KINETICS OF GLISEROLYSIS REACTION OF SILKWORM PUPAE OIL ON SYNTHESE SURFACTANT BIODEGRADABLE

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Abstract. Continuing previous research entitled “The Innovation of Making MAG-DAG Biodegradable Surfactants Based on Silkworm Waste: Raw Material for Animal Oil”. So this study aims to determine the kinetics of the reaction. Determining the order of the reaction can only be done experimentally, the second-order reaction is not always bimolecular, but the bimolecular reaction must be of second order. The reaction is carried out at various temperature variations namely 65°C, 75°C, and 85°C at 1 atm pressure. Each interval of one hour, samples were taken from the process up to 4 hours of reaction time, to then be analyzed the residual content of triglycerides in each sample. The results showed that the higher the reaction temperature, the faster the reaction. Further analysis showed that the reaction that occurred was an alternating second-order reaction, the deviation was respectively 8.84% and 16.71%, with the values of $k_1$ and $k_2$:

$$k_1=1.1625 \times 10^5 \exp \left( \frac{-6946.06}{T} \right) \left( \frac{L}{mol.s} \right)$$

$$k_2=7.4306 \exp \left( \frac{-4038.74}{T} \right) \left( \frac{L}{mol.s} \right)$$

The general equation for the reaction speed of pupa oil glycerolysis is

$$r = k_1 \,(C_A) \,(C_B) - k_2 \,(C_C) \,(C_D)$$

1. Introduction

Silkworm pupae (Bombbyx mori), which have died to the drying process, are untreated waste, though people know that silkworm pupae have high protein, fat and vitamin content, some people still feel less appetite for consuming them directly, people use it more as animal feed. The use of pupae that have been carried out is used as fertilizer, as a source of lecithin which can be used as antioxidants in vegetable oil and fish oil. The silkworm pupa protein source can also be a more acceptable food processed product, such as by making it as a pupa powder and applying it as a water-soluble protein source in the process of making instant cream soup [1]. Various attempts were made by several researchers to utilize silk pupa waste into products that have more economic value.
One of the efforts to increase the economic value of silkworm pupa waste is its use as a surfactant product that has biodegradable properties. Using the glycerolysis process, pupa oil that has been extracted can be processed into monoglycerides and diglycerides as a raw material for surfactants, this can be seen from the test results using GCMS. Pupa oil contains fatty acids among others: palmitic acid-\(\alpha\)-monoglyceride; \(\alpha\)-monopalmitin; \(\alpha\)-monoolein; and some other fatty acids that are possible to convert into mono-diglycerides.

The silkworm pupae (\textit{Bombyx mori}) which have been processed in the form of powder contain 7.18% water, 29.57% lipids, 48.98% protein, 4.65% glycogen, 3.37% chitin, and the rest is ashes [2]. Extraction of pupa powder to obtain silk pupa oil which has physico-chemical properties as follows: viscosity = 30.88 Cp; pH 5.2; \(\rho = 0.935\) g/ml; acid number 12.54%; iod number 126.89/100 gr; saponification number 215.56 mg KOH/gr; peroxide number 17.57 gr/100 gr; FFA 0.42%; and 36.17% unsaturated fatty acids [3].

Monoglycerides (MG) are widely used as emulsifiers in the food, pharmaceutical, and cosmetic industries. In the pharmaceutical industry, MG is used as a binder in tablets. In the food industry, MG is generally used as an emulsifier for bakery products, margarine, gravy, butter, pudding, bread, biscuits, and pastries. Meanwhile, in the cosmetic industry, it is used to increase the consistency of creams and lotions. Monoglycerides also provide lubrication and plasticity which are good for use in the textile industry, plastic industry [4], [5], [6]. Currently, surfactant products are still dominated by palm oil raw materials, whose availability is quite abundant. So it is necessary to research to study other alternative materials that can be converted into surfactants.

The manufacturing process is based on the glycerolysis process, which is the reaction between glycerol and triglycerides from oil or fat to produce monoglycerides and diglycerides. Based on the literature reaction rate or reaction speed can only be determined if the stoichiometric reaction is known and there is experimental data on changes in the components involved in the reaction each time [7]. Based on the experiments that have been carried out, the rate of a chemical reaction is influenced by or is a function of (i) The concentration of the components involved in the reaction; (ii) Reaction temperature; (iii) -Reaction system pressure; and (iv) Catalysts. In simple mathematics it can be written in the form of an equation:

\[
\text{r} = f (C_i, T, P, \text{Katalis})
\]

In this study, a solvent is used which is thought to increase the solubility of oil in glycerol. It is hoped that the glycerolysis reaction can be carried out at a low temperature to avoid the formation of brown color and unpleasant odors to the burning of materials and products [8]. Solvents that can increase the solubility of oil in alcohol are long-chain aliphatic alcohol compounds which have a high enough boiling point (above 100°C). In this study, the solvent used was n-butanol which has a TD of 117.73°C.

Monoglycerides consist of one fatty acid radical and two glycerol molecules, while diglycerides consist of only one glycerol molecule. [9] The glycerolysis reaction that occurs is as follows:

![Glycerolysis Reaction Stage (Noureddini et al., 2004)](image-url)
The equation for the overall reaction rate of glycerolysis is as follows:
\[
r = -\frac{dC_A}{dt} = k_1 (C_A) (C_B) - k_2 (C_C) (C_D)
\]  
\(^{(1)}\)

\[
C_A = C_{A0} (1 - X_A)
\]  
\(^{(2)}\)

\[
C_B = C_{B0} - (C_{A0}.X_A)
\]  
\(^{(3)}\)

\[
C_C = C_{C0} + (C_{A0}.X_A)
\]  
\(^{(4)}\)

\[
C_D = C_{D0} + (C_{A0}.X_A) \text{ and } X_A = \text{konversi A}
\]  
\(^{(5)}\)

At equilibrium conditions \((X_{Ae})\), \(r = 0\):
\[
\frac{k_1}{k_2} = \frac{C_CC_D}{C_AC_B}
\]  
\(^{(6)}\)

\[
\frac{k_1}{k_2} = \frac{C_CC_D}{C_AC_B}
\]  
\(^{(7)}\)

Each \(C_A\): residual triglyceride concentration; \(C_B\): residual glycerol concentration; \(C_C\): the resulting monoglyceride concentration; \(C_D\): the resulting concentration of diglycerides. Whereas \(k_1\) and \(k_2\) are reaction velocity constants. \(X_A\) is the conversion of triglycerides is the reaction time. Mathematically, the relationship between the constant value of reaction velocity and the temperature is expressed by the Arrhenius equation \([10]\).
\[
k = A \cdot e^{-\frac{E_a}{RT}}
\]  
\(^{(8)}\)

Where \(k\)=constant rate of reaction, \(A\)=impact factor, \(E_a\)=activation energy \((J/mol)\), \(R=8.314\) \(J/mol\) \(K\), \(T\)=temperature \((K)\).

This study to examine the reaction kinetics of the glycerol process of silk pupa oil, the results of which will be useful as a basis for a design for the production of surfactant monoglycerides and diglycerides as biodegradable surfactants on a larger scale.

2. Materials and Method

2.1 Materials

The materials used in this research were: silk pupa oil, glycerol 87.72%, MgO p.a catalyst Merck, and solvent n-butanol with a purity of 74.28%. The research equipment used is shown in Figure 2.

![Glycerolysis Equipment](image)

**Explanation:**
1. Cooler
2. Mixer Motor
3. Stative
4. Waterbath
5. Stove Heater
6. Thermocontrol

**Figure 2. Glycerolysis Equipment**

2.2 Research Procedure

100 grams of pupa oil, 50 grams of glycerol, 4.5 grams of MgO catalyst, and 200 ml of n-butanol are put into a three-neck flask. The motor mixer is driven at 400 Rpm. The mixture was then heated to a
temperature of 65 °C, then 4.5 grams of MgO catalyst was added, keeping the temperature constant. The first sample was taken at zero hours (t₀). The glycerolysis process was run for four hours, 10 ml samples were taken every hour. The same procedure is carried out for temperature variations of 75 °C and 85 °C. The samples were then analyzed to determine the levels of monoglycerides, diglycerides, and remaining triglycerides from the glycerolysis reaction using the AOAC (Association of Analytical Chemist) analysis method.

3. Result and Discussion

From the results of research for the synthesis process of silk pupa oil into mono-diglyceride surfactant through the glycerolysis process, the results of the triglyceride conversion value (Xₐ) in percent are presented in Table 1.

| No | Temperature (°C) | Time (hours) | 1 | 2 | 3 | 4 |
|----|------------------|--------------|---|---|---|---|
| 1  | 65               | 39.70        | 37.03 | 35.75 | 31.87 |
| 2  | 75               | 35.89        | 33.10 | 32.09 | 31.05 |
| 3  | 85               | 39.10        | 32.73 | 28.79 | 27.15 |

Table 1 shows that the triglyceride conversion increases with increasing reaction time and reaction temperature. The higher the reaction temperature, the kinetic energy the molecules will increase. The collision of many molecules causes chemical reactions to accelerate. The decrease in triglycerides indicates the higher conversion obtained in the glycerolysis reaction. The longer the reaction time, the higher the triglycerides from silk pupa oil.

Theoretically, it can be seen that the triglyceride glycerolysis reaction is a reversible second-order reaction. If CA₀ = CB₀ then the reaction speed equation for a reversible second-order reaction is as follows:

\[
\ln \frac{X_{Ae}^2 (2X_{Ae} - 1)X_A}{X_{Ae}^2 X_A} = 2k_1 \left( \frac{1}{X_{Ae}} - 1 \right) C_{A0} t
\]

When in graphic form:

\[
\ln \frac{X_{Ae}^2 (2X_{Ae} - 1)X_A}{X_{Ae}^2 X_A} = y
\]

\[
2k_1 \left( \frac{1}{X_{Ae}} - 1 \right) C_{A0} = \text{slope}
\]

\[
t = x
\]

If the glycerolysis reaction is true second order is reversible, then a graph will be obtained with the experimental results approaching a straight line. With Microsoft Excel, a linear trendline was selected to see if the experimental data matched with the initial analysis.

From the data obtained, it is processed with a graphical method, to determine the reaction order based on the R² value approach using the Program Excel 2013. The results obtained are presented in Figures 3, 4, and 5. The three figures provide a straight line equation with R² approaching the value of 1, this shows that the glycerolysis reaction of silk pupa oil is reversible[10].
**Figure 3.** Graphic relationship between time (second) and value \(\ln\left(\frac{X_{AE} - (2X_{AE} - 1)X_A}{X_{AE} - X_A}\right)\) at temperature 65oC.

\[ y = 1.0955E-04x + 2.1667E-01 \\
R^2 = 0.9173E-01 \]

**Figure 4.** Graphic relationship between time (second) and value \(\ln\left(\frac{X_{AE} - (2X_{AE} - 1)X_A}{X_{AE} - X_A}\right)\) at Temperature 75oC.

\[ y = 2.1881E-04x + 4.8051E-01 \\
R^2 = 0.9685E-01 \]

**Figure 5.** Graphic relationship between time (second) and value \(\ln\left(\frac{X_{AE} - (2X_{AE} - 1)X_A}{X_{AE} - X_A}\right)\) at temperature 85oC.

\[ y = 2.0066E-04x - 2.0978E-02 \\
R^2 = 0.9958E-01 \]
Table 2. Reaction Rate Constants (k₁ and k₂) following the value of the Equilibrium Constants (K) at Various Temperature.

| Temperature | k₁ data (x10⁻⁴) | k₁ Count (x10⁻⁴) | Rectify (%) | k₂ data (x10⁻⁴) | k₂ count (x10⁻⁴) | Rectify (%) | K = k₁/k₂ |
|-------------|-----------------|-----------------|-------------|-----------------|-----------------|-------------|----------|
| 338         | 1.2971          | 1.3818          | 6.1313      | 0.4272          | 0.4805          | 11.0794     | 3.0359   |
| 348         | 2.8408          | 2.4940          | 13.9051     | 0.8626          | 0.6773          | 27.3487     | 3.2936   |
| 358         | 4.0732          | 4.3555          | 6.4819      | 0.8271          | 0.9366          | 11.6951     | 4.9247   |
| Total       |                 |                 | 26.5182     |                 |                 | 50.1232     |          |
| Average Deviation | 8.8394        |                 | 16.7077     |                 |                 |            |          |

Table 2 it can be seen that the higher the temperature, the greater the reaction rate constant (k₁ or k₂). the equilibrium constant value increases with increasing temperature. The effect of temperature on reaction speed is strengthened by the analysis of the equilibrium constant value (K = k₁/k₂), a low equilibrium constant value indicates that the reaction is reversible reaction. If a relationship is made between the constant rate of reaction and temperature according to Arrhenius's Law [10], the following equation is obtained, with the deviation was respectively 8.84% and 16.71%.

\[
k₁ = 1.1625 \times 10^6 \exp \left( \frac{-6946.06}{T} \right) \left( \frac{L}{mol.s} \right) \tag{13}
\]

\[
k₂ = 7.4306 \exp \left( -\frac{4038.74}{T} \right) \left( \frac{L}{mol.s} \right) \tag{14}
\]

The general equation for the reaction speed of pupa oil glycerolysis is as follows:

\[ r = k₁ (Cₐ) (C₉) – k₂ (C₇) (C₉) \]

Where:
- \( r \) = reaction rate, mol/(L.s)
- \( k₁, k₂ \) = constant reaction rate, L/(mol.s)
- \( Cₐ \) = concentration of triglyceride, mol/L
- \( C₉ \) = concentration of glicerol, mol/L
- \( C₇ \) = concentration of diglyceride, mol/L
- \( C₉ \) = concentration of monoglyceride, mol/L

4. Conclusion

The pupa oil glycerolysis reaction kinetics follow as 2nd order and reaction is a reversible with the highest reaction rate constant occur at 358oK with \( k₁ = 4.0732 \times 10⁻⁴ \) L mol⁻¹ s⁻¹. Validation indicate that laboratory data (kdata) and calculation (kcount) result in similarity, so the reaction kinetics model is acceptable. The effect of temperature on the value of the reaction rate constant on surfactant production from silkworm waste is that the higher the temperature, the value of the reaction rate constant is the greater or proportional this is in accordance with the Arrhenius equation.

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Reference

[1] Haryasyah, Catherine, Gunawan, Stella A, Artianti, Astrisia H, Stephanie G.,2009, “Utilization of Silkworm Waste (Bombyx Mori) in the Production of High Protein Instant Cream Soup”, [https://repository.ipb.ac.id/handle/123456789/19890](https://repository.ipb.ac.id/handle/123456789/19890).
[2] Yang, X., Huang, L., and Li, T., 2004, “Effects of Silkworm Pupa Oil on Serum Lipids Anp Platelet Fuction in Rats”, Departement of Nutrition and Hygiene, Tongji Medical College of Huangzhong University of Science and Technology, Wuhan, China.

[3] EryFatarina P, Mega K, Sri Mulyaningsih, T.Nina Da Silva, 2016, “The Potential of Silkworm Waste as Biodegradable Raw Materials”, JurnalIlmiah Dasar, Volume 17, Nomor 1, Page 35-38, http://jurnal.unej.ac.id/index.php/JID.

[4] Negi, D.S., Sobotka, F., Kimmel, T., Wozny, G., and Schomacker, R., 2007, “Glycerolysis of Fatty Acid Methyl Esters: Investigation in A Batch Reactor”, Journal of American Oil Chemist’s Society, Volume 84, 83-90.

[5] Potter, M.R., 1994, “Handbook of Surfactants”, 2nd edition., Chapman and Hall, Glasgow.

[6] Holmberg, K., Jonsson, B; Kronberg, B, dan Lindman, B., 2004, “Surfactants and Polymers in Aqueous Solution”, 2nd edition., John Wiley and Sons Inc., New York.

[7] Christina, D., 2006, “Characterization and Application of Emulsifier Mixture of Mono-diacylglycerol from Palm Oil Fatty Acid Distillate, Research of the Department of Food Technology and Nutrition”, Faculty Agricultural Technology, IPB, Bogor.

[8] Anggoro, D.D; Budi, F.S., Noviana, S.M dan Hapsari, Y.S., 2008, “Glycerolysis Process of Palm Oil Glycerolysis Process of Palm Oil to Mono-diacylglycerol with n-Butanol Solvent and MgO Catalyst”, Proceeding National Seminar on Chemical and Process Engineering, Department Chemical Engineering, UNDIP, Semarang.

[9] Noureddini, H., and Medikonduru, V., 1997, “Glycerolysis of Fats and Methyl Esters”, Journal of The American Oil Chemist’s Society, Volume 74, Number 4.

[10] Levenspiel, O., 1999, “Chemical Reaction Engineering”, John Wiley and Sons, Inc., New York.