

Research Article

Catalytic Synthesis of Diethanolamide Surfactant from Used Cooking Oil

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Abstract: The synthesis of diethanolamide surfactant from used cooking oil was systematically studied using modified zeolite as catalyst. The activated zeolite was obtained by dispersing natural zeolite in sulfuric acid (H₂SO₄) solution. Potassium carbonate (K₂CO₃) was loaded into activated zeolite by wet impregnation method. The methyl ester obtained from transesterification reaction of used cooking oil was refluxed with diethanolamine (C₄H₁₁NO) solution over K₂CO₃/zeolite catalyst in the production of diethanolamide surfactant. The amidiation reaction over K₂CO₃/zeolite effectively produced 92% of diethanolamide surfactant with the highest selectivity of methyl oleate. Diethanolamide surfactant showed stable foam and emulsion with the reduction of surface tension as much as 3.3 dyne/cm.

Keywords: Zeolite, Potassium carbonate, Diethanolamide surfactant, Used cooking oil

Introduction

Biodiesel is an alternative energy source to replace or reduce the use of petroleum-based diesel. Biodiesel is known as a renewable, biodegradable and non-toxic energy source. In chemical terms, biodiesel is produced from lipid sources with alcohol through transesterification reaction in the presence of a base, acid, enzyme or solid catalyst [1–4]. The use of used cooking oil in the production of biodiesel has become an effective way that offers solutions to economic and environmental problems [5–7].

Biodiesel obtained from transesterification reaction can be further processed to be neutral or ionic surfactant. Neutral surfactant has been widely produced as it is not affected by pH conditions, i.e. diethanolamide surfactant. The reaction between diethanolamine and methyl ester gives the well-known diethanolamide [8]. Diethanolamide is an important surfactant used in cosmetics as foaming agent or emulsifier. The most used catalysts of this amidiation reaction are potassium hydroxide (KOH), sodium methylate (CH₃ONa) and sodium hydroxide (NaOH) [9–11]. The homogeneous catalysts are generally better to interact with reactant molecules and show attractive selectivity under mild condition. Nevertheless, it has consequence of harmful wastes due to the difficult product recovery and environmental pollution, lead to the use of heterogeneous catalyst as possible and desirable solution [4].

Zeolite consists of three-dimensional structures of aluminosilicate with uniform pore size. It has been widely utilized as catalyst, ion-exchange resin and absorbent due to its physico-chemical properties [2],[12–14]. In addition, potassium carbonate (K₂CO₃) as a heterogeneous catalyst has been used for transesterification reaction for biodiesel production with a much higher yield than unmodified zeolite [15–16]. This study aims to synthesize K₂CO₃ modified zeolite as catalyst for the manufacture of diethanolamide surfactant from used cooking oil.

Materials and Methods

Materials

The materials used in this research were methanol (CH₃OH), potassium hydroxide (KOH), hydrochloric acid (HCl), sulfuric acid (H₂SO₄), potassium carbonate (K₂CO₃), diethanolamine (C₄H₁₁NO₂)

and phenolphthalein indicator supplied by E-Merck. The natural zeolite was obtained from CV Fruitanol Energy and the used cooking oil was collected from household waste.

A set of reflux apparatus, separatory funnel, analytical balance (Matrix), oven (Mettler Germany), hotplate magnetic stirrer (Amtast), magnetic bar, vacuum filter, thermometer, centrifuge (Kokusan Ogawa Seiki), microscope (Shenstone), evaporator Buchi (Oilbath B-485), capillary tube, furnace and test sieve 150 mesh. X-Ray Diffraction (XRD) data of catalyst were obtained with a Rigaku Miniflex 600. Fourier transform infrared spectroscopy (FTIR) analysis were carried out by a Shimadzu IR Prestige-21. Gas chromatography-mass spectrometry (GC-MS) characterizations were performed using a Shimadzu QP.

Methods

Acid Treatment of Natural Zeolite

Natural zeolite was soaked in distilled water for 24 h and dried at 105 °C for 4 h, then crushed and sieved to 150 mesh size. The calculated amount of natural zeolite was dispersed in H₂SO₄ for 3 h. The product is filtered, washed and neutralized using distilled water until the pH range of 7, then dried at 130 °C for 4 h and sieved to 150 mesh size.

Synthesis of K₂CO₃/Zeolite Catalyst

The calculated amount of activated zeolite and K₂CO₃ were dispersed in distilled water. The mixture was refluxed at 60 °C for 2 h, then dried at 110 °C for 24 h and calcined at 450 °C for 4 h. The obtained materials were referred to herein as K₂CO₃/zeolite catalyst.

Synthesis of Diethanolamide Surfactant

The used cooking oil was dissolved in CH₃OH and titrated by KOH for free fatty acid (%FFA) analysis using the following equation:

$$\%FFA = \frac{V_{KOH} \times M_{KOH} \times Mr_{fatty\ acid}}{\text{sample weight} \times 1000} \times 100\%$$

The mixture was heated at 60 °C for 2 h and extracted for 24 h and completely forms 2 separate layer. The methyl ester was separated from water, then neutralized using distilled water and HCl until the pH range of 7.

The calculated amount of methyl ester was refluxed with C₄H₁₁NO over K₂CO₃/zeolite catalyst at 120 °C for 4 h. The centrifugal separation of catalyst from surfactant was carried out at 1100 rpm for 20 min. The effectiveness and properties of diethanolamide surfactant was assessed by foam stability, emulsion index and surface tension tests.

Results and Discussions

Catalyst Preparation and Characterization

Acid treatment of natural zeolite aims to remove the mineral impurities and increase the acid strength by reducing the amount of Al in the framework of zeolite (dealumination). Fig. 1 shows the FTIR spectra of natural zeolite, activated zeolite and K₂CO₃/zeolite. The peak position shifted from 1033 cm⁻¹ to 1056 cm⁻¹ is assigned to the dealumination process, thus the ratio of Si/Al is increased. A broad band at 3448 cm⁻¹ and 1635 cm⁻¹ are corresponded to stretching and bending modes of adsorbed water molecules. The peak intensity of water molecule after acid treatment decreases due to the impurities removal in the framework. The spectra contain the peaks in the range of 1211-1219 cm⁻¹ and 455-462 cm⁻¹, which are ascribed to stretching and bending vibrations of TO₄ group (T= Si or Al) [17]. The weak band at 702 cm⁻¹ in K₂CO₃/zeolite spectrum is attributed to exchangeable cations in the framework [18]. The typical peak at 1450 cm⁻¹ is ascribed to C–O vibration that confirms the presence of CO₃²⁻ ions from K₂CO₃ [19].

Fig. 2 presents XRD pattern for K₂CO₃/zeolite. The characteristic peaks at 2θ = 31.48°, 31.98°, 32.23° and 39.71° correspond to K₂CO₃. The data show that K₂CO₃ was successfully impregnated on zeolite, producing a highly active solid acid catalyst.

Surfactant Preparation and Characterization

The used cooking oil after purification process showed 1.8% free fatty acid (FFA) tolerance in transesterification step. The transesterification reaction consists of the conversion of triglyceride contained in used cooking oil into methyl ester and glycerol as the final products using KOH catalyst. The reaction between KOH and methanol produced methoxide ion, which reacts reactively with carbonyl group in triglyceride then produced methyl ester and glycerol.

Table 1 lists product distribution of methyl ester obtained from transesterification of used cooking oil. According to GC-MS data, it was estimated as much as methyl myristate ($C_{15}H_{30}O_2$), methyl palmitoleate ($C_{17}H_{32}O_2$), methyl palmitate ($C_{17}H_{34}O_2$), methyl linoleate ($C_{19}H_{34}O_2$), methyl oleate ($C_{19}H_{36}O_2$), methyl stearate ($C_{19}H_{38}O_2$) and methyl arachidate ($C_{21}H_{42}O_2$). The transesterification reaction of used cooking oil effectively produced 46.8% of methyl oleate.

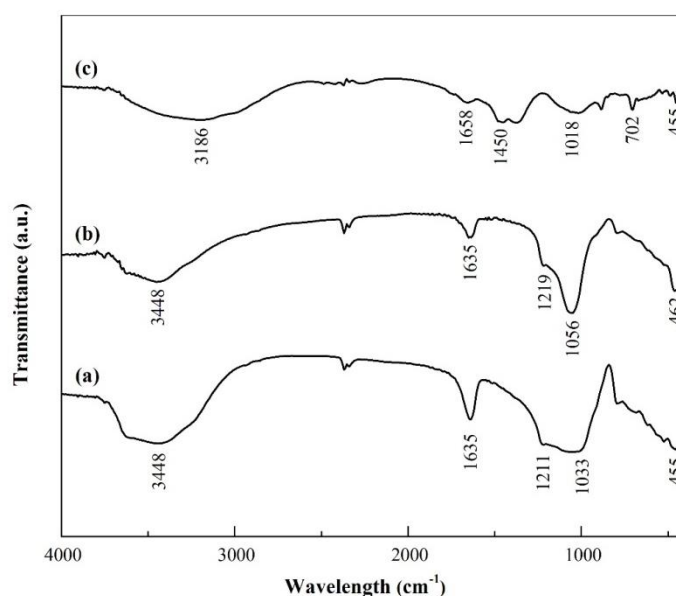


Figure 1. FTIR spectra of (a) natural zeolite, (b) activated zeolite and (c) K_2CO_3 /zeolite

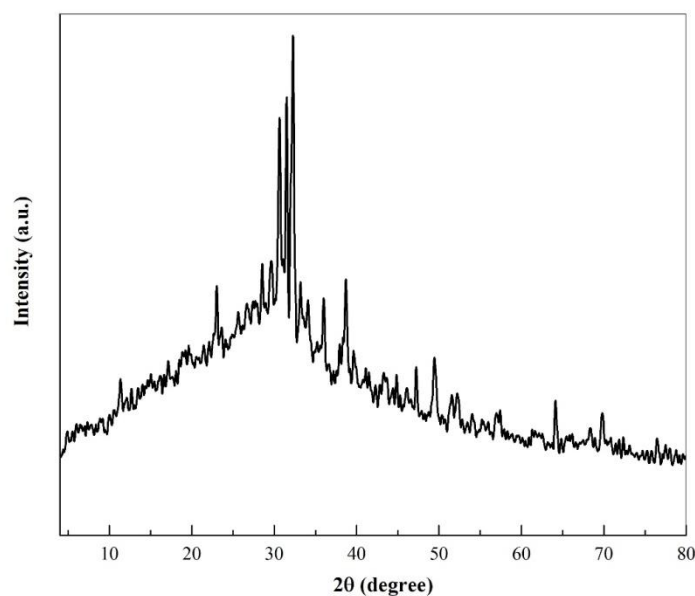


Figure 2. XRD pattern of K_2CO_3 /zeolite

Table 1. Product distribution of methyl ester obtained from transesterification of used cooking oil

Peak No	Retention time (min)	Compound	Content (%)
1	31.3	Methyl myristate	1.0
2	35.2	Methyl palmitoleate	0.3
3	35.7	Methyl palmitate	36.5
4	39.0	Methyl linoleate	9.9
5	39.2	Methyl oleate	46.8
6	39.6	Methyl stearate	5.2
7	43.2	Methyl arachidate	0.3

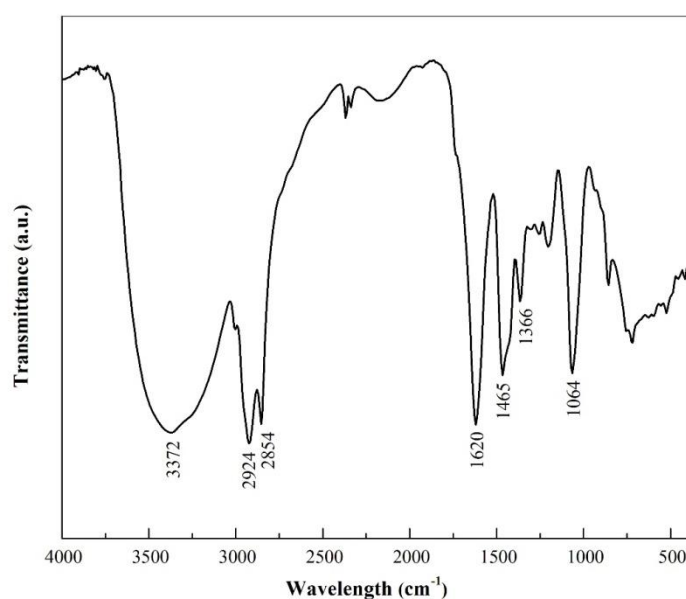


Figure 3. FTIR spectra of diethanolamide surfactant

The reaction between methyl ester obtained from transesterification and diethanolamine using K_2CO_3 /zeolite successfully produced diethanolamide surfactant with the yield of 92%. Fig. 3 shows the FTIR spectrum of non-ionic diethanolamide surfactant. The band at 3372 cm^{-1} is attributed to O–H vibration. The characteristic bands at 1620 and 1064 cm^{-1} result from amide groups of C=O and C–N vibrations, respectively. The typical two peaks appear at 2924 and 2854 cm^{-1} correspond to C–H vibrations in methyl ester from transesterification step. The bands at 1465 and 1366 cm^{-1} shows the functional groups of $-CH_2-$ and $-CH_3$, respectively [8][10].

The characterization of diethanolamide surfactant consists of foam stability, emulsion index and surface tension tests. Foam can possess reasonable stability only if it does not easily disappear and has uniform size. The stability of the foam can be determined by monitoring the changes in volume of foam until it completely disappears (Sharma). The effect of observation time to the foam stability is showed in Fig. 4. The result indicates that a relatively long observation time led to decrease the volume of foam.

Emulsion is a colloidal system in which two phases include immiscible or partially miscible [19, 20]. This characterization aims to analyze the effectiveness of diethanolamide surfactant as dispersing agents of two immiscible liquids. Fig. 5 presents the effect of observation time to emulsion index. Prolonged observation time led to decrease the emulsion index. According to the results, the addition of diethanolamide surfactant caused the formation of stable emulsion. This occurred due to the reduction of surface tension between two immiscible liquids.

The surface tension test of diethanolamide surfactant aims to determine the ability of surfactant to reduce surface tension. Surfactants can reduce the surface tension between two immiscible because its ability

to interact with oil and water phases [21]. Diethanolamide surfactant significantly reduced the surface tension of solution from 50.3 to 47.0 dyne/cm.

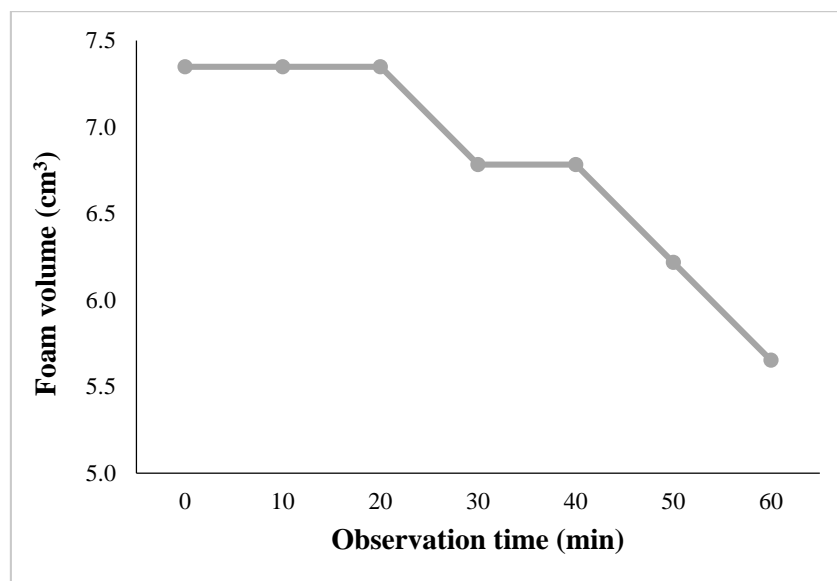


Figure 4. Graph of observation time vs foam volume

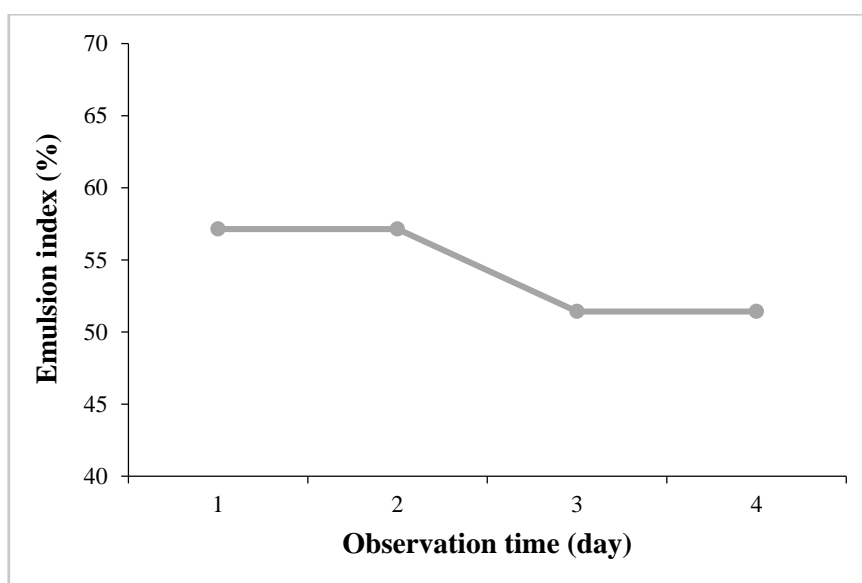


Figure 5. Graph of observation time vs emulsion index

Conclusions

The K_2CO_3 modified zeolite was successfully employed as a solid heterogenous catalyst in the production of diethanolamide surfactant from used cooking oil. The impregnation of K_2CO_3 on zeolite was believed to be an active site for amidiation reaction between diethanolamine and methyl ester. The surfactant characterization data revealed that diethanolamide surfactant led to the formation of stable foam and emulsion, also reduced the surface tension of solution.

Acknowledgements

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