SYNTHESIS OF WAX ESTERS FROM PALM OIL AND CETYL ALCOHOL BY ALKALI-CATALYZED TRANSESTERIFICATION

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ABSTRACT

In this study, alkali-catalyzed transesterification of palm oil and cetyl alcohol for preparation of wax esters was presented. The effect of palm oil to cetyl alcohol molar ratios and the catalyst concentrations on the production of wax esters were investigated. The transesterification reaction was carried out in three-necked round bottle flask at 100°C under stirring condition for 15 minute. The molar ratios of palm oil to cetyl alcohol were varied at 1:1, 2:1 and 3:1. The percentages of the catalyst (KOH) were varied from 0.5% to 3.0% (w/w of alcohol). The transesterification reactions were monitored by high performance size exclusion chromatography (HPSEC) equipped with evaporative light scattering detector (ELSD) using a 100-Å Phenogel column. The optimum condition for preparation of palm oil wax esters was 1:1 molar ratio of palm oil to cetyl alcohol and 1.0% KOH. The maximum yield of palm oil cetyl ester was 46.98% (w/w of total reaction mixture).

Keyword: Alkali-catalyzed transesterification, Cetyl alcohol, Palm oil cetyl esters

1. INTRODUCTION

Wax esters are esters that derived from a long chain fatty acid and a long chain fatty alcohol. The physical characteristics of wax have maximized their usage in various industrial purposes such as in cosmetics, foods, pharmaceuticals, and polishing applications. Natural wax esters can be extracted from animal and plant materials such as beeswax, carnuba wax, sperm whale oil, and jojoba oil. However, due to the high price and limitation of natural waxes thus several attempts have been made to synthesize wax esters with cheap starting materials.

Synthetic wax esters can be synthesized by transesterification (or esterification) of triglycerides (or fatty acids) with long chain fatty alcohols by using either chemical (Sánchez, et al., 1992, Sunitha et al., 2007) or enzymatic catalysis (Salis and Monduzzi, 2003). Among transesterification reactions, alcoholysis of triglycerides is simple and is practical for industrial application due to the starting material is cheap.

The objective of the present study was to synthesis wax esters by KOH-catalyzed transesterification of palm oil with cetyl alcohol. The effects of palm oil to alcohol molar ratio and catalyst concentration on the transesterification were investigated.

2. EXPERIMENT

2.1 Chemical

Cetyl alcohol was obtained from Honghuat Co., Ltd. (Bangkok, Thailand). Palm oil was purchased from local supermarket in Bangkok, Thailand. KOH was analytical grade from Carlo Erba (Val de Reuil, France). All solvents were analytical grade from Merck (Germany) and RCI-Labscan (Bangkok, Thailand).

2.2 Experimental Apparatus

High performance size-exclusion chromatography (HPSEC)

The HPLC system consisted of a pump model 510 (Waters Associates, Milford, MA, USA), a Rheodyne 7125 valve injector, a 20-µl loop and a Sedex 75 Evaporative Light Scattering Detector (ELSD; Sedere, Alfortville, France). Detector temperature was set at

30^oC and N_2 gas was at 2 bar. Data were collected and processed by CSW32 HPLC software (DataApex Ltd, Prague, Czech Republic). Sample was analyzed on a 100-Å Phenogel column (300 mm x 7.8 mm ID, 5µm) (Phenomenex, Torrance, CA) protected with a Bondapak C18 Guard Pak (Millipore Co., Milford, MA, USA). The column and injector were in an oven set at 65^oC. The mobile phase was at a flow rate of 1.0 ml/min, its composition is reported in the text. Peaks were identified by comparison with reference standards.

2.3 Technique

Transesterification of palm oil with cetyl alcohol

Transesterification of palm oil with cetyl alcohol was carried out in a round bottom flask equipped with a condenser and a mechanical stirrer at 100^oC with the rate of stirring of 200 rpm. The molar ratio of palm oil to cetyl alcohol was set at 1:1, 2:1 and 3:1. The catalyst concentration was varied between 0.5 and 3.0% KOH (w/w of alcohol).

Briefly, the pre-calculated amount of cetyl alcohol was melt in a 250 ml round bottom flask. The KOH was added to the melted alcohol and stirred at 200 rpm, 100^oC for 15 min. The preheated palm oil was added into the reaction flask and the reaction was started. An aliquot (~2 ml) was taken at 1, 3, 5, 7 and 9 min and neutralized with glacial acetic acid, washed and analyzed by HPSEC to check the completeness of transesterification.

2.4 Sample preparation

Lipid standards including palm oil, cetyl alcohol, palmityl palmitate and palmitic acid (1,000 ppm each) and reaction mixtures were dissolved in toluene. The samples were kept at 70^oC heating box before analysis.

3. ANALYSIS

3.1 Lipid analysis by HPSEC

According to Aryusuk et al. (2011), the triglyceride and wax ester of rice bran wax could be separated on a 100-Å Phenogel column protected with a Bondapak C18 Guard Pak by using 65:35:0.10 (v/v/v) of isooctane/toluene/acetic acid as mobile phase. However, palm oil (Mw = 840.38 g/mol) and cetyl palmitate (Mw = 480.85 g/mol) could not be separated by this chromatographic condition. They are separated on a 100-Å Phenogel column protected with 1-cm Spherisorb silica guard column by using 30:70:0.05 (v/v/v) of isooctane/toluene/acetic acid as mobile phase (Fig.1).

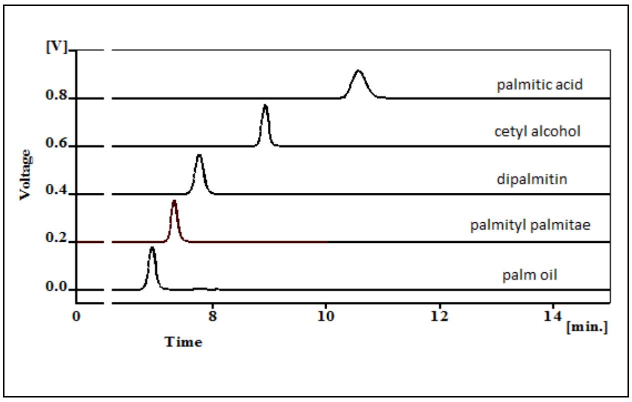

Fig.1 Chromatograms of lipid standards separated on a 100-Å Phenogel column protected with 1-cm Spherisorb silica guard column using 30:70:0.05 (v/v/v) of isooctane/toluene/acetic acid as mobile phase.

3.2 Effect of palm oil to cetyl alcohol molar ratio

In transesterification of vegetable oils and animal fats, three moles of short chain alcohol (e.g. methanol and ethanol) is required to convert one mole of triglyceride to three moles of ester. Since the reaction is reversible thus, excess amount of alcohol is required to push the reaction forward and enhance the ester yield (Jothiramalingam and Wang, 2009). The unreacted alcohol is preferably separated from the ester by evaporation. However, separation of long chain alcohol from its ester is much difficult due to its high melting and boiling point. Separation of palm oil from its ester by solvent extraction and/or crystallization is much easier. Thus, in this study, synthesis of palm oil cetyl ester using excess palm oil molar ratio to cetyl alcohol was varied at 1:1, 2:1 and 3:1 using 1% KOH as catalyst. Table 1 shows the percentage of palm oil wax esters observed in the transesterification reaction at different reaction time.

Table 1 Effect of molar ratio on the percentage of palm oil wax esters. (1% KOH, temperature 100^oC, rate of stirring 200 rpm).

Time (min)	Palm oil wax esters (%, w/w)		
	1:1	2:1	3:1
0	0.00	0.00	0.00
1	40.53	18.49	11.15
3	42.29	18.37	11.00
5	44.32	18.59	11.59
7	43.97	19.27	11.69
9	46.98	22.09	11.96

At 1:1 molar ratio of palm oil to cetyl alcohol, one mole of cetyl alcohol was completely reacted with one mole of palm oil and there remained two mole of palm oil unreacted in the reaction. For the molar ratio of 2:1 and 3:1, cetyl alcohol was not completely reacted with palm oil. This may be due to the difficulty in mixing homogeneously added palm oil and cetyl alcohol. Together with higher excess content of the oil and

incomplete of the reaction, low percentages of palm oil wax esters were observed in the reactions of 2:1 and 3:1 molar ratio of palm oil to cetyl alcohol.

3.3 Effect of catalyst concentration

Catalyst has emerged as the most important factor to determine the overall ester yield in transesterification reaction (Lam and Lee, 2011). Fig. 2 shows percentage of palm oil wax esters versus time at different catalytic concentrations. The molar ratio of palm oil to cetyl alcohol was set at 1:1. The KOH used as catalyst was varied at 0.5, 1.0, 2.0 and 3.0% (w/w of alcohol). From the figure, the esters yield was found to increase as the percentage of catalyst increased. The highest esters yield was observed when 1.0% KOH was used as catalyst. However, at 2.0 and 3.0% KOH, there was decrease in the yield of wax esters due to hydrolysis of the oil was occurred. This was in accordance with the results of Encinar et al. (2007) and Rashid and Anwar (2008).

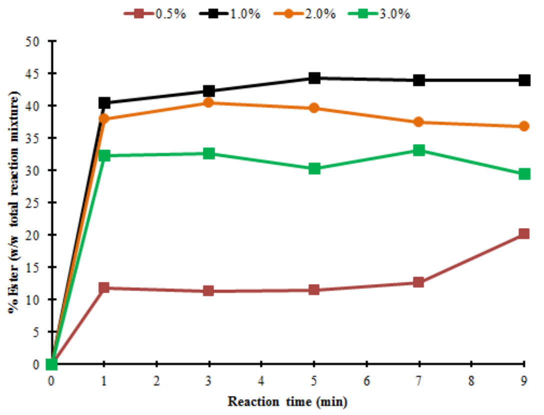

Fig. 2 Effects of KOH concentration on the percentages of palm oil wax esters. (palm oil/cetyl alcohol molar ratio 1:1, temperature 100°C, rate of stirring 200 rpm).

CONCLUSION

The optimum condition for preparation of palm oil wax esters was 1:1 palm oil to cetyl alcohol molar ratio, 1% KOH (w/w of alcohol) as catalyst with a stirring rate of 200 rpm at 100°C. The developed HPSEC method for determination of the transesterification reaction mixture was simple, rapid and reliable.

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NOMENCLATURE

Å: Angstrom

°C: Degree Celsius

ELSD: Evaporative light scattering detector

HPLC: High performance liquid chromatography

HPSEC: High performance size exclusion chromatography

KOH: Potassium hydroxide

ml: Milliliter

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