Separation of glycerolysis product using hexane

S Mujdalipah*, A H Sasmita2, I K Amalia3 and A Suryani3
1 Program Studi Pendidikan Teknologi Agroindustri, Universitas Pendidikan Indonesia, Jl. Setiabudi No. 207, Bandung, Indonesia
2 Jurusan Pendidikan Teknik Mesin, Universitas Pendidikan Indonesia, Jl. Setiabudi No. 207, Bandung, Indonesia
3 Departemen Teknologi Industri Pertanian, Institut Pertanian Bogor, Kampus IPB Darmaga, Bogor, Indonesia

*Corresponding author: siti.mujdalipah@upi.edu

Abstract. Hexane is non-polar solvent and it can dissolve triglyceride and free fatty acid. The aim of this research is to get the hexane ratio to the glycerolysis product that can produce product that has the best characteristics. The study was conducted in five stages. In the first stage, the physicochemical properties of palm oil were analysed. In the second stage, palm oil glycerolysis was conducted. In the third stage, glycerolysis product was extracted by using hexane in various concentrations. In the following stage, physicochemical properties of extracted products were analysed. In the last stage, data were subjected to an analysis of variance. Results showed that ratio between glycerolysis product to hexane in this work did not significantly ($\alpha=0.05$) affect the yield, the free glycerol content, and the ability of extracted products to reduce the surface tension of water. It was also found that the best treatment had yield of 28.5%. It was able to lower water surface tension from 72.00 to 31.80 dynes/cm and had free glycerol content of 2.40%. Base on this work, we found that further research need to be done.

1. Introduction

Monoglyceride (MAG) and diglyceride (DAG) is the emulsifier that can be gotten from palm oil. They are many used as emulsifier in the various food products, such as margarine, bread, ice cream, and chewing gum. There are 20 kinds of food emulsifiers today and 70% of them are MAG and DAG [1]. Bakery is the most food product that uses these two kinds of emulsifier.

Product glycerolysis contains many impurities such as unreacted glycerol, unreacted triglyceride, and catalyst. This process produces a lot of excess glycerol. Hui [2] described that the finished product generally contains 35 -50% mono-glycerides and the rest are mostly di-glycerides, some unreacted triglycerides (10%), residual glycerol (3-4%), and free fatty acid (1-3%). Purification process to get a product that contains a high purity of mono-glycerides in the food industry is needed. Mono-glycerides have better emulsifying properties than a mixture of different acylglycerols. Some methods to remove excess glycerol and impurities in glycerolysis product were found by the writers.

Some of them are a vacuum or molecular distillation [3 – 7], column chromatographic purification [8], decantation [4], and thin layer chromatographic purification [3]. Distillation process is an energy intensive process [5] and purification process by decanting it takes a time. Some kinds of organic solvent can dissolve oil or fat. Some of them are benzene, methanol, ethanol, isopropanol, diethyl ether, carbon tetra chloride, and trichloroethylene. Hexane is non-polar solvent. It can dissolve...
triglyceride and free fatty acid. Hexane has been used for decades to extract oil from oilseeds with massive construction and operational costs [9]. However, information of the use of hexane to separate excess glycerol from glycerolysis product is rarely found. The information about impact of the use of hexane information on the characteristics of the glycerolysis product is also rarely. The aim of this research is to get the hexane ratio to the glycerolysis product that produce product that has the best characteristics as an emulsifier.

2. Methodology

Main materials used in this study were palm oil, glycerol, and solvent. Chemicals used for analysis were chloroform, iodine, glacial acetic acid, potassium iodide, KOH, HCl, ethanol, phenolphthalein, K_2Cr_2O_7, NaOH, alcohol 95%, and ethanol. Equipment including four-neck flask, condenser, rotary evaporator, vacuum pump, hotplate stirrer, Du Nuoy tensiometer, analytical balance, separatory flask, heater bath, desiccators, beaker glass, Buchner funnel, Erlenmeyer flask, burette, separator funnel, and other glass equipment were used. The study was done in five stages, namely 1) analysis of palm oil physicochemical properties, 2) glycerolysis of palm oil, 3) extraction of monoglyceride and diglyceride by using hexane in various concentrations, 4) analysis of physicochemical properties of extracted products, and 5) data analysis.

2.1 Analysis of palm oil physicochemical properties

Palm oil was analyzed for its physicochemical properties including acid value and water content. The acid value was analyzed volumetrically by 0.1 N NaOH as titrant and phenolphthalein as an indicator. The water content was analysed using oven method at 105 °C for 1 hour until a constant weight.

2.2 Glycerolysis of palm oil

Glycerolysis process was conducted for two hours by using KOH as catalyst. The glycerolysis was done by using solvent with a glycerol/palm oil ratio of 3.5 in 80°C.

2.3 Extraction of monoglyceride and diglyceride by using hexane in various concentrations

Extraction process was done by using hexane with hexane/glycerolysis product ratios of 1, 2, and 3. The process was conducted at room temperature and was continued by separating extracted product from residue of glycerol by using centrifugation.

2.4 Analysis of physicochemical properties of extracted products

Products resulted from glycerolysis were tested for their ability to lower the surface tension of water by using DuNouy tensiometer and free glycerol content [10].

2.5 Data analysis

Data were subjected to an analysis of variance by using Microsoft Excel application software.

3. Results and Discussion

3.1 Acidity and water content of Palm oil

Ma and Hanna [11] noted that free fatty acid and water can inactivate the alkali catalyst. They will consume the catalyst and reduce catalyst efficiency by causing soap formation. Atadashi et al. [12] noted the same thing that water from feedstock or produced during course of reaction may lead to deactivation of the alkali catalyst by hydration. Presence of water also speeds up hydrolysis of triglycerides and increases FFAs content in vegetable oils [12]. Kombe et al. [13] and Ding et al. [14] also noted those free fatty acids are not easily converted by homogeneous base trans esterification, because of the concurrent soap formation of the free fatty acids with the catalyst. The free fatty acids of 0.05% or 0.11 mg KOH/g sample in oil can inactivate catalyst as much as 0.1 kg/ton oil. Meanwhile, 0.01% of water in oil will inactivate 0.3 kg catalyst/ton oil. The acid value of palm oil was 1.31 mg KOH/g sample. Meanwhile, the water content of palm oil was 0.1%. The palm oil had acid value and water content which will bother activity of KOH as catalyst. High acid value of palm oil can lead the formation of soap as a result of the reaction between free fatty acids and KOH which will
cause emulsion. The emulsion makes the product hard to separate. It was the reason why the search method for separating excess glycerol from the product needs to be done.

3.2 Effects of Concentration of Hexane on the Yield of Extracted Products

Oil or fat are soluble in organic solvent. Extraction using solvent is the standard technique. It is widely used technique because it is simple and easy to run. In this study, the yields of extracted products were from 32% to 28.25% (Figure 1). The highest yield was obtained at glycerolysis to solvent ratio of 1:3. We can see from the figure that the product yield increases with increasing concentration of solvent. Ratio of solvent to solid is one of important parameter for extraction process [15]. Dasari and Goud [15] said that extraction depends on the nature of the solvent and oil, contact time of sample with solvent, extraction temperature, particle size and solvent ratio. Increasing solvent to glycerol ratio will increase the yield. It is due to the concentration gradient becomes greater which favors good mass transfer [16].

![Figure 1. Relationship between ratio hexane to glycerolysis product on the yield of extracted products](image)

Results showed that the concentration in this research did not significantly (confidence level 95%) affect the yield of extracted products. The extracted products which were extracted by using hexane with hexane/glycerolysis product ratio of 3 produced the highest yield.

3.3 Effects of Concentration of Hexane on the Ability of Extracted Products to Lower Water Surface Tension

Glycerolysis process was done as the research result of Kumoro [17]. In this study, the glycerolysis was conducted by using KOH as catalyst and isopropyl alcohol solvent at 80°C for two hours. The products were then extracted by using hexane with hexane/glycerolysis product ratios of 1, 2, and 3. In this study, the extracted products could lower water surface tension from 72 to 31.8-33.75 dynes/cm or 53.125%-55.764% (Figure 2). This proved that the products had surface active properties. Active groups contained in the products were able to lower water surface tension.

![Figure 2. Relationship between ratio hexane to glycerolysis product on the ability of extracted products to lower water surface tension](image)
Results showed that the concentration did not significantly (confidence level 95%) affect the ability of extracted products to lower water surface tension. The extracted products which were extracted by using hexane with hexane/glycerolysis product ratios of 2 and 3 had better ability to lower water surface tension than commercial emulsifier (tween).

3.4 Effects of Concentration of Hexane on the Free Glycerol Content of Extracted Products

Allowed free glycerol content in commercial glycerolysis products is no more than 7% [4]. Meanwhile, Hui [2] described that the finished product from glycerolysis process generally contains 3 – 4 % residual glycerol. Chetpattananondh and Tongurai [6] found that the impurities in monoglycerides product will reduce its emulsifying properties. Extracted products in this study contained free glycerol at a level of 2.40-3.05%. This indicated that the amount of glycerol that does not bind to fatty acid or residual glycerol which is still contained in the product was fairly low.

![Figure 3. Relationship between ratio hexane to glycerolysis product to the free glycerol content of extracted products](image)

Results showed that the concentration of hexane did not significantly (confidence level 95%) affect free glycerol content of extracted products. However, we can see from the figure that the free glycerol content of the product decreases with increasing concentration of hexane. Increasing solvent concentration will increase mass transfer [18]. It is also will increase contact area between products and solvent.

4. Conclusion

Hexane can extract monoglycerida and diglyceride from glycerolysis product. Concentration of hexane did not significantly (confidence level 95%) affect the yield and the free glycerol content of extracted products. It also did not affect the ability of extracted products to lower water surface tension. The extracted products was extracted with hexane/glycerolysis ratio of 2 had the best characteristics.

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