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Directed Interesterification of Coconut Oil to Produce Structured Lipid

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Abstract

Structured lipid is triglycerides composed of medium chain saturated fatty acids and unsaturated fatty acids. Coconut oil contains adequate amounts of medium chain and unsaturated fatty acids. The objective of this research is to evaluate a new method of producing structured lipid directly from coconut oil through directed interesterification in a solvent at three successively decreasing temperatures. The tested solvents are cellosolve and acetone. The results of the research showed that the new method is indeed effective and acetone is the better solvent. Three stages directed interesterification of coconut oil in acetone solvent could deliver around 24% of structured lipid.

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Keywords: medium chain triglyceride; structured lipid; coconut oil; directed interesterification; cellosolve; acetone

1. Introduction

Coconut (*Cocos nucifera*) is a plant species of the tribe of *Palma* and is the member of the genus *Cocos*. These plant parts starting from the root to the tip of the rod can be used for various purposes from industrial to household needs. Indonesia is one of the biggest coconut producing countries in the world. Thus, the utilization of the coconut is very wide open to be developed. Coconut oil is one of the processed results of coconuts that still can be further

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processed to produce useful products and high economic value. These can be used as raw material for the manufacture of food products, cosmetic products, and pharmaceutical products.

Coconut oil contains around 15% of medium chain fatty acids (C_6, C_8, and C_{10}). These fatty acids are raw materials for producing Medium Chain Triglyceride (MCTs) which is has high value because known as healthy food/fat. Structured lipids are composed of saturated fatty acids of medium chains and/or unsaturated fatty acids (especially those that are essential). Coconut oil also contains about 9% unsaturated fatty acids that can be generated around 24% structured lipids. The production of structured lipids is using conventional methods that are similar to the way the making of MCTs.

1.1. Structured lipid

Structured lipids are beneficial fats in food which is when it is consumed would not only produces nutritional benefits but also other health benefits such as a reduction in calories, weight control and others (Babayan, 1987). Structured lipids are rarely found in nature, but it can be produced by synthesis or modification of natural triglycerides. Constituent fatty acids of structured lipids are medium chain fatty acids and unsaturated fatty acids (oleic, linoleic acid, polyunsaturated fatty acids etc.).

Observations by Babayan (1987) on the composition of fatty acids on coconut oil showed that in addition contains approximately 15% of medium chain fatty acids and about 9% unsaturated fatty acids (oleic, linoleic, and palmitoleat). So, based on theory, coconut oil can be generated around 24% of structured lipids. Structured lipid has a relatively low melting point, so it appears ass fluid phase. The production of coconut oil is using conventional methods similar to the way of making of MCTs: methanolysis/hydrolysis of coconut oil, separation of methyl ester (medium chain and unsaturated fatty acids), and repeated esterification of fatty acids with glycerol. However, the directed interesterification method seems to allow the shorter and simpler method.

1.2. Directed interesterification

Interesterification is a general term of exchanged reaction between fatty acids from some fatty acid esters (e.g. triglycerides) with fatty acids, alcohol, or other fatty acid esters, to produce a new ester. Reaction of esters with acids is called acidolysis, the reaction of esters with alcohol called alcoholysis, and the reaction of esters with another called transesterification or ester exchange (Mattil et al.., 1964).The last group of reactions (transesterification or ester exchange) is a reaction which can be used to alter the distribution of fatty acids in oil or fat (triglycerides) without the addition of new fatty acids.

Chemical directed interesterification occurs if one or more of the triglyceride from interesterification reaction, selectively removed from the phase of reaction (the oil phase). The disappearance of these products from the reaction causing the reaction equilibrium always distracted, so interesterification continue and produce the maximum eliminated product. The commonly practiced procedure is carrying out the reaction at relatively low temperatures, until the more saturated triglycerides (with higher melting point) selectively precipitated/crystallized as solid fats (Marangoni and Rousseau, 1995). The main factor that reduce the acquisition of crystallized solid fat is the solubility of solid fat in liquid oils..

2. Methodology

This research consists of two main stages, namely the interesterification reaction and analysis. Solvent was added into coconut oil during the interesterification reaction. The solvents were cellosolve and acetone. The reaction carried out in 3 stages of decreased temperatures and solid fats were removed from solution every the end of each stage.

2.1. Tools and materials

This study used a set of distillation tools, a three-necked flask, one-necked Erlenmeyer flask, magnetic stirrer, electric heater, thermometer, filter paper, Buchner funnel, and stopwatch. Materials needed were coconut oil (saponification value 248-265 mg KOH/g), cellosolve and acetone solvent, potassium methoxide catalyst, aquades, reagents and solutions for iodine value and saponification value test.

2.2. Research Procedure

Put 100 grams of solvent, 100 ml of coconut oil, and potassium methoxide catalyst on a three-necked flask with a magnetic stirrer. Directed interesterification carried out in three stages decreased temperature and solid fats are removed from solution every the end of each stage. The oil at the end of the process still dissolved in the solvent is re-obtained by vaporize solvent.

Firstly, the flask that contains solvent and coconut oil is heated up to the temperature of the first phase (60^{o}C for cellosolve solvent and 45^{o}C for acetone solvent), using the electric heater while stirring with magnetic stirrer. Next put the catalyst of potassium metoxide and continued warming for 2 hours. Then, splitting solid phase from solution using a Buchner funnel and filter paper in a controlled temperature (still hot). The oil phase was returned to in three-necked flask for the second phase of the interesterification reaction. The second stage took place on the temperature of 50^{o}C for cellosolve solvent and 35^{o}C for acetone solvent. Warming and stirring is carried out for 4 hours. Splitting solid phase at the end of the second stage separated again by using a Buchner funnel. The third stage is the last stage in which the oil phase as filtering result is re-heated on temperature 40^{o}C for cellosolve solvent and 25^{o}C for acetone solvent, for 6 hours. The oil phase as result of the last interesterification process in the third stage allegedly as lipids structured.

Iodine value and saponification value test are needed to identify splitting solid phase and oil phase which is structured lipid as final product.

2.3. Experimental Variations

Variation in this research was the type of solvent used during directed interesterification process (i.e. acetone and cellosolve solvent). There were 3 stages of decreased temperatures and solid fats were removed from solution every the end of each stage. Respectively temperature of the reaction for acetone solvent in each phase were 45^{o}C (2 hours), 35^{o}C (4 hours), and 25^{o}C (6 hours). While the respectively temperature of the reaction for acetone solvent in each phase were 60^{o}C (2 hours), 50^{o}C (4 hours) and 40^{o}C (6 hours).

3. Results and Discussion

3.1. Sample testing of coconut oil

Coconut oil as raw material in this research was tested in advance of acid value, saponification value, and iodine value. Experiment results showed acid value of the sample was 0.342, so it did not need to reduce the level of acid number. High acid number indicates high level of free fatty acids in the oil that can interfere interesterification process because free fatty acids will consume catalyst which is alkaline. Based on experiment results, iodine value and saponification value consecutively were 6.99 and 259.33. According to O' Brien (1998), normal ranges of iodine value on coconut oil is 6-11, while the saponification value is 248-265.

3.2. Directed interesterification of coconut oil

Directed interesterification reaction is carried out by temperatures below the melting point of triglycerides to be separated, which is the triglycerides with long chains of fatty acids (trimyristin, tripalmitin, and trilaurin). At each stage of the reaction should has obtained a splitting of triglycerides in solid form (fats). Melting points of trimyristin, tripalmitin and trilaurin respectively are 65.5; 57.0 and 46.5°C (Thomas, 2005). The highest heating temperature (60^{o}C) is still relatively safe, considering the normal boiling point of cellosolve solvent is 135^{o}C. Directed interesterification using acetone solvent was carried out at the sequentially temperature of 45^{o}C (2 hours), 35^{o}C (4 hours), and 25^{o}C (6 hours). With boiling point of acetone which is only about 56^{o}C, removal of solvents from structured lipids product can be more efficient.

3.3. Structured lipid testing results

The experiment was done twice with their respective solvents. At each stage of directed interesterification process, there was splitting triglyceride in solid form, whereas structured lipid as final product in the form of liquid (oil). Furthermore, those solid triglycerides and structured lipids were tested for each iodine value and saponification value. The testing results of interesterification process with acetone solvent and cellosolve solvent, respectively, are presented in Figure 1 (a) and Figure 1 (b) (first trial).

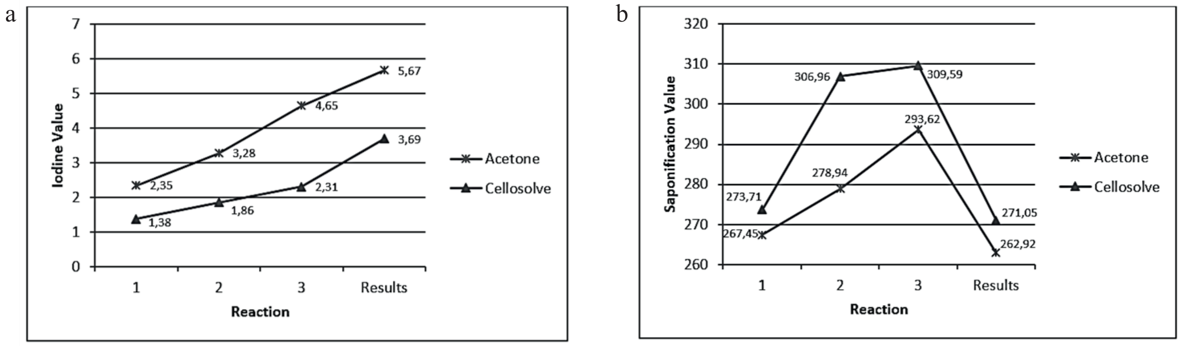

Fig. 1. (a) Iodine values of coconut oil after interesterification; (b) Saponification values of coconut oil after interesterification.

The iodine values of separated triglycerides (first reaction, second reaction, and third reaction) increased in a row, both in directed interesterification with acetone solvent and cellosolve solvent. For example, in interesterification reaction with cellosolve solvent on first reaction stage (temperature of 60^{o}C), the splitting triglycerides are triglycerides contain fatty acids with melting point above 60^{o}C, such as tripalmitin which has melting point 65.5^{o}C. Tripalmitin is one of long chain triglycerides that should be separated in order to obtain structured lipids containing triglycerides with medium chain fatty acids and unsaturated fatty acids. On the second reaction stage (temperature of 50^{o}C), the splitting triglycerides are triglycerides contain fatty acids with melting point above 50^{o}C, such as trimyristin. Increase of iodine values on each temperature decrease according to the results of previous research that had been done by 2 Sweden companies, Aktiebolaget Svenska Oljeslageri Aktiebolaget and Separator (1952).

The number of saponification values increased in every stage of temperature decrease in directed interesterification stage. It shows that separated triglycerides at each temperature decrease have increasingly low molecular weight. The repetition of directed interesterification of coconut oil showed the identical results to the first experiment. Shown in Fig. 2 (a) and Fig. 2 (b).

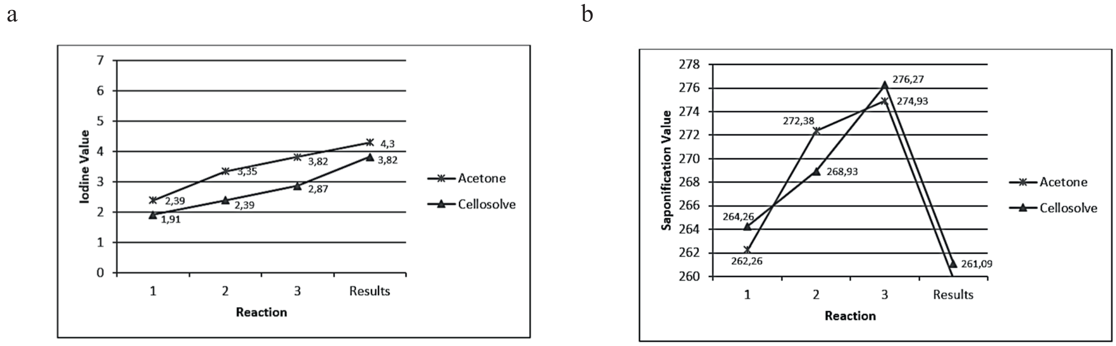

Fig. 2. (a) Iodine values of coconut oil after interesterification (looping); (b) Saponification values of coconut oil after interesterification (looping)

Iodine values increased in line with temperature decrease at each stage of the reaction. Iodine value of structured lipid as final product has the highest value compared with the results of iodine values of splitting triglycerides on solid form. On the other hand, saponification values also increased in line with temperature decrease. As in the first experiment, the saponification values of structured lipid has the lowest value compared with the results of iodine values of splitting triglycerides on solid form.

The result is identical between the first and second trials. Then comparison can be done between interesterification reactions with acetone solvent and cellosolve solvent. Comparison is done by taking the average of data from the results of the first and second trials for reaction with acetone and cellosolve solvents, i.e. the comparison of iodine values (Table 1 and Table 2) and the comparison of saponification values (Table 3 and Table 4).

Table 1. The average of iodine values of directed interesterification results (with acetone solvent).

Reaction Stages	Iodine Values		Averages
	Trial 1	Trial 2	
1	2.34	2.39	2.37
2	3.28	3.35	3.31
3	4.65	3.82	4.23
Results	5.58	4.30	4.94

Table 2. The average of iodine values of directed interesterification results (with cellosolve solvent).

Reaction Stages	Iodine Values		Averages
	Trial 1	Trial 2	
1	1.38	1.91	1.65
2	1.86	2.39	2.13
3	2.31	2.87	2.59
Results	3.69	3.82	3.76

Comparison profile of iodine values average of directed interesterification results on the first and second trials for both solvents, shown in Figure 3.

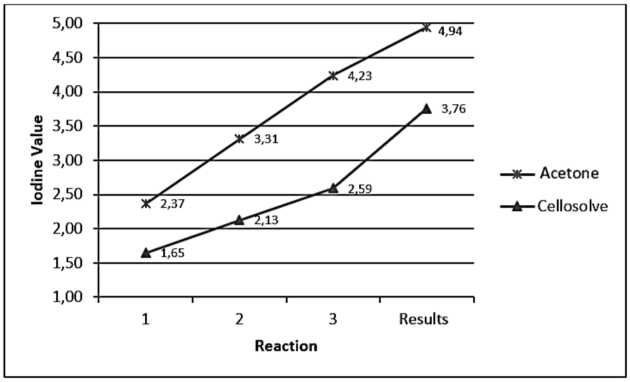

Fig. 3. Comparison between iodine values of directed interesterification results with acetone and cellosolve solvents.

Iodine values of directed interesterification results with acetone solvent is higher than the results of directed interesterification with cellosolve solvent. It showed that the amount of unsaturated fatty acids contained in structured lipids from interesterification process with acetone solvent are more than the results with cellosolve solvent. Based on these results, the use of acetone solvent in directed interesterification reaction of coconut oil is more effective because it produced higher iodine value.

Table 3. The average of saponification values of directed interesterification results (with acetone solvent).

Reaction Stages	Saponification Values		Averages
	Trial 1	Trial 2	
1	267.45	262.26	264.85
2	278.94	272.38	275.66
3	293.62	274.93	284.28
Results	262.92	259.76	261.34

Table 4. The average of saponification values of directed interesterification results (with cellosolve solvent).

Reaction Stages	Saponification Values		Averages
	Trial 1	Trial 2	
1	273.71	264.26	268.98
2	306.96	268.93	287.95
3	309.59	276.27	292.93
Results	271.05	261.09	266.07

Comparison profile of saponification values average of directed interesterification results on the first and second trials for both solvents, shown in Figure 4.

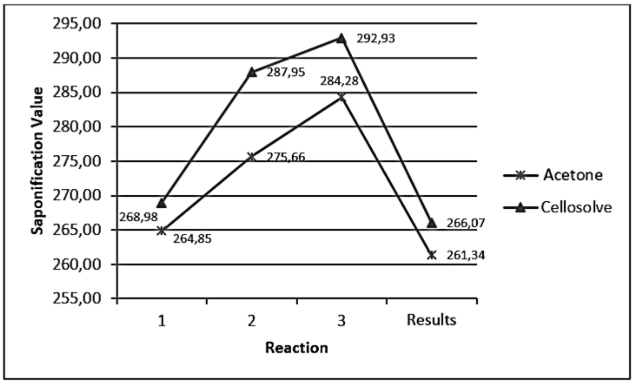

Fig. 4. Comparison between saponification values of directed interesterification results with acetone and cellosolve solvents.

Saponification values of directed interesterification results with acetone solvent is lower than the results of directed interesterification with cellosolve solvent. Most of the triglycerides with long-chain saturated fatty acids were already separated through the temperature decrease (first reaction, second reaction, and third reaction), so the final product left were triglycerides with medium-chain fatty acids and unsaturated fatty acids. The amount of unsaturated fatty acids contained in structured lipid affected the saponification values which is have low values. Based on these results, the use of acetone solvent in directed interesterification reaction of coconut oil is more effective because it produced lower saponification value.

4. Conclusions and Suggestions

From the results of iodine value testing, acetone solvent usage in the structured lipid production with directed interesterification of coconut oil is more effective when compared with the use of cellosolve solvent. Iodine value of structured lipid by directed interesterification with acetone solvent is higher than the results by directed interesterification with cellosolve solvent. The effectiveness of the use of acetone solvent is also evidenced by the results of the saponification value which is lower than the process results with cellosolve solvent. With the use of acetone solvent, separation of triglycerides during the interesterification process took more effective, proven by quantity of splitting triglycerides were more than interesterification process with cellosolve solvent. The solvent acetone has a pretty low boiling point (56^{o}C), so the removal process of solvents from structured lipid products would more efficient in energy usage. Three-stages directed interesterification of coconut oil in acetone solvent is capable to produce structured lipid with acquisition close to the theoretic estimation, i.e. 24%.

Gas chromatography analysis needs to be conducted to further analysis of fatty acids contained in the splitting triglycerides during the process and content of fatty acids in structured lipid product. Time and temperature variation during the interesterication process also needs to be conducted to get the most effective operating conditions in the production of structured lipid.

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