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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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Keywords: Glycerol, Propylene Glycol, 1,2-Propanediol, Raney® Copper, Hydrogenolysis, Fixed Bed Reaction **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 by-product 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/cc 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.

TOC Graphic



1. INTRODUCTION

The increasing world-wide 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 which 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 which 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 ethers⁹ 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, 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 by-products in this reaction is ethylene glycol (EG). One possible route to its formation is that initiated by the dehydrogenation of GLY to glyceraldehde (**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 which also contained Pt¹³ 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,²⁰⁻²⁴modified with Cr²⁵⁻²⁹or as a component in a mixed oxide system³⁰⁻³² 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 since 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 °C to 270 °C; hydrogen pressures from 150 psi to 1500 psi with one patent³¹ describing the use of 3700-4400 psi of H₂. The batch reactions were run for 5 to 40 hours giving widely different results, reporting **GLY** conversions ranging from 23% to 100% and selectivities to **PG** from 20% to 95% as well as giving varying amounts of by-products, 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 Suppes³³⁻⁴⁰ 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 by-product 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 CO_2 and, thus, minimizing any equilibrium constraints which may have led to the low yields observed in most batch reactions. We report here an examination of the effect which 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

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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 re-investigation 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



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 cc/min and a H₂ pressure of 300 psig and a flow rate of 150 cc/min.



Figure 2. Effect of H_2 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 cc/min and a H_2 flow rate of 150 cc/min.

Raney® Cu promoted reactions were run in a continuous mode using a fixed bed reactor.

Research was initiated by an examination of the effect which 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. Figure 1 and Figure 2 depict the effect of temperature and hydrogen pressure, respectively, on the **GLY** conversion and reaction selectivity while 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 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 the 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

Table 1. Effect of H_2 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*}

ataryzed conver		111.				
H ₂ Flow,	100	150	200	100	150	200
cc/min						
GLY Feed	0.025	0.025	0.025	0.075	0.075	0.075
Flow, cc/min						
% 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
^{<i>i</i>} Temp. 190 °C,	H ₂ pressu	ıre, 600 p	si, 80% a	queous (GLY.	

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 °C to 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

Table 2. Temperature effect on Raney® Cucatalyzed conversion of GLY to PG.^a

°C	% Conv. ^b	% PG Yield	% PG Sel. ^c	% EG Sel. ^c
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

^{*a*} Reactions run at a H_2 flow rate of 150 cc/min and pressure of 200 psi and 80% aqueous **GLY** at a flow rate of 0.05 cc/min.

- ^b Conversion
- ^c Selectivity

Table 3. Effect of GLY feed flow rate and H ₂ flow rate and pressure on the
Raney [®] Cu catalyzed conversion of GLY to PG . ^{<i>a</i>}

GLY Feed Flow Rate cc/min	H ₂ Flow Rate cc/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

^{*a*} Reactions run using an 80% aqueous GLY at 205 °C.

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 rates above 0.1 cc/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% 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 liquidsolid 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. **Table 4.** Effect of glycerol concentration onthe Raney $\ensuremath{\mathbb{R}}$ Cu catalyzed conversion of**GLY** to **PG**.^{*a*}

GLY	%	% PG	% EG
Conc. ^b	Conv. ^c	$\mathrm{Sel.}^d$	Sel. ^d
80%	100	96.7	1.1
90%	100	91.4	1.5

^{*a*} Reactions run at 205 °C with a H_2 flow rate of 375 cc/min and pressure of 200 psi and a **GLY** feed flow rate of 0.05 cc/min.

- ^b Concentration.
- ^c Conversion.
- ^{*d*} Selectivity.

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

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the first days of operation with this catalyst the product mixture was strongly colored suggesting

Table 5. Percent conversions and product compositions from **GLY** hydrogenolysis over copper catalysts.^a

% Selectivities

Catalyst	TOS ^b (Days)	% Conv.	PG	EG	MeOH	EtOH	n- PrOH	ACT	1 ,3 PG
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

^a Reactions run at 205 °C with a H₂ flow rate of 375 cc/min and pressure of 200 psi and an 80% GLY feed flow rate of 0.05 cc/min.

^b Time on Stream.

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 grams of PG/cc 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 effect on the **GLY** conversion. The **PG** selectivity was stable between 210 °C 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 cc/min.

Table 6. Effe	ect of higher ter	nperatures on
the Raney® C	u catalyzed co	nversion
of GLY to PC		
Temperature	%	% PG
°C	Conversion	Selectivity
210	100	96.2
225	100	96.3
240	100	83.8

^{*a*} Reactions run with a H_2 flow rate of 300 cc/min and pressure of 600 psi and a **GLY** feed flow rate of 0.10 cc/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 which 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 WHSV's are shown in Figures 3 and 4. These data indicate that there is a combination of factors involved in the GLY to PG reaction. Among these is the effect which 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 which 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.



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 cc/min.

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 cc/min (WHSV = 0.35) while with the 65% **GLY** it was at a flow rate of about 0.19 cc/min (WHSV = 0.57) and with 80% **GLY** about 0.15 cc/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.



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 H_2 pressure of 600 psig and a flow rate of 300 cc/min.

The product compositions shown in Figure 4, though, appear to depend on the effect which 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 which 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.

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Table 7. Prcatalyzed by	oduct comp A Ranev® C	osition fron u. ^a	n 24 d (580 h)	continuous	GLY hydrog	enolysis
,	, <u>)</u>		% Selec	tivities		
% Conv.	PG	EG	МеОН	EtOH	n-PrOH	ACT
100	94.6	2.5	0.4	0.7	0.6	1.0

• , • c

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

In Table 7 are shown the average product compositions for a reaction run continuously for 24 d using 80% aqueous GLY over a Raney® Cu catalyst at 225 °C, a H₂ flow rate of 300 cc/min, a H_2 pressure of 600 psi and a GLY feed flow rate of 0.12 cc/min (WHSV = 0.440). Product compositions varied by less than 1% throughout the reaction. The STY, under these conditions, was 0.49 g PG/cc 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 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 to 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"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 by-pass 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 \mathbf{C} was a 0.5 inch id tube reactor fitted with three band-heaters and quarter inch 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

Figure 5. Fixed bed reactor

controllers connected in series enabled maintaining the temperature of each zone within ± 0.2 °C. The top, pre-heating, zone was fitted with 2 µm 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 inch into the catalyst bed. The third zone was the catalyst bed temperature zone with a second thermocouple placed 0.5 inch 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, gas and liquid flows) varied by more than 10% from the pre-set values, the system was programmed to enter an "abort regime" which terminated the power to the heaters and the pump and vented the reactor to a by-pass 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 cc (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 de-ionized 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, 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 which 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 ID and film thickness of 1 μ m). 1,4-Butanediol was used as the internal standard with the response factor (RF) calibrations for the reaction products obtained using 5 point curves.

FORMULAS

% Conversion of **GLY** = [mmol converted **GLY**] * 100 / [mmol **GLY**]_o % Selectivity to PRODUCT = [mmol PRODUCT formed] * 100 / [mmol converted **GLY**] Space-Time-Yield (STY) = g PRODUCT/cc catalyst/h Weight Hourly Space Velocity (WHSV) = g **GLY**/g catalyst/h

Liquid Hourly Space Velocity (LHSV) = cc GLY/cc catalyst/h

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