



Optimization of transesterification of palm-based methyl palmitate and triethanolamine towards maximum di-esteramine content



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ABSTRACT

This study involved optimization of transesterification of palm-based methyl palmitate with triethanolamine towards maximum di-esteramine content for an ideal performance of esterquats. This reaction was aided by Ca–Al, a hydrotalcite-like compound (HTLC) as the heterogeneous catalyst and the reaction was conducted in a 500 mL reaction unit. Response surface methodology (RSM) in combination with face-centered design was used to optimize the operating parameters. Results show that temperature was the most significant variable affecting the di-esteramine composition, followed by Ca–Al dosage, quadratic effect of Ca–Al dosage, vacuum and interaction of vacuum and Ca–Al dosage. The optimum reaction conditions obtained were at temperature of 169 °C, Ca–Al dosage of 0.74% and vacuum of 278.6 mbar. The result from ICP-OES exhibited insignificant leaching of Ca and Al active species into fatty esteramine mixtures and the reusability of Ca–Al catalyst was successfully sustained for three subsequent cycles.

1. Introduction

Nowadays, esterquats cationic surfactant is commonly derived from biological resources such as vegetable oils and animal fats. Excellent environmental profile and the good softening effect of the esterquats have made this surfactant a better replacement for the conventional distearyl (tallow) dimethyl ammonium compounds as an active ingredient in fabric softeners. Esterquats is an interesting class of quaternaries, which are characterized by the presence of hydrophobic alkyl chains that link to the positively charged nitrogen molecule via ester bonds. The presence of this ester link will provide easy hydrolysis into fatty acids and short chain quats (Tyagi et al., 2006; Puchta et al., 1993). Generally, esterquats are produced via a two-stage process in which, triethanolamine is first esterified with fatty acid in the presence of homogeneous acid catalyst or transesterified with ester using a base catalysts to produce the desired esteramine. Esteramine, which consists of mixtures of mono, di and tri-esteramine is then quaternized with methylating agent to introduce a positive charge onto the esterquats molecule. Optimization of the esterification or transesterification process for maximum conversion into esteramine is the key step in the preparation of esterquats. However, homogeneous catalysts employed in the process are difficult to be separated from the product (Jiang et al., 2012). Besides, homogeneous acid catalysts such as

hypophosphorous acid, para-toluenesulfonic acid and sulfuric acid are toxic and corrosive, while sodium methoxide used in transesterification process can be a serious health hazard to humans upon contact. These homogeneous catalysts are also not reusable. Due to these limitations, heterogeneous catalysts have been proposed as alternative to the homogeneous catalysts for the production of esteramine.

Production of esteramine via fatty acid route using solid catalysts has been reported in several literatures. Lipase-catalyzed esterification of oleic acid and triethanolamine for esteramine production was reported, whereby response surface methodology (RSM) was used to optimize the enzymatic process conditions. The optimum conditions were established at enzyme amount of 4.77%, reaction time of 24 h, temperature of 61.9 °C, mole ratio of 1:1 (oleic acid to triethanolamine) and agitation speed of 480 rpm with the highest conversion of 63.57% obtained (Masoumi et al., 2013). However, the study did not reported on the optimization of the operating parameters towards maximum di-esteramine content. Esterification between stearic acid and triethanolamine to produce esteramine catalyzed by 20% loaded zirconium sulfate supported on SBA-15 and aluminium on SBA-15 mesoporous molecular sieves have been reported (Geng et al., 2010, 2011; Jiang et al., 2012). The optimum operating conditions employing these catalysts were reported at temperature of 190 °C, catalyst dosage of 0.25%, mole ratio of 1.8:1 of stearic acid to triethanolamine and 6 h reaction time. The

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solid acid catalyst of 20% loaded zirconium sulfate supported on SBA-15 (with pore diameter of 6 nm) was reported to give higher composition of mono and di-esteramine of 16.61% and 67.45% respectively as opposed to the homogeneous catalyst H_3PO_3 , with tri-esteramine composition of 15.94%. Meanwhile, aluminium supported on SBA-15 catalyst also appeared to be selectively produced higher di-esteramine content of 68.49% as compared to H_3PO_3 , with mono and tri-esteramine content of 16.30% and 15.21% respectively. Although several development of selective catalysts to produce higher di-esteramine contents were reported, the production of esteramine via direct esterification of fatty acids and triethanolamine in the presence of solid acid catalyst will requires expensive corrosion-resistant equipment. Furthermore, the preparation of the fatty acid substrates produces many impurities, which lead to formation of dark-coloured product. As such, further downstream processes such as bleaching and distillation are needed to improve the purity and colour of the products that will increase the production cost [Narula (1995)].

Due to drawbacks of the direct esterification of fatty acids, alternative route of producing esteramine from methyl ester has been explored. Production of palm-based fatty esteramine from a novel heterogeneous transesterification process from palm-based methyl palmitate has been revealed in which, Ca-Al catalyst was employed as the heterogeneous catalyst (Haliza et al., 2016). The previous research work reported on the optimum transesterification operating conditions towards achieving maximum conversion of methyl palmitate of approximately 98%. Among the various HTLC investigated, Ca-Al catalyst showed the best catalytic activity as it gave the highest conversion of methyl palmitate and yielded mono, di and tri-esteramine compositions of 23.50%, 47% and 23.90% respectively. Further effort to obtain the optimum operating conditions with maximum di-esteramine content will be highlighted in this present study, which has not been previously reported based on the scope of our knowledge. Esteramine derived from triethanolamine will consists of a mixture of mono, di and tri-esteramine. Higher mono-esteramine content would give better dispersibility and formulation stability but exhibits low softening effects, whereas higher tri-esteramine content results in better softening but give poor formulation stability (Mishra et al., 2007). Ideally, higher di-esteramine content is desirable as it exhibits both excellent softening and good stability of fabric softeners formulation. As such, optimization of the transesterification process towards obtaining maximum di-esteramine content will be investigated in this present study.

Interaction among the process parameters as well as optimization of the operating conditions towards maximum di-esteramine content using multivariate statistic technique will be highlighted in this present study. Face-centered cube design was used to design the experiment and RSM was used as the optimization tools. A mathematical model was generated to demonstrate the relationship between the operating parameters and di-esteramine content. Stability of Ca-Al catalyst in terms of its reusability as well leaching of the calcium and aluminium active species into the fatty esteramine mixtures shall also be discussed in this paper.

2. Materials and methods

2.1. Materials

Palm-based methyl palmitate (purity, 98%) was purchased from Carotino Sdn Bhd and triethanolamine (purity, 99%) was purchased from Fisher Scientific (M) Sdn Bhd. Ca-Al solid catalyst was prepared in-house by the Malaysian Palm Oil Board.

2.2. Catalyst preparation and characterization

The Ca-Al catalyst system was prepared by co-precipitation technique at high supersaturation in a single container of two diluted

solutions A and B, in which solution A contained Ca^{2+} (67 g) and Al^{3+} (150 g) dissolved in 1 L deionized water. Solution B acting as precipitating reagents was prepared by dissolving Na_2CO_3 (42.4 g) and NaOH (16 g) in 0.5 L deionized water. The prepared solutions A and B were then mixed with high supersaturation technique for 18 h at 80 °C with vigorous stirring. Finally, the precipitate was filtered, washed with deionized water up to pH 7 and dried at 120 °C for overnight. The morphology of Ca-Al was examined by scanning electron microscopy (SEM) using FEI Quanta 200 modal. Leaching of the calcium and aluminium metals of the catalyst into the reaction medium was determined using the Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) conducted using Perkin Elmer Emission Spectrometer Model Plasma 1000.

2.3. Transesterification reaction

The process was performed in a 500 mL reaction flask equipped with magnetic stirrer, vacuum line and a heating jacket. The reaction was carried out under the optimum mole ratio of 1.8:1 (methyl palmitate: triethanolamine) and duration of 2 h as reported in previous study (Haliza et al., 2016). The reactants were mixed and heated to the desired reaction temperature and vacuum. When the reaction was completed, Ca-Al solid catalyst was separated via vacuum filtration and the product was then analyzed using gas chromatography. For reusability study of Ca-Al, several reactions were performed under the optimum operating conditions by recycling Ca-Al from one cycle to the subsequent cycle without washing or drying the catalyst cake after its separation from the reaction mixture. Leaching of Ca-Al catalyst active species into fatty esteramine was tested, whereby the Ca and Al metals content in the product were measured after first, second, third and forth cycles in the recycling process. For samples preparation, 1 g of fatty esteramine was added into 10 mL nitric acid (50% concentration) and the sample mixture was heated for 10 min at 95 °C. 5 mL of concentrated nitric acid (HNO_3) was then added to the mixture and heated for another 30 min at 95 °C. After the mixture was cooled down, 2 mL of deionized water and 3 mL of hydrogen peroxide (30% concentration) were added into the mixture and heated again for 2 h at 95 °C. Subsequently, 7 mL of hydrogen peroxide (30% concentration) and 10 mL of concentrated hydrochloric acid were added into the mixture and heated again for 15 min at 95 °C. Finally, the sample mixture was cooled down, filtered and marked up to 100 mL with deionized water.

2.4. Analytical method

Compositions of mono, di and tri-esteramine were determined via gas chromatography analysis, performed using the capillary column ZB-5HT inferno (12 m × 530 μm × 15 μm). The oven temperature was set initially at 100 °C, held for 3 min, and then increased at 6 °C/min to 350 °C. Helium was used as the carrier gas at a flow rate of 20 mL/min. Injector temperature was set at 350 °C with split ratio set at 10: 1. Flame Ionization Detector (FID) was used and temperature was set at 360 °C.

2.5. Design of experiments and optimization method

Design-Expert software (version 8) was employed in design the experimental works and optimizing the operating conditions. The experimental design was a three-level face-centered cube design involving 30 experiments. Face-centered design is usually used in order to avoid the experimental regions over the process limit (Norhazimah et al., 2012). Reaction temperature, vacuum, agitator speed and Ca-Al dosage were chosen as the independent variables while the di-esteramine content was chosen as the response for the optimization study. These independent variables were studied at three levels with 6 replications of central point and 8 axial points. The value of alpha

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