

KINETICS STUDY DEGRADATION OF GLYCEROL IN SUBCRITICAL WATER

Yuyun Yuniati, Sumarno, Mahfud

Departement of Chemical Engineering

Institute Technology of Sepuluh Nopember Surabaya

Email : yuniati73@gmail.com

ABSTRAK

Penelitian ini bertujuan untuk mempelajari kinetika reaksi degradasi gliserol dalam media air subkritis. Hal ini diperlukan untuk mengetahui sejauh mana gliserol dapat didegradasi dalam media air subkritis. Penelitian dilakukan dalam reaktor batch yang terbuat dari stainless steel. Reaktor dilengkapi dengan thermocouple, indikator tekanan, dan pemanas listrik. Gliserol dan air dengan perbandingan massa 1:10 direaksikan pada temperatur 250, 300, dan 350°C. Waktu reaksi divariasikan antara 10-60 menit dengan interval 10 menit. Hasil reaksi dianalisis kadar gliserol sisa dengan metode gas chromatograph pada setiap variabel. Konstanta kecepatan reaksi dapat didekati dengan persamaan Arrhenius dengan $k = 0,48836 \exp(-4378,4/RT)$. Energi aktivasi yang diperoleh pada penelitian ini adalah 4378,4 kal/mol dan faktor frekuensi sebesar 0,48836 menit⁻¹. Reaksi degradasi gliserol mengikuti kinetika reaksi orde satu. Hasil penelitian ini memberikan konversi gliserol tinggi memberikan harapan terhadap peluang degradasi gliserol menjadi produk kimia lainnya berupa asetaldehid, metanol, dan etanol.

Kata kunci : subkritis, degradasi, gliserol, kinetik

ABSTRACT

The aims of this research is to study the degradation kinetics of glycerol in subcritical water media. This is necessary to know the extent to which glycerol can be degraded by subcritical water media. The study was conducted in a batch reactor made of stainless steel. Reactor was equipped with thermocouple, pressure indicator, and electrical heaters. Glycerol and water with mass ratio of 1:10 was reacted at a temperature of 250, 300, and 350°C. Reaction time was varied between 10-60 minutes at intervals of 10 minutes. Products were analyzed by Gas Chromatograph method. Reaction rate constants can be approximated by the Arrhenius equation with $k = 0.48836 \exp(-4378.4/RT)$. Activation Energy is 4378.4 cal / mol and frequency factor is 0.48836 min⁻¹. Glycerol degradation reactions follow first order reaction kinetics model. The study provides a high glycerol conversion to give hope to the chances of degradation of glycerol to other chemical products as acetaldehyde, methanol, and ethanol.

Key words : subcritical, degradation, glycerol, kinetics.

Introduction

Declining fossil oil reserves and the environmental problems caused by the usage of oil lead scientists to find new energy sources. Increasing world population will also result in increased energy needs. Issues related to world climate changes caused by soaring levels of carbon dioxide in the atmosphere also needs to get serious attention. Fossil-based fuels are considered as the largest contributor to carbon dioxide levels, especially in the industrial city. The possibility is to use biomass for fuel.

One of the preferred alternative fuel is biodiesel. This synthetic fuel produced by transesterification of triglycerides (derived from plants such as *jatropha curcas*, palm oil, sunflower seeds, etc.) and alcohol with base catalyst. The main products of this reaction is a methyl ester (biodiesel) and side products is glycerol. Crude glycerol generated from the transesterification process is 10% of biodiesel produced (Dasari et al., 2005). An abundance of glycerol production would likely reduce the price of glycerol in the market (1.28 to 1.5 U \$ per kilogram). Crude glycerol can not be used directly by industry and the purification process of crude glycerol requires a high cost (Pachauri et al., 2006).

The molecule structure of glycerol and many of biodiesel industry cause glycerol have the opportunity to be exploited further. Various studies have been done related to transformation of glycerol into a new compound which has a higher sale value. Glycerol is a compound that can be transformed into other chemical product, for example: glycerol convert to 1,3 propanediol by fermentation (Xiu et al., 2004), acrolein through the hot compressed water (Watanabe et al., 2007).

Glycerol degradation with water medium in the the subcritical and supercritical condition give product like acetaldehyde, propionaldehyd, acrolein, carbon dioxide, and hydrogen (Buhler et al., 2002). Others research provide information on the formation of CO, H₂, CO₂, CH₄, and C₂H₄ through pyrolysis (Valliyappan et al., 2007; Adhikari et al., 2007; Slinn et al., 2007).

Water as a reaction medium in the region subcritical (temperatures above the boiling point of water and below the critical point, the pressure above 22.1 MPa) very profitable with a variety of considerations..

In addition, limitation of the operating conditions in the area of subcritical water provide an alternative implementation of appropriate operating conditions. Reaction kinetics are strongly influential in the near critical point of water at various temperatures and pressures, and even allows for the occurrence of "jumping reaction" which is very favorable for reactions with very high activation energy. Water at subcritical conditions behaves like a catalyst, either acidic or alkaline. (Broll et al., 1999).

Currently a lot of organic material synthesis process used subcritical water as the medium of technology, especially for the degradation reaction. Research had been done by Bicker, et al (2005) concerning degradation reactions of carbohydrates in subcritical water conditions (25 Mpa, 300°C) using transition metal ions such as Co, Cu, Ni, and Zn as catalyst. Results of this research showed the increasing of lactic acid yield between 42% to 86%. Khajavi, et al (2003) showed that the kinetics of maltose decomposition in subcritical water (260°C, 10 MPa) followed first order reaction and overall reaction is influenced by the pH

(acidity). Demirbas (2008) reported that transesterification of linseed oil (linseed) with methanol and alcohol in supercritical conditions increase the yield of ester conversion. Celulosa hydrolysis in subcritical and supercritical conditions was carried out by Sasaki, et al (2007) using a continuous reactor at a temperature of 290-400°C and pressure of 25 MPa. At supercritical conditions, a higher yield (75%) can be obtained.

There are not many reviews about the kinetics of glycerol degradation kinetics using subcritical water media, whereas data relating to the kinetics is needed in the reactor design. Therefore, this study aims to determine the parameters in glycerol degradation kinetics at various reaction temperatures. Knowing the reaction kinetics is expected to provide information primarily for the reactor design in a larger scale and to prove that the glycerol have big chances to be transformed to other products.

Experimental

a.Materials

Glycerol was obtained from PT. Brataco Chemical with purity 87% (in weight) and HPLC water was obtained from CV. Mitra Gemilang. Nitrogen was obtained from PT. Tri Gases with purity 98%.

b.Apparatus

The experiment were carried out using batch reactor made of stainless steel with super duplex type from Swagelok. The reactor was 4.7 in long with 0.5 in outside diameter and 0.402 in internal diameter. The thermocouple for temperature indicator was K-type from As One Korea and temperature controller was SR 64-type from Shimaden.

The temperature was controller regulates the temperature inside the reactor to match the setting point. Pressure Indicator use a pressure gauge with a maximum pressure reading of 500 kgf/ cm² obtained from Nagano. Fig.1 shows the schematic diagram of apparatus.

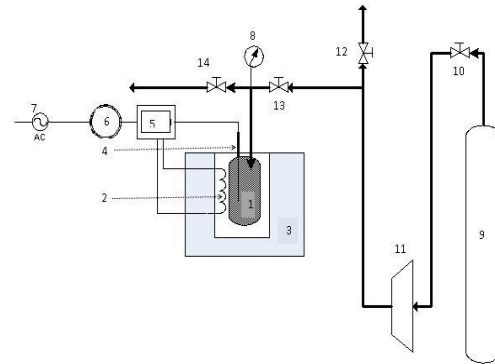


Fig.1. Schematic diagram of the apparatus of glycerol degradation. 1) Reactor, 2).Heater, 3). Isolator, 4). Termocouple, 5). Temperature controller, 6). Regulator, 7). Power electric, 8). Pressure gauge, 9). Nitrogen, 10). Valve to booster, 11). Booster hydraulic, 12). Valve to air, 13). Valve to reactor, 14). Safety valve

c.Procedure

The experiment on degradation reaction were carried out in batch reactor. The reactant was made from glycerol and water in mass ratio 1:10. Removing the gases in the solution process was carried out by heating the solution (degassing) to boiling for a few moments. Furthermore, as many as 10 ml of solution was filled in a batch reactor. After the equipment was ready to run, nitrogen gas was flow using hydraulic booster to achieve the desired initial pressure and the pressure was keep constant at 250 kgf/ cm².

To start the reaction, the heating was set at the desired reactor temperature. The reaction temperature was varied between 250°C to 350°C at intervals of 50 degree. Reaction time also was varied between 10 to 60 minute with intervals 10 minute. When the reaction was complete, the reactor was quenched by quickly immersing it in a cool water. After the cooling process was complete, the solution was removed from the reactor and analyzed. Quantitative analysis of the reaction products was carried out by GC-FID method.

Result and Discussion

In subcritical water media, glycerol can be transform through degradation reaction into other product as acetaldehyde, methanol, and ethanol.

The effect of temperature on glycerol conversion with various time of reaction was studied for 250°C, 300°C, and 350°C. The glycerol conversion profiles were shown in Fig.1.

Media subcritical water behave as a reactant to give considerable influence on the glycerol conversion in this reaction. This is caused by the properties of water which also acts as a catalyst in that condition.

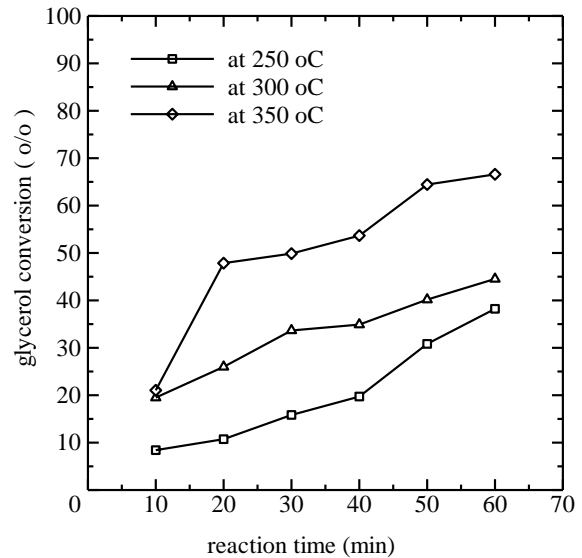


Fig.2. Effect of reaction time on glycerol conversion

High reaction temperatures cause reactant molecules activity very high, so that collisions between molecules fast enough. Thus, with increased activity of reactant molecules also can function as a mechanical stirrer in the this system.

Water behaves as a catalyst can directly reduce the activation energy of degradation reaction. The high reaction temperature and pressure cause the formation of product ions from water molecules. The high ionization product ions of water molecules causes the molecules to attack the bond between atoms on the glycerol so that the glycerol can be split into smaller compounds.

Equation of glycerol degradation rate can be approximated with first order kinetic model and could be expressed by the this equations.

$$-\frac{dG}{dt} = k \cdot G \quad (1)$$

$$-\int \frac{d(1-x)}{(1-x)} = k \cdot \int dt \quad (2)$$

$$-\ln(1-x) = k.t \quad (3)$$

Where G is glycerol concentration (mol/l), x is the conversion of glycerol (%) and t is reaction time (min). Kinetic parameters be reaction rate constant, k is determined by making a line that describes the relationship between $-\ln(1-x)$ and t at each reaction temperature. Slope of the line shows the value was of the reaction rate constant

Figure 3. shows the relationship between $-\ln(1-x)$ at various times to determine the reaction rate constants.

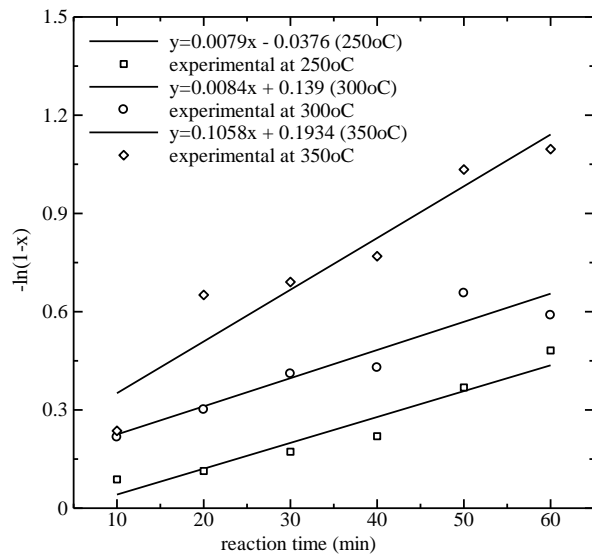


Fig.3. Relationship between $-\ln(1-x)$ with reaction time (min)

The rate constant of this reaction for degradation of glycerol at 250°C, 300°C, and 350°C were 0.0079/ min; 0.0084/ min; and 0.0158/ min. Reaction rates at temperatures of 250°C and 300°C showed a slight increase, but at a constant temperature of 350 increase in reaction speed is high enough. It is possible because of the jumping reaction when the reaction temperature approached the critical point of

water. Increased conversion of glycerol was also improves reaction rate constant value.

This research, can determine the relationship between the temperature of the reaction with the rate constant value.

The activation energy and activation factor (k_o) can be determined using the Arrhenius equation: $k = k_o \cdot \exp(-E/RT)$.

Calculation results can be seen in the table 1.

Table.1. Calculation Results for Arrhenius equation

T	k	$-\ln k$	1/T (1000)
523	0,0079	4,84089	1,91205
573	0,0084	4,7559	1,7452
623	0,0158	4,14775	1,60514

The kinetic parameters as $-\ln k$ were plotted versus $(1000/T)$ in Fig 4.

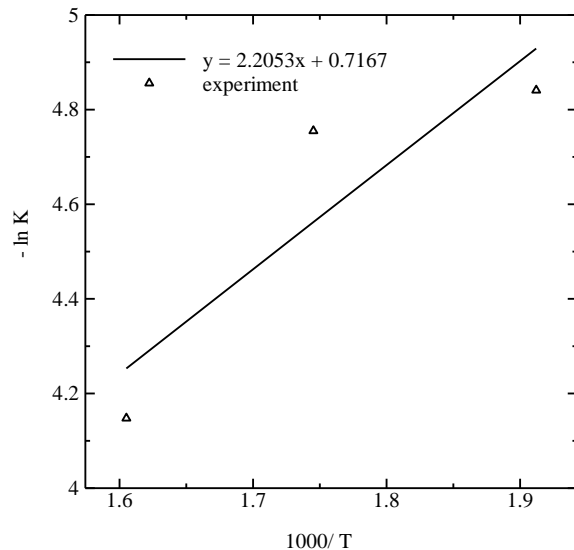


Fig 4. Relationship $-\ln k$ and $1000/T$

From the picture above obtained the following equation can be obtained.

$$-\ln k = \frac{2203.3}{T} + 0.7167 \quad (4)$$

If the R value of 1.9872 cal / mol.K, and $E/R = 2203.3$, then the Arrhenius equations for glycerol degradation reaction is $\ln k = 0.48836 \exp (-2203.3 / T)$. The activation energy obtained in this experiment was 4378.4 cal / mol and frequency factor is 0.48836 / min.

CONCLUSION

Glycerol can be transform through degradation reaction into other product as acetaldehyde, methanol, and ethanol.

Conversion of glycerol degradation reaction was increased when the temperature is increased. The largest reaction conversion was obtained when the reaction is run at a temperature of 350°C and time of 60 minutes was 66.59%. In this research, the higher the temperature, the reaction rate constant value was also greater.

The study also showed existence of jumping reaction when the reaction temperature approached the critical point of water. Reaction rate constants can be approximated by the Arrhenius equation with $k = 0.48836 \exp (-2203.3/T)$. Activation Energy was 4378.4 cal / mol and frequency factor was 0.48836 min⁻¹. Glycerol degradation reactions follow first order reaction kinetics model. The study provides a high glycerol conversion to give hope to the chances of degradation of glycerol to other chemical products.

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