



Synthesis of Triacetin Catalyzed by Activated Natural Zeolite Under Microwave Irradiation

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Abstract

Esterification of glycerol with acetic acid under microwave irradiation in the presence of activated natural zeolite was investigated. Natural zeolite was collected from Ujung Pancu (Aceh Besar) and chemically activated with hydrochloric acid. The reaction was carried out in a stirred glass flask reactor placed inside microwave oven. Experimental variables include microwave transmission time, molar ratio of glycerol to acetic acid, and catalyst loading. XRD profile of activated zeolite showed an increase of Si/Al ratio to 6.042 and the crystallinity decreased slightly by 12.23%, mainly due to dealumination during chemical treatment. Qualitative analysis by FTIR shows that the reaction product obtained by microwave heating contains ester group (triacetin) at wavelength 1706.669 cm^{-1} , while the quantitative analysis by acidi-alkalimetry titration indicates the highest glycerol conversion of 93.033% at the reaction condition of the molar ratio of 1:9, catalyst loading of 3%, and microwave transmission of 10 minutes. The present work suggests that microwave can be utilized as efficient heating technique in esterification of glycerol to triacetin.

INTRODUCTION

Glycerol is the main by-product of transesterification of triglycerides to biodiesel (Liao et al., 2010). Global production is expected to reach around 3.7 million tons of crude glycerol produced as a biodiesel by-product by 2020 (Katryniok et al., 2013). The rapid increase in biodiesel production has resulted in a large surplus of raw glycerol and a price decline. However, the use of glycerol has been limited due to toxic methanol and fatty acids contaminants (Yuan et al., 2010). To overcome excessive glycerol problem, it is highly recommended to convert glycerol to valuable chemical products, i.e. triacetin so that it can reduce environmental impacts and economic losses.

Triacetin ($\text{C}_9\text{H}_{14}\text{O}_6$) can be obtained through complete esterification of glycerol with acetic acid using an acid catalyst. Triacetin has great industrial applications. It can be used as an

aroma ingredient in sweets and soft drinks. Whereas for non-food applications, triacetin may function as a solvent in perfumes, co-polymers, and polymers, as well as fuel additives (Nuryoto et al., 2010). Biodiesel mixed with triacetin can reduce the emission of nitrogen oxide to an acceptable amount, making the transportation fuels will be more environmentally friendly and free of tetraethyl lead (TEL) and methyl tertiary butyl ether (MTBE) (Mufrodi et al., 2014).

Triacetin synthesis reaction commonly involves strong acid catalysts in the form of liquid phase, which may leads to difficulty in separation and purification of the product. For example, Windrianto & Satriadi (2012) observed a maximum conversion of 67.63% in homogeneous esterification using H_2SO_4 catalyst 5% (v/v) at a molar ratio of glycerol and acetic acid of 1:7, temperature of 120°C , and reaction time of one hour. The problems can be overcome by using solid

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catalysts. Several reports have been found dealing with solid catalysts. Luque et al. (2008) reacted acetic acid and glycerol in the presence of Starbon-400-SO₃H catalyst and obtained a glycerol conversion value of 99%. Sari et al. (2015) used modified natural zeolite and the reaction for 4 hours gave glycerol conversion of 90.02% at the ratio of glycerol and acetic acid of 1:7 and temperature 100°C. Meanwhile, Sun et al. (2016) achieved 99% selectivity towards triacetin at complete glycerol conversion for the reaction using Fe-SnTi(SO₄²⁻)-400. Wang et al. (2016) reported similar results from moderate conditions with polysulfone catalysts.

So far, no work is found using microwave in esterification of glycerol. Heat for reactions with conventional heating is usually supplied through a coil or jacket recirculation system. Since the heat flows across the heating media by convection and conduction, the reaction medium requires longer time to reach the set point and often experiences uneven distribution of heat. Recently alternative heating methods have been sought; one of them is microwave due to advantages to accelerate many chemical reactions (Marwan et al., 2015; Marwan & Indarti, 2016; Martín & Navarrete, 2018). Energy from the microwave is delivered directly to molecules that involve in a chemical reaction, so heat transfer will be much more effective and efficient than conventional heating (Lertsathapornsuk et al., 2004).

This study aims to investigate uses of microwave irradiation and local natural zeolite as alternative catalyst in esterification of glycerol with acetic acid. However, natural zeolite has weakness due to its impurities and poor crystallinity. Chemical treatment can be used to improve its characteristics (Udyani et al., 2014). The research will determine composition and crystallinity of the natural zeolite before and after activation, and investigate effect of catalyst loading, molar ratio of glycerol and acetic acid and microwave irradiation time to the conversion of glycerol towards triacetin.

EXPERIMENTAL

Chemicals used are natural zeolite from Ujung Pancu (Aceh Besar), glycerol (85% technical grade), acetic acid (glacial), hydrochloric acid (reagent grade), AgNO₃, phenolphthalein and sodium hydroxide, used as purchased without further purification. All chemicals were obtained

from Merck (Germany), except for acetic acid purchased from Bratachem (Indonesia).

The equipment used are 250 mL beaker glass, 250 mL erlenmeyer, glass funnel, 100 mL measuring cup, three neck flask, thermocouple, condenser, stirring hot plate (Thermo Scientific Cimarec Model SP88857107), microwave (Panasonic Model NN-ST 342M), muffle furnace (Nabertherm Model L5/11), oven (Gallenkamp), ball mill, and 200/325 mesh sieve. The analytical tools are X-ray diffraction or XRD (Shimadzu Model D6000) and Fourier transform infrared (FTIR) spectroscopy (Shimadzu Model 8400S). Diffractogram XRD is evaluated using the Match 3 App! Version 3.5.3.109 (Shimadzu) to identify and calculate the composition of SiO₂ and Al₂O₃.

The fixed variable in this study was size of the natural zeolite catalyst 200/324 mesh, volume of glycerol as much as 20 mL, initial temperature of glycerol and acetic acid 100°C, microwave power 520 watts (medium), and stirring speed 400 rpm. While the independent variables were molar ratio of glycerol and acetic acid 1:3, 1:6 and 1:9, ratio of catalyst amount and acetic acid volume 1, 3 and 5% (w/v) and microwave irradiation time 5, 10 and 15 minutes.

Chemical Treatment of Natural Zeolite

Natural zeolite was collected in a traditional mining area at Ujung Pancu (Aceh Besar). Natural zeolite was activated chemically and physically. Catalyst preparation began with refining the natural zeolite using a ball mill and screening with a 200/325 mesh sieve. The zeolite particles was soaked with distilled water for 24 hours and filtered. Natural zeolite was then dried in an oven at 120°C for 24 hours. Furthermore, natural zeolite was immersed in 3 N HCl and stirred at 110 rpm for 2 hours, filtered, and washed with distilled water to remove Cl⁻ ions completely. The loss of Cl⁻ ion was tested with 0.5 N AgNO₃ 0. Finally, natural zeolite was activated physically by heating treatment in a furnace at 400°C for 4 hours and the activated natural zeolite (ZA) was stored in a closed plastic container.

Triacetin Synthesis

Experiment was started by heating glycerol and glacial acetic acid using a stirring hot plate separately to 100°C. Variation of the molar ratio of glycerol to acetic acid was 1:3, 1:6 and 1:9, so that

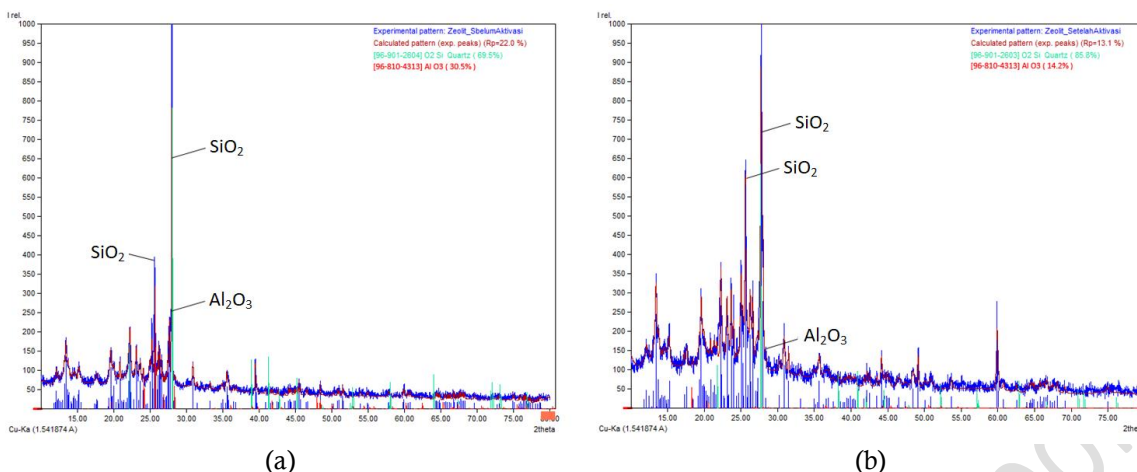


Figure 1. XRD profiles of ZA catalysts before activation (a) and after activation (b)

for glycerol which was filled into the reaction flask by 20 mL, the volume of acetic acid used was 43.2 mL, 86.4 mL and 129.6 mL.

After each reactant reached temperature of 100°C, they were poured into the reaction flask which was then placed inside microwave oven. The reactor system consisted of microwave, triple neck flask (for reaction solution), condenser, thermocouple, and magnetic stirrer. Then the ZA catalyst was loaded into the reaction flask by 1%, 3% or 5% of the volume of acetic acid. The microwave was turned on and set irradiation time for 5, 10 or 15 minutes, and its stirrer was switched on at 400 rpm. After reaction proceeded for the required time, the reaction flask was removed and the reaction solution was filtered to separate the catalyst and a reaction sample containing triacetin was obtained.

Characterization of Catalyst and Reaction Products

Several analyzes were carried out to characterize catalysts and reaction products. The first analysis was to calculate the value of Si/Al ratio and crystallinity of natural zeolite and ZA catalyst by interpreting the XRD diffractogram using the Match 3! Application. Furthermore, identification of the presence of acetin products was performed by analyzing FTIR spectra. Glycerol conversion (X) was determined by the FBI A01-03 method, namely acidi-alkalimetry titration with 2N NaOH based on the residual value of acetic acid, and then calculated by using Eq. (1).

$$X = \frac{M_o - M_t}{M_o} \quad (1)$$

where M_o is mole of glycerol at the beginning of the reaction and M_t is mole of glycerol after a given reaction time.

RESULTS AND DISCUSSIONS

Characterization of Natural Zeolite (ZA) Catalyst

The success of chemical activation of natural zeolite can be studied by comparing XRD of natural zeolite (ZA) samples before and after activation. XRD profile can identify the content and crystallinity of ZA catalysts that may affect its performance in the esterification. Figure 1 shows that in general there was no change in the main components of zeolite, namely SiO_2 and Al_2O_3 which were identified in each zeolite before and after activation. The diffractogram of the ZA sample before activation (Figure 1a) shows main peaks at 27.98° and 25.62° for SiO_2 and 27.64° for Al_2O_3 . While the ZA sample after the activation process (Figure 1b) produces a diffractogram with the main peaks at 27.77° and 25.63° for SiO_2 and 28.00° for Al_2O_3 . Lestari et al. (2010) states that Si and Al are the main constituents of ZA whose composition depends on their origin and generally natural zeolites found in Indonesia contain mostly mordenite and clinoptilolite types.

Table 1 shows an alteration in the composition of SiO_2 and Al_2O_3 with the activation treatment of ZA. Composition of SiO_2 in ZA increased from 69.5% to 85.8% with the rest being Al_2O_3 . It corresponds to an increase in SiO_2 composition by 16.3%. The Si/Al ratio calculated based on the composition of SiO_2 and Al_2O_3 before and after activation was 2.278 and 6.042, respectively. This ratio is greater than expected 5.00

Table 1. The main peak intensity of components in ZA catalysts and its composition

Component	ZA before activation			ZA after activation		
	2 θ (%)	Intensity	Composition (%)	2 θ (%)	Intensity	Composition (%)
SiO ₂	27.98	1000	69.5	27.77	1000	85.8
	25.62	252.89		25.63	647.50	
Al ₂ O ₃	27.64	398.5	30.5	28.00	159.69	14.2

so that this ZA catalyst can have fairly stable acidity (Lestari, 2010). An increase in Si/Al ratio by 3.764 makes this activated zeolite has potential to be a good catalyst because many active sites have been formed resulting from the dealumination process (Kurniasari et al., 2011).

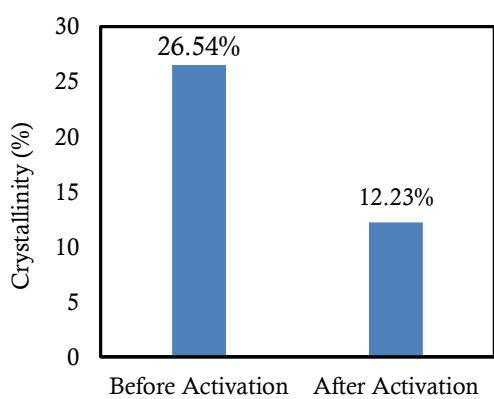


Figure 2. Crystallinity of ZA catalysts before and after activation.

Crystallinity of ZA catalysts as shown in Figure 2 is calculated based on the value of 2 θ and the intensity value (I) used in the equation in Darmansyah et al. (2013). The crystallinity of ZA

before activation was 26.54% and after activation it changed to 12.23% which showed a decrease in crystallinity by 14.31%. It indicates that SiO₂ crystal structure was slightly decreased and the porous sizes become wider. This decrease was due to chemical activation or dealumination process by concentrated hydrochloric acid (Ertan & Ozkan, 2005).

Characterization of Triacetin in Reaction Solution

FTIR analysis of reaction products aims to recognize the functional groups presence in the samples from experiments with a molar ratio of glycerol and acetic acid of 1:3, catalyst loading of 3% and irradiation time of 10 minutes. Figure 3 shows FTIR profiles of a reaction solution for the esterification with microwave heating method and a sample for pure glycerol, and identification for the functional groups based on the ATR-FTIR Database.

FTIR spectra of a triacetin sample having functional group C₉H₁₄O₆ belong to an ester group with wave numbers of 1700-1750 cm⁻¹ (Vogel, 1989). Figure 3 suggests that FTIR profile of the

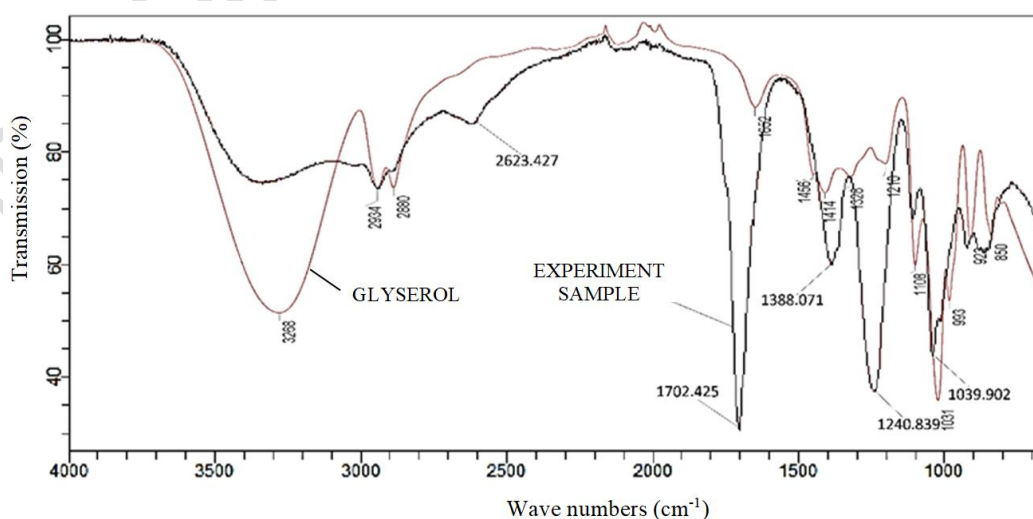


Figure 3. FTIR spectra of the reaction solution and pure glycerol

Table 2. FTIR spectra of reaction solution and identification of bonding types based on the ATR-FTIR Database

Bonding type	Wave numbers (cm ⁻¹)	
	ATR-FTIR Database	Reaction solution
C – O (Alcohol)	1050-1300	1039.9
C – O (Alcohol)	1050-1300	1240.8
C – H (Alkane)	1340-1470	1388.1
C = O (Ester)	1690-1760	1702.4
O – H (Carboxylic Acid)	2500-2700	2623.4

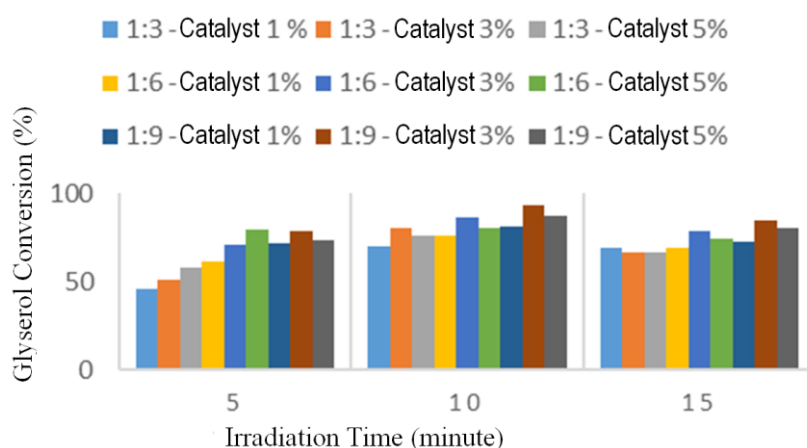


Figure 4. Effect of microwave irradiation time on glycerol conversion

reaction solution in this study indicates the presence of an ester group at a wavelength of 1690 - 1760 cm⁻¹, precisely a peak at 1702.4 cm⁻¹. Table 2 shows the FTIR spectra interpretation of the existence of bond groups in the reaction sample containing acetin resulting from esterification of glycerol with acetic acid assisted by the ZA catalysts and microwave heating methods. While the glycerol spectra in Figure 3 do not show the existence of an ester group so it can be concluded that in the reaction sample there is certainly triacetin (ester group).

Glycerol Conversion to Triacetin

Glycerol content was evaluated by acid-alkalimetry titration according to FBI A02-03 Standard Method. Figure 4 shows the effect of microwave irradiation time on glycerol conversion with catalyst loadings of 1, 3 and 5% and molar ratio of glycerol to acetic acid of 1:3, 1:6 and 1:9. The highest glycerol conversion reached 93.03% which was obtained in the reaction with the molar ratio of 1:9, irradiation time of 10 minutes and a catalyst loading of 3%. This conversion was assessed to be quite high compared to the results of Sari et al. (2015) who used activated natural zeolite as catalyst with the molar ratio of 1: 7 to give a conversion of 90.04%. Use of 3% catalyst loading

gave the highest conversion value, which indicates excessive catalyst may not necessarily increase product yield (Mufrodi et al., 2014). Furthermore, there is a tendency for glycerol conversion at the irradiation time of 15 minutes always decreasing possibly because of the esterification reaction being a reversible reaction. Instability of the microwave temperature which causes the steric (unstable molecule) effect in the reaction process can also reduce the rate of ester formation so that the ester yield becomes reduced (Fessenden & Fessenden, 1986).

CONCLUSION

Esterification of glycerol using activated zeolite (ZA) catalyst and microwave heating proved to be able to produce acetin ester compounds, one of which is triacetin. Activated ZA is suitable for the esterification catalyst because of highly ratio of Si/Al, reaching 6.042. The reaction product shows the effective conversion of glycerol to acetin ester with a conversion attaining 93.03% for the reaction conditions of molar ratio of 1:9, ZA loading of 3% and irradiation time of 10 minutes. This study shows the esterification of glycerol to triacetin can effectively utilize microwave heating which has been revealed to accelerate reaction significantly in

a number of organic syntheses. Further research needs to be developed to achieve both complete conversion of glycerol and high selectivity towards triacetin as the desired final product.

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