MODELING AND OPTIMIZATION OF ALKYL POLYGLUCOSIDE SURFACANTS FROM FATTY ALCOHOL BY RESPONSE SURFACE METHODOLOGY

Department of Chemical Engineering, Faculty of Engineering, Universitas Sumatera Utara, Medan, Indonesia
E-Mail: zuhrina@yahoo.com

ABSTRACT
Application of Response Surface Methodology (RSM) in the modeling and optimization of the synthesis of alkyl polyglucosides (APG) is presented. Two different sets of alkyl polyglucoside from glucose (G) have been synthesized using an acid catalyst. Decanol (C10) and dodecanol (C12) are used as sources of fatty alcohol (FA), and the interactions effect of catalyst concentration, substrate molar ratio and reaction time on the density of APG is observed. The optimum density in decyl polyglucosides (APG-C10) synthesis was obtained at a catalyst concentration of 1.5 % (w/wG), a substrate ratio of 3 (mol FA/G) and a reaction time of 3 h. While in dodecyl polyglucosides (APG-C12) synthesis, optimum density was obtained at a catalyst concentration of 1 % (w/wG), substrate ratio of 2 (mol FA/G) and 13 h reaction time. The substrate ratio and reaction time are significant variables that influence the acquisition of APG density in both reactions. A quadratic polynomial model was fitted to the data with an R² of more than 0.95 so that the model obtained can be said to be very significant.

Keywords: alkyl polyglucoside, fatty alcohol, glucose, response surface methodology.

INTRODUCTION
Surface and interface phenomena are very widely used in industrial processes for the manufacture of various food products, pharmaceuticals, detergents, textile and agro-chemical industries [1]. For this reason, surfactant compounds are one of the ingredients used because they can reduce surface tension and interfaces, making it easier to spread and equalize [2,3].

In terms of molecular structure, surfactant molecules are absorbed to the surface or interface, because surfactant molecules have two opposing characters, namely lipophilic organic groups and hydrophilic inorganic groups [4]. So that surfactants are elements that play a role to unite water and oil, for example, fatty alcohol sulfate products for detergents, fatty ester products for cosmetics, and fatty sulphasucinates for the plastics industry [5].

One of the surfactants from fatty alcohol which has been developed is alkyl polyglucoside (APG) surfactant. APG are non-ionic surfactants in which the surface-active part of the surfactant is uncharged or molecular ionization does not occur. This surfactant does not dissociate in water but depends on its structure to change hydrophilicity, which makes the substance dissolved in water [6,7].

Alkyl polyglucoside is environmentally friendly surfactants because they are more biodegradable. This compound has been known for a long time but is only available for academic purposes and is considered not too applicable and useful [8]. The birth of alkyl polyglucoside is due to the increasing threat to decreasing energy sources, so the world needs to find alternative renewable energy sources. APG is a renewable surfactant because fatty alcohol can be obtained from various vegetable oil derivatives, and glucose can be obtained from various carbohydrates such as starch [9,10].

Glucose is an important monosaccharide and is used as a source of energy for animals and plants. Glucose is an aldehyde that has five carbons and one oxygen that forms a ring called a pyranose ring. Glucose can be formed from formaldehyde in an abiotic state so that it will be easily available to primitive biochemical systems. More important for upper organisms is the tendency for glucose, compared to other hexose sugars, which do not readily react non-specifically to the amino group of a protein [6,11].

The usefulness of the surfactants produced can be known through a standard called Hydrophilic Lipophilic Balance (HLB). HLB is a standard scale for the balance of lipophilic-hydrophilic surface-active ingredients. With the help of this equilibrium price, we can optimally form the HLB range of each surfactant. The greater the HLB value of an ingredient, the more hydrophilic the material will be [4,12].

Alkyl polyglucosides are mostly produced through the process of trans-acetylation (indirect method) between glucose and alcohol using a two-stage process. This process requires equipment and expensive costs. For this time, synthesis of alkyl polyglucosides was carried out using the acetylation process (indirect method), where fatty alcohol along with glucose was reacted with HCl as a catalyst with a one-step process [9].

One method for modeling and optimizing acquisition is to use the Response Surface Methodology (RSM). RSM is a set of mathematical methods and statistical techniques aimed at making models and measuring the strength of relationships and the effect of response variables and predictor variables [13,14,15].

This method has been widely used in engineering, using a variety of experimental designs, and what is often used is Central Composite Design and Box Behnken Design [16,17]. For this reason, this study
observed the interaction effect of catalyst, substrate ratio and reaction time on the APG density using Box Behnken Design. catalyst.

The acetylation process is influenced by temperature, reaction time, a ratio of raw materials and the amount of catalyst [8,11]. For this reason, this study observed the effect of catalyst concentration, the molar ratio of substrate and reaction time on the synthesis of APG-C10 and APG-C12 with D-glucose using HCl catalysts. Therefore, it is hoped that important information can be concluded related to the influence of the three variables on the density of APG produced.

MATERIALS AND METHODS

Materials

The main raw materials used are fatty alcohols C10 (decanol) and C12 (1-dodecanols) obtained from PT. Ecogreen Oleochemicals, Batam Indonesia. D-glucose, hydrochloric acid, n-hexane, and sodium hydroxide were obtained from E. Merck.

Experimental Design

Box Behnken Design is used to analyze the effect of the interaction between catalyst concentration, substrate ratio and reaction time on the response variable, namely density. Variables and levels developed for the synthesis of APG are shown in Table-1. The experimental data in Table-1 were analyzed by response surface regression procedures to fit the following second-order polynomial equation [3,14]. The regression analysis, statistical significance and response contour plot were done using Minitab 17® trial version.

Acetylation Process

In a three-neck flask, glucose is dissolved with 200 ml n-hexane and then added to C10 or C12 with a molar ratio of substrates of 1 to 4 (mol FA/G). The flask is equipped with a magnetic stirrer, reflux condenser, and thermometer. Furthermore, the HCl catalyst was added in the range of 1 to 2% (w/wG). Distilled at 100 °C for 3-5 hours for decyl polyglucoside (APG-C10) synthesis and 12-16 hours for dodecyl polyglucoside (APG-C12) synthesis. The results of the reaction are cooled and filtered using a Buchner funnel and a vacuum pump. The filtrate obtained was evaporated by a liquid cooler. The top and bottom layers are separated using a separating funnel, and an analysis of the two layers is carried out [7,12].

Table-1. Variables and levels developed for synthesis of APG.

<table>
<thead>
<tr>
<th>Variables</th>
<th>Level for Decyl polyglucoside (APG C-10)</th>
<th>Level for Dodecyl polyglucoside (APG-C12)</th>
</tr>
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<tr>
<td>Catalyst (% w/wG)</td>
<td>-1  0  1</td>
<td>-1  0  1</td>
</tr>
<tr>
<td>Substrate ratio (mol FA/G)</td>
<td>2  3  4</td>
<td>1  2  3</td>
</tr>
<tr>
<td>Reaction time (hr)</td>
<td>3  4  5</td>
<td>12  14  16</td>
</tr>
</tbody>
</table>
Table-2: The results of optimization of APG synthesis in the APG density values.

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Catalyst (X₁)</th>
<th>Substrate ratio (X₂)</th>
<th>Reaction time (X₃)</th>
<th>APG-C10 Density (mg/mL)</th>
<th>APG-C12 Density (mg/mL)</th>
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</thead>
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<tr>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>0</td>
<td>1.42</td>
<td>1.13</td>
</tr>
<tr>
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<td>-1</td>
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<td>1.54</td>
<td>1.14</td>
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<tr>
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<td>0</td>
<td>1.50</td>
<td>1.13</td>
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<tr>
<td>4</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>1.82</td>
<td>1.14</td>
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<td>1.13</td>
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<td>1.42</td>
<td>1.13</td>
</tr>
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</table>

RESULTS AND DISCUSSIONS

Analysis of Variance (ANOVA)

The results of the optimization of APG synthesis in the APG density values are shown in Table-2. Data in Table-2 were further analyzed using RSM with the response variable being the density of APG (mg/mL) and the predictor variables were catalyst concentration, substrate molar ratio and reaction time.

Based on the results of the analysis of variance, the equation model that can show the relationship between reaction variables and their interactions with the density of APG-C10 is as follows:

\[
\text{Density} = 0.073 - 1.528 \text{Catalyst} + 0.224 \text{Substrate Ratio} + 0.837 \text{Reaction Time} + 0.477 \text{Catalyst}^2 + 0.0142 \text{Substrate Ratio}^2 - 0.0583 \text{Reaction Time}^2 + 0.1000 \text{Catalyst} \times \text{Substrate Ratio} - 0.0050 \text{Catalyst} \times \text{Reaction Time} - 0.0875 \text{Substrate Ratio} \times \text{Reaction Time} \quad (1)
\]

Whereas the equation model that can show the relationship of the reaction variable to the density of APG-C12:

\[
\text{Density} = 1.1070 - 0.01175 \text{Catalyst} + 0.224 \text{Substrate Ratio} + 0.000500 \text{Catalyst} \times \text{Reaction Time} + 0.000375 \text{Substrate Ratio} \times \text{Reaction Time} \quad (2)
\]

For the predicted model, the model verification test is carried out, to check the suitability of the residuals with the assumptions required [16]. Assumptions commonly taken in ANOVA are the assumption of normality, the assumption of homoscedasticity and the assumption of independence [13]. The assumption of normality can be determined by the Kolmogorov-Smirnov test. Normal interpretation using the Kolmogorov Smirnov (KS) test was performed using a significance value (\(\alpha\)) = 0.05 [15]. Obtained from the normal plot in Figures 1 and 2, that the distribution of residual data is in a straight-line plot. If distribution tends to form a straight line, then the assumption of normality can be said to not be violated.

To determine the homogeneity of variance, a homoscedasticity test was performed. From the residual plot with fitted values in Figures 1 and 2 shows that the data distribution tends to be random and does not form a specific pattern so that it can be said that the assumption of homogeneity of variance (homoscedasticity) is fulfilled. The assumption of independence aims to find out whether the independent variables are interconnected or correlated. From the Figure 1 and 2 above it can also be seen that the distribution of residual versus sequence data tends to be random and not patterned, so it can be said that the assumption of independence is fulfilled. So that from all the results of the model verification test it was concluded that the regression model predicted and the regression model created was appropriate and could be used.
Interaction Effects of Catalyst and Substrate Ratio

The solubility of monosaccharides, oligosaccharides, and polysaccharides to fatty alcohol is one of the problems in APG synthesis. For this reason, excess alcohol is used in APG synthesis, so that sugar oligomerization can be minimized. The success of the acetylation process is strongly influenced by the type of acid catalyst used. HCl catalyst has the advantage of being easily soluble in water and available in large quantities. Reaction without using a catalyst is more difficult to do because the reaction rate is very slow and the collected glucose will produce a larger particle size so that it can cause caramelization. Besides that, the reaction of acetal formation occurs because one of the oxygen is protonated by an acid so that the synthesis process of APG requires an acid catalyst in its formation.

Figure-3 shows the contour plot to determine the density response for the interactions between catalyst and substrate ratio in APG-C10 synthesis. The APG density increases linearly with increasing substrate ratios when there is a trend of decreasing density if observed simultaneously between the ratio substrate and catalyst concentration. On a constant ratio substrate, increasing the amount of catalyst will reduce the density of the product. This is expected because, at a constant reaction time of 4 hours, the overall density obtained is still above the APG density range.

The interaction effect of catalyst concentration and substrate ratio on the APG-C12 density is explained in Figure-4. In general, the density increases on increasing the amount of catalyst and the amount of fatty alcohol. Density is directly proportional to the mass of the particle. The higher the ratio of the substrate molar ratio, the greater the mass of APG particles formed so that the density will be even greater.
The addition of the amount of catalyst will further activate the reactants, thus increasing the chances of reactants to collide with each other. It is seen that the maximum density obtained is still within the expected APG density range of 0.9-1.2 (mg/mL). If the catalyst concentration is less than 1.5 % (w/wG) and the substrate ratio is less than 3 (mol FA/G) the optimum density response field will be obtained which is less than 1.13 mg/mL. So that for the synthesis of APG-C12 the optimum density is obtained at minimum substrate ratio and catalyst interactions.

**Interaction Effects Catalyst and Reaction Time**

The In APG-C10 synthesis, the density response for the interaction of catalyst concentration and reaction time is shown in Figure-5. It is seen that the optimum density is obtained in the reaction time range of 3-3.5 h, with a catalyst concentration range of 1-1.5% (w/wG). A density response that is far from the APG density limit is obtained if the reaction time is more than 4 hours and the catalyst concentration is more than 1.8% (w/wG). From Figure-5 it can be concluded that the interaction of the amount of catalyst with time will increase the APG density value and the optimum density is at the lower limit of the interaction of both.

APG-C12 synthesis runs for 12-14 h with a catalyst concentration of 1-2% (w/wG). The interaction between the two variables is shown in Figure-6. It is generally seen that in the entire range of values used, the density response obtained is still in the APG density range.

More particularly it was found that the increase in density was faster at increasing the catalyst concentration. This is in line with the results of the analysis of variance that the reaction time is more significant in increasing the density response compared to the increase in the amount of catalyst.

**Interaction Effect of Substrate Ratio and Reaction Time**

The Density is one of the physical properties and also the parameters that can provide information on the physical and chemical state of a material. In APG-C10 synthesis, density gain is affected by substrate ratio and reaction time. This is seen in Figure-7. Adding a substrate ratio or adding fatty alcohol to the reaction will increase density. Increasing the concentration of dissolved solids can increase the density of a liquid. The greater molar ratio of glucose-fatty alcohol will increase the chance of fatty alcohol to bind with aldehyde groups in glucose to form an acetal group.
Likewise, the reaction time. It is expected that throughout the reaction up to 5 hours will be obtained density in the APG density range. It's just that the density obtained shows that the response will increase with increasing reaction time to 5 h. However, by observing the interaction of the substrate ratio with the reaction time to obtain the best density, it is found that the minimum optimum density is at the reaction time of 3-3.5 h and the substrate ratio is 3 (mol FA/G). Increasing the substrate ratio and catalyst concentration to the upper limit of the observation will increase APG density, which is not expected.

Substrate ratio and reaction time are significant variables to obtain the optimum APG density. For this reason, observations of density responses to interactions between the two are interesting to observe, as seen in the contour of the plot in Figure-8. This contour illustrates the optimum density field at the reaction time of less than 14 h and substrate ratio of 1-2 (mol FA/G). It was also found that the increase in reaction time was more significant in increasing APG-C12 density compared to substrate ratio. It is also concluded from this figure that for the entire reaction time and substrate ratio, the density response obtained is entirely in the APG density range.

**CONCLUSIONS**

Synthesis of two types of APG namely APG-C10 and APG-C12 can be modeled using Box Behnken Design in RSM with the acquisition of $R^2$ reaching more than 0.95. From the results of the analysis of variance, it was found that the ratio of the substrate and the reaction time were very significant variables to get the optimum APG density. Optimum results for APG- synthesis were obtained at catalyst concentration of 1-1.5 % (w/wG), substrate molar ratio of 2-3 (mol FA/G) and reaction time of 3-13 h. The longer the alkyl chain is used, the longer the reaction time is needed, where for APG-C10 the reaction time is 3 h and for APG-C12 is 13 h.

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REFERENCES


