

Conversion of glycerol waste from biodiesel plant to high-value product

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Abstract: Glycerol is waste from biodiesel production processes in which glycerol amounts to about 10 wt% of the total biodiesel produced. Currently, many researchers have attempted to develop the process for utilization of glycerol as a potential source of biochemicals, rather than as a waste. This research proposal aims to develop the conversion process to produce high-value chemical i.e. 1,2-propanediol (1,2-PDO) through catalytic hydrogenolysis reaction. The catalytic hydrogenolysis of glycerol was studied at several operating conditions with the presence of metal catalysts. 35%Cu/ γ -Al₂O₃ was prepared and evaluated in this work. Liquid products were intensively analyzed to understand the influences of catalyst and operating parameters on the product characteristics. Moreover, the characterization of synthesized metallic catalysts were evaluated using X-ray diffraction (XRD), temperature-programmed reduction with hydrogen (H₂-TPR), and N₂ sorption to study the relationship between their catalytic activity and physical-chemical properties. 35%Cu/ γ -Al₂O₃ with oven-drying method was the suitable catalyst for glycerol hydrogenolysis. It was observed that the reaction at 240°C for 5 hours under a hydrogen pressure of 50 bar with catalyst loading of 6wt% gave the maximum 1,2-PDO yield of 80.16% and selectivity of 85.44%.

Keywords: Glycerol; Hydrogenolysis; Catalyst; 1,2-Propanediol.

1. Introduction

Nowadays, the need of energy is increasing continuously, but the rate of new crude oil discoveries is declining. The limitation of fossil fuels has stimulated the development of alternative resources to substitute fossils [1-2]. Thailand is an agriculture-based country that has a variety of agricultural products. Therefore, biomass is a primary candidate as a potential substitute for petroleum for the production of fuels and chemicals. The current commercialized liquid biofuels in Thailand are bioethanol and biodiesel. Majority of ethanol production is produced by the fermentation of molasses which is a by-product of sugar industry, while biodiesel is obtained from the transesterification of palm oil. In Thailand, biodiesel is typically produced from vegetable oil or animal fat through the process called transesterification. The process uses vegetable oil or animal fat with an alcohol to form fatty acid methyl esters (FAMES). Glycerol is a waste from biodiesel plant. For every 1 ton of biodiesel that is manufactured, 110 kg of glycerol are produced. Therefore, glycerol is very interesting as a feedstock for the production of high value-added products due to its high availability and low price in the market [3].

Recently, potential glycerol derivatives have been widely considered in global market for the transformation of bioglycerol into value-added chemicals which can use in various industries. **Figure 1** shows commercially available products from glycerol via different routes. For example, propylene glycol or 1,2-propanediol (1,2-PDO) is a one of potential derivatives of glycerol which derived from catalytic hydrogenolysis route and widely applied in unsaturated polyester resins, functional fluids (e.g., antifreeze, de-icing and heat transfer), pharmaceuticals, foods, personal care, paints and animal feeds. Epichlorohydrin (ECH) is mainly used in the production of epoxy resins. Polyglycerols can be used for the manufacture of cosmetic ingredients, polymer additives, nutritional additives [4-5]. Conventionally, propylene glycol is produced from propylene oxide derived from petroleum resources.

The conventional methods for the propylene glycol production are normally non-catalytic processes at high temperature (150–250°C) and high pressure (>100 psi). Therefore, the production of propylene glycol from bio-derived glycerol is attractive [6].

The transformation of glycerol to derivatives has been widely investigated. From previous researches, it was found that operating conditions and catalysts affected on glycerol derivative products. For example, Guo et al. [7] studied the catalytic efficiency of Cu catalysts on various supports (γ -Al₂O₃, HY zeolite, 13X zeolite, HZSM-5 zeolite, H β zeolite) for the selective hydrogenolysis of glycerol to propanediols. They found that Cu supported on γ -Al₂O₃ with metal loading of 2.7 mmol/g of support at 300°C showed the best catalytic performance for production of propylene glycol and presented a 97% selectivity to propanediols with a 50% glycerol conversion under mild reaction conditions (220°C, 1.5 MPa initial H₂ pressure, 10 h, Cu/glycerol molar ratio 3:100) [7]. Hirunsit et al. [8] investigated the hydrogenolysis of glycerol into 1,2-propanediol (1,2 PD) over Cu/ γ -Al₂O₃ with 35% loading of Cu on gamma-alumina as catalyst. The results showed that these conditions led to high selectivity (93.3%) and yield (56.9%) for 1,2-propanediol, and high glycerol conversion rate (61%) [8]. Ma and co-workers studied the influence of Re addition to Ru catalyst during glycerol hydrogenolysis. They found that Re could promote the activity and the selectivity for production of propanediols due to the dispersion of Ru on support was improved [9].

This research work aims to develop the process and catalyst for conversion of glycerol waste to high-value product. In this work, glycerol was converted to high-value chemical i.e. propylene glycol (1,2-propanediol, 1,2-PDO) by catalytic hydrogenolysis. The suitable types of catalyst, synthesis processes, and operating conditions to maximize the yields of desired products were identified. In addition, the characterization of synthesized metallic catalysts was evaluated to study the relationship between their catalytic activity and physical-chemical properties.

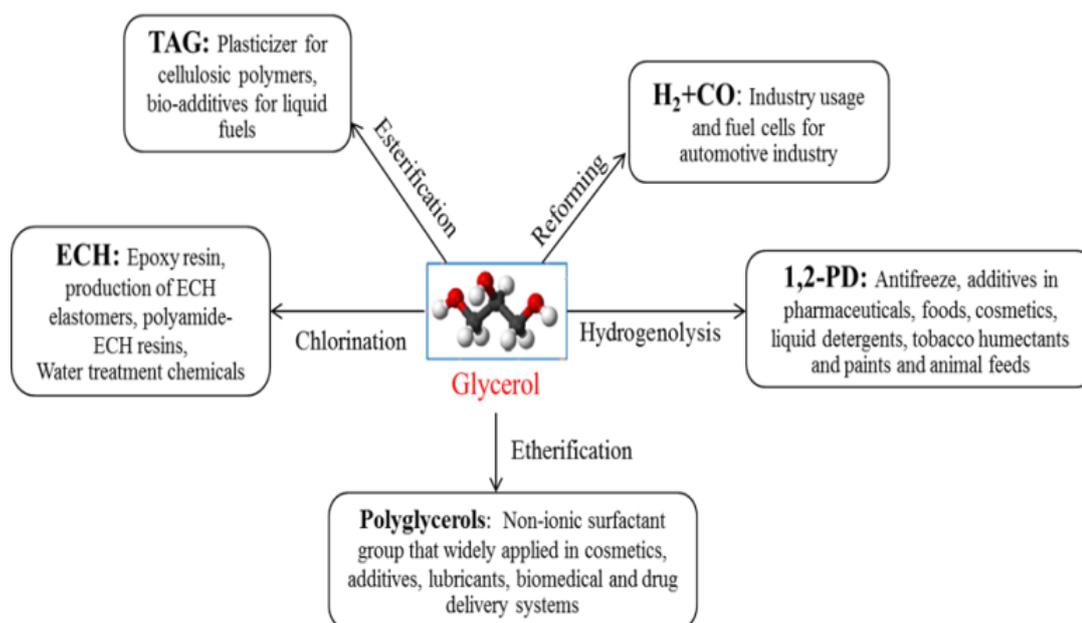


Figure 1. Commercial available products from glycerol via different pathways.

2. Materials and methods

2.1 Raw material

Copper(II)nitrate ($\text{Cu}(\text{NO}_3)_2$) from Ajax Finechem was used as a precursor. The commercial $\gamma\text{-Al}_2\text{O}_3$ with 1.8 mm diameter was obtained from Sasol Company. Milli-Q water (18 M Ω) obtained from a Milli-Q water purification system (Elix® Advantage system, Merck Millipore) was used to prepare various solutions. Moreover, the standard of chemicals (glycerol, 1,2-PDO, 1,3-PDO, acetol, ethylene glycol (EG), propanol) were purchased from Sigma-Aldrich.

2.2 Catalyst preparation

The 35%Cu/ $\gamma\text{-Al}_2\text{O}_3$ catalyst was prepared by impregnation method. The $\gamma\text{-Al}_2\text{O}_3$ was crushed and sieved to obtain 0.42 mm particle size before using as a support. The metal precursor was calculated by desired weight and dissolved in deionized water. Then, the metal aqueous solutions were impregnated on $\gamma\text{-Al}_2\text{O}_3$ followed by drying overnight in an oven at 105°C and calcined with a ramping rate of 5°C min⁻¹ from room temperature to 450°C for 4 hours. Before testing reaction, the prepared catalysts were reduced under H₂ atmosphere at 300°C for 3 hours.

2.3 Catalyst characterization

Catalysts were analyzed to study phase, reducibility, surface area, pore volume, and pore diameter by various techniques including X-ray diffraction (XRD), temperature-programmed reduction with hydrogen (H₂-TPR), and N₂ adsorption-desorption, respectively. XRD patterns of samples were collected on an X-ray diffractometer (Philips P.W. 1830, Philips) using a CuK α radiation. The XRD spectra was observed at 40 kV and 30 mA over the range of 10° < 2 θ < 80° with a step size of 0.02° s⁻¹. H₂-TPR was acquired on a CHEMBET-Pulsar Quantachrome Instruments with a thermal conductivity detector (TCD). Before analyzing, 0.2 g of catalyst was treated at 120°C for 1 hour. After that, the catalyst was reduced in 5% H₂/Ar at a flow rate 30 cm³min⁻¹ from 30°C to 800°C at a heating rate of 10°C min⁻¹. The Nova 2000e, Quantachrom Instruments, Germany was used for N₂ adsorption-desorption. 0.2 g of sample was degassed at 180 °C for 3 hours.

2.4 Reaction procedure

Glycerol hydrogenolysis reaction testing was operated in Parr batch reactor 300 ml. 50 g of glycerol feedstock and 5 g of

reduced catalyst were added in the reactor and then the reactor was pressurized with H₂ (50 bar) and heated to the desired temperature (200-240°C) with various reaction times (1-7 h). At the end of test, the reactor was cooled down until room temperature by cooling system. The gas-phase product was collected in a gasbag and liquid-phase product was centrifuged to remove the solid catalyst powder and analyzed by gas chromatography (GC-2014, Shimadzu) equipped with a flame ionization detector and a capillary column (Rtx-WAX, 30 m in length with 0.32 mm i.d. and 0.5 μm film thickness). Conversion, selectivity, and product yield were calculated for evaluating catalyst performance as shown in following below.

$$\text{Conversion (\%)} = \frac{\text{Mole of glycerol converted}}{\text{Total mole of glycerol in the feed}} \times 100$$

$$\text{Yield (\%)} = \frac{\text{Mole of product}}{\text{Mole of glycerol}} \times 100$$

$$\text{Selectivity (\%)} = \frac{\text{Yield (\%)}}{\text{Conversion (\%)}} \times 100$$

3. Results and discussion

3.1 Catalyst characterizations

The reducibility of catalyst was observed by H₂-TPR, as shown in Figure 2. From the TPR pattern, we found that oxide phase of Cu was reduced to metallic phase at a temperature range from 200°C to 350°C and hydrogen was consumed maximally at 275°C. Figure 3 shows the XRD patterns of $\gamma\text{-Al}_2\text{O}_3$ and catalysts after calcination. The oxide phase of Cu was clearly observed (see in Figure 3). After reducing the synthesized catalyst, sharp reflection of metallic Cu was observed at 2 θ = 43.3°, 50.5°, and 74.1° corresponding to (111), (200) and (220) planes of the cubic pore structure (JCPDS: 85-1326), respectively. From the XRD results, it could be confirmed that oxide phase of Cu was completely reduced to Cu metallic phase at temperature of 300 °C under 100% H₂. Surface area, pore volume and pore diameter are shown in Table 1. From the surface analysis data, it can be seen that surface area significantly decreased from the support around 30 % because metallic phase covered the pore of support which pore volume also decreased minimally.

3.2 Catalytic performance

In this research, the effect of the catalyst preparation process (catalyst drying process) and operating conditions (reaction time, reaction temperature, and catalyst loading) were studied. The effect of drying process during catalyst preparation step on the catalytic performance of 35% Cu/ γ -Al₂O₃ in glycerol hydrogenolysis was studied as shown in Table 2. It can be seen that the values of glycerol conversion, yield, and selectivity of the products of both catalysts which were synthesized by different methods were similar. Therefore, 35% Cu/ γ -Al₂O₃ catalyst which was synthesized from oven drying process method was further studied as presented in the next session.

The effect of reaction temperature was studied as shown in Table 3. Glycerol conversion significantly increased when reaction temperature increased from 200 to 240°C. The 1,2-PDO was a main product. At 240°C, the 1,2-PDO yield was highest at 75.85%. Moreover, other products such as 1,3-propanediol (1,3-PDO), ethylene glycol (EG), acetol, and propanol were detected.

The effect of reaction time on glycerol conversion, product yield, and selectivity from glycerol hydrogenolysis in the presence of 35%Cu/ γ -Al₂O₃ catalyst was investigated. As presented in Table 4, glycerol conversion monotonously increased with increasing reaction time. However, 1,2-PDO yield peaked at 3 h and decreased at prolonged time, due to the consecutive decomposition to fragmentation products such as propanol.

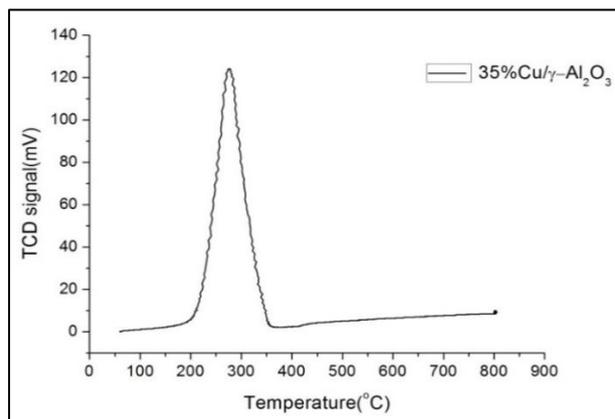


Figure 2. TPR profiles of the 35%Cu/ γ -Al₂O₃ catalyst.

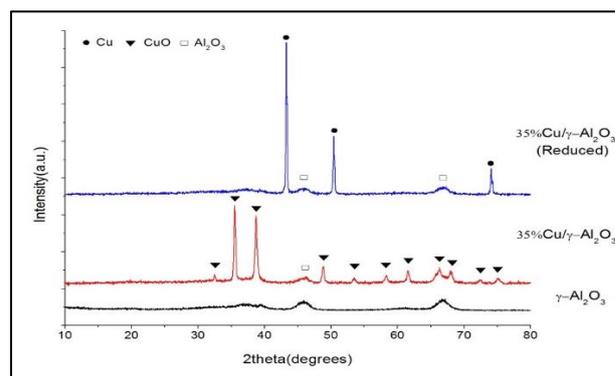


Figure 3. XRD patterns of γ -Al₂O₃ and 35%Cu/ γ -Al₂O₃ catalysts at calcined and reduced states.

Table 1. Surface area, pore volume, and pore diameter of supporting material and catalysts with different drying methods.

Sample	Surface Area ^a (m ² /g)	Pore Volume ^b (cc/g)	Pore Diameter ^b (nm)
γ -Al ₂ O ₃	198	0.05	2.13
35%Cu/ γ -Al ₂ O ₃ (oven)	139	0.04	2.13
35%Cu/ γ -Al ₂ O ₃ (microwave)	141	0.04	2.13

^a Specific surface area were calculated using the BET method

^b Pore volumes and pore diameter were calculated using the BJH method

Table 2. Effect of drying process of catalysts on the catalytic performance of 35%Cu/ γ -Al₂O₃ catalysts in glycerol hydrogenolysis.

Drying processes	Glycerol conversion (%)	1,2-PDO yield (%)	Selectivity (%)				
			1,2-PDO	1,3-PDO	EG	Acetol	Propanol
Microwave 200 watt	76.33	61.06	79.99	0.11	1.04	2.36	0.11
Oven 105 °C	78.89	62.22	78.88	0.11	0.98	1.79	0.13

Reaction conditions: 5 g of catalyst, 50 bar of initial H₂ pressure, 220°C, 5 h.

Table 3. Effect of reaction temperature on the catalytic performance of 35%Cu/ γ -Al₂O₃ catalysts in glycerol hydrogenolysis.

Temperature (°C)	Glycerol conversion (%)	1,2-PDO yield (%)	Selectivity (%)				
			1,2-PDO	1,3-PDO	EG	Acetol	Propanol
200	21.97	14.52	66.11	0.00	0.00	4.87	0.71
220	78.89	62.22	78.88	0.11	0.98	1.79	0.13
240	98.68	75.85	76.87	0.09	1.50	4.11	0.51

Reaction conditions: 5 g of catalyst, 50 bar of initial H₂ pressure, 5 h.

Table 4. Effect of reaction time on the catalytic performance of 35%Cu/ γ -Al₂O₃ catalyst in glycerol hydrogenolysis.

Time (hour)	Glycerol conversion (%)	1,2-PDO yield (%)	Selectivity (%)				
			1,2-PDO	1,3-PDO	EG	Acetol	Propanol
1	74.44	62.17	83.52	0.13	1.18	3.31	0.37
3	95.25	76.72	80.55	0.09	1.43	3.73	0.39
5	98.68	75.85	76.87	0.09	1.50	4.11	0.51
7	98.70	60.06	60.85	0.10	1.07	4.02	0.87

Reaction conditions: 5 g of catalyst, 50 bar of initial H₂ pressure, 240 °C.

Table 5. Effect of catalyst loading on the catalytic performance of 35%Cu/ γ -Al₂O₃ catalysts in glycerol hydrogenolysis.

Catalyst loading (wt%)	Glycerol conversion (%)	1,2-PDO yield (%)	Selectivity (%)				
			1,2-PDO	1,3-PDO	EG	Acetol	Propanol
4	77.84	50.80	65.27	0.13	0.91	2.63	0.76
6	93.82	80.16	85.44	0.10	1.61	3.00	0.62
8	97.37	75.89	77.93	0.09	1.47	4.13	0.81
10	98.68	75.85	76.87	0.09	1.50	4.11	0.51
12	99.26	75.53	76.09	0.09	1.43	4.22	0.81

Reaction conditions: 50 bar of initial H₂ pressure, 240°C, 5 h.

Table 5 shows the effect of catalyst loadings in the range of 4 to 12 wt%. Glycerol conversion increased from 77.84 to 99.26% when the catalyst loading increased from 4 to 12 wt%. At 6 wt% catalyst loading, we found that the 1,2-PDO yield and selectivity reached a maximum, and then decreased afterward at 8-12 wt% loading.

4. Conclusions

The catalytic activities of 35%Cu/ γ -Al₂O₃ catalysts prepared by different drying methods (oven and microwave methods) toward the hydrogenolysis of glycerol to 1,2-PDO were comparatively studied. We found that the values of glycerol conversion, yield, and selectivity of the products of both catalysts were similar. Therefore, we selected 35%Cu/ γ -Al₂O₃ catalyst for further studies. From the experimental results, the optimized condition was found at 240°C for 5 h under H₂ initial pressure at 50 bar with 6 wt% of catalyst loading, providing the glycerol conversion, 1,2-PDO yield, and 1,2-PDO selectivity of 93.82%, 80.16%, and 85.44%, respectively.

Acknowledgement

The authors acknowledge financial supports from the Joint Graduate School of Energy and Environment (JGSEE) and the technical supports from National Nanotechnology Center (NANOTEC), National Science and Technology Development Agency (NSTDA).

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