SYNTHESIS OF NONIONIC SURFACTANT ALKYL POLYGLUCOSIDES (APGs) USING MICROWAVE ASSISTED FISCHER'S TWO STAGES METHOD

TỔNG HỢP CHẤT HOẠT ĐỘNG BỀ MẶT KHÔNG ION ALKYL POLYGLUCOSIDES (APGs) VỚI SỰ HỖ TRỢ VI SÓNG THEO PHƯƠNG PHÁP FISCHER HAI GIAI ĐOẠN

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TÓM TẮT

Alkyl polyglucosides (APGs) là sản phẩm của phản ứng giữa glucose và rượu béo với xúc tác acid. Tính chất bề mặt của APG có mạch alkyl dài (C_8-C_{16}) được đánh giá. APG là được xem là chất hoạt động bề mặt an toàn cho môi trường sinh thái vì có tính chất dễ phân hủy sinh học. Các nhà khoa học gọi chúng là "chất hoạt động bề mặt tương lai". APG có thể được tổng hợp từ các nguyên liệu tái sử dụng nên an toàn cho sức khỏe, không độc hại. Nó được sử dụng rộng rãi trong sản xuất dược phẩm, mỹ phẩm và nông nghiệp.

- APG được tổng hợp bằng phản ứng Fischer hai giai đoạn sử dụng lò vi sóng tại chế độ Defrost.
- Khi so sánh với phương pháp thông thường, phương pháp có sự hỗ trợ vi sóng có nhiều ưu điểm: rút ngắn thời gian phản ứng, giảm các phản ứng phụ và làm tăng hiệu suất phản ứng, giảm dung môi, xúc tác, tiết kiệm năng lượng, thời gian, và chi phí.

ABSTRACT

Alkyl Polyglucosides (APGs) is product of the reaction of glucose with fatty alcohol with acid catalyst. The surface properties of APG that has long alkyl chain (C_8-C_{16}) were evaluated. APG awas considered as ecologically safe surfactant because of their biogradable properties. Scientists call it "future surfactant". APG can be prepared starting from renewable raw materials so safety for health, not hazardour, it is widely used in manufacturing pharmaceutical products, cosmetics, agricultural chemistry and so on.

❖ APG is synthesized by the Fisher's two stages reaction motivated with microwave oscilation (carrying out in a microwave oven at Defrost mode)

❖ Compare to heating traditional method, this new method shows many advantages : Reduce chemical reaction times, reduce side reactions, and increase reaction yields. Reduce solvents and catalysts. Save energy, save time and costs.

Keywords: *Synthesis of APG, microwave assisted method*

1. INTRODUCTION

Alkyl polyglucosides (APGs) is a new class of nonionic surfactants with many applications because of their non-toxic and biodegradability in all condition (aerobic and anaerobic) [1]. APG is prepared from renewable, good dermatologically compatible, biodegradable raw materials glucose (or starch) and fatty alcohol [2,3]. Although APG is a nonionic surfactant, its foaming property is equal to that of anionic surfactant [4].

Exploring new method for enhancing reaction reaction yield, saving energy, decreasing

environmental pollution becomes more interested nowadays. Microwave technique is considered as a clean, cheap and convenient synthetic method [5]. This "non-classical heating" technique is moving from lab to production. [6]

People focus on researching and finding more applications which relate to APG in domestic and industry. Vietnam has huge sources of raw materials, but most of APG products used in cosmetic are imported.

Based on some results obtained with esterification reaction by microwave method [7], we continue to investigate the synthetic reaction of APG, and compare to heating traditional method.

2. MATERIALS AND METHODS

2.1 Materials

* *D – glucose*
n – buthanol
Lauryl alcohol is provided by TICO Enterprise, HCMC.
The other chemicals are analysis grade.
* TLC : 25DC – Alufolein 20 X 20 cm Kiesegel $60F_{245}$

2.2 Methods

2.2.1 Synthesis of Lauryl Polyglucosides by Fisher motivated with microwaves interaction

Studying factors affect on synthetic reaction of Lauryl polyglucosides (LaPGs) such as temperature, reaction time, catalyst, ratio of raw materials.

Reaction reaction yield is evaluated by remaining glucose content [8].

Qualitative analysis is done by TLC method [9] :

Solvent system : $CHCl_3 – CH_3OH = 8 : 2$.

Reagent : solution of thymol + 5% H_2SO_4 + C_2H_5OH.

Carrying out two experiments in a microwave oven at Defrost mode for every point of studying, using 0.1mol glucose (22,30 g) for each. Catalyst is H_2SO_4.

a. Step 1 : Raw materials are added into a glass flask in order : 0,1 mol glucose, n – buthanol, catalyst H_2SO_4. The experiment is followed under heating regulation for step 1 (Table 1). Record water volume separated.

b. Step 2 : Later Lauryl alcoholhol is added. The experiment is followed under heating regulation for step 2 (Table 2). Record buthanol volume separated.

c. *Collection product :* Collect compound and investigate.

Table 1 *- Heating regulations for step 1*

Time of activating microwave (min)	Temperature (^{0}C)	Water seperated
0'00 → 1'30	~ 95^{0}C	Begin to have humidity
2'30 → 3'00	~ 98^{0}C	Begin to have humidity
4'00 → 4'30	~100^{0}C	Water seperated
5'30 → 6'00	~ 102^{0}C	Water and little of buthanol seperate
7'00 → 7'30	~ 104^{0}C	Water and little of buthanol seperated
9'30 → 10'00	~ 102^{0}C	Water and buthanol seperated
12'00 → 12'30	~ 102^{0}C	Water and buthanol seperated
14'30 → 15'00	~ 102^{0}C	Much water and buthanol seperated
17'00 → 17'30	~ 102^{0}C	Much water and buthanol seperated
19'30 → 20'00	~ 102^{0}C	Much water and buthanol seperated
22'00 → 22'30	~ 102^{0}C	Much water and buthanol seperated
24'30 → 25'00	~ 102^{0}C	Much water and buthanol seperated
27'00 → 27'30	~ 102^{0}C	Water and buthanol seperated
29'30 → 28'00	~ 102^{0}C	Water and buthanol seperated
30'00 → 30'30	~ 102^{0}C	Water and buthanol seperated
32'30 → 33'00	~ 102^{0}C	Water and buthanol seperated
35'00 → 35'30	~ 102^{0}C	Water and buthanol seperated
37'30 → 38'00	~ 102^{0}C	Water and buthanol seperated

Table 2 - Heating regulations for step 2

Time of activating microwave (min)	Temperature (^{0}C)	Water seperated
0'00 → 1'00	~ 110^{0}C	Buthanol seperated
2'00 → 2'30	~ 116^{0}C	Buthanol seperated
3'30 → 4'00	~ 120^{0}C	Much buthanol seperated
6'00 → 6'30	~ 116^{0}C	Much buthanol seperated
8'30 → 9'00	~ 116^{0}C	Much buthanol seperated
11'00 → 11'30	~ 116^{0}C	Much buthanol seperated
13'30 → 14'00	~ 116^{0}C	Much buthanol seperated
16'00 → 16'30	~ 116^{0}C	Much buthanol seperated
18'30 → 19'00	~ 116^{0}C	Much buthanol seperated
21'00 → 21'30	~ 116^{0}C	Buthanol seperated
23'30 → 24'00	~ 116^{0}C	Buthanol seperated

Studying factors

- τ_1 = 4 – 10 mins
- τ_2 = 3 – 6 mins
- Ratio of catalyst H_2SO_4 : glucose = 0,05% : 1 – 0,15% : 1

- Ratio of n - buthanol : glucose = 3 : 1 – 1 : 1
- Ratio of lauryl : glucose = 2 : 1 – 0.8 : 1

2.2.2 Comparisions synthesis of APG by Fisher with and without microwaves interaction :

Comparions were evaluated by qualification of reaction productivity, reaction time, ratio of raw materials.
Bleaching products and measuring color (^{0}Klette). Evaluating the color change after each step.

3. RESULTS AND DISCUSSIONS

Effect of the ratio of Buthanol – Glucose and Reaction time on reaction yield of stage I

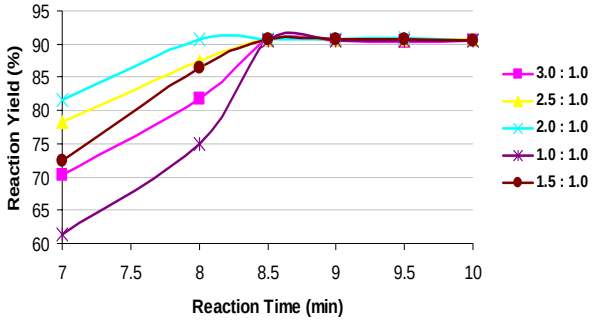

Figure 1 - Effect of the ratio of Buthanol – Glucose and Reaction time on reaction yield of stage I

Reaction time is one of the most important factors affect on synthetic reaction.
Reaction is fast in first 8 minutes, then it becomes slower in the next 30 seconds and reaches the highest value (91%).

When used lower volume of buthanol (from 3:1 – 2:1), reaction rate increases, reaction reaction yield reaches a higher value faster. However, if the ratio of buthanol : glucose is lower than 2:1, reaction reaction yield decreases.

→ The product is a light yellow, clear liquid. The suitable parameter for stage I :

- ✓ Ratio of n – buthanol:glucose = 2.0:1
- ✓ Reaction time 1 : = 8’

Effect of the ratio of Buthanol – Glucose and Reaction time on reaction yield of stage II

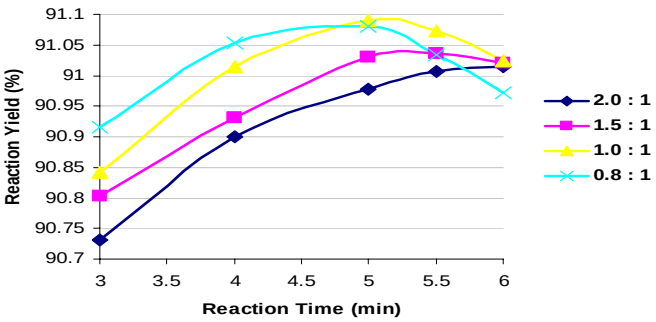

Figure 2 - Effect of the ratio of Lauryl alcohol – Glucose and Reaction time on reaction yield of stageII

When increased reaction time, reaction yield increases, reach the highest, then decreases because the products - Lauryl polyglucosides, Lauryl glucoside, Polyglucosides – are reversible hydrolysed in acid and high temperature condition. The longer reaction time is, the higher the product’s viscosity is and the darker product is, however.

When used lower volume of lauryl alcohol, reaction rate increases, but reaction yield decreased so fast after reach the highest value.

→ The suitable parameter for stage II :

- ❖ Ratio of n – buthanol : glucose = 2.0 : 1
- ❖ Reaction time I : τ_1 = 8’
- ❖ Ratio of lauryl alcohol : glucose = 1.0 : 1
- ❖ Reaction time II : τ_2 = 5’

Effect of the concentrate of catalyst on reaction yield :

The concentrate of catalyst using affects on synthetic reaction - reaction yield, reaction time, product’s quality and their color.
When used lower volume of catalyst (0.05% - 0.075%), reaction time might reach 12 minutes (total time for step 1 is about 48 minutes, including break time). If a little higher volume of catalyst is used (0.01%), reaction time could reduce dramatically – 8 minutes (total time for step 1 is just 28 minutes, including break time). However, the product will be darked fast and side reactions (polymerization reaction, reversible hydrolysis, …) are also stronger if used higher catalyst (0.125% - 0.15%).
Using 0.1% of catalyst will be logical for restraint undesired factors such as dark product, side reactions, oxidation of glucose, …

Comparisions of method with and without microwave assisted:

* *Reaction time :*

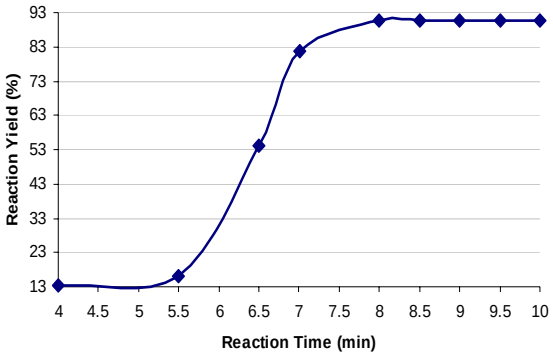

Figure 3 *- Effect of reaction time on yield (stage I) Microwave assisted*

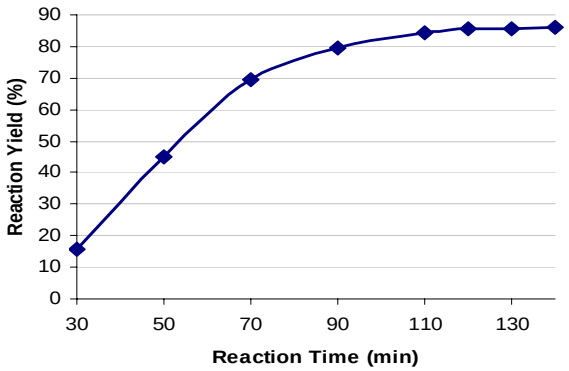

Figure 4 *- Effect of reaction time on yield (stage I) Traditional method*

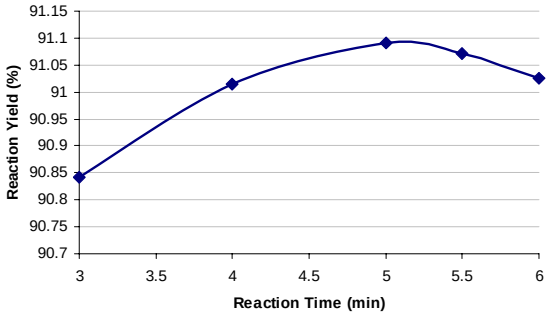

Figure 5 *- Effect of reaction time on yield (stage II) Microwave assisted*

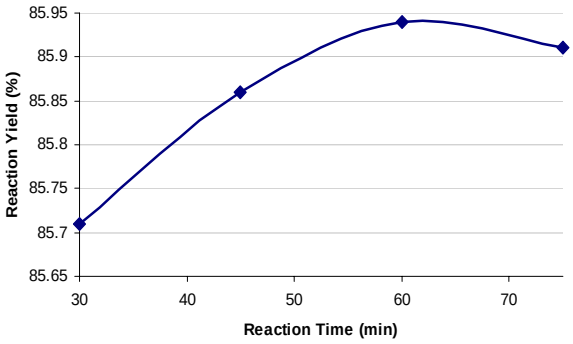

Figure 6 *- Effect of reaction time on yield (stage II) Traditional method*

Table 3 - *Comparisions of angular co-efficient*

	Stage I	**Stage II**
Microwave assisted (k_{vs})	51.546	0.126
Traditional method (k_{co})	1.402	0.008
k_{vs}/k_{co}	36.766	15.75

→ By microwave technique, reaction yield increases (reaction time decreases dramatically).

* ***Comparisions of some factors affect on synthesis by two method****:*

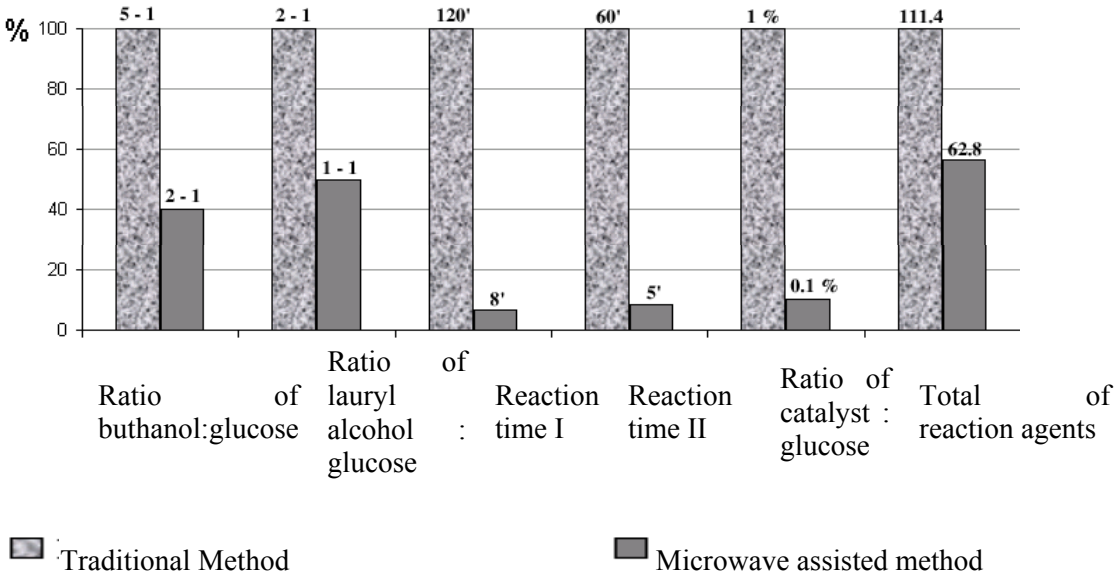

Figure 7 - *Comparisions of some factors affect on synthesis*

* *Product 's color :*

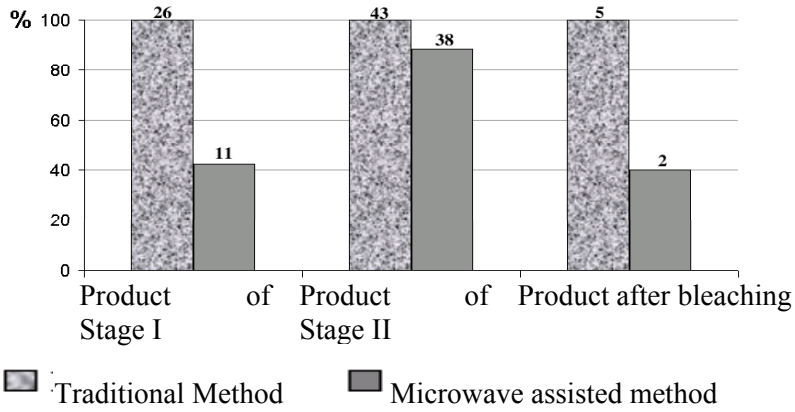

Figure 8 - *Comparision of product's color of two methods after each stage*

* *TLC analysis :*

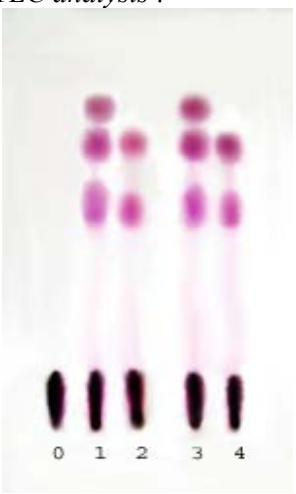

Figure 9 - *TLC analysis results*

0 : Glucose
1 : Product of stage I (traditional method)
2 : Product of stage II (traditional method)
3 : Product of stage I (microwave method), darker than spot 1
4 : Product of stage II (microwave method), darker than spot 2

CONCLUSION

This new method has showed many advantages : Reduce chemical reaction times, reduce side reactions, and increase reaction yields. Reduce solvents and catalysts. Save energy, save time and costs, ...

Compare to traditional heating method, microwave technique could help enhance reaction (TLC analysis shows better results), reduce remarkably chemical reaction time (from 170 mins to 13 mins, in both stage), and catalyst (just 1/10 volume required). Reaction times in traditional heating method and in microwave assistant method in first stage were 110 mins and 8 mins; in second stage were 60 mins and 5 mins. Because of short reaction time, microwave assisted method also helps limit side reactions and time of product in acid condition.

By microwave assisted method, the volume of buthanol and lauryl alcohol required are also lower. Reaction yield increases from 85.9% to 91%. APG products has lighter color and helps bleaching more easily.

The suitable parameter for synthesis of APG by microwave assisted method :

* Ratio of n-buthanol : glucose = 2.0 : 1
* Reaction time I : τ_1 = 8'
* Ratio of lauryl alcohol : glucose = 1.0 : 1
* Reaction time II : τ_2 = 5'

In the process of synthesis of alkyl polyglucosides (APGs), the high costs of solvent and refining final products are obstacles for its development. Microwave technique shows a potential therefore.

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