effectively used in esterification reaction palmitate fructose. Based on study of Saber et al [14] used molecular sieve 12 % (w/w) can increase conversion 76 %, reaction time 72 h concentration of Novozym −435 10 % (w/w), 60 °C, molar ratio fructose:palmitate (1 : 6), adding co-solvent 2−methyl 2−butanol and stirring speed 600 rpm in stirrer batch reactor.

This matter, water adsorbent is effective binding water, which is produced from glycerolysis reaction and raw materials. That is a side product of glycerolysis reaction can support hydrolysis of mono and diacylglycerol [13]. It is supported data from Fig. 4. That concentration of free fatty acid decrease become 0.00 % ± 0.00 % after adding water adsorbent. If it is compared without adding water adsorbent the concentration of free fatty acid is 17.35 % ± 0.27 %. The free fatty acid is a side product of mono and diacylglycerol hydrolysis.

4.5. Determination of the best fractionation temperature

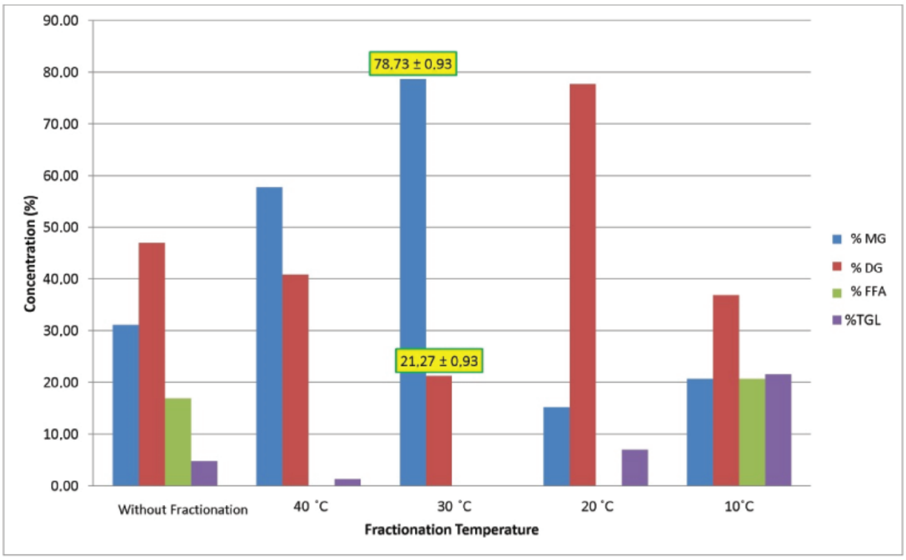


Figure 5: The Effect Of Fractionation Temperature (40 °C, 30 °C, 20 °C and 10 °C) to Monoacylgylcerol (% MG), Diacylglycerol (% DG), Free Fatty Acid (% FFA) and Triglyceride (% TGL) Concentration.

Based on Fig. 5, the best fractionation temperature can be produced the highest monoacylglycerol concentration (78.73 % ± 0.93 %) is 30 °C with diacylglycerol concentration 21.27 % ± 0.93 %, concentration of free fatty acid and triglyceride is 0.00 % ± 0.00 %. This matter shows that all of the monoacylglycerols crystallize at 30 °C. It matches with the study of Mustafa [17] fractionation of high triglyceride diacylglycerol from enzymatic glycerolysis reaction from Refined Bleached, and Deodorized Palm Oil that increasing fractionation temperature makes increasing monoacylglycerol content at 15 °C. increasing monoacylglycerol content is caused less of triglyceride and diacylglycerol because of the melting point of triglyceride and diacylglycerol lower than monoacylglycerol. So, at this temperature triglyceride and diacylglycerol dissolves in hexane.

This study, the highest monoacylglycerol concentration at 30 °C because increasing crystallization temperature makes the size of the crystal is big. So, the crystal is accommodated in filtration paper increases. It makes solid fat content in stearin fraction increases in coconut oil fractionation. Furthermore, critical cooling velocity influences of fractionation effectiveness, decreasing critical cooling velocity makes big crystal. So, the crystal is accommodated in filtration paper increases and monoacylglycerol content in filtration paper increases [32].

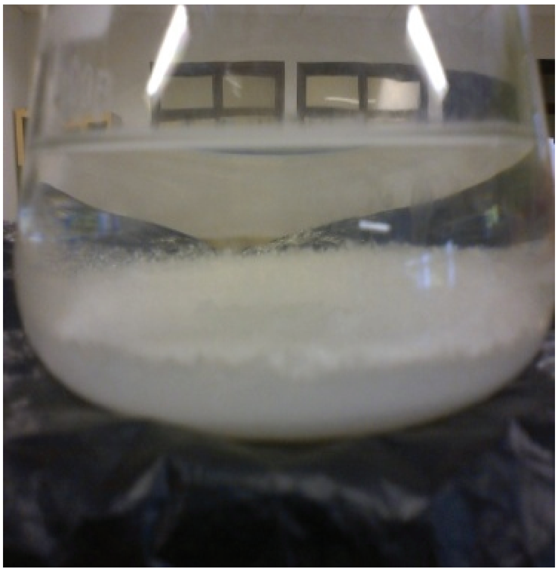


Figure 6: Crystal of Mono and Diacylglycerol at 30 °C.

Based on Fig. 6, the temperature of 30 °C has a concentration of monoacylglycerol less 100 %. It means little of monoacylglycerol fraction dissolves in hexane. It is caused that palm stearin has a variation of fatty acid, so it makes a variation of monoacylglycerol melting point [33, 34]. Furthermore, the different of melting point is influenced by the position of fatty acid, that changes hydroxyl group in the glycerol. They are between 1-monoacylglycerol and 2-monoacylglycerol have different polymorphism crystal shape 1-monoacylglycerol (asymmetric monoacylglycerol). The crystal forms α polymorphism until β' (not stable). 2-monoacylglycerol (symmetric monoacylglycerol), its crystal forms β polymorphism more stable [31].

Table 2: Yield of Mono and Diacylglycerol from The Best Condition Process in BSTR Yield and Concentration of Mono and Diacylglycerol of Product from The Best Condition Process.

The weight of Fractionation Product 30 °C (g)	The weight of Raw Materials (g) Palm Stearin	Yield (%)
28.75	46.8	61.43

Based on Table 2, the yield of synthesis mono and diacylglycerol using the best condition process in Batch Stirrer Tank Reactor is 61.43 %. Yield is still low because the fractionation process is not maximum.

The key factor that influences the effectiveness of fractionation are crystallization temperature, crystallization time and critical cooling velocity. Increasing temperature and time of crystallization makes big crystal. So, increasing of the crystal is accommodated in the filtration paper, and yield will increase. Increasing critical cooling velocity makes small crystal. So, many crystals run out from filtration paper and yield will decrease [32]. From many factors, the factor cause decreasing yield is critical cooling velocity. This study the value of critical cooling velocity in the fractionation process is 0.925 °C · min-^{1}. Based on a study of Hariyadi [35] if we can maintain the critical cooling velocity less from 0.125 °C · min-^{1}. It makes increase solid fat content in stearin fraction in fractionation process of coconut oil because decreasing of critical cooling velocity makes big crystal. So, all of the crystal can be accommodated in filtration paper, and yield will increase.

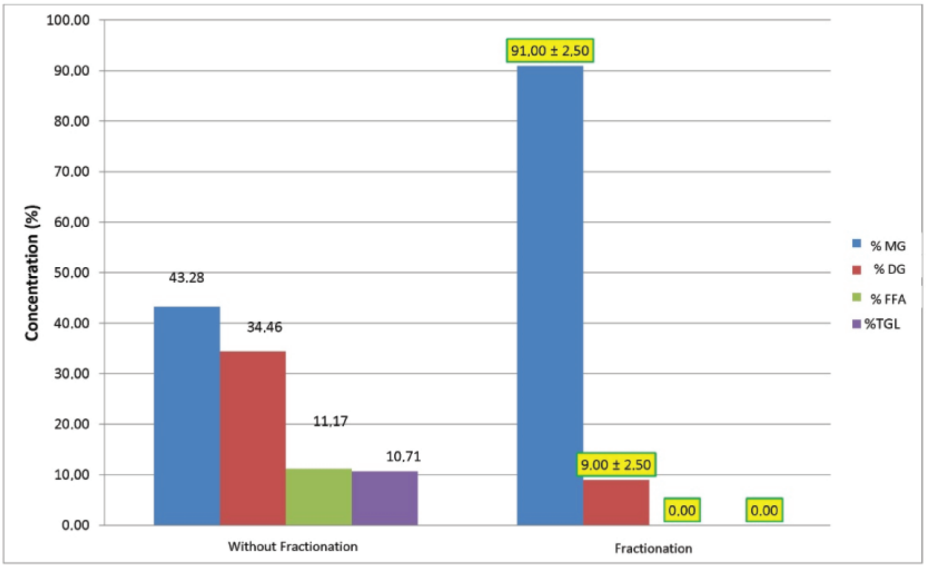


Figure 7: The concentration of Product (monoacylglycerol, diacylglycerol, free fatty acid, and triglyceride) Synthesis Mono and Diacylglycerol from The Best Condition Process with Fractionation Process and Without.

Based on Fig. 7, that product from the fractionation process has high purity 91.00 % ± 2.50 % (concentration of monoacylglycerol) and 9.00 % ± 2.50 % (concentration of diacylglycerol). If it is compared from the product without fractionation process. It still contents desirable component like free fatty acid 11.17 % ± 0.72 % and triglyceride 10.71 % ± 0.57 %. It is caused the fractionation method of oil is based on differences of melting point of triglyceride component and separation by thermomechanical. It means, that triglyceride has a higher melting point will separate from triglyceride has a lower melting point through crystallization partial, and then it is continued filtration step. So, it produces purity product [34, 36–37].

4.6. Emulsification characteristics of mono and diacylglycerol

Based on Table 3, control showed emulsification activity with emulsion capacity 38.28 % ± 1.11 %. The emulsion of control is formed from homogenization of molecule

TABLE 3: The result of capacity and stability emulsion testing in control (without emulsifier), emulsifier commercial and monoacylglycerol.

Sample	Emulsion Capacity (%)	Emulsion Stability (%)
Control	38.28 ± 1.11	0.00 ± 0.00
Emulsifier Commercial	100 ± 0.00	100 ± 0.00
Monoacylglycerol	95.55 ± 0.71	90.44 ± 1.24

breaking from water and oil by temporary. That is evidenced after heating. The emulsion system goes through a separation 2 layer (oil phase: top layer and water phase: bottom layer) with emulsion stability is 0.00 % ± 0.00 %. While commercial emulsifier has good emulsification, the emulsification is very stable because after heating of emulsion. Emulsion system does not change. But, emulsifier mono and diacylglycerol has enough stable of emulsification. If it is compared with commercial emulsifier because emulsion capacity 95.55 % ± 0.71 %, after heating emulsion stability decrease become 90.44 % ± 1.24 %.

TABLE 4: Emulsification characteristic of mono and diacylglycerol.

Parameter	Value
Emulsion Capacity (%)	95.55 ± 0.71
Emulsion Stability (%)	90.44 ± 1.24
HLB Value	10.25 ± 0.44
Emulsion Type	o/w
Melting Point	62.67 ± 2.52°C – 70.33 ± 0.58 °C

5. Conclusion

Glycerolysis reaction from refined, bleached and deodorized Palm Stearin with glycerol in Batch Stirrer Tank Reactor system using homogenous base catalyst NaOH is the best catalyst because that catalyst can produce mono and diacylglycerol concentration is higher and faster than heterogenous acid catalyst Amberlyst-15. The best glycerolysis reaction condition in Batch Stirrer Tank Reactor system is reaction time 6 h, concentration catalyst NaOH 3 % (w/w), using molecular sieve 12 % (w/w), 90 °C, adding co-solvent tert-butanol 20 mL · 10 gr^{-1} oil, molar ratio oil:glycerol (1 : 5), velocity of stirrer 400 rpm. The best fractionation temperature is 30 °C. Concentration of product are 43.26 % ± 0.90 % (monoacylglycerol), 34.46 % ± 0.41 % (diacylglycerol), 11.17 % ± 0.72 % (free fatty acid) and 10.71 ± 0.57 % (triglyceride). After fractionation product, rendement of the product is 61.43 % contain 91.00 ± 2.50 % monoacylglycerol dan 9.00 ± 2.50 % diacylglycerol. Emulsification characteristic of product mono and diacylglycerol are emulsion capacity

95.55 ± 0.71 %, emulsion stability 90.44 % ± 1.24 %, Hydrophilic and lipophilic balance value 10.25 ± 0.44, type of emulsion o/w and melting point 62.67 °C ± 2.52 °C to 70.33 °C ± 0.58 °C.

References

[1] Hasenhuetti GL. Food emulsifiers and their application. Second Edition. Springer, Madison, Wisconsin; 2008. https://www.springer.com/gp/book/9780387752839

[2] Kaewthong W. Continuous production of monoacylglycerols by glycerolysis of palm olein with immobilized lipase. Journal of Process Biochemistry. Elsevier; 2005:40:1525–1530. http://pirun.ku.ac.th/$\sim$fagissi/research/PalmOlein/monoacylglycerols.pdf

[3] Kimmel, T. Kinetic investigation of the base-catalyzed glycerolysis of fatty acid methyl esters [Thesis]. Faculty of Mathematics and Science. Technical Berlin University (2004). https://www.depositonce.tu-berlin.de/handle/11303/1283

[4] Kamel BS. Emulsifiers. Food additive user's handbook. J. Smith (ed.). Blackie Academic & Profesional, Glasgow, UK; 2004. http://gtu.ge/Agro-Lib/[Fatih_Yildiz]_Advances_in_Food_Biochemistry(BookFi.org).pdf.

[5] Malaya KN, Naik SN, Monty S. Enzymatic glycerolysis for conversion of sunflower oil to food based emulsifiers. Catalysis Today. Science Direct 2014;237:145–149. https://www.sciencedirect.com/science/article/pii/S0920586113006081

[6] Endalew AK, Kiros Y, dan Zanzir R. Inorganic heterogeneous catalysts for biodiesel production from vegetable oils. Biomass Bioenergy 2011;35(3):787–809. https://www.sciencedirect.com/science/article/pii/S0961953411003357

[7] Harismawati A, Prasetyo F. Produksi mono dan digliserida dengan proses gliserolisis pseudohomogen dari minyak goreng bekas. [Production of mono and diglyceride with pseudohomogen glycolysis process from used cooking oil]. [Thesis]. Universitas Diponegoro (2008). http://eprints.undip.ac.id/36791/1/89.Jurnal_Penelitian.pdf [in Bahasa Indonesia].

[8] Boz N, Degirmenbasi N, Kalyon DM. Esterification and transesterification of waste cooking oil over amberlyst-15 and modified amberlyst-15 catalyst. INFONA 2015;165:723–730. https://www.infona.pl/resource/bwmeta1.element.elsevier-319decf4-8fb1-3d22-b0ae-5c52faa2d076?locale=en

[9] Fan G. Liao C, Fang T, Luo S, Song G. Amberlyst-15 as a new and reusable catalyst for the conversion of cellulose into cellulose acetate. Carbohydrate Polymers. ResearchGate; 2014:112:203–209.

https://www.researchgate.net/publication/263317417_Amberlyst_15_as_a_new_and_reusab _catalyst_for_the_conversion_of_cellulose_into_cellulose_acetate

[10] Jeenpadiphat S, Tungasmita DN. Acid-activated pillar bentonite as a novel catalyst for the esterification od high FFA oil. Powder Technology. CAB Direct 2013;237:634–640. https://www.cabdirect.org/cabdirect/abstract/20143050468

[11] Suyin G, Hoon KN, Park HC, Fook LL. Heterogeneous free fatty acids esterification in waste cooking oil using ion-exchange resins. Infona; 2012:102:67–72. https://www.infona.pl/resource/bwmeta1.element.elsevier-d09ed0ea-da66-3b55-ae08-348840a840f3

[12] Yanuar, S.P. dan Mulyani, S. Proses gliserolisis CPO menjadi mono dan diasilgliserol dengan pelarut tert-butanol dan katalis MgO. [CPO glycolysis process into mono and diacylglycerol with butanol-tert-solvent and MgO catalyst] Universitas Diponegoro, Semarang; 2013. [in Bahasa Indonesia] http://eprints.undip.ac.id/3486/

[13] Ulfa A. Sintesis monoester gliserol asam palmitat menggunakan H2SO4 etanolat-amberlyst-15 dalam stirrer tank reaktor. [Synthesis of Monoester Glycerol Palmitic Acid Using H2SO4 Ethanolate-Amberlyst-15 In Stirrer Tank Reactor] Universitas Gadjahmada; Yogyakarta (2015). [in Bahasa Indonesia]

[14] Sabeder S, Habulin M, Knez Z. Lipase-catalyzed synthesis of fatty acid. Elsevier 2006;77(4):880–886. https://www.sciencedirect.com/science/article/pii/S0260877405005674?via%3Dihub

[15] Soheila Z, Sahari MA, Barzegar M, Esfehani ZH. Production of cocoa butter replacer by dry fractionation, partial hydrogenation, chemical and enzymatic inter-esterification of tea seed oil. Scirp 2012;3(2):184–189. http://file.scirp.org/Html/7-2700318_17513.htm

[16] Zaelani, A. Sintesis Mono dan Diasilgliserol dari Refined Bleached and Deodorized Palm Oil. Departemen Ilmu dan Teknologi Pangan. [Synthesis of Mono and Diasilglycerol from Refined Bleached and Deodorized Palm Oil. Department of Food Science and Technology] Institut Pertanian Bogor; Bogor. 2007. https://anzdoc.com/skripsi-sintesis-mono-dan-diasilgliserol-dari-refined-bleach.html [in Bahasa Indonesia]

[17] Musthofa, C. Mempelajari proses pemekatan diasilgliserol dari fraksi kaya diasilgliserol dari hasil gliserolisis enzimatis refined bleached and deodorized palm oil. [Study of diacylglycerol concentration from diasilgliserol rich fraction of enzymatic glyceroline result refined bleached and deodorized palm oil,Skripsi]. Departemen Ilmu dan Teknologi pangan. Institut Pertanian Bogor, Bogor; 2009. http://repository.ipb.ac.id/handle/123456789/11230 [in Bahasa Indonesia]

[18] Francisco J, Andrade, Jacob T, Shelley, William C, Wetzel, Michael R. Webb, Gerardo Gamez, Steven J, Ray, Gary M, Hieftje. 2008. Atmospheric pressure

chemical ionization source 2. Desorption-ionization for the direct analysis of solid compounds. ACS Publication 2008;80(8):2654–2663. https://pubs.acs.org/doi/abs/10.1021/ac800210s

[19] Lopez DE, Goodwin JG, Bruce DA, Lotero E. Transesterification of triacetin with methanol on solis acid and base catalysts. Academia 2005;295;97–105. http://www.academia.edu/28685612/Transesterification_of_triacetin_with_methanol_on_solid_acid_and_base_catalysts

[20] Kholifaturrosyidah F. Sintesis biosurfaktan ester fruktosa oleat secara enzimatis menggunakan lipase amobil pada matrik modifikasi hidrofobik dalam fluidized bed reactor. [Synthesis of enzymatic esther fructose oleic oleic synthesis using amobil lipase in a hydrophobic modification matrix in a fluidized bed reactor,Thesis] Department of Food Technology and Agricultural Products. Gadjah Mada University; Yogyakarta. 2014. http://etd.repository.ugm.ac.id/index.php?mod=penelitian_detail&sub=PenelitianDetail&act=view&typ=html&buku_id=78019&obyek_id=4 [in Bahasa Indonesia].

[21] Gupta RK, James K, Smith FJ. Sucrose ester and sucrose ester/glyceride blends as emulsifiers. Springer 1983;60:862. https://link.springer.com/article/10.1007/BF02787451

[22] Winarno, F. G. Kimia pangan dan gizi. [The Chemical of food and nutrient] PT Gramedia Pustaka Utama, DKI Jakarta; 2002. http://onesearch.id/Record/IOS3341.siprus-0000000000000046021 [in Bahasa Indonesia].

[23] Vlada BJ, Ivana BB, Olivera SS. Purification of crude biodiesel obtained by heterogenously-catalized transesterification. ScienceDirect 2015;49:500–516. https://www.sciencedirect.com/science/article/pii/S1364032115003676

[24] Margareth N, Purba RD, Ritonga MY. Pengaruh jumlah katalis abu cangkang telur ayam dan waktu reaksi gliserolisis pada pembuatan mono Dan diasilgliserol dengan menggunakan co-solvent tert-butanol. [Influence of amount of chopped egg shell catalysts and time of glycolysis reaction on preparation of mono and diasilglycerol by using a co-solvent tert-butanol] University of North Sumatra; Medan. 2014:3:43. http://download.portalgaruda.org/article.php?article=275631&val=4138&title=PENGARUH%20JUMLAH%20KATALIS%20ABU%20CANGKANG%20TELUR%20AYAM%20DAN%20WAKTU%20REAKSI%20GLISEROLISIS%20PADA%20PEMBUATAN%20MONO%20DAN%20DIASILGLISEROL%20(MDAG)%20DENGAN%20MENGGUNAKAN%20CO-SOLVENT%20%20TERT-BUTANOL [in Bahasa Indonesia].

[25] Zulfikar. Pengaruh kalsium karbonat dan gliserol terhadap produk gliserolisis refined bleached deodorized palm oil (RBDPO). [Effects of calcium carbonate and glycerol

on refined bleached deodorized palm oil (RBDPO) glyceroline products] Department of Chemistry, Faculty of Mathematics and Natural Sciences, University of North Sumatera. Medan. 2009. [in Bahasa Indonesia] http://repository.usu.ac.id/bitstream/123456789/13958/1/10E00367.pdf

[26] Widiyarti G, Hanafi M. Pengaruh konsentrasi katalis dan perbandingan molaritas reaktan pada sintesis senyawa alpha-monolaurin. [Effect of catalyst concentration and comparison of reactant molarity in synthesis of alpha-monolaurin Compounds] PUSPIPTEK, Serpong; Tangerang. 2008;12:2. https://ejournal.undip.ac.id/index.php/reaktor/article/view/1509 [in Bahasa Indonesia].

[27] Kaewthong W. Continuous production of monoacylglycerols by glycerolysis of palm olein with immobilized lipase. Journal of Process Biochemistry. Elsevier 2005;40:1525–1530. https://www.sciencedirect.com/science/article/pii/S0032959204000081?via%3Dihub

[28] Hingu SM, Gogate PR, Rathod VK. Synthesis of from waste cooking oil using sono-chemical reactors. Europe PMC 2010;17:827–832. https://europepmc.org/abstract/med/20303314

[29] Koh MY, Mohd TJ, Ghazi M. 2011. A review of production from jatropha curcas L. oil. IDEAS 2011;11:2240–2251. https://ideas.repec.org/a/eee/rensus/v15y2011i5p2240-2251.html

[30] Wang R, Zhou WW, Hanna MA. Preparation, optimization and fuel properties from non-edible feedstock, datura stramonium L. fuel. Science Direct 2012;91:182–186. https://www.sciencedirect.com/journal/fuel/vol/91/issue/1

[31] Gunstone FD, Harwood JL, Padley FB. Lipid handbook. Chapman and Hall. 1995. https://onlinelibrary.wiley.com/doi/abs/10.1002/lipi.19950970720

[32] Fardiaz D. Pengaruh laju pendinginan, suhu dan lama kristalisasi terhadap profil triasilgliserol dan sifat melting produk fraksinasi minyak kelapa. [Effect of cooling rate, temperature and length of crystallization on triacylglycerol profile and melting properties of coconut oil fractionation products] Department of Food Science and Technology. Faculty of Agricultural Technology. Bogor Agricultural Institute; Bogor. 2013;18:1. http://journal.ipb.ac.id/index.php/JIPI/article/view/8348 [in Bahasa Indonesia].

[33] O'Brien RD. Fats and Oils: Formulating and processing for applications. CRC, Boca Raton; 2004. https://www.crcpress.com/Fats-and-Oils-Formulating-and-Processing-for-Applications-Third-Edition/OBrien/p/book/9781420061666

[34] Huey SM, Hock CC, Lin SW. Characterization of low saturation palm oil products after continuous enzymatic interesterification and dry fractionation. NCBI 2009;74:E177-E183. https://www.ncbi.nlm.nih.gov/pubmed/19490322

[35] Hariyadi MP, Purnomo EH, Andarwulan. Fraksinasi kering minyak kelapa menggunakan kristalisator skala 120 kg untuk menghasilkan fraksi minyak kaya triasilgliserol rantai menengah. (Dry practionation of coconut oil using a 120 kg crystallizer scale to produce a rich oil fuel fraction triacylglycerol chain) IPB, Bogor; 2013:19(1):1–50 lhttps://repository.ipb.ac.id/handle/123456789/64111 [in Bahasa Indonesia].

[36] Timms RE. Fractional crystallisation – the fat modification process for the 21st century. European Journal of Lipid Science and Technology 2005;107(1):48-57. https://doi.org/10.1002/ejlt.200401075

[37] Calliuw G, Fredrick E, Gibon V, De Greyt W, Wouters J, Foubert I, Dewettinck K. On the fractional crystallization of palm olein: solid solutions and eutectic solidification. Food Research International 2010;43:972–981. https://lib.ugent.be/en/catalog/pug01:979618