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Low-Pressure Packed-Bed Gas Phase Conversion of Glycerol to Acetol

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This article describes the investigations carried out on the vapor-phase hydrogenolysis of glycerol to acetol over a copper-chromite catalyst in a packed bed flow reactor. The effects of reaction method (liquid-phase vs. vapor-phase mode), vapor-phase reaction with gas feed, reaction temperature, catalyst loading, and hydrogen feed rate were studied to arrive at optimum conditions. Operating the reactor in vapor-phase mode dramatically reduced the amount of undesired by-product formation, and thereby increased the overall yield of acetol and propylene glycol. The optimum reaction temperature is near 220°C. Higher hydrogen feed rates increased propylene glycol selectivity. The proposed production scheme has application for production of both acetol and propylene glycol from the crude glycerol that contains various soluble salts.

Keywords: catalyst, reactor, glycerol, acetol

Introduction

There is considerable interest in developing biodiesel as an alternative fuel in recent years because of its environmental benefits and because it is derived from renewable resources including vegetable oils or animal fats.[1–4] As the production of biodiesel increases, the amount of crude glycerol which is generated as a byproduct from transesterification will also increase.

In biodiesel production, ~1 pound of glycerol by-product is produced for every 9 pounds of biodiesel produced. In the U.S., the 2007 production of biodiesel was about 400 million gallons. The U.S. consumption of glycerol is about 400 million pounds per year, which was met by existing capacity in the industry (before the relatively new biodiesel industry). At current production trends, the amount of glycerol produced in the U.S. in 2008 will be about double the recent demand. New glycerol uses are needed.

Propylene glycol is currently produced in large scale by hydration of propylene oxide (from petroleum) through either the chlorohydrin process or the hydroperoxide process.[5,6] Propylene glycol is employed in numerous industrial and commercial applications, for example, moistening agent in the cosmetic and food industries, functional fluids (antifreeze, deicing, and heat-transfer agents), and as a solvent for fats, oils, resins, and dyestuffs. It also serves as raw product for manufacture of other products. The recent propylene glycol market is twice that of glycerol, and the antifreeze market is five times that of glycerol. The hydrogenolysis of biodiesel's crude glycerol to propylene glycol used as antifreeze could sustain prices better than recent glycerol markets and would have a positive economic impact on biodiesel production.

Reaction mechanism

Much is published on the hydrogenolysis of glycerol to propylene glycol. In an earlier work,[7] we proposed the novel reaction mechanism for converting glycerol to propylene glycol via a reactive intermediate as shown in Figure 1. Relatively pure acetol was isolated from dehydration of glycerol as the transient intermediate. The isolation of this intermediate and similarity of reactions using either glycerol or acetol as the fed reagent validated this two-step reaction process for copper chromite catalysis at temperatures less than 250°C.[8]

Several publications and patents document multiple schemes for hydrogenating glycerol to propylene glycol.

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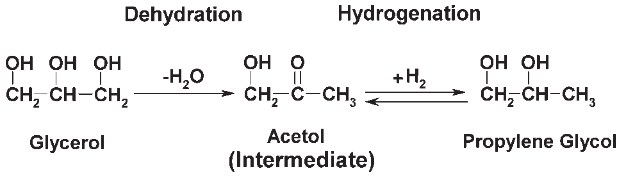

Figure 1. Proposed reaction mechanism for conversion of glycerol to propylene glycol.

Casale et al.[9,10] described a method of hydrogenating glycerol using copper and zinc catalyst as well as sulfided ruthenium catalyst at a pressure of 150 bar and temperatures in the range of 240–270°C. Schuster et al.[11] described a method for production of propane diols using a catalyst containing cobalt, copper, manganese, molybdenum, and an inorganic polyacid achieving a 95% yield of propylene glycol at a pressure of 250 bar and a temperature of 250°C. Che et al.[12] described a method for 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.[13] 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 the production of propanediol from glycerol and sugars.[14,15]

Fleckenstein et al.[16] used a copper-chromite catalysis in a packed-bed. They ran the reactor as two phases (technically three, liquid-gas-catalyst). Their system required 250 bars of pressure. They had far greater product degradation. Liquid in this system promotes side reactions and creates a barrier between the gaseous hydrogen and catalyst surface.

However, these previously patented approaches have several drawbacks including higher temperatures and pressures than may be necessary or optimal, low production efficiency from using diluted solutions (with water) of glycerol, low selectivity to propylene glycol, and relatively high selectivity to ethylene glycol and other by-products.

Unnecessarily, high selectivities to ethylene glycol have several drawbacks. Separation of propylene glycol and ethylene glycol is costly because of the close proximity of their boiling points. Additionally, by utilizing only two, instead of three, carbons the atom economy for ethylene glycol formation is also lower. Finally, ethylene glycol does not carry the premium price associated with propylene glycol.

A new gas-phase, lower pressure approach has been developed for propylene glycol production.[17] The technology has been developed to the point of commercial viability for converting glycerol to propylene glycol based on copper-chromite catalysis. The preferred method for preparing acetol and propylene glycol from glycerol includes a vapor-phase reaction over a copper-chromite catalyst in a packed bed reactor. In the presence of hydrogen, the vapor-phase reaction approach allows glycerol to be converted to propylene glycol in a single reactor. This approach was demonstrated in a continuous process to address the concerns of scalability and catalyst recycle.

Earlier work in our group has demonstrated that copper-based catalysts exhibit higher selectivity toward propylene glycol with little or no selectivity toward ethylene glycol and other degradation by-products.[7] In the absence of hydrogen, glycerol can be dehydrated to hydroxyacetone (acetol) via a reactive-distillation technique. From our previous studies, high acetol selectivities were obtained by using copper-chromite mixed oxide catalysts.[8] It is known that these catalysts exhibit poor hydrogenolytic activity toward C—C bonds and efficient activity for C—O bond hydrodehydrogenation.[18,19]

An alternative method uses a two-step synthesis involving a reactive-distillation step to form acetol followed by acetol hydrogenation.[20] This approach reduces oligomer by-product formation and the associated catalyst deactivation that occurs in slurry-phase reactions.

The present study focuses on preparing acetol from glycerol in vapor-phase reactions using a packed bed reactor maintained above the reaction mixture dew point temperature. The effects of liquid vs. gas phases, hydrogen vs. nitrogen gases, and reaction temperature were experimentally studied using copper-chromite catalyst.

Experimental Methods

Materials

Glycerol (99.9%) propylene glycol (99.5%), acetol (90% in water), *n*-butanol (99.9%), and Karl Fisher titrant were purchased from Sigma-Aldrich (Milwaukee, WI). Methanol (HPLC grade, 99.9%) was purchased from Fisher Scientific Co. (Fairlawn, NJ). Copper-chromite catalyst containing a mixture of copper and chromium impregnated on an activated carbon support was purchased from Sud-Chemie. Table 1 gives the specification of copper-chromite catalyst. The copper-chromite catalyst used in this study was reduced prior to reaction per the suppliers recommended procedures.

Catalyst activation procedures

Nitrogen and hydrogen were used to remove the heat generated during the activation process. The catalyst bed was heated while purging the system with nitrogen until the minimum activation temperature of 130°C was reached. The catalyst was then activated by a slow, stepwise, hydrogen addition, beginning with hydrogen concentrations of 1% until over 95% hydrogen was present. An exotherm was observed each time the hydrogen concentration increased; thus, the hydrogen addition was controlled carefully to limit the temperature in the catalyst bed to a maximum temperature of 170°C. After the hydrogen had reached the 95% concentration, and after all exotherms had passed through the catalyst

Table 1. Specifications of Copper-Chromite Catalyst

Type	Cu/Cr
Form	Tablets
Size (mm)	3 × 3
Surface area (BET, m^2/g)	30
Porous volume (cm^3/g)	0.2
Bulk density (g/cm^3)	0.8
Cu content (calculated as CuO in weight percent)	45%
Cr content (calculated as Cr_2O_3 in weight percent)	47%
MnO_2	3.5%
BaO	2.7%

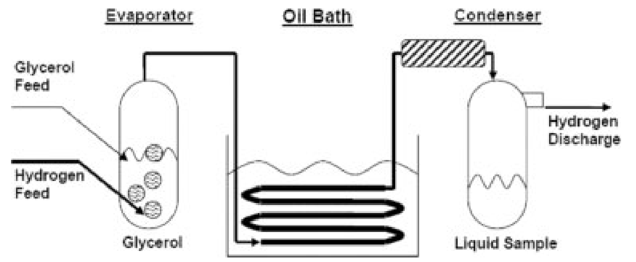

Figure 2. Experimental setup for converting glycerol to propylene glycol.

The packed bed reactor is indicated by the coil in the oil bath.

bed, the catalyst was slowly heated to a hold temperature of 180°C for 4 h.

Vapor-phase packed bed experiment

The experiments were carried out in a stainless steel tube reactor having a length of 6 m with an inner diameter of 19 mm. The reactor was packed with 3 mm × 3 mm pellets of copper-chromite catalyst. Figure 2 provides a schematic of the reaction system.

The glycerol was loaded into the evaporator at the start of the experiment and continuously introduced through an auxiliary feed to the evaporator during the experiment. The gas (hydrogen or nitrogen) flow rates were measured and controlled by a rotameter. They were introduced at the bottom of the evaporator to promote evaporation through gas–liquid contact. The evaporator was operated at a temperature of 230°C to promote evaporation of glycerol and form a vapor reactor influent.

The packed bed reactor was heated by immersing it in a constant temperature oil batch, the temperature of which was maintained within ±1°C of the desired temperature via a fluid temperature control unit. Thermocouples were placed concentrically in the reactor to measure the temperature in the catalyst bed. A condenser was attached to the end of the packed bed reactor through which chilled water was circulated.

The steady-state conditions were achieved by passing the reactants through the reactor kept at the operating temperature for 1 h. The product samples were collected for 30 min and were analyzed by gas chromatography. Glycerol was loaded into the evaporator at the start of the experiment and continuously introduced through an auxiliary feed to the evaporator during the experiment. All experiments were carried out under steady-state isothermal conditions. The copper-chromite catalyst was reduced by the procedures described in the section on catalyst activation procedures.

For the experiments conducted at pressures below 1 bar (vacuum), an aspirator was connected to the gas phase discharge of the condenser at the end of the process. A vacuum environment promoted evaporation of glycerol at a temperature of 230°C to form a vapor reactor influent. The reduced pressure literally caused the reactants to be drawn through the system and allowed the ratio of hydrogen to glycerol that entered the reactor to be reduced below what is possible at atmospheric pressure.

For liquid-phase reactions, the preheated glycerol was continuously fed into the reactor at a constant rate of 90 g/h over a period of about 2 h.

Liquid-phase packed bed experiment

Liquid-phase packed bed experiments were carried out in the same packed bed reactor setup as described in the section of vapor-phase packed bed experiment. The preheated glycerol was continuously introduced into the packed bed reactor with a constant flow rate by a peristaltic pump. All liquid-phase experiments were conducted at a reduced pressure of 0.1 bar by using an aspirator.

Analytical methods

The liquid samples in the distillate were weighed and 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.

For preparation of the GC samples, 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. Two microliters of the sample was injected into the column. The oven temperature program consisted of an initial condition of 45°C (0 min), ramp at 0.2°C/min to 46°C (5 min), ramp at 30°C/min to 220°C (5.5 min). Figure 3 shows a typical gas chromatogram of the 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. The concentration of water was measured by a Metrohm 758 KFD Titrino (Herisau, Switzweland) with Karl Fisher titrant. The samples were diluted with methanol before titration.

For each data point, the conversion of glycerol and the yield of product were calculated. The conversion of glycerol is defined as the moles of glycerol reacted divided by moles introduced into the reactor. The yield was calculated as the moles of the product (acetol, ethylene glycol, or propylene glycol) produced divided by the moles of glycerol introduced into the reactor.

Results and Discussion

A series of experiments were conducted to evaluate the process variables that could impact the performance of low-pressure vapor-phase packed bed reactor. The effects of reaction method (liquid-phase vs. vapor-phase mode), vapor-phase reaction with gas feed (hydrogen vs. nitrogen feed), catalyst loading, reaction temperature, and hydrogen feed rate for the glycerol hydrogenolysis reaction were determined using copper-chromite catalyst.

Liquid-phase vs. vapor-phase packed bed method

Glycerol was reacted on each of liquid-phase and vapor-phase reactions over a copper-chromite catalyst to form acetol in the same packed bed reactor.

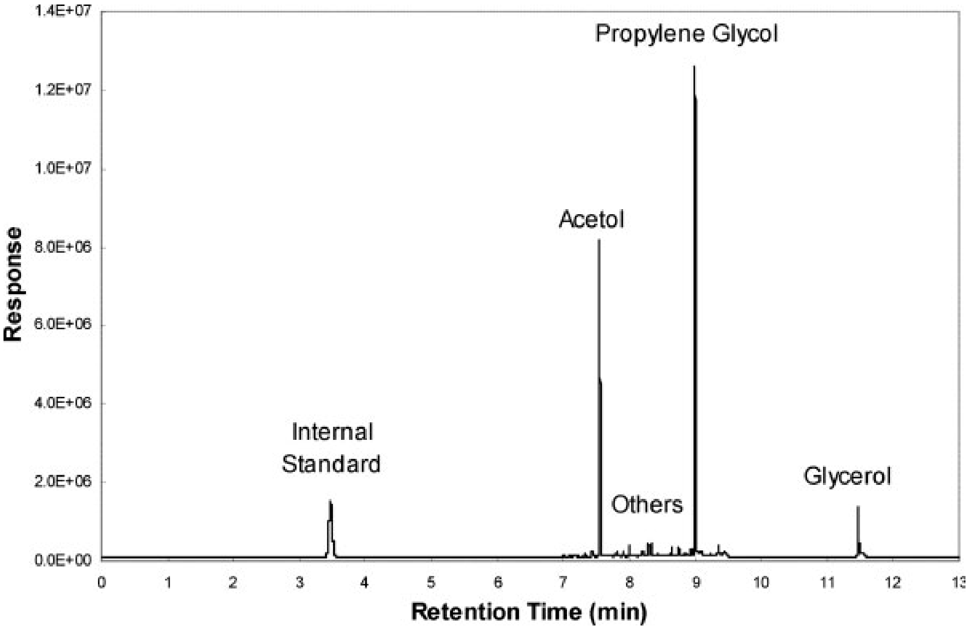

Figure 3. Gas chromatogram of the reaction product.

Table 2 provides an example of the conversion data over copper-chromite catalyst. The decrease of by-products and high acetol formation for the vapor phase illustrates the effectiveness of the vapor-phase reaction over a packed bed of catalyst for producing acetol in high yield and selectivity relative to the liquid-phase reaction.

From experimental observation during these studies, acetol tends to polymerize into dark gel at temperatures above 150°C. At the reaction conditions and by analogy, in the absence of inhibitors, acetol has a high tendency to polymerize to highly crosslinked solids which are infusible and insoluble in common solvents.[21] Acetol and acrolein are both possible dehydration products of glycerol. The vapor phase reaction reduces the polymer or oligomer formation through two mechanisms. First, the residence time for the gas is much less than for the liquid. Second, the density of acetol is less in the gas phase, and lower densities dramatically reduce polymerization reactions (which tend to be higher order reactions).

Vapor-phase packed bed reaction with gas feed

It was observed that propylene glycol was produced even in the absence of hydrogen. Since the only source of hydrogen for reacting with acetol or glycerol to form propylene glycol was from another acetol or glycerol molecule, it was hypothesized that the absence of free hydrogen in the system led to scavenging of hydrogen from the glycerol and that this scavenging led to undesired by-products and loss in yield. To overcome the hypothesized problem with scavenging of hydrogen from glycerol, hydrogen was introduced to the system.

When glycerol is evaporated in the presence of gas, the gas will tend to dilute the glycerol vapors (constant pressure assumption). Glycerol has a vapor pressure of 0.15 bar at 230°C. In view of this, hydrogen was fed into the evaporator, rather than after the evaporator, and thus the gas diluent promoted evaporation of glycerol.

Table 3 provides example conversion data illustrating the beneficial impact of a hydrogen feed (feed) with the glycerol feed in the packed bed reactor. A higher yield to acetol and propylene glycol was observed with the hydrogen feed compared to that without a hydrogen feed.

Dehydration of glycerol to acetol produces one water molecule for every acetol molecule that is formed. Water present in excess indicates excess dehydration and lower selectivities. The ratio of the amount of water produced to the stoichiometric amount that would be generated at 100% selectivity to acetol (and propylene glycol) is a good indicator of by-product formation. Based on the data in Table 3, the ratio of

Table 2. Comparison of Liquid-Phase and Vapor-Phase Packed Bed Reaction on Formation of Acetol and Propylene Glycol from Glycerol*

		Product Distribution (wt %)			
	Glycerol Conversion (%)	Acetol	Propylene Glycol	Water	By-Products[†]
Liquid-phase	20.4	6.1	0.9	8.1	5.3
Vapor-phase	22.1	13.7	1.1	6.5	0.8

*All the reactions were performed over a copper-chromite catalyst of 50 g at a reaction temperature of 230°C and a reduced pressure of 0.1 bar in the packed bed reactor. Reactions were run for 2 h rather than 30 min as indicated in the section on experimental methods.

[†] The sum of unidentified compounds.

Table 3. **Comparison of Vapor-Phase Packed Bed Reaction with Gas Feed and Without Gas Feed on Formation of Acetol and Propylene Glycol from Glycerol**

Gas Feed	Glycerol Conversion (%)	Product Distribution (wt %)				Total Acetol and Propylene Glycol Yield (%)
		Acetol	Propylene Glycol	Water	By-Products*	
No gas[†]	22.1	13.7	1.1	6.5	0.8	18.3
Hydrogen[‡]	25.6	18.4	1.5	5.4	0.4	24.7
Nitrogen[‡]	20.7	11.2	0.5	6.9	2.1	14.6

*The sum of unidentified compounds.

[†] All the reaction was performed on the vapor-phase reaction over a copper-chromite catalyst of 50 g at a reaction temperature of 230°C and a reduced pressure of 0.1 bar.

[‡] All the reactions were performed on the vapor-phase reaction over a copper-chromite catalyst of 50 g at a reaction temperature of 230°C and atmospheric pressure, with a gas feed rate of 0.1 L/min.

actual to theoretical water content decreased from 1.47 to 1.05 as a result of hydrogen being present during the dehydration reaction. In addition, the ratio of undesired by-product to desired products (acetol and propylene glycol) decreased from 0.05 to 0.02 as a result of hydrogen being present during the dehydration reaction.

In order to confirm that the desired results were a result of hydrogen rather than any other diluent gas in the system, a control experiment was performed using nitrogen as the gas diluent. The ratio of actual to theoretical water increased to 1.66 with nitrogen. In addition, the ratio of the undesired by-product "others" to desired products (acetol and propylene glycol) increased to 0.18. The result demonstrates that nitrogen was not as good as hydrogen based on higher water content and undesired by-products.

The yields in Table 3 are for propylene glycol, acetol, and those by-products that are present in concentrations of about 0.25 wt % or higher. The yield is on a carbon basis, and discrepancies between the sum of the yields and conversion can be attributed to vapor-phase products that do not completely condense (e.g., methanol) and to a multitude of products at less than 0.25%. The carbon balances are near 100%.

Dilute reaction studies

Reactions were performed at 2.5% glycerol in water as compared to reactions without water present as reported in Tables 2 and 3. Reactions at 2.5% glycerol in water are better able to approach isothermal behavior for this highly exothermic reaction, since this large excess of water provides a large heat capacity to moderate any temperature changes. In addition, 2.5 wt % glycerol (MW = 92.1) in water (MW = 18) is equivalent to 0.5 mol %. At 1 bar of operating pressure, this is equated to 0.005 bars of partial pressure. Addition of hydrogen to this reaction system further lowers the partial pressure.

For reactions operated at feed of 2.5% glycerol in water, no initial loading of glycerol was placed in the evaporator. Also, no liquids were observed to accumulate in the evaporator (they all evaporated).

Table 4 summarizes conversion as a function of temperature and hydrogen flow rate. Glycerol conversion was

Table 4. **Impact of Temperature and Flow Rates on Conversion of Glycerol at 1 bar Over 92 g of Copper-Chromite Catalyst with a Feed of 2.5 wt % Glycerol in Water**

Feed (g/h)	H_2 (L/min)	T (°C)	Acetol (wt %)	Propylene Glycol (wt %)	Glycerol (wt %)
300	0	230	94.7	0.00	0.00
150	0	230	96.7	0.00	0.00
150	0	200	85.5	0.00	0.00
300	0.27	230	89.6	6.13	0.00
150	0.27	230	84.4	15.6	0.00
300	0.27	200	96.7	3.27	0.00
150	0.27	200	77.5	22.5	0.00
150	1	230	69.3	15.2	0.00
300	1	230	86.0	8.69	0.00
150	1	200	76.1	22. 7	0.00
300	1	200	76.5	23.5	0.00
300	3	230	70.0	30.0	0.00
150	3	230	61.7	37.3	0.00
300	3	200	64.8	35.2	0.00
150	3	200	44.5	55.5	0.00
150	3	170	41.7	48.1	5.79

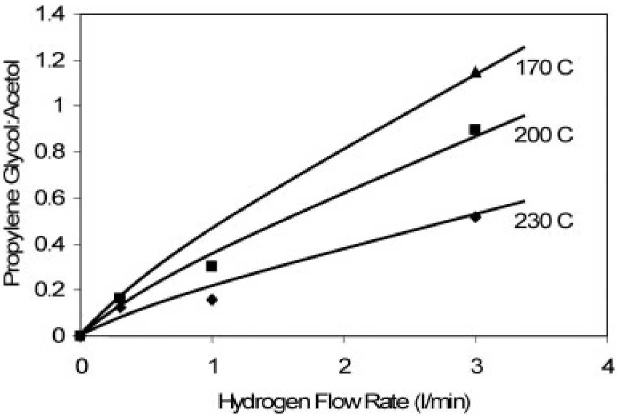

Figure 4. Impact of hydrogen flow rate and temperature on the ratio of propylene glycol to acetol in the product.

Values at different liquid flow rates were averaged.

complete except at 170°C. The impact of doubling the liquid feed flow rate was within the standard deviation of the data (no impact detected). Higher hydrogen flow rates shifted the equilibrium to favor propylene glycol formation as expected based on the reaction mechanism of Figure 1, which shows the acetol hydrogenation as being equilibrium limited. Higher temperatures shifted the equilibrium in favor of acetol as would be expected for the exothermic hydrogenation step.

In contrast to the nitrogen control experiment of Table 3, at zero hydrogen loading, the zero-hydrogen loading conversions of Table 4 show no yield to propylene glycol. In the absence of hydrogen, acetol is hypothesized to scavenge hydrogen from glycerol or other acetol molecules. This scavenging is hypothesized as a second-order process that produces more by-products. At greater dilutions, these second-order reactions would be expected to markedly decrease, as is observed in the highly dilute reaction system at 2.5% glycerol in water.

Figure 4 illustrates the impact of temperature and hydrogen flow rate on the ratio of propylene glycol to acetol in the product. The data supports the equilibrium-limited step of the reaction scheme of Figure 1 for exothermic hydrogenation.

Effect of catalyst loading

To estimate catalyst utilization, catalyst loadings from 50 to 150 g using crushed small catalyst (9–40 mesh) were evaluated. Table 5 summarizes the conversion results. Doubling the catalyst mass doubled the conversion. Tripling the catalyst mass (50–150 g) tripled the conversion. To a first approximation, this reaction is zero-order.

Further catalyst loadings of 770, 1160, 1350, and 1560 g were evaluated in the manufactured 3-mm pellets. The data at higher loadings indicated full glycerol conversion at 230°C and loadings greater than about 1000 g of catalyst for a glycerol feed rate of 90 g/h condensate accumulation (no water other than that formed during reaction).

At catalyst loadings greater than 1160 g, yields of acetol and propylene glycol decreased. It was also observed that the amount of water and undesired by-product formation increased with increasing catalyst loading. This indicates that acetol and propylene glycol undergo further hydrogenolysis and dehydration reactions to form additional by-products. The excess catalyst promotes excessive reaction, converting acetol, and propylene glycol to degradation products. Hence, to get a desirable conversion of glycerol with high selectivity to acetol and propylene glycol, an optimal amount of catalyst should be used depending on feed flow rate.

It should be noted that subsequent reactions using catalyst that was prereduced by the manufacturer led to improved catalyst utilization, up to about 1.5 (grams of catalyst/grams of glycerol conversion per hour).

Effect of reaction temperature

Experiments were conducted on the vapor-phase reaction over a copper-chromite catalyst at 200, 210, 220, 230, and 240°C and at atmospheric pressure with hydrogen feed in the packed bed reactor. Table 6 shows the effect of temperature on the conversion and yield of the reaction.

The glycerol conversion of 78% was obtained at a reaction temperature of 200°C. A 100% glycerol conversion was achieved at 220°C. At 210°C and 200°C, the conversion of glycerol was less than 100% due to the insufficient lower reaction rates. The selectivity to acetol and propylene glycol decreased as the temperature was further increased from 220

Table 5. Effect of Catalyst Loading on Formation of Acetol and Propylene Glycol from Glycerol

Catalyst Loading (g)	Glycerol Conversion (%)	Product Distribution (wt %)				Total Acetol and Propylene Glycol Yield (%)
		Acetol	Propylene Glycol	Water	Others[*]	
Catalyst size: 9–40 mesh[†]						
50	31.9	23.1	1.7	6.5	0.6	30.8
100	63.5	44.7	2.4	13.0	3.4	58.5
150	92.9	64.1	6.4	18.8	3.6	87.4
Catalyst size: 3 × 3 mm[‡]						
760	84.5	41.9	23.2	17.0	2.6	80.2
1160	100.0	44.0	28.6	21.4	5.8	89.3
1350	100.0	43.6	27.5	22.2	6.5	87.5
1560	100.0	42.3	26.9	22.9	7.9	85.1

[*] The sum of unidentified compounds.

[†] All the reactions were performed on the vapor-phase reaction over a copper-chromite catalyst at 230°C and atmospheric pressure with a hydrogen feed rate of 0.1 L/min.

[‡] All the reactions were performed on the vapor-phase reaction over a copper-chromite catalyst at 220°C and atmospheric pressure with a hydrogen feed rate of 2.4 L/min.

Table 6. Effect of Reaction Temperature on Formation of Acetol and Propylene Glycol from Glycerol*

Temperature (°C)	Glycerol Conversion (%)	Product Distribution (wt %)				Total Acetol and Propylene Glycol Yield (%)
		Acetol	Propylene Glycol	Water	Others†	
200	78.1	26.1	35.3	15.8	2.3	78.0
210	91.6	30.6	39.3	18.6	3.2	85.6
220	100.0	32.1	42.4	20.9	4.6	91.2
230	100.0	32.3	38.7	23.2	5.9	87.0
240	100.0	31.4	35.1	25.6	8.3	81.5

*All the reactions were performed on the vapor-phase reaction over a copper-chromite catalyst of 1160 g at atmospheric pressure with hydrogen feed rate of 5 L/min.

†The sum of unidentified compounds.

to 230 and 240°C. These trends indicate that at these higher temperatures (>220°C) excessive reaction converts the acetol and propylene glycol into undesired by-products which upon further degradation form degradation products appeared on the GC chromatogram as by-product peaks. Under the present reaction conditions, the optimum reaction temperature for converting glycerol to acetol and propylene glycol is near 220°C on the basis of glycerol conversion and selectivity to desired products.

Effect of hydrogen feed rate

Figure 5 summarizes the effect of hydrogen flow rate on conversion of glycerol to acetol and propylene glycol products at 220 and 230°C. For this system, the pressure was constant at 1 atm and the catalyst loading was at 1160 g.

Since the evaporator contains a reservoir of glycerol, increasing the hydrogen flow rate is equivalent to decreasing the space time in the reactor. Space time is defined as the ratio of reactor volume to volumetric flow rate in the reactor. The results displayed in Figure 5 support the conclusion that lower space times lead to more degradation products in this reaction system, with 1160 g of catalyst being a marginally high amount.

Catalyst life

The catalyst was found to perform satisfactorily for 15 reaction cycles of 4-h duration. When operating at proper conditions (no liquid-phase in the reactor) the catalyst worked well for 15 cycles with no sign of deactivation. Catalyst coking and deactivation was observed when liquid phase chemistry was present in the system. As a general observation of more than a year of studies on these catalysts, the catalyst is able to retain high activity for months when conditions are controlled to assure liquids do not condense and temperatures are maintained below 230°C. These months of operation included frequent shutdown and startup of the reactor.

Conclusions

The formation of acetol and propylene glycol from glycerol through the novel reaction mechanism was performed in a low-pressure vapor-phase packed bed reactor using copper-chromite catalyst. This catalytic process has been demonstrated as feasible for producing propylene glycol from glycerol. Effects of various reaction parameters on the products yield were tested. Operating the reactor in vapor-phase mode dramatically reduced the amount of undesired by-product

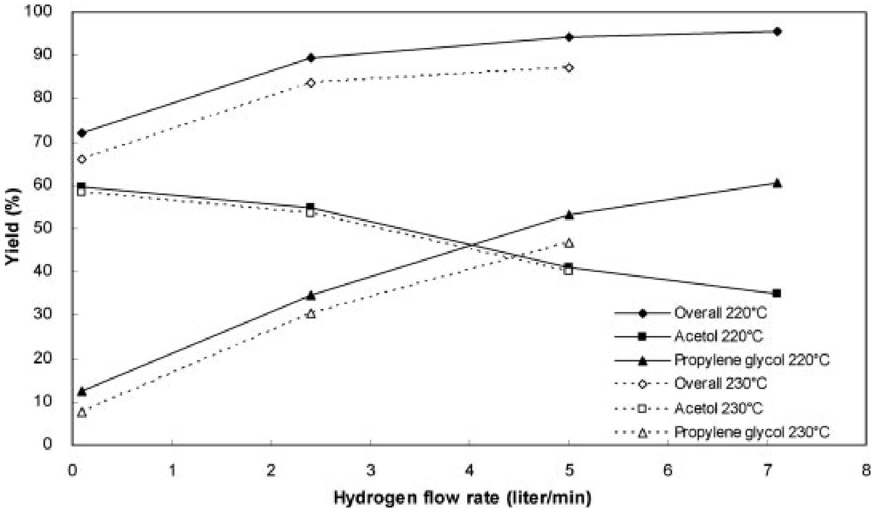

Figure 5. Effect of hydrogen feed rate on formation of acetol and propylene glycol from glycerol.

All the reactions were performed on the vapor-phase reaction over a copper-chromite catalyst of 1160 g at atmospheric pressure with hydrogen feed.

formation. Higher yields of propylene glycol were observed at higher hydrogen feed rates. At temperatures of greater than 220°C excessive reaction takes place resulting in undesired by-product formation, which upon further degradation forms degradation products. Hundred percent glycerol conversion and single-pass yields of propylene glycol $>50\%$ were attained at the temperature range of 220–230°C and atmospheric pressure with hydrogen feed. A two-step reaction process to produce propylene glycol from the glycerol via an acetol intermediate was proposed and validated.

Many of the decomposition products are formed in second-order mechanisms, and so, lower partial pressures of glycerol in the feed reduces by-product formation. Discrepancies in by-product formation between systems operated at the same temperature but at different partial pressures of glycerol can often be attributed to higher-order by-product formation mechanisms. The reaction of glycerol to acetol was generally zero order in glycerol concentration and first order in catalyst concentration. This mechanism is valid until rather low glycerol concentrations at which point the reaction would be expected to approach being first order in glycerol concentration.

Acknowledgments

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