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SYNTHESIS OF AMIDE-BASED SURFACTANTS FROM FATTY ACID METHYL ESTER: EFFECT OF SOLVENT RATIO AND STIRRING SPEED

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ABSTRACT

The synthesis of surfactant fatty alkanolamidei.e. coco mono-ethanolamide was observed in this study. The fatty acid methyl ester (FAME) resulted from trans-esterification of coconut oil, treated with mono-ethanolamine to be coco mono-ethanolamide, using $ZrCl_4$ as a catalyst and tert-amyl alcohol as a solvent. The observed reaction variables are the solvent ratio and stirring speed, and their effect on the converted FAME. The results showed that the 4:1 (v/w FAME) solvent ratio, and 300 rpm stirring speed gave the best results. Structural tests performed with FT-IR spectroscopy show that the surfactant obtained includes the fatty alkanolamide group. The results of this study are expected to produce cheap fatty alkanolamide surfactants obtained from renewable raw materials.

Keywords: fatty acid methyl ester, coco mono-ethanolamide, solvent ratio, stirring speed.

INTRODUCTION

Surfactant demand continues to increase, among which are used as emulsifiers, corrosion inhibitors, foaming agents, anti-slip, additive lubricants and printing inks [1,2]. Now the surfactant is the backbone of the modern industry. Fatty alkanolamides are widely used as surfactants such as cleaning agents and emulsifiers [3,4].

Coconut (*Cocosnucifera Linn.*) belongs to the *Arecaceae* family. Coconuts are cultivated primarily in the tropics with high humidity, regular rainfall, and sandy soil. Countries like India, Sri Lanka, Indonesia and the Philippines have a big share for the global coconut production. Copra is a dry coconut kernel with low water content (6-8%) and processed into coconut oil using organic solvents. Coconut oil is rich in medium chain fatty acids and easy to digest [5,6].

Coconut Oil consists of 45-52% lauric acid, which is converted to monoglyceride called monolaurin; 16-11% myristic acid which is a saturated fatty acid; 5-10% caprylic acid and other components such as palmitic acid, oleic acid, linoleic acid, vitamin E and protein [7]. All of these components provide health benefits [5]. Coconut oil is excellent oil for the skin that acts as an effective moisturizer. Coconut oil is widely used in the manufacture of various products such as cosmetics products [8].

Coconut fatty acids derived from coconut oil, coco mono-ethanolamide (Cocamide MEA), are abrasive solids that dissolve easily in water. The pH of cocamide MEA at a concentration of 10% in water is 9.5-10.5. Cocamide MEA has an acid and alkali value of 1 (maximum) and 10-20 respectively and melts at a temperature of 60-64°C [5,9].

Mono-ethanolamine (MEA) is often referred to 2-aminoethanol commonly used by the natural gas processing industry to remove acid gas from natural gas (eg. H_2S and CO_2). Mono-ethanolamine is a group of chemicals known as alkanolamines. Alkanolamines are bi-functional molecules with functional groups of amines and alcohols in the same compound. As a result, they experience a variety of beneficial reactions that are common to amines and alcohols [10,11].

An economical method for synthesizing amides has been studied lately [12,13]. Heterogeneous catalysts can be an alternative and are particularly suitable because of low consumption and are easily separated from the solution mixture [14]. Zirconium (IV) chloride ($ZrCl_4$) is a catalyst with abundant availability in the earth's crust so $ZrCl_4$ is a cheap and widely available catalyst. In addition, zirconium (IV) is a compound having low toxicity [15,16]. Based on this, this study used a heterogeneous $ZrCl_4$ catalyst to obtain the best result of getting fatty alkanolamide surfactant.

Methyl ester fatty acids used are obtained from the coconut oil trans-esterification reaction. The trans-esterification process takes place between oil and alcohol where the short chain of alcohol is converted to glycerol from each triglyceride unit of the oil. This process can be given acidic catalysts, bases, and enzymes. In the trans-esterification process using a base catalyst, the glyceride and alcohol should be anhydrous to avoid a soap-forming reaction This soap can be produced from ester derivative products and will make the process difficult both separation and purification. In addition, the process which has a small free fatty acid should use a trans-esterification process using an alkaline catalyst [17].

Bearing the explanation above, the objectives of the study reported in this paper are observed the effect of solvent ratio and stirring rate on the converted FAME on the amidation reaction of FAME with mono-ethanolamine using a $ZrCl_4$ catalyst.

MATERIALS AND METHODS

Materials

The coconut oil used as commercial oil that is Braco®. Mono-ethanolamine, zirconium (IV) chloride ($ZrCl_4$), sulfuric acid, methanol, tert-amyl alcohol, sodium

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hydroxide, sodium sulfate, potassium hydroxide, ethanol and chloride acid are obtained from E Merck, Darmstadt Germany.

Methods

The study began by trans-esterification of coconut oil with methanol into coconut oil fatty acid methyl ester and glycerol. Trans-esterification method using the following variables: reaction time 120 minutes, mole ratio methanol/coconut oil 6:1, catalyst concentration 1% NaOH, 50°C reaction temperature and 200 rpm stirring speed [9]. The fatty acid methyl ester obtained is then reacted with mono-ethanolamine to obtain fatty alkanolamide. The reaction of fatty alkanolamide from FAME is given in Figure-1.

A further study was conducted by observing the effect of solvent ratio, tert-amyl alcohol: methyl ester of 1:1, 2:1, 3:1, 4:1, 5:1 (v/b FAME), as well as the effect of stirring speed of 100-400 rpm. The reaction method is as follows. Mono-ethanolamine with methyl esters dissolved in tert-amyl alcohol at various variations of the solvent ratio is reacted with a 2:1 -mole substrate ratio in a three-neck flask. The catalyst added into solution with concentration 5% total weight of the solution. Stirred at various stirring speeds and treated at 75°C for 60 minutes.

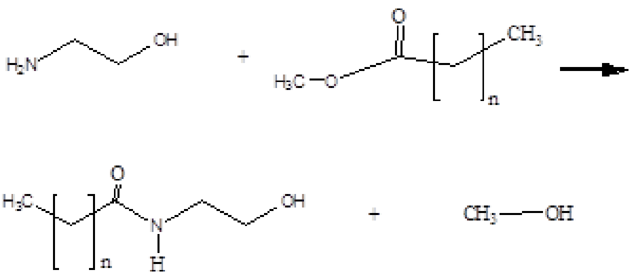

Figure-1. The reaction of fatty alkanolamide from mono-ethanolamine and fatty acid methyl ester (FAME).

The mixture was separated from the catalyst by filtration, the solvent and methanol were evaporated. Followed by the analysis of the acid number of the product to determine the converted fatty acid. Qualitative analysis was performed using FT-IR spectroscopy.

RESULTS AND DISCUSSIONS

In the preliminary study, the trans-esterification reaction of coconut oil to fatty acid methyl ester was carried out. Thereafter followed by the synthesis of surfactant cocamide mono-ethanolamine from FAME and mono-ethanolamine (MEA). This study aims to determine the best results of process variables. Observations were made on variations of stirring speed and solvent ratio. Followed by acid number analysis for all samples. From this acid number then calculated the conversion value for each variable.

Determination the type of solvent

In the preliminary study, suitable solvent types were observed using lauric acid with diethanolamine. The research aims to determine the best solvent to be used. For that, four types of organic solvents of isopropyl alcohol (log P = 0.05), tert-butanol (log P = 0.4), tert-amyl alcohol (log P = 1.5) and n-hexane (log P = 3.5), selected for use in synthesis.

The four types of an organic solvent is shown in Figure-2 where the reaction gives a good result on n-hexane solvent (log P = 3.5), and further tert-amyl alcohol (log P = 1.5). However, the solvents chosen for use in FAME amidation are tert-amyl alcohol, with the consideration that tert-amyl alcohol is also a solvent which gives good results on alkanolamide synthesis, and not many studies use tert-amyl alcohol [12]. In addition, the use of tert-amyl alcohol has several advantages including low toxicity and does not reduce the product mixture.

Effect of solvent ratio

The proper use of the solvent ratio can increase the homogeneity of the substrate, positively affect the performance of the catalyst and ultimately be expected to provide a good product yield. The best solvent ratio determination result is shown in Figure-3. It can be seen that the highest conversion of cocamide mono-ethanolamine is obtained in the solvent ratio of 4:1 (v/wFAME) and that is 85.29%.

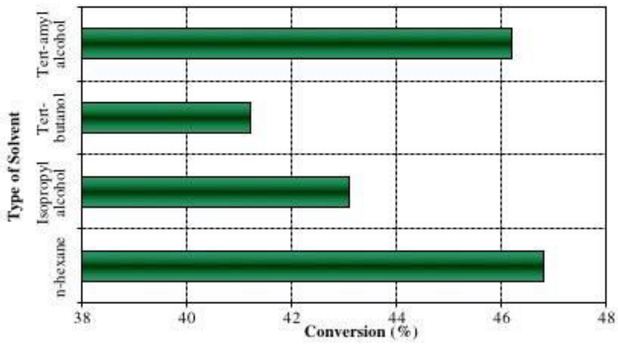

Figure-2. The four types of an organic solvent.

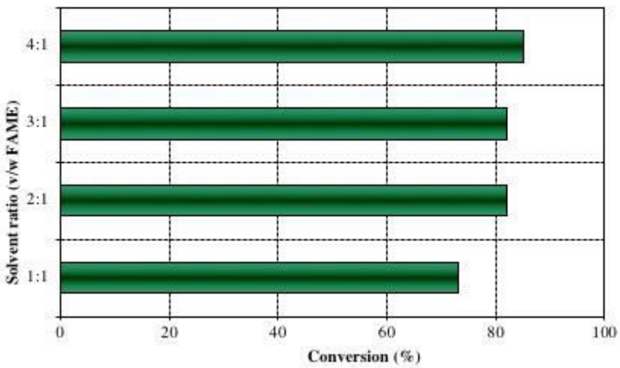

Figure-3. The determination of solvent ratio on coco-monoethanolamide synthesis.

From the figure, it is found that at a ratio of 1:1 (v/wFAME), the conversion of the fatty acid obtained is still below 80%.

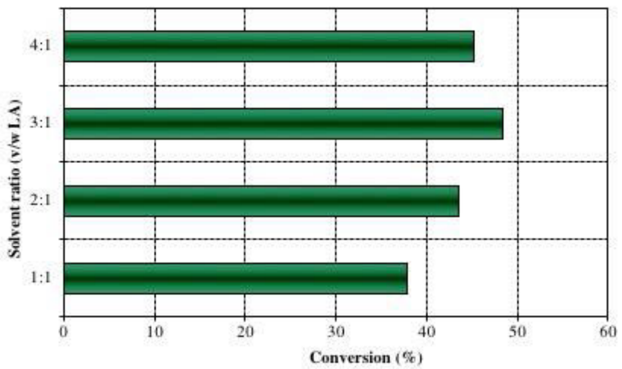

Figure-4. The determination of solvent ratio for long-chain alkanolamide synthesis.

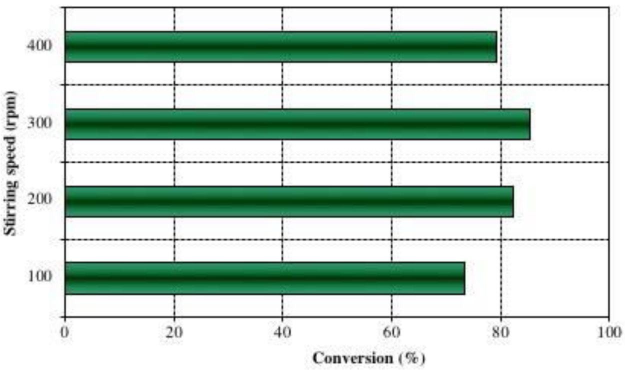

Figure-5. The effect of stirring speed on the percent conversion of fatty acid.

It seems at a ratio of 1:1 (v/wFAME), the amount of solvent present is not sufficient to completely dissolve the substrate. At a 4:1 (v/wFAME) ratio, the available solvent is sufficient so that the raw material is completely dissolved and the catalyst is maintained its reactivity so that the conversion of fatty acids becomes high. The amine and FAME substrate are molecules with different polarities and solubilities [18]. FAME dissolves in a hydrophobic solvent, whereas alkanol amine is slightly soluble in some solvents.

Selected amyl alcohols may be used for further research because they provide optimum results [19]. Similar observations were also obtained in the synthesis of α-butyl glucoside using lipase in a tert-amyl alcohol solvent. It is observed that tert-amyl alcohol is an inert solvent and suitable for use because it can dissolve both the acyl and alcohol substrate.

In comparison, the solvent ratio determination results for long-chain alkanolamide synthesis are shown in Figure-4. It is found that at a ratio of 3:1 (v/wLA) the conversion reaches the optimum value when at a ratio of 4:1 (v/wLA), the available solvent is excessive so that the solvent tert-amyl alcohol actually takes the essential water which required the catalyst to maintain its activity so that the conversion of fatty acids became low.

The effect of stirring speed

The effect of stirring speed on the conversion of fatty acid is shown in Figure-5. The observation of stirring speed is done on four types of motor rotation that is 100, 200, 300 and 400 rpm. Based on Figure-5 it can be seen that the highest conversion of cocamidemonoethanolamine obtained at 300 rpm. So for the advanced research used 300 rpm stirring speed as it gives optimum results.

The opposite result is found only after 300 rpm stirring speed, where increasing the stirring speed to 400 rpm decreases the fatty acid conversion. From the figure, it was observed that the increase in stirring rate actually decreased the percent conversion of fatty acids. It was concluded that higher stirring speeds of 300 rpm seemed to disrupt the amidation reaction and decrease fatty acid conversion in the synthesis of fatty alkanolamide.

The FT-IR analysis

As an ester, alkanolamide compounds also have carbonyl groups. Carbonyl recharge of the infra-red spectrum is at 1630-1840 cm^{-1} [20]. However, the carbonyl positions for alkanolamides and esters have a difference, wherein the position of alkanolamide recharge is at 1630-1700 cm^{-1} when the ester absorption is at 1740 cm^{-1}. Specifically, the infrared spectra for cocamide mono-ethanolamide compounds are given in Figure-6.

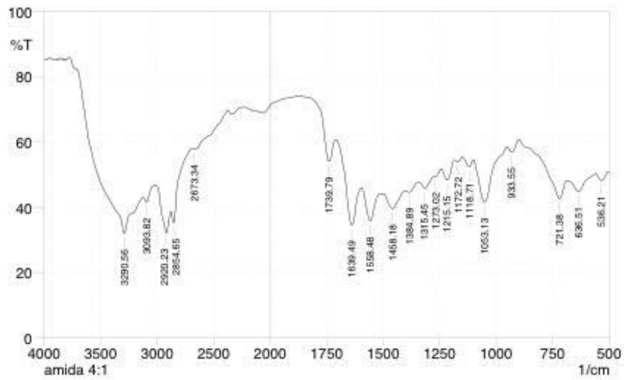

Figure-6. The infrared spectra for cocamidemonoethanolamide.

Visible peak absorption in the region of the wave number 3290.56 cm^{-1}, indicating the presence of OH group. The presence of OH is supported by an OH bend at 1458.18 cm^{-1}. The vibration of CH sp3 appears in the area of the wave number 2920.23 cm^{-1} supported by the emergence of absorption at the 1558.48 cm^{-1} wave number region indicating the presence of vibration of CH sp^3.

The spectrum shows the vibration peak at the wave number region 721.38 cm^{-1} which is the rocking vibration (CH2) n for n> 4. The vibration of C = O (carbonyl) groups appears in the regions of wave numbers 1739.79 cm^{-1} and C-N at 1639.49 cm^{-1} which is a typical group of N-C = O amides. The C-N bond is also expressed by the C-N stretch at 1053.13 cm^{-1}.

CONCLUSIONS

Based on the results of the research and discussion on the synthesis of surfactant fatty alkanolamide it was found that the amidation reaction gave the best fatty acid conversion if using 4:1 (v/wFAME) solvent ratio, and 300 rpm stirring rate. So it can be concluded that the amount of converted fatty acids is affected by the stirring speed and the ratio of solvent.

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