



APPLICATION OF SUPER BASE CALCIUM OXIDE CATALYST IN THE SYNTHESIS OF STEARAMIDE SURFACTANTS BY AMIDATION

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ABSTRACT

Surfactant is a substance that can reduce surface tension, which has two groups in one molecule: hydrophilic and hydrophobic. These two groups, in the same molecule, have different degrees of polarity. In this study, stearic acid was amidated with urea using a super base calcium oxide catalyst in a mixture of hexane and isopropanol solvents. The study was carried out by observing two process-independent variables: the reaction temperature in the range of 55°C, 65°C, and 75°C, and the reaction time in the range of 2 hours, 3 hours, and 4 hours. Optimum conditions were obtained at a temperature of 75°C and a reaction time of 3 hours, where a conversion of 89.88% was obtained. Then the research samples were analyzed using FT-IR and super base calcium oxide catalyst and analyzed for morphological properties using SEM.

Keywords: amidation, stearic acid, super base calcium oxide, urea, stearamide.

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INTRODUCTION

Surfactants are very useful in everyday life in households and industry. Surfactants in the industry can be used as emulsifiers, corrosion inhibition, foaming, detergency, and hair conditioning. Surfactants are widely used in hospitals because they contain anti-germs that can be used as a clean washing agent [1-3].

Surfactants are also used in the petroleum industry because they can reduce interfacial tension, change wettability, reduce viscosity, shrink droplets in water, clean dispersion of oil droplets, and clean oil wells in highly depleted wells, thereby facilitating the flow of oil from reservoir-to-reservoir production wellbore [4, 5].

However, the use of surfactants can also have a negative impact. Against the environment, surfactants can cause water pollution because surfactants can kill microorganisms in the environment and inhibit the degradation of other toxic substances. Certain surfactant toxicity can enter animals through their food and skin penetration. Long-term use of detergents can cause skin irritation, and surfactants can damage enzyme activity and impact human physiology [6, 7].

Surfactants are active compounds that can be used to reduce surface tension and interfacial tension. In general, surfactants can be produced by chemical synthesis as well as biochemical synthesis. The main characteristic of surfactants is that they are amphiphilic. Amphiphilic is a compound that has two groups that are opposite each other in one molecule. This group is a hydrophilic group that is polar and a hydrophobic group that is non-polar, so it can unite two materials with different polarities. The hydrophobic group is usually a long chain of hydrocarbons, and this group has a non-polar nature which is commonly referred to as an R (alkyl) group and is soluble in oils and fats. The hydrophobic group is in the tail. The hydrophobic group binds impurities in the cleaning process, while the hydrophilic group is useful as

a wetting agent and is found in the head. Some groups of surfactants that can dissolve in water include carboxyl groups (CO₂), hydroxyl (OH-), and sulfones (SO₂-) [8, 9]. Most of the surfactants are obtained from petroleum and natural gas derivatives, so the resulting surfactants are difficult to degrade by the environment and will eventually pollute the environment. An alternative that can be used to overcome this is to use vegetable oil. Most vegetable oils contain saturated and unsaturated fatty acids. In saturated fatty acids, there are several compounds: caproic acid, caprylic acid, myristic acid, palmitic acid, and stearic acid. In contrast, the compounds in unsaturated fatty acids are cyclo-propane pentanoic acid, oleic acid, and sapiens acid [10-12].

An amide surfactant from stearic acid, known as stearamide, has begun to be developed because stearic acid can be obtained in large quantities from vegetable oil derivatives such as palm oil. Stearic acid has a crystalline appearance and is white or yellowish, has a slight odor, and has a fat-like taste. Stearic acid is a saturated fatty acid, in which saturated fatty acids are more stable than unsaturated fatty acids. Stearic acid can be used as a stabilizer so that the flexibility of the polymer matrix can be increased, and it can also be used as a dispersant and lubricant [13, 14].

Several catalysts can be used to synthesize surfactants, such as sodium methoxide, calcium oxide, and sulfuric acid. Calcium oxide (CaO) catalyst is a heterogeneous catalyst. The advantage of using heterogeneous catalysts such as CaO is that they are readily available in nature, do not cause side reactions, are easily separated from reaction products, and can be used again after activation. Early studies on calcium metal oxide for the transesterification reaction showed that the development of CaO into superbase CaO showed higher activity and stability than CaO [15, 16].



Catalysts are compounds that can speed up reactions. In manufacturing a compound, we generally use homogeneous and heterogeneous catalysts. The advantage of using heterogeneous catalysts in transesterification is to reduce wasted water, and the catalyst can be reused for further processes. Calcium Oxide (CaO) is a type of heterogeneous catalyst [17, 18].

A good heterogeneous catalyst must have several qualities, namely being able to catalyze both transesterification and esterification reactions, not being deactivated in the presence of water in the mixture, being active at low temperatures, and having high selectivity, stability, and not requiring product washing. The surface of this heterogeneous material must display some hydrophobic character. This is useful for promoting preferential triglyceride adsorption and for avoiding catalyst deactivation due to the strong adsorption power of side products, such as glycerol and water, which are polar [19, 20].

Calcium Oxide (CaO) is the most widely used chemical compound for the transesterification process because of its low price, low solubility in methanol, mild toxicity, abundant availability in nature, so the price is relatively low, and high basicity it can produce high ester yields. In research that has been done, the CaO catalyst can increase the number of collisions between palm oil methyl ester (POME) and Na₂S₂O₅. Increasing the number of collisions can accelerate the sulfonation reaction by lowering the activation energy so that more and more Na₂S₂O₅ is bound to POME to produce surfactant methyl ester sulfonate (MES). The conversion obtained in the sulfonation reaction with 1% CaO catalyst was 87% [21].

Stearamide is part of the primary fatty acid amides. Stearamide is usually granular and can be produced on a large scale. Stearamide is white and crystalline at room temperature, with the molecular formula C₁₈H₃₇NO. The maximum temperature of stearamide is 220 °C, and stearamide is often used in industrial applications such as the rubber industry [22, 23]. The stearamide structure is shown in Figure-1.

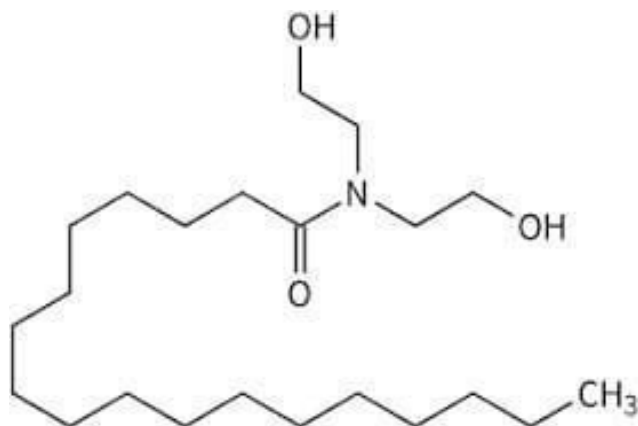


Figure-1. Stearamide Surfactant Structure.

Stearamide surfactant can be obtained through an amidation reaction, and it is necessary to continue to seek optimal results because stearamide has many uses, is easily degraded, and can be obtained from renewable raw materials. Efforts that can be made include observing the effect of the super base calcium oxide (CaO) catalyst and the characteristics of the catalyst obtained, as well as observing the effect of the reaction variables on the characteristics of the resulting stearamide surfactant.

MATERIALS AND METHODS

Materials

Research materials include stearic acid (C₁₈H₃₆O₂), hexane, isopropanol, calcium oxide (CaO), urea (CH₄N₂O), and ammonium carbonate-purification materials in the form of citric acid and acetone. The analytical materials are potassium hydroxide (KOH), Phenolphthalein, 2-propanol, and hydrochloric acid (HCl).

Preparation of Super Base Calcium Oxide Catalyst

This stage begins by measuring the pH of CaO. Next, soak CaO in ammonium carbonate solution to precipitate calcium metal as carbonate compounds. Stir the marinade for 30 minutes, then filter. The collected solids were heated at 110°C and calcined at 800°C for 1.5 hours. The pH of CaO was measured (pH ≥ 11.45 in the superbase state) and put in a desiccator to prevent a decrease in the base strength of the catalyst.

Preparation of Stearamide Surfactants

Add 5 grams of stearic acid to a three-neck flask and heat it. Hexane isopropanol solvent was added with a solvent: substrate ratio (1:1). Into the beaker glass, a super base calcium oxide catalyst was added with a weight percent ratio of 3%, 5%, and 7% to stearic acid. Wait until the stearic acid dissolves, then put it in a three-neck flask. It was heated with variations in heating temperature of 55°C, 65°C, and 75°C. Stir with a stirring speed of 200 rpm. They were reacted for 2 hours, 3 hours, and 4 hours. Then purification is carried out, and the percent conversion is calculated

Purification

5 ml of 10% citric acid was added to the mixture to precipitate the catalyst, and the precipitate formed was separated by filtration. The product mixed with the solvent is separated by evaporating at 90 °C. The product containing excess urea is then washed with acetone twice the volume of the product mixture, which will dissolve the urea. The product will be obtained as the bottom layer, while the excess urea will dissolve with acetone as the top product. The excess acetone was evaporated, and the volume obtained was measured. Calculated conversion percentage and product mass.

Analysis

Analysis was carried out by determining the acid number, the saponification number, identifying



compounds by FT-IR spectroscopy, and the number of Hydrophilic-Lipophilic Balance (HLB value).

RESULTS AND DISCUSSIONS

Super Base Calcium Oxide pH Analysis

The results of the analysis of the pH of super base calcium oxide, after the activation of the catalyst, obtained a pH of 13.1. The activated CaO catalyst has reached the standard of a super base catalyst from the pH obtained. The advantages of calcium oxide as a catalyst are high activity, mild reaction conditions, long catalyst life, and low cost [15, 18].

Catalyst Morphology Analysis

Analysis of morphological characteristics using SEM on super base calcium oxide without activation compared to activation is shown in Figure-2. Figure-2, with a magnification of 3,000 times, shows the particle morphology of the calcium oxide catalyst, the result of a calcination temperature of 700°C, where Figure-2 (a) shows that the catalyst, before activation, has a small surface and small pores, whereas, in Figure-2 (b), it shows that the catalyst after being calcined, a catalyst that has an expanding surface and wide open pores will be obtained. Madhumanchi *et al.* (2016) explained that the calcination effect of a temperature of 700°C not only removes fat and protein so that the color of the catalyst becomes white but also increases the porosity of the catalyst structure.

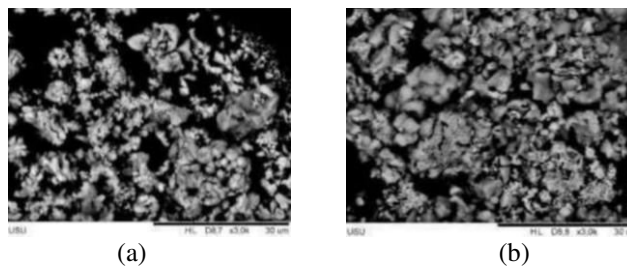


Figure-2. Morphological characteristics using SEM with a magnification of 3,000 times, (a) the morphology before treatment, (b) the morphology after calcination.

Functional Group Analysis

To find out the functional groups present in the sample, it is necessary to do an FT-IR analysis [24]. The different peaks identify chemical bonds. The results of the stearic acid spectrum can be seen in Figure-3. The spectrum in Figure 3 shows that the vibration for the C-H bond with a wave number of 2912.76 cm⁻¹ is a strong alkane. The O-H bond vibration with wave number 2846.66 cm⁻¹ is a carboxylic acid. The vibration for the C=O bond with wave number 1694.17 cm⁻¹ is for aldehydes, ethers, carboxylic acids, and esters. C-H bond vibration with wave number 1429.12 cm⁻¹ is a strong alkane compound.

Urea spectrum analysis using FT-IR can be seen in Figure-4. The vibration of the C=H bond with a wave number of 940.26 cm⁻¹ is an alkene compound. The vibration for the C-H bond with a wave number of 1354.86 cm⁻¹ is an alkane compound. The vibration for the O-H bond with wave number 2846.68 cm⁻¹ is that of a carboxylic acid compound. C-H bond vibration with wave number 718.38 cm⁻¹ is an aromatic ring. The N-H bond vibration with wave number 2946.48 cm⁻¹ is for amine and amide compounds.

The spectrum analysis of the stearamide with the highest conversion is shown in Figure-5. It is shown that the vibration of the C-N bond with a wave number of 1220.42 cm⁻¹ is an amide compound. The vibration for the C-H bond with a wave number of 1428.87 cm⁻¹ is an alkane compound. The vibration of the C=C bond with a wave number of 1694.40 cm⁻¹ is an alkene compound. The N-H bond vibration with wave number 2946.87 cm⁻¹ is for an amine compound.

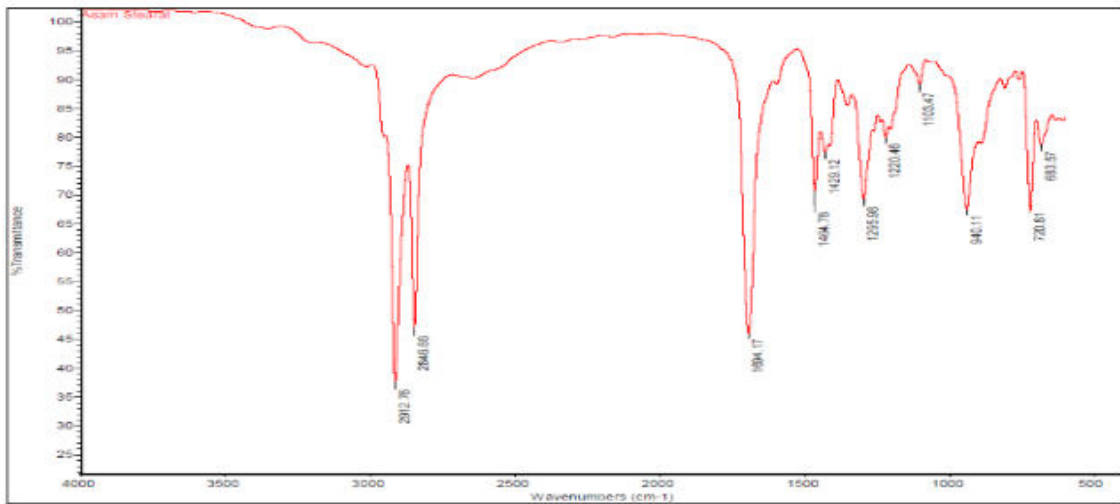


Figure-3. The results of the stearic acid spectrum.

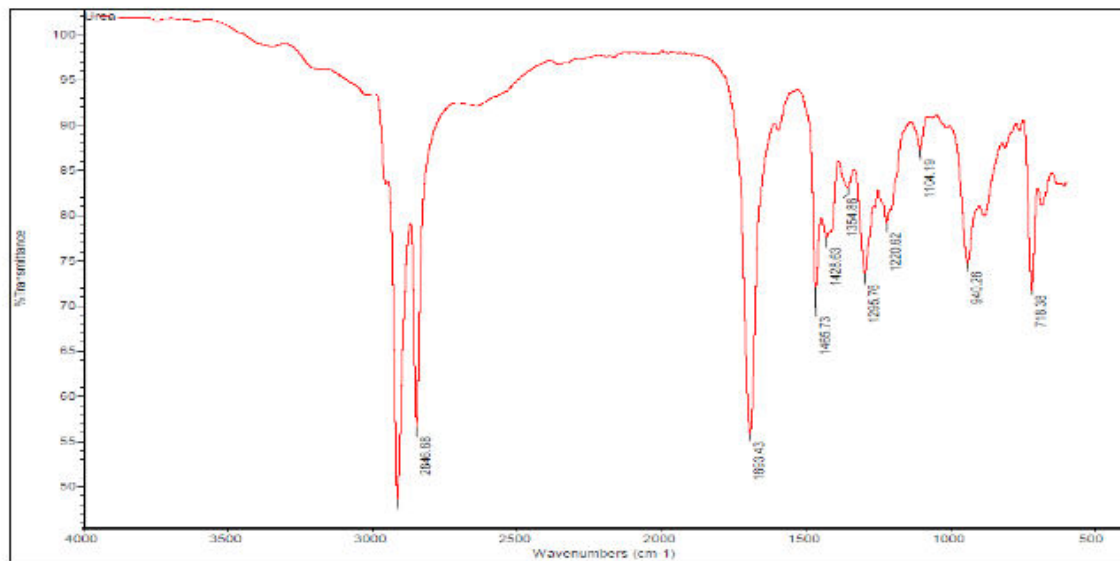


Figure-4. Urea spectrum using FT-IR.

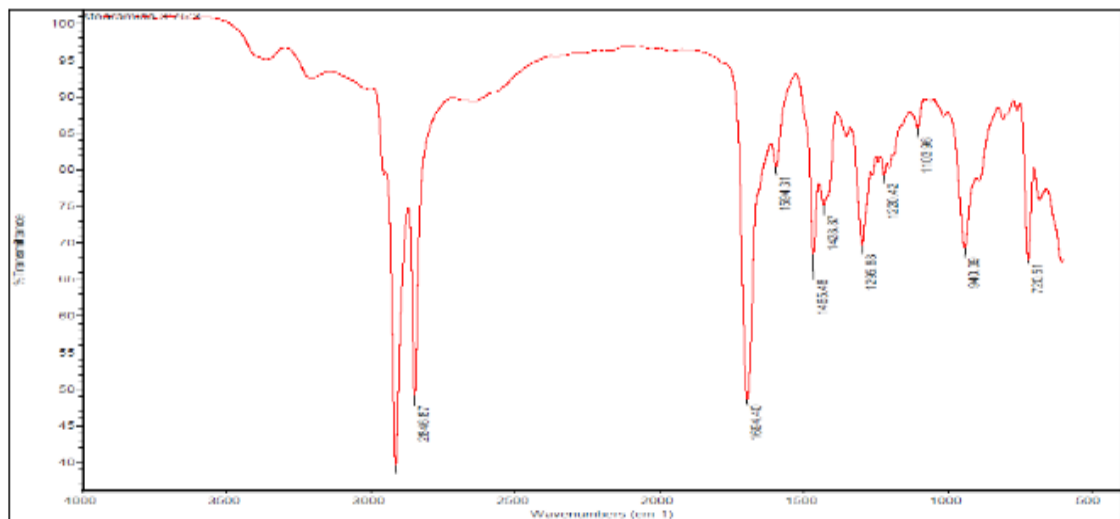


Figure-5. The spectrum of stearamide.



Effect of Reaction Temperature

In this study, the catalytic activity of the super base calcium oxide catalyst was tested for the formation of stearamide surfactant. The relationship between temperature and catalyst concentration for the converted stearic acid can be seen in Figure-6. Figure-6 shows that at various catalyst concentrations for 3 hours, the trend of fluctuations in the conversion of stearic acid was shown. This can happen because the side reactions in the transesterification reaction have different optimum conditions for various variables.

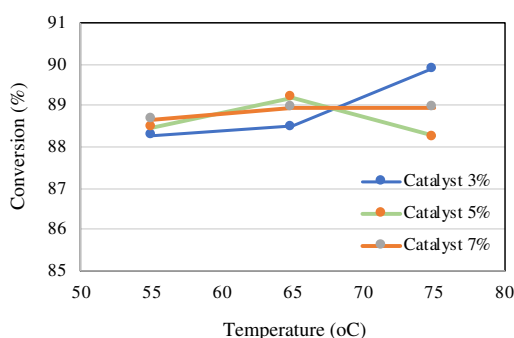


Figure-6. Effect of temperature on the conversion of stearic acid.

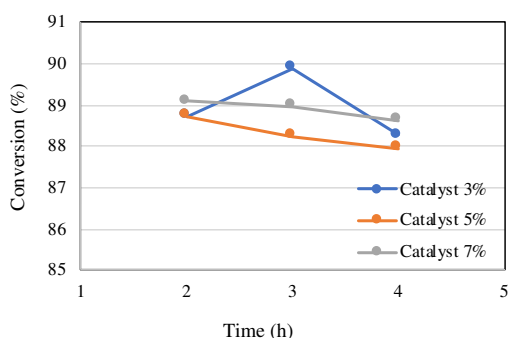


Figure-7. Effect of reaction time on stearic acid conversion.

Observations of stearamide synthesis in Figure-6 show the effect of temperature on the conversion of stearic acid. The optimum temperature was obtained at 75°C, which resulted in the best conversion of 89.88%, with a super base calcium oxide catalyst concentration of 3% for 3 hours. The lowest conversion was at 55°C with a 3% super base calcium oxide catalyst concentration for 3 hours, namely 88.35%. The transesterification reaction takes place at a temperature of 50°C-80°C. Temperature is an important factor in endothermic reactions because endothermic reactions require heat. Of course, the reaction cannot run properly if the temperature does not meet the existing conditions, such as at 55°C. Decreased conversion due to transesterification can occur because it is a reversible reaction [14]. It can be concluded that the optimum temperature for stearamide synthesis is 75°C.

Effect of Reaction Time

The relationship between reaction time and stearic acid conversion at various catalyst concentrations can be seen in Figure-7. In Figure-7, it is shown that the largest conversion occurred at a reaction time of 3 hours, with a catalyst concentration of 3%, namely 89.88%. The smallest conversion occurred at a reaction time of 4 hours with a catalyst concentration of 5%, namely 87.95%. There was a decrease in the conversion obtained due to side reactions such as saponification [14]. The increase in reaction time did not significantly affect the amide gain [8]. It can be concluded that the optimum reaction time for stearamide synthesis is 3 hours.

Effect of Solvent Ratio

Observation of the influence of the solvent ratio was observed in three categories of substrate ratios, namely 2:1; 3:1; and 4:1. The results obtained are shown in Figure-8. At a substrate ratio of 2:1, it can be seen that if the solvent ratio is increased to 2, the conversion of stearic acid will increase. Meanwhile, the reaction conversion will decrease if the solvent ratio becomes three times the amount of raw material. The same was observed at a substrate ratio of 3:1.

For a substrate ratio of 4:1, adding solvent up to three times will reduce the conversion of stearic acid. From

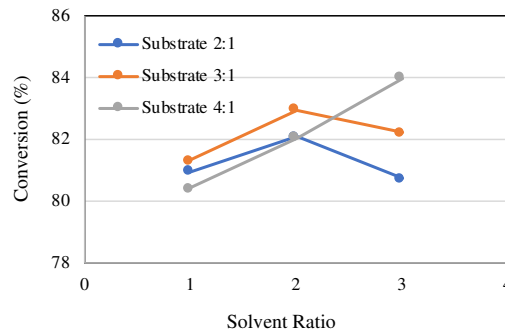


Figure-8. Effect of solvent ratio on stearic acid conversion.

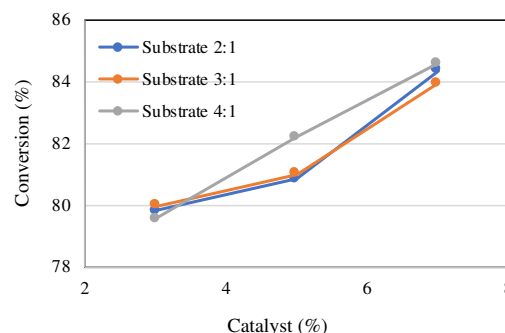


Figure-9. Effect of the amount of catalyst on the conversion of stearic acid.



Figure-8, it can be concluded that of the three existing substrate ratios, the solvent ratio of twice the substrate amount provides a high stearic acid conversion. If a solvent ratio of 3 times is used, it does not increase the amount of stearic acid converted to stearamide. A solvent ratio of 2 times the amount of substrate is sufficient for the solvent to dissolve all stearic acid and urea [7].

Effect of Amount of Catalyst

Observation of the effect of the amount of CaO catalyst added on the amidation reaction of stearic acid with urea is shown in Figure-9. Overall, it was observed that the conversion of stearic acid would increase if the amount of catalyst added also increased [16]. Observations were also grouped on the three substrate ratios, at the amount of catalyst 3%, 5%, and 7%. It can be seen that the optimum amount of catalyst added is 7% of the amount of stearic acid and urea used. For this combination, the conversion of stearic acid can reach 85.2%.

Analysis of HLB Value (Hydrophile-Lipophile Balance)

To determine the use of surfactants, the HLB value is usually determined first [25]. From the results of this research, the HLB value of the stearamide surfactant product was obtained, which was measured using the acid number and saponification number approach. The HLB value of the surfactant product obtained is 13.181. The value of this HLB indicates that stearamide surfactant can be used as an industrial material, as it is widely used in detergent, pulp, and paper production applications.

CONCLUSIONS

The conclusions of the studies conducted are as follows. The best reaction conditions for synthesizing stearamide surfactant were at a temperature of 75°C, a reaction time of 3 hours, and a super base calcium oxide catalyst concentration of 7%. Observations from the stearamide synthesis process showed that at a temperature of 75°C, a reaction time of 3 hours, and a concentration of 7% super base calcium oxide catalyst produced the best conversion, reaching 89.88%. A decrease in conversion can occur because the amidification reaction is reversible. A decrease in conversion can also occur due to a side reaction, namely saponification.

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