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Low-pressure hydrogenolysis of glycerol to propylene glycol

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Abstract

Hydrogenolysis of glycerol to propylene glycol was performed using nickel, palladium, platinum, copper, and copper-chromite catalysts. The effects of temperature, hydrogen pressure, initial water content, choice of catalyst, catalyst reduction temperature, and the amount of catalyst were evaluated. At temperatures above 200 °C and hydrogen pressure of 200 psi, the selectivity to propylene glycol decreased due to excessive hydrogenolysis of the propylene glycol. At 200 psi and 200 °C the pressures and temperaures were significantly lower than those reported in the literature while maintaining high selectivities and good conversions. The yield of propylene glycol increased with decreasing water content. A new reaction pathway for converting glycerol to propylene glycol via an intermediate was validated by isolating the acetol intermediate.
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1. Introduction and background

Over the past couple of decades fatty acid methyl esters derived from vegetable oil and animal fat have assumed importance as potential diesel fuel extenders known as ‘‘biodiesel’’ [1–4]. For every 9 kg of biodiesel produced, about 1 kg of a crude glycerol by-product is formed; and today, biodiesel production plants are in need of methods to realize increased income from this glycerol. If crude natural glycerol could be converted to propylene glycol, this technology could be used in biodiesel production plants to increase profitability. Preferred technology would convert crude natural glycerol at moderate temperatures and pressures.

Propylene glycol, i.e. 1,2 propanediol, is a three-carbon diol with a steriogenic center at the central carbon atom. Propylene glycol is a major commodity chemical with an annual production of over 1 billion pounds in the United States [5] and sells for about $0.71 [6] per pound with a 4% growth in the market size annually. The commercial route to produce propylene glycol is by the hydration of propylene oxide derived from propylene by either the chlorohydrin process or the hydroperoxide process [7,8]. There are several routes to propylene glycol from renewable feedstocks. The most common route of production is through hydrogenolysis of sugars or sugar alcohols at high temperatures and pressures in the presence of a metal catalyst producing propylene glycol and other lower polyols [9–14]. Some typical uses of propylene glycol are in unsaturated polyester resins, functional fluids (antifreeze, de-icing, and heat transfer), pharmaceuticals, foods, cosmetics, liquid detergents, tobacco humectants, flavors and fragrances, personal care, paints and animal feed. The antifreeze and deicing market is growing because of concern over the toxicity of ethylene glycol-based products to humans and animals as well.

Fig. 1 summarizes the overall reaction of converting glycerol to propylene glycols. In the presence of metallic catalysts and hydrogen, glycerol can be hydrogenated to propylene glycol, 1,3 propanediol, or ethylene glycol. Several publications and patents document multiple schemes for hydrogenating glycerol to propylene glycol. Casale and Gomez [10,11] described a method of

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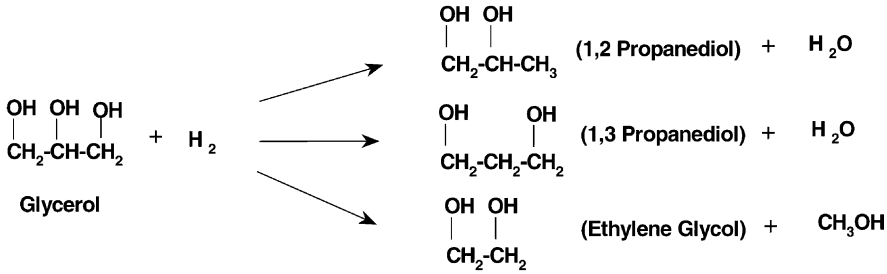

Fig. 1. Summary of the overall reaction of converting glycerol to propylene and ethylene glycols.

hydrogenating glycerol using copper and zinc catalyst as well as sulfided ruthenium catalyst at a pressure of 2175 psi and temperature in the range of 240–270 °C. Ludvig and Manfred [12] described a method for the production of propanediols using a catalyst containing cobalt, copper, manganese, molybdenum, and an inorganic polyacid achieving a 95% yield of propylene glycol at pressures of 3625 psi and a temperature of 250 °C. Tessie [13] describes a method of production of propanediols over homogeneous catalyst containing tungsten and Group VIII transition metals at a pressure of 4600 psi and a temperature of 200 °C. Haas et al. [14] described a process of simultaneous production of propylene glycol and 1,3 propanediol from gaseous glycerol solutions at a temperature of 300 °C using two stages. Cameron et al. proposed a biocatalytic fermentation technique for production of propanediol from glycerol and sugars [15,16].

In spite of several research efforts, this potentially important reaction was limited to a laboratory scale production because of common drawbacks of existing technologies. One drawback is the use of high temperatures and pressures that would necessitate expensive high-pressure equipment, thereby increasing the capital cost of the process. Typical hydrogen pressures anywhere between 1450 and 4700 psi and temperatures in the range 200–350 °C were being used for this reaction.

An additional drawback is the use of dilute solutions of glycerol for this reaction. Typically, 10–30 wt.% glycerol solutions were predominantly used which will be further diluted through the water from the reaction. This will reduce the average space–time yield of the reaction increasing the energy consumption of the process and in turn decreasing the process profitability. However, not much has been reported about the positive effect of using dilute glycerol solutions instead of 100% glycerol.

A final drawback is the low selectivity towards propylene glycol. Most of the literature reports high selectivity towards ethylene glycol and other by-products like lactic acid, acetol, acrolein, and degradation products like propanol, methanol, carbon dioxide, methane, etc.

In an effort to overcome these drawbacks, our research focuses at developing a technology to perform the reaction at lower temperatures and pressures using concentrated glycerol while simultaneously achieving high selectivity towards propylene glycol and little or no selectivity towards ethylene glycol or other by-products. An additional objective of this paper is to validate our proposed novel reaction mechanism for converting glycerol to propylene glycol via a reactive intermediate.

1.1. Recommended catalysts

Traditional practices of hydrogenating carbonyl groups to form alcohols along with the common practice of hydrogenating ester groups in fats and oils to form fatty alcohols indicate that the alcohol groups are stable and do not readily react at normal hydrogenating conditions. Moreover, the alcohols are also known as excellent solvents for the hydrogenation [17], which imply that they very much resist reaction. Hence conventional hydrogenation catalysts such as nickel, ruthenium, and palladium are not very effective for hydrogenating glycerol. Copper is potentially a good catalyst for alcohol hydrogenation. It is known for its poor hydrogenolytic activity towards C–C bond and an efficient catalyst for C–O bond hydro-dehydrogenation [18,19].

2. Experimental methods

2.1. Materials

Glycerol (99.9%), propylene glycol, acetol, and *n*-butanol were purchased from Sigma-Aldrich (Milwaukee, WI). High purity grade hydrogen and nitrogen were obtained from Praxair. Table 1 gives the description of various catalysts used in this study and their suppliers.

2.2. Experimental setup

All reactions were carried out in a specially designed stainless steel multi-clave reactor capable of performing eight reactions simultaneously. Each reactor with a capacity of 150 mL is equipped with stirrer, heater and a sample port for liquid sampling. The temperature of the reactors was controlled by CAMILE 2000 control and data acquisition system using TG 4.0 software. The reactors were flushed several times with nitrogen followed by hydrogen. Then the system was pressurized with hydrogen to the necessary pressure and heated to the desired reaction temperature.

Table 1
Summary of conversion of glycerol, yield and selectivity of propylene glycol from glycerol over various metal catalysts

Supplier	Description	Conversion	Yield	Selectivity
Johnson Matthey	5% Ru/C	43.7	17.5	40.0
Johnson Matthey	5% Ru/alumina	23.1	13.8	59.7
Degussa	5% Pd/C	5	3.6	72.0
Degussa	5% Pt/C	34.6	28.6	82.7
PMC Chemicals	10% Pd/C	8.9	4.3	48.3
PMC Chemicals	20% Pd/C	11.2	6.4	57.1
Grace Davision	Raney nickel	49.5	26.1	52.7
Grace Davision	Raney copper	48.9	33.8	69.1
Sud-Chemie	Copper	53	21.1	39.8
Sud-Chemie	Copper-chromite	54.8	46.6	85.0
Johnson Matthey	Ni/C	39.8	27.3	68.6
Alfa-Aesar	Ni/silica-alumina	45.1	29.1	64.5

Reactions were carried using 80% glycerol solution at 200 °C and 200 psi hydrogen pressure for 24 h.

The speed of the stirrer was set constant at 100 rpm throughout the reaction. All the catalysts used in this study were reduced prior to the reaction in the same reactor by passing a stream of hydrogen over the catalyst bed at 300 °C for 4 h. The reactants were immediately transferred to the reactor without further delay.

2.3. Method of analysis

The samples were taken at desired time intervals, cooled to room temperature and centrifuged using an IEC (Somerville, MA) Centra CL3R centrifuge to remove the catalyst. These samples were analyzed with a Hewlett-Packard 6890 (Wilmington, DE) gas chromatograph equipped with a flame ionization detector. Hewlett-Packard Chemstation software was used to collect and analyze the data. A Restek Corp. (Bellefonte, PA) MXT® WAX 70624 GC column (30 m × 250 μm × 0.5 μm) was used for separation. A solution of *n*-butanol with a known amount of internal standard was prepared a priori and used for analysis. The samples were prepared for analysis by adding 100 μL of product sample to 1000 μL of stock solution into a 2 mL glass vial. Fig. 2 shows a typical gas chromatogram of the hydrogenolysis reaction product. Using the standard calibration curves that were prepared for all the components, the integrated areas were converted to weight percentages for each component present in the sample.

For each data point, selectivity of propylene glycol, conversion of glycerol, and yield of propylene glycol were calculated. Selectivity is defined as the ratio of the number of moles of the product formation to that of the glycerol consumed in the reaction, taking into account the stoichiometric coefficient. Conversion of glycerol is defined as the ratio of number of moles of glycerol consumed in the reaction to the total moles of glycerol initially present. Yield of propylene glycol is defined as the ratio of the number of moles of propylene glycol produced to the theoretical number of moles of the propylene glycol.

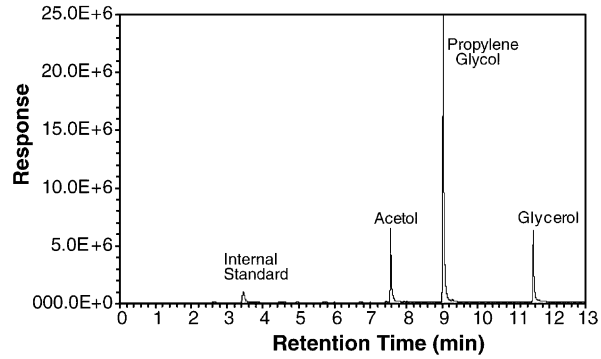

Fig. 2. Gas chromatogram of the hydrogenolysis reaction product.

3. Results and discussion

3.1. Reaction mechanism

The primary goal of this study is to develop a technology that would allow production of propylene glycol from glycerol at milder hydrogenation conditions. To achieve this, it is necessary to understand the fundamental chemistry and mechanism behind the hydrogenolysis of crude glycerol to propylene glycol.

Preliminary investigations in our work indicated that hydroxyacetone (acetol) was formed and is possibly an intermediate of an alternative path for forming propylene glycol. GC analysis of the reaction product showed the presence of acetol in trace amounts. Acetol is formed by dehydration of a glycerol molecule, which further reacts with hydrogen to form propylene glycol with 1 mol of water by-product. The proposed mechanism is shown in Fig. 4. Studies to investigate the effect of water on the hydrogenolysis reaction indicated that the reaction takes place even in the absence of water with a 49.7% yield of propylene glycol. Moreover, since the copper-chromite catalyst is reduced in a stream of hydrogen prior to the reaction there will be no surface hydroxyl species taking part in the reaction.

Both the above observations contradict the mechanism proposed by Montassier et al. [19] who proposed the reaction mechanism for the conversion of glycerol to propylene glycol shown in Fig. 3. According to this mechanism, dehydrogenation of glycerol on copper can lead to glyceric aldehyde in equilibrium with its enolic tautomer. The formation of propylene glycol was explained by a nucleophilic reaction of water or adsorbed OH species, a dehydroxylation reaction, followed by hydrogenation of the intermediate unsaturated aldehyde. The mechanism shown in Fig. 3 supported by our data does not include water present in the form of surface hydroxyl species or as apart of reactants.

In order to validate the mechanism in Fig. 4, preliminary reactions were conducted in two steps. In step 1, relatively pure acetol was isolated from glycerol at 200 °C in the absence of hydrogen at 9.4 psi pressure in the presence of

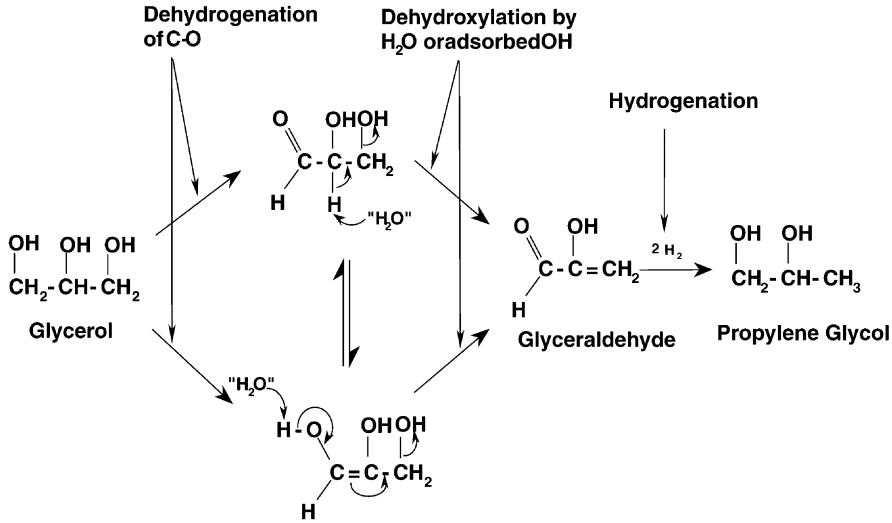

Fig. 3. Reaction mechanism for conversion of glycerol to propylene glycol proposed by Montassier et al. [19].

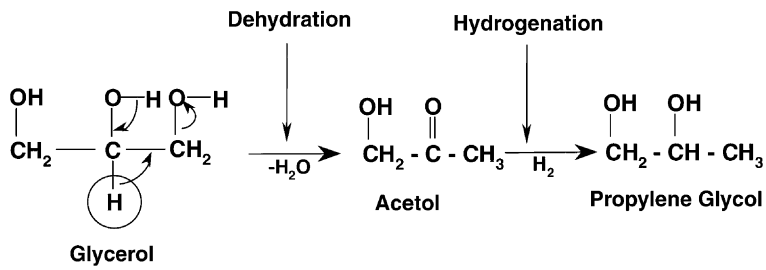

Fig. 4. Proposed reaction mechanism for conversion of glycerol to propylene glycol.

copper-chromite catalyst. In step 2, the acetol formed in step 1 was further hydrogenated to propylene glycol at 200 °C and 200 psi hydrogen pressure using similar catalyst that is used for the formation of acetol. The combination of these reactions gave high product yields and results were shown in Table 2. This mechanism was supported by the studies of Cameron et al. [15,16] in which propanediols were made using biocatalytic routes from glycerol and sugars via formation of a reactive acetol intermediate. Optically active propylene glycol is currently prepared by the biocatalytic reduction of acetol [20].

3.2. Catalyst screening and selection

Heterogeneous catalysts, including ruthenium, nickel, platinum, copper, raney copper, raney nickel, palladium, and copper-chromite in the form of metallic powders, metal oxides, and activated metals (metal sponge) were impregnated on an activated carbon support. Reactivities were tested at 200 psi hydrogen pressure and at a temperature of 200 °C. Table 1 shows the performance comparision of these catalysts. Catalysts like ruthenium and palladium showed low selectivities, less than 50%, due to competitive hydrogenolysis of C–C and C–O bonds leading to excessive degradation of glycerol at lower pressures to form lower alcohols and gases. On the other hand, copper or copper-based catalysts exhibited higher selectivity towards propanediols with little or no selectivity towards ethylene glycol and other degradation by-products. Copper-chromite catalyst was selected for further studies.

3.3. Parametric studies

The effect of catalyst reduction temperature, reaction temperature, hydrogen pressure, initial water content and

Table 2
Summary of reactions performed to validate the proposed reaction mechanism

	Initial loading (g)	Best possible (g)	Final product (g)
Step 1: formation and isolation of acetol intermediate from glycerol using copper-chromite catalyst			
Glycerol	50	0	0
Acetol	0	40.22	30.72
Propylene glycol	0	0	2.23
Step 2: formation and isolation of propylene glycol from acetol intermediate from step 1 using same catalyst			
Glycerol	0	0	0
Acetol	20	0	0.8
Propylene glycol	0	20.5	18.3

amount of catalyst for the hydrogenolysis reaction were determined using copper-chromite catalyst and the results are discussed in the following sections.

3.4. Effect of catalyst reduction temperature

Copper-chromite catalyst obtained in an oxide form is partially or fully reduced in the presence of hydrogen to increase its activity. Literature [21] reports that the coordinately unsaturated sites of cuprous ions on the catalyst surface are the active sites for hydrogenation. Studies were performed in order to determine the activity of the catalyst as a function of catalyst prereduction temperature. The catalyst was reduced in an atmosphere of hydrogen at different temperatures: 150, 200, 250, 300, 350, 400 °C for 4 h. Fig. 5 provides the summary of the conversions of 80% glycerol solution at 200 °C and 200 psi using copper-chromite catalyst reduced at different temperatures. The yield and selectivity of propylene glycol increase with catalyst reduction temperatures up to 300 °C and decrease for temperatures greater than 300 °C. Hence, reducing the catalyst at 300 °C for 4 h was detemined as the optimum conditon for the hydrogenolysis reaction and is used for further studies.

3.5. Effect of catalyst weight

It was observed that the activity of the copper-chromite catalyst is lost even before the reaction goes to completion. This catalyst can be regenerated by washing with a polar solvent and reducing it in a stream of hydrogen and in some cases has to be replaced with fresh catalyst. In order to minimize the high cost of catalyst replacement and addition of fresh catalyst, a minimum amount of fresh catalyst could be used in each batch, which can be discarded after use. Reactions were carried out to find the minimum weight of the catalyst required to achieve the necessary conversion. Table 3 shows the effect of catalyst weight on overall conversion of glycerol to propylene glycol. The glycerol conversion and the yield of propylene glycol increased with catalyst concentration. As the concentration of the catalyst increases, more surface area is available for the hydrogenolysis reaction to take place. The initial rates of conversion of glycerol and formation of propylene glycol have a proportional increase with the catalyst amount. However, as the reaction time increases, the excess catalyst further promotes excessive hydrogenolysis reaction converting propylene glycol to lower alcohols and gases. Hence, to get a good conversion of glycerol with high selectivity to propylene glycol an optimal amount of catalyst should be used depending on the reaction time.

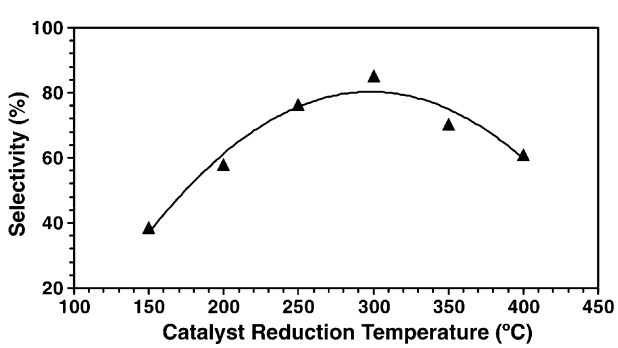

Fig. 5. Effect of catalyst reduction temperature on formation of propylene glycol from glycerol. All the reactions were performed using 80% glycerol solution at 200 °C and 200 psi hydrogen pressure for 24 h.

Table 3
Effect of weight of catalyst on formation of propylene glycol from glycerol

wt.% of catalyst	%Conversion	%Yield	%Selectivity
1	28.3	17.9	63.3
2.5	33.5	26.2	78.2
5	54.8	46.6	85.0
10	58	45	77.6
15	70.1	45.2	64.5
20	78.5	48.7	62.0

All the reactions were performed using 80% glycerol solution at 200 psi hydrogen pressure for 24 h.

3.6. Effect of reaction temperature

Temperature has a significant effect on the overall yield of the propylene glycol. Reactions were carried out at 150, 180, 200, 230, and 260 °C and at a pressure of 200 psi of hydrogen in the presence of a copper-chromite catalyst. Table 4 shows the effect of temperature on the conversion and yield of the reaction. As the temperarture of the reaction increases from 150 to 260 °C there is a uniform increase in the glycerol conversion from 7.2 to 87%. However, the overall yield of propylene glycol increased until 200 °C and began to decrease as the temperature was increased further. A similar trend is also observed in the case of the selectivity of the propylene glycol. This indicates that at a hydrogen pressure 200 psi, temperatures >200 °C lead to excessive hydrogenolysis converting the propanediols into lower alcohols like methanol, ethanol, which upon further degradation form gaseous products like methane, ethane, propane, carbon dioxide, etc. Moreover, from our initial screening studies (data not presented) it was observed that it

Table 4
Effect of reaction temperature on formation of propylene glycol from glycerol

Temperature (°C)	%Conversion	%Yield	%Selectivity
150	7.2	2.3	31.9
180	28	9.8	35.1
200	54.8	46.6	85.0
230	72	35.1	48.7
260	87	7.7	8.8

All the reactions were performed using 80% glycerol solution at 200 psi hydrogen pressure for 24 h.

is necessary to operate at higher pressures to prevent degradation of glycerol at temperatures >200 °C.

3.7. Effect of hydrogen pressure

Reactions were carried out at 50, 100, 150, 200, 300 psi at a constant temperature of 200 °C to determine the effect of hydrogen pressure on the overall reaction. Table 5 provides the summary of the conversions of 80% glycerol solution at 200 °C under different hydrogen overhead pressures. As expected the conversion of the glycerol increased as the hydrogen pressure increased from 50 to 300 psi. The pressures were significantly lower than those reported in the literature. Lower pressure hydrogenolysis can be improtant to maximize the utility of existing equipment for performing hydrogenolysis.

3.8. Effect of initial water content

Water is generated in this reaction and it is always preferable to eliminate the water from the initial reaction mixture to drive the equilibrium in the forward direction. Previous literature used very dilute glycerol solutions (10–30%), the reason being unknown. In order to isolate propylene glycol, it is therefore necessary to first remove large amounts of water by distillation, which means expenditure of large amounts of energy. In addition, as the concentration of glycerol decreases from 100 to 50%, the size of the reactor doubles to produce the same amount of product. Hence, reactions were performed using glycerol solutions made up of different water contents to study the effect of initial water content on the overall reaction. Table 6 provides the summary of effect of initial water content on overall glycerol conversion at 200 °C and 200 psi. As the initial water in the reaction increases, both the glycerol conversion and the yield of propylene glycol decreased. Morover, for glycerol solutions with concentration >80% a decrease in the selectivity was observed due to the degradation of reaction product due to polymerization. Hence it is essential to have atleast 10–20% of solvent (water, methanol) to minimise the degradation.

This demonstrates that high yields of propylene glycol can be achieved by using only 10–20% water in glycerol instead of 70–90% water as reported earlier. This would increase the space–time yield of the reaction (yield of propylene glycol product produced per unit volume per unit time) and reduce the size and pressure ratings of the reactor vessels. At these conditions, it is preferred to operate at low water contents to improve conversion and simultaneously reduce the reactor volumes. This was a valuable observation not previously reported in the literature.

Table 5
Effect of hydrogen pressure on formation of propylene glycol from glycerol

Pressure (psi)	%Conversion	%Yield	%Selectivity
50	25	9.1	36.4
100	37	15.7	42.4
150	44	22.3	50.7
200	54.8	46.6	85.0
300	65.3	58.5	89.6

All the reactions were performed using 80% glycerol solution at 200 °C for 24 h.

Table 6
Effect of initial water content in the reactants on formation of propylene glycol from glycerol

Water (wt.%)	%Conversion	%Yield	%Selectivity
80	33.5	21.7	64.8
40	48	28.5	59.4
20	54.8	46.6	85.0
10	58.8	47.2	80.3
0	69.1	49.7	71.9

All the reactions were performed at 200 °C and 200 psi hydrogen pressure for 24 h.

4. Conclusion

Copper-chromite catalyst was identified as the most effective catalyst for the hydrogenolysis of glycerol to propylene glycol. The mild reaction conditions of 200 °C and 200 psi used in these studies give the process based on copper-chromite catalyst distincitve competitive advantages over traditional process using severe conditions of temperature and pressure. A novel mechanism to produce propylene glycol from glycerol via an acetol intermediate was proposed and validated. In a two-step reaction process, the first step of forming acetol can be performed at atmospheric pressure while the second requires a hydrogen partial pressure. Propylene glycol yields >73% were achieved at moderate reaction contions.

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