

Non-Catalytic and MgSO_4 Catalyst based Degradation of Glycerol in Subcritical and Supercritical Water Media

Yuyun Yuniati¹, Sumarno², and Mahfud²

Abstract—This research aims to study the glycerol degradation reaction in subcritical and supercritical water media. The degradation of glycerol into other products was performed both with sulphate salt catalysts and without catalyst. The reactant was made from glycerol and water with the mass ratio of 1:10. The experiments were carried out using a batch reactor at a constant pressure of 250 kgf/cm², with the temperature range of 200-400°C, reaction time of 30 minutes, and catalyst mol ratio in glycerol of 1:10 and 1:8. The products of the non-catalytic glycerol degradation were acetaldehyde, methanol, and ethanol. The use of sulphate salt as catalyst has high selectivity to acetaldehyde and still allows the formation alcohol product in small quantities. The mechanism of ionic reaction and free radical reaction can occur at lower temperature in hydrothermal area or subcritical water. Conversion of glycerol on catalytic reaction showed a higher yield when compared with the reaction performed without catalyst

Keywords—glycerol, degradation, catalyst, subcritical, supercritical

Abstrak—Penelitian ini bertujuan untuk mempelajari reaksi degradasi gliserol dalam media air pada kondisi subkritis dan superkritis. Reaksi degradasi gliserol dilakukan dengan bantuan katalis garam sulfat maupun tanpa katalis. Reaktan dibuat dari campuran gliserol-air dengan rasio massa 1:10. Percobaan dilakukan dalam se buah reaktor batch pada tekanan tetap 250 kgf/cm², range temperatur antara 200-400°C, waktu reaksi 30 menit serta rasio mol katalis-gliserol adalah 1:10 dan 1:8. Produk yang dihasilkan melalui reaksi degradasi non katalitik adalah asetaldehid, metanol, dan etanol. Sedangkan pada reaksi degradasi menggunakan katalis garam sulfat memberikan hasil dengan selektivitas tertinggi pada produk asetaldehid dan sedikit produk alkohol. Dengan menerapkan kondisi operasi tersebut, membuktikan bahwa mekanisme reaksi ionik dan radikal bebas dapat berlangsung di daerah temperatur rendah atau daerah subkritis. Konversi gliserol yang dihasilkan pada reaksi degradasi berkatalis memberikan nilai yang lebih tinggi jika dibandingkan dengan reaksi degradasi tanpa katalis.

Kata Kunci—gliserol, degradasi, katalis, subkritis, superkritis

I. INTRODUCTION

Today biodiesel has been considered as one of the preferred alternative fuels in the world. Biodiesel can be produced by trans-esterification reaction of triglycerides and alcohol with base catalyst. Glycerol as a by-product in this process can contribute to about 10% weight of diesel oil. Based on this fact, glycerol obviously has the opportunity to be transformed into other chemical products which have higher selling prices. Glycerol has a complex molecular structure and thus, making it possible to crack the carbon bond into other chemical products.

Glycerol compounds are colorless, odorless, and appear as dilute solutions of a very extensive use. In food and beverages, glycerol is served as a humectant (hygroscopic compound), solvent and sweetener, food preservatives, low-calorie food ingredients, liquid thickener/viscous, and sugar substitute. Glycerol can also be used as an anti-freeze compound for plants.

Commercially, glycerol has another name: glycerin, or commonly referred to as alcohol sugar. Glycerol has three hydrophilic hydroxyl groups of alcohol which greatly affect the solubility of water (hygroscopic properties).

Various studies have been carried out in regards with the transformation of glycerol. Consequently, a large amount of energy would be required for this reaction to proceed. To supply the energy requirement, glycerol degradation process needs to be performed in various conditions, such as at high temperature and low pressure [1], high temperature and high pressure in water media at near critical point without catalyst [2], as well as with acid catalyst [3].

One of the fluid that has the potential to degrade glycerol is water. Water can serve as a medium as well as reactant. Water in subcritical and supercritical conditions can increase the kinetics of reaction by varying pressure and temperature. By using water at subcritical and supercritical conditions as a media, the temperature and pressure limits can be sufficiently large to change the polarity and solubility so that it is possible to obtain a high yield or conversion [4-7].

In general, the kinetics of reaction is strongly affected at the subcritical to the supercritical areas by varying the pressures in the process. This is especially true for the reactions which involve different phases of reactants, such as non-polar materials with significant solubility in

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subcritical to supercritical water medium. This causes mass transfer limitations is no longer effective. Likewise, the water properties/characteristics will also change in their structure and enable water to act as solvents, catalysts, and even reactants. It is very possible because the bonding ability of hydrogen structure increases [8].

Dielectric constant (ϵ) and pK_w are properties that will affect the polarity and nature of the medium as acid or base catalyst. Static dielectric constant at 25° C which is in value of 78.5 drastically decreases to 6 when it reaches a critical point. This value sufficiently explains the differences of the solution property at supercritical conditions if compared with normal water. The low value of dielectric constant is caused by the reduced strength of hydrogen bonds because of the effect of either the temperature or pressure. In the case of chemical reactions, water at supercritical conditions can undergo dissociation or becomes radical and will significantly decrease the activation energy [8].

Water in supercritical area shows its very large specific heat capacity (C_p), which is 29.2 kJ/kg.K at 4.000C and 29 MPa. Depending on the temperature and pressure, this C_p can vary in a wide range limits. At subcritical to supercritical conditions, the C_p causes a high compressibility on water that subsequently facilitates the reaction to easily take place, especially in reducing the problem of mass transfer in heterogeneous reactions [8].

Various studies on glycerol degradation are reported, among others :

The degradation of glycerol using supercritical water medium to produce various chemical compounds which have high selling prices, such as acrolein, acetaldehyde, allyl alcohol, methanol and gas products like CO, CO₂ and H₂ [2].

Valliyappan et al [1] performed glycerol pyrolysis at various rates of N₂ (30-70 mL/minute), temperature (650-800°C), as well as the type and the size of packing in the atmospheric reactor tube. Most products are gases, mainly containing CO, H₂, CO₂, CH₄, and C₂H₄. It has been researched that the temperature, the inert gas velocity, as well as the particle diameter of packing have given effects on glycerol as well as on its product distribution. Composition of gas products are of: 70-93% mole syngas, 3-15% mole C₂H₄ and "heating value" between 13-22 MJ/m³. This study indicates that bio-glycerol is potentially used in producing syngas and gases with medium "heating value".

Slinn, et al conducted a study of glycerol degradation by using alumina platinum catalyst [9]. This study aims to know the influence of the process if pure glycerol and glycerol as byproduct of trans-esterification reaction are used. In addition, other variables studied included temperature, input concentration and input rate of glycerol. The optimum process condition is achieved at a temperature of 880°C with a feed rate of 0.12 mol/minute of glycerol per kg catalyst and steam-carbon ratio below 0.5. Non-pure glycerol gives poor results and lower yields, and in such reaction, more carbon decomposition will be likely to occur.

The use of hot-compressed water in glycerol degradation using batch processes have been studied by [3]. The operating conditions used were 573-673K tempera-

ture and pressure of 25 to 34.5 MPa. Research variables included temperature, H₂SO₄ catalyst, glycerol concentration, and pressure. The main products of this research is acrolein; acrolein yield increased with the use of high concentrations of glycerol and high pressure with a selectivity of 80% and 90% glycerol conversion at supercritical temperature and pressure conditions of 673K and 34.5 MPa respectively.

Various ZSM-5 catalysts in the reaction of gas phase dehydration of glycerol in the temperature range 265-340° C [10]. According to the research, the highest selectivity was found to be that of *acrolein*. This is different from that carried out by Corma et al, stating that the process of gas-phase dehydration of glycerol at temperature range 500-720° C gives the highest selectivity in acetaldehyde [11].

Various studies on subcritical to supercritical water were reported as follow:

Ott, et. al. conducted a study on degradation reactions of carbohydrates in subcritical water by using catalytic transition metal ions such as Co, Cu, Ni, and Zn [4]. From this research, it was found that the use of catalyst can increase the yield of lactic acid produced, i.e. between 42% to 86%. Operating conditions applied were the temperature of 300°C and a pressure of 25 MPa.

Krammer and Herbert studied the ester hydrolysis reactions in sub and supercritical water in order to obtain the typical reaction at a temperature of 250-400°C and 23-30 MPa pressure by using a continuous reactor with a residence time between 6 to 400 seconds [6].

Demirbas has conducted trans-esterification reaction of linseed oil with methanol and alcohol to produce biodiesel (methyl ester) in supercritical conditions [12]. The parameters affecting the process include temperature and pressure, molar ratio, water content, and content of FFA (Free Fatty Acid). At subcritical conditions, the reaction rate was still low and gradually increased with increasing temperature and pressure up to supercritical. These conditions also increased the yield of ester conversion. The ester alcylyl yield increased with the increasing of oil molar ratio towards alcohol.

Lehr et al conducted research on dehydration of various polyols derivatives (1,2 and 1,3 propanediol, 1,2 butanediol, glycerol, and m-erythritol) in subcritical and supercritical water [7]. During the dehydration process, a variety of aldehydes and furan derivatives are formed, both of which are important compounds in industries.

Cellulose hydrolysis in subcritical and supercritical water was carried out by Sasaki et al using a continuous reactor at a temperature of 290-400°C and pressure of 25 MPa. A higher yield of about 75% was obtained at supercritical conditions [13].

Many previous researchers have been using the medium of water at conditions near the critical point to degrade glycerol [2-3]. In response, it is necessary that further research is conducted by using water as a media in glycerol degradation at a lower condition than it is in the subcritical region (hydrothermal) as this is very important to greatly reduce energy demand in the degradation reaction. This research aims to study the degradation reactions of glycerol either without or with

catalyst in subcritical region (hydrothermal) and supercritical.

II. METHOD

This research was done by specifying the material and set up experimentally.

A. Materials

Glycerol in this research was obtained from PT. Brataco Chemical with purity 87% (in weight). Water for Chromatograph used to solvent in glycerol was obtained from CV.Mitra Gemilang. The solution of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ used as catalyst. Nitrogen used to pressurization gas was obtained from PT. Tri Gases with purity 99.99%.

B. Apparatus

The experiment of glycerol degradation without and with catalyst were carried out using batch reactor made of stainless steel with tubing type of super duplex obtained from Swagelok. The reactor was 12.5 cm in long; 1.27 cm in outside diameter; and 1.02 cm in internal diameter. The thermocouple for temperature indicator was K-type from As One Kore and temperature controller was SR 64-type from Shimaden to regulate the temperature inside the reactor in accordance with the setting point. Pressure indicator use a pressure gauge with a maximum pressure reading of 500 kgf/cm^2 obtained from Nagano. Nitrogen gas was kept in tanks and used to raise the pressure in the reactor. Figure 1. shows the schematic diagram of apparatus.

C. Procedure

The reactant was made from glycerol and water in mass ratio 1:10. To remove the gases in this solution it was carried out by degassing (heating solution to boiling) for a few moment. Futhermore, as many as 10 ml of solution was filled in a batch reactor. After the equipment was ready to run, nitrogen gas was flown using hydraulic booster to achieve the desired initial pressure for reaction pressure in 250 kgf/cm^2 . In glycerol degradation with catalyst used sulfate salt solution $\text{MgSO}_4 \cdot 10\text{H}_2\text{O}$ in mol ratio catalyst-glycerol were 1:8 and 1:10. The reaction temperature was varied between 200°C to 400°C at intervals 50 degree and batch time was 30 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 Gas Chromatograph method.

III. RESULTS AND DISCUSSION

A. Non Catalytic Glycerol Degradation

As shown in the chromatogram of Figure 2-3, several liquid products have been identified as the products of glycerol degradation reaction without catalyst, such as acetaldehyde, methanol, and ethanol, whereas some other products remain unidentified.

The effect of temperature on the glycerol which was converted into products was studied in the temperature

range of 200 to 400°C and 10-60 minutes processing time. The results are shown in Figure 4.

Calculation of glycerol conversion was obtained as molar fraction of a reaction glycerol to the sum of initial mole glycerol.

From Figure 4, it is known that at the reaction temperature range of 250 - 350°C , higher temperatures will lead to increase the glycerol conversion. It can be explained that high reaction temperatures will enhance reactant molecules activities, and resulted in higher collisions between molecules. Increased activity of the reactant molecules will also serve as a mechanical stirring in a mixed system.

Water at subcritical and supercritical conditions which acts as a catalyst will directly decrease the activation energy of degradation reaction. Therefore, the rate of reaction and conversion will also increase.

When the reaction occurs at 400°C , conversion of glycerol decreased. This was caused by the change on reaction performance in supercritical region/areas; at the temperature range of 250°C to 350°C , the reactions still occur in the liquid phase, whereas at 400°C , the reaction is estimated to occur in gas phase. This is possible because the mixture critical point at the higher mass ratio of H_2O is 376.3°C . This value is quite close to the critical point of water at 374°C . This condition causes the pathway (mechanism or reaction steps) to change as well. Therefore, the conversion and the products formed will also be affected. The highest glycerol conversion was 59.61% which was obtained at the conditions of operating temperature at 350°C and a processing time of 60 minutes.

From Figure 4. it can also be noted that the conversion of glycerol increases with the duration of degradation process. The adequate process time will provide more chances for the reactant molecules to react into products. The longer processing time will also provide more chance for reactant molecules to be more degraded.

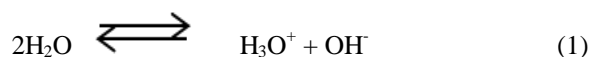
The effect of temperature on the product distribution of glycerol degradation reaction was studied at 30 min batch time and a temperature range of 200 - 400°C . The results are presented in Figure 5, where the amount of products yielded is expressed as molar yield, i.e. moles of each product divided by moles of initial glycerol.

Figure 5. shows that the formation of acetaldehyde product starts at the temperature of 200°C , while the methanol product formed at a temperature of 250°C and methanol at 300°C .

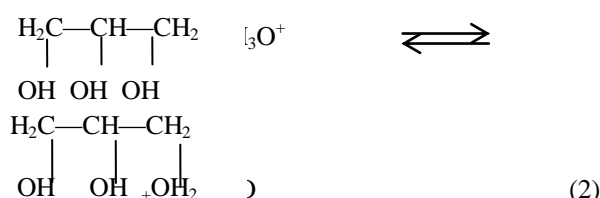
Acetaldehyde, as can be seen, was abundantly produced at 350°C and this is consistent with the experiment of Buhler et al [2], in which the reaction started at 357°C until 477°C , which is a region near the critical point of water. The most abundant acetaldehyde product was obtained at 357°C and decreased at a reaction temperature of 477°C .

Based on the reaction steps reported by Buhler et al [2], the mechanism of the acetaldehyde formation was assumed following ionic mechanism. Reaction steps to be proposed were:

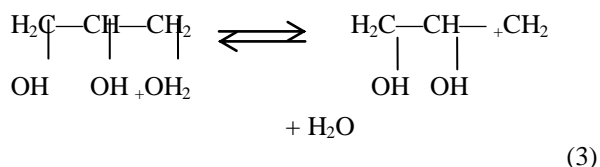
1. Dissosiation of water



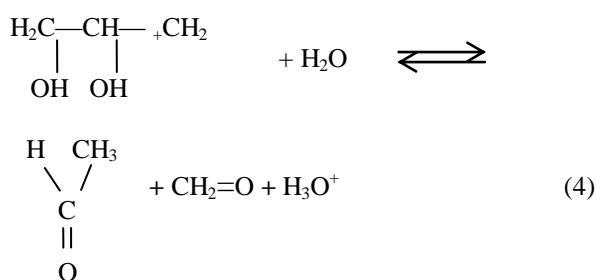
2. Glycerol protonation



3. Dehydration reaction



4. Acetaldehyde formation



Acetaldehyde is formed by the protonated glycerol and then followed by water abstraction to form the carbenium ion. The reaction start with one of the C3-radicals (from glycerol) and the decomposition to C1 and C2 fragments [2].

In this work, the glycerol degradation reaction was carried out at lower temperature, i.e. from 200°C (hydrothermal/subcritical water) until 400°C (supercritical water). The acetaldehyde started to form at temperature 200°C and kept increasing until the reaction temperature reached 350°C, and remained constant at 400°C. Thus, it can be concluded that acetaldehyde is the major product from glycerol degradation in the subcritical and supercritical water.

The use of massive water quantity in this research, i.e. 10 times that of glycerol, has been found to have effect on ionic activities. This was indicated by the high acetaldehyde production from 200 to 400°C. This is consistent with the research of [2], i.e. ionic and free radical reactions took place in the hydrothermal (subcritical) area. In addition, the authors suggest that in their research ionic and free radical activities started at the temperature near critical point of water, which was signified by the high acetaldehyde production in that area [2].

Methanol started to form at the temperature of 250°C and kept increasing until 400°C. Significant difference has been identified between this research and that of [2], with their research stating that the methanol was formed by a free radical reaction which normally occurs within the critical point of water, i.e. about 374°C.

Furthermore, this research also shows a fairly good agreement with that of [2], where free radical reaction has already occurred at a temperature lower than that of critical of water. However, in this research ethanol started to form at 300°C, a contrast to what authors have found, in which no ethanol was identified in the products of glycerol degradation [2].

From the above discussion, it can be concluded that acetaldehyde, methanol, and ethanol have been produced in the degradation reaction of glycerol without catalyst in subcritical to supercritical region. This indicates that the reaction mechanism of ionic and free radical can indeed take place at lower temperature region, i.e. hydrothermal (subcritical) region.

B. Catalytic Glycerol Degradation

In this experiment, the initial amount of glycerol was used 1.00467 molar and MgSO₄·7H₂O solution as catalyst.

Glycerol degradation reaction with MgSO₄ catalyst give some liquid product like acetaldehyde and methanol, while ethanol cannot find as a product as shown by the chromatogram in Figure 6-7.

In Figure 6-7 there are some degradation products that can not be identified. Effect of temperature on liquid product glycerol degradation with catalyst studied in the temperature interval between 200 to 400°C. The mol ratio MgSO₄ catalyst and glycerol was 1:10 and 1:8, while the time was 10- 30 min.

The MgSO₄ catalyst was contribute to lowering ther activation energy and it increasing the selectivity of glycerol degradation products. Acetaldehyde has a high selectivity towards MgSO₄ when compared with ethanol and methanol.

In the most of catalytic reaction, acrolein is the main product from double dehydration of glycerol, and acetol as a result of mono dehydration. The other products of the glycerol degdration are acetaldehyde and acetone [14].

Figure 8 shows the dehydration of glycerol in two parallel reaction pathway.

In that mechanism, acetaldehyde can be obtained from the catalytic C-C bond cleavage of acetol [14].

The effect of glycerol conversion in catalytic degradation was studied and the results are shown in Figure 9.

From Figure 9, it is obvious that the higher the temperature, the more conversion of glycerol would be obtained. The highest glycerol conversion was reached at 63.54% in operating condition 400 °C and processing time 30 minutes. Conversion of glycerol on catalytic degradation showed a higher yield when compared with the degradation without catalyst. This proves that the catalyst causes more degradation products resulted and lowering the activation energy during the reaction process.

Figure 10 and 11 shows the molar yield of acetaldehyde product as function of temperature at constant time.

In Figure 10 and 11, the yield of acetaldehyde increase with reaction temperature and this result is higher when compared with the non catalytic degradation reaction.

Similarly with the non catalytic reaction, the main product of glycerol degradation was acetaldehyde. The high of acetaldehyd yield is caused by dehydration reaction one molecule of water (H_2O) from the group of glycerol ($C_3H_8O_3$). The results of this study have similarities with several studies that have been reported, although there are different types of catalyst used, where the studies were using acid catalysts such as ZSM-5 [3, 13-14].

Figure 12-13 shows the molar yield of methanol product as function of temperature at constant time.

In Figure 12-13, indicates that the higher the reaction temperature did not cause an increase in the methanol product. The use of sulfate salt catalyst causes of methanol product lower than the reaction without catalyst. On the use of acid catalysts such as research that has been reported previously Watanabe et al support the occurrence of dehydration reaction that causes bond rupture of alcohol molecule (OH) [3,7,11]. In that study found no alcohol in the reaction products of glycerol degradation. If anything, alcohol compound produced in very small concentrations (tracer) with a molar selectivity value of less than 0.2% [10]. When compared with this study, the formation of alcohol products due to the persistence of effects of free radicals are mutually competitive with the influence of the catalyst.

In this research, it can conclude that the use of sulfate salt catalyst ($MgSO_4$) give the highest selectivity in the acetaldehyde product and the formation of methanol still possible although in small yield.

IV. CONCLUSION

1. Non catalytic glycerol degradation in water media at subcritical and supercritical condition can produce other product as acetaldehyde, methanol, and ethanol. Mechanism of ionic and free radical can occur at a lower temperature which is in hydrothermal (subcritical) area.
2. The use of $MgSO_4$ catalyst can result the highest selectivity in acetaldehyd and there is methanol products in small yield.
3. Glycerol conversion on catalytic reaction gives higher yields compared with the reaction without catalyst at various operating conditions
4. Similarly with the reaction without catalyst, the main product of glycerol degradation with catalyst was acetaldehyde with a higher yield. The $MgSO_4$ catalyst can not increase the yield of methanol.

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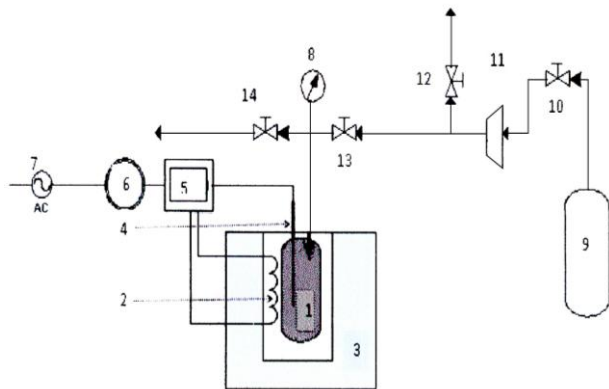


Figure 1. Schematic diagram of the apparatus of glycerol degradation. 1) Reactor, 2).Heater, 3). Isolator, 4). Thermocouple, 5). Temperature controller, 6). Regulator, 7). Power electric, 8). Pressure gauge, 9). Nitrogen, 10). Valve to booster, 11). Booster hydraulic, 12). Valve to air, 13). Valve to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

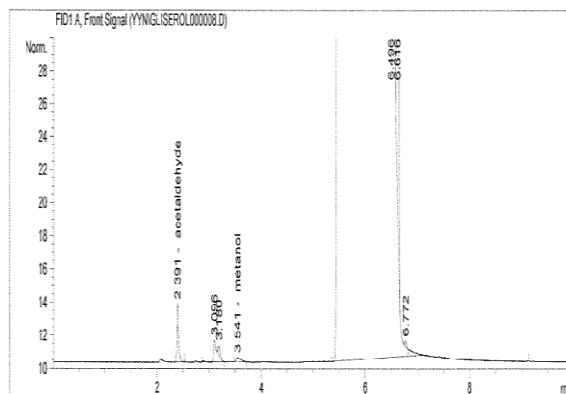


Figure 2. Chromatograph liquid product in glycerol degradation without catalyst in subcritical water

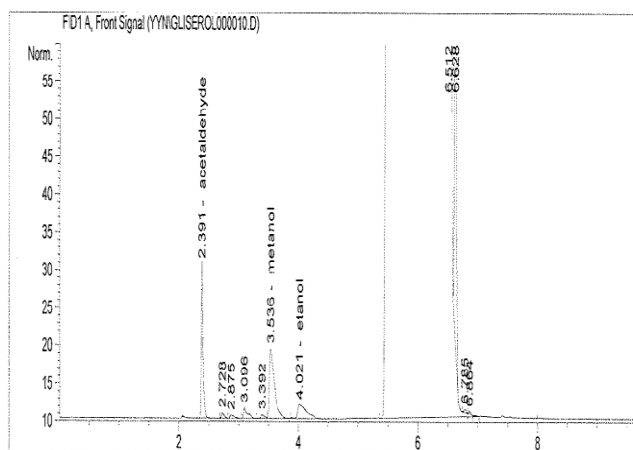


Figure 3. Chromatograph liquid product in glycerol degradation without catalyst in supercritical water

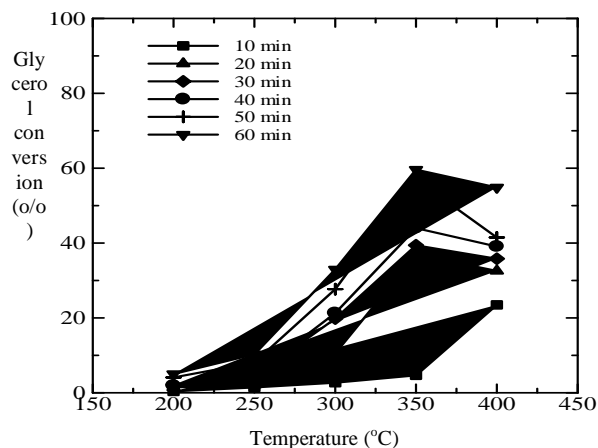


Figure 4. Glycerol conversion versus temperature at various time. The amount of glycerol before reaction was 1.00467 molar.

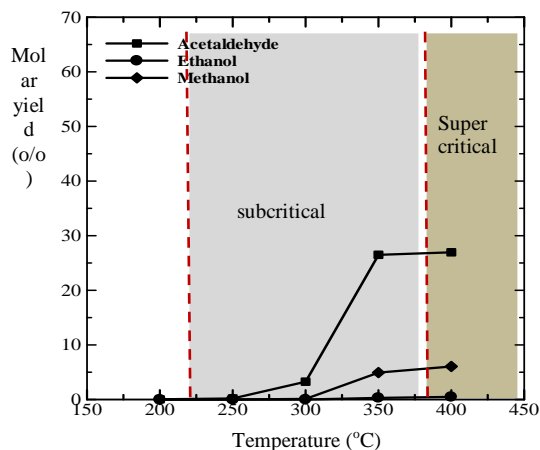


Figure 5. Molar yield of liquid product versus temperature. The batch time was 30 min. The amount of glycerol before reaction was 1.00467 molar

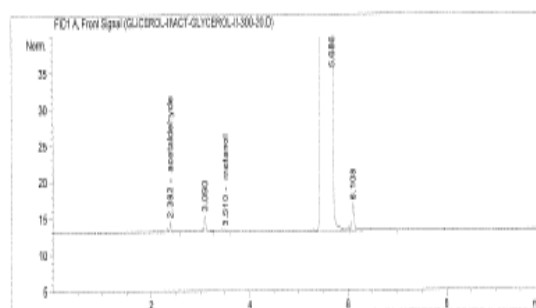


Figure 6. Chromatograph liquid product in glycerol degradation with catalyst in subcritical water

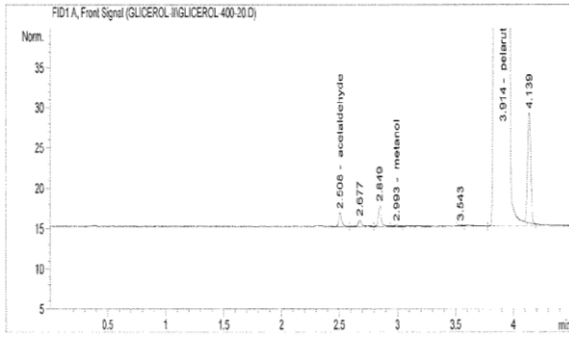


Figure7. Chromatograph liquid product in glycerol degradation with catalyst in supercritical water

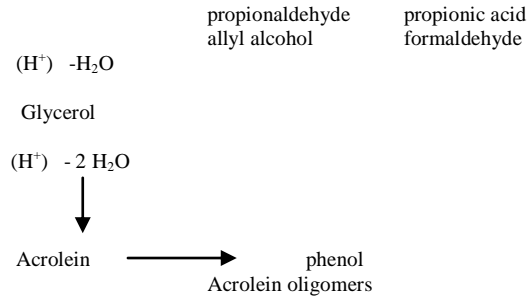


Figure 8. General reaction scheme of the dehydration of glycerol [14].

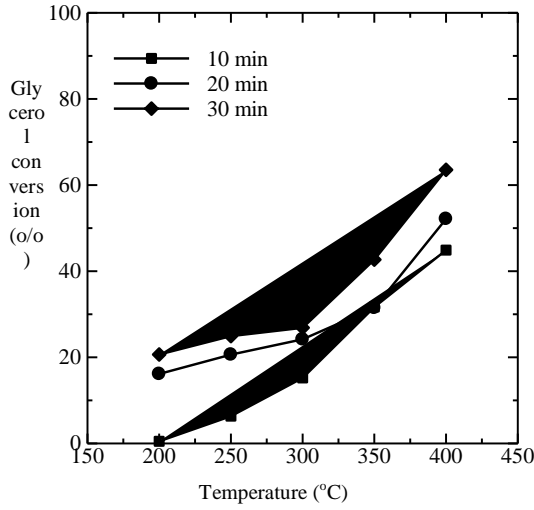


Figure9. Glycerol conversion versus temperature at various time. The mol ratio $MgSO_4$ catalyst and glycerol was 1:8

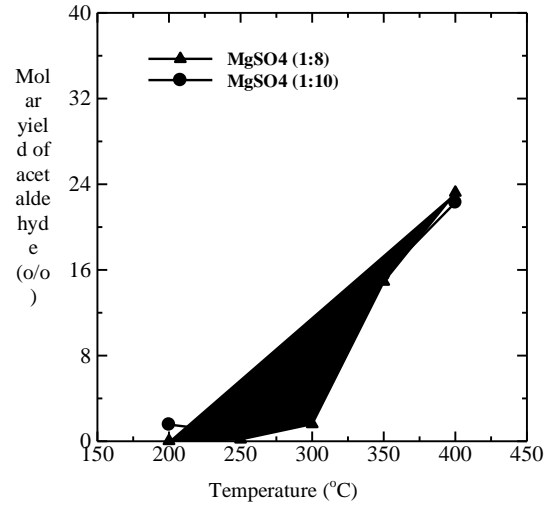


Fig 10. Molar yield of acetaldehyde versus temperature at 10 min. The mol ratio $MgSO_4$ catalyst and glycerol were 1:8 and 1:10.

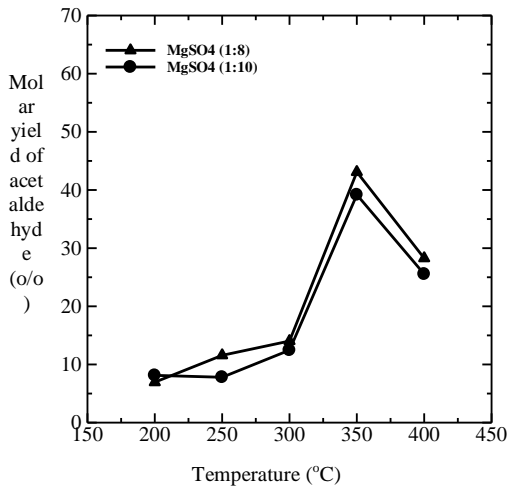


Fig 11. Molar yield of acetaldehyde versus temperature at 30 min. The mol ratio $MgSO_4$ catalyst and glycerol were 1:8 and 1:10.

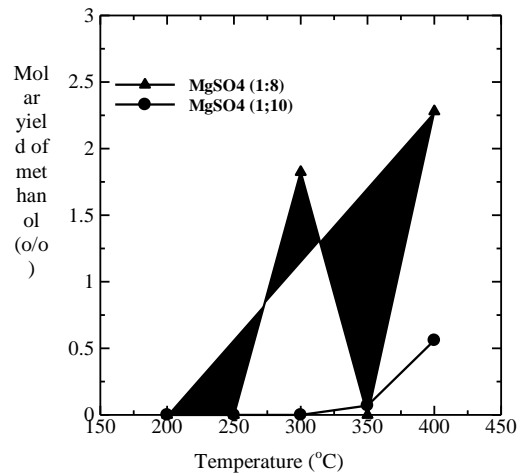


Figure12. Molar yield of methanol versus temperature at 10 min. The mol ratio $MgSO_4$ catalyst and glycerol were 1:8 and 1:10.

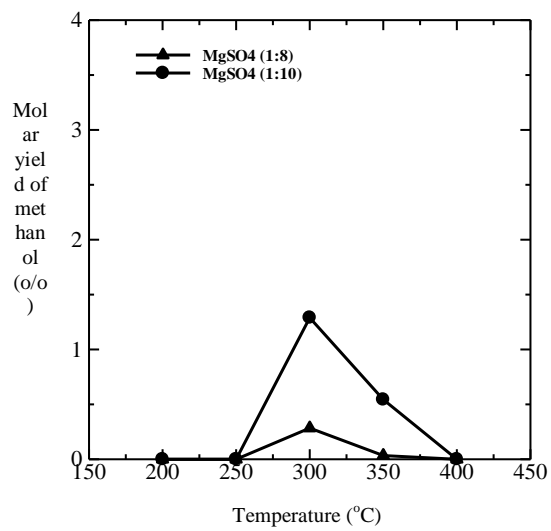


Figure13. Molar yield of methanol versus temperature