Potential of Ketapang Seed Oil (*Terminalia catappa* Linn) as Basic Material Mono-diglyceride Biodegradable Surfactant

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Abstract. Surfactants are widely used in pharmaceuticals, perfumes, cosmetics, food and beverages. One type of surfactant produced from the synthesis of palm oil is mono-diglyceride which can function as an emulsifier. Ketapang (*Terminalia catappa* Linn) is a beach tree with a wide spread area, whose seeds have not been utilized optimally. The content of Ketapang seed oil has the potential to be converted into mono-diglyceride surfactant. This study uses experimental laboratory methods, while parameter optimization is done by the two level factorial design method. The raw materials used were Ketapang seeds from around the campus of Semarang 17 Augustus 1945 University, n-butanol solvents, glycerol, MgO catalysts. During the glycerolysis process, 8 run experiments were carried out with 3 variables which changed in temperature (60 & 90°C); MgO catalyst (2 & 4%) and solvent / 10 g oil volume 20 and 40 ml, while the variable is the weight of 25 gram ketapang seed oil; stirring speed of 400 rpm; reaction time of 4 hours; ratio of glycerol 2.5 ml / 10 g oil; and 24-hour deposition time. From the results of the study, the influential variable is temperature. The optimum results were obtained at conditions of 90°C, 4% MgO catalyst, solvent volume of 20 ml / 10g ketapang seed oil and yield 97.9% %. The resulting surfactant has the characteristics of acid number 57.2 mg KOH / gr, saponification number 218 mg KOH / gr. Surfactant has HLB value 14.75, meaning that the surfactant functions as an O / W type emulsifier or as detergent agent.

1. Introduction

Ketapang (*Terminalia catappa* Linn) is a beach tree with a fairly wide distribution area. Originating from the tropics in India, then spread to Southeast Asia, North Australia, and Polynesia in the Pacific Ocean. Besides growing wildly on the beach, this tree is often planted as a shade tree in the lowlands. Therefore, ketapang trees are also planted as ornamental trees in cities. Ketapang tree is also one type of shade tree. Ketapang tree is one of the trees that are often found in the city of Semarang, one of which is in the UNTAG Semarang campus area as a parking area shade plant, or a road shade.

Until today, the utilization of ketapang trees has not been explored to the fullest, especially the fruit. The shape of the fruit of this ketapang tree is like an almond fruit, its fruit is roughly 4 - 5.5 cm. Ketapang seeds when unripe are green and turn brownish red when ripe. Utilization of seeds so far is only limited to direct consumption or processed into snacks, it is still very rarely extracted oil content [1]. Ketapang seeds contain 50% - 60% oil. Ketapang seed oil has not been used optimally, in some countries Ketapang seed oil is used as a substitute for Almond oil, the oil is tasteless and odorless so it is not tasty for consumption, its use is new as a remedy for skin diseases such as scabies. [1]
According to research by Ravensca I., et al. [5]. The making of surfactant based on Ketapang seed oil with Triethanolamine obtained a yield of 20%. The surface tension test results are 34,947 dyne/cm. In the chemical properties test for esteramine, the acid number is 5.61 mgKOH/gr, the saponification number is 98.175 mgKOH/gr and the HLB value is 5.25.

Based on research that has been done, it is possible that ketapang seed oil is converted into surfactants. This study aims to examine whether it is possible for Ketapang oil to be converted into "biodegradable" surfactant type Mono-diglyceride; know the most influential variables; know the optimum conditions of the glycerolysis process and determine the characteristics of the physico-chemical properties, the functional properties of the emulsifier based on HLB values.

| Table 1. Composition of Ketapang seed fatty acids [6] |
|-----------------------------------------------|
| Fatty acid     | Composition (%) |
| Palmitic Acid  | 35,26           |
| Palmitoleic Acid | 0,38           |
| Stearic Acid   | 4,55            |
| Oleic Acid     | 38,72           |
| Linoleic Acid  | 20,57           |
| Arachidic Acid | 0,51            |

Glycerolysis is the reaction between glycerol and oil or fat to produce mono and di-acyl glycerol (MAG and DAG). The purpose of the catalyst in addition to getting a relatively short reaction time is also to direct the OH group toward the formation of MAG and DAG. Reactions with base catalysts (NaOH) usually run faster. Characteristics of the glycerolysis reaction from oils/fats will (predominantly) produce monoglycerides. Monoglycerides with a 2-acyl structure or β-monoglycerides will generally be obtained between 5-8% (at low temperatures) and above 30% (at very high temperatures) [10].

The main characteristic of surfactants is their surface activity. Surfactants can increase the ability to reduce surface tension and interface of a liquid, increase the ability to form oil emulsions in water, change the speed of aggregation of dispersed particles by inhibiting and reducing flocculation and coalescence of dispersed particles, so that the stability of dispersed particles increases.

Hydrophilic Lipophilic Balance (HLB) is a number that shows the comparison between hydrophilic groups and lipophils in surfactants. Griffin set up a HLB surfactant size scale that can be used to compose the optimum HLB efficiency region for each surfactant function. The higher the HLB value of a surfactant, its polarity properties will increase. Different Hydrophilic - Lipophilic Balance (HLB) values of surfactants, HLB values range from 0-20, each value has a different function [12].
Table 2. Function of surfactants based on HLB values [12]

| Characteristic dalam air | HLB | Ratio | Funksi |
|--------------------------|-----|-------|--------|
| Tidak terdispersasi      | 0   | 0     | 100    |
| Sedikit terdispersasi    | 2-3 | 10    | 90     |
| Milky dispersion         | 4-5 | 20    | 80     |
| Stable milky dispersion  | 6   | 30    | W/O emulsification |
| Transparent dispersion   | 5-9 | 40    | O/W emulsification |
| Larutan liquor           | 10-11 | 50 | 60 |

2. Research Method

Materials used: Ketapang seeds, MgO catalyst, aquadest, n-butanol, n-hexane, Glycerol. Equipment used: a series of extraction and glycerolysis devices, ovens, thermometers, electric scales, glass ware.

2.1. Fixed Variable

| Changed Variable | High Level (+) | Low Level (-) |
|------------------|----------------|---------------|
| Glycerol Ratio   | 2.5 ml / 10 gr of oil |              |
| Oil Weight       | 25 gr           |               |
| Solvent type     | n-butanol       |               |
| Separation Time  | 24 hours        |               |

| Temperature      | 90°C            | 50°C           |
| Solvent Volume   | 40 ml/10 gr oil | 20 ml/10 gr oil |
| Catalyst         | 4 %             | 2 %            |

2.2. Procedure

Extraction Process:
Ketapang seeds are dried, mashed, then weighed 30 grams. They are then wrapped in filter paper and inserted into the extractor tube. Extraction is carried out for 1.5-2 hours with 250 ml n-hexane as solvent. Extraction stops when the oil has been completely extracted and then the recovery solvent process is performed. Then the result oil is roasted to evaporate the remaining solvent.

Glycerolysis Process:
Ketapang seed oil is put with n-butanol solvent into a three-neck flask, in a certain amount according to the variable. Then it is heated to the specified temperature. A certain amount of glycerol is heated in a separate place until the operating temperature. Glycerol and MgO catalyst were put into a mixture of ketapang seed oil and n-butanol solvent in a three-neck flask and stirring was carried out. Heating and stirring stopped after the reaction time was reached. Separate the catalyst by filtering. Then the product left in the separating funnel for 24 hours to create two perfect layers, the remaining glycerol is separated from the product and its weight and volume are measured.
3. Results and Discussion

The variable test results show that the temperature variable is the variable whose farthest point of effect shows that the temperature variable is the most influential variable on the glycerolysis process of ketapang oil. Providing the same results as research conducted by Purwaningtyas, et al. [11].

The optimization stages of the glycerolysis process gave the following results: at a glycerolysis temperature of 90°C, a solvent volume of 20 ml / 10 g of oil, a 4% MgO catalyst and a stirring time of ± 4 hours with a stirring speed of 400 rpm gave the largest yield of 97.7%. Figure 1 shows the relationship between the glycerolysis temperature and the % yield obtained, the results show a tendency to increase glycerolysis results at increasingly rising temperatures. But decreased after a temperature of 90°C. The cause is after reaching the optimum point the results of the glycerolysis decrease with increasing temperature. An increase in temperature will cause the solvent n-butanol to be in the vapor phase so that the solubility of the ketapang seed oil in glycerol decreases, the temperature can increase the homogeneity of the reaction mixture.

![Figure 1. Graphic optimization of the relationship of temperature to yield.](image)

The results of the HLB surfactant test values produced gave a value of 14.75. HLB values indicate that mono diglyceride surfactants can be used as O/W emulsifiers, namely at HLB values 8-18, these surfactants can dissolve in water and are used to make oil-in-water emulsions (O/W). Examples of Polyoxyethylenesorbitanmonoooleate emulsifiers (Polysorbate 80 USP) or commonly referred to by the trade name tween 80, in addition to being used as an emulsifier are also used as cleaning agents (detergents) where HLB detergent 13-15.[12]

4. Conclusion

The most influential variable on the glycerolysis process of ketapang seed oil is temperature. The optimum conditions for the glycerolysis process are achieved in:

- Solvent type: n-butanol
- Content: 70%
- Volume: 20 ml / 10 gr oil
- Sample weight: 25 grams
- Temperature: 90 °C
- Time: 4 hours
- Stirring Speed: 400 rpm
- Yield: 97.9%
- MG content: 31.83%

Characteristics of surfactants produced:

- Acid number: 57.2 Mg KOH / gr
- Saponification Number: 218 Mg KOH / gr
- HLB value: 14.75 (O/W emulsifiers being used as an cleaning agents).
References

[1] Handayani, M.P. and S. Wahyuono., 2008. Analisis Biji Ketapang (Terminalia catappa L.) Sebagai Suatu Alternatif Sumber Minyak Nabati. Majalah Obat Tradisional, July-September. 13/45. Page 101-107.

[2] Suwarso W.P., Gani I.Z., and Kusyanto., 1999, Sintesis Biodiesel Dari Minyak Biji Ketapang (Terminalia catappa L.) Yang Berasal Dari Tumbuhan Di Kampus UI Depok, Laboratorium Kimia Organik – Departemen Fakultas Matematika dan Ilmu Pengetahuan Alam - Universitas Indonesia, Depok.

[3] Balogun, A. M. and Fetuga, B. L., 1985, Fatty Acid Composition of Seed Oils of Some Members of the Meliaceae and Combretaceae Families. JAOCs, Vol. 62, no. 3, Hal. 539 – 531. In Handayani, M.P. dan S. Wahyuono., 2008. Analisis Biji Ketapang (Terminalia catappa L.) Sebagai Suatu Alternatif Sumber Minyak Nabati. Majalah Obat Tradisional, July-September. 13/45. Page 101-107.

[4] Nuryanto E, 1997, Surfactant yang Ramah Lingkungan dari Minyak Kelapa Sawit, Warta Pusat Penelitian Kelapa Sawit, volume 5 (1), page 37-45.

[5] Ravensca I., Saleh C., and Daniel., 2017, Pembuatan Surfactan Berbahan Dasar Minyak Biji Ketapang (Terminalia catappa) Dengan Trietanolamina, Jurnal Atomik 02 (2) hal 183-189, Program Studi Kimia FMIPA Universitas Mulawarman, Samarinda.

[6] http://isjd.pdii.lipi.go.id/admin/jurnal/12084250.pdf downloaded on May 23rd, 2019.

[7] Oktaviany H., 2006. Analisis Mutu Minyak Biji Ketapang (Terminalia catappa Linn).FMIPA, Universitas Sriwijaya, Inderalaya.

[8] Negi, D.S ; Sobotka, F ; Kimmel, T; Wozny, G and Schomacker, R, 2007, Glycerolysis of Fatty Acid Methyl Esters : 1. Investigations in a Batch Reactor, Journal of American Oil Chemist’s Society, Volume 84, Page 83 – 90. (www.springerlink.com)

[9] Hassanaudin A, 2001, Kajian Teknologi Pengolahan Minyak Sawit Mentah untuk Produksi Emulsifier Mono-diaisilgliserol dan Konsentrat Karotenoid, Makalah Falsafah Sains, page 17, Universitas Tadulako, Palu.

[10] Anggoro ,D.D., Budi, F.S., Noviana, S.M and Hapsari, Y.S., 2008, Proses Gliserolisis Minyak Kelapa Sawit menjadi Mono-diacylgliserol dengan Pelarut n-butanol dan Katalis MgO, Prosiding Seminar Nasional Rekayasa Kimia dan Proses, Teknik Kimia UNDIP, Semarang.

[11] Purwaningtyas E.F., Kasmiyatun M., Mulyaningsih S.MF and Indah,WN., 2015 , Optimization of Glycerolysis Temperature Process for the Synthesis of Monoglyceride-Diglyceride Surfactants Derived from oil of Silkworm Pupae, Prosiding Seminar Nasional “Kejuangan”, UPN Yogyakarta, 18 Maret 2015.

[12] Holmberg ,K., Jonsson, B., Kronberg ,B and Lindman, B., 2004, Surfactants and Polymers in Aqueous Solution, 2nd edition, John Wiley & Sons Inc. USA.