Synthesis and Characterization of Diethanolamide (Surfactant) from CaO/Zeolite-Catalysed Used Cooking Oil

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Abstract

Synthesis of diethanolamide (surfactant) from CaO/zeolite-catalysed used cooking oil has been conducted. The results showed that the yields of the reactions between methyl esters and diethanolamine with CaO concentration at 3%, 5%, and 7% were 64.47%, 92.91%, and 87.05%, respectively. The characterization showed that the higher surfactant concentration, the greater the capability of decreasing surface tension. The watersurfactant-pertalite system had an emulsion index of 67%. The new liquid mixture system (water-surfactant-pertalite) was observed for 4 days to investigate the emulsion stability. The CMC and HLB values were 1.5 g/L and 10.59, respectively. These results show that surfactant is applicable as a cleaning solution with a good emulsion stability.

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Introduction

Surface-active agents (surfactants) are compounds with an amphipathic structure consisting of hydrophilic groups (water-loving) and hydrophobic groups (oil/fat-loving) on the same molecule to unite mixture of liquids (water and oil) and improve the dispersion properties by lowering the surface tension between the liquids [1,2].

Surfactants can be synthesized from palm oil. Indonesia, in this case, as the largest palm oil-producing country in the world, has a great potential to produce palm oil-based surfactants.

Palm oil is one of vegetable oil that can be used as the raw material for the synthesis of surfactants. It is an important economic and business commodity in Indonesia, in which 3.5 million families are working in oil palm cultivation.

Indonesian people generally use vegetable oils such as palm oil for cooking. Repeated use of cooking oil will cause oxidation on its unsaturated fatty acids, which then form peroxide groups. The use of used cooking oil can cause oxidative damage in body, including damage to DNA, proteins, and cell membranes [3].

Used cooking oils are abundant at minimal cost than fresh vegetable oils [4,5,6] and can be processed into biodiesel and utilized as raw material for surfactants production. Vegetable oils are the best raw material for producing biodiesel because the conversion of pure triglycerides gives result to high fatty acid methyl esters within relatively short reaction times [7].

Many researches have been conducted to synthesis new surfactant in many applications. Samanta et al. [8] synthesized a triethanolamine derivative sodium dodecyl sulfate as an Alkali-Surfactant-Polymer (ASP) flooding in an enhanced oil recovery (EOR). The result shows that the derived surfactant has lower surface tension than the pure surfactant [8]. To be ecologically acceptable, diethanolamide, one of the fatty acid amides (surfactants), can be synthesized from renewable and degradative raw materials [9]. Its formation reaction involves amidation using alkanolamines [10] and requires high temperature and long time. The use of catalyst can lower the temperature and pressure as well as time of reaction. In this regard, zeolites have been widely used in reaction requiring the use of catalyst due its large pores, high surface areas, and empty spaces. The latter is the most notable feature that can form channels in zeolite structures and play a significant role in catalytic reactions that are specific and selective [11].

This study is focused to utilize used cooking oil as basic ingredient in the production of diethanolamide surfactant by heterogeneous catalyst CaO applied to zeolites.

Experimental Section
Materials and apparatus

The materials used in this research are used cooking oil, natural zeolite, phenolphthalein indicator, methanol, potassium hydroxide, hydrochloric acid, sulfuric acid, calcium oxide, filter paper, diethanolamine, and distilled water.

The equipment used in the study included a set of glassware, a set of reflux apparatus, 150 mesh sieve, centrifugation equipment, furnace tools, sliding microscope, IR spectrometer, X-ray diffractometer, conductometer and GC-MS.

Determination free fatty acid levels

Two grams of used cooking oil was put into Erlenmeyer, followed by the addition of 50 mL of methanol and 2 drops of phenolphthalein indicator. The mixture was titrated with 0.1 M KOH solution until the colour changed from yellowish to pink.

Activation of natural zeolite

A total of 100 g of natural zeolite (150 mesh) was immersed in 100 mL of distilled water for 24 hours, dried at 110 °C. Natural zeolite was activated by 500 mL of 0.5 M H2SO4 and stirred for 3 hours. The yield was filtered and washed by distilled water until neutral pH. The activated natural zeolite was dried at 130 °C for 4 hours.

Synthesis of activated CaO/zeolite

Fifteen grams of zeolite were divided into three parts, each 5 g was refluxed with 3%, 5% and 7% (w/w) CaO at 90 °C for 3 hours. Each zeolite was separated from the solutions and dried at 130 °C for 3 hours and calcined at 500 °C for 3 hours. The activated CaO/zeolite was characterized by FTIR and XRD.

Transesterification of used cooking oil

A total of 300 mL of used palm oil waste was put into a 500 mL three-neck flask, then 1% (w/w) KOH
dissolved in 75 mL methanol was added. The mixture was refluxed for 2 hours at 60 °C. The mixture was added into 100 mL distilled water and 1 mL of 1 M HCl in separating funnel. The mixture was shaken, the top layers was washed using distilled water until neutral pH. The yield was characterized by FTIR and GC-MS.

Manufacture non-ionic surfactant diethanolamide

A total of 50 g of methyl ester from used cooking oil and 36.75 g of diethanolamine were put into a 500 mL three-neck flask and heated until 150 °C for 5 hours. 1, 3, 5, and 7% (w/w) catalyst CaO/zeolite was added. Products were separated from catalysts by centrifuge. Each of the solutions was dissolved with 50 mL chloroform-methanol (1:1) and 50 mL distilled water. Each solution was put into separating funnel to facilitate the formation of two layers and their separation. The lower layer was re-dissolved with chloroform-methanol (1:1), while the solvent was evaporated with a rotary evaporator. Each viscous liquid and its properties, including emulsion stability, surface tension, CMC, and HLB values were characterized.

Results and Discussion

Based on Indonesian Industrial Standards number 00069 - 75 of 1975 [12], the content of free fatty acids (FFAs) in palm oil reach 0.27%. The conversion of used cooking oil to produce methyl ester compounds, with FFAs less than 1%, can be conducted by transesterification process.

The activation of natural zeolite was done by chemical and physical process. Chemically, it was conducted by the addition of 0.5 M H2SO4 to create uniform zeolite’s cations. In this case, H+ ions took the cations’ position giving result to zeolite being surrounded by H+ cations [13,14]. Physical process occurs by heating to remove organic impurities and water in zeolite framework giving result to dehydrated zeolite, in which case H+ ions bond with zeolite to form H-zeolite and alter its pore size. The natural zeolite before and after activation was characterized by FTIR. In Figure 1, a shift in peak of internal vibration occurs.

The peak shift occurs from 1034 to 1057 cm⁻¹, leading to a higher wavenumber in the internal stretching vibrational region. Besides, there was also a shift in peak at 3448 cm⁻¹ to 3433 cm⁻¹, which shows the level of silanol groups and corresponds to zeolite’s framework [15].

![Figure 1. FTIR spectra of natural zeolite before and after activation.](image)

Synthesis of CaO/ZAA catalysts was carried out by impregnating CaO at concentrations of 3%, 5%, and 7% to zeolites through wet impregnation process at 90 °C. The results were characterized using FTIR and XRD. The following are the IR spectra of CaO/zeolite with CaO at concentrations of 3%, 5%, and 7%.

![Figure 2. FTIR spectra of (a) activated natural zeolite, (b) CaO/zeolite with 3%, (c) 5%, and (d) 7% CaO concentration.](image)
FTIR spectra shows a strong absorption at 2924 and 2855 cm\textsuperscript{-1} which is characteristic of alkyl group by the vibration of the C-H \textsuperscript{sp3}. The presence of a sharp absorption at 1744 cm\textsuperscript{-1} indicates a stretching vibration of carbonyl group (-C=O) which is reinforced by the absorption at 1173 and 1018 cm\textsuperscript{-1} which shows the C-O ester bond. In addition, a weak absorption appears in 1658 cm\textsuperscript{-1} which is typically from unsaturated alkene group (-CH=CH\textsuperscript{-}) which is strengthened by the presence of a sharp absorption at 725 cm\textsuperscript{-1}. In the region of 1443 cm\textsuperscript{-1} the absorption of the methylene group (-CH\textsubscript{2}-) and 1366 cm\textsuperscript{-1} was the absorption of the methyl group (-CH\textsubscript{3}). Based on FTIR spectra, the results of used cooking oil transesterification contain ester, alkene, alkane, methylene, and methyl groups.

Figure 5 shows an analysis by GC-MS has 7 peaks and 2 main peaks. Results of GC chromatogram peaks identified from transesterification process of used cooking oil are shown in Table S2. Based on GC-MS analysis, the results of transesterification of used cooking oil contain seven fatty acids with two main components, which are methyl palmitate and methyl oleate at 36.54\% and 46.76\%.

Figure 3 shows diffraction patterns of CaO/zeolites. The X-ray diffraction patterns of CaO/ZA catalyst impregnated with 3\% of CaO shows major peak at 2\(\theta\) = 25.62\(^{\circ}\), indicating the presence of clinoptilolite minerals. The other peaks are seen at 2\(\theta\) = 26.32\(^{\circ}\), 19.62\(^{\circ}\), and 27.63\(^{\circ}\) as the characteristics of mordenite. The higher the concentration of CaO being impregnated into zeolite, the lower the peak intensity due the the presence of CaO on zeolite surface leading to decrease zeolite crystallinity. However, CaO impregnation does not change the structure of activated natural zeolite. The CaO diffraction patterns was absence in zeolite because CaO is evenly dispersed on zeolite surface and forms single layer which resulted in no CaO/ZA diffraction patterns [16].

The result of transesterification reaction was a mixture of methyl esters and glycerol with 91.20\% methyl esters yields. The methyl esters were analysed by FTIR and GC-MS. FTIR results are shown in Figure 4.

Figure 4. FTIR spectrum of the results of used cooking oil transesterification.
catalyst in the solution was in excess and clumped together to form an aggregate. Conversely, inadequate CaO would not be sufficient to stick to zeolite and as a consequence the distribution of metal oxide CaO was low. The formation of aggregate and uneven distribution of CaO affect the number of active sites of catalyst, thus affecting the catalytic properties of catalyst.

Analysis of diethanolamide (surfactant) was carried out with IR spectrometer. Based on Figure 6 the spectra shows absorption at wavenumbers of 2924 and 2855 cm\(^{-1}\), indicating \(\text{C}-\text{H}\) group characteristics. Wavenumber of 3379 and 3402 cm\(^{-1}\) indicate the presence of unchanged \(\text{–OH}\) alcohol groups in the main chain with no reaction during the amidation reaction. Strong absorption occurred in the region of 1620 cm\(^{-1}\), which is the characteristic of the amide carbonyl groups \((\text{C}=\text{O})\), strengthened by the appearance of absorption at 1057 cm\(^{-1}\) as the characteristics of \(\text{–C-N}\).

![Figure 6. FTIR spectra of diethanolamide.](image)

The liquid mixture system resulted in the synthesis constituted water and hydrocarbon compounds (pertalite) formed unstable emulsion system. The addition of diethanolamide as a dispersing agent was expected to form a stable emulsion by decreasing the surface tension between pertalite and distilled water. Increasing time would cause the emulsion index to decrease. The new liquid mixture system (water-surfactant-pertalite and distilled water) made of fatty acid methyl esters. The HLB value of diethanolamide (surfactant) was 10.59, thus can be used as a translucent cleaning solution and solvent.

The CMC values were determined by measuring the electrical conductivity of solutions at different concentrations diethanolamide solutions in water solvents. The electrical conductivity of surfactant solutions from synthesis using CaO catalyst at concentration of 3%, 5% and 7% is increased by the increasing concentration. This is due to the higher concentration, the more number of ions interacting with conductor, thus increasing the measured electrical conductivity.

**Conclusions**

Diethanolamide (surfactant) obtained from synthesis can reduce surface tension and has CMC, emulsion index, and HLB values of 1.5 g/L, 67%, and 10.59, respectively. The results indicate the ability of surfactant as translucent cleaning solution and solvent with good emulsion stability. The synthesis of diethanolamide (surfactant) gave an optimum results by the use of 5% CaO with a resulting yield of 92.91%.

**Conflict of Interest**

The authors declare there is no conflict of interest.

**References**


