I&EC research
Industrial & Engineering Chemistry Research

ARTICLE

pubs.acs.org/IECR

Catalytic Thermochemical Conversion of Glycerol to Simple and Polyhydric Alcohols Using Raney Nickel Catalyst

Randy L. Maglinao[†] and B. Brian He[*]

Biological and Agricultural Engineering, University of Idaho, Moscow, Idaho 83844, United States

ABSTRACT: The crude glycerol from biodiesel production possesses low economic values and alternative ways of converting it to valuable chemicals are needed to sustain the biodiesel industry. This study aimed to investigate the production of primary alcohols and propylene glycol from glycerol through a catalytic thermochemical process without an external supply of hydrogen. The effects of reaction time, water to glycerol ratio, and doses of catalyst on glycerol conversion and alcohol yields were investigated using a batch pressure reactor and Raney nickel catalyst. The presence of alcohols and gases in the products confirmed that hydrogen was produced and was utilized in the formation of propylene glycol through hydrogenolysis. Ethanol and propylene glycol yields of up to 10.4 ± 0.2 and 33.2 ± 1.4 mol %, respectively, were observed. It was also concluded that ethanol is formed through hydrogenolysis of propylene glycol and its yield improves at extended reaction time and increased initial water content of the feed.

INTRODUCTION

Biodiesel is an alternative fuel produced by transesterification of an alcohol and a plant oil or animal fat. With the introduction of the next generation feedstocks such as jatropha and algae, it is predicted that the biodiesel production will be tripled by 2020.[1] However, along with the success of the biodiesel industry, the global production of glycerol, a byproduct of biodiesel production, also increased. The rapid increase in crude glycerol greatly affected the market price of glycerol, which dropped from \$0.43/kg in 2003 to \$0.18/kg in 2010 for pure glycerol, and to only \$0.02/kg for crude glycerol.[2,3] Although various products can be derived from glycerol for different applications, the demand for these products is still not enough to handle the increasing supply of crude glycerol. Thus, new technologies of producing valuable products with relatively large markets from glycerol are urgently needed.

Converting glycerol to primary alcohols such as ethanol and methanol, and polyhydric alcohols such as propylene glycol, through a thermochemical process is a potential way to increase the value of crude glycerol. Thermochemical processes can use heat only to break down organic matter into desired products. The problem with thermochemical processes is, however, the low selectivity toward desired products. Conventional thermochemical conversions involve high operating temperatures. Such conditions also favor further decomposition and repolymerization of the desired products to undesired compounds such as char and tar. This problem can be avoided if appropriate catalysts are employed to increase the selectivity and efficiency of the chemical process. Catalysts have the capability to decrease the energy required by lowering the activation energy of a chemical reaction and to increase the selectivity by breaking specific chemical bonds to produce the intended products. It is logical, therefore, to apply catalysts to the thermochemical decomposition of glycerol to improve the selectivity toward the desired alcohol products.

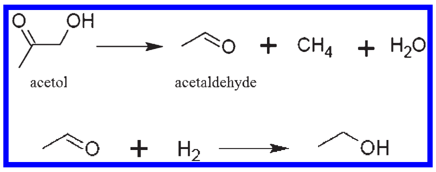
Metal catalysts have been used in converting glycerol to polyhydric alcohols and hydrogen through hydrogenolysis and reforming, respectively. Ethylene glycol and propylene glycol are examples of useful polyhydric alcohols that can be derived from glycerol using metal catalysts. However, the production of propylene glycol from glycerol has received more attention and is mostly researched as compared to the production of other polyhydric alcohols such as 1,3-propanediol and ethylene glycol.[4−8] Propylene glycol is also the preferred product rather than ethylene glycol because of the less desired toxic characteristics of ethylene glycol. Suppes and co-workers performed research on the conversion of glycerol to propylene glycol and patented a process of selectively producing propylene glycol.[9−11] In producing propylene glycol, one of the primary hydroxyl groups in glycerol is selectively removed through hydrogenolysis using a metal catalyst. There are two theories in hydroxyl group selective removal, namely, the acetol pathway and the glyceraldehyde pathway,[4] of which the acetol pathway has been the most widely investigated. According to the theory of acetol pathway, the secondary hydroxyl group of glycerol is dehydrated to acetol followed by catalytic hydrogenation to propylene glycol. Therefore, hydrogen presence in the system is a must.

In addition to polyhydric alcohols, ethanol and methanol are other valuable products that can be derived from glycerol. In producing propylene glycol from glycerol, degradation of acetol and propylene glycol to other products has been reported.[10] However, secondary reactions such as the decomposition of acetol and propylene glycol can be utilized in a favorable way to produce valuable compounds in addition to propylene glycol. Wojcik and Adkins[12] used hydrogenolysis to prepare specific hydrocarbons from long-chain alcohols. In their process, the carbon with the hydroxyl group is cleaved at the carbon to carbon bond from the long-chain alcohol, producing a hydrocarbon, methane, and water. Based on this concept, further hydrogenolysis of acetol could lead to ethanol formation, as shown in Scheme 1.

Theoretically, hydrothermal cracking of glycerol, i.e., the high-temperature reaction of glycerol with water, can produce

Received: December 28, 2010
Accepted: March 31, 2011
Revised: March 30, 2011
Published: March 31, 2011

Scheme 1. Hydrogenolysis of Acetol to Ethanol



methanol. The advantage of co-producing these low boiling point alcohols along with propylene glycol is that they can be easily separated through distillation. Still, to produce these alcohols from glycerol through this pathway, hydrogen is needed.

Hydrogen is essential for hydrogenolysis of glycerol to occur, but it can come from the reactant itself. Studies have reported successful production of hydrogen from glycerol.[13−16] Several processes have been employed to convert glycerol to hydrogen, including steam reforming, autothermal reforming, and aqueous-phase reforming.[17−19] Steam reforming uses steam to react with an organic compound to produce carbon dioxide and hydrogen.[20−23] Autothermal reforming is the combination of steam reforming and oxidation of glycerol.[18] This is achieved by preheating a glycerol/water mixture at 300 ± 10 °C and feeding the vaporized mixture with lean air to a reactor with a catalyst.[18] The heat produced by the oxidation of glycerol is used by the steam reforming reactions to produce hydrogen, and such a system reduces the overall energy requirement of the process. The above-mentioned processes are typically operated at temperatures over 400 °C at atmospheric pressure. On the other hand, aqueous-phase reforming operates at higher pressures (∼2.5 MPa) but at relatively lower temperatures (∼220 °C).[19,24] These conditions are similar to those required for the hydrogenolysis of glycerol to propylene glycol. If hydrogen can be produced from glycerol at conditions where hydrogenolysis occurs, it can be hypothesized that glycerol can undergo hydrogenolysis to catalytically produce valuable primary and polyhydric alcohols without external hydrogen supply, which is an ideal process with significant economic advantages.

Currently, there is no in-depth investigation reported on converting glycerol to alcohols using a catalytic thermochemical process without external hydrogen supply. This study aimed to investigate the production of primary alcohols and propylene glycol through catalytic thermochemical process with no external hydrogen supply and to determine the favorable conditions for maximizing the same.

■ METHODS

Materials and Equipment. Reagent grade glycerol (BDH distributed by VWR, West Chester, PA) with 99.5% purity was used throughout the experiments in our first phase research to avoid the interference of impurities found in crude glycerol from biodiesel. Active Raney nickel catalyst was purchased from Sigma-Aldrich (St. Louis, MO) and used. Standards of methanol, ethanol, *n*-propanol, 2-propanol, propylene glycol, acetol, and glycerol were prepared for calibrating the gas chromatograph. Methanol (99.8% purity), acetone (99.7%), and 2-propanol (99.99%) were purchased from EMD (Gibbstown, NJ). Acetol (95%) and propylene glycol (99.5%) was purchased from Alfa Aesar (Ward Hill, MA), and 1-propanol (99.9%, J.T. Baker) was purchased from VWR (West Chester, PA). Ethanol was bought from AAPER, Alcohol and Chem. Co. (Shelbyville, KY). Diethel ether (99.0%, BDH) was purchased from VWR.

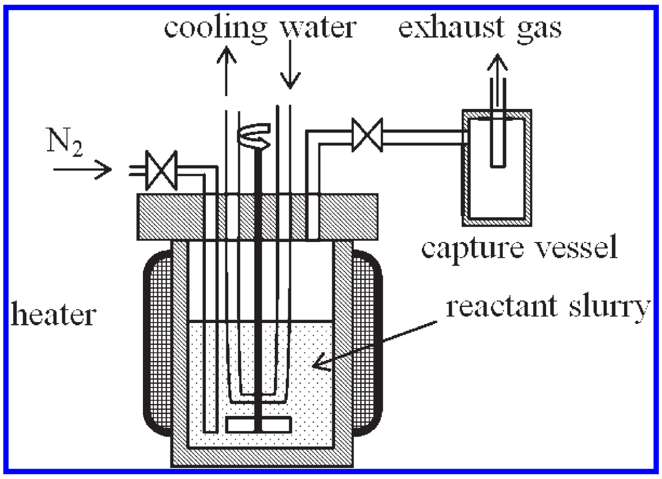


Figure 1. Schematic diagram of the reactor system used in the study.

A 300 mL pressure reactor from Parr Instruments (Moline, IL) was used for conducting the experiments in this study. The reactor is capable of handling up to 20 MPa (3000 psig) of pressure and 350 °C of temperature. The reactor is equipped with a controller to regulate and monitor the operating temperature, pressure, and agitation motor speed. A capture vessel (a vacuum flask) was installed along the exhaust line to capture any condensables escaping during removal of gases after reaction (Figure 1).

Analysis of Samples. An Agilent 6890N gas chromatograph with a flame ionization detector (FID) was used for analyzing the primary and polyhydric alcohols and residual glycerol. For this purpose, the column was a 30 m by 0.32 mm inside diameter DB-wax column with 0.5 μm film thickness. A 5 g amount of the sample and 100 mg of the internal standard (diethyl ether) were mixed and deionized water was added to make up 10 mL of solution. The solution was then diluted by adding HPLC grade acetone to the solution to make up 50 mL of the final solution. The oven temperature was programmed to begin at 30 °C for 10 min before ramping to 220 °C at 30 °C/min with a final hold time of 13 min. Samples of 1 μL were injected with a split ratio of 60:1 and with an inlet port temperature of 250 °C. The inlet port temperature was set slightly lower than 290 °C to prevent any glycerol decomposition. Slight and complete decomposition below its boiling point have been reported.[25,26] Helium was used as the carrier gas with its pressure programmed to start at 48 kPa (7 psig) with a holding time of 10 min and then ramped to 103 kPa (15 psig) at 34.5 kPa/min (5 psi/min) to increase the flow rate of glycerol. The FID was set at 300 °C with a nitrogen makeup gas of 30 mL/min.

Experimental Procedures. Experiments of catalytic thermochemical conversion of glycerol to alcohols were conducted using the batch reactor as described in Figure 1. Glycerol, water, and the metal catalyst were mixed in the reactor. Nitrogen gas was used to purge the headspace of the reactor for 1 min to remove oxygen. The reactor was then heated to 230 °C and maintained at the set reaction time. Upon the completion of the reaction, the reactor was cooled to room temperature by the equipped cooling mechanism. The noncondensable gases formed during the reaction were removed through the exhaust valve and vented out. The final weight of the liquid product and catalyst was determined by measuring the reactor with the product (liquid and catalyst) and taking the difference of the premeasured weight of the empty reactor. The liquid product collected from the reactor was separated from the catalysts using a vacuum filtration at constant vacuum pressure of 16.9 kPa (5 in.Hg).

Table 1. Conversion Rates of Glycerol and Yields of Gases at 230 °C Using Raney Nickel Catalyst[a]

reaction time (min)	WGMR[b]	rate of conversion (mol %)	pressure diff[c] (MPa)	yield of gas (mol %)
15	1:1	91.1 ± 2.3	2.314 ± 0.158	13.1 ± 1.7
45	1:1	98.6 ± 0.2	3.240 ± 0.137	18.2 ± 0.7
75	1:1	99.6 ± 0.5	4.904 ± 0.458	30.9 ± 3.9
105	1:1	99.9 ± 0.1	5.216 ± 0.123	33.9 ± 0.2
45	7:3	99.9 ± 0.1	3.493 ± 0.258	35.5 ± 2.8
45	3:7	95.3 ± 0.2	2.893 ± 0.042	12.3 ± 0.3

[a] Each treatment was conducted in triplicate. Data are presented as *average* ± *standard* deviation. [b] WGMR = water to glycerol mass ratio in the feed. [c] Measured at 30 °C before and after the reaction.

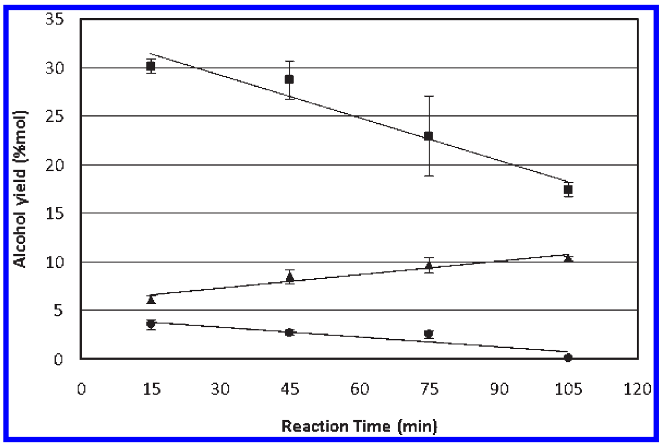


Figure 2. Alcohol yields versus reaction time. Each treatment was conducted in triplicate, and the error bars represent the standard deviations. The symbols in the plot are as follows: ■, propylene glycol; ▲, ethanol; ●, acetol.

Whatman Qualitative No. 2 filter paper (8 μm pore size) was used throughout the study.

The amount of gas evolved was estimated using the modified Benedict–Webb–Rubin gas equation for real gas mixtures (eq 1). The intermediate parameters were evaluated on the basis of the critical parameters such as temperature, density, and acentric factor of its pure species as described by Starling and Han.[27] The difference in the pressure of the reactor before and after the reaction at the same temperature, specifically at 30 °C, was assumed to represent the contribution of gas formed. Thus, this pressure difference was used in the gas equation. Also, it was assumed that carbon dioxide was the dominant gas formed due to the inability to determine the composition of the gaseous products in this study.

Benedict–Webb–Rubin equation of state:

$$P = \rho RT + \left(B_o RT - A_o - \frac{C_o}{T^2} + \frac{D_o}{T^3} - \frac{E_o}{T^4}\right)\rho^2 + \left(bRT - a - \frac{d}{T}\right)\rho^3 + \alpha\left(a + \frac{d}{T}\right)\rho^6 + \frac{c\rho^3}{T^2}(\beta + \gamma\rho^2)\exp(-\gamma\rho^2) \qquad (1)$$

where P is the absolute pressure, Pa; T is the absolute temperature, K; ρ is the gas density, mol/m^3; R is the gas constant, 8.314 m^3 Pa/(mol/K); and A_o, B_o, C_o, D_o, E_o, a, b, c, d, α, β, and γ are intermediate parameters.

The experimental data were processed and analyzed according to the following definitions:

$$\text{glycerol conversion rate}/(\text{mol }\%) = \frac{n_{\text{i,gly}} - n_{\text{f,gly}}}{n_{\text{i,gly}}} \times 100$$

where $n_{\text{i,gly}}$ is the moles of glycerol before the reaction (initial quantity) and $n_{\text{f,gly}}$ is the moles of glycerol after the reaction (residual quantity).

$$\text{yield of alcohol j}/(\text{mol }\%) = \frac{n_{\text{j,p}}}{n_{\text{i,gly}}} \times 100$$

where $n_{\text{j,p}}$ is the moles of compound j in the product and j = methanol, ethanol, or propylene glycol.

$$\text{yield of gases}/(\text{mol }\%) = \frac{n_{\text{gas}}}{n_{\text{c,feed}}} \times 100$$

where n_{gas} is the moles of gases formed and $n_{\text{c,feed}}$ is the moles of initial carbon in the feed.

■ EXPERIMENTAL RESULTS

Effect of Reaction Time. Table 1 summarizes the experimental results of the overall glycerol conversion and gaseous products at different reaction time and water to glycerol mass ratio. Water to glycerol mass ratio, WGMR, is defined as the ratio of water and glycerol used in the feed. It shows that at 45 min and longer into the reaction, more than 98 mol % glycerol was converted (Table 1). In addition to liquid products, gaseous compounds were also formed during the reaction. The results also show that more gaseous compounds were formed at extended reaction time. Pairwise analysis on the pressure readings using the least significant difference test (LSD test) at 95% confidence level by the Statistical Analysis System software (SAS Institute Inc., Cary, NC) suggested that there were significant differences in the amount of gases formed from 15 to 75 min while no differences were observed thereafter.

Propylene glycol and ethanol were the major liquid products of the process. Other simple alcohols, such as methanol and 2-propanol, were also produced but in small amounts. Acetol, which is the proposed intermediate compound for producing propylene glycol and ethanol, was also present in the liquid product. The alcohol yields against the reaction time are shown in Figure 2. Ethanol yield increased from 6.1 ± 0.4 to 10.4 ± 0.2 mol % while propylene glycol decreased from 30.2 ± 0.7 to 17.4 ± 0.7 mol %. Similarly to that of propylene glycol, the yield of acetol dropped at extended reaction time.

Table 2. Alcohol Yields at Different Water to Glycerol Mass Ratios[a]

	for given water to glycerol mass ratio		
alcohols	7:3	1:1	3:7
methanol	3.919 ± 0.645	2.658 ± 0.463	2.115 ± 0.125
2-propanol	0.149 ± 0.024	0.547 ± 0.425	0.065 ± 0.006
ethanol	10.911 ± 0.387	8.519 ± 0.733	7.249 ± 0.326
n-propanol	0.456 ± 0.012	0.388 ± 0.028	0.380 ± 0.012

[a] Each treatment was conducted in triplicate. Data are presented as *average* ± *standard* deviation.

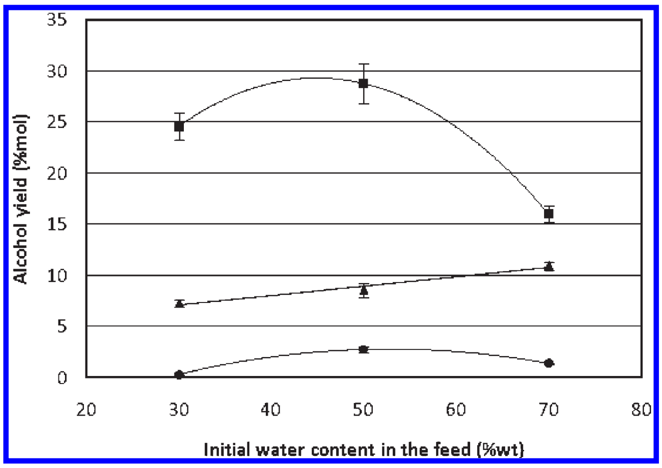


Figure 3. Alcohol yields at different initial amounts of water in the feed. Each treatment was conducted in triplicate, and the error bars represent the standard deviations. The symbols in the plot are as follows: ■, propylene glycol; ▲, ethanol; ●, acetol.

Effect of the Initial Amount of Water. Water is an essential ingredient in producing hydrogen from glycerol through the water-gas shift reaction. Thermodynamic analysis on steam reforming of glycerol showed that more hydrogen can be produced at higher water to glycerol mass ratios.[20,21] For example, Luo et al.[19] obtained higher hydrogen yields at 5 wt % glycerol than that at 10 wt % in water solutions at 220 °C. In addition, water also helps maintain a homogeneous temperature profile throughout the liquid-phase reaction and inhibits chemical dehydration of glycerol to unwanted intermediates and products in hydrogenolysis.[10] Table 2 summarizes the yields of primary alcohols at different water to glycerol mass ratios. The ethanol yield increased as the water content in the solution increases. A similar trend was observed for methanol and gaseous products. On the other hand, less propylene glycol was produced at higher water to glycerol mass ratios (Figure 3). Comparing the cases of 7:3 and 1:1 of water to glycerol mass ratios, the decreasing trend of propylene glycol can be attributed to the production of more gaseous compounds as manifested by the increasing operating pressures (Table 1). However, this trend does not hold when the initial amount of water was further decreased. As shown in Figure 3, propylene glycol peaked near the water to glycerol mass ratio of 1:1 but the amount of gaseous products still kept decreasing as shown in Table 1.

Effect of Catalyst. Figure 4 summarizes the yield trends of alcohols at different amounts of nickel catalysts at 230 °C for 45 min of reaction and 1:1 water to glycerol mass ratio. Increasing the doses of the catalysts resulted in the increases of the yields of both ethanol and propylene glycol. The yield of propylene glycol followed a quadratic path and reached its peak at 6.4 wt % nickel catalyst.

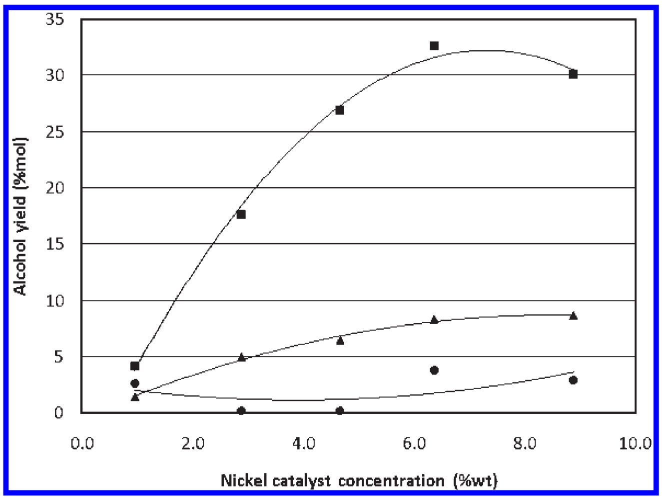


Figure 4. Alcohol yields of at different doses of nickel catalyst. The symbols in the plot are as follows: ■, propylene glycol; ▲, ethanol; ●, acetol.

The decrease in the alcohol yields from using 6.4−8.9 wt % suggest that increasing the concentration of nickel catalyst to above 6.4 wt % would not significantly improve the yields of propylene glycol and ethanol under the studied conditions. The overall conversion of glycerol and formation of gases were also affected by the dosage of catalyst applied. The glycerol conversion rate increased from 49.04 to 98.59 mol % and the gas yields increased from 3.69 to 17.60 mol % when increased concentrations of nickel catalyst were applied (Table 3).

■ DISCUSSION

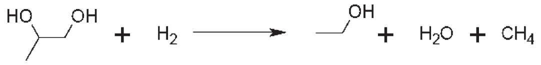
The presence of significant amounts of ethanol and propylene glycol in the liquid product confirms that hydrogenolysis had occurred in the catalytic thermochemical conversion of glycerol. The formation of gaseous products also supported the authors' hypothesis that a portion of glycerol has been converted to hydrogen and utilized simultaneously in the production of alcohols. Although the presence of hydrogen was unconfirmed due to a lack of tests for this study, we have no other explanation for the formation of gases other than the aqueous-phase reformation of glycerol that occurs at the same conditions as in this study, which typically produces carbon dioxide and hydrogen.[24] Methanol and *n*-propanol were also produced in the process. The low yields of methanol and *n*-propanol, however, suggest that the conditions explored in the study favor other competing reactions such as formation of propylene glycol.

Effect of Operating Parameters. The yield of propylene glycol was significantly affected by the parameters tested in this study. At 230 °C, the highest yield of propylene glycol was observed at the shortest reaction time, i.e., 15 min. Extending the reaction time resulted in degradation of propylene glycol to other products as indicated by the increasing yields of ethanol and gases (Table 1 and Figure 2). Maris and Davis[6] also observed a decreasing trend in propylene glycol yields when the reaction time was prolonged. In their study, the yield of propylene glycol peaked at the same time when almost all of the glycerol has been converted to products and then the yield continuously decreased thereafter. Although it took 100 min of reaction to achieve a conversion rate of glycerol greater

Table 3. Conversion Rates of Glycerol and Gas Yields at 230 °C for 45 min and 1:1 Water to Glycerol Mass Ratio Using Raney Nickel Catalyst

catalyst concentration (wt %)	glycerol conversion rate (mol %)	yield of gas (mol %)	catalyst concentration (wt %)	glycerol conversion rate (mol %)	yield of gas (mol %)
1.0	49.04	3.69	6.4	95.75	16.36
2.9	77.19	8.31	8.9	98.59	17.60
4.7	87.95	12.12			

Scheme 2. Hydrogenolysis of Propylene Glycol to Ethanol



than 90 mol % in the study of Maris and Davis, almost all glycerol has been converted to products after 45 min in our study, as summarized in Table 1. Comparing it to the results from the study of Maris and Davis,[6] it can be concluded that the production of propylene glycol had reached its maximum at or earlier than 15 min. The degradation of propylene can also be explained by the increase of gaseous products. The inverse trend between the molar conversion of propylene glycol and gaseous products at different reaction time supports this claim (Table 1 and Figure 2). One of the possible reactions that lead to the formation of gases is the hydrocracking of propylene glycol to ethylene glycol and methane as suggested by Chiu and co-workers.[10]

On the other hand, increasing the water to glycerol mass ratio favored more the reformation reactions than the hydrogenolysis to propylene glycol. This explains the low yield of propylene glycol and the high yield of gaseous products at 7:3 water to glycerol mass ratio (Table 1 and Figure 3). Though water thwarted the yield of the process toward propylene glycol at higher water to glycerol mass ratios, water was still essential in inhibiting other reactions such as dehydration of the intermediates to unwanted compounds. As shown in Figure 3, the yield of propylene glycol decreased as the water content in the reactant mixture was decreased from 50 to 30 wt %.

Ethanol production was also affected by the operating parameters but in a different way. The yield of ethanol increased as the reaction time increased while it decreased at lower water to glycerol mass ratios. As shown in Scheme 1, ethanol was produced from hydrogenolysis of acetol. However, the results of this study suggest that ethanol may have been produced from different reaction routes. The observed decreasing trend of acetol was caused by the decreasing of glycerol in the reactant rather than being consumed in a reaction to form ethanol. More than 98 mol % glycerol had already been converted at 45 min of reaction (Table 1). Thus, there was no more glycerol to replenish acetol that was then further converted to propylene glycol beyond 45 min. Instead of acetol, propylene glycol reformation to ethanol could have occurred. Following the same reaction mechanism discussed by Wojcik and Adkins,[12] hydrogenolysis of propylene glycol can also produce ethanol, as shown in Scheme 2.

However, there was no direct correlation between the ethanol produced and the propylene glycol degraded (Figure 2). Other reactions such as reformation of propylene glycol to hydrogen and carbon monoxide may have competed with the reaction suggested in Scheme 2. Moreover, possible reformation of ethanol to gaseous products may have occurred while it was produced simultaneously.

The initial water content in the reactant mixture affected ethanol yield favorably by the reformation reactions at higher water to glycerol mass ratios. The trend observed in Figure 3 reinforces this hypothesis, in which more ethanol and gases but less propylene glycol were produced.

In the case of methanol formation, unlike the other alcohols, no significant change in methanol yield in the liquid product was observed under different operating conditions. This may lead to the conclusion that methanol was a minor intermediate product or possibly already in equilibrium with all other compounds present in the system.

Effect of Catalyst. The application of Raney nickel catalysts was effective in providing the activated sites for the reactions of producing hydrogen and converting glycerol to propylene glycol and ethanol. The direct relationship between the catalyst doses and the glycerol conversion to propylene glycol, ethanol, and gaseous products indicates this inference. A higher dose of catalyst increases the pore surfaces and the active sites, thus improving the conversion rate of glycerol. The yield of acetol was affected by the doses of catalyst. At the low application rate of 1.0 wt % catalysts, the acetol yield was higher than the acetol yields at 2.9 and 4.7 wt % catalyst. It is the authors' interpretation that there were not enough reactive sites to promote hydrogenation of acetol to propylene glycol; in turn, not all of the acetol produced through dehydration of glycerol was consumed to the formation of propylene glycol. By increasing the mass of the catalysts, the rate of hydrogenation reactions increased, which caused immediate consumption of acetol and led to the decrease of acetol in the liquid product.

■ CONCLUSIONS

The results of this study confirmed that propylene glycol and ethanol can be produced from glycerol in the absence of external hydrogen supply. Hydrogen was produced under the operating conditions as explored in this study. Higher yield for propylene glycol was observed at shorter reaction time and water to glycerol mass ratio of 1:1. Water is essential in inhibiting side reactions, such as dehydration of intermediate compounds, in propylene glycol production. Water also promotes additional reformation reactions that make propylene glycol degrade to other products. On the other hand, competing with these reactions is the hydrogenolysis of propylene glycol to ethanol. Thus, longer reaction time and increased initial water results in higher ethanol yield.

On the basis of the results of this study, it can be proposed that the reactions of glycerol reformation to hydrogen and hydrogenolysis to propylene glycol via the acetol pathway occur simultaneously in the catalytic thermochemical conversion of glycerol. These reformation reactions include carbon-to-carbon and hydrogen—carbon bond cleavages, which produce carbon monoxide and hydrogen, and the water-gas shift reaction, which produces hydrogen. The hydrogen produced initiates immediately the hydrogenation of acetol to propylene glycol. On the basis of the results of the study, it can be concluded that ethanol is produced through the hydrogenolysis of propylene glycol instead of acetol in the system.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: bhe@uidaho.edu.

Notes

†E-mail: rmaglinao@vandals.uidaho.edu.

■ ACKNOWLEDGMENT

This study was supported financially by the National Institute of Advanced Transportation Technology (NIATT) and the Biological and Agricultural Engineering Department at the University of Idaho. The authors also express their gratitude to Dr. Joe Thompson for his great assistance in the study. Valuable discussions with and advice from Dr. Peter Griffiths (professor of Chemistry), Dr. Jon Van Gerpen (professor of Biological and Agricultural Engineering), and Dr. Roger Korus (professor of Chemical Engineering) are also gratefully acknowledged.

■ REFERENCES

(1) Biofuels Market to Triple by 2020, Jun. 15, 2009. *Biodiesel Magazine*, http://www.biodieselmagazine.com (accessed Aug. 7, 2010).

(2) Lefebvre, B. Glycerine (US Gulf) ICIS Pricing, June 2010, ICIS Pricing, www.icispricing.com (accessed Dec. 20, 2010).

(3) Hartenbower, B.; French, W.; Hernandez, R.; Licha, M.; Benson, T. Biogas Production Using Glycerol, the Biodiesel By-Product, as the Carbon Source, http://aiche.confex.com/aiche/2006/techprogram (accessed Apr. 25, 2010), The 2006 Annual Meeting: Fuels and Petrochemical Division.

(4) Allhanash, A.; Koszhevnikova, E.; Kozhevnikov, I. Hydrogenolysis of Glycerol to Propanediol over Ru:Polyoxymetalate Bifunctional Catalyst. *Catal. Lett.* **2008**, *120*, 307.

(5) Huang, Z.; Cui, F.; Kang, H.; Chen, J.; Zhang, X.; Xia, C. Highly Dispersed Silica-Supported Copper Nanoparticles Prepared by Precipitation-Gel Method: A Simple but Efficient and Stable Catalyst for Glycerol Hydrogenolysis. *Chem. Mater.* **2008**, *20*, 5090.

(6) Maris, E.; Davis, R. Hydrogenolysis of Glycerol over Carbon-supported Ru and Pt Catalysts. *J. Catal.* **2007**, *249*, 328.

(7) Meher, L.; Gopinath, R.; Naik, S.; Dalai, A. Catalytic Hydrogenolysis of Glycerol to Propylene Glycol over Mixed Oxides Derived from a Hydrotalcite-type Precursor. *Ind. Eng. Chem. Res.* **2009**, *48*, 1840.

(8) Miyazawa, T.; Koso, S.; Kunimoro, K.; Tomishige, K. Glycerol Hydrogenolysis to 1,2-Propanediol Catalyzed by a Heat-Resistant Ion-Exchange Resin Combined with Ru/C. *Appl. Catal., A* **2007**, *329*, 30.

(9) Chiu, C.; Dasari, M.; Suppes, G.; Sutterlin, W. Dehydration of Glycerol to Acetol via Catalytic Reactive Distillation. *AIChE J.* **2006**, *52*, 3543.

(10) Chiu, C.; Tekeei, A.; Ronco, J.; Banks, M.; Suppes, G. Reducing Byproduct Formation during Conversion of Glycerol to Propylene Glycol. *Ind. Eng. Chem. Res.* **2008**, *47*, 6878.

(11) Suppes, G.; Sutterlin, W. Method of Producing Lower Alcohols from Glycerol. *World Intellectual Property Organization*, WO 2007/053705 A2, 2007.

(12) Wojcik, B.; Adkins, H. Hydrogenolysis of Alcohols to Hydrocarbons. *J. Am. Chem. Soc.* **1933**, *55*, 1293.

(13) Hirai, T.; Ikenaga, N.; Miyake, T.; Suzuki, T. Production of Hydrogen by Steam Reforming of Glycerin on Ruthenium Catalyst. *Energy Fuels* **2005**, *19*, 1761.

(14) Slinn, M.; Kendall, K.; Mallon, C.; Andrews, J. Steam Reforming of Bio-diesel By-product to Make Renewable Hydrogen. *Bioresour. Technol.* **2008**, *99*, 5851.

(15) Valliyappan, T.; Ferdous, D.; Bakhshi, N. Production of Hydrogen and Syngas via Steam Gasification in a Fixed-Bed Reactor. *Top. Catal.* **2008**, *49*, 59.

(16) Zhang, B.; Tang, X.; Li, Y.; Xu, Y.; Shen, W. Hydrogen Production from Steam Reforming of Ethanol and Glycerol over Ceria-Supported Metal Catalysts. *Int. J. Hydrogen Energy* **2007**, *32*, 2367.

(17) Buffoni, I.; Pompeo, F.; Santori, G.; Nichio, N. Nickel Catalysts Applied in Steam Reforming of Glycerol for Hydrogen Production. *Catal. Commun.* **2009**, *10*, 1656.

(18) Dauenhauer, P.; Salge, J.; Schmidt, L. Renewable Hydrogen by Autothermal Steam Reforming of Volatile Carbohydrates. *J. Catal.* **2006**, *244*, 238.

(19) Luo, N.; Fu, X.; Cao, F.; Xiao, T.; Edwards, P. Glycerol Aqueous Phase Reforming for Hydrogen Generation over Pt Catalysts—Effect of Catalyst Composition and Reaction Conditions. *Fuel* **2008**, *87*, 3483.

(20) Adhikari, S.; Fernando, S.; Gwaltney, S. R.; Filip To, S. D.; Bricka, R. M.; Steele, P.; Haryanto, A. A Thermodynamic Analysis of Hydrogen Production by Steam Reforming of Glycerol. *Int. J. Hydrogen Energy* **2007**, *32*, 2875.

(21) Adhikari, S.; Fernando, S.; Haryanto, A. A Comparative Thermodynamic and Experimental Analysis on Hydrogen Production by Steam Reforming of Glycerin. *Energy Fuels* **2007**, *21*, 2306.

(22) Adhikari, S.; Fernando, S.; Haryanto, A. Production of Hydrogen by Steam Reforming of Glycerin over Alumina-Supported Metal Catalysts. *Catal. Today* **2007**, *129*, 355.

(23) Adhikari, S.; Fernando, S.; To, S.; Bricka, R.; Steele, P.; Haryanto, A. Conversion of Glycerol to Hydrogen via a Steam Reforming Process over Nickel Catalysts. *Energy Fuels* **2008**, *22*, 1220.

(24) Wen, G.; Xu, Y.; Ma, H.; Xu, Z.; Tian, Z. Production of Hydrogen by Aqueous-Phase Reforming of Glycerol. *Int. J. Hydrogen Energy* **2008**, *33*, 6657.

(25) Hodgman, C.; Weast, R. S.; Selby, S. *CRC Handbook of Chemistry and Physics: A Ready-Reference Book of Chemical and Physical Data*, 44th ed.; Chemical Rubber: Cleveland, OH, 1962.

(26) Miall, L. *A New Dictionary of Chemistry*, 3rd ed.; InterScience: New York, 1961.

(27) Starling, K.; Han, M. Thermo Data Refined for LPG—14. Mixtures. *Hydrocarbon Process. (1966–2001)* **1972**, *51*, 129–132.