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An Efficient, Selective Process for the Conversion of Glycerol to Propylene Glycol Using Fixed Bed Raney Copper Catalysts

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ABSTRACT: Propylene glycol is formed in yields of up to 95% at 100% conversion using a Raney Cu catalyst in a fixed bed reactor. The reaction uses an 80% aqueous glycerol solution and a hydrogen pressure of 600 psi. The primary byproduct is ethylene glycol formed in 1–3% yield. In a reaction run continuously for 24 d using a sample of a commercial preparation of Raney Cu, the selectivity to propylene glycol at 100% glycerol conversion was 94.6% with a space–time yield (STY) of 0.49 g of 1,2-propylene glycol/mL Raney Cu/h. Ethylene glycol was formed in 2.5% yield, while methanol, ethanol, *n*-propanol 1,3-propylene glycol, and acetol were present in less than 1% yield.

1. INTRODUCTION

The increasing worldwide production of biodiesel by the transesterification of fats and oils has resulted in a corresponding increase in the production of glycerol. One gallon of glycerol is produced for every nine gallons of biodiesel. Even though there are over 2000 different applications for which glycerol is used,¹ new high volume commercial processes are needed to improve the economics of biodiesel production. Some early work in this area concentrated on the selective oxidation of glycerol² to compounds such as dihydroxyacetone, hydroxypyruvic acid, and glyceric acid. For a variety of reasons this approach was not sufficiently effective to utilize much of the glycerol that was being produced. Other research was directed toward finding commercially applicable procedures for the conversion of glycerol into commodity chemicals.^{3–5} Processes have been developed that use a glycerol feedstock to replace the petrochemical feedstock for the preparation of acrolein⁶ and epichlorohydrin.⁷ More recently procedures have been reported for converting glycerol to glycerol carbonate,⁸ a practical, ecofriendly solvent, and glycerol alkyl ethers,⁹ which are safe and effective fuel additives.

The most recent research efforts, though, have been directed to developing practical methods for the conversion of glycerol (GLY) to 1,2-propylene glycol (PG), which is used primarily in polymer synthesis but is also an ingredient in antifreeze and de-icing solutions. Since PG is considered as Generally Recognized As Safe (GRAS) by the USFDA, it has also found use in pharmaceuticals and personal care products and as a preservative in food.

The commonly proposed mechanistic pathways for the conversion of glycerol to glycols are shown in Scheme 1. The formation of PG apparently takes place through an initial dehydration of one of the primary hydroxyl groups on GLY to give the enol, **1**, which is in equilibrium with the hydroxy ketone, acetol (ACT). Hydrogenation of ACT gives PG. Dehydration of the secondary hydroxyl group in GLY gives the enol, **2**, which is in equilibrium with the hydroxyl aldehyde, **3**.

Hydrogenation of **3** produces 1,3-propylene glycol (1,3PG), while dehydration gives acrolein (ACR). One of the most common byproducts in this reaction is ethylene glycol (EG). One possible route to its formation is that initiated by the dehydrogenation of GLY to glyceraldehyde (**4**). A retro-Aldol reaction leads to the formation of formaldehyde and the enol, **5**, which on hydrogenation give EG and MeOH. Other potential routes to EG are the direct hydrogenolysis of a C–C bond of GLY and the decarbonylation of **4**, which would form EG directly. A dehydration–hydrogenation sequence on EG leads to the formation of EtOH.

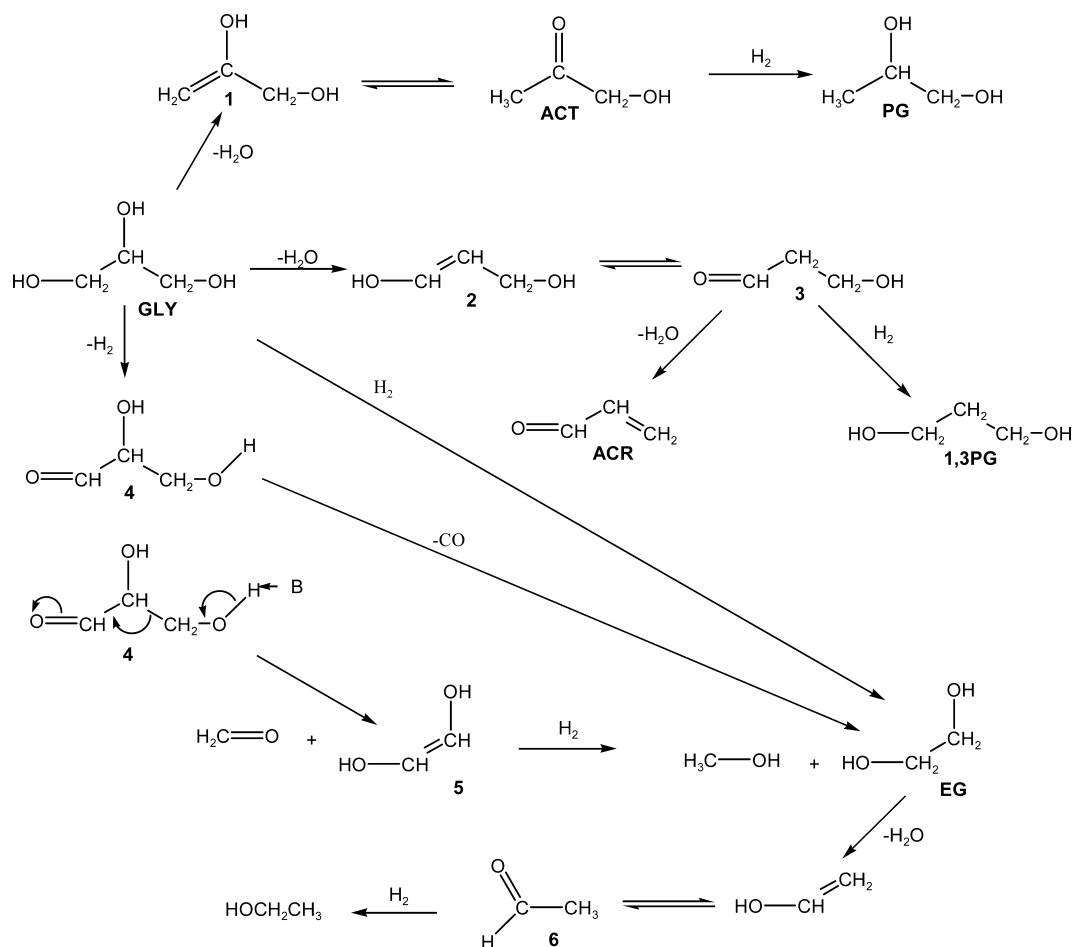
The catalysts involved in the conversion of GLY to PG generally contain Ru, Ni, or Cu. Supported Ru was used in conjunction with an acidic ion-exchange resin to facilitate the initial dehydration step.^{10–12} Other reports cited the use of supported Ru catalysts that also contained Pt,¹³ Au,¹³ or Fe.¹⁴ Supported Ni catalysts included Ni/C,¹⁵ Ni-Ce/C,¹⁶ and Ni/NaX.¹⁷ Co/MgO was also used as a catalyst for this reaction.¹⁸ The most commonly used catalysts, however, contained copper,¹⁹ usually either supported on ZnO,^{20–24} modified with Cr^{25–29} or as a component in a mixed oxide system^{30–32} such as copper-chromite (Adkins catalyst) (Cu–CrO).^{33–38} Most of these reports described the use of batch processes for this reaction, but some, primarily patents, also discussed the use of continuous reactions.^{19,20,31,34,38}

It is difficult to compare these procedures because they were run using a wide range of reaction conditions: glycerol concentrations ranging from 10% aqueous GLY to pure GLY and technical grade GLY; reaction temperatures from 140 to 270 °C; hydrogen pressures from 150 to 1500 psi with one patent³¹ describing the use of 3700–4400 psi of H₂. The batch reactions were run for 5–40 h giving widely different results,

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Scheme 1. Glycerol Hydrogenolysis Reactions



reporting GLY conversions ranging from 23% to 100% and selectivities to PG from 20% to 95%, as well as giving varying amounts of byproducts, primarily EG, ACT, *n*-propyl alcohol, ethanol and methanol. The continuous processes utilized primarily copper containing catalysts, again with differing reaction conditions making any comparisons difficult.

Probably the most extensive study of batch and continuous reactions for this transformation was that reported by Suppes,^{33–40} which used Cu-CrO as the catalyst. His approach was unique in that it involved a two-stage reaction sequence in which ACT was formed first and then hydrogenated in a separate step. Both batch³⁹ and continuous reactions⁴⁰ were used in this approach.

Little has been published on the use of Raney catalysts for the conversion of GLY to PG. One paper described using Raney Ni as the catalyst for batch reactions comparing the extent of PG formation between pure GLY and the GLY obtained from a biodiesel reaction.⁴¹ Another reported using Raney Ni in a batch process to yield selectivities of 77% PG, 15% ethanol, and 8% CO₂ at 63% conversion after 20 h.⁴² In a survey of catalysts screened for the GLY to PG conversion it was reported that with 80% aqueous glycerol, 200 °C, and 200 psi of H₂ a Raney Ni catalyst gave a selectivity of 53% for PG at 50% conversion after 24 h. Under the same conditions a Raney Cu catalyst yielded 69% selectivity to PG at 49% conversion. Some ACT was also produced.³³ Interestingly, no EG formation was reported in these articles even though EG was the primary byproduct observed in reactions run over

supported Ni catalysts.^{15–17} An early paper describing GLY conversion over Raney Cu at 240 °C and 750 psi of H₂ reported an 80% yield of PG and 20% EG at 85% conversion.⁴³

Most of what has been published in the open literature described the use of batch reactions for the GLY to PG reaction. However, continuous fixed bed processes are preferred over batch procedures because the former provide a higher catalyst/feed ratio, which offsets the low specific activity of catalysts, such as those containing Cu, as well as having the ability to remove byproducts such as water and CO₂ and, thus, minimizing any equilibrium constraints that may have led to the low yields observed in most batch reactions. We report here an examination of the effect that reaction variables have on the activity and selectivity of these Raney catalysts in the continuous conversion of GLY to PG. A preliminary report on the use of Raney Cu for the valorization of glycerol has been published.⁴⁴ The data cited in this previous report have been modified in the present description by the use of an improved analytical procedure involving five point curves for the internal standard calibrations.

2. RESULTS AND DISCUSSION

2.1. Raney Ni Catalysts. Relatively little has been published on the use of either Raney Ni^{33,41,42} or Raney Cu^{33,43,44} for the conversion of GLY to PG. This seeming discrepancy indicated that a reinvestigation of the use of Raney Ni and Raney Cu catalysts in this reaction was warranted, but given the reported relative inactivity of these catalysts in batch

processes^{33,41–43} as well as the advantages of fixed bed reactions cited above, the Raney Ni and Raney Cu promoted reactions were run in a continuous mode using a fixed bed reactor.

Research was initiated by an examination of the effect that the individual reaction parameters, temperature, H₂ pressure, GLY feed flow rate, and H₂ flow rate, had on the outcome of the Raney Ni-catalyzed reaction. Figures 1 and 2 depict the

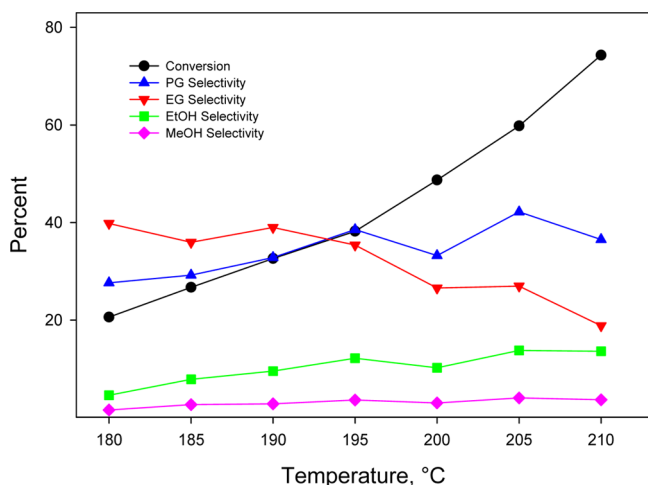


Figure 1. Effect of reaction temperature on the percent conversion and product composition for the GLY to PG reaction run over Raney Ni with an 80% aqueous GLY solution flow rate of 0.075 mL/min and a H₂ pressure of 300 psig and a flow rate of 150 mL/min.

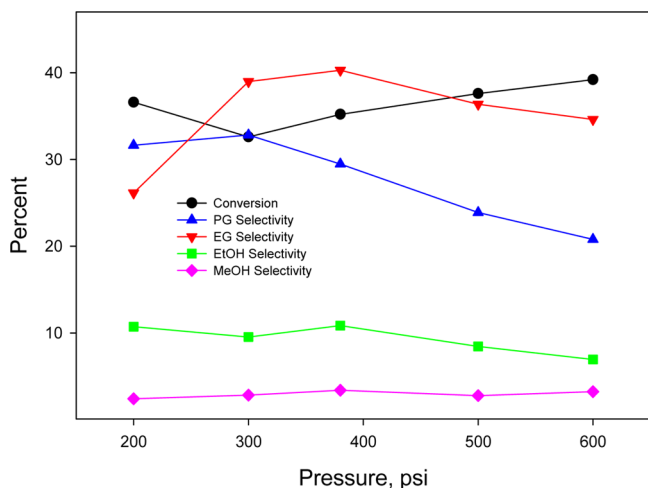


Figure 2. Effect of H₂ pressure on the percent conversion and product composition for the GLY to PG reaction run over Raney Ni at 190 °C, with an 80% aqueous GLY solution flow rate of 0.075 mL/min and a H₂ flow rate of 150 mL/min.

effect of temperature and hydrogen pressure, respectively, on the GLY conversion and reaction selectivity, and the effect of hydrogen and GLY feed flow rates are shown in Table 1. As Scheme 1 illustrates, the overall reaction sequence for GLY conversion is complex with the potential of having several reactions taking place simultaneously. In the equation at the top of Scheme 1, the dehydration of GLY followed by hydrogenation of ACT leads to the production of PG. The pathways at the bottom of Scheme 1 are responsible for the degradation of GLY to EG, EtOH, and MeOH. The totality of these

Table 1. Effect of H₂ and GLY Feed Flow Rates on Percent Conversion and Selectivity of PG, EG, EtOH, and MeOH in a Raney Ni-Catalyzed Conversion of GLY^a

H ₂ flow (mL/min)	100	150	200	100	150	200
GLY feed flow (mL/min)	0.025	0.025	0.025	0.075	0.075	0.075
conversion (%)	77	75.4	73	46	39.2	38
selectivity (%)						
PG	17.0	17.8	20.7	18.8	20.8	22.7
EG	20.0	24	32.3	25.1	34.6	39.5
EtOH	14.9	13.5	11.1	7.1	7.0	7.7
MeOH	7.6	7.4	6.1	2.8	3.2	3.6

^aTemp 190 °C, H₂ pressure, 600 psi, 80% aqueous GLY.

reactions is indicated by the percent conversion of GLY with the most significant effect on this aspect of the reaction being brought about by changes in the reaction temperature since this factor influences virtually all reactions in Scheme 1. Increasing the hydrogen pressure, however, had a more modest effect on the percent conversion since not all of the reactions used hydrogen. A faster GLY flow rate can cause a decrease in conversion because the reactants have insufficient time in contact with the catalyst to react completely.

The effect of these variables on the product composition, though, is more complex. A low GLY feed flow rate resulted in the reaction mixture being in contact with the catalyst longer, thus giving more degradation products. Increasing the hydrogen flow rate also increased the extent of degradation since there was more hydrogen available for hydrogenolysis. An increase in temperature apparently favored the hydrogenation steps over the C–C hydrogenolysis, while increasing the hydrogen pressure appeared to have the opposite effect. The *n*-PrOH and ACT selectivities were less than 1%, and the 1,3PG selectivity was between 1% and 1.5% in all of these reactions.

2.2. Raney Cu Catalysts. The large amount of EG, EtOH, and MeOH formed in the Raney Ni-promoted reactions showed that it was not a viable catalyst for the selective conversion of GLY to PG. It seemed, therefore, that since the use of other Raney-type catalysts had not been explored to any great extent primarily because of their commercial rarity and obscurity to date, a non-Ni catalyst would be a prime candidate for further study especially when used in continuous reactions. Given the interest in the use of Cu-containing catalysts for the GLY to PG conversion,^{19–38} it was decided to investigate the use of Raney Cu and modified Raney Cu catalysts for this reaction.

The ranges of the reaction parameters investigated in the Raney Cu-promoted reactions were based on the data obtained with Raney Ni. The effect of temperature in the range of 190–205 °C on the conversion and product composition in the Raney Cu-catalyzed reactions are shown in Table 2. As expected, increasing the temperature increased the conversion and the yield of PG. The amount of EG observed was significantly less than that formed during the Raney Ni-catalyzed reactions. Table 3 lists the percent conversion and the PG and EG selectivities observed from reactions run with varying GLY feed and H₂ flow rates as well as H₂ pressures. In all reactions the amounts of MeOH, EtOH, and ACT were less than 1% with no *n*-PrOH or 1,3PG observed. Increasing the GLY feed flow rate, with the concomitant decrease in residence time in the catalyst bed, resulted in a decrease in PG selectivity regardless of the H₂ flow rate. Increasing the GLY feed flow

Table 2. Temperature Effect on Raney Cu-Catalyzed Conversion of GLY to PG^a

temp (°C)	conversion (%)	PG yield (%)	PG selectivity (%)	EG selectivity (%)
190	86.3	73.2	84.9	2.6
200	99.9	80.5	80.6	2.3
205	100	81.4	81.4	1.7

^aReactions run at a H₂ flow rate of 150 mL/min and pressure of 200 psi and 80% aqueous GLY at a flow rate of 0.05 mL/min.

Table 3. Effect of GLY Feed Flow Rate and H₂ Flow Rate and Pressure on the Raney Cu-Catalyzed Conversion of GLY to PG^a

GLY feed flow rate (mL/min)	H ₂ flow rate (mL/min)	H ₂ pressure (psi)	conversion (%)	PG selectivity (%)	EG selectivity (%)
0.05	375	200	100	96.3	1.5
0.06	375	200	100	95.3	2.3
0.075	375	200	100	93.9	1.9
0.10	375	200	99.1	93.7	2.2
0.10	375	175	98.6	90.1	2.1
0.10	375	150	97.0	89.3	1.9
0.10	450	175	98.7	90.2	1.9
0.10	450	150	98.5	88.9	1.9
0.125	450	150	94.9	85.8	1.9
0.125	515	150	95.5	85.3	2.0
0.125	515	125	95.1	83.5	1.7

^aReactions run using 80% aqueous GLY at 205 °C.

rates above 0.1 mL/min decreased the percent conversion as well. As anticipated from the reactions shown in Scheme 1, decreasing the hydrogen pressure resulted in lower GLY conversions and PG formations. A higher H₂ flow rate somewhat compensated for a lower pressure. The data in Table 4 show that increasing the GLY concentration to 90%

Table 4. Effect of Glycerol Concentration on the Raney Cu-Catalyzed Conversion of GLY to PG^a

GLY concn (%)	conversion (%)	PG selectivity (%)	EG selectivity (%)
80	100	96.7	1.1
90	100	91.4	1.5

^aReactions run at 205 °C with a H₂ flow rate of 375 mL/min and pressure of 200 psi and a GLY feed flow rate of 0.05 mL/min.

resulted in a decrease in PG selectivity. Since virtually all of the previous research cited in the Introduction used aqueous solutions of GLY, it would appear that the presence of some water may be needed for this reaction. One possible scenario is that sufficient water in the GLY solution is needed to facilitate

the passage of the substrate and hydrogen through the liquid–solid barrier at the catalyst surface. If this is the case, then it would appear that the 90% GLY does not contain sufficient water for this to happen.

Since the addition of Cr has been shown to increase the activity and selectivity of supported Cu catalysts,²⁵ some Cr-modified Raney Cu catalysts were also used to promote the GLY to PG reaction. They were Raney Cu containing 2% Cr and Raney Cu containing 0.75% Cr and 2.8% Ni. These catalysts along with a commercial CuCrO catalyst and the unmodified Raney Cu were used in long-term GLY to PG reactions with the results shown in Table 5. While all of the reactions went to complete conversion, the use of the unmodified Raney Cu catalyst resulted in the highest PG selectivity. The drop in PG selectivity using Raney Cu-Cr suggests that the final hydrogenation step shown in Scheme 1 takes place primarily on the Cu surface. With the Raney Cu-Cr catalyst, the Cu is probably partially covered by CrO_x moieties. This decrease in hydrogenation ability allows time for the competing degradation reactions to take place. The Cu-CrO catalyst gave a differing product distribution, less PG, and more EtOH. In the first days of operation with this catalyst the product mixture was strongly colored, suggesting either some leaching or the presence of colored unanalyzed oligomers. This later is more consistent with the lower material balance observed with Cu-CrO (~92%) as opposed with 98.5% with Raney Cu. Since there was no interest in pursuing the use of Cu-CrO or the other modified catalysts, this matter was not investigated further.

The unmodified Raney Cu was stable under these same reaction conditions in runs of up to 24 d with the conversion remaining at 100% and a stable PG selectivity at 95%. However, under these reaction conditions the STY was only 0.17 g of PG/mL of catalyst/h. Data in the literature on the use of supported Cu catalysts show that higher temperatures could be used with Cu catalysts, but this was usually associated with higher H₂ pressures because the increase in temperature would decrease the H₂ coverage of the catalyst.^{19–21,25} With this in mind, the effect of increasing the reaction temperature was examined using a 50% aqueous GLY solution. The data in Table 6 show that increasing the temperature to 240 °C had no

Table 6. Effect of Higher Temperatures on the Raney Cu-Catalyzed Conversion of GLY to PG^a

temp (°C)	conversion (%)	PG selectivity (%)
210	100	96.2
225	100	96.3
240	100	83.8

^aReactions run with a H₂ flow rate of 300 mL/min and pressure of 600 psi and a GLY feed flow rate of 0.10 mL/min.

Table 5. Percent Conversions and Product Compositions from GLY Hydrogenolysis over Copper Catalysts^a

catalyst	TOS ^b (days)	conv (%)	selectivity (%)						
			PG	EG	MeOH	EtOH	<i>n</i> -PrOH	ACT	1,3PG
Raney Cu	6.2	100	95.0	1.9	0.9	0	0.2	0.4	0
Raney Cu-Cr	4.9	100	87.4	0.6	1.0	3.9	0	0.5	1.0
Raney Cu-Cr-Ni	3.9	100	82.9	1.8	0.2	0	0.2	0.4	0
Cu-CrO	5.0	100	82.5	0.7	0.9	2.2	0	0.5	0.5

^aReactions run at 205 °C with a H₂ flow rate of 375 mL/min and pressure of 200 psi and an 80% GLY feed flow rate of 0.05 mL/min. ^bTime on Stream.

effect on the GLY conversion. The PG selectivity was stable between 210 and 225 °C but decreased at the higher temperature. It was decided that further reactions would be run at 225 °C with the H₂ pressure increased to 600 psi and a H₂ flow of 300 mL/min.

With these changes the effects of GLY feed concentration and flow rate would have to be reexamined. In comparing the effect of different GLY feed concentrations, though, the flow rate is not a useful parameter since the use of different concentrations of GLY feed at the same flow rate would result in differing amounts of GLY feed passing through the catalyst over a given time. The factor that should be used is the weight hourly space velocity (WHSV), which is defined as the grams of substrate/gram of catalyst/h. The results from reactions run using 50%, 65%, and 80% aqueous GLY feeds at different WHSVs are shown in Figures 3 and 4. These data indicate that

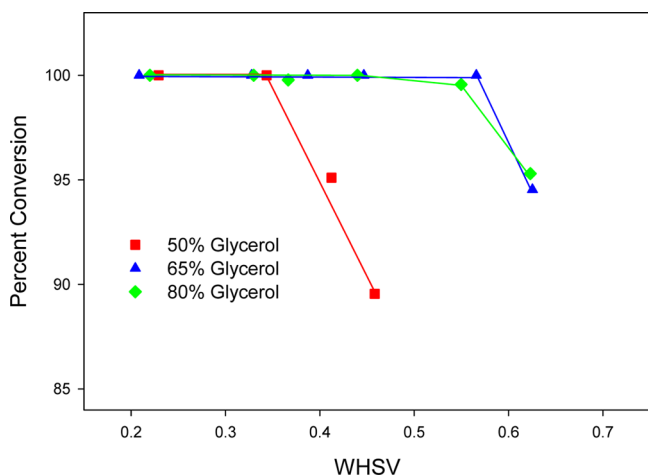


Figure 3. WHSV effect on the percent conversion observed using different aqueous GLY concentrations for the GLY to PG reaction run over Raney Cu at 225 °C with a H₂ pressure of 600 psig and a flow rate of 300 mL/min.

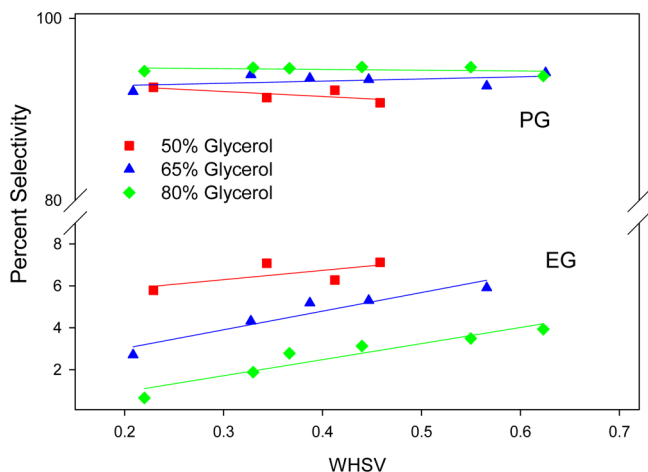


Figure 4. WHSV effect on the PG and EG selectivities observed using different aqueous GLY concentrations for the GLY to PG reaction run over Raney Cu at 225 °C with a H₂ pressure of 600 psig and a flow rate of 300 mL/min.

there is a combination of factors involved in the GLY to PG reaction. Among these is the effect that increasing the water concentration has on the competitive adsorption on the catalyst

surface between water and GLY. Another factor is the changing of the contact time (flow rate or WHSV) of the reactants with the catalyst and the effect it has on the kinetics of the reaction. A third factor is the effect that increasing the water concentration had on the reactions shown in Scheme 1. There are two separate aspects of this reaction which are summarized in Figures 3 and 4, the percent conversion of GLY and the selectivity in the formation of PG and EG from the GLY.

Increasing the flow rate will decrease the contact time of the water and GLY on the catalyst surface. This fact, combined with the competitive adsorption of water on the Cu surface, would indicate that at a particular flow rate GLY adsorption could be diminished to the extent that the conversion of GLY decreased. As shown in Figure 3, this point was reached with the 50% aqueous GLY at a flow rate of about 0.15 mL/min (WHSV = 0.35), while with the 65% GLY it was at a flow rate of about 0.19 mL/min (WHSV = 0.57) and with 80% GLY about 0.15 mL/min (WHSV = 0.55). This was not an indication of catalyst deactivation since when the flow rate was decreased, the conversion returned to 100%. This type of behavior was observed at other times when changes in the GLY feed flow rate was being examined. When a decrease in GLY conversion was noted with an increase in the GLY feed flow rate, the conversion could be recovered by returning to the original flow rate.

The product compositions shown in Figure 4, though, appear to depend on the effect that water had on the different reaction pathways depicted in Scheme 1. It is possible that an increase in the water content of the feed could inhibit the initial dehydration of GLY to form ACT, and this would decrease the formation of PG while shifting the catalytic activity to those paths that lead to the formation of EG, pathways in which water does not play a role. As the water content of the feed decreased, the amount of PG increased, though slightly, while the EG selectivity decreased significantly.

In Table 7 are shown the average product compositions for a reaction run continuously for 24 d using 80% aqueous GLY

Table 7. Product Composition from 24 d (580 h)
Continuous GLY Hydrogenolysis Catalyzed by Raney Cu^a

conv (%)	selectivity (%)					
	PG	EG	MeOH	EtOH	n-PrOH	ACT
100	94.6	2.5	0.4	0.7	0.6	1.0

^aReaction run at 225 °C with a H₂ flow rate of 300 mL/min and pressure of 600 psi and an 80% GLY flow rate of 0.12 mL/min.

over a Raney Cu catalyst at 225 °C, a H₂ flow rate of 300 mL/min, a H₂ pressure of 600 psi, and a GLY feed flow rate of 0.12 mL/min (WHSV = 0.440). Product compositions varied by less than 1% throughout the reaction. The STY, under these conditions, was 0.49 g PG/mL catalyst/h corresponding to 3.98 kg of PG being produced over the course of this reaction. The catalyst used for the reaction was a sample obtained from a commercial scale production of Raney Cu.

3. CONCLUSION

A commercially prepared Raney Cu catalyst has been shown to be an efficient and selective catalyst for the conversion of glycerol to propylene glycol under moderate conditions: 80% aqueous glycerol, 225 °C, H₂ pressure of 600 psig in a liquid phase fixed bed reactor. The unmodified Raney Cu catalyst was

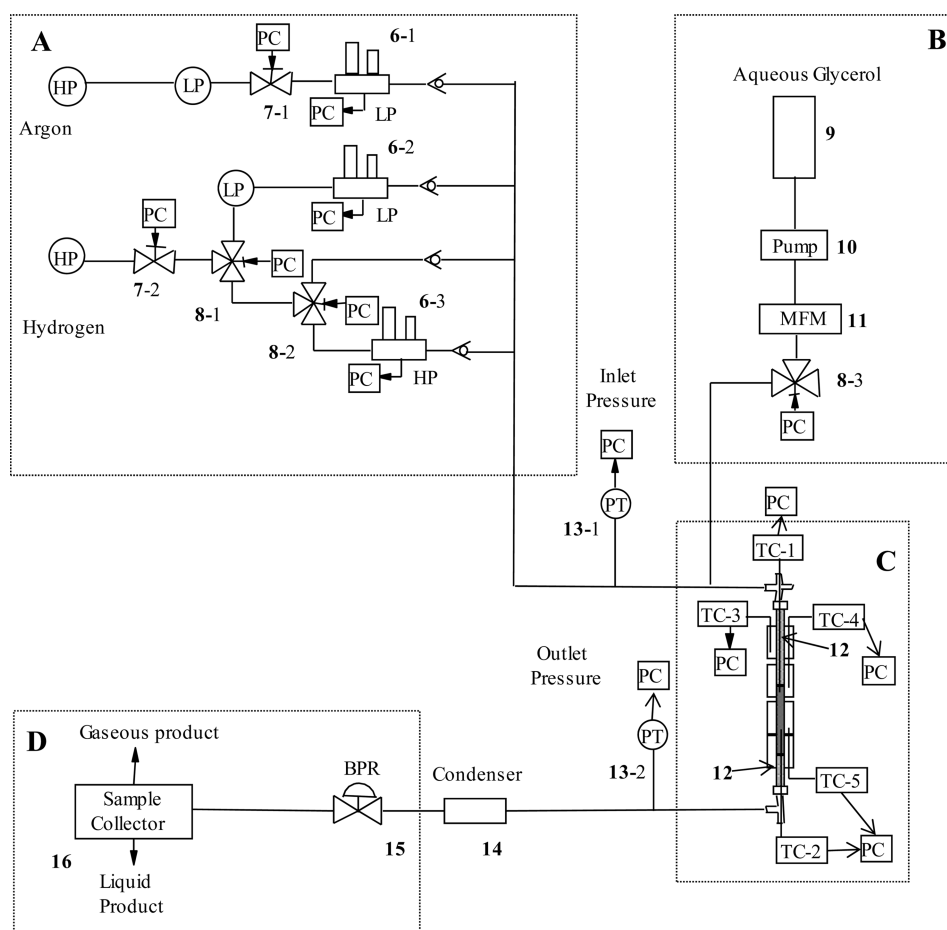


Figure 5. Fixed bed reactor.

shown to be superior to Raney Ni, Cu-CrO, and Raney Cu catalysts containing Cr and Ni modifiers.

4. EXPERIMENTAL SECTION

4.1. Materials. The Raney catalysts used in this study were made using proprietary techniques involving the partial leaching of Al from 8–12 mesh sized particles of Ni-Al, Cu-Al, Cu-Al-Cr, and Cu-Al-Ni-Cr alloys using dilute NaOH solutions. The copper chromite (Cu-CrO) catalyst was a 1/8 in. extrudate obtained from BASF, Elyria, OH. The sample used was obtained by first crushing the extrudates and sieving the resulting material to 10–20 mesh before packing the catalyst in the reactor. The Cu-CrO catalyst was reduced, in situ, in a 20 mL/min flow of hydrogen at 205 °C for 2 h, after raising the temperature at 20°/h from ambient to 205 °C. The Raney catalysts did not require any in situ activation.

4.2. Description of the Fixed Bed Reactor System. The continuous hydrogenation of glycerin over particulate Raney catalysts was carried out in the fixed bed reactor depicted in Figure 5. The gas control section, A, consisted of a channel for low pressure inert gas, a low pressure hydrogen line, a bypass channel for pressurizing the system, and a high pressure hydrogen delivery channel. All four channels were fitted with Brooks mass flow controllers (6) and high pressure two-way (7) and three-way (8) solenoid valves (Parker Instruments). All controllers and the solenoid valves were interfaced to an in-house developed data acquisition and control system.

Section B was the GLY feed unit. The GLY solution, in a glass reservoir (9), was kept under 30 psi nitrogen pressure and placed on a balance for continuous monitoring and recording of the amount of feed added over time. The solution was pumped into the reactor using a high precision Shimadzu LC-10AT pump (10), while the liquid flow rate was also monitored by a Brooks liquid mass flow meter (11).

Section C was a 0.5 in. i.d. tube reactor fitted with three band-heaters and 0.25 in. inlet and outlet ports. The reactor was partitioned into three zones with the temperatures in each zone controlled by two Omega temperature controllers, one for the internal reactor temperature and the second for controlling the temperature of the band heater. This combination of two controllers connected in series enabled maintaining the temperature of each zone within ± 0.2 °C. The top, preheating zone was fitted with 2 μ m stainless steel filters, 12, and used for preheating and mixing the aqueous glycerin and hydrogen. The second zone was the “hot catalyst” temperature zone with a thermocouple inserted 0.5 in. into the catalyst bed. The third zone was the catalyst bed temperature zone with a second thermocouple placed 0.5 in. into the lower section of the catalyst bed. The reactor inlet and outlet pressure were monitored by Omega pressure transducers (13).

The fourth section, D, consisted of a condenser (14), a domed back pressure regulator (15), and a gas–liquid separator (16) operated at a temperature of 6 °C. The excess hydrogen flow was directed to a trap kept in dry ice.

All two- and three-way valves, the mass flow controllers and meters, the reactor temperatures, the inlet and outlet pressures,

and the balance reading were constantly under computer control and monitoring. Special attention was paid to the safety of the flow system so when any one of the process parameters (temperatures in the reactor, pressure, and gas and liquid flows) varied by more than 10% from the preset values, the system was programmed to enter an “abort regime” that terminated the power to the heaters and the pump and vented the reactor to a bypass line.

4.3. Hydrogenolysis of GLY. Three filtering elements, **12**, were inserted over the bottom thermocouple to serve as a catalyst support (Figure 5). The catalyst, **14** mL (16.5 g), was suspended in water and carefully transferred into the reactor under a constant flow of water for uniform packing and protection from direct contact with air. A GC vibrator was used to avoid gaps between the particles. The reactor was sealed on the top with three additional filtering elements, **12**, to contain the catalyst bed. The reactor was attached to the feed and the exit lines.

The GLY solutions were prepared using deionized water at pH 7. At each set of reaction conditions the catalyst performance was stabilized by running the reaction for 6–7 h after which time 3 collections were made; 2 day-time collections for an average TOS of 8 h each and one overnight collection with an approximate 15 h TOS. All reactions were run in a down flow mode with both the aqueous GLY and the hydrogen introduced at the top of the reactor. The product flow exited the reactor and passed through a condenser, **14**, which was kept at 25 °C, and then to the BPR, **15**, which lowered the pressure to ambient. The exit flow was switched to a waste flask during the stabilization steps or to a collection flask during the reaction steps and analyzed offline. The gas phase was passed through a liquid trap held at –36 °C to condense low boiling products that may have been in the hydrogen flow.

4.4. GC Analysis. was done using an HP 5890 with FI detector and an RTX1701 capillary column (60 m, 0.53 mm i.d. and film thickness of 1 µm). 1,4-Butanediol was used as the internal standard with the response factor (RF) calibrations for the reaction products obtained using 5 point curves.

5. FORMULAS

% conversion GLY

$$= [\text{mmol conv GLY}] \cdot 100 / [\text{mmol GLY}]_0$$

% selectivity to product

$$= [\text{mmol product formed}] \cdot 100 / [\text{mmol conv GLY}]$$

space–time yield (STY) = g product/mL catalyst/h

weight hourly space velocity (WHSV)

$$= \text{g GLY} / \text{g catalyst} / \text{h}$$

liquid hourly space velocity (LHSV)

$$= \text{mL GLY} / \text{mL catalyst} / \text{h}$$

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Notes

The authors declare no competing financial interest.

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