Dehydration of Glycerol to Acetol via Catalytic Reactive Distillation

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Dehydration of glycerol was performed in the presence of various metallic catalysts including alumina, magnesium, ruthenium, nickel, platinum, palladium, copper, raney nickel, and copper-chromite catalysts to obtain acetol in a single-stage reactive distillation unit under mild conditions. The effects of operation mode, catalyst selection, glycerol-feed flow rate, catalyst loading, and initial water content were studied to arrive at optimum conditions. High-acetol selectivity levels (> 90%) were achieved using copper-chromite catalyst, and operating in semi-batch reactive distillation mode. A small amount of water content in glycerol feedstock was found to reduce the tendency for residue to form, therein extending catalyst life. The acetol from this reaction readily hydrogenates to form propylene glycol, providing an alternative route for converting glycerol to propylene glycol. © 2006 American Institute of Chemical Engineers *AIChE J,* 52: 3543–3548, 2006
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Introduction

Use of fatty acid methyl esters (FAME) derived from vegetable oils and animal fats as diesel fuel extenders known as biodiesel, has received considerable attention in recent years.[1,2,3,4] The U.S. production of biodiesel is 120 – 160 million L, which is expected to grow at a rate of 50 – 80% per year, with a projected 1.6 billion L of production by the year 2012. A major drawback of biodiesel is its high cost when compared to diesel—the production costs for biodiesel range from $0.17– $0.40 per L.[5]

For every 9 kg of biodiesel produced, about 1 kg of a crude glycerol byproduct is formed. Most of the larger biodiesel producers refine the glycerol for sale in the commodity glycerol market. However, the price of glycerol is already (2005) about half the price of past averages in Europe where biodiesel production exceeds 1.6 billion L per year. Increased biodiesel production is expected to further suppress glycerol prices, and so, conversion of glycerol to other consumer products is desirable.

Propylene glycol is a major commodity chemical with an annual production of over 450 million kg in the United States,[6] and sells for $1.56 to over $2.20 per kg with a 4% growth in the market size annually.[7] If crude glycerol could be used to produce propylene glycol, this technology could increase the profitability of biodiesel production plants and, thereby, reduce the costs of producing biodiesel.

The commercial petroleum-based propylene glycol is produced by either the chlorohydrin process or the hydroperoxide process that hydrates propylene oxide to propylene glycol.[8,9] Conventional processing of glycerol to propylene glycol uses metallic catalysts and hydrogen as reported in several United States patents.[10,11,12,13] These research efforts report the successful hydrogenation of glycerol to form propylene glycol. However, none of the processes that can suitably commercialize the resultant reaction products due to some common

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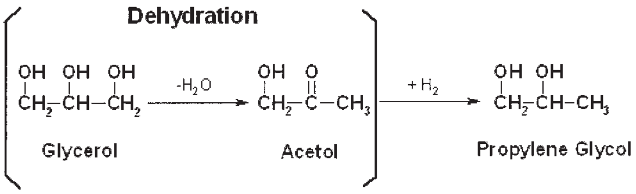

Figure 1. Proposed reaction mechanism for converting glycerol to acetol, and then to propylene glycol.

drawbacks of existing technologies, for example, high-temperatures and high-pressures, low-production efficiency from using diluted solutions of glycerol, and low-selectivity toward propylene glycerol.

In earlier work we proposed the novel reaction mechanism for converting glycerol to propylene glycol via a reactive intermediate as shown in Figure 1. [14] Relatively pure hydroxyacetone (acetol) is isolated from dehydration of glycerol as the transient intermediate indicates that the reaction process for producing propylene glycerol with high-selectivity can be done in two steps. In the broader sense, this process may potentially advance the art and overcome those problems outlined above by the novel reaction mechanism to convert glycerol to acetol, and then acetol is hydrogenated in a further reaction step to produce propylene glycol.

In the absence of hydrogen, glycerol can be dehydrated to acetol via a reactive-distillation technique. Acetol is considerably more volatile than glycerol. Reaction product vapors (acetol and water) are simultaneously removed or separated from the reaction mixture as they are formed during the step of heating. The possibility of degrading acetol by continuing exposure to the reaction conditions is commensurately decreased by virtue of this removal. In addition, the acetol is inherently removed from the catalysts to provide relatively clean acetol. Since removal of products allows the equilibrium to be shifted far to the forward direction, and high-acetol yields to be achieved under relatively mild operation conditions, this reactive-distillation technique is particularly advantageous for reactions which are equilibrium limited.

Several prior works have been published on reactive distillation by Gaikar and Sharma[15] and Doherty and Buzad.[16] Reactive-distillation technique is now commercially exploited for the manufacture of methyl *tert*-butyl ether (MTBE), ethyl *tert*-butyl ether (ETBE), and *tert*-amylmethyl ether, which are used as octane number enhancers.[17] Reactive distillation is also used for esterificaiton of acetic acid with alcohols like methanol and ethanol, and hydrolysis reactions of esters like methyl acetate.

There are only a limited number of publications documenting schemes for converting glycerol to acetol and none of these are based on reactive distillation. This study focused on demonstrating the feasibility of producing acetol by dehydration of glycerol using heterogeneous metallic catalysts in a single stage reactive distillation unit. Performance of operating in batch and semi-batch mode, and effect of various reaction parameters were investigated.

Experimental Section

Materials

Glycerol (99.9%) and n-butanol were purchased from Sigma-Aldrich (Milwaukee, WI). Methanol (HPLC grade) was purchased from Fisher Scientific Co. (Fairlawn, NJ). Table 1 gives the description of various catalysts used in this study and their suppliers. All catalysts used in this study were used in the condition in which they arrived.

Experimental Setup

Batch-reactive distillation

The experiments on batch reactive distillation were carried out in a fully agitated glass reactor of capacity 1.25×10^{-4} m^3. A magnetic stirrer at an agitation speed of 100 rpm was used to create a slurry reaction mixture. A condenser was attached to the top of a glass reactor, through which chilled water was circulated. The glass reactor was immersed in a constant temperature oil batch, the temperature of which was maintained within ±1 °C of the desired temperature. In the glass reactor, the catalyst was first heated to the reaction temperature of 240 °C, and then the amount of glycerol solution was charged immediately to the reactor. Complete addition of the glycerol

Table 1. Summary of Conversion of Glycerol, Selectivity of Acetol and Residue to Initial Glycerol Ratio from Glycerol over Various Metal Catalysts

Supplier	Description	Conversion (%)	Selectivity (%)	Residue: Initial-Glycerol Ratio (%)
	Mg/Alumina	0	0	—
	Mg/Chromium	0	0	—
Johnson Matthey	5% Ru/C	89.18	31.72	36.54
Johnson Matthey	5% Ru/Alumina	88.24	33.81	34.14
Degussa	5% Pd/C	87.12	4.68	12.33
Degussa	5% Pt/C	0	0	—
PMC Chemicals	10% Pd/C	86.98	3.32	10.51
PMC Chemicals	20% Pd/C	85.14	2.69	9.87
Sud-Chemie	Alumina	0	0	—
Sud-Chemie	Copper	85.19	51.54	15.03
Sud-Chemie	Copper-chromite	86.62	80.17	13.37
Grace Davision	Raney Nickel	82.40	30.38	7.99
Johnson Matthey	Ni/C	79.47	52.97	6.81
Alfa-Aesar	Ni/Silica-Alumina	89.37	57.29	3.33

All reactions were performed in batch reactive distillation at 240°C and 98 kPa (vac).

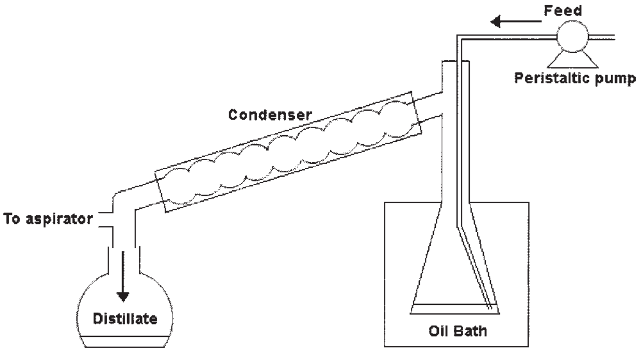

Figure 2. Semi-batch reactive distillation experimental setup.

solution was taken as zero time for the reaction. All experiments were conducted at a reduced pressure of 98 kPa (slight vacuum) by using an aspirator.

Semi-batch-reactive distillation

The same reactive distillation setup was used as described in the section of batch-reactive distillation. Experiments were carried out in a continuous mode of operation in the reactive distillation setup as shown in Figure 2. Glycerol solution was continuously introduced at the bottom of the glass reactor with different feed flow rates by a peristaltic pump. All experiments were conducted at a reduced pressure of 98 kPa (slight vacuum) by using an aspirator.

Analytical Methods

In the batch mode, the completion of reaction was considered when additional condensate ceased to collect. In the semi-batch mode, a digestion of the mixture was induced by stopping the feed and allowing the reaction to proceed for about 30 min to an hour at the end of the reaction—during this digestion the volume of the reaction mixture decreased, and the residue became more apparent. The residues in the glass reactor were weighed. 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 (30m × 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 2mL glass vial. Two microliters of the sample was injected into the column. The oven temperature program consisted of: start at 45 °C (0 min), ramp at 0.2 °C/min to 46 °C (0 min), ramp at 30 °C/min to 220 °C (2.5 min). 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, conversion of glycerol and selectivity of acetol were calculated. 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. Selectivity is defined as the ratio of the number of moles of product formation to the moles of glycerol consumed in the reaction, considering the stoichiometric coefficient.

For the semi-batch mode, the terms "conversion" and "selectivity" defined by the following expressions were used to present the performance of reactive distillation.

$$\text{Conversion} = \frac{\text{Molar flow rate of glycerol reacted}}{\text{Feed molar flow rate of glycerol}} \times 100\% \tag{1}$$

$$\text{Selectivity} = \frac{\text{Molar flow rate of acetol in distillate}}{\text{Molar flow rate of glycerol reacted}} \times 100\% \tag{2}$$

Results and Discussion

Catalyst screening and selection

Reactivities of heterogeneous catalysts, including alumina, magnesium, ruthenium, nickel, platinum, palladium, copper, raney nickel and copper-chromite were tested in the batch mode of reactive distillation at a reaction temperature of 240 °C, and a reduced pressure of 98 kPa. Table 1 shows the performance comparison of these catalysts and their suppliers. Conventional dehydration catalysts like alumina were not effective for dehydrating glycerol to acetol since these catalysts with high-acidic sites favor the dehydration of glycerol to acrolein.[18] Ruthenium catalysts showed low-selectivities and high-residue to initial glycerol ratios, greater than 30%, due to the polymerization (condensation) of hydrocarbon free radicals leading to further deactivation of catalyst. Low-selectivities and low-residue to initial glycerol ratios were observed in nickel and palladium based catalysts, since they tend to be too active which results in excess reaction (degradation) of glycerol to form lower-molecular alcohols and gases.

On the other hand, copper or copper-based catalysts are superior to the other catalysts studied here in both acetol selectivity and residue formation. The superiority is enhanced by mixing copper with chromite. A high-acetol selectivity of 86.62% was obtained by using copper-chromite mixed oxide catalyst. Copper increases the intrinsic catalyst activity; however, copper favors sinterization leading to catalysts with low-surface areas. Chromium acts as a stabilizer to preventing sintering (reduce the sintering rate), and, thus, maintains catalysts in high activity.[19] Copper-chromite catalyst was selected for further studies.

Batch vs semi-batch processing

Glycerol was reacted in the presence of copper-chromite catalyst to form acetol in each of batch and semi-batch process modes. Relatively pure acetol was isolated from glycerol in the absence of hydrogen at a reaction temperature of 240 °C and a reduced pressure of 98 kPa. The theoretical maximum 100% yield of glycerol dehydration would be achieved if 50 g of glycerol would form a maximum of 40.2 g of acetol.

In batch mode, glycerol and catalyst were loaded into the reactor at the start of the reaction. In semi-batch mode, the reactor was changed with catalyst and glycerol was continu-

Table 2. Comparison of Batch Reactive-Distillation and Semibatch (Continuous) Reactive-Distillation on Formation of Acetol from Glycerol

Mass Balance Details on Batch Reactive Distillation Using 5% Copper-Chromite Catalyst Loading. Initial Loading of Glycerol, 42.48; Glycerol in Distillate, 3.64; Residue, 5.68; and Amount of Glycerol Reacted, 38.84 All in Grams. The Glycerol Reacted as Described Below.

	Reacted Glycerol (g)	Best Possible (g)	Distillate (g)
Glycerol	38.84	0	3.64
Acetol	0	31.24	23.73
Propylene glycol	0	0	1.67
Water	0	7.6	6.99

Mass Balance Details on Semibatch Reactive-Distillation Using 5% Copper-Chromite Catalyst Loading. Initial Loading of Glycerol, 54.29; Glycerol in Distillate, 4.91; Residue, 3.80; and Amount of Glycerol Reacted, 49.38 All in Grams. The Glycerol Reacted as Described Below.

	Reacted Glycerol (g)	Best Possible (g)	Distillate (g)
Glycerol	49.38	0	4.91
Acetol	0	39.71	35.99
Propylene glycol	0	0	1.65
Water	0	9.66	5.79

Mass Balance Details on Semibatch Reactive-Distillation Using 2.5% Copper-Chromite Catalyst Loading. Initial Loading of Glycerol, 52.8; Glycerol in Distillate, 3.85; Residue, 4.91; and Amount of Glycerol Reacted, 48.95 All in Grams. The Glycerol Reacted as Described Below.

	Reacted Glycerol (g)	Best Possible (g)	Distillate (g)
Glycerol	48.95	0	3.85
Acetol	0	39.37	33.51
Propylene glycol	0	0	1.63
Water	0	9.58	6.24

All reactions were performed at 240°C and 98 kPa (vac). Glycerol feed rate was 33.33 g/h for semibatch reaction.

ously fed into the reactor at a uniform rate of 33.33 g/h over a period of about 1.25 h. 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 byproducts and loss in selectivity. Either process mode produced a residue which was a dark solid coated on the catalyst that was not soluble in water. Table 2 shows the semi-batch reactive-distillation exhibits higher yield and selectivity, and lower-residue formation than batch due to the semi-batch operation has a higher-catalyst loading to glycerol ratio in the reaction.

Effect of glycerol feed flow rate

Reactions were performed to study the effect of glycerol feed flow rate on semi-batch operation-mode with 2.5% copper-chromite catalyst loading. It can be seen in Table 3 that increasing the flow rate decreases acetol selectivity and increases the residue to initial-glycerol ratio. As the amount of catalyst is fixed, an increase of the glycerol feed flow rate results in an accumulation of fed glycerol in the reaction mixture, hence, reduces the catalyst loading to glycerol ratio during the reaction. This decrease in the catalyst loading to glycerol ratio results in lower-acetol selectivity and higher-residue formation, reinforcing the afore-conclusion in the section of comparison of batch and semi-batch operation modes. It was also observed that decreasing the flow rate from 33.33 g/h decreases the conversion of glycerol because the glycerol could be easily vaporized and appear in the distillate as an unconverted glycerol.

Table 3. Effect of Glycerol Feed Flow Rate on Conversion of Glycerol to Acetol in Semibatch Reactive-Distillation

Glycerol Feed Flow Rate (g/h)	Conversion (%)	Selectivity (%)	Residue: Initial-Glycerol Ratio (%)
100	88.94	60.92	20.45
50	91.49	65.21	19.81
33.33	92.71	85.11	9.30
18.75	91.58	87.32	8.73
14.29	90.15	87.49	7.59

All reactions were performed in semibatch reactive-distillation at 240°C and 98 kPa (vac).

Effect of catalyst loading

For copper-chromite catalyst, it was generally observed that as reaction proceeded, the reaction rate tended to decrease and the amount of residue increased. During the digestion time induced at the end of semi-batch reaction, the volume of the reaction mixture decreased, and the residue became more apparent. It indicates that the activity of copper-chromite catalyst is lost before the reaction goes to completion.

In order to find the minimum catalyst loading required to achieve necessary conversion, lowering catalyst loadings from 5% to 0.83% was evaluated to determine the impact of catalyst loading on conversion of glycerol to acetol and residue formation. Reactions were carried out by reacting various amounts of glycerol: 25g (5%), 50g (2.5%), 75g (1.67%), 100g (1.25%), 150g (0.83%) to 1.25g of copper-chromite catalyst in semi-batch reactive-distillation mode. Table 4 summarizes the conversion results. These data illustrate that the formation of residue increased with increasing throughput of glycerol over the catalyst. Also, the acetol selectivity decreased with increasing throughput of glycerol over a fixed catalyst loading in the reactor due to residue increasing with reaction time leading to further deactivation of catalyst.

Table 4. Effect of Catalyst to Glycerol Throughput Ratio on Conversion of Glycerol to Acetol in Semibatch Reactive-Distillation

Wt. % of Catalyst	Conversion (%)	Selectivity (%)	Residue: Initial-Glycerol Ratio (%)
5	90.96	90.62	7.00
2.50	92.71	85.11	9.30
1.67	90.44	76.94	9.76
1.25	89.23	73.50	11.07
0.83	86.87	59.76	11.32

All reactions were performed in semibatch reactive-distillation with glycerol feed rate of 33.33 g/h at 240°C and 98 kPa (vac).

Effect of initial water content

Reactions were performed to study the effect of initial water content on the overall reaction. Glycerol was reacted in the presence of 2.5% copper-chromite catalyst to form acetol in a semi-batch reactive-distillation method. Water was added to the glycerol to evaluate if water would decrease the accumulation of the water-insoluble residue. Table 5 summarizes the conversion results. As the initial water in the reaction increases, the residue to initial glycerol ratio decreased. The initial water content reduces the residue formation by stripping of the acetol along with water vapors from the reaction mixture before it can degrade/polymerize to form residue—water boils and provides the near-ideal diffusion of acetol in the reaction.

In addition, those reactions with initial water content have higher-acetol selectivities compared with the reaction without initial water. For glycerol solutions with water concentration >5%, a decrease in the glycerol conversion was observed due to the entrained glycerol presented in distillate. It demonstrates that high yields of acetol can be achieved and formation of residue can be controlled by using a small amount of water in glycerol.

Catalyst stability—ability to reuse catalyst

The residue was taken as a solid form at room-temperature, and a slurry form at the reaction temperature during the long period of reaction time. The solid was soft and tacky in nature and readily dissolved in methanol to form slurry. Reactions were carried out to find the stability of the copper-chromite catalyst. After each run the catalyst was washed with methanol until the wash was clear, and then the catalyst was dried in a furnace at 80 °C to remove the methanol for the subsequent runs. The physical appearance of this catalyst after washing was similar to that of the new catalyst. The data of Figure 3 demonstrate the copper-chromite catalyst can be used repeatedly. The conversion of glycerol and the selectivity of acetol were slightly decreased over repeated usage.

Methanol wash is effective to remove the residue, allowing the catalyst to be reused multiple times. However, it was observed that residue started foaming on the catalyst at 30 min after total glycerol was fed (during the digestion time). Once the reaction mixture started foaming, a methanol wash was not effective for removing the residue from the catalyst. If the reaction was stopped prior to commencement of foaming, the methanol was effective for removing the residue from the catalyst. When catalyst loading less than 2.5%, the reaction mixture started foaming while the glycerol was still being fed into the reactor, hence, the catalyst could not be recovered at end of the reaction.

Table 5. Effect of Initial Water Content in the Glycerol Feedstock on Residue Formation

Water (Wt. %)	Conversion (%)	Selectivity (%)	Residue: Initial-Glycerol Ratio (%)
0%	92.71	85.11	9.30
5%	90.74	90.65	7.02
10%	84.80	89.87	6.13
20%	82.58	89.84	5.31

All reactions were performed in semibatch reactive-distillation with glycerol feed rate of 33.33 g/h at 240°C and 98 kPa (vac).

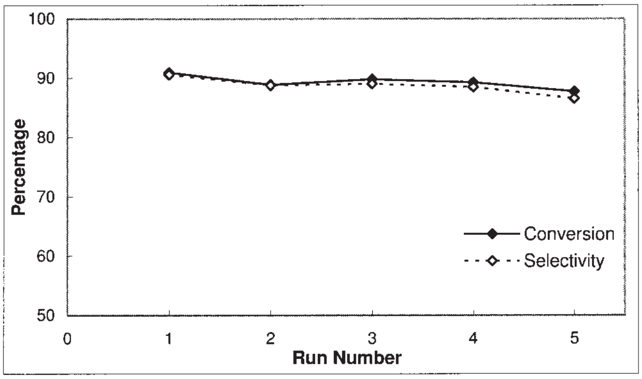

Figure 3. Copper-chromite catalyst reuse for conversion of glycerol to acetol. All reactions were performed using 5% copper-chromite catalyst loading in semi-batch reactive distillation with glycerol feed rate of 33.33 g/h at 240 °C and 98 kPa (vac).

Conclusions

Acetol was successfully isolated from dehydration of glycerol as the transient intermediate for producing propylene glycerol. This catalytic process provided an alternative route for the production of propylene glycol from renewable resources. In this study, selective dehydration of glycerol to acetol has been demonstrated using copper-chromite catalyst under mild conditions. Reactive distillation technology was employed to shift the equilibrium toward the right and achieve high-yields. High-acetol selectivity levels (>90%) have been achieved using copper-chromite catalyst in semi-batch reactive-distillation. This reactive distillation technology provides for higher yields than is otherwise possible for producing acetol from glycerol feedstock. In parametric studies, the optimum conditions were delineated to attain maximum acetol selectivity, as well as high-levels of glycerol conversion.

Acknowledgments

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