PRODUCTION OF 3-METHOXY,1,2,PROPANEDIOL AND HYDROXYACETONE
BY THE SUBCRITICAL HYDROTHERMAL LIQUEFACTION OF GLYCEROL

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By
Bander Ebraheem Jaffary
Regina, Saskatchewan
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Bander Ebraheem Jaffary, candidate for the degree of Master of Applied Science in Process Systems Engineering, has presented a thesis titled, *Production of 3-Methoxy,1,2-Propanediol and Hydroxyacetone by the Subcritical Hydrothermal Liquefaction of Glycerol*, in an oral examination held on April 10, 2014. The following committee members have found the thesis acceptable in form and content, and that the candidate demonstrated satisfactory knowledge of the subject material.

External Examiner: Dr. Farshid Torabi, Petroleum Systems Engineering

Supervisor: Dr. Raphael Idem, Process Systems Engineering

Committee Member: Dr. Hussameldin Ibrahim, Process Systems Engineering

Committee Member: *Dr. David D. deMontigny, Industrial Systems Engineering

Committee Member: Dr. Terradet Supap, Adjunct

Chair of Defense: Dr. Chris Street, Faculty of Business Administration

*Not present at defense*
ABSTRACT

Research on the use of crude glycerol, a byproduct of bio-diesel production has received strong interest within the last several years. The objective has been to add value to or utilize this byproduct, as a measure to remove one of the major obstacles encountered in the production and widespread application of bio-diesel. The present study was focused on the hydrothermal liquefaction of glycerol in subcritical water conditions for the production of 3-methoxy,1,2,propanediol and hydroxyacetone. The production of 3-methoxy, 1,2,propanediol was selected to be the major objective of this study because of its value as well as its importance in the medical sector. In the study, the molar ratio of water to glycerol in the feed to the process was in the range of 3 – 12 mol/mol. These experiments were performed at temperatures in the range of 200 – 325 ºC, initial gauge pressure ranging from autogenous to 60 bar. The reaction retention time was recorded after the process had reached the desired temperature, which was typically in the range of 0 – 120 min. The liquid product was analyzed using GC-MS while an online GC was used to quantify the gas products. The results showed that as the temperature increased, the yield of 3-methoxy,1,2, propanediol increased until 225 ºC before decreasing. Therefore, the optimum temperature for producing 3-methoxy,1,2, propanediol is 225 ºC. Similarly, the yield of hydroxyacetone increased as the operating temperature increased until 250 ºC and then decreased after this temperature. An increase in the retention time resulted in a decrease of the yield of 3-methoxy,1,2,propanediol while that of hydroxyacetone increased until 60 min then decreased. The optimum retention time for producing 3-methoxy,1,2, propanediol was 0 min. It was observed that the gas products started to appear at between 275 and 325 ºC. The trend of the gas yield was: CO₂>CO>H₂
and zero yield for CH$_4$ and C$_2$H$_6$. Furthermore, the optimum initial gauge pressure for
producing 3-methoxy,1,2,propanediol and hydroxyacetone was 40 bar. On the other hand, the optimum
molar feed ratio (water to glycerol) for 3-methoxy,1,2,propanediol and hydroxyacetone were 6 and 9, respectively. Two types of solid acid catalysts (H-ZSM-5 and γ–alumina) were investigated for the production of 3-methoxy,1,2, propanediol. It
was observed that H-ZSM-5 inhibited the production of 3-methoxy,1,2, propanediol while γ–alumina increased the yield compared with the non-catalytic experiments. On the other hand, the yield of hydroxyacetone increased using the two acid catalysts with the
trend: H-ZSM-5> γ–alumina> non-catalytic experiment. Compared with the non-catalytic experiments, the yields of the two target liquid products increased with γ–alumina within
the range of catalyst weight used in the study (0.5 – 1 g). A non-catalytic kinetic study
was performed using an empirical power-law rate model to interpret the kinetic data. Three temperatures (225, 275, 325 °C) at four different retention times (0, 60, 90, 120
min) were used to get the maximum glycerol conversion in the subcritical water
condition. The feed molar ratio (water to glycerol) was fixed as 6 and the initial gauge
pressure was kept autogenous in all of the kinetic experiments. The kinetic parameters
(A, E, n) were regressed using NLREG software. The highest glycerol conversion in this
study was observed at 325 °C as 65%. The values of the pre exponential factor, activation
energy, and the overall reaction order were 1.61 min$^{-1}$, 21.922 KJ/mol, and 3,
respectively. The kinetic data were in a good fitness with the kinetic model with $R^2$ of
90 %. The experimental and predicted rates were also in good agreement giving an
AAD% of 10.9. The final form of the rate model with the substitution of the kinetic
parameters is: $-r_A = \frac{dx_A}{dt} = 1.61 e^{-21922/RT} (1 - X_A)^3$. 
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NOMENCLATURE AND ABBREVIATIONS

T: Temperature
K: Kelvin
°C: Degree Celsius
AAD: Average Absolute Deviation
%: Percent.
CO₂: Carbon Dioxide
CO: Carbon Monoxide
H₂: Hydrogen
A: Collision or Pre-exponential Factor
J: Joule
n: Reaction order
N₂: Nitrogen
g: Gram
C₃H₈O₃: Glycerol
C₄H₁₀O₃: 3-methoxy,1,2, propanediol
C₃H₆O₂: Hydroxyacetone
OH⁻: Hydroxide ion
mL: Millilitre
mm: Millimetre
t: Reaction time, min
mg: Milligram
w%: Weight Percent
k: Rate constant
i.d: Internal diameter

NLREG: Non-Linear Regression

P: Pressure
bar: pressure Unit

C₂H₆: Ethane
CH₄: Methane
H⁺: Hydrogen ion
H₂O: Water
H-ZSM-5: Zeolite catalyst

GC/MS: Gas Chromatograph /Mass Spectrometer

GC: Gas Chromatograph
Ea: Activation Energy

R: Molar gas constant (8.314 J/mol/K)

Psi: Pounds per square inch

Xₐ: Glycerol conversion

Cₐᵢ: initial concentration of glycerol
Cₐᵢₙ: final concentration of glycerol
CHAPTER 1
INTRODUCTION

1.1 PETRODIESEL AND BIODIESEL FUELS

It has been mentioned that there is always a necessity of finding other resources of fuels and chemicals to overcome the expected shortage of conventional fuel sources over long period of usage. In this context, renewable resources such as vegetable oils are promising sources, which can be used to produce fuels such as biodiesel. Even though, biodiesel is a fuel with less air pollution but petrodiesel is widely used in the industrial sector because it is cheaper (Haas, 2005).

The production of biodiesel can be conducted through the trans-esterification process. Glycerol is a by-product that is produced through the formation of biodiesel in the reaction of fatty acids with alcohols (Dalai et al., 2000). The chemical reaction and the schematic pathway of producing biodiesel through the trans-esterification process are shown in Figures 1.1 and 1.2 respectively. Glycerol is considered as a waste product because it cannot be used in the industrial applications directly without purification process, which is not economical to cover the high cost of biodiesel production. Economically, the high price of biodiesel production can be compensated by extracting valuable liquids or gases out of glycerol (Claude, 1998). The usage of glycerol as a feed to obtain valuable products needs to focus on the economics of the end products as a guide to selecting an appropriate processing method. Hydrothermal liquefaction in subcritical water is one of the methods for treating glycerol to produce valuable liquid products. In this process, water acts as a reactant and as a catalyst through the
hydrothermal liquefaction. The hydrothermal process saves the energy used for drying when compared with other processes such as pyrolysis process. According to the literature, which is covered in chapter two, most of the studies in the hydrothermal processes of glycerol were made in the supercritical water condition with a just few studies in the subcritical water condition. Therefore, this study will focus on subcritical water condition, which is suitable to increase the liquid yield of some important liquid products for use in the industry.
Figure 1.1: Chemical equation of trans-esterification (adapted from Sarma et al., 2012)
**Figure 1.2:** Schematic pathway of biodiesel production by trans-esterification (modified from Sarma et al., 2012)
1.2 SCOPE OF THE THESIS

Nowadays, many researchers are interested to find clean and safe sources of energy in order to decrease emissions and environmental pollution. Hydrogen, biodiesel, and ethanol are examples of these clean sources (Quintana et al., 2011). Biodiesel is a fuel, which has a long chain of fatty acids and is produced from vegetable oil and animal fat (Chang and Liu, 2010). It can be produced through transesterification of animal fat or vegetable sources such as sunflower, cottonseed, soybean, canola and palm oil (Janaun and Ellis, 2010). In this process, the reaction of the vegetable oil or the fat with alcohol produces an ester and glycerol as a by-product. The by-product glycerol cannot be used directly in any industrial application without purification. Figure 1.1 shows some of the industrial applications of glycerol (Claude, 1998). The purification process is costly; however, producing useful chemicals and fuels out of glycerol could eliminate this need. There are many useful products that can be produced from glycerol such as hydrogen and syngas, lactic and citric acids, surfactants, acrolein, hydroxyacetone, formaldehyde, esters, ethers, propanediol, and acrylonitrile (Pathak 2005; Klepacova et al., 2007; Valliyappan et al., 2008; Guerrero-Perez et al., 2009; Fan et al., 2010). There are many technologies that can be used to process glycerol such as steam gasification, catalytic cracking, pyrolysis, and sub/supercritical hydrothermal liquefaction or gasification. Generally, sub/supercritical hydrothermal processes are suitable for any feed because there is no need to consume energy to dry the material. The presence of water is an important factor to increase the efficiency of these processes (Pathak, 2005).
Figure 1.3: Glycerol uses in industry (adapted from Claude, 1998)
1.3 RESEARCH OBJECTIVES

The objectives of this research can be summarized as:

- Screening and selecting target liquid products based on their industrial applications and their value.
- Optimizing the production of 3-methoxy,1,2, propanediol and hydroxyacetone by varying the process conditions such as temperature, initial gauge pressure, retention time, and the molar feed ratio of water to glycerol.
- Performing catalytic experiments aimed at selecting a suitable catalyst to increase the yield of 3-methoxy,1,2, propanediol.
- Studying the kinetics of a non-catalytic hydrothermal liquefaction of glycerol in subcritical water.
CHAPTER 2
LITERATURE REVIEW

This chapter focuses on hydrothermal liquefaction processes for glycerol as well as other techniques that can be used to process glycerol. The water properties in sub and supercritical conditions are also included. Moreover, this chapter reviews the literature of 3-methoxy,1,2, propanediol to show its importance and its value as well as the contribution of this project toward its production using the hydrothermal liquefaction of glycerol. The reaction pathways of producing 3-methoxy,1,2,propanediol and hydroxyacetone are also explained in details.

2.1 POTENTIAL IMPORTANT LIQUID PRODUCTS THAT CAN BE PRODUCED FROM THE GLYCEROL:

2.1.1 PRODUCTION OF HYDROXYACETONE

Hydroxyacetone is an organic component with a formula of C₃H₆O₂ and a molecular weight of 74.08 g/mol. Hydroacetone has a high market price of 7.96 CAD/mL, which indicates its value compared with glycerol. It can be applied in the industry to produce many important chemicals such as propylene glycol, acrolein and acetone (Mohamad et al., 2011). Hydroxyacetone can be produced from glycerol using different processes.

Wolosiak-Hnat et al. (2012) studied the effect of glycerol hydrogenolysis on hydroxyacetone selectivity using Cu/Al₂O₃ catalyst. Different parameters were investigated such as temperature, retention time, and concentration of glycerol. These authors observed that the hydroxyacetone selectivity gave the highest value as 2.2
compared with the lowest selectivity of 0.4 at 20 wt% glycerol 200 °C, 24 hr retention time, 6 wt % Cu/Al₂O₃, and 100 rpm. However, as the temperature increased the hydroxyacetone selectivity decreased. On the other hand, Stosic et al. (2012) examined the effect of glycerol dehydration on hydroxyacetone production using calcium phosphate catalysts. The results showed that as the amount of the catalyst increased the yield of hydroxyacetone increased. The highest selectivity of hydroxyacetone was 29 mol% using 1.66 HAP catalyst compared with the lowest selectivity of 13 mol% using W/HAP catalyst at 350 °C. Feng et al. (2012) studied the glycerol conversion by the hydrogenolysis process using different types of catalysts. The catalysts were Cu/Al₂O₃, Cu/TiO₂, and Cu/ZnO. The results showed that Cu/TiO₂ and Cu/ZnO had the highest activity and selectivity of 90% for hydroxyacetone production.

Chieregato et al. (2012) investigated the effect of glycerol oxidehydration on hydroxyacetone production using continuous flow glass reactor. They observed that the selectivity of hydroxyacetone decreased as the temperature increased. Meanwhile, Mane et al. (2012) studied the glycerol conversion by hydrogenolysis process to produce hydroxyacetone. The study showed a high selectivity of hydroxyacetone using CAP(K₂CO₃ and CAF(KOH) at 220 °C. Also, Tao et al. (2012) investigated the production of hydroxyacetone by the dehydration of glycerol. The experiments were carried out using Tantalum oxides catalysts. The study showed that the hydroxyacetone selectivity increased as the temperature increased up to 700 °C. In addition, Mane and Rode (2012) investigated the effect of glycerol dehydration on hydroxyacetone production over Cu–Al oxide catalyst. The investigation indicated that the selectivity of
hydroxyacetone increased to reach 100 mol% at 230 °C, 3 hours retention time, and 1 g of 20% Cu/Al₂O₃.

Possato et al. (2013) studied the dehydration of glycerol over micro/mesoporous MFI zeolites for the production of hydroxyacetone. The highest selectivity of hydroxyacetone was 3.4 wt% after 8 hr reaction retention time. Delgado et al. (2013) examined the hydrogenolysis of glycerol over Pt-based catalysts. The catalysts used were Pt/Al₂O₃, Pt/Al₂O₃–SiO₂, and Pt/TiO₂ at the temperature of 210 °C. The catalyst of Pt/TiO₂ had the highest activity and selectivity for hydroxyacetone production as compared with the other two catalysts. The highest selectivity for hydroxyacetone was 32.3 wt%. Meanwhile, Massa et al. (2013) has explained the effect of glycerol dehydration on hydroxyacetone production. The study was performed using niobium and tungsten oxide supported over monoclinic zirconia. The highest yield of hydroxyacetone was found to be 26.4 % with 91.3 % glycerol conversion at 305 °C, retention time of 3 hours, 0.8 g ZrO₂, and a feed of 20 wt% of aqueous glycerol.

In another study, Gu et al. (2013) investigated the dehydration of glycerol for producing hydroxyacetone using supported sulfated catalysts. Hydroxyacetone reached the highest selectivity of 14% when using cesium carbonate-modified 29NiSO₄-550 at 340 °C with a cesium content of 12 wt%. However, the study showed that 16.5 wt% of hydroxyacetone selectivity was reached by using 29NiSO₄-550 at the same temperature. On the other hand, Hulteberg et al. (2013) discussed glycerol dehydration using WO₃/ZrO₂ catalyst. The results indicated that the catalyst was deactivated through the formation of hydroxyacetone at 553 K. The usage of WO₃/ZrO₂ increased the production of hydroxyacetone. Liebig et al. (2013) studied the dehydration of glycerol using
catalysts WO$_3$/TiO$_2$, Sb-V-O, and Sb-Fe-O. The experiments were carried out using a continuous gas flow reactor. The results showed that the use of WO$_3$/TiO$_2$ increased the selectivity toward hydroxyacetone from 1.1% after 1 hour to 2.2% after 5 hours at a temperature of 280 °C. Moreover, Manfro et al. (2013) studied glycerol reforming using Ni-Cu for producing hydroxyacetone. The study showed that the highest conversion of glycerol of 70% was obtained at 250 °C and 35 atm. The results showed that the increase in the amount of catalyst used increased the yield of hydroxyacetone

2.1.2 PRODUCTION OF 3-METHOXY,1,2, PROPANEDIOL

The chemical, 3-methoxy,1,2,propanediol, is an organic compound with the molecular formula of C$_4$H$_{10}$O$_3$ and a molecular weight of 106.12 g/mol. 3-methoxy,1,2,propanediol has a market price of CAD 39.10 /mL with a very important medical application. According to Shuaff-Werner and Miler (1988), 3-methoxy,1,2,propanediol is used as a cryoprotector in low-temperature preservation of reinoculated cell cultures, bone marrow, and blood cells.

This chemical can be produced from glycerol through a number of reactions. Koshchii (2002) studied the methylation of glycerol to produce 3-methoxy,1,2,propanediol using NaOH. In this study the yield of the 3-methoxy,1,2,propanediol increased up to 59% using a molar feed of glycerol to NaOH of 3:1. On the other hand, Fauhl and Wittkowski (2004) examined the effect of adding glycerol to wine and detecting the amounts of 3-methoxy,1,2,propanediol in the solutions. The study showed that the amount of 3-methoxy,1,2,propanediol was in the range of 0.1–0.8 mg/L. Meanwhile, Mota, and Goncalves (2008) (published in Portuguese Language) studied
glycerol etherification for the production of 3-methoxy,1,2, propanediol using different catalysts. The catalysts were Me sulfate, di Me sulfate, chloromethane, bromomethane, and iodomethane. The experiments were carried out at the temperature of 200 °C. The results showed that as the temperature increased the yield of 3-methoxy,1,2, propanediol decreased.

Thibault et al. (2011) investigated a different type of process called glycerol hydrogenation for producing 3-methoxy,1,2, propanediol using ruthenium aqua complexes catalysts in the presence of methanol. The results showed that the highest yield of 3-methoxy,1,2, propanediol was 47 % at 200 °C, a pressure of 3.45 MPa (34.5 bar), and a glycerol concentration of 500 mmol/L. Marulanda (2011) studied the transesterification process of fat to produce methyl esters and glycerol. The experiments were performed using a continuous unit at temperatures range of 350 to 400 °C and pressures up to 300 bars. The results indicated that the samples from the decomposition of glycerol included 3-methoxy,1,2, propanediol as one of the products. Li et al. (2012) (the study was published in Chinese Language) studied the reaction of glycerol with methanol using acid to produce 3-methoxy,1,2, propanediol. The experiments were performed at a temperature range of 100- 300 °C and a retention time of 0.5- 6 hr. The results showed that the yield of 3-methoxy,1,2, propanediol increased by using an acid agent. As has been observed in the current literature, the use of hydrothermal liquefaction of glycerol to produce 3-methoxy,1,2, propanediol has not been reported. Therefore, this study will contribute to adding a new process to produce 3-methoxy,1,2, propanediol from glycerol.
2.2 TECHNOLOGIES USED TO PROCESS GLYCEROL

There are many processes that can be used for treating glycerol to produce valuable products. The processes for converting glycerol can be classified in two groups, which can be either thermal conversion processes or biological processes. Steam reforming, pyrolysis, and hydrothermal gasification or liquefaction are examples of the thermal conversion processes. Steam reforming of glycerol using a catalyst is widely used to produce hydrogen from glycerol. The main reason for using a catalyst in this process is to increase hydrogen selectivity as well as the rate of the reaction. This process is an endothermic reaction carried out at a high temperature and atmospheric pressure (Cheng et al., 2012). Furthermore, carbon dioxide is produced through steam reforming by the water gas shift reaction (Davda et al., 2005). According to Zhang et al. (2007), the glycerol conversion reached 100% at 400 °C to produce hydrogen (85 % selectivity) using the process of steam reforming with a metal catalyst of Ir/ CeO₂. Moreover, basic supports were recommended in this process for hydrogen production. On the other hand, the pyrolysis process is one of the processes that need the application of the drying process to the feed before starting the reaction. Many studies have been performed using the pyrolysis of glycerol. Chaudhari and Bhakshi (2002) used the pyrolysis of glycerol process and found out that about 70 mol % of the production was synthesis gas. Another study was performed by Valliyappan et al. (2008) at different temperatures and gas flow rates which resulted in about 70 wt % of the glycerol being converted to synthesis gas at a gas flow rate of 50 ml/min and 800 °C. The second group of processes is the biological processes, which aim to produce hydrogen from glycerol through fermentation reactions.
The fermentation reactions must be applied in anaerobic systems to produce hydrogen, which is different than the aerobic systems that result in producing CO$_2$ (Tymchyshyn, 2010). The fermentation of glycerol has been used in different studies to produce some useful chemicals such as lactic acid, citric acid, and 1,3- propanediol (Guerrero-Perez et al., 2009; Fan et al., 2010; Tisserat et al., 2012). This project focuses on the hydrothermal liquefaction process, which is considered to be a good choice for processing glycerol. Hydrothermal processes depend on water as a reaction medium. This is advantageous in that the feed drying step is eliminated. The presence of water in the feed is important and even necessary because water can work as a reactant as well as a catalyst to enhance glycerol conversion. Another advantage of using water in this process is that it is safe to the environment and it is also already available in the feed (Kumar, 2010).

2.3 WATER PROPERTIES AT SUB/ SUPERCRITICAL CONDITIONS:

The water properties depend on the operational temperature and pressure and any change in these parameters could result in a huge change in the properties of water. The critical point of water is a temperature of 374 °C and a pressure of 22 MPa (220 bar) (Kumar, 2010). The hydrothermal processes can be classified as subcritical processes or supercritical processes. The process is considered to be subcritical if the operational temperature and pressure are below the critical point whereas if the operational temperature and pressure are higher than the critical point, the process is deemed to be a supercritical process. In the subcritical region, water is known as subcritical water with a clear distinction between the liquid and gas phases, while in the supercritical region, water is considered as one homogenous phase of liquid and gas, which is known as a supercritical fluid (Dolan, 2010). Furthermore, the supercritical region is used to increase
gas production whereas the subcritical condition is preferred if an increase in the liquid yield is desired. Water can become a good solvent for the organic compounds by increasing its temperature to the critical point or higher (Brunner, 2009). Table 2.1 shows the water properties at ambient, subcritical and supercritical conditions. In the critical region, the ionization constant, density, and dielectric constant of water change significantly compared with water properties in the ambient temperature (Dolan, 2010). The dissociation constant of water (Kw) reflects the formation of OH⁻ and H⁺ ions. The chemical equation of water dissociation is:

$$\text{H}_2\text{O} \rightleftharpoons \text{OH}^- + \text{H}^+ \quad (2.1)$$

The ionic constant of water in the subcritical condition is higher than that at ambient or supercritical conditions (Dolan, 2010). The acid-base reactions can be accelerated in the subcritical condition because water produces the acidic and basic ions of H⁺ and OH⁻, respectively (Yu et al., 2008). Increasing the water temperature decreases its pH and dipole moment. In addition, the dielectric constant, polarity, and viscosity of water also decrease (Brunner, 2009). The decrease in water polarity is the reason for the ability of water in dissolving non-polar components such as alkanes when the operational temperature increases to the critical temperature or higher. Therefore, the cooling of water to the ambient temperature leads to separation of the alkanes because of the increase in water polarity (West et al., 2008). In the subcritical water condition the ionization constant ($K_w$) increases and the ionic reactions become dominant (Tester et al., 1993; Kruse and Gawlik, 2003).
The concentration of water ions at this condition increases and this leads to an increase in the liquid products yield (Kumar, 2010). On the other hand, the supercritical condition decreases the water density, which increases the rates of the free-radical reactions (Kruse and Gawlik, 2003). The subcritical and supercritical regions of water are shown in Figures 2.1 and 2.2, respectively.
Table 2.1: water properties at ambient, subcritical and supercritical conditions (Goldstein, 1981; Marshall and Franck, 1981; Franck, 1983; Krammer and Vogel, 2000; Kruse and Dinjus, 2007):

<table>
<thead>
<tr>
<th></th>
<th>Ambient water</th>
<th>Subcritical water</th>
<th>Supercritical water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (K)</td>
<td>298</td>
<td>523</td>
<td>673</td>
</tr>
<tr>
<td>Pressure (bar)</td>
<td>1</td>
<td>50</td>
<td>250 - 500</td>
</tr>
<tr>
<td>pKw</td>
<td>14</td>
<td>11.2</td>
<td>19.4 – 11.9</td>
</tr>
<tr>
<td>Heat Capacity (kJ kg(^{-1}) K(^{-1}))</td>
<td>4.22</td>
<td>4.86</td>
<td>13 – 6.8</td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>78.5</td>
<td>27.1</td>
<td>5.9 – 10.5</td>
</tr>
<tr>
<td>Dynamic Viscosity (m Pa s)</td>
<td>0.89</td>
<td>0.11</td>
<td>0.03 – 0.07</td>
</tr>
<tr>
<td>Density (g cm(^{-3}))</td>
<td>1</td>
<td>0.8</td>
<td>0.17 – 0.58</td>
</tr>
<tr>
<td>Heat conductivity (mW m(^{-1}) K(^{-1}))</td>
<td>608</td>
<td>620</td>
<td>160 - 438</td>
</tr>
</tbody>
</table>
Figure 2.1: Water properties at subcritical condition (Maria et al., 2011)
Figure 2.2: Water properties at supercritical condition (Chowdhury et al., 2010)
2.4 REACTION PATHWAYS FOR PRODUCING 3-METHOXY,1,2, PROPYANEDIOL AND HYDROXYACETONE

According to D’Hondt (2008), the formation of 3-methoxy,1,2, propanediol and hydroxyacetone from glycerol undergoes two dehydration processes. The formation of hydroxyacetone takes a shorter pathway and is formed by direct dehydration of glycerol. The formation of hydroxyacetone can be catalyzed using acid catalysts. On the other hand, 3-methoxy,1,2,propanediol follows a longer pathway, which starts by the formation of glyceraldehyde from glycerol through a dehydrogenation process. Then, the glyceraldehyde is oxidized to form hydroxyethanal followed by the oxidation of hydroxyethanal to form formaldehyde. Moreover, formaldehyde is hydrogenated to form methanol. Finally, methanol reacts with the unconverted glycerol to form 3-methoxy,1,2, propanediol under dehydration process. The hydroxide ion is removed from the methanol while the proton is extracted from glycerol to form 3-methoxy,1,2,propanediol, which can be catalyzed using acid catalysts. The reaction pathways for producing 3-methoxy, 1,2,propanediol and hydroxyacetone are shown in Figure 2.3.
**Figure 2.3:** Reaction pathways for producing 3-methoxy,1,2, propanediol and hydroxyacetone (modified from D’Hondt, 2008).
2.5 HYDROTHERMAL PROCESSES INVOLVING GLYCEROL:

Glycerol is a polyalcohol with a molecular formula of $C_3H_8O_3$ and a molecular weight of 92 g/mol. Glycerol is a viscous liquid with a freezing point of 17 °C and a boiling point of 290 °C. Glycerol can be produced either chemically from epichlorohydrin or biochemically by microbial fermentation (Frost and Sullivan Market Insight, 2006; Wang et al., 2001). Glycerol is produced as a by-product with a low level of purity from the production of fatty acids and the production of biodiesel, which represents 10wt% of plant product (Pagliaro et al., 2007). Glycerol cannot be used directly in food or cosmetics without purification. Actually, the purification process is expensive, and the increase in biodiesel production leads to increase the production of glycerol. The ratio of glycerol to the produced biodiesel is 1 Kg glycerol / 9 Kg biodiesel produced (Dasari et al., 2005). The high production of crude glycerol decreased its price from $ 2.5/ lb to 30 ¢/lb between 2004 and 2006 (Yazdani and Gonzalez, 2007). Therefore, it is more desirable to search for processes that can extract useful components out of glycerol. Hydrothermal processes are examples of such useful processes, which can be classified as either liquefaction when it is applied in the subcritical water region, or gasification when the water properties are in the supercritical condition. Here is a literature review about the hydrothermal gasification and liquefaction of glycerol.

Xu et al. (1996) implemented a catalytic hydrothermal process of glycerol by using charcoal and activated carbon catalysts. The experiments were carried out at 600 °C and 34.5 MPa (345 bar) in a supercritical flow reactor. The results showed that without using swirl in the entrance of the reactor, the carbon catalysts were deactivated after 4 hours. However, the carbon catalysts gave 100% stability for more than 6 hours using a
swirl in the entrance of the reactor. Buhler et al. (2002) examined the hydrothermal process of glycerol at 622–748 K. The investigation was conducted in a tubular reactor at pressures of 25, 35 and 45 MPa (450 bar). The retention time was in the range of 32 – 165 s. The results showed that the liquid phase included methanol, acetaldehyde, propionaldehyde, acrolein, allyl alcohol, ethanol and formaldehyde. The gas yield was mainly carbon oxides and hydrogen. Kambayashi et al. (2003) utilized a continuous supercritical water (SCW) test equipment to study the hydrothermal gasification of glycerol at a temperature range of 573- 773 K. The experiments were carried out at a pressure range of 15-25 MPa (150-250 bar) with a solution concentration of 1 wt% and a reaction time of 7.5 min. The main product in this study was hydrogen.

Moreover, Ott et al. (2006) used a plug flow reactor to process glycerol hydrothermally at a temperature range of 300 – 390 °C and a pressure range of 25 – 34 MPa (250 – 340 bar) using retention time in the range of 10 – 60 seconds. The main product was observed to be acrolein. Meanwhile, Watanabe et al. (2007) investigated the usage of H$_2$SO$_4$ to catalyze the hydrothermal processing of glycerol. The experiments were performed at a temperature range of 573 – 673 K at a supercritical pressure range of 25 – 34.5 MPa (250 – 345 bar). Two types of reactors, namely, a batch reactor and a flow reactor were used in order to increase the yield of the target product, acrolein. The results showed that the yield of acrolein increased as the glycerol concentration, H$_2$SO$_4$ concentration, and the pressure increase. The selectivity of acrolein reached 80 % with a 90 % glycerol conversion at 673 K and 34.5 MPa (345 bar) in the presence of H$_2$SO$_4$. In contrast, Chai et al. (2007) studied the subcritical hydrothermal liquefaction of glycerol at 315 °C and 0.1 MPa (1 bar) in a vertical fixed-bed quartz reactor over a solid acid-based
catalysts. The main liquid product in this condition was acrolein. Similarly, Wen et al. (2008) tested the effect of using metallic catalysts (Pt, Ni, Co and Cu) in the subcritical hydrothermal liquifaction of glycerol. The experiments were conducted in a fixed-bed flow reactor at 503 K, 3.2 MPa (32 bar) and a retention time of 4 hrs. The results showed that the main gas product in this condition was hydrogen. However, Corma et al. (2008) applied zeolite catalysts in order to increase the yield of acrolein by subcritical hydrothermal liquifaction of glycerol at 290 – 650 °C. Two types of reactors were used: a moving-bed reactor and a fixed-bed to perform the reactions at retention time in the range of 0.5 – 30 seconds.

Byrd et al. (2008) studied a catalytic supercritical hydrothermal gasification a of glycerol using a tubular fixed-bed flow reactor at a temperature range of 700 – 800 °C and pressure of 24.1 MPa (241 bar). The catalyst used in this study was Ru/Al₂O₃ at a retention time of lower than 5 seconds. The main products were hydrogen, carbon dioxide, methane and a small amount of carbon monoxide. In contrast, Xu et al. (2009) studied the effect of using a base catalyst, Na₂CO₃, also under supercritical hydrothermal conditions using a continuous tubular-flow reactor at 380 – 500 °C and 25MPa (250 bar). The retention time was 0.98 min. The main product was hydrogen. In addition, May et al. (2010) investigated the supercritical hydrothermal gasification of glycerol using a continuous isothermal fixed-bed reactor. Inert non-porous ZrO₂ and 1 wt% Ru/ZrO₂ were used to catalyze the reactions at 510 – 550 °C and 35 MPa (350 bar) at a retention time in the range of 2 – 10 seconds. The liquid products obtained included acetaldehyde, acetic acid, hydroxyacetone, acrolein, allyl alcohol, propionaldehyde and acrilic acid while the gas products were hydrogen, carbon oxides and methane.
Xiu et al. (2010) investigated the hydrothermal reaction of mixing crude glycerol with swine manure at 340 °C. The experiments were performed in a batch reactor at a retention time of 15 min. The production of bio-oil was the main goal of this research. Yuksel et al. (2010) used NaOH to catalyze the subcritical hydrothermal liquifaction of glycerol at 280 °C and 10 MPa (100 bar) in a continuous flow reactor with a retention time in the range of 30 – 120 min. The gas obtained was mainly hydrogen while the liquid products were glycolaldehyde, lactic acid and formic acid. Meanwhile, Onwudili and Williams (2010) studied the possibility of applying a hydrothermal process on crude glycerol with and without using alkaline catalyst. The experiments were performed using a batch reactor at 300 – 450 °C and 8.5 – 31 MPa (85 – 310 bar). The results showed that the main liquid product in the non-catalytic experiments was oil/wax whereas the gas products included carbon dioxide, methane, and hydrogen with low amounts of carbon monoxide and C2-C4 hydrocarbons. On the other hand, the catalytic reaction using NaOH increased the yield of hydrogen gas.

Qadariyah et al. (2011) used a batch reactor to study the hydrothermal process of glycerol at 473 – 673 K and 30 MPa (300 bar). The retention time was in the range of 20 – 60 min. The liquid products were mainly acetaldehyde, acrolein and allyl alcohol. On the other hand, Azadi (2012) used a molten salt as a heating medium to supply heat to the supercritical hydrothermal gasification of glycerol. The molten salt was heated by solar energy and then used to supply heat to the process. The catalytic reactions by Ru and Ni catalysts were performed in a fixed-bed flow reactor at 773 K and 25 MPa (250 bar). The gaseous products were hydrogen, methane, and carbon dioxide. Meanwhile, Guo et al. (2012) tested the use of alkali catalysts to increase hydrogen yield for the supercritical
hydrothermal gasification of glycerol. Four alkali catalysts, namely, NaOH, Na$_2$CO$_3$, KOH and K$_2$CO$_3$, were used in this study. The reactions were performed in a continuous flow tubular at a residence time in the range of 3.9 – 9 seconds using the supercritical conditions of 25 MPa (250 bar) and the temperature range of 445 – 600 °C. The results indicated that the order of the catalysts based on the yield of hydrogen was NaOH > Na$_2$CO$_3$ > KOH > K$_2$CO$_3$.

Bennekom et al. (2012) studied the effect of different catalysts in the supercritical hydrothermal gasification of glycerol using Pt/CeZrO$_2$, Ni/ZrO$_2$, Ni/CaO-6Al$_2$O$_3$, NiCu/CeZrO$_2$ and CuZn alloy catalysts. The experiments were carried out in a continuous flow reactor at a temperature range of 375 – 700 °C, pressure range of 25.5 – 27 MPa (255 – 270 bar), and a retention time range of 8 – 87 seconds. The highest decomposition of glycerol was recorded at 674 °C. The conversion of glycerol was only 40 % without using catalysts while complete conversion was achieved in the catalytic experiments. Water-gas shift reaction was enhanced by all the catalysts whereas methanation reaction was increased using Ni based catalysts. However, deactivation of Ni/ZrO$_2$ and Pt/CeZrO$_2$ was observed because of coke formation after a long time of using the catalysts. Except for Ni Cu/CeZrO$_2$, all the catalysts supports showed good stability at the supercritical condition of water based on XRD analysis of the used catalysts.
2.6 EXAMPLES OF SOLID ACID CATALYSTS USED IN THIS STUDY:

The usage of acid catalysts was recommended to increase the yield of 3-methoxy, 1,2, propanediol and hydroxyacetone (D’Hondt, 2008; Li et al., 2012). Two types of solid acid catalysts were used in this study, which were γ-alumina and H-ZSM-5. The first type is γ-alumina, which is a crystalline microporous catalyst (Pinto et al., 2004; Wolverton and Hass, 2000; Gutierrez et al., 2001). Moreover, γ-alumina is widely used in many processes such as petrochemical processes, clauss process, refinery processes and alcohols dehydration (Digne et al., 2004). The second catalyst used in this study was H-ZSM-5, which is one of the zeolite solid acid catalysts. H-ZSM-5 has porous structure and it consists of AlO₄ and SiO₄ (Bhatia, 1989). The ion exchange of Na⁺ by H⁺ in ZSM-5 will result in formation of H-ZSM-5. H-ZSM-5 has more acidity comparing with ZSM-5 because of the high number of protons in H-ZSM-5. Furthermore, H-ZSM-5 has more selectivity and acidity comparing with other solid acid catalysts (Furrer, 1988). H-ZSM-5 is widely used in the hydrocarbons formation through the reactions of alcohols (Derouane et al., 1978).
CHAPTER 3
EXPERIMENTAL SECTION

3.1 OVERVIEW

In this study, a total of 60 experiments were performed to investigate the effect of different experimental parameters (such as temperature, initial gauge pressure, retention time, and the feed molar ratio of water to the glycerol) on the production of 3-methoxy 1,2 propanediol, and hydroxyacetone. The experiments were carried out using an autoclave batch reactor through a subcritical hydrothermal liquefaction of glycerol process. The experimental setup and the procedure of the typical experimental run are described in the following sections. Moreover, the feed preparation and products analysis are also included in this chapter.

3.2 CHEMICALS, GASES AND EQUIPMENT

The following gases, chemicals, and equipment were used in this project:

3.2.1 GASES

- Nitrogen (UHP, Praxair) (Purity: > 99.998%)
- Helium (UHP, Praxair) (Purity: > 99%)

3.2.2 CHEMICALS

- Ethylene glycol bath fluid (Cole-Parmer)
- Glycerol (VWR international, PA)
- 3-Methoxy,1,2 propanediol (Sigma Aldrich) for calibration curve only
- Hydroxyacetone (Sigma Aldrich) for calibration curve only
3.2.3 EQUIPMENT

- A 600 ml stainless steel batch reactor (Model 5523, Parr Instrument Co., obtained from Illinois, USA).
- A temperature Controller (Model 4836, Parr Instrument Co., obtained from Illinois, USA).
- Gas chromatograph – Mass spectrometer (GC-MS, Model 6890/5073, Hewlett-Packard Canada Ltd., Canada).
- Auto injector (Model 7683, Hewlett-Packard Canada Ltd., Canada)
- Gas chromatograph/thermal conductivity detector (GC/TCD, Agilent 6890 N, USA).

3.3 FEED MATERIALS AND PREPARATION

The feed used in this study was an aqueous solution of analytical grade glycerol, which was obtained from (VWR international, PA with purity of 99.7%). Different molar feed ratios (i.e. water/glycerol ratios 3, 4.5, 6, 7.5, 9, 12) were used in this process. The total mass of the solution used in each experiment was 100 g.

3.4 CATALYST USED IN THE PROJECT

Two types of solid acid catalysts were also used in this study. These were: H-ZSM-5, and γ–alumina. H-ZSM-5 was purchased from ZEOCHEM AG, Switzerland whereas γ–alumina was obtained from EM Science, Merck KGa A, Darmstadt Germany. The catalysts weights obtained using a chemical balance (PB602-S, Mettler Toledo, Switzerland) and were 0.5 and 1 g with 1.18 mm average particle size.
3.5 OPERATING CONDITIONS

This study was performed to investigate the effect of different experimental parameters (temperature, retention time, initial gauge pressure, and molar feed ratio of water to glycerol) on the production of 3-methoxy,1,2 propanediol, hydroxyacetone, and useful gases using the hydrothermal liquefaction of glycerol under subcritical water conditions. The reaction retention time was considered as the length of time used in holding the reaction after it had reached the desired temperature. The cooling process starts when the desired temperature is reached and the residence time is completed. The experiments were classified into autogenous pressure and non-autogenous pressure experiments. The initial gauge pressure of the reactor was kept at atmospheric pressure while varying the other experimental parameters in the autogenous experiments. However, in the non-autogenous pressure experiments, an external initial gauge pressure was applied to the reactor using nitrogen cylinder, while other experimental parameters were maintained at the optimum values. The optimum values of the other parameters were obtained previously from the autogenous experiments to determine their effect on the production of 3-methoxy,1,2 propanediol, hydroxyacetone and gases. The values of the experimental parameters of this study are as follows:

- Temperature: 200, 215, 225, 240, 250, 275 and 325 °C.
- Initial gauge pressure: 0, 10, 15, 20, 40 and 60 bar.
- Retention time: 0, 30, 60, 90 and 120 min.
- Molar feed ratio of water to glycerol (W/G): 3, 4.5, 6, 7.5, 9 and 12.
3.6 EXPERIMENTAL SETUP AND PROCEDURE

3.6.1 SCHEMATIC DIAGRAM AND DESCRIPTION OF EXPERIMENTAL SETUP:

The schematic diagram of the experimental setup of this study is shown in Figure 3.1. The experiments were carried out using a 600 mL stainless steel batch reactor (model 5523, Parr Instrument Co., Moline, IL). The batch reactor has a removable head containing a magnetic drive, which attached to the stainless steel stirring shaft (T316). There are two impellers of (1.5 inch diameter) in the stirring shaft with four rectangular blades. One impeller is located in the bottom and the other is 2.5 inch above the bottom one. A Bourdon-type presser gauge is placed in the head of the reactor with a capacity of 0- 3000 psi (0- 200 bar). There are three valves in the head of the reactor, which are used for gas inlet, gas release, and liquid sampling with the presence of a safety rupture disk for releasing the pressure in the case of over-pressurizing. Furthermore, the reactor is equipped with a J-type thermocouple for measuring the reaction temperature and a cooling coil for keeping the temperature constant throughout the reaction. The reactor is also equipped with a dip tube for sample removal and gas introduction. A solenoid valve is used in the cooling system for regulating the process. There is a temperature controller with an accuracy of (± 0.1%) (model 4836, Parr Instrument Co., Moline, IL) used for controlling the furnace to provide the desired amount of heat to the reactor. Ultra-high-purity (UHP) nitrogen cylinder provided from Praxair (Ontario, Canada) was used for purging the reactor.
Figure 3.1: Schematic diagram of the experimental setup of this study (modified from Harry, 2012)
3.6.2 TYPICAL EXPERIMENTAL RUN

Six different molar feed ratios of water to glycerol (3, 4.5, 6, 7.5, 9, 12) were prepared previously and a 100 g solution was weighed using a chemical balance and used in each experiment. The aqueous solution of glycerol was placed in the autoclave batch reactor. The reactor was purged for 10 min using nitrogen gas from a cylinder to remove any air before starting the experiment. The reactor was heated to the desired temperature in the range of 200-325 °C and was kept at this temperature for the specific retention time of (0, 60, 90 and 120 min). After the completion of the reaction, the reactor was cooled to room temperature. The gas products were analyzed and their compositions were recorded using a gas chromatograph (GC), which was equipped with a thermal conductivity detector (GC-TCD). After cooling the process mixture, the liquid sample was filtered and then analyzed using GC–MS and the target products were quantified. However, in the non-autogenous experiments, a specific initial gauge pressure (10, 15, 20, 40, and 60 bar) was supplied from the nitrogen cylinder to the reactor before starting the experiment.
3.7 SAFETY PRECAUTIONS

The experiments were performed while considering the safety precautions listed below:

- Lab jacket and eyeglasses were used throughout the experimental study.
- A leak test of the reactor was performed prior to the start of each experiment by applying nitrogen pressure in the reactor and checking for any pressure drop with the time.
- The nitrogen cylinder was firmly closed after purging the reactor.
- Any contact between the hot metal and the cooling plastic tubes during the reaction, which can lead to leaking of the cooling fluid, was avoided.

3.8 PRODUCT ANALYSIS

3.8.1 GASEOUS PRODUCT ANALYSIS

The gases were analyzed by a gas chromatograph (Agilent Technologies 6890), which was equipped with two columns (Hayesep Q and molecular sieve) and a thermal conductivity detector (TCD). In the GC analysis, helium was used as the carrier gas. Standard gas mixtures containing H₂, CO₂, CH₄, CO, C₂H₆, N₂, and O₂ were used to calibrate the GC for quantifying the compositions of the gases in the gas yield. The initial oven temperature was 80 °C with a holding time of 15 min. Therefore, the total time of the injection was 15 min to ensure that all of the gases were separated and quantified completely.
3.8.2 LIQUID PRODUCTS ANALYSIS

The identification of the target liquid products (3-methoxy-1,2, propanediol, and hydroxyacetone) was achieved using a gas chromatograph attached to a mass selective detector (GC-MS). The gas chromatograph (GC) was used to separate the chemicals in the liquid sample. The mass spectrometer (MS) was used to identify the components in the liquid sample. The combination of GC and MS provides the separation and the identification of the components in one injection. GC-MS (model 6890/5073) was used in this study and was obtained from Hewlett-Packard Canada Ltd., Montreal, Quebec, Canada. The type of the column was HP- INNOWAX polyethylene glycol capillary (Agilent 19091N-133) with dimensions of 30 m length x 250 µm i.d x 0.25 µm thickness. Nylon membrane of 0.2 µm was used to filter the liquid sample before the injection to the GC-MS. A volume of 1 mL was used in the auto sampler/auto injector (model 7683, Hewlett-Packard Canada Ltd., Montreal, Quebec, Canada). The reproducibility of the auto injector volume was 0.3% relative standard deviation (RSD) of the peak area percentage. The inlet temperature was 250 °C with a split ratio of 20:1. The initial temperature of the oven was 40 °C with a holding time of 5 min, which was then ramped at the rate of 5 °C/min to a final temperature of 200 °C. This temperature was maintained for 15 min to ensure that all of the liquid chemicals were separated and eluted the column completely. Helium gas with ultra high purity (UHP) at a flow rate of 1mL/min was used as the carrier gas in the GC-MS. The temperature of MS quadrupole, MS source, and GC-MS interface were 150, 230, 250 °C, respectively. A mass range of 10-300 was applied in MS scan mode with EM voltage of 1858 V. The chemical components were identified using the commercial database of the national institute of standards and technology.
(NIST, 1998 version) and the peak mass spectra of the component was compared with the mass spectra in the standard database NIST. The verification of the target products was applied by matching the peak mass spectra and the GC retention time of the commercial pure standards of the products with the peak mass spectra and GC retention time of the components in the experimental liquid sample. The NIST database was used to compare the peaks mass spectra of the commercial pure standards with those of the products in the experimental liquid sample. A percentage matching of 90% was accepted as a good match. The peaks of hydroxyacetone and 3-methoxy,1,2,propanediol are shown in figures 3.2 and 3.3 respectively.
**Figure 3.2:** Gas chromatograph/ Mass spectrometer analysis for liquid sample (Hydroxyacetone is the highest peak and appears at time of 14.387 min).
**Figure 3.3:** Gas chromatograph/ Mass spectrometer analysis for liquid sample

(3-methoxy,1,2,propanediol appears at time of 27.021 min).
3.9 EQUATIONS USED TO CALCULATE YIELD AND CONVERSION

The general equation that explains the hydrothermal liquefaction of glycerol at subcritical water is

\[
\text{Glycerol} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO} + \text{CO}_2 + \text{Liquid products} + \text{tar} + \text{H}_2\text{O} \quad (3.1)
\]

The yield of liquid was calculated as mg of component divided by g of glycerol while the gas yield was calculated as mole of gas divided by g of glycerol. The yield of gas or liquid can be calculated as:

\[
\text{Yield of "A"} = \frac{\text{milligram or mole of "A"}}{\text{gram of glycerol used}} \left( \frac{\text{mg liquid}}{\text{g Glycerol}} \right) \text{ or } \left( \frac{\text{mol gas}}{\text{g Glycerol}} \right) \quad (3.2)
\]

where “A” is the gas or liquid product.

The glycerol conversion was calculated as the difference between the initial concentration of glycerol and the final concentration of glycerol divided by the initial concentration of glycerol. The glycerol conversion can be calculated by the following formula:

\[
X_A = \frac{C_{Ai} - C_{Af}}{C_{Ai}} \quad (3.3)
\]

where:

\(X_A\): the glycerol conversion (g/g)

\(C_{Ai}\): initial concentration of glycerol (g/mL)

\(C_{Af}\): final concentration of glycerol (g/mL)
CHAPTER 4
RESULTS AND DISCUSSION

4.1 OPTIMIZATION OF LIQUID PRODUCTS

4.1.1 EFFECT OF THE TEMPERATURE IN THE LIQUID PRODUCTS

The effect of temperature on the yield of 3-methoxy,1,2, propanediol and hydroxyacetone for the subcritical hydrothermal liquefaction of glycerol was evaluated using different temperatures in the range of 200–275 °C. This temperature range includes the optimum region for producing 3-methoxy,1,2, propanediol and hydroxyacetone. The experiments were performed at autogenous initial gauge pressure, retention time of 0 min, and feed ratio of 6 mol/mol (water to glycerol). Figure 4.1 shows that as the temperature increased, the yield of hydroxyacetone increased until 250 °C before decreasing which means that 250 °C is the optimum temperature for producing hydroxyacetone. Furthermore, the yield of 3-methoxy,1,2,propanediol increased until 225 °C after which the yield decreased. Therefore, 225 °C was considered to be the optimum temperature for producing 3-methoxy,1,2,propanediol. The yield of hydroxyacetone was higher than that of 3-methoxy,1,2,propanediol because hydroxyacetone is produced from a direct dehydration from glycerol while 3-methoxy,1,2,propanediol needs a longer pathway to be formed during dehydration from the methanol (intermediate product) and glycerol. The rate of the dehydration reaction for forming 3-methoxy,1,2,propanediol decreased after 225 °C whereas the rate of the dehydration reaction for producing hydroxyacetone continued until 250 °C then decreased.
Figure 4.1: The effect of temperature in the liquid products at retention time of 0 min, autogenous initial gauge pressure, and ratio of 6 mol/mol (water to glycerol).
4.1.2 EFFECT OF THE RETENTION TIME ON THE LIQUID AND GAS PRODUCTS

The effect of retention time was investigated at the temperature of 225 °C for the liquid products and the temperatures of 275 and 325 °C for the gas products since gas products start to appear at 275 °C. The experiments were carried out at the retention time in the range of 0 – 120 min, autogenous initial gauge pressure, and the feed ratio of 6 mol/mol (water to glycerol). Figure 4.2 shows that the yield of 3-methoxy,1,2,propanediol decreased with increasing retention time, and 0 min was found to be the optimum retention time for producing 3-methoxy,1,2,propanediol. On the other hand, the yield of hydroxyacetone increased until 60 min, and then decreased after then. The optimum retention time for producing hydroxyacetone was 60 min. The effect of retention time was tested at 225 °C which is the optimum temperature of producing the 3-methoxy,1,2,propanediol. In general, the yield of hydroxyacetone was higher than that of 3-methoxy,1,2,propanediol. The increase in retention time leads to an inhibition of the rate of the dehydration reactions of methanol and glycerol which, results in the reduction in the production of 3-methoxy,1,2,propanediol. Moreover, the rate of the direct dehydration of glycerol for producing hydroxyacetone increased with increasing retention time until 60 min then decreased. On the other hand, the effect of the retention time on the gas products at 275 and 325 °C are shown in Figures 4.3 and 4.4, respectively. In the two figures the highest yield was observed for CO₂ while the lowest yield of zero was for CH₄ and C₂H₆. The trend for the gas products is as follows: CO₂ > CO > H₂ > CH₄ and C₂H₆.
Figure 4.2: The effect of retention time in the liquid products at 225 °C, autogenous initial gauge pressure, and feed ratio of 6 mol/mol (water to glycerol).
Figure 4.3: The effect of retention time on the gas products at 275 °C, autogenous initial gauge pressure, and feed ratio of 6 mol/mol (water to glycerol).
**Figure 4.4:** The effect of retention time on the gas products at 325 °C, autogenous initial gauge pressure, and feed ratio of 6 mol/mol (water to glycerol).
4.1.3 EFFECT OF THE PRESSURE IN THE LIQUID PRODUCTS

Six different initial gauge pressures were applied on the reactor to investigate the effect of pressure on the liquid products. The initial gauge pressures were (0, 20, 30, 40, 50, 60 bar) at a temperature of 225 °C, retention time of 0 min, and a feed ratio of 6 mol/mol (water to glycerol). Figure 4.5 shows that the optimum initial gauge pressure for producing the 3-methoxy,1,2-propanediol and the hydroxyacetone is 40 bar. As the initial gauge pressure increased beyond 40 bar, the rates of the dehydration reactions for producing the target products are inhibited while other side reactions could take place to form other liquid products.
**Figure 4.5:** The effect of the initial gauge pressure on the liquid products at 225 °C, retention time of 0 min, and feed ratio of 6 mol/mol (water to glycerol).
4.1.4 EFFECT OF MOLAR FEED RATIO OF WATER TO GLYCEROL

The effect of the water to glycerol ratio on the liquid products was examined at 225 °C, autogenous initial gauge pressure, and a retention time of 0 min. Six molar ratios (3, 4.5, 6, 7.5, 9, 12) were used to obtain the optimum feed ratio for producing the target liquid products. Figure 4.6 shows that the yield of 3-methoxy,1,2,propanediol increased until the ratio of 6 mol/mol (water to glycerol) then decreased, implying that the molar feed ratio of 6 is the optimum feed ratio for producing 3-methoxy,1,2,propanediol. On the other hand, the molar ratio of 9 mol/mol (water to glycerol) was observed to be the optimum feed ratio for producing hydroxyacetone. The rates of both dehydration reactions increased until the molar feed ratio of 6. After this molar ratio, the dehydration reaction of methanol and glycerol was inhibited leading to a decrease in the yield of 3-methoxy,1,2,propanediol whereas the direct dehydration of glycerol for producing hydroxyacetone continued to increase until the feed ratio of 9, after which it decreased.
**Figure 4.6**: The effect of the water to glycerol ratio on the liquid products at 225 °C, autogenous initial gauge pressure, and retention time of 0 min.
4.2 EFFECT OF SOLID ACID CATALYSTS ON LIQUID PRODUCTS

The experiments in this section were performed for the purpose of selecting a suitable catalyst for producing the target products. Based on the literature, acid catalysts are suitable for producing 3-methoxy, 1,2-propanediol and hydroxyacetone (D’Hondt, 2008; Li et al., 2012). Two solid acid catalysts (γ–alumina, and H-ZSM-5) were used in these experiments at 275 °C, a retention time of 0 min, autogenous initial gauge pressure, and a feed molar ratio of 6 (water to glycerol). Figure 4.7 shows that both solid acid catalysts increased the yield of hydroxyacetone compared with the non-catalytic experiment. H-ZSM-5 gave the highest yield of hydroxyacetone followed by γ–alumina. The weight of catalyst was 1 g for each of the catalysts. On the other hand, the production of 3-methoxy, 1,2-propanediol was inhibited by using H-ZSM-5, resulting in a zero yield. In contrast, γ–alumina increased the yield of 3-methoxy, 1,2-propanediol compared with the non-catalytic experiment. Therefore, γ–alumina is suitable for the two target liquid products while H-ZSM-5 can only be used to increase the yield of hydroxyacetone alone.

Figure 4.8 focused on γ–alumina by using two weights of the catalyst (0.5 and 1 g) at 275 °C, a retention time of 0 min, autogenous initial gauge pressure, and feed molar ratio of 6 (water to glycerol). It can be seen from the figure that as the catalyst weight increases, the yields of 3-methoxy,1,2-propanediol and hydroxyacetone increase. The acid sites in γ–alumina are Lewis acid sites which work as electron acceptors. These sites attract the hydroxide ions to be adsorbed on the surface of γ–alumina. In the case of hydroxyacetone, the direct dehydration of glycerol can be accelerated by γ–alumina. The hydroxide ions form glycerol will be attracted and adsorbed on the lewis acid sites on γ–alumina. The adsorbed hydroxide ions on γ–alumina will work as proton acceptors and
which lead to the removal of more water molecules from glycerol resulting in higher yield of hydroxyacetone. However, the dehydration process for producing 3-methoxy, 1,2-propanediol needs the availability of methanol molecules, which provides the hydroxide ions. The hydroxide ions coming from the methanol molecules will react with the protons coming from the glycerol molecules to form water molecules. The methanol molecules, which can be formed as intermediate products, can participate in forming many products that contain methyl groups in their structures. The role of γ–alumina in this process is to attract more of the methanol molecules to provide the hydroxide ions and release the methyl groups. These will then follow the reaction pathway for forming 3-methoxy, 1,2-propanediol. The hydroxide ions will withdraw the protons from the glycerol molecules while the methyl molecules will take the position of the proton connecting to the oxygen atom to form methoxy group in the glycerol molecule.
Figure 4.7: The effect of different solid acid catalysts on the liquid products at 275 °C, retention time of 0 min, water to glycerol ratio of 6 and autogenous initial gauge pressure.
Figure 4.8: The effect of the catalyst weight of $\gamma$–alumina in the liquid products at 275°C, retention time of 0 min, water to glycerol ratio of 6 and autogenous initial gauge pressure.
4.3 KINETIC MODELING IN THE HYDROTHERMAL LIQUIFICATION OF GLYCEROL IN SUBCRITICAL WATER

4.3.1 KINETIC MODELING

This section was included to study the kinetics of the non-catalytic hydrothermal liquefaction of glycerol in subcritical water. This study was conducted at a fixed feed molar ratio of 6 (water to glycerol) which is the optimum feed ratio of producing 3-methoxy,1,2-propanediol. The initial gauge pressure was kept autogenous throughout all of the kinetic experiments. Three different temperatures (225, 275, 325 °C) at four different retention times (0, 60, 90, 120 min) were used to obtain conversion of glycerol in the subcritical hydrothermal liquefaction of glycerol. An empirical power law rate model was used to interpret the kinetic data. The rate of the reaction in a batch reactor can be obtained from the following equation (Levenspiel, 1999):

\[ -r_A = \frac{dX_A}{dt} = k \left(1 - X_A\right)^n \]  

where:

\[ k = A e^{-E/RT} \]  

By substituting equation 4.2 in equation 4.1, the final form of the rate model can be written as:

\[ -r_A = \frac{dX_A}{dt} = A e^{-E/RT} \left(1 - X_A\right)^n \]  

where:

A = pre exponential factor (or collision factor)

E = activation energy (J/mol)

T = reaction temperature (K)

R = gas constant (8.314 J/mol K)
4.3.2 CALCULATION OF GLYCEROL CONVERSION AND REACTION RATE

The conversion of glycerol in the hydrothermal liquefaction in subcritical water was obtained from the following equation:

\[ X_A = \frac{C_{Af} - C_{Ai}}{C_{Ai}} \]  

(4.4)

where:

- \( X_A \): the glycerol conversion (g/g)
- \( C_{Ai} \): initial concentration of glycerol (g/mL)
- \( C_{Af} \): final concentration of glycerol (g/mL)

The equation depends on the difference between the initial concentration of glycerol and the final concentration of glycerol divided by the initial concentration of glycerol. The final concentration of glycerol was obtained from GC-MS measurements. The conversions of glycerol at different temperatures (225, 275 and 325 °C) were plotted versus the retention time. The glycerol conversions versus the retention time at 225, 275 and 325 °C are shown in Figures 4.9, 4.10 and 4.11, respectively. Glycerol conversions at the three temperatures are combined in Figure 4.12. As can be seen, the highest glycerol conversion was obtained at 325 °C as 65 %. Microsoft Excel was used to fit the curves of the conversion versus the retention time. The polynomial equation at each temperature was differentiated to make the function equivalent to \( \frac{dX_A}{dt} \) which is equal to the rate of the reaction. The retention times were substituted in the equations of different temperatures to get the rate in each retention time. The kinetic data of the hydrothermal liquefaction of glycerol in subcritical water is shown in Table 4.1.
Figure 4.9: The glycerol conversion at 225 °C at different retention times

\[ y = -1E-05x^2 + 0.0029x + 0.3368 \]

\[ R^2 = 0.9884 \]
Figure 4.10: The glycerol conversion at 275 °C at different retention times
Figure 4.11: The glycerol conversion at 325 °C at different retention times

\[ y = -2E^{-05}x^2 + 0.0048x + 0.3812 \]
\[ R^2 = 0.9967 \]
Figure 4.12: The glycerol conversion at 225, 275, 325 °C at different retention times
Table 4.1: The kinetic data of the hydrothermal liquefaction of glycerol in subcritical water at 225, 275, 325 °C.

<table>
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<th>Experimental rate (min⁻¹)</th>
<th>Temperature (K)</th>
<th>X (glycerol conversion)</th>
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</tr>
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<td>548.15</td>
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<tr>
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</tr>
<tr>
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<td>598.15</td>
<td>0.60</td>
</tr>
<tr>
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<td>598.15</td>
<td>0.63</td>
</tr>
<tr>
<td>0.0009</td>
<td>598.15</td>
<td>0.65</td>
</tr>
</tbody>
</table>
4.3.3 ESTIMATION OF THE KINETIC PARAMETERS

The kinetic parameters (A, E, n) were regressed using NLREG software. Table 4.2 shows the values of the estimates of the kinetic parameters. The values of the pre-exponential factor, activation energy, and the overall reaction order are 1.61 min\(^{-1}\), 21.922 KJ/mol, and 3 respectively. The kinetic data showed a good fit with the kinetic model and gave R\(^2\) statistics of 90\%. The experimental and predicted rates were also in a good agreement with an absolute average deviation (AAD) % of 10.9 as shown in the parity plot of Figure 4.13. The absolute average deviation was calculated as:

\[
\text{AAD} = \left( \frac{1}{12} \sum_{i=1}^{12} \frac{\text{ABS}(\text{Experimental rate} - \text{Predicted rate})}{\text{Experimental rate}} \right) / 12
\]

(4.5)

Therefore, the final rate model after substitution of the kinetic parameters is:

\[
-r_A = \frac{dX_A}{dt} = 1.61 e^{-21.922/RT} \left( 1 - X_A \right)^3
\]

(4.6)
**Table 4.2:** The estimate of the kinetic parameters

<table>
<thead>
<tr>
<th>A (min(^{-1}))</th>
<th>E (KJ/mol)</th>
<th>n</th>
<th>AAD%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.61</td>
<td>21.922</td>
<td>3</td>
<td>10.9</td>
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</table>
Figure 4.13: Parity plot comparing the experimental and predicted rates
CHAPTER 5
CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

This project was focused on the subcritical hydrothermal liquefaction of glycerol for producing 3-methoxy,1,2,propanediol and hydroxyacetone. The feed molar ratio of water to glycerol was in the range of 3 – 12 mol/mol. The experiments were carried out at temperatures in the range of 200 – 325 °C, initial gauge pressure ranging from autogenous to 60 bar. The following conclusions were drawn from the study:

As the reaction temperature increased, the yield of 3-methoxy,1,2, propanediol increased until 225 °C, after which the yield decreased. Therefore, the optimum temperature for producing 3-methoxy,1,2, propanediol is 225 °C. On the other hand, the yield of hydroxyacetone increased until 250 °C and then decreased as the operational temperature increased.

An increase in the retention time resulted in a decrease of the yield of 3-methoxy,1,2,propanediol whereas hydroxyacetone increased until 60 min then decreased. The optimum retention time for producing 3-methoxy,1,2, propanediol was 0 min. Gas products start to appear at 275 °C. The trend of the yield of different gas components was: CO₂>CO>H₂ and zero yield for CH₄ and C₂H₆. Furthermore, the optimum initial gauge pressure for producing 3-methoxy,1,2,propanediol and hydroxyacetone is 40 bar. The optimum molar feed ratio (water to glycerol) for 3-methoxy,1,2,propanediol and hydroxyacetone were 6 and 9, respectively.

Two solid acid catalysts (H-ZSM-5 and γ–alumina) were investigated to find the suitable catalyst for producing 3-methoxy,1,2, propanediol. The production of 3-
methoxy,1,2, propanediol was inhibited to give zero yield when using H-ZSM-5 while γ-alumina increased the yield compared with the non-catalytic experiment. On the other hand, the yield of hydroxyacetone increased using any of the two acid catalysts with the trend as H-ZSM-5 > γ-alumina > non-catalytic experiment.

The yields of the two liquid products were increased using γ-alumina. As the weight of γ-alumina increased the yields of 3-methoxy,1,2, propanediol and hydroxyacetone increased more than the non-catalytic yields.

A non-catalytic kinetic study was performed using an empirical power law rate model to interpret the kinetic data obtained at three temperatures (225, 275, 325 °C) at four different retention times (0, 60, 90, 120 min), feed molar ratio (water to glycerol) of 6 and the initial gauge pressure kept autogenous. The highest glycerol conversion in this study was observed at 325 °C to be 65%. The values of the pre-exponential factor, activation energy, and the overall reaction order were 1.61 min⁻¹, 21.922 KJ/mol, and 3.0 respectively. The kinetic data were in a good fit with the kinetic model with $R^2$ of 90%. The experimental rates and the predicted rates were in good agreement with AAD% of 10.9%. The final form of the rate model with the substitution of the kinetic parameters is:

$$-r_A = \frac{dX_A}{dt} = 1.61 \ e^{-21922/RT} (1 - X_A)^3 .$$
5.2 RECOMMENDATIONS

The recommendations for the future work can be summarized as:

• Selecting more solid acid catalysts to investigate their effect on the yield of 3-methoxy,1,2, propanediol.

• Applying Langmuir-Hinshelwood-Hougen-Watson (LHHW) or Eley-Rideal (ER) approaches on the hydrothermal liquefaction of glycerol in subcritical water to interpret the formation of 3-methoxy,1,2, propanediol.

• Searching for more useful liquid products by investigating other experimental parameters such as the agitation speed.

• Using the crude glycerol which includes methanol in its compositions and that could help to increase the yield of 3-methoxy,1,2, propanediol.

• Performing long term stability tests for γ-alumina and H-ZSM-5.
REFERENCES


APPENDICES

APPENDIX (A)

- The calculation of liquid and gas yields

The yield of liquid or gas can be calculated from the following formula:

\[
\text{the yield of component} = \frac{\text{mole or gram of component}}{\text{gram of glycerol}}
\]

The yield of gas was calculated as moles while the liquid was calculated as grams

- Liquid yield

The liquid sample was injected in the GC-MS. The integration parameters were (initial Area reject “0”, initial peak width “0.125”, shoulder Detection “OFF”, initial threshold “15”). The peak areas of the target liquid products were converted to concentrations using calibration lines, which were made previously using standard solutions of the components.

- Example of liquid yield calculation

For example if the concentration of the component is equal to 1.03 X 10^{-4} g/ml and the amount of water is 54 mL when the molar feed ratio (steam to glycerol) is 6. The grams of the component can be calculated by multiplying the concentration by the milliliters of water (1.03 X 10^{-4} g/mL * 54 mL = 0.005562 g of the liquid component). The grams of glycerol in the feed is 46 g. the liquid yield can be calculated as grams of component per grams of glycerol (0.005562 g of the liquid component/ 46 g glycerol = 1.21 X 10^{-4} g/g).
Figure A-1: Calibration line of Hydroxyacetone

\[ y = 5 \times 10^8 x \]

\[ R^2 = 0.9992 \]
Figure A-2: Calibration line of 3-methoxy,1,2, propanediol

\[ y = 5 \times 10^{10}x \]

\[ R^2 = 0.9847 \]
Figure A-3: Calibration line of glycerol

$y = 2E+10x$

$R^2 = 0.993$
- **Gas yield**

  The volume fractions of the gas components were taken from the online GC. The volume fraction of the component was multiplied by the volumetric flow rate of the total gas. The final unit of the gas yield was mole of gas per gram of glycerol.

- **Example of gas yield calculation**

  The unit of time was considered as 1 min, therefor, the calculation was performed based on 1 min basis. For example for the hydrogen gas the volume fraction is 0.10875 and the total volumetric flow rate of gas is 305 cm$^3$/min. the volumetric rate of hydrogen will be $(0.10875 \times 305 = 33.17 \text{ cm}^3/\text{min} = 33.17 \text{ mol/min}$. if the molar feed ratio is 3 (steam to glycerol), which contains 63.01 g glycerol. The yield of hydrogen will be $(33.17/63.01 = 0.5264 \text{ mol/g})$.

- **Calculation of glycerol conversion**

  The glycerol conversion can be calculated as the difference between the initial and the final concentrations of glycerol divided by the initial concentration of glycerol.

  $$X_A = \frac{C_{Ai} - C_{Af}}{C_{Ai}}$$

  where:

  $X_A$: the glycerol conversion (g/g)

  $C_{Ai}$: initial concentration of glycerol (g/mL)

  $C_{Af}$: final concentration of glycerol (g/mL)
• **Example of glycerol conversion calculation**

If the feed molar ratio (steam to glycerol) is 6, the initial concentration of glycerol is 0.8519 g/mL. The final concentration of glycerol can be obtained from the peak area of glycerol using GC-MS, which can be converted to concentration using the calibration line of glycerol. If the final glycerol concentration is 0.5659 g/mL, the glycerol conversion will be:

\[
X_A = \frac{0.8519 - 0.5659}{0.8519} = 0.3356 \text{ (g/g)}
\]
APPENDIX (B)

- **Calculation of reaction rates**

  The reaction rates were calculated by the differentiation of the curve equation of the conversion versus the retention time, which gives the slop of the curve. The slop of the curve is equal to the reaction rate.

- **Example of calculating the reaction rate**

  At 275 °C:

  The fitness equation of the curve of conversion versus retention time is:

  \[ Y = -1 \times 10^{-5} X^2 + 0.0031 X + 0.3551 \]

  Where:

  \( Y \) = glycerol conversion  

  \( X \) = retention time  

  By taking the differentiation of the equation

  \[ \frac{dy}{dx} = \text{Slop} = \frac{dX}{dr} = \text{reaction rate} = 2 (-1 \times 10^{-5})X + 0.0031 \]

  At retention time of 0 min the reaction rate will equal 0.0031 min\(^{-1}\)
• **The determination of kinetic parameters using NLREG software.**

The following formula was used for the regression of the kinetic parameters \( (A, E, n) \)

\[
-r_A = \frac{dX_A}{dt} = A e^{-E/RT} \left( 1 - X_A \right)^n
\]

The following code was used in the NLREG software for determining the kinetic parameters:

```plaintext
Title "Rate Model of the Hydrothermal liquifaction of glycerol";

variable r, T, XA;

parameter A, E, n;

function \( r = A \times \exp \left( -\frac{E}{8.314 \times T} \right) \times (1 - X_A)^n \);

plot;

data;

where:

\( R = 8.314 \)

\( X_A = \) is the glycerol conversion

\[
-r_A = \frac{dX_A}{dt}
\]

The run of the software is shown in the next page

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Figure C-1: The Run of NLREG software

--- Final Results ---

NLREG version 6.5
Copyright (c) 1992-2000 Phillip H. Sherrod.

Rate Model of the Hydrothermal liquefaction of glycerol
Number of observations = 11
Maximum allowed number of iterations = 500
Convergence tolerance factor = 1.00000E-010
Stopped due to: Relative function convergence.
Number of iterations performed = 29
Final sum of squared deviations = 1.6430004E-006
Final sum of deviations = -3.5554345E-008
Standard error of estimate = 0.000453306
Average deviation = 0.000328203
Maximum deviation for any observation = 0.000687073
Proportion of variance explained (R^2) = 0.9004 (90.04%)
Adjusted coefficient of multiple determination (Ra^2) = 0.8755 (87.55%)
Durbin-Watson test for autocorrelation = 1.250
Analysis completed 31-May-2014 08:23. Runtime = 0.49 seconds.

--- Descriptive Statistics for Variables ---

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--- Calculated Parameter Values ---

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--- Analysis of Variance ---

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