THE INFLUENCE OF THE ADDITION H₃PO₄ ON DEGRADATION OF GLYCEROL WITH VIBRATING HORN

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ABSTRACT

Indonesia is currently developing a renewable energy-based vegetable oils include the development of biodiesel. One way of making biodiesel is the transesterification process from vegetable oils and ethanol/methanol. The transesterification process will produce primary products such as methyl ester and byproducts/waste in the form of glycerol approximately 10-15 % so that glycerol is quite abundant. Degradation of glycerol were processed by the method of sonication can produce many other compounds include acrolein. The purpose of this study was to determine the effect of phosphoric acid catalyst in the degradation of glycerol. The process of production is done in sonication reactor type 316 stainless steel is equipped with an ultrasonic wave generator. The operating conditions of research are atmospheric pressure with water glycerol mass ratio is 1: 8. Research variable is the temperature of sonication 30, 40 and 50 °C, sonication time is 10, 30, 50, 70 and 90 minutes with and without the use of catalysts. Results of the experiment were analyzed by using Gas Chromatography (GC). The results showed that the ultrasonic wave radiation for glycerol degradation process can be used to produce other compounds such as acrolein and others. With the use of H₃PO₄ catalyst conversion is greater than without using a catalyst and increases with sonication time. The highest conversion obtained with the use of catalysts H₃PO₄ is 72.68 % in the sonication time of 90 minutes and a temperature of 50 °C, while the highest yield obtained was 49.50 % with the use of a catalyst H₃PO₄ at sonication time of 90 minutes and a temperature of 50 °C.

Keywords: glycerol, vibrating horn, acrolein, phosphoric acid.

INTRODUCTION

In the processing of biodiesel can produce glycerol approximately 10-15% as a byproduct. Biodiesel production in Indonesia has reached 4 million Kl / year [1] that will produce glycerol rough around 400,000-600,000 tonnes / year. Processing glycerol to produce high-purity glycerol or to be converted into other compounds need to be done, one of which is the degradation giseral to produce acrolein which are widely used in the ceramics industry, paper and electroplatting.

Research on processing glycerol to obtain other compounds have been done which could increase the economic value of glycerol. Various processes are being developed include steam reforming [2, 3], hydrothermal [4, 5], the catalytic hydrogenation [6], the catalytic dehydration [7], Pyrolysis [4, 8], hydrogenolysis [9, 10]. The process requires harsh operating conditions that operate at high temperatures and high pressures and high costs as well. Therefore, the development process is softer and efficiently as processes using ultrasonic waves (sonication process).

Sonication process is a process that uses ultrasonic waves with frequencies between 20-100 kHz. The process is easily applied to a variety of destinations such as degradation and modification reactions [11]. One of the benefits of ultrasonic process is to accelerate the reaction process [12, 13].

In the degradation process of glycerol, one important thing is the use of a catalyst. Various kinds of catalysts commonly used among other things Cu/SiO₂[14], Cu/MgO [15], Al₂O₃[16], HZSM [17], γ-Al₂O₃ [18], CuSO₄[19], H₃PO₄[20]. All these catalysts produce chemical compounds in the form of gas phase and liquid phase one of which is acrolein.

This study aims to determine the effect of phosphoric acid catalyst (H₃PO₄) to acrolein produced. At this degradation process using atmospheric reactor equipped with an ultrasonic wave generator.

MATERIAL AND METHODS

MATERIAL

Glycerol used in this work, was obtained from BRATACO Chemical Co. Ltd. with a purity of 91% (w/w) and the γ-Al₂O₃ catalyst was purchased from MERCK and the pure water was used as solvent.

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 of 1.3
cm, part number 630-0219, 5.5micrometersinlength. 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.

EXPERIMENTAL PROCEDURE
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, 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.

RESULTS AND DISCUSSIONS
Effect of Glycerol Conversion Against Time
The influence of time on the conversion at various temperatures with and without the use of catalysts can be seen in the following figure:

From Figures 2 and 3 can be seen that the conversion of glycerol has increased along with increasing sonication time, both without the use of catalysts and the use of catalysts. This is because the sonication time effect on the intensity of the ultrasonic waves, where the longer period of sonication can extend the time of the intensity of the waves so that the cavitation process also becoming more frequent. This is in accordance study [21] which states that the cavitation effect is influenced by several
things, among others, temperature, time and pressure. Also [4] in his research states that increasing the reaction time can increase the conversion reaction. Similarly, [15] of the results showed that the longer the reaction time, the conversion obtained is also greater. From Figure-2 shows that the largest conversion was obtained at the time of 90 minutes and a temperature of 40 °C with conversion of 37.36%. While in figure 3 shows that the largest conversion is also obtained at the time of 90 minutes and a temperature of 40 °C with conversions by 59.62%.

Effect of Acrolein Yield Against Time

The influence of time on the yield of acrolein without the catalyst at a various sonication temperature can be seen in the following Figure:

![Figure-4](image)

**Figure-4.** Effect of sonication time to acrolein yield without a catalyst at various temperature.

From Figure-4. It can be seen that for the process without catalyst, the yield value of 10 to 50 minutes increased from 3.44% to 9.60%, but at the time of 70 minutes decreased to 8.97% and then rose back into 14.24% at the time of sonication 90 minutes. The occurrence of such fluctuations due acrolein decompose into other compounds during the reaction [22, 23]. The results also fluctuating in accordance with the research [17] with acrolein yield fluctuates in line with increasing time and operating temperature. Similarly, the [7, 19] resulted in a yield of acrolein which fluctuate according increasing time and operating temperature.

Results are fluctuating due to glycerol as initial components can be broken / degraded using ultrasonic waves, but how and what fraction of the glycerol molecule can not be determined with certainty as a result of the degradation of the components that form the radical very difficult to estimate the final product [12]. As for the temperatures 40 and 50 °C, the product yield increased with increasing sonicating time.

The effect of yield over time with the use of a catalyst at various sonication temperature can be seen in the following Figure:

![Figure-5](image)

**Figure-5.** Effect of sonication time to acrolein yield at various temperatures with a catalyst.

From Figure-5 it can be seen that the use of catalysts H3PO4, product yield at temperatures of 30, 40 and 50 °C increased with increasing sonication time (10, 30, 50, 70 and 90 min.).

CONCLUSIONS

From the results of research conducted the conclusion as follows:

1. Ultrasonic wave radiation for glycerol degradation process can be used to produce other compounds such as acrolein and others.
2. The biggest conversion is obtained by the use of catalysts H3PO4 is 72.68% in the sonication time of 90 minutes and a temperature of 50 °C.
3. The highest yield obtained is 92.50% with the use of catalysts H3PO4 at 90 min sonication time and temperature 50 °C.

REFERENCES


