



Research Article

# Production of Triacetin by Microwave Assisted Esterification of Glycerol Using Activated Natural Zeolite

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## Abstract

Triacetin, an alternative biodiesel additive, was prepared by esterification of glycerol with acetic acid in the presence of chemically activated natural zeolite. The esterification was carried out in a small reaction flask under microwave irradiation. The catalyst was characterized for its morphology by SEM and its chemical composition by X-ray Diffraction (XRD). The Scanning Electron Microscopy (SEM) micrograph indicates improved surface area of the zeolite, while the XRD analysis shows an increase in Si/Al ratio from natural zeolite to 6.042 and its crystallinity value of 12.23%. The Fourier Transform Infra Red (FTIR) analysis obtained showed that microwave-heated samples have an esters group spectrum of triacetin at 1702 cm<sup>-1</sup>. The conversion value of glycerol was more than 95% at molar ratio of the reactants 1:9 and catalyst loading of 3%. The selectivities for monoacetin, diacetin, and triacetin were 80.1%, 15.4%, and 4.5% at 60 minutes, and 43.0%, 48.6%, and 8.3% at 90 minutes. It shows that the conversion took place in consecutive steps and the use of microwave allows the reaction proceeding at milder condition. Copyright © 2019 BCREC Group. All rights reserved

**Keywords:** Triacetin; Glycerol; Biodiesel Additive; Zeolite; Microwave

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## 1. Introduction

Microwave has emerged as new tool to accelerate many chemical synthesis including catalytic or complex heterogeneous reactions [1,2]. Microwave interacts directly with the molecules that exist in the reaction mixture and it provides an evenly disseminated energy to the reac-

tion, leading to an instantaneous heating process. Moreover, microwave effect may be not purely thermal since the selective absorption of microwave energy by polar molecules occurs, yielding alterations to the orientation of the molecular collisions, to the thermodynamic properties of the reaction systems, and to the activation energy [3]. As the results, the microwave assisted reaction also offers simple, clean, economic, efficient, and more environmentally friendly technique [4,5].

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Improved reaction rates have been reported in many publications, including in our previous works. Marwan [6] has shown the benefit of microwave in one step preparation of biodiesel directly from microalgae biomass. Microwave assisted transesterification of lipid from microalgae took place at fast rate, reaching an equilibrium conversion of more than 94% within 6-10 min. In this case, microwave irradiation also contributed to more effective destruction of the cells, thus helping fast release of oil prior to the reaction. Later, Marwan and Indarti [7] found microwave assisted transesterification of palm oil using hydrated calcined seashell as solid catalyst proceeded to completion in a very short time with a maximum yield of 96.0% at much milder conditions than in the conventional reactor. The commonly low reactivity of such solid catalysts was enhanced by the effects of microwaves at an intermolecular level.

In the present work, we offer a new approach in esterification of glycerol towards triacetin using microwave irradiation. The reaction involved acetic acid and a chemically activated natural zeolite. Triacetin is an alternative additive that could be used to improve cold and viscosity properties of biodiesel. Esterification of glycerol with acetic acid is reported using several solid catalysts, however the triacetin selectivity was rather low [8,9]. So far, no report is found on esterification of triacetin involving microwave as source of heating.

## 2. Materials and Methods

### 2.1 Materials

The catalyst precursor was natural zeolite which was traditionally mined from Ujung Pancu, Aceh Besar (Indonesia). Glycerol of technical grade (85%) was obtained from Bratachem (Indonesia). Acetic acid (glacial) 100%, hydrochloric acid 37%, and sodium hy-

droxide of reagent grade were obtained from Merck (Germany). All chemicals were used without further purification.

### 2.2 Catalyst Synthesis

Natural zeolite was crushed in a ball mill and followed by sieving to obtain particle size of 200/325 mesh. The zeolite particle was dipped in distilled water for 24 hours and then was filtered to remove water. Wet zeolite was dried in an oven at 120 °C overnight. Zeolite was mixed into 3 N hydrochloric acid solution and stirred at 110 rpm for 2 hours. Later, the solids were filtered to separate the solution and washed with distilled water to remove the remaining chloride ion. Finally, the zeolite was calcined at 400 °C for 4 hours in a furnace. The activated natural zeolite was then cooled and stored in sealed plastic bags prior to its use for the experiments and the characterization. The catalyst was characterized for its surface morphology by Scanning Electron Microscope (SEM) and its crystal profile by X-ray Diffraction (XRD) apparatus with software Match! 3 (Version 3.5.3.109) to identify mineral species.

### 2.3 Esterification of Glycerol

The esterification was carried out in a 250 ml flask, placed inside a household oven type microwave (Model NN-ST 342M, Panasonic) operating at frequency 2.45 GHz with maximum output 800 W. Figure 1 shows arrangement of the experimental equipment. Preparation of the reaction was initiated by heating glycerol and acetic acid separately in hot plate to temperature of 90 °C. Both reactants were mixed in a reaction flask. Molar ratio of glycerol and acetic acid was adjusted to 1:9 based on 20 mL glycerol. The activated zeolite catalyst was loaded into the reaction solution as much as 3% (w/v) of acetic acid. The reaction flask was transferred to the microwave chamber. The mixture was continuously stirred using a magnetic stirrer at 400 rpm. The reaction was started by switching on the microwave at low-micropower setting. The reaction was run for 60 and 90 minutes with intermittent operation. After the reaction was stopped, the mixture was cooled down to room temperature and the solid catalyst was removed. The liquid phase was then transferred to sampling bottle and stored for further analysis. Chemical composition of the sample was determined by Fourier Transformed Infra-red (FTIR) Analyzer and Gas Chromatography-Mass Spectroscopy (GC-MS).

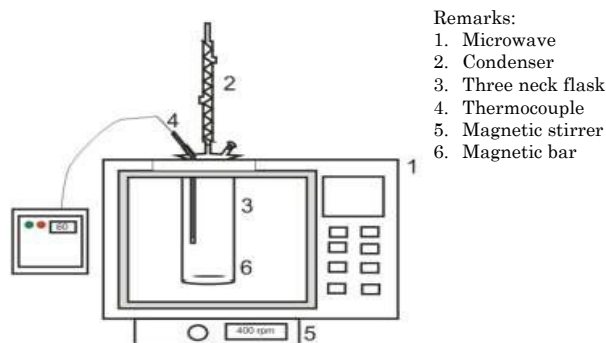


Figure 1. The schematic diagram of experimental equipment.

### 3. Results and Discussion

#### 3.1 Surface Morphology

Effect of treating the natural zeolite with hydrochloric acid can be observed from its morphological change. SEM image shown in Figure 2 indicates similar particle sizes of the natural zeolite prior to and upon the activation treatment. However, surface of the treated zeolite became rough due to surface opening and increasing porosity. Kongnoo [10] and Chen [11] reported that during the acid treatment, leaching of  $\text{Al}_2\text{O}_3$  and organic species of natural zeolite into the acid solution and then the solution evaporated and the organics were oxidized during calcination making the treated zeolite surface more porous.

#### 3.2 XRD Analysis

XRD pattern of the untreated natural zeolite and the activated natural zeolite is shown in Figure 3. Although no shift in the position of main peaks of the natural zeolite and the activated one were observed, significantly increased in the intensity of the  $\text{SiO}_2$  main peak of the activated natural zeolite can be found. In the other hand, the  $\text{Al}_2\text{O}_3$  main peak decreased. This suggests, as a result of acid treatment, dealumination taking place led to the destruction of the zeolite framework forming an amorphous aluminosilicate structure [12]. Attack of  $\text{H}^+$  ions on the zeolite caused hydrolysis of some of the O-Al-O bonds, the tetrahedrally coordinated Al is depleted from the framework sites, while hydroxyl groups were attached around the aluminum vacancies [13]. Moreover, inhomogeneous elimination of Al led to formation of a non-crystalline silicon enriched layers in the zeolite crystals [12]. The later fact was revealed in this work as crystallinity of the natural zeo-

lite was decreased from 26.54% to 12.23%. The crystallinity was determined from Cullity's equation [14].

Si/Al atomic ratio of the activated natural zeolite was 6.042, which is higher than one of the untreated natural zeolite due to dealumination power of the acid treatment. As the result, the activated natural zeolite became more acidic. According to Chen [11], the zeta potential of hydrochloric acid treated stellerite decreased with the increase of acid concentration due to part of cations substituted by  $\text{H}^+$  ions. Hence, the adsorptivities for the adsorption of reacting species may be improved. Testa [15] also suggests that medium acidic sites as found in silica based catalysts are preferred to give good selectivity to triacetin.

#### 3.3 Glycerol Conversion

Esterification of glycerol under microwave irradiation was run at 60 and 90 minutes. The progress of reaction was evaluated regarding

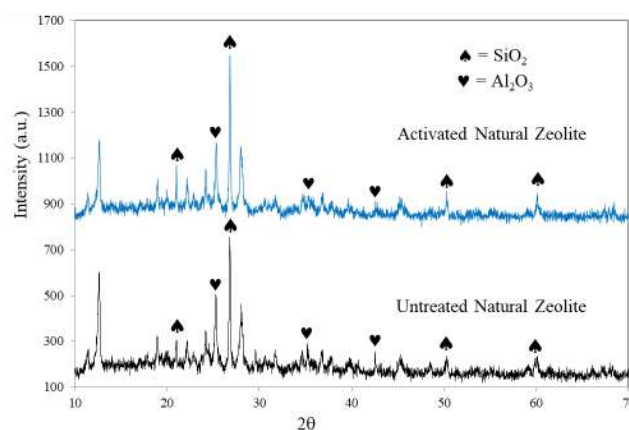


Figure 3. XRD profiles of untreated natural zeolite and activated natural zeolite

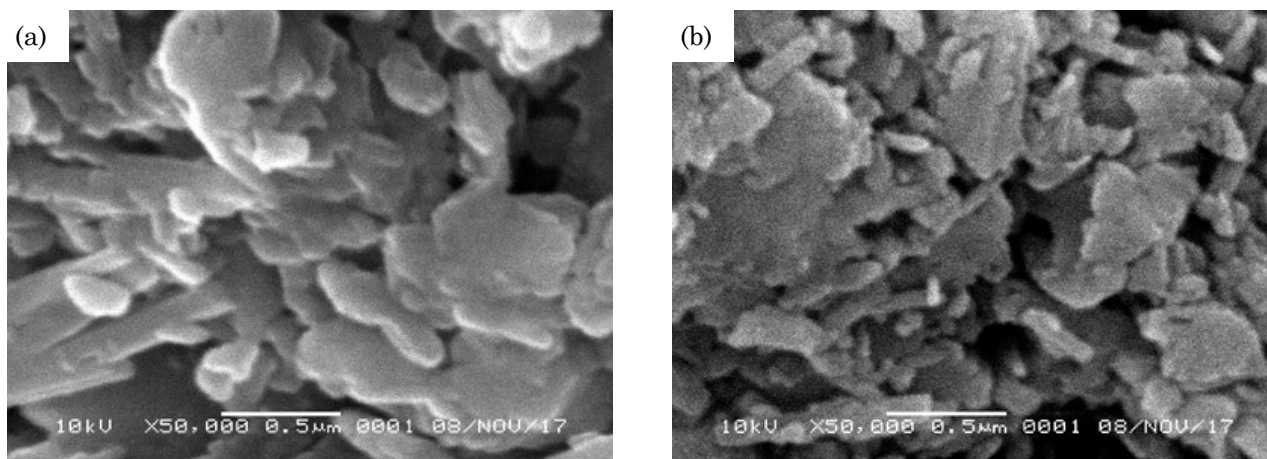
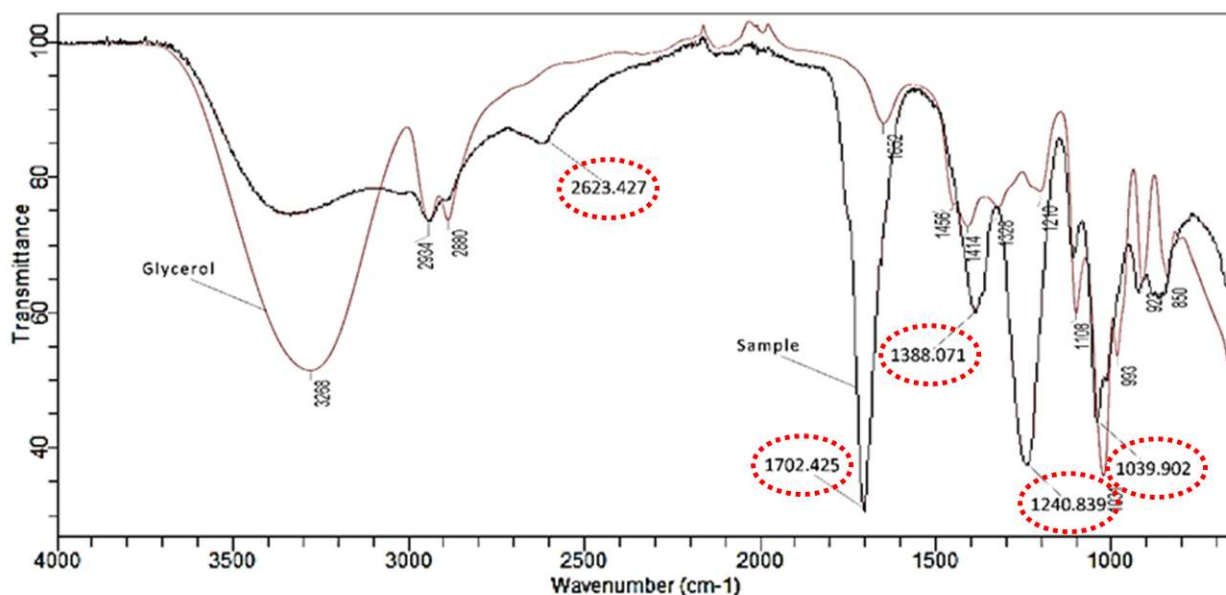


Figure 2. SEM images of untreated natural zeolite (a) and activated natural zeolite (b)

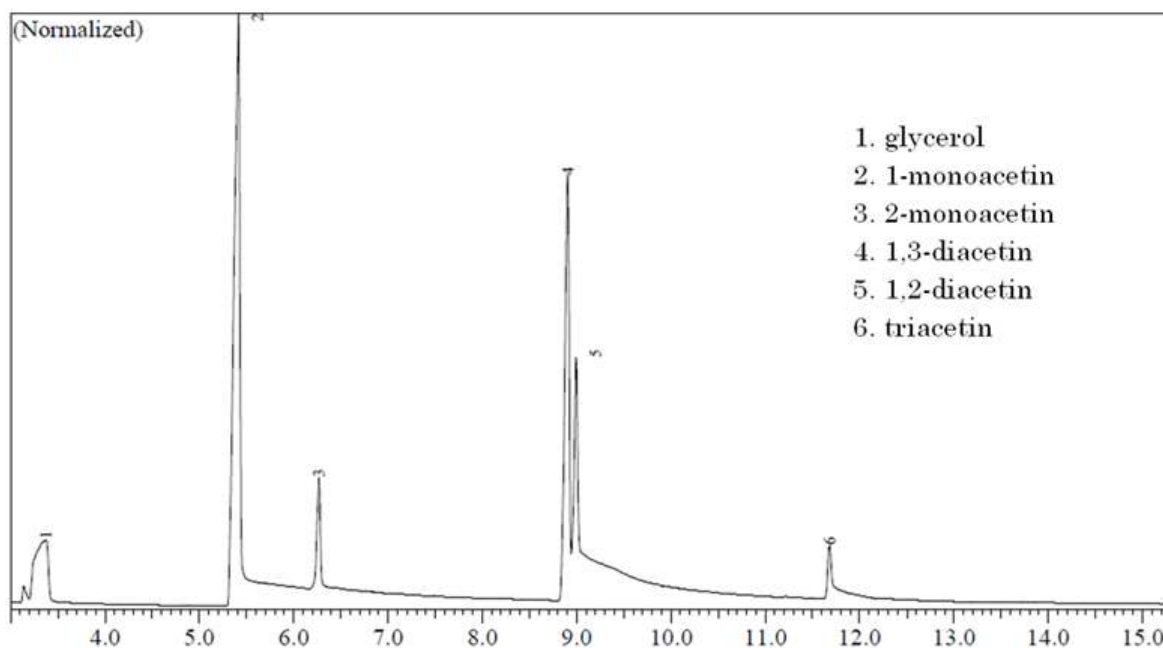
with glycerol conversion and triacetin selectivity. In the initial stage of experiment, FTIR analysis was carried out to identify the presence of ester groups upon the reaction. Figure 4 shows a significant difference of FTIR functional groups presence in a reaction sample and pure glycerol suggesting glycerol conversion under microwave irradiation. O-H stretch of glycerol at 3100-3400  $\text{cm}^{-1}$  decreased significantly compared with the case of triacetin since glycerol loss its hydroxyl group during the reaction to form water. On the other hand, a major peak at 1702.4  $\text{cm}^{-1}$  represents a C=O stretch of

the ester molecules [16]. Then, the peak at 1240.8  $\text{cm}^{-1}$  indicates a C-C(O)-C stretch of ester of acetates group, further verifying the existence of triacetin in the product.

The conversion values of glycerol reached more than 95% at molar ratio of the reactants 1:9 and catalyst loading of 3% for the reaction times 60 and 90 minutes. High conversion of glycerol suggests that the microwave irradiation was able to facilitate conversion close to 100% in around one hour which is not much different with those in conventional approaches, but the later often requires temperature



**Figure 4.** FTIR spectra of a reaction sample and glycerol



**Figure 5.** GC-MS spectra of reaction products

higher than 90 °C and even with pressure above atmospheric. Testa [15] reports a conversion of 100% in one hour using sulfonic amorphous and mesoporous silicas as solid catalysts using temperature of 105 °C. Kale [17] also found the same conversion in one hour reaction with Amberlyst type catalyst.

The reaction selectivity was determined from GC profile as given in Figure 5. The selectivity towards monoacetin, diacetin, and triacetin was 80.1%, 15.4%, and 4.5% at 60 minutes, and 43.0%, 48.6%, and 8.3% at 90 minutes, respectively. It suggests that a fast conversion of glycerol to monoacetin taking place during first one hour, and followed by further conversion of monoacetin to diacetin. Later, diacetin was esterified to triacetin. This trend represents the typical consecutive reaction. However, the formation of triacetin seems very slow even after 90 minutes only selectivity of 8.3% reached.

The Si/Al ratio of the catalyst was improved upon the acid treatment. Silva [18] observed at high Si/Al ratio of zeolite catalyst, its pore environment becomes hydrophobic and minimizes the adsorption of water on the active sites. Water released during the glycerol esterification is not desirable since it may stimulate the reverse reaction. In this work, further consecutive step to form the triacetin was facilitated with the activated natural zeolite.

Similar profile of the esterification progress was also reported by Testa [15] and Kale [17], who observed selectivity to triacetin of 11% and 7%, respectively, at 60 minutes of the reaction. Low rate of triacetin formation is possibly due to water of glycerol solution and water formed as by-product of the reaction that might shift the equilibrium towards the reactants or deactivate of the catalytic sites. In addition, Testa [15] also found that the spacing between the acidic groups inside catalyst pores is possibly not enough to allow the formation of the bulky acetin.

In the present work, microwave generates a thermal effect since the microwave energy can be directly adsorbed by the reacting species and the superheating induced by molecular vibration and rotation can further promote the reaction [2,3,19]. Such thermal effect could contribute to enhancing an endothermic reaction. Liao [20] suggests that esterification of glycerol with acetic acid is an endothermic process, demanding high energy for the introduction of the third acetyl group to produce triacetin as the desired product.

#### 4. Conclusions

Triacetin was successfully prepared under microwave irradiation in the presence of activated natural zeolite. The overall reaction follows three consecutive steps. Although the glycerol conversion reached more than 95% after 90 minutes of the reaction, the selectivity towards the desired product was only 8.3%. Longer reaction time is required and water presence need to be dealt to allow a complete selectivity to triacetin. At least, the process at such milder condition was shown to be potential for further development.

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