



Original Article

Synthesis of high purity monoglycerides from crude glycerol and palm stearin

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Received 28 November 2007; Accepted 11 June 2008

Abstract

The optimum conditions for the glycerolysis of palm stearin and crude glycerol derived from biodiesel process were found to be a reaction temperature of 200°C with a molar ratio of crude glycerol to palm stearin of 2.5:1, and a reaction time of 20 minutes. The yield and purity of monoglycerides obtained under these conditions was satisfactory as compared with the glycerolysis of pure glycerol. To increase the purity of monoglycerides a two-step process, removal of residual glycerol and crystallization, was proposed instead of either vacuum or molecular distillation. Residual glycerol was removed by adding hydrochloric acid followed by washing with hot water. Optimum conditions for crystallization were achieved by using isooctane as a solvent and a turbine impeller speed of 200 rpm at a crystallization temperature of 35°C. A purity not exceeding 99 percent of monoglycerides was obtained with monopalmitin as the major product.

Keywords: glycerolysis, glycerol, monoglycerides, palm stearin, biodiesel

1. Introduction

Biodiesel is a widely accepted liquid alternative fuel that can be produced from a variety of fat, oil, and waste grease feedstocks (Nelson and Schrock, 2006). The production cost of biodiesel depends mainly on the cost of raw materials (Kapilakarn and Peugtong, 2007). In Thailand, the sales price of biodiesel is about US \$0.03/liter cheaper than that of petroleum-based diesel (PTT Plc., 2008), due to a subsidy of about US \$0.5/liter by the Thai government. However, the high cost for the biodiesel production has been a major factor for its slow commercialization. Reducing this cost by using low-cost lipid feedstocks has been extensively investigated (Chongkhong *et al.*, 2007). Furthermore, in the production of biodiesel, a large amount of crude glycerol is generated. If this could be utilized for the production of higher valued derivatives of glycerol, such as monoglycerides, the economic viability of the biodiesel process might improve.

The interest in monoglycerides resides in their structure comprising an aliphatic lipophilic chain and two hydroxyl groups in the hydrophilic part. This structure causes surfactant action, which stabilizes emulsions (Eychenne and Mouloungui, 1999). Their abilities to form stable emulsions make the monoglycerides suitable as internal and external lubricants in fiber and textile technologies. In addition, monoglycerides are important emulsifiers used in food, pharmaceutical, and cosmetic industries (Bornscheuer, 1995; Negi *et al.*, 2007). Monoglycerides and their derivatives represent 75 % of the world production of food emulsifiers (Sagalowicz, 2006); in the USA, about 100 million kg are used annually (Birnbbaum, 1981).

The most common method for production of monoglycerides is a glycerolysis reaction (Campbell-Timperman *et al.*, 1996), which is the transesterification of triglyceride with glycerol to monoglyceride (Muniyappa *et al.*, 1996). Conventional batch-type glycerolysis operates at high temperatures (200-250°C) employing inorganic alkaline catalysts under a nitrogen gas atmosphere (Sonntag, 1982). The finished product generally contains 35-50% monoglycerides

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and the rest are mostly diglycerides, some unreacted triglycerides (10%), residual glycerol (3-4%), and free fatty acid (1-3%) (Hui, 1996).

Monoglycerides need to be of high purity in the food industry, because they have better emulsifying properties than a mixture of different acylglycerols. To remove impurities and to increase the purity of monoglycerides up to more than 90% a vacuum or molecular distillation is conventionally applied (Kaewthong *et al.*, 2004, 2005); at laboratory scale, column chromatographic purification is a choice (Yang *et al.*, 2003).

The glycerolysis of pure glycerol has been extensively studied whereas information on the glycerolysis of crude glycerol from biodiesel is rare. In this work, the feasibility of glycerolysis of crude glycerol with palm stearin was studied and the optimum conditions obtained. In addition, a two-step process, removal of residual glycerol and crystallization, was applied in place of conventional methods, vacuum and molecular distillation, to obtain high purity monoglycerides.

2. Materials and Methods

2.1 Materials

Pure glycerol (95% purity) purchased from Witayasom Ltd. Company, Hat Yai, is of commercial grade. The crude glycerol (70% purity) obtained from biodiesel production in the Department of Chemical Engineering, Prince of Songkla University, contains about 3.7% monoglycerides and about 2% sodium hydroxide catalyst per unit mass of crude glycerol. Palm stearin (Iodine value 38 and saponification value 202) provided by Chooporn Palm Oil Company comprises 98.7% triglycerides and 1.3% diglycerides. The molecular weight of palm stearin calculated from the saponification value is 834 (Gardner *et al.*, 2002). Hydrochloric acid, hexane and isooctane used in this study are all of analytical grade.

2.2 Equipment

Batch glycerolysis was conducted in a two layer-stainless steel reactor, an inner vessel (capacity of 10 liter) with a top agitator is for the reaction and an insulated outer vessel is for the cooling process. The inner reactor is a pressure vessel, capable of withstanding full vacuum as well as positive pressure, which is typically 620 kPa abs, with an inner diameter of 20 cm and a wall thickness of 4 mm.

A vacuum pump is used to reduce the pressure inside the pressure vessel to below atmospheric pressure. The condenser, which contains cooling water, is used to condense glycerol and water vapors from the pressure vessel to protect clogging of the vacuum pump. A controller on the gas-heater controls the temperature of the inner reactor. The control valve for the nitrogen gas is on the lid of the reactor.

A batch crystallization unit was constructed from an acrylic sheet with 0.5 liters capacity of the inner tube. The

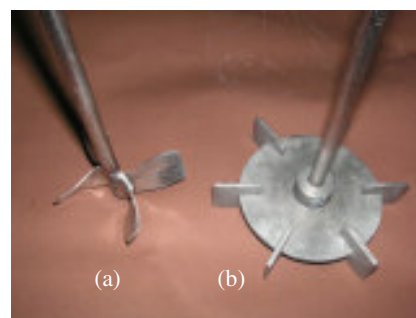


Figure 1. Two types of impellers; (a) propeller and (b) turbine used in the crystallization process.

outer tube is connected to a programmable bath for water circulation. A turbine or propeller with a diameter of 8 cm was used as a stirrer (Figure 1).

2.3 Glycerolysis process

Glycerol and palm stearin (being solid at room temperature) were firstly melted outside the reactor. The reactor itself was under vacuum condition. Then melted glycerol was charged to the reactor followed by melted palm stearin. The mixture was agitated at 200 rpm and heated to 120°C. Then, nitrogen gas was fed to the reactor to reduce oxidation. The mixture was continuously heated to the desired temperature and was maintained for the desired reaction time. The operating pressure was maintained at 3.5 kPa abs. It is noted that no catalyst addition is necessary for the reaction with crude glycerol, but for the reaction with pure glycerol, the amount of sodium hydroxide required was also 2% by mass of glycerol.

2.4 Optimum condition for glycerolysis process

The operating parameters to be investigated were reaction temperatures, reaction times, and molar ratios of glycerol to palm stearin. The reaction temperatures were 180, 200, 230, and 250°C. The reaction times chosen were 15, 20, 30, 60, and 90 minutes. The molar ratios of glycerol to palm stearin were 2:1, 2.5:1, and 3:1.

2.5 Reverse reaction

Two sets of experiments were conducted to study the effect of the reverse reaction of glycerolysis. For the first set, the reaction mixture was rapidly cooled down to a temperature of 75°C in 5 minutes by water-cooling. For the second set, there was no cooling water used, and the reaction mixture was cooled down to the temperature of 75°C in 210 minutes.

2.6 Residual glycerol removal process

One hundred grams of product from the glycerolysis process were melted and then 1 mL of 35% hydrochloric

acid was added to neutralize the catalyst. The mixture was stirred and heated to 80°C. Then the mixture was allowed to settle into two phases. Residual glycerol separated at the bottom was withdrawn while the top phase product was extracted with water at 90°C. This top-product was stirred and again heated to 80°C. The mixture was settled with the water phase at the bottom and monoglycerides phase on the top.

2.7 Crystallization process

The product from residual glycerol removal process was fed to the crystallization unit and mixed with solvent (isooctane or hexane) in the ratio of 80 g to 400 mL. The mixture was heated and stirred using a turbine or propeller with a speed of 200, 250, 300, 350, or 400 rpm. The mixing Reynold's numbers are presented in Table 1. The temperature of the mixture was raised to 70°C and then kept constant for 10 minutes. After that, the temperature was decreased to 40°C at a rate of 1°C/min and remained at this value for 90 minutes. The precipitate was removed by filtration. The crystallization process was then repeated for the other crystallization temperatures (34, 35, 36, 37, 38, and 39°C).

2.8 Analytical methods

The production compositions, monoglycerides (MG), diglycerides (DG), triglycerides (TG), and fatty acid (FA), were analyzed by thin layer chromatograph with flame ionization detection (TLC/FID; Iatroscan MK5, Iatron Laboratories Inc., Tokyo) (Rosu, 1997). The MG and DG contents were expressed as the sum of the mass percentage of their regioisomers. The amount of glycerol was determined by sodium periodate oxidation method (TISI 337, 2002).

Crystallization temperature was studied using a differential scanning calorimeter (DSC; DSC7, Perkin Elmer). The product after crystallization process was transformed to monoesters and analyzed for the type of MG using a gas chromatography-mass spectrometer (GC-MS).

2.9 Statistic analysis

All experiments were repeated three times. Therefore, the experimental results were average values from three replications with standard deviations on the error bars. The imprecision, coefficient of variation (CV) was calculated to be $\leq 5\%$. In addition, analysis of variance (ANOVA) was

carried out by Microsoft Excel tool package within 95% confidence interval.

3. Results and Discussion

3.1 Effect of temperature and time

The primary object in glycerolysis process under study is to obtain a high yield of MG at the lowest possible reaction time. The reaction at 180°C temperature gave low yields of MG for all reaction times. The yields were similar at reaction temperatures of 200 and 230°C, while slightly lower yields were observed for a temperature of 250°C at each reaction time, except for 15 minutes reaction time (Figure 2). The lower yields were probably due to polymerization as reported by Hui (1996). In addition, there were reports on undesirable taste and color of MG due to decomposition of TG at higher temperatures (Hui, 1996; Muniyappa *et al.*, 1996). With the reaction temperatures of 200 and 230°C, resembling MG yields were provided at the reaction times of 20 and 30 minutes. The reaction time of 20 minutes is chosen for economic reasons. One-Factor ANOVA was then carried out to test the difference between the MG yields obtained with temperatures at 200 and 230°C at a reaction time of 20 minutes. It was found that there was no significant difference of yields at both temperatures. To determine the optimum temperature, not only the maximum yield of MG was considered, but also energy consumption was taken into account.

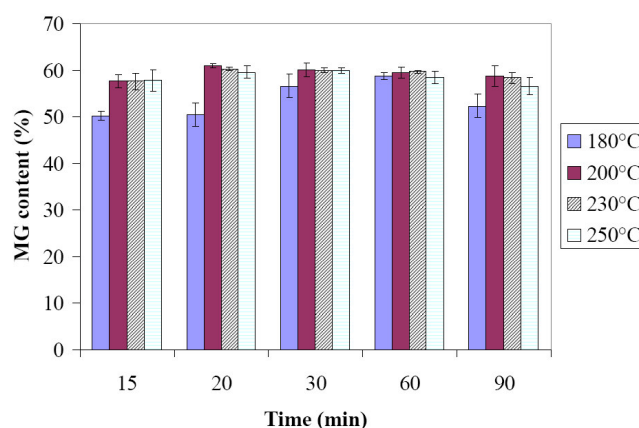


Figure 2. MG content in the products from the glycerolysis of crude glycerol at different temperatures using a molar ratio of crude glycerol to palm stearin of 2.5:1 and 2% NaOH of crude glycerol.

Table 1. Mixing conditions for the crystallization process.

Solution	Reynold's number				
	200 rpm	250 rpm	300 rpm	350 rpm	400 rpm
Mixed MG product + Isooctane	4,631	5,789	6,947	8,105	9,263
Mixed MG product + Hexane	4,432	5,540	6,648	7,756	8,864

Consequently, a reaction temperature of 230°C is not preferred. Therefore, the optimum temperature is decided to be 200°C.

3.2 Effect of molar ratio of substrates and time

Hui (1996) showed that when a greater amount of glycerol reacts with fat, the finished product has higher monoglyceride content. From our results, the MG content was found to be very low, using a ratio of 2:1, the stoichiometric molar ratio of glycerol to triglyceride required for the formation of MG, compared to the molar ratios 2.5:1 and 3:1 (Figure 3). For the reaction times of 15 and 20 minutes, the greatest MG production was observed at the molar ratio of 2.5:1, with a maximum yield of 60.9% at 20 minutes. When increasing the reaction time above 20 minutes, the highest MG content was obtained with the ratio 3:1, having a maximum yield of 61.1% at 30 minutes. One-Factor ANOVA was done to find out the difference between the MG contents obtained at these two conditions. The results show that there was no significant difference between them. From an economic point of view, a molar ratio of 2.5:1 at a reaction temperature of 200°C for a reaction time of 20 minutes are the best conditions. The finished product, which contained about 61% MG, 25% DG, 3% TG, 2% FA, 8% glycerol, and 1% sodium hydroxide is quite satisfactory, as in the most manufacturing plant the MG concentration is only 35-50 wt% (McNeil and Yamane, 1991 and McNeil *et al.*, 1991).

3.3 Glycerolysis of pure glycerol

Glycerolysis of pure glycerol was done in order to compare the results with glycerolysis of crude glycerol at the optimum conditions. The results are presented in Table 2. Purity and yield of MG obtained from glycerolysis of crude glycerol were 5.5% and 4.6%, respectively, lower than the glycerolysis of pure glycerol. The lower purity and yield of MG came from the impurities in the crude glycerol itself, which were not removed before the glycerolysis reaction. To remove the impurities distillation is conventionally applied, which is a high-cost method. Therefore, using crude glycerol

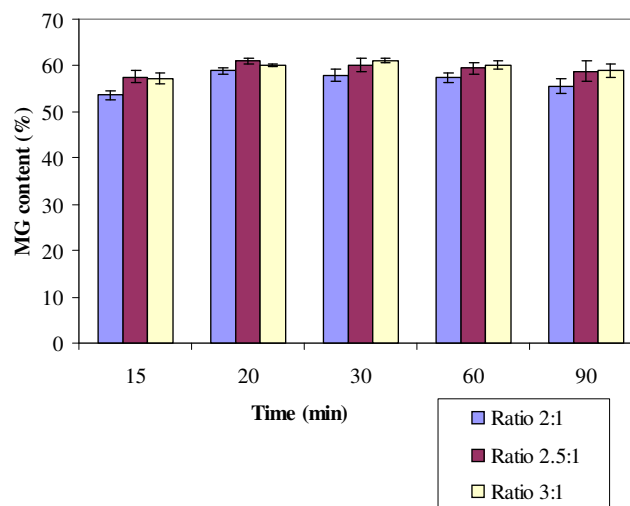


Figure 3. MG content in the products from the glycerolysis of crude glycerol at different molar ratios of crude glycerol to palm stearin at a reaction temperature of 200°C and 2% NaOH of crude glycerol.

Table 2. Comparison of MG production from the glycerolysis of pure glycerol and glycerolysis of crude glycerol at 200°C, the molar ratio of glycerol to palm stearin = 2.5:1 and reaction time of 20 minutes.

Type of glycerol	Purity of MG (%)	Yield of MG (%)
Pure	67.7	65.4
Crude	62.2	60.8

without purification before the glycerolysis provides an accepted level of purity and MG yield with lower cost.

3.4 Effect of reverse reaction

The effect of the reverse reaction of glycerolysis was studied. Table 3 shows the compositions of the reaction mixture at different conditions for cooling down. By rapidly

Table 3. The compositions of reaction mixture at different conditions of cooling down, the initial reaction mixture was from the glycerolysis at the optimum conditions.

Cooling down conditions	Composition of reaction mixture (% from TLC/FID)			
	TG	DG	MG	FA
Initial reaction mixture	2.7	23.0	72.4	1.9
Using cooling water for 5 minutes	3.6	23.8	71.2	1.4
No cooling water for 60 minutes	3.7	24.9	69.5	1.9
No cooling water for 120 minutes	5.3	33.4	57.3	4.0
No cooling water for 180 minutes	5.8	34.3	56.0	3.9
No cooling water for 210 minutes	6.5	34.8	54.0	4.7

cooling down the reaction mixture from 200 to 75°C with cooling water, the MG content reduced from 72.4 to 71.2%, which is a 1.2% reduction. By cooling down the reaction mixture without any cooling water, the MG content decreased from 72.4 to 54.0%, which is a 18.4% reduction. In addition, the amount of DG and TG increased 11.8 and 3.8%, respectively, in the case of no cooling water. These results indicated that there was a significant reversion when cooling down the reaction mixture without cooling water. Sonntag (1982) stated that the reversion of glycerolysis could occur to the extent of about 30%. Thus, the mixture reaction must be rapidly cooled to a temperature at which the reversion velocity is nil (below 75°C from our study).

3.5 Residual glycerol removal

The purity of MG in the product from the glycerolysis process was 61.5 wt%. By adding 1 mL of 35% HCl followed by hot water washing, most of the residual glycerol was removed from the reaction mixture and only 2.4% of monoglycerides were lost in the washing step (Table 4).

3.6 Optimum condition for crystallization

After removal of residual glycerol, the purity of MG was increased by the crystallization process. With a DSC chromatogram, the temperature at the lowest point of the dip is usually considered the crystallization temperature. Then, the studied crystallization temperature was set to start at 40°C as shown in Figure 4. In addition to the crystallization temperature, the choice of crystallization solvent is critical, which depends on the solubility of the compound. In any crystallization technique, the idea is to exceed the saturation level of the solution and force the solute to solidify in form of good quality crystals. Two types of solvent (isooctane and

Table 4. The amount of monoglycerides and residual glycerol before and after adding 1 mL of 35% HCl following by hot water washing.

Condition	MG (%)	Glycerol (%)
After glycerolysis process	61.5	11.2
After removal of residual glycerol	59.1	0.1

hexane) were compared in this study. From Table 1, the mixing Reynold's numbers are in the range of 4,432-9,263, which is turbulent condition. Turbulent flow results in a random eddying motion that causes efficient mixing and convective heat transfer (Rieke, 1997). It can be seen from Figure 5 that the optimum crystallization temperature for isooctane and hexane were different. The highest purity of MG was 93% at 35°C for isooctane and 73% at 39°C for hexane. With isooctane, higher purity of MG was obtained at every crystallization temperature. In addition, the significant differences of MG purity obtained by the two solvents were confirmed by a Single-Factor ANOVA test. Thus, crystallization with isooctane at a temperature of 35°C was further investigated.

Two types of impellers were tested. A turbine was more suitable than a propeller as it gave higher MG purity (Figure 6). The impeller speed was another parameter controlling the purity of MG. Figure 7 shows that at a speed higher than 250 rpm low purity MG was obtained. This was probably because some crystals were fractured from that high speed. The greatest purity of MG was observed with a mixing speed of 250 rpm followed by a mixing speed of 200 rpm. Single-Factor ANOVA indicated that the purity of MG was not significant different with a mixing speed of 200 and 250 rpm. Therefore, the speed of 200 rpm was chosen for economic reason.

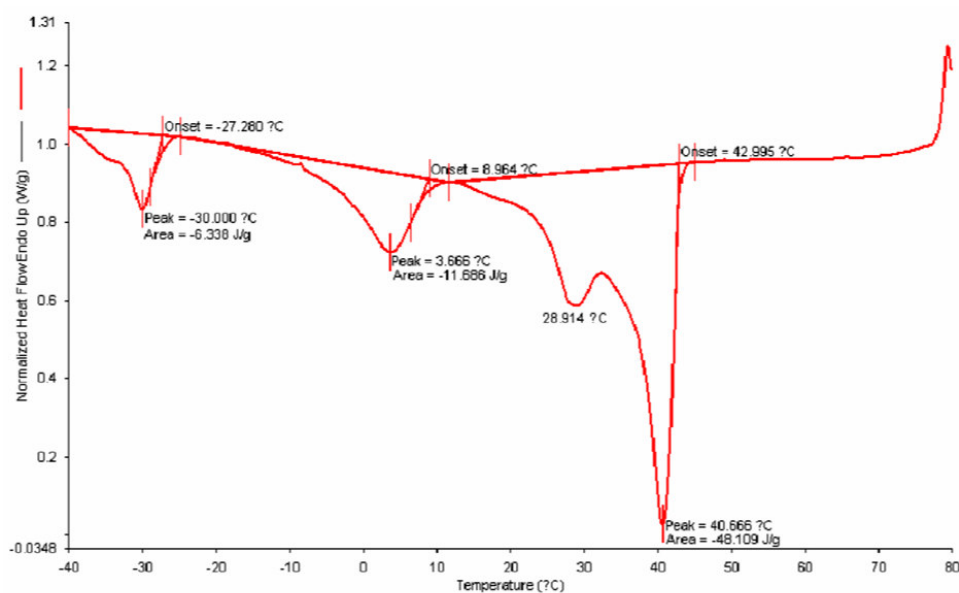


Figure 4. DSC chromatogram of a product after removal of residual glycerol.

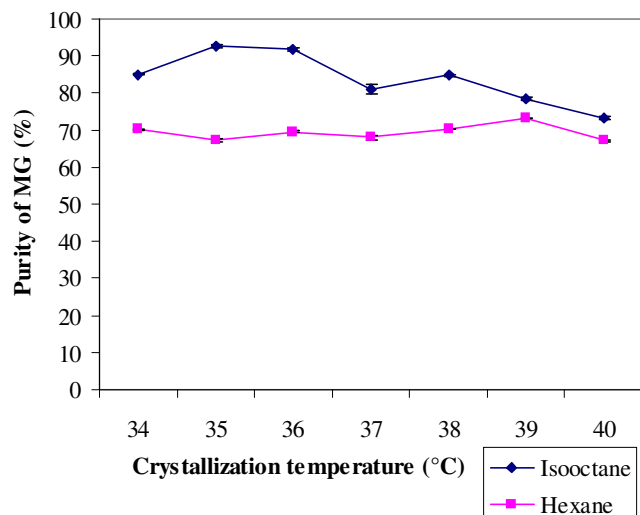


Figure 5. Purity of MG with different crystallization temperatures by using isooctane or hexane as a solvent and a turbine impeller at a speed of 200 rpm for 90 minutes.

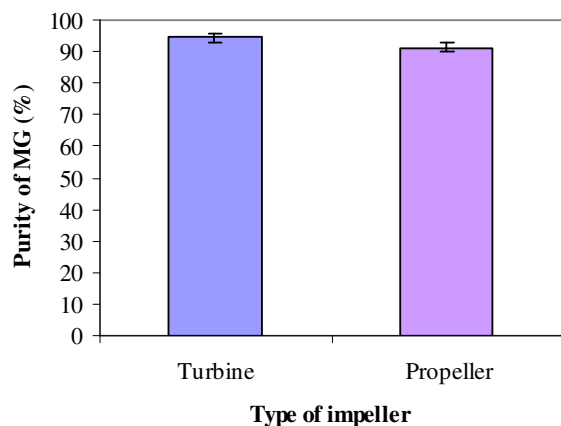


Figure 6. Purity of MG with different types of impeller by using isooctane as a solvent at a crystallization temperature of 35°C for 90 minutes.

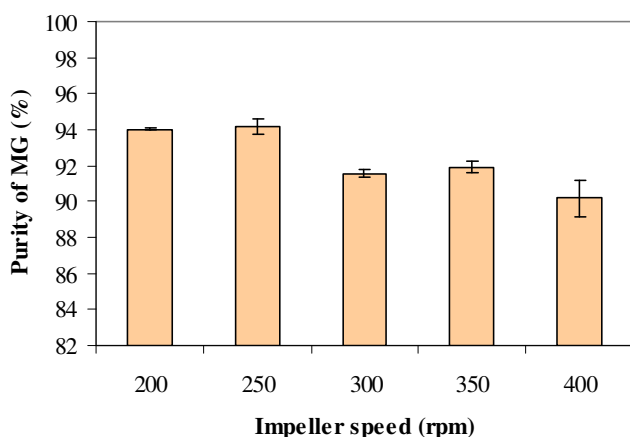


Figure 7. Purity of MG at different speeds of the turbine impeller by using isooctane as a solvent at a crystallization temperature of 35°C for 90 minutes.

At the optimum conditions for the crystallization process: using isooctane and a turbine impeller speed of 200 rpm and a crystallization temperature of 35°C, the finished product contained 95% MG and 5% DG. By transforming this product to monoesters and analyzing it with GC-MS, there was 98% monopalmitate and 2% monostearate. Thus, at these conditions, monopalmitin was obtained as the major MG and monostearin was a minor. The MG purity can be further increased by repeating the crystallization process. With a second crystallization, up to 99 wt% purity of MG was reached.

4. Conclusion

At the optimum conditions for glycerolysis of crude glycerol about 61% MG yield and 62% MG purity was obtained. This is quite satisfactory compared to the glycerolysis of pure glycerol in this study and compared to most manufacturing plants. After the glycerolysis reaction was carried out for 20 minutes, the reaction mixture must be rapidly cooled down below 75°C to minimize the reversion process. Then the residual glycerol was removed, which caused a slightly reduction in MG. To increase the MG purity the crystallization process was proposed instead of vacuum or molecular distillation. Carrying out the first crystallization with isooctane at 35°C for 1.30 hrs, up to 95% purity was gained, and with the second crystallization, up to 99% purity was reached. Monopalmitin was the major product with monostearin as a minor.

The glycerolysis of crude glycerol has two major benefits. Firstly, it will make the production of biodiesel more competitive with the existing diesel fuel market, and second, it will produce monoglycerides, which are the most important emulsifiers used in food industry with lower cost compared to the conventional process, as the crude glycerol can be obtained as a by-product from the biodiesel process.

Acknowledgements

The Prince of Songkla University financially supported this research. The Department of Chemical Engineering and the Faculty of Engineering, Prince of Songkla University are gratefully acknowledged for their support.

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