Hydrogenolysis of Glycerol into Propylene Glycol Over 
Cu/ZnO/Al₂O₃ Catalyst via Gel Co-precipitation

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Introduction
Biodieseldriven from vegetable oil and animal fat have been assumed to be an important 
supplement to conventional diesel fuel for a number of its environmentally friendly features 
such as biodegradability, nontoxic and free of sulfur. However, the major obstacle to biodiesel 
large scale commercialization is the high production cost. Glycerol is the major byproduct 
produced via transesterification with an alcohol. Glycerol is an important commodity chemical 
that is primarily used in food, cosmetic and pharmaceutical industries. As the biodiesel 
production dramatically increases, the large amount of surplus glycerol has made the current 
cost of storage handling and transportation of crude glycerol exceed its market value; therefore, 
converting glycerol into value-added products is an efficient way to promote biodiesel 
production and reduce the economical waste and environmental pollutions. Propylene glycol is 
an important commodity chemical which is mainly used for anti-freeze, polyester resins and 
pharmaceuticals. The current market value of propylene glycol is reported to be around 80 
cents/lb; this is much higher than that of crude glycerol which is reported to be only 7–8 
cents/lb. Cu/ZnO/Al₂O₃ catalyst has exhibited a good selectivity towards 1,2-propandiol under 
mild conditions and it is less toxic compared with the Cu/Cr₂O₃ catalysts [1,2].

Materials and Methods
The catalyst was prepared by a novel gel co-precipitation method. The catalysts were also 
prepared by impregnation for comparison. The experiment was carried out in a 300ml batch 
auto-clave. Samples were taken via a sampling valve in a certain time interval and analyzed by 
a GC integrated with a FID detector. The physicochemical properties of the catalysts are 
characterized by BET, XRD, TG/DTA, NH₃-TPD.

Results and Discussion
The metal composition has been investigated and with the optimum Cu/Zn/Al composition, he 
experimental results show that at 200°C and 400psi hydrogen pressure, the glycerol conversion 
and propylene glycol selectivity catalyzed by the Cu/ZnO/Al₂O₃ catalyst prepared through 
oxalate gel-coprecipitation are 86.0% and 91.9% respectively after 24 hours, which are higher 
than those by the catalysts prepared by the other two methods (Figure 1). It was also found that 
that the propylene glycol selectivity strongly depends on hydrogen pressure and the low 
selectivity at a lower hydrogen pressure is mainly due to the side reaction caused by acetol, 
which is the intermediate of the reaction system [3]. The by-products were found to be the 
same in both glycerol hydrogenolysis and acetol hydrogenation reaction systems (Figure 2). 
The catalytic characterizations show that the catalyst prepared by gel co-precipitation can have 
more homogeneous distribution for all the metal component and finer Cu particle size.

Figure 1 Kinetics of Glycerol Conversion Using Cu/ZnO/Al₂O₃ Catalysts Prepared by 
Different Methods. Reaction Conditions: 200°C, 80wt% aqueous glycerol, 5wt% of catalyst 
with respect to glycerol weight, 400psi H₂

Figure 2 GC Chromatogram Comparison for the Final Product of Glycerol hydrogenolysis and 
Acetol Hydrogenation

Significance
This work has shown that the Cu/ZnO/Al₂O₃ catalyst prepared by gel coprecipitation has 
exhibited a very high activity for glycerol hydrogenolysis process. The experimental results 
showed that the undesired by-products are formed due to the side reaction when acetol is 
present. Therefore, a highly active hydrogenation catalyst or higher hydrogen pressure are 
needed if a high selectivity of propylene glycol is desired.

References