Proceeding of Chemistry Conferences, Volume 2 (2017) ISSN: 2541-108X

Selection of PTSA Catalyst Concentration for the Synthesis Alkyl Polyglycosides from Fatty Alcohol (C16) and Glucose Syrup 85%

Mira Rivai[1], Yuni Astuti[2], Erliza Hambali[1,2], Pudji Permadi[1,3], Ani Suryani[1,2], Ari Imam Sutanto[1]

[1] Surfactant and Bioenergy Research Center, Bogor Agricultural University, Bogor, Jawa Barat, Indonesia
[2] Department of Agroindustrial Technology, Faculty of Agricultural Technology, Bogor Agricultural University, Bogor, Jawa Barat, Indonesia
[3]Program Study of Petroleum Engineering, Institute Technology of Bandung, Bandung, Jawa Barat, Indonesia

E-mail: me_rarivai@yahoo.com

Abstract. Alkyl polyglycosides (APG) is a non-ionic surfactant that is environmental friendly and used in the formulations of several products such as herbicides, cosmetics, personal care products and petroleum displacer. The aims of this research were to obtain the best concentration of p-toluene sulfonic acid (PTSA) catalyst for the synthesis of APG from fatty alcohol (C_{16}) and glucose syrup (85%) and to determine the performance of APG surfactant produced. The concentrations of PTSA catalyst used were 0.6; 0.9; 1.2; and 1.5% from the weight of glucose used. Results showed that catalyst concentration had no significant effect on the density, pH, and foaming performance, but gave significant effect on interfacial tension. It was also shown that catalyst concentration of 0.6% was different significantly from that of 0.9; 1.2; and 1.5%. However, there were no differences among 0.9; 1.2; and 1.5%, respectively. The best catalyst concentration was 1.2% which gave the interfacial tension value of $4.5x10^{-2}$ dynes/cm, pH of 7.9, density of 0.9839 gr/cm^3, and height of foam of 2.3%.

1. Introduction

Alkyl Polyglycoside (APG) can be synthesized through two ways: with prior and without prior butanolysis. APG synthesis without prior butanolysis is done to materials containing dextrose or starch-based sugar with long chain fatty alcohol. APG synthesis with prior butanolysis is done to materials containing starch with long chain fatty alcohol [3]. APG surfactant synthesis always requires an acid catalyst. According to McCurry et al. [6], acid catalysts that can be used in this synthesis include inorganic acids such as HCl, H_2SO_4, H_3PO_4, HNO_3, organic acids such as methane sulfonic acid, trifluoromethanesulfonic acid, and surfactant acids such as para-toluene sulfonic acid and methyl ester sulfonic acid.

One of the catalysts commonly used in APG surfactant synthesis is p-toluene sulfonic acid (PTSA). PTSA is white solid which is soluble in water, alcohol, and organic solvent. Another characteristic of PTSA is that, different from nitric acid, sulfuric acid, and perchloric acid, it is a non-oxidizing acid [2]. The catalyst used in surfactant synthesis is a weak acid such as PTSA as strong acid may cause hydrolysis of glucose. The use of weak acid also makes neutralization process easier to carry. In addition, PTSA is not corrosive on the iron pipe or stainless steel [3].

Gibson and Leedy [8] determined a catalyst for use based on the following calculation.

1. The first catalyst was about 0.7-1.4% of glucose/starch weight.
2. The second catalyst was about 25-50% of the first catalyst.

APG is a non-ionic surfactant which is environmentally friendly and in extensive use. APG surfactant is used in formulation of various products including herbicides, cosmetics, personal care products, and textile bleaching agent. One of the latest applications of it is as an oil pusher in the enhanced oil recovery (EOR) technique. The study was aimed at determining the best PTSA concentration in APG synthesis from fatty alcohol (C_{16}) and liquid glucose 85% and assessing the performance of APG produced.

2. Methods

2.1. Materials and Equipment

Materials used in this study included oil palm fatty alcohol (C_{16}), liquid glucose 85%, para-toluene sulfonic acid (PTSA) catalyst, NaOH, and technical butanol. For analysis used xylene, pyridine, and benzene. Butanolysis and acetalization/trans-acetalization reactors were used for APG surfactant synthesis from liquid glucose 85% and fatty alcohol (C_{16}). The reactors were equipped with heat control, stirring control, and vacuum pump. Spinning drop interfacial tension meter, density meter, and pH meter were used for the analysis.

2.2. Methods

Alkyl Polyglycoside (APG) Surfactant Synthesis. This trial was focused on obtaining the best concentration of PTSA catalyst for APG synthesis using fatty alcohol C_{16} with liquid glucose 85% as the reactant. Treatments consisted of PTSA concentration of 0.6; 0.9; 1.2; and 1.5% of the weight of glucose used during butanolysis. A completely randomized design with 4 concentrations of PTSA as treatments were used. PTSA catalyst used for transacetalization was 50% of the first catalyst. The mole ratio of glucose and butanol used was 1:5.9 and that of glucose and fatty alcohol was 1:3.

In butanolysis, liquid glucose 85% was reacted with butanol and PTSA catalyst was added in accordance to the concentration treatments. Butanolysis was done for 2 hours at 140-150°C and 1-4 bars pressure. Then, PTSA catalyst (50% the amount of the first catalyst) was added in to transacetalize the result of butanolysis. Transacetalization process was done for 2 hours at 120°C and 10-15 bars pressure. The next stage was neutralization process. This process was done by adding NaOH until pH 7-9 was reached at 80-90°C and 1 atm pressure in 30 minutes. Distillation was then conducted to separate fatty alcohol which was not reacted by evaporating it in a vacuumed condition ($1.33x10^{-4}$-$2.67x10^{-3}$) at 180°C for 2 hours. The flow chart of APG production is depicted in Figure 1.

Analysis of APG Surfactant. The resulted APG surfactant was analyzed for its physicochemical properties including interfacial tension, density, pH, foam height, and HLB values.

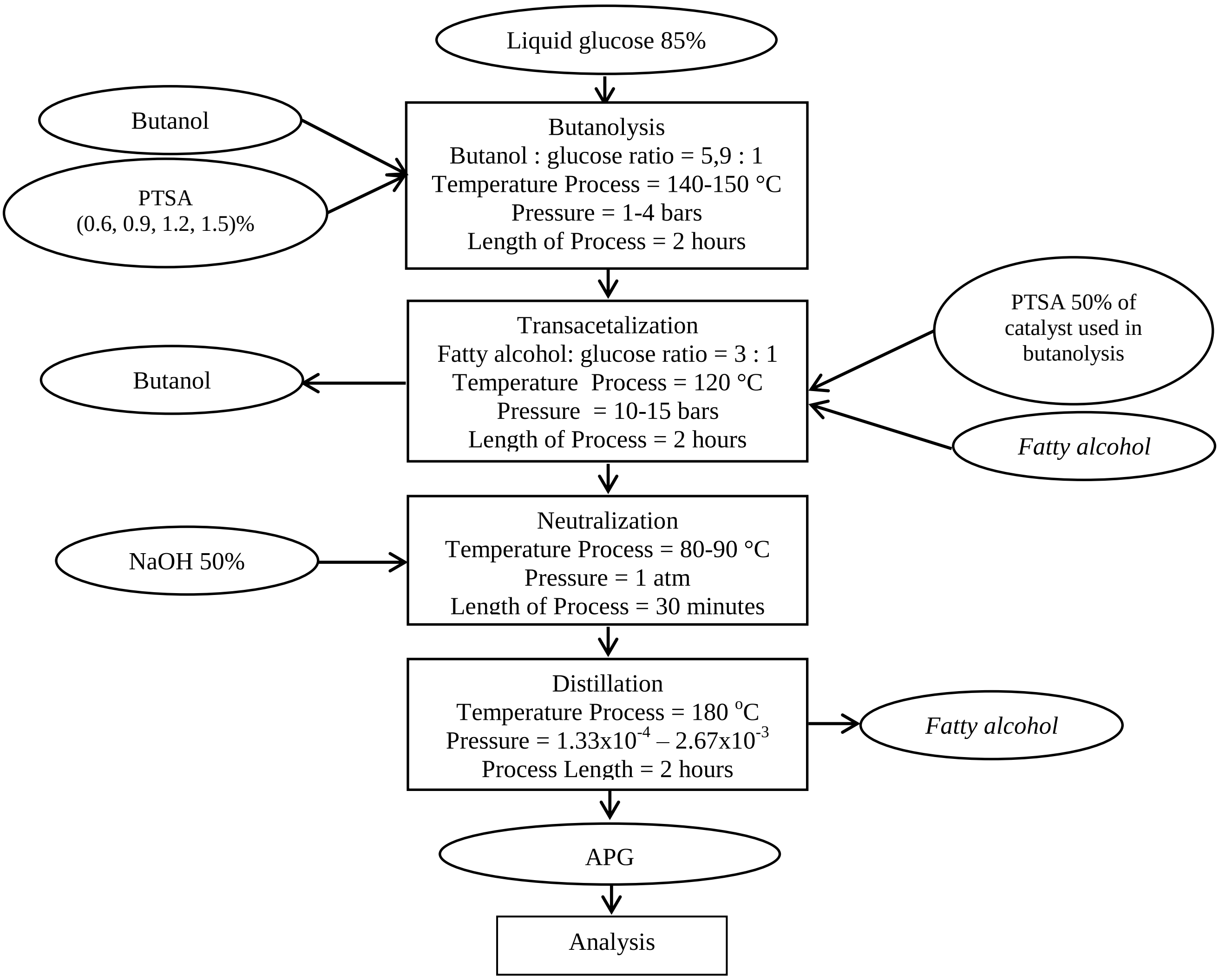

Figure 1. Flow chart of APG production process.

3. Result and Discussion

APG surfactant synthesis was done through the following processes: butanolysis of liquid glucose 85%, transacetalization with fatty alcohol C_{16}, neutralization with NaOH, and distillation at high temperature in a vacuumed condition. In butanolysis, butanol was reacted with liquid glucose and PTSA catalyst in concentrations was added. The final product of this process was butyl glucoside solution which was brownish yellow in color. In transacetalization, long chain fatty alcohol was reacted with butyl glucoside with an addition of PTSA catalyst. This reaction resulted in crude APG which was still mixed with excess fatty alcohol and butanol as a by-product which was evaporable. The resulted APG was a brown solid.

This APG was acidic so that it needed to be neutralized with NaOH until pH values of 7-9 was reached. NaOH was easier to use as it was available in solution and it did not need filtration to remove the formed salt [10]. Neutralization was needed as saccharides were easy to get damaged in acidic condition during the distillation process done at high temperature. The resulted APG still contained excess fatty alcohol which could interfere with surfactant performance. This excess fatty alcohol had to be removed through a distillation process. The resulted APG was a dark brown solid.

3.1. Interfacial Tension (IFT)

IFT is a force per unit length occurring on an interface between two liquid phases which cannot be mixed. Surfactant reduces cohesive force and increases adhesive force so that it can reduce interfacial tension [5]. Results showed that catalyst concentrations significantly (α=5%) affected IFT values. However, IFT value was only different in catalyst concentration of 0.6% but not in 0.9; 1.2; and 1.5%.

It was shown in Figure 2 that higher PTSA concentration resulted in lower IFT values. Lower IFT values indicated better surfactant performance. The best IFT value of $4.5x10^{-2}$ dynes/ cm was shown by APG concentration of 1.2%.

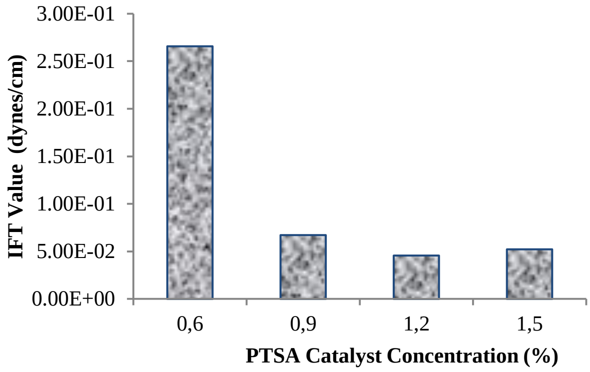

Figure 2. The capacity of resulted APG surfactant in lowering interfacial tension.

3.2. Density

Density is mass per volume. It was found that APG surfactant synthesized in this study had a lower density than water. Catalyst concentrations were not found to give different effect (α=5%) on density levels of produced APG. APG density values were about 0.98 g/cm^3 indicating that this APG was highly water soluble.

3.3. Acidity Level (pH)

APG surfactant should have neutral acidity level as acidic or basic surfactant might be reacted with equipment or skin when it is applied. Catalyst concentration was not found to significantly affect APG surfactant pH values (α=5%) which were about 7-8.

3.4. Foam Stability

Liquid foam is a colloid in which a gas is dispersed in a liquid dispersion medium. Foam stability is resulted from the existence of a foaming agent (surfactant). This foaming agent is adsorbed in the interphase area and binds air bubbles so that stability is obtained [7]. Foam stability was measured by diluting APG surfactant in a formation water 0.5%. This solution was shaken in a vortex mixer. The decline in foam height was observed every 5 minutes. The resulted APG was found to produce less foam. It was shown that there was no significant effect (α=5%) of catalyst concentration on APG foam stability. The ability of APG to form foam was very low, only 2.3%.

This low ability of APG to produce foam might be caused by the long carbon chains it got from fatty alcohol, its main constituent. Yuliasari et al. [9] stated that the ability of surfactant to produce foam was affected by length of carbon chains of its constituents. C_{16}-C_{18} played a significant role in shaping the detergency property while C_{12}-C_{14} in shaping the foaming effect. Ware et al. [1] tested the foaming ability of Sodium Lauryl Sulfate (SLS), APG C10, and APG C_{12} surfactants and they found that APG surfactant had lower foaming ability than SLS surfactant.

3.5. Hydrophilic and Lipophilic Balance (HLB)

HLB is a value showing the balance between hydrophilic and hydrophilic group of a surfactant. HLB value is used to determine the solubility property of surfactant in water or oil. According to Homberg et al. [4], HLB value determined the type of application a surfactant can be used in. In this study, no significant difference (α=5) was found in the HLB values which were around 10. Based on the concept of Holmberg et al. [4], the resulted APG surfactant could be used as an emulsifier of oil in water (O/W) and had a good detergency ability.

4. Conclusion

Catalyst concentration of 1.2% resulted in the best performance APG with IFT value of $4.5x10^{-2}$ dynes/cm, pH 7.9, density of 0.9839 g/cm^3, HLB of 10.18, and foam height of 2.3%.

Acknowledgments
Funding assistance from Ministry of Research and Technology the Republic of Indonesia and facility and equipment assistance from Surfactant and Bioenergy Research Center IPB were acknowledged.

References
[1] A M Ware, J T Waghmare and S A Momin 2007 *J. Dispers Sci Technol* **28** p 473-444
[2] D D Perrin and W L F Armarego 1988 Purifification of Laboratory Chemicals (Oxford : Pergamon Press)
[3] K Hill, W V Rybinski and G Stoll 2000 Alkyl Polyglicoside: Technology, Properties and Applications (New York : VCH Publishers)
[4] K Holmberg, B Jonsson, B Kronberg and B Lindman 2003 Surfactants and Polymers In: Aqueous Solution (New York: 2nd ed. Wiley)
[5] K L Matheson 1996 In: L. Spitz (ed), Surfactant Raw Materials: Classification, Synthesis, and Uses. *Soap and Detergents*: *A Theoretical and Practical Review,* (Illinois: AOCS Press–Champaign)
[6] McCurry, M Jr Patrick, E Rainer, S Paul 1996 U.S. Patent **5** 512 666
[7] M Noerdin 2008 Undergraduate Thesis, Department of Agroindustrial Technology, Faculty of Agricultural Technology, Bogor Agricultural
[8] M W Gibson and C Leedy 2001 Patens: *Process for Reducing Cycle Times in Reaction During The Production of Alkyl Polylicosides*. www.uspto.gov, 2012.
[9] R Yuliasari, P Guritno and T Herawan 1997 *Indonesian J. Of Oil Palm Research* **5** p 205 – 213
[10] W Wuest, E Rainer, W K Josef, H Karlheinz and B Manfre 1992 U.S. Patent No. **5** p 138 046.