AJChE 2018, Vol. 18, No. 2, 62 – 69

Optimization for Production Tert-Butyl Oleyl Glycoside Nonioic Surfactant Using Response Surface Methodology

***Harsa Pawignya** *,1,2*
***Tutuk Djoko Kusworo** 1*
***Bambang Pramudono** 1*

[1] *Department of Chemical Engineering, Diponegoro University, Jl. Prof. Soedarto, Kampus UndipTembalang, Semarang 50239, Indonesia*

[2] *Department of Chemical Engineering, University of Pembangunan Nasional "Veteran" Yogyakarta, Jl. SWK 104 Condongcatur, Yogyakarta, 55283, Indonesia*

**e-mail:* harsaprawignya@upnyk.ac.id

The development of surfactant production process strongly influenced by the potential use of raw materials and products that are environmentally friendly. For raw materials such as surfactants are carbohydrate-based material utilization example, glucose, which is reacted with tert-butanol, to form tert-butyl glycoside (TBG), then TBG can be esterified with oleic acid forming surfactant tert-butyl oleyl glycoside (TBOG). This study aims to obtain the optimum conditions TBOG production process of esterification reactions TBG and oleic acid catalyst the para toluene sulfonic acid using response surface method to reach optimum yield TBOG. The independent variable used is the mole ratio of TBG with oleic acid, percent of the catalyst and a temperature. Optimization results obtained optimum conditions of mole ratios of 1: 4.096; 2.33 percent of the catalyst and the temperature of 96.04 °C with a TBOG yield of 92.46%, with a TBOG content of 91.72 %. Based on the HLB value of the surfactant TBOG is 3.87, then these surfactants can be used as an emulsifier of water-in-oil.

Keywords : Optimization, Emulsifier, Surfactant, Tertbutyl, Oleyl, Glycoside

INTRODUCTION

In the present day, due to environmental problems and regulatory pressures that have provided the driving force for replacing petrochemical based surfactants in part with those based on natural renewable sources (Ware *et al.* 2007). Carbohydrate-containing agricultural products can be used as raw materials in the surfactant industry. Surfactants made from carbohydrate feedstocks can provide benefits that are easily degraded, environmentally friendly and non-toxic. Nonionic surfactants can be used as detergents, solubilizing agents, emulsifying agents, dispersing agents, and potency biomaterials applications (Schick 1987, Sela *et al.* 1993, Zaijun *et al.* 2005). Surfactant alkyl polyglycoside (APG) is a non-ionic surfactant that made from renewable natural materials, namely carbohydrates and fatty alcohol (Ware *et al*. 2007, El-Sukkary *et al*. 2008). APG can be used as an additive in the formulation of some products such as herbicide formulations, personal care products, cosmetics and for bleaching fabrics/textiles (Hill and Rhode 1999). Usefulness of surfactant depends on the value hydrophilic-lipophilic balance (HLB), for examples of HLB value of 1-3 for antifoaming, HLB 2-7 for emulsifier type W/O, HLB 7-9 for wetting, HLB 8-18 for emulsifier type O/W, HLB 13-15 for detergents and HLB 15-18 for a solvent agent. HLB is a number that indicates the ratio between the hydrophilic and lipophilic groups in a surfactant (Rosen 2004). The addition of the surfactant in the solution would cause a decrease in surface tension, once it reaches a certain concentration, surface tension will be constant even if the surfactant concentration increased, when a surfactant was added beyond this concentration, the surfactant aggregates to form molecules. At the concentration of molecule formation called the Critical Micelle Concentration (CMC) (Hait and Moulik 2001). Various surfactant APG other types made from base ingredients carbohydrates such as surfactants ter-butyl oleyl glycoside (TBOG), made from the reaction of acetalization of glucose with tert-butanol to produce tert-butyl glycosides (TBG) are then TBG esterified with oleic acid forming surfactant TBOG, TBOG surfactants including APG surfactant group.

In this study, a new thing is synthesizing surfactant TBOG, from TBG esterification reaction with oleic acid using a para toluene sulfonic acid (p-TSA) catalyst and to use a solvent benzene (Sembiring 2007). APG surfactant results of previous studies have a dark brown color that is not desirable because using petroleum ether, while this study using solvent benzene to produce better color surfactant that is a bright yellow.

The experimental design optimization of the process conditions in production TBOG, using Response Surface Methodology (RSM) and research using composite design centered. It is suitable for determining squared surfaces and helps to optimize effectiveness parameters with a minimum number of tests, and also to analyze the interaction between the parameters (Khuri and Mukhopadhyay 2010). Optimization is to determine the process parameters that are optimum mole ratio of reactants, percent p-TSA catalyst and temperature, which produces the maximum yield TBOG.

METHODOLOGY

Materials

The materials were oleic acid 99 % (Merck), benzene 99.7 % (Merck), p-TSA 98.5 % (Merck), NaOH 98 % (Merck), sodium acetate 98 % (Merck), sodium sulfate 98 % (Merck) and TBG 49 % (made from the reaction of glucose with tert-butanol) (Sembiring 2007, Zhang *et al.* 2013).

Methods

Synthesis tert-ButilOleylGlikosida (TBOG)

Taken 2.82 grams (0.01) moles TBG added oleic acid pour into the reactor, which equipped with a stirrer, thermometer, heater, and coolant. Then added p-TSA catalyst, plus 50 ml of benzene as a solvent, and then heated (mole ratio of oleic acid/TBG, percent of catalysts and the temperature made variations). Subsequently, the solution is refluxed, then cooled to room temperature and neutralized with sodium hydroxide 50% and stirred. Further purified by evaporation until its weight is constant. This residue is TBOG surfactant were analyzed Yield (100% x (TBOG weight/weight TBG)). TBOG content analysis using GCMS. The TBOG, was then used to prepare the TBOG solution at various concentrations, then the solution measured surface tension by using Du Nouy Tensiometer, HLB value can be calculated by Eq. (1).

$$HLB = 7 - 0.36\ x\ ln\ \frac{100 - CMC}{CMC} \qquad (1)$$

Design experiment

Experimental design, synthesis optimization TBOG using Response Surface Method and research using composite design centralized with the software Statistical 6. Using the software can be determined the model equation, to graph the 3-D contour of the response and to predict the interaction between the parameters (Sembiring 2007). In this experimental design, all the independent variables presented in **Table 1**.

Table 1. The area level and the independent variable level code are used in the RSM

Independent variables	Coded Factor	Level		
		Low (-1)	Center (0)	High (1)
Mole Ratio, mole oleic acid/TBG	X_1	3	4	5
Percent Catalyst ,%	X_2	1.5	2	2.5
Temperature,°C	X_3	85	90	95

It is used to develop an empirical model linking the response to the independent variables by using the following polynomial Eq. (2):

$$Y = \beta_0 + \beta_1X_1 + \beta_2X_2 + \beta_3X_3 + \beta_{12}X_1X_2 + \beta_{13}X_2X_3 + \beta_{23}X_1X_3 + \beta_{11}X_1^2 + \beta_{22}X_2^2 + \beta_{33}X_3^2 \qquad (2)$$

RESULT AND DISCUSSIONS

Use of models to predict TBOG yields

Response Surface Methodology is a way of processing statistical data using a minimum set of experimental data to determine the coefficients of the mathematical model and optimization (Yemis and Mazza 2012, Vuong *et al.* 2011). An analysis of the variance of the experimental results is presented in **Table 3**. The relationship of the independent variable to the response variable is presented in Eq. (3):

$$Y = 90.1385 + 1.1201\ X_1 - 5.3806\ X_2 + 4.2030\ X_3 - 3.1850\ X_1X_2 + 1.4514\ X_2X_3 - 0.6165\ X_1X_3 - 0.2237\ X_1^2 + 0.0437\ X_2^2 + 0.0462\ X_3^2 \qquad (3)$$

By using centralizing composite design, experimental design matrix show in **Table 2**. The ANOVA results can be seen in **Table 3** (Raymond and Douglas 2016, Bezerra *et al.* 2008, Raji and Oluwole 2014).

The effect of parameters on yield

From Eq. (3) shows that indicated that the mole ratio and temperature at the same provide a positive effect. It is because the larger the mole ratio and temperature will accelerate the rate of reaction formation TBOG, in which the effects of temperature is greater than the effect of mole ratio. The percent of the catalyst negative effect this is because the percent of the catalyst is too much would interfere with the reaction. **Table 3** obtained R^2 of the model is 0.98 it shows that 98 % of the amount of data can be adjusted to the predicted yield rate of the model and only 2 % wrong data. The p and F-values of the respective models are 0.000001 and 62.27, that the model predictions are significant (Adisalamun *et al.* 2012, Voung *et al.* 2015). The specific relationship between each parameter illustrated visually in the 3D profile shown in **Figures 1, 2** and **3**.

Table 2. Matrix of experimental design

No	Mole Ratio (oleic acid /TBG)	Percent Catalyst (%)	Temperature (°C)	Yield (%) Observed	Yield (%) Predicted
1	3.00	1.50	85.00	73.05	74.05
2	3.00	1.50	95.00	75.88	76.77
3	3.00	2.50	85.00	82.98	82.81
4	3.00	2.50	95.00	85.11	85.72
5	5.00	1.50	85.00	75.89	76.65
6	5.00	1.50	95.00	78.01	79.55
7	5.00	2.50	85.00	84.04	84.51
8	5.00	2.50	95.00	87.23	87.59
9	2.32	2.00	90.00	73.76	73.04
10	5.68	2.00	90.00	78.01	76.80
11	4.00	1.16	90.00	75.89	74.06
12	4.00	2.84	90.00	88.30	88.19
13	4.00	2.00	81.59	86.52	85.95
14	4.00	2.00	98.41	92.20*	90.84
15 (C)	4.00	2.00	90.00	90.07	90.14
16 (C)	4.00	2.00	90.00	91.13	90.14
17 (C)	4.00	2.00	90.00	90.43	90.14
18 (C)	4.00	2.00	90.00	89.36	90.14
19 (C)	4.00	2.00	90.00	89.36	90.14
20 (C)	4.00	2.00	90.00	90.15	90.14

Table 3. Variance analysis of the regression model

Source	Sum of Squares	Df	Mean Square	F Value	P Value	Signifi-cance
Model	792.1835	9	217.181	62.2708	0.000001	**
(A) Mole ratio	17.1355	1	17.1355	11.2124	0.007384	*
(B) Percent catalyst (%)	417.2272	1	417.2272	273.0000	0.000001	**
(C) Temperature (ºC)	241.2620	1	241.1992	157.8671	0.000001	**
AB	146.1992	1	146.1992	95.6638	0.000002	**
AC	28.7720	1	28.7720	18.8266	0.001469	*
BC	5.4777	1	5.4777	3.3843	0.087597	
A^2	0.4005	1	0.4005	0.02621	0.619815	
B^2	0.0153	1	0.0153	0.0100	0.922245	
C^2	9.0171	1	0.0171	0.0112	0.917820	
Residual	15.2828	9	1.5283			
Lake of Fit	13.0159	5	2.6032	5.7421	0.0389	*
Pure Error	2.2667	5	0.4533			
Cor Total	822.7489	19				
R^2 = 0.98						

Notes: "*" represented p< 0.05, "**" represented p< 0.0001.

Effect of mole ratio and percent of catalyst p-TSA on the yield

From **Figure 1**, yield increases with the increasing mole ratio and percent of the catalyst. It is because the larger the mole ratio, the faster the reaction shifted to the right, so that the yield increases, two percent greater catalyst activation, the power will be reduced so that the reaction rate increases. After the mole ratio of 4, the yield reduced it is reaction close to balance. After the catalyst reached 2 %, the yield decreased, because was not able to lower the activation energy.

Effect of mole ratio and temperature on the yield

From **Figure 2**, yield increases with the increasing mole ratio and temperature, it is because the larger the mole ratio, the faster the reaction shifted to the right, so that the yield increases, also the temperature the greater the reaction speed is accelerating. After the mole ratio of 4, the yield is reduced it is a reaction close to balance. After the temperature 90 °C, the yield decreased, because, the reaction product started to break down.

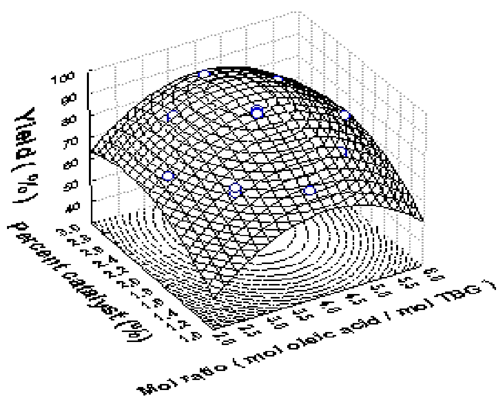

Fig. 1. The effect of mole ratio and percent of catalyst on the TBOG yield shown by the surface and contour plot

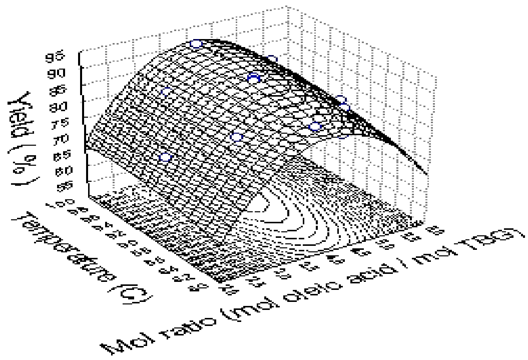

Fig. 2. The effect of mole ratio and temperature on the TBOG yield shown by the surface and contour plot,

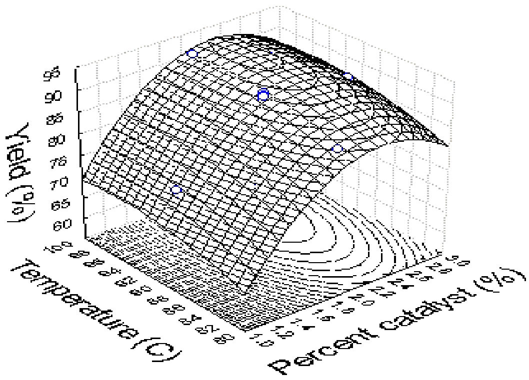

Fig. 3. The effect of percent catalyst and temperature on the TBOG yield shown by the surface and contour plot

Effect of percent of catalyst and temperature on the yield

From **Figure 3** shows that greater the percent catalyst, the activation energy, reduced so that the faster the reaction, also the temperature the greater the reaction speed is accelerating. After the catalyst reached 2 %, the yield decreased, because was not able to lower the activation energy. After the temperature 90 °C, the yield decreased, because, the reaction product started to break down.

Analysis of the nature of the TBOG surfactant

TBOG surfactant obtained in optimum conditions hereinafter set its value HLB and CMC, by way of surfactant TBOG dissolved in aquades at various concentration values were analyzed surface tension, the result showed in **Figure 4**. Surface tension reduced in line with the increase in the concentration and finally, it becomes constant. It is because TBOG solution is aggregated to form micelles, **Figure 4** shows CMC about 0.017 %. The surface tension decreases from 67mN/m to 34.6 mN/m. The HLB value obtained is 3.87 indicates that the TBOG can function as water in oil type of emulsifier (Khuri and Mukhopadhyay 2010).

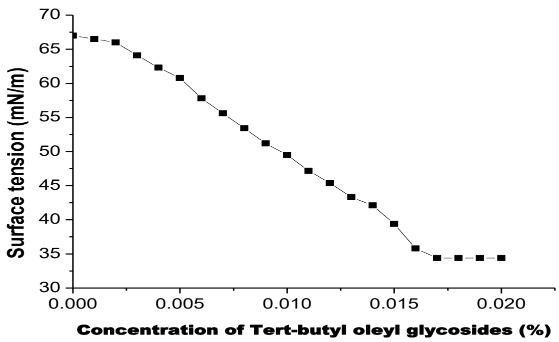

Fig. 4. Effect of TBOG concentration on surface tension

CONCLUSION

Variables that significantly influence the synthesis of TBOG are mole ratio and temperature. Temperature and the mole ratio of positive impacts on yield, while the percent of the catalyst has a bad impact on yield. Optimal conditions at mole ratio 1: 4.096, percent of catalyst 2.333 %, temperature 96.03 °C and obtained TBOG yield 92.46 %, content 91.72 %, HLB value = 3.87 that can function as water in oil type of emulsifier.

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