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Research Article

Non-Catalytic and γ-Al_2O_3 Catalyst-based Degradation of Glycerol by Sonication Method

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Abstract

This research aims to study the effect of the addition of the catalyst γ-Al_2O_3 on the degradation of glycerol with using sonication method. This degradation reaction performed with the aid of a catalyst γ-Al_2O_3 or without a catalyst. Reactants were prepared from glycerol-water mixture with a mass ratio of 1:8. Experiment was carried out in a batch reactor at atmospheric pressure, temperature range between 30-70 °C for 10-90 min. The products, which were degraded from glycerol, were analyzed by gas chromatography (GC). The results showed that the ultrasonic wave radiation could degrade glycerol. The glycerol conversion was 2.92%-59.95% without employing catalyst, while the conversion of glycerol increased with adding γ-Al_2O_3.catalyst. It was found that methanol, allyl alcohol and acrolein were degradation products.

Keywords: Glycerol; degradation; sonication; γ-Al_2O_3; methanol

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1. Introduction

Indonesia is developing a renewable energy based vegetable oils include the development of biodiesel. The transesterification process is the established method to prepare biodiesel by reacting vegetable oils and ethanol / methanol and produce primary products such as methyl ester and byproducts / waste in the form of glycerol.

The one kilogram of biodiesel yielded about 125 grams of glycerol waste. Currently, the rate of biodiesel production in Indonesia has reached 4 million Kl / year [1]; it is equal to around 500,000 tonnes glycerol per year. If the production of biodiesel is intensified to replace diesel fuel, the glycerol will be more abundant. The utilization of glycerol can be increased further through the purification process, or glycerol degradation into other valuable chemicals. While, the use of pure glycerol was not much so that the process of degradation becomes very important to be developed. Even though its complex molecular structure, glycerol is possible to break carbon bonds into other chemical products.

Glycerol substance is colorless, odorless and dissolved in water. In the food and beverages industries, glycerol acts as a humectant material (hydroskopic compound), solvent, sweetener, preservatives, thickening (viscous fluid)

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and sugar substitutes. Glycerol can also be used as anti-freeze compounds for plants. Glycerol, as commercial product, has another name: glycerin or commonly referred to as sugar alcohols. That compound has three hydrophilic alcoholic hydroxyl groups, which greatly affect the solubility of water (hygroscopic).

Various studies have been conducted in connection with the transformation of glycerol, such as steam reforming [2,3], hydrothermal [4,5], catalytic hydrogenation [6], the catalytic dehydration [7], pyrolysis [4,8], hydrogenolysis [9,10]. Those previous investigations produced both liquid compounds (methanol, formaldehyde, acetaldehyde and others) and gas compounds (CO_2, butane, hydrogen and others).

The sonication process has been widely used for the process of degradation of other chemicals, such as: ultrasonics synthesis of 5-(Pyrazol-4-yl)-4.5-Dihydropyrazoles [11], Methyl Violet [12], Carbon tetrachloride [13]. One of the advantages of the ultrasonic process is to speed up the reaction process [14,15]. In the sonication process occurs an acoustic cavitation that can generate free radicals and molecules in a liquid medium such as OH and H radicals accumulated on the surface of the cavitation bubbles, which can lead to the formation of degradation products and trigger radical chain reaction [16-18].

The catalyst employed in the degradation process accelerates the chemical reaction. The catalyst used as follows: Cu/SiO_2, Cu/MgO, Al_2O_3, HZSM, γ-Al_2O_3, $CuSO_4$, H_3PO_4 [19-25]. However, these processes still require operating conditions at high temperature and pressure thus requiring a high operating cost.

There is an alternative process to degrade glycerol that is degradable by using ultrasonic waves, known as sonication process. The sonication process can be operated at lower temperatures and be performed without catalysts. In this study, degradation of glycerol with and without catalyst was investigated. This research aims to study the degradation reactions of glycerol both with and without catalyst in the method of sonication.

2. Materials and Method

2.1. Material

Glycerol used in this work, was obtained from BRATACO Chemical Co. Ltd. with a purity of 91% (w/w) and the γ-Al_2O_3 catalyst was purchased from MERCK and the pure water was used as solvent.

2.2. Apparatus

The experiment of glycerol degradation with and without catalyst was carried out by using a batch reactor made of 316 stainless steel 400 ml volume equipped with an ultrasonic wave generator (High Intensity Ultrasonic Processor VCX 500 Sonics and Materials Inc. USA 500 W, 20 kHz). The probe sonicator tip has a diameter

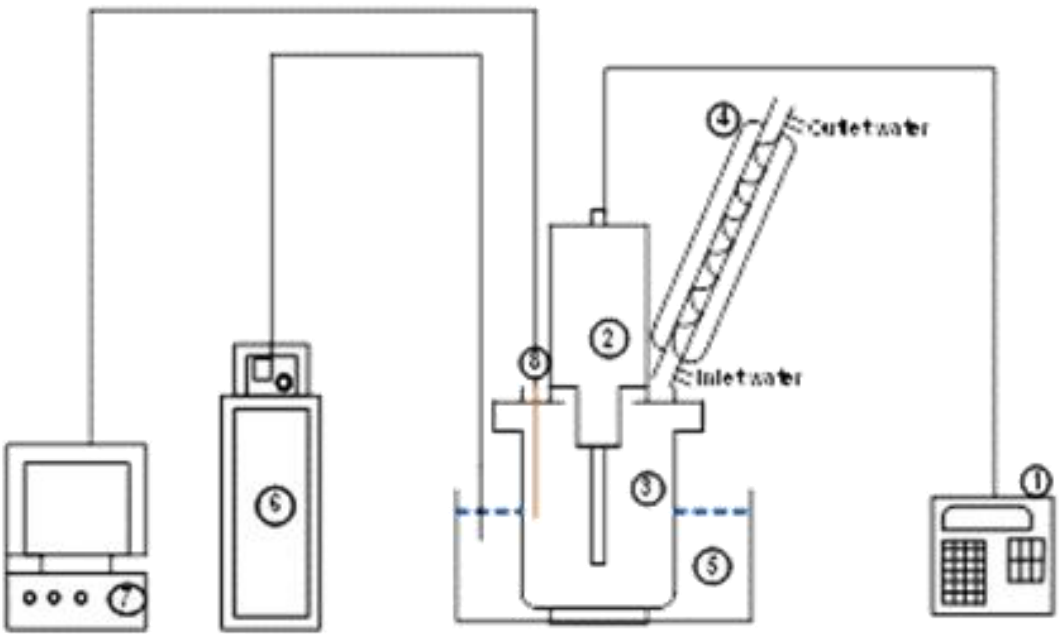

Figure 1. Experimental apparatus. Descriptions: (1). Ultrasonic Power; (2). Sonicator Probe; (3). Reactor; (4). Condensor; (5). Water bath; (6). Chiller; (7). Data Recorder; (8). Thermocouple

of 1.3 cm, part number 630-0219, 5.5 micrometers in length. The temperature inside the reactor was measured using a type K thermocouple, size 1/16 in (As One, Korea) and recorded using the Data Taker. To minimize loss of solution due to evaporation, the reactor was equipped with a reflux condenser. Figure 1 shows a schematic diagram of the equipment used in this work.

2.3. Experimental Procedure

Before being employed, the γ-Al_2O_3 catalyst was activated through calcination at temperature of 550 ˚C for 5 h then analyzed by XRD. The analysis performed was to identify the crystalline phases in the material. Peak pattern as shown in Figure 2 describes the relative intensity of the crystal contained in the inside catalyst. Table 1 is the data of angles appearing of catalyst and compared to those of standard. The angles of peaks of catalyst (γ-Al_2O_3) after calcination were relatively similar to those of JCPDS standard. The catalyst, which has been prepared, showed the clear peaks in XRD pattern at 37.19°, 38.90°, 43.57° and 45.51°. Those values were close to JCPDS standard, 37.60°, 39.49°, 45.79° and 48.93°. It was indicative that the γ-Al_2O_3 catalyst has been successful activated performing a calcination.

The physical properties of the catalyst, the surface area and pore diameter, were also characterized using BET method. The BET analysis found that activated catalyst has a surface area of 123.004 m²/g with a pore diameter of 6.072 nm. The surface area on the catalyst was high category (100-500 m²/g) and the pore diameter was ranged from 2-10 nm, which was mesoporous (medium). Degradation was carried out by inserting glycerol-water mixture into reactor with a mass ratio of 1:8. The three percent catalyst of glycerol (w/w) was added into solution, and the sonication equipment was run. Figure 1 shows the equipment design used in this work. The degradation process was started when the sound wave was generated. The process stopped when time attained as previously set. Operating conditions were atmospheric pressure and glycerol-water mass ratio was 1:8. Research variables were as follows: the temperatures of sonication were 30,

Table 1. The data of angles appearing of catalyst and compared to those of standard.

Position [2θ]	γ-Al_2O_3 (JCPDS standard)
37.19	37.60
38.90	39.49
43.57	45.79
45.51	48.93

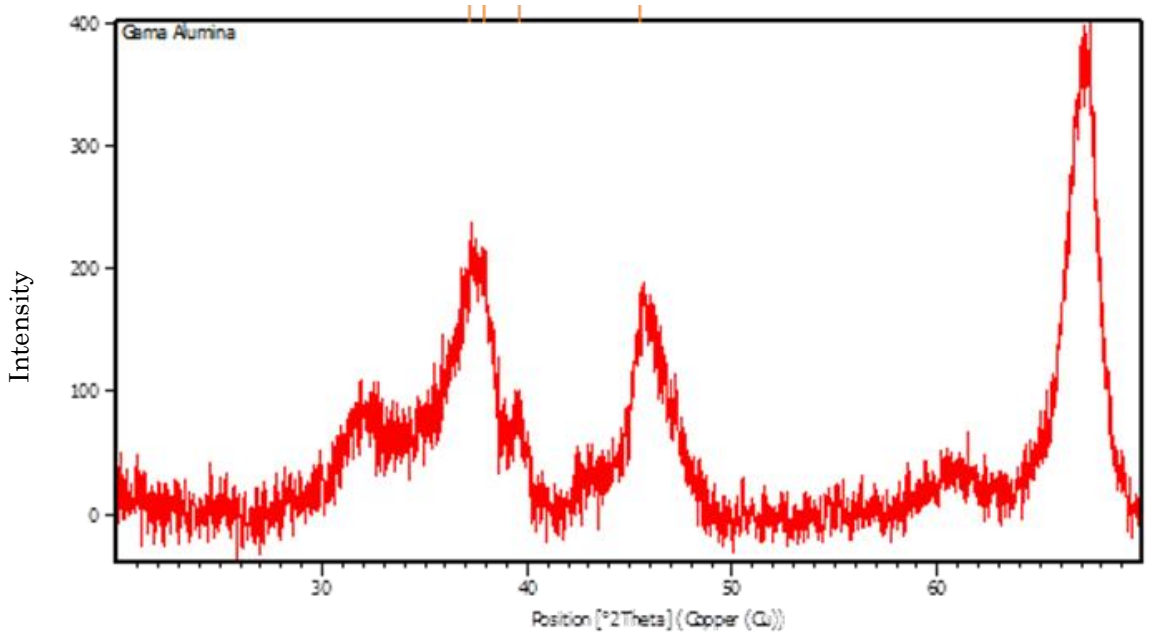

Figure 2. The results of XRD analysis of γ-Al_2O_3 catalyst

40, 50, 60 and 70 °C, sonication times were 10, 30, 50, 70 and 90 min for catalyst treatment and those were compared to without catalyst.

Products obtained were analyzed using GC with Agilent column type 19091Z-213, with operating conditions were as follows: maximum column temperature 325°C, the maximum oven temperature of 325 °C, a temperature of 300 °C front detector, FID detector type (front) and TCD (rear), feed rate of 1.6 ml/min, an air flow of 300 ml / min, the hydrogen rate of 30 ml/min, the carrier gas is helium, the run time of 7.5 minutes.

3. Results and Discussion

3.1. The effect of sonication time against glycerol conversion with and without catalyst

The influence of sonication time on the conversion of glycerol with- and without using the catalysts is shown in Figure 3. In figure shows that for the process without catalyst, the conversion of glycerol increased as sonication time inclined. The significant improvement of conversion was occurred at the range 10 to 90 min.

The increase in conversion was due to the effect of ultrasonic wave intensity. The longer period of sonication occurred, the longer process of cavitation took place. The cavitation influence on the physical and chemical conditions, was quite extreme in the mixture. The reactants destruction was caused by the bursting of sound waves during cavitation, which reduced the concentration of glycerol and then increased the conversion until a certain time [26]. It was found that sonication time is very influential on the cavitation, so that conversion significantly increased as previously reported [4,20,27].

By adding γ-Al_2O_3 catalyst, the conversion of glycerol increased until 70 min, and then stabilized until 90 min.

3.2 The effect of sonication time against temperature

In general, the reaction conversion increases as the temperature adds. In the sonication process, temperature rose caused by the effect of ultrasonic wave emission as displayed in Figures 4 and 5. Figure 4 shows the effect of sonication time versus temperature initiated at 30 °C. Temperature increase (40-46 °C) occurred from 10-70 min, and then was constant until 90 min. While, in Figure 5 describes the temperature rise against sonication time conditioned at 50 °C and compared with water. The temperature went up from 61-63 °C undergone at 10-30 min and was constant until 90 min. In this study, external heating to raise the operating temperature (40, 50, 60 and 70 °C), was performed.

3.3. The liquid phase reaction products

Figure 6 shows the chromatogram of product whose temperature and time were set at 50 °C and 50 min without catalyst. The chromatogram pattern shows the products, which were degraded from glycerol with and without using

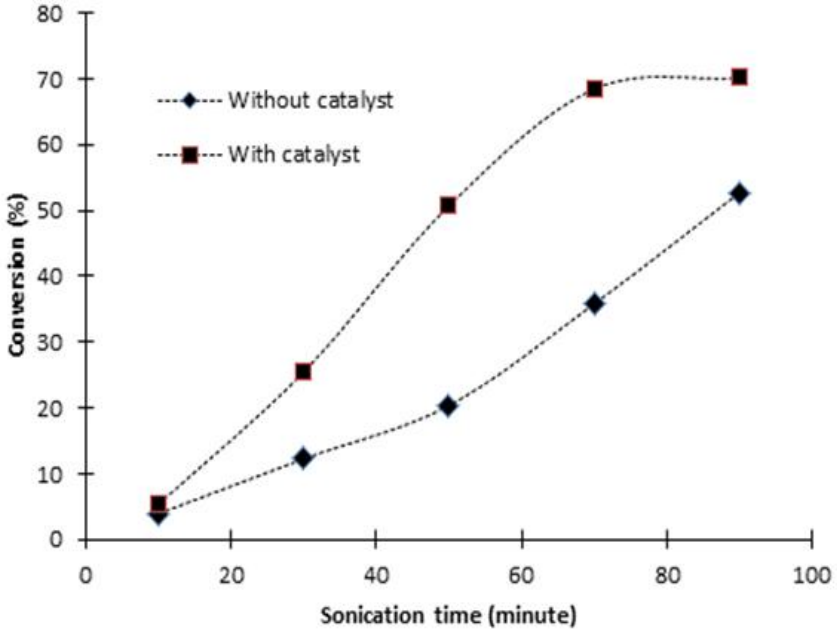

Figure 3. The effect of sonication time against glycerol conversion with and without catalyst at 60 °C

catalyst. Products identified were methanol, allyl alcohol and acrolein, while, other products appeared on the diagram but not known. Based on that diagram, yield of product was calculated through performing an equation, which stated mass of product per mass of initial glycerol.

Influence of sonication time on the yield of product is shown in Figure 7. The yield of each product either methanol, acrolein, or allyl alcohol increased as sonication time inclined. Yield of allyl alcohol obtained was relatively small compared to that of methanol, or acrolein.

Figure 8 shows the effect of adding catalyst vs the percentage of product obtained. It was discovered that yields of products, acrolein, methanol and allyl alcohol using catalyst was lower compared with those of employing cata-

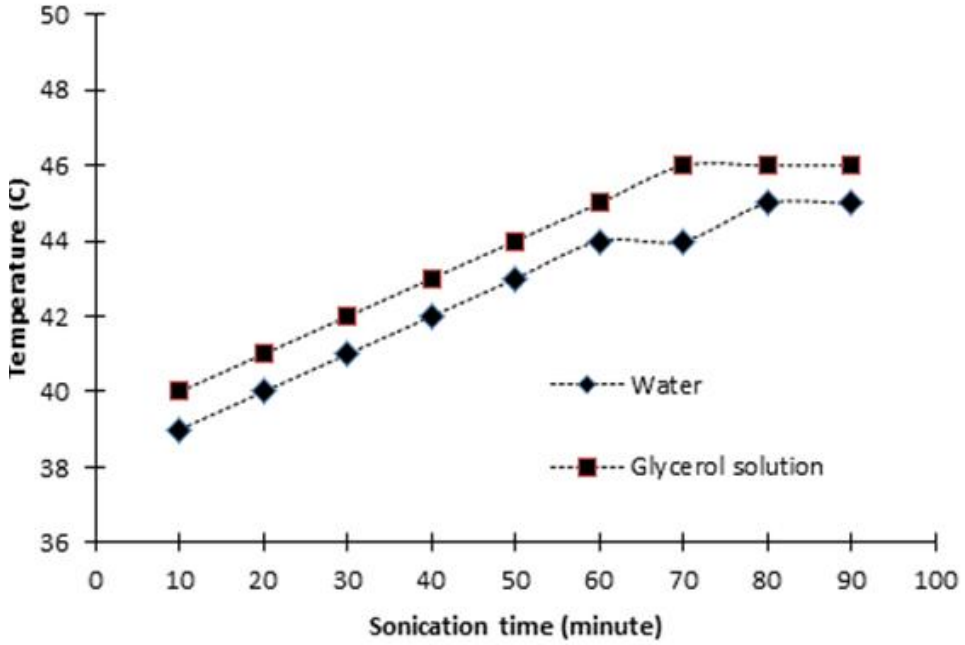

Figure 4. The effect of sonication times againt reaction temperature at 30 °C

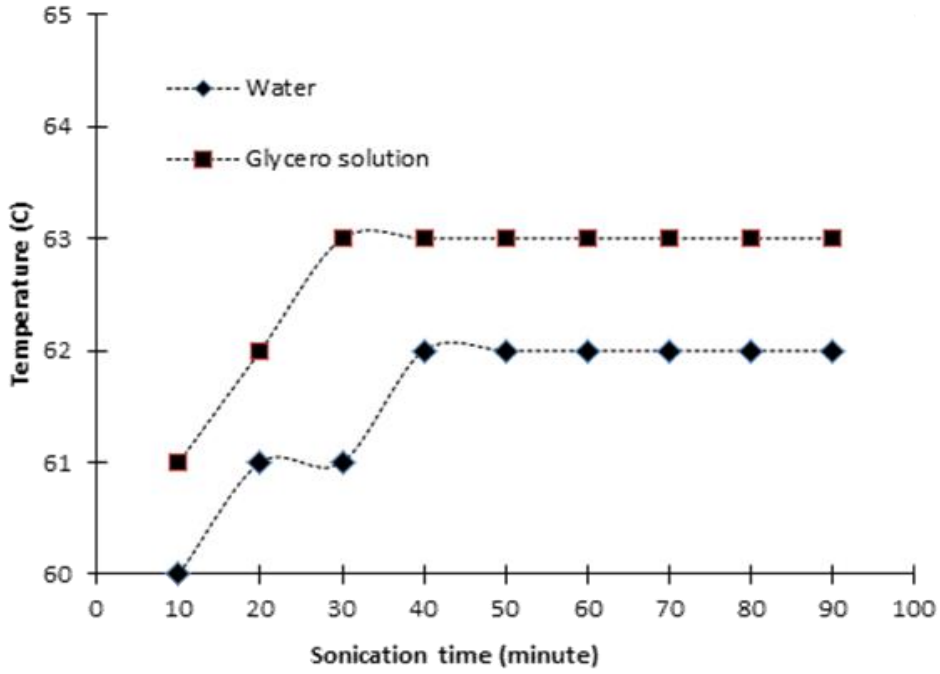

Figure 5. The effect of sonication times againt reaction temperature at 50 °C

lysts. These were comparable and consistent with previous investigations [23-25].

3.4. The effect of temperature toward yield of products

Figure 9 describes the effect of temperature toward the yield of products, methanol, acrolein and allyl alcohol. The yields of methanol and acrolein increased as temperature went up, meanwhile yield of allyl alcohol decreased at 40 ˚C and improved at 50-70 ˚C. A decrease in the yield of allyl alcohol possibility was caused by decomposing product (allyl alcohol) into CO, CO_2 and H_2 [28, 29]. It was found that the products have been successfully obtained from degrading glycerol. It was indicative that glycerol was broken down into products by using ultrasonic waves.

4. Conclusions

Glycerol has been degraded into valuable products, acrolein, methanol and allyl alcohol enhanced by sonication (ultrasonic wave). The γ-Al_2O_3 catalyst was employed to accelerate the

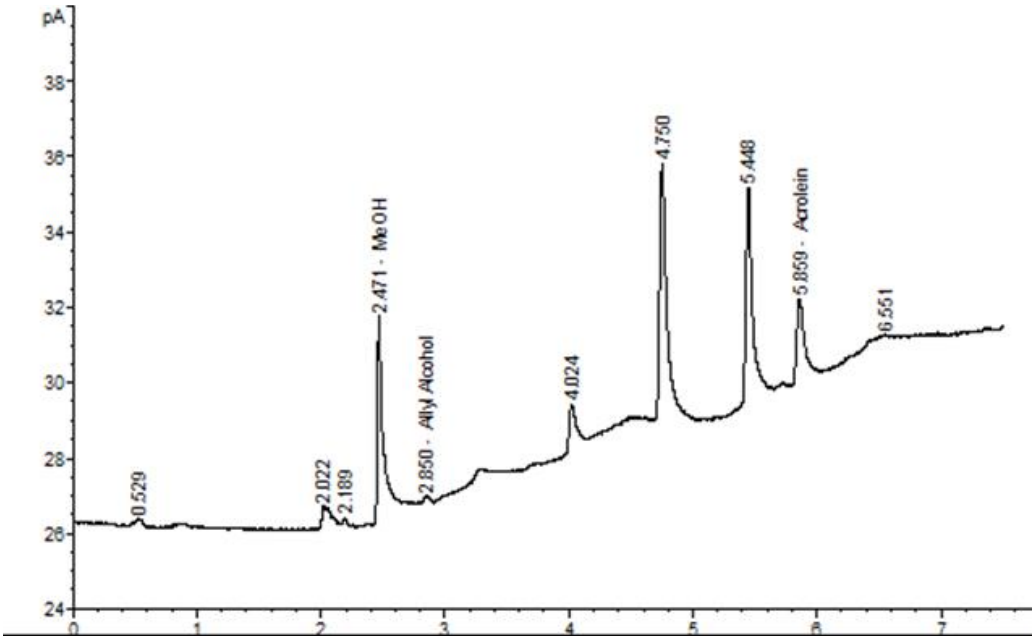

Figure 6. Chromatogram of product at temperature 50 °C, time sonication 50 minutes without catalyst

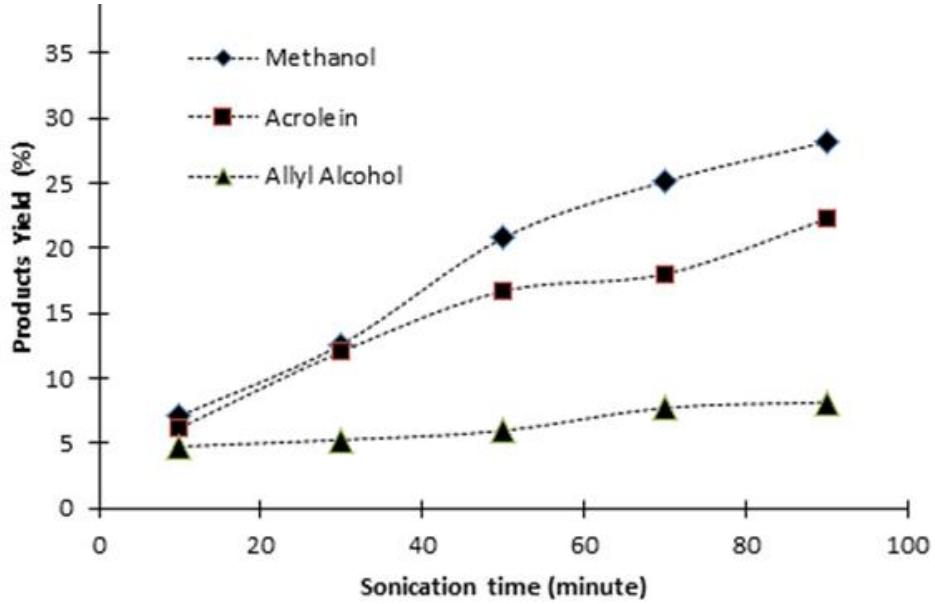

Figure 7. The effect of sonication time against products yield at temperature 60 °C without catalyst

degradation rate. In general, the glycerol conversion increased as reaction time inclined with-, or without using catalyst. The yield of product using catalyst was bigger than that of without catalyst. Even though there was an addition of catalyst, the conversion was relatively constant in certain time. Meanwhile, the yield was improved when sonication time and temperature were added.

Acknowledgments

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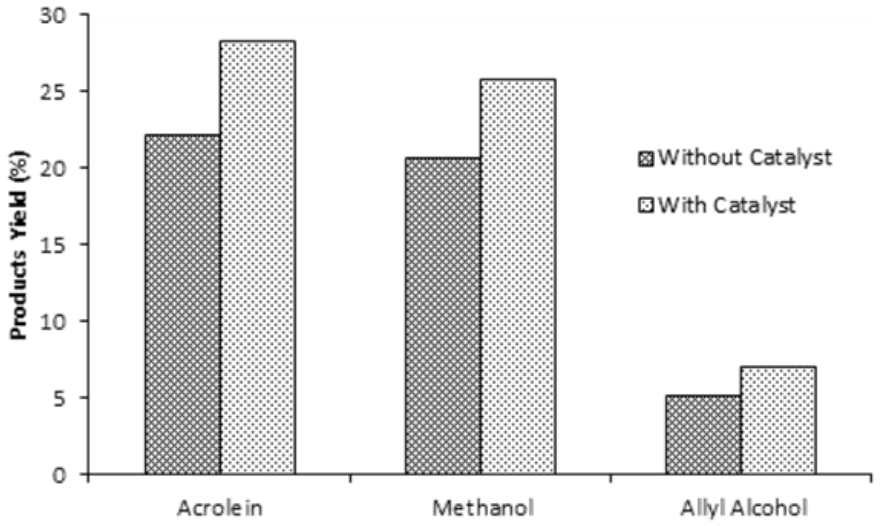

Figure 8. The effect of adding a catalyst to the products yield at temperature 70 °C and sonication time 10 minutes

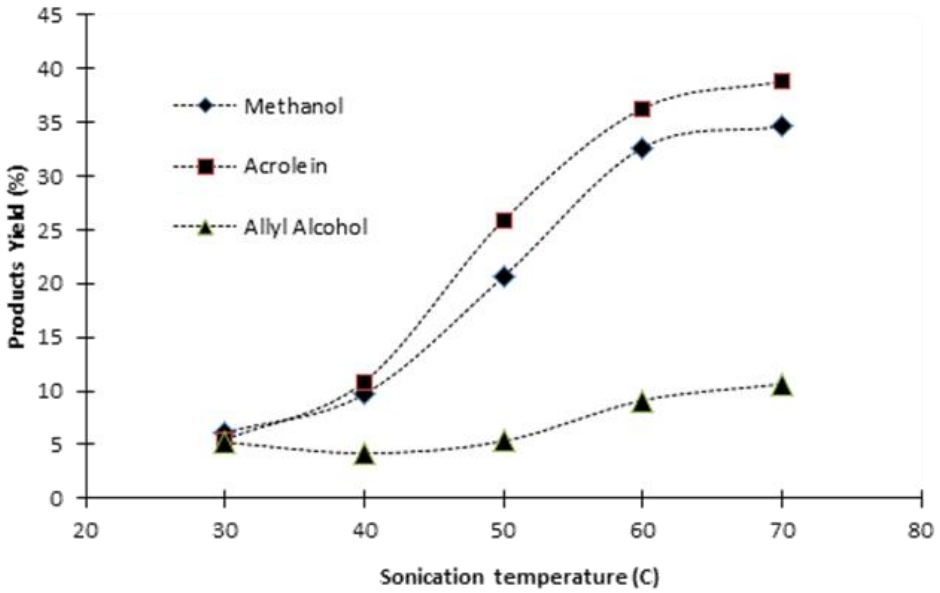

Figure 9. The effect of temperature to the products yield at sonication time 90 minutes with catalyst

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