EQUILIBRIUM LIMITATIONS AND SELECTIVITY ON CONVERSION OF GLYCEROL TO PROPYLENE GLYCOL

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Master of Science

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by

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The undersigned, appointed by the Dean of the Graduate School, have examined the thesis entitled

EQUILIBRIUM LIMITATIONS AND SELECTIVITY ON CONVERSION OF GLYCEROL TO PROPYLENE GLYCOL

presented by Lizanette Rivera-Ramos

a candidate for the degree of Master of Science

and hereby certify that in their opinion it is worthy of acceptance.

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Dr. Thomas R. Marrero

Dr. Hsieh

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CHAPTER 1

1. INTRODUCTION

1.1 Introduction to Bio-Based Products

Over the past couple of decades fatty acid methyl esters derived from vegetable oil and animal fat have become importance as potential diesel fuel extenders known as "biodiesel".[1, 2, 3, 4] The burgeoning U.S. biodiesel industry collects millions of gallons of crude glycerin per year as a byproduct, most of which is disposed as waste.[5] The production of biodiesel utilizes surplus vegetable oils, fats, and waste restaurant greases while reducing the US dependence on foreign crude oil. For every 9 kilograms of biodiesel produced, about 1kilogram of crude glycerol byproduction is formed; and today, biodiesel production plants are in need of methods to realize increased income from this glycerin.[6] Increased biodiesel production is expected to further suppress glycerol prices, and so, conversion of glycerol to other value-added consumer products is desirable.[7]

Biodiesel production and the use of glycerin byproduct produce antifreeze. Figure 1.1 illustrates a biodiesel production and use of glycerin byproduct to produce antifreeze.

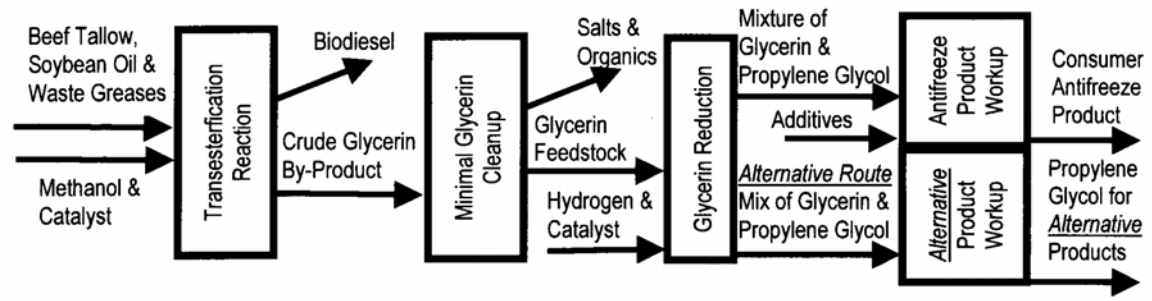

Figure 1.1. Block flow diagram for biodiesel and antifreeze production.

The U.S. production of biodiesel is 30-40 million gallons, which is expected to grow at a rate of 50-80% per year.[7] The projected amount of the crude glycerol byproduct of the process will increase to over 400 million liters per year.[7] Experimentally it has been proved that crude natural glycerol can be converted to propylene glycol, this technology could be used in biodiesel production plants to increase profitability.[6] Preferred technology would convert crude natural glycerol at moderate temperatures and pressures.

Propylene glycol is a three carbon diol with alcohols on the 1 and 2 carbons as illustrated by the following diagram.

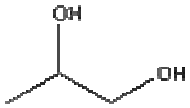

Figure 1.2. Propylene Glycol structure.

Propylene glycol is a major commodity chemical with an annual production of over 1 billions pounds in the U.S., with a 4% growth in the market size annually.[8] There are several routes to propylene glycol from renewable feedstocks.[6] The most commonly research is through hydrogenolysis of sugars alcohols at high temperatures and pressures in the presence of a metal catalyst

producing propylene glycol and other lower polyols.[10, 11, 12, 13, 14, 15] The hydrogenolysis of biodiesel's crude glycerol to propylene glycol is one process being evaluated to increase the profitability of biodiesel production. In the presence of metallic catalyst and hydrogen, glycerol can be hydrogenated to propylene glycol or ethylene glycol.[6] Figure 1.3 summarizes the overall reaction of converting glycerol to glycols.

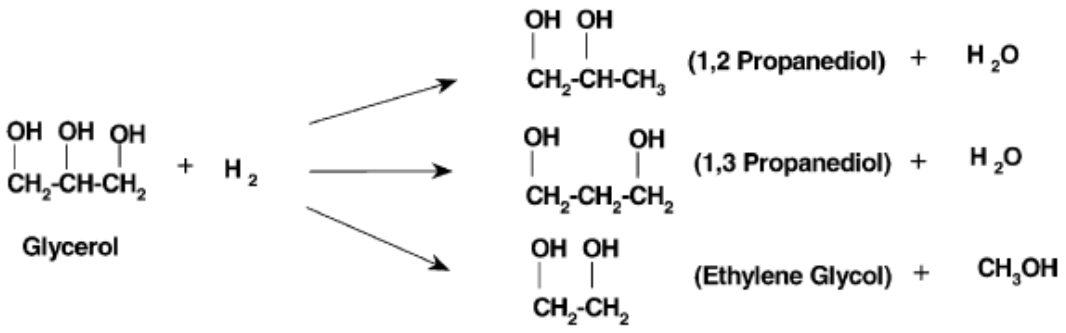

Figure 1.3. Summary of the overall reaction of converting glycerol to propylene (propanediol) and ethylene glycols.

1.2 Propylene Glycol

1.2.1 Physical and Chemical Properties

Propylene glycol ($CH_3CHOHCH_2OH$) is a colorless and odorless liquid at room temperature with a chemical name of 1,2-propanediol. The molecular weight is 76.095 g/mol. The normal boiling point is 187ºC. Additional propylene glycol properties are provided in Appendix D.

1.2.2 Uses

Some propylene glycol uses are in unsaturated polyesters resins, functional fluids (antifreeze, de-icing, and heat transfer devices), pharmaceuticals, foods, cosmetics, liquid detergents, tobacco humectants, flavor and fragrances, personal care, paints and animal feed[7]. The antifreeze and de-icing market is growing because of concern over the toxicity of ethylene glycol-based products to humans and animals as well[7].

1.3 Background Literature

The uses of catalyst to convert glycerol to propanediols[9] have been published in patents: U.S. Patents Nos. 5,616,817, 4,642,394, 5,214,219 and 5,276,181. These patents report a successful hydrogenation of glycerol to form propanediols. But the patented processes indirectly provide a mixture of reaction products that are suitable for use as antifreeze (e.g. propylene glycol). These patents **do not** include the use of unrefined crude natural glycerol feedstock.

A direct method of producing lower alcohols from glycerol feedstock to provide glycerol-based and/or propylene glycol based antifreezes has been reported in US Patent Application # 2005-0244312.[9] The glycerol-based and/or propylene glycol based antifreezes displace the use of toxic and no renewable ethylene glycol with non-toxic and renewable glycerol-derived antifreeze. The process converts natural glycerol to propylene glycol which is also known as 1, 2-propanediol through an acetol intermediate at temperatures from 150º to 250ºC, at a pressure ranging from 1 and 25 bar.[9] The process uses copper-chromium

powder as a catalyst. The U.S. Patent Application 2005-0244312 inventor is Dr. G. Suppes, the supervisor of this research study.

1.4 Research Emphasis

This research focuses on developing a technology to quantify the glycerol to propylene glycol reaction at lower temperatures and pressures using concentrated glycerol while simultaneously achieving high selectivity towards propylene glycol and little or no selectivity towards ethylene glycol or other byproducts. Figure 1.4 shows the reaction mechanism for conversion of glycerol to propylene glycol used.

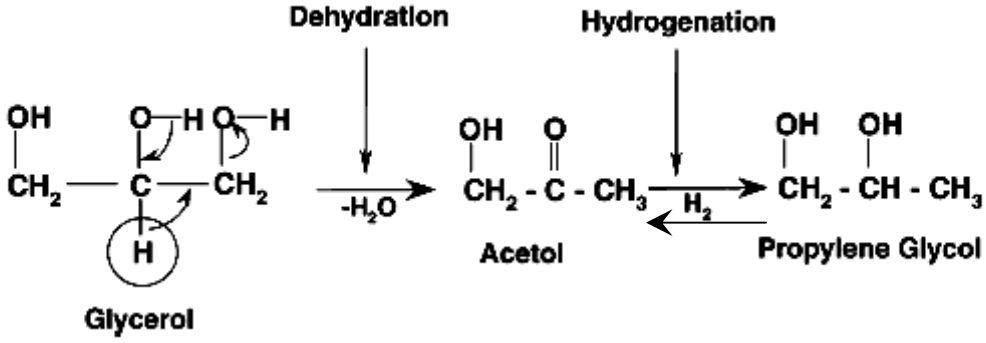

Figure 1.4. Reaction mechanism for conversion of glycerol to propylene glycol.

In Figure 1.4 hydroxyacetone (acetol) is proposed as an intermediate for forming propylene glycol. The acetol is formed by dehydration of a glycerol molecule that undergoes intramolecular rearrangements. In a subsequent hydrogenation step, the acetol further reacts with hydrogen to form propylene glycol with one mole of water byproduct resulting from dehydration step of a

glycerol molecule. The first step on the above mechanism is an irreversible reaction of glycerol to acetol. The second step of the reaction (the reaction of acetol to propylene glycol) is expected to be equilibrium limited.

The research emphasis of this project was to verify the equilibrium limitations and selectivity on conversion of glycerol to propylene glycol. For this emphasis during the research, glycerol, acetol, and propylene glycol were used as reagents.

The scope of this research is as follows:

(1) Determine the effect of temperature on the glycerol to propylene glycol reaction, propylene glycol to acetol reaction, and acetol to propylene glycol reaction.

(2) Determine the effect of pressure on the glycerol to propylene glycol reaction, propylene glycol to acetol reaction, and acetol to propylene glycol reaction.

(3) Determine the effect of residence time on the glycerol to propylene glycol reaction, propylene glycol to acetol reaction, and acetol to propylene glycol reaction.

(4) Determine the effect of water content on the glycerol to propylene glycol reaction

(5) Determine the effect of H_2: Glycerol mole ratio on the glycerol to propylene glycol reaction.

The trends of these effects were plotted in Chapters 3 to 5 and focus on reaction selectivity and and byproduct formation.

The organization of this thesis is as follows. In Chapter 2 the materials, equipment, and procedures used in this research are described. Chapters 3, 4, and 5 present the results of the research. The conclusions and recommendation are presented in Chapter 6. Additional detailed information is provided in the appendices of the thesis.

CHAPTER 2

2. EXPERIMENTAL MATERIALS AND METHODS

2.1 Introduction

Experimental methods are described in three parts: materials, apparatus, and procedures. All the experiments were conducted with bench scale equipment. The description of procedures includes a detailed explanation of experimental planning.

2.2 Materials

2.2.1 Glycerol

The glycerol used was a 99.7% Moon glycerol purchased from Chem Organics (Houston, TX). Physical properties of glycerol and additional data from Material Safety Data Sheets are available in Appendix D.

2.2.2 Propylene Glycol (PG)

The propylene glycol used in this study was a 99.9% propylene glycol. Physical properties of glycerol and additional data from Material Safety Data Sheets are available in Appendix D.

2.2.3 Hydroxyacetone (Acetol)

The acetol used in this study was a 65% acetol as synthesized in our laboratory to a purity of about 90%. The GC chromatogram of this acetol is available in Appendix D.

2.2.4 Hydrogen

High purity grade hydrogen was purchased from Praxair.

2.2.5 Catalyst

Pre-reduced copper-chromite catalyst was purchased from Engelhard Corporation (Elyria, Ohio).

2.2.6 *n*-Butanol

The *n*-butanol used as a solvent to analyze the samples in GC was purchased from Sigma Aldrich (Milwaukee, WI). Additional data are available from Material Safety Data Sheets, see Appendix D.

2.3 Chemical Reaction Apparatus

2.3.1 Introduction

The apparatus system can be divided into three distinct areas: feed, pre-heat and evaporation, reactor and condenser.

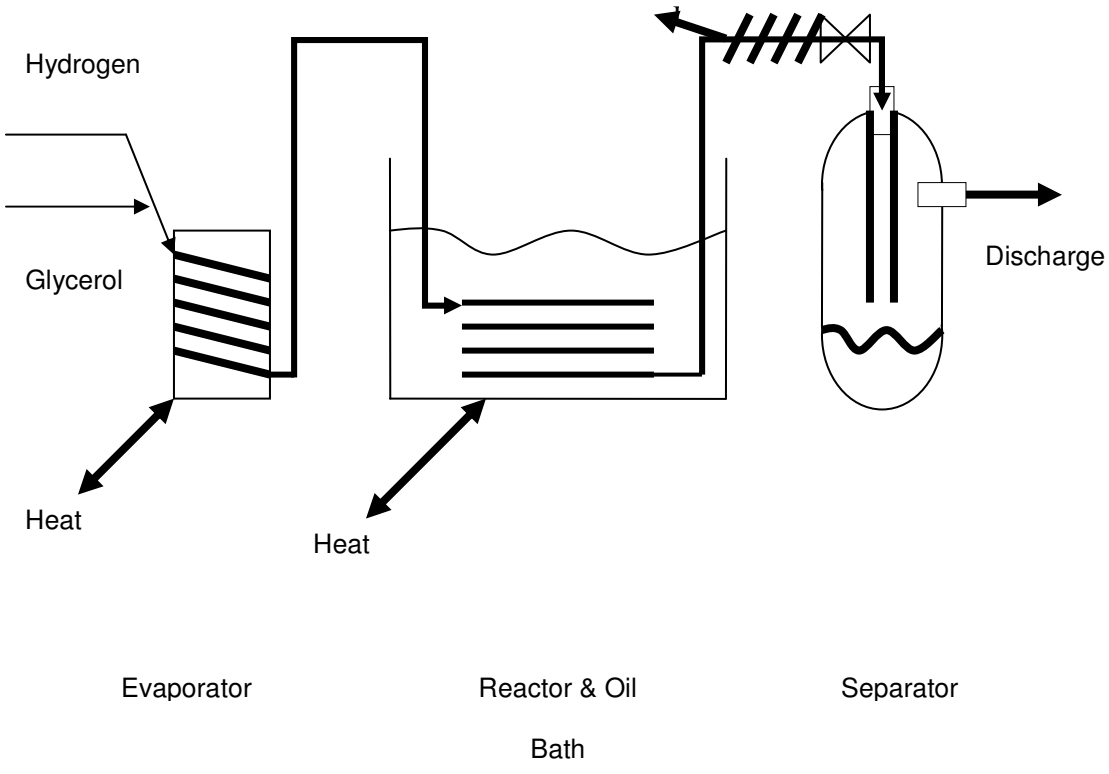

Figure 2.1. System Design Diagram to produce Propylene Glycol.

2.3.2 Feed Area

A FMI Metering Lab Pump Model RP-SY pump was used to feed the liquid reagents into the system.

2.3.3 Pre-heat and Evaporation

The pre heated system consists of one coil (soft refrigerated copper tubing of ¼ inches obtained from a local supplier) with an electric heating tape wrapped

around a stainless steel pipe to preheat the hydrogen and the glycerol lines. The evaporator consists of this coil.

A knockout vessel is located after the coil to trap any liquids remaining in the feed, and to prevent these liquids from going into the reactor. The knockout vessel consists of a stainless steel vessel with a volume of one liter wrapped with a heating tape. This vessel has one inlet and one outlet equipped with thermocouples.

2.3.4 Reactor

The reactor used for this system is a continuous packed-bed reactor. In a continuous reactor the chemical reaction proceeds as the reagents flow through the reactor. This reactor consists of four sections of high temperatures and pressure resistant tubing equipped with thermocouples. Each tubing reaction has four feet of length. The diameter of this pipe is of 0.0625 feet for a total volume of 0.05 cubic feet.

2.3.5 Condenser

The condensation part consists of a wrapped coil (soft refrigerated copper tubing of ¼ inches) submerged in ice followed by a glass condenser. The flow around a glass condenser is cooled using a VWR refrigerator recirculator.

2.4 Procedures

2.4.1 Experimental Procedures

All reactions were carried out in a continuous reactor of 0.0014 m^3 of capacity equipped with a thermocouple. The reactor was packed with 650 grams of pre-reduced catalyst. The temperature of the reactor was controlled by OMEGA controller. All the reactions were conducted in one step at temperatures of 180ºC, 200ºC, 220ºC, and 240ºC. The reactor was purged continuously with hydrogen and heated to the desired temperature. The reagent was introduced continuously into an evaporator equipped with a thermocouple using a FMI metering pump. The temperature of the evaporator was controlled by OMEGA controller at a range of 220ºC to 230ºC. Hydrogen was added to hydrogen line to promote conversion of the reagent to propylene glycol. The system was pressurized at 1, 2, and 4 bars. The mixture was cooled through a condenser to about 25℃ and collected.

2.4.2 Method of analysis

The samples of each reactions were taken at 10 minutes of time intervals. These samples were analyzed with a Hewlett-Packard 6890 (Wilmington, DE) gas chromatograph equipped with a flame ionization detector. Hewlett-Packard Chemstation software was used to collect and analyze the data. A Restek Corp. (Bellefonte, PA) MXT® WAX 70694 GC column (30 m × 250 µm × 0.5 µm) was used for separation. A solution of *n*-butanol with a known amount of internal standard was prepared a priori and used for analysis. The samples were

prepared for analysis by adding 100 µL of product sample to 1000 µL of stock solution into a 2mL glass vial. 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.

2.6 Data Reduction

In order to study and identify the trends in the data collected, EXCEL program was used to plot, tabulate, and calculate the results. The data was divided into three different sets depending of the reaction (glycerol to propylene glycol, propylene glycol to acetol, and acetol to propylene glycol).

For each set data were collected to evaluate,

- the effect of temperature on propylene glycol production and byproducts,
- the effect of pressure on propylene glycol production and byproducts, and
- the effect of residence time on byproducts were tabulated and plotted

For the glycerol and propylene glycol reaction data were collected to evaluate,

- the effect of water content on byproducts and,
- the effect of H_2: Glycerol Mole Ratio on catalyst productivity were plotted and calculated

Experimental data with water content higher than 30% in the product formation for the glycerol to propylene glycol reaction was neglected in this study.

CHAPTER 3

3. VERIFYING EQUILIBRIUM OF GLYCEROL TO PROPYLENE GLYCOL REACTION

The focus of this chapter is to study the equilibrium of the reactions discussed in Figure 1.3 (see Chapter 1). Hydrogenolysis reactions were performed at temperatures of 180ºC to 240ºC and pressure of 1, 2, and 4 bars. These reaction temperatures and pressures were significantly lower than those reported in patents previous mentioned (see Chapter 1) where the reactions were carried out at higher temperatures and pressures.

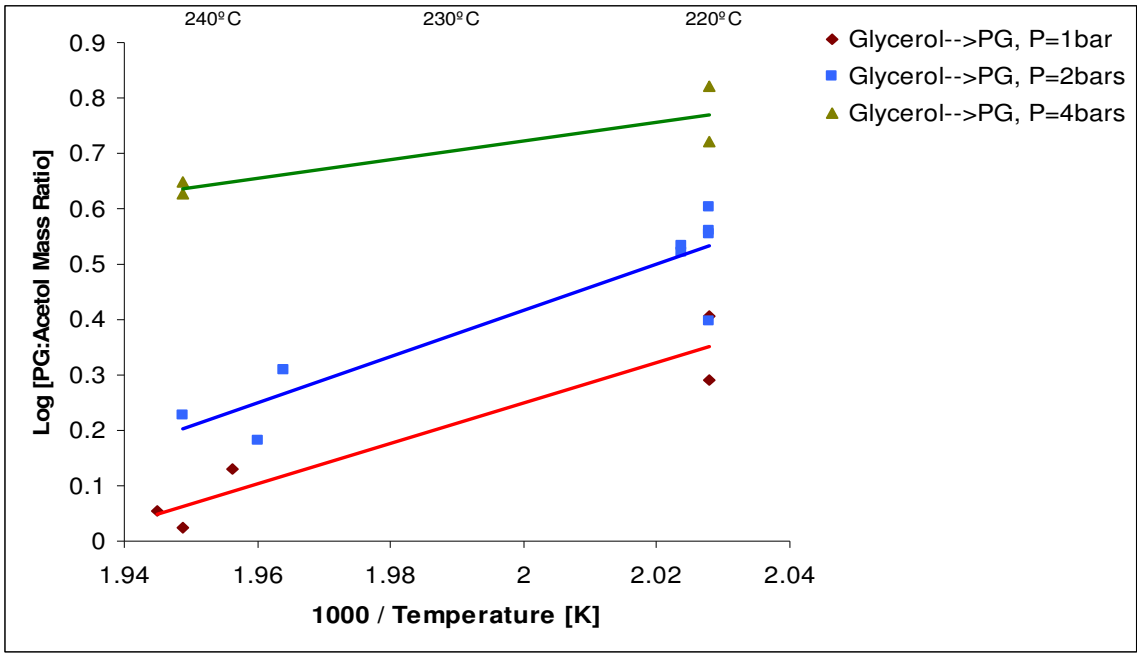

Figure 3.1. Temperature Dependence of the Glycerol to Propylene Glycol Reaction, at System Pressures of 1, 2 and 4 bar.

3.1 Reaction of Glycerol to Propylene Glycol

Figure 3.1 presents the Log [PG: Acetol Mass Ratio] values as a function of temperature (220 ºC to 240 ºC) of the glycerol to propylene glycol reaction at three pressures (1, 2, and 4 bars). This figure indicates that decreasing the temperature of reaction increases the mass ratio of propylene glycol to acetol. In other words, at lower temperatures the more desired product (propylene glycol) is produced. This effect was evident at each of the three pressures. At the higher pressures the conversion of propylene glycol increased. The experimental data plotted in Figure 3.1 are listed in Table 3-1.

Table 3-1 lists the Log [PG: Acetol Mass Ratio] for each temperature of reaction of the glycerol to propylene glycol reaction. Table 3-1 indicates that by decreasing the temperature of reaction and by increasing the system pressure more weight percent of propylene glycol is produced.

Table 3-1 Effect of Temperature and Pressure on the Formation of Propylene Glycol from Glycerol.

Reactor Temperature [ºC]	Pressure of Discharge [bar]	Acetol [wt%]	PG [wt%]	[PG:Acetol Mass Ratio]	Reactor Temperature [K]	1000 / Temperature [K]	Log [PG:Acetol Mass Ratio]
220	1	26.00	50.84	1.96	493	2.03	0.29
220	1	18.58	47.29	2.55	493	2.03	0.41
238	1	20.29	27.31	1.35	511	1.96	0.13
241	1	24.45	27.73	1.13	514	1.94	0.05
240	1	29.70	31.35	1.06	513	1.95	0.02
220	2	22.64	56.31	2.49	493	2.03	0.40
220	2	17.56	63.71	3.63	493	2.03	0.56
220	2	18.34	65.75	3.59	493	2.03	0.55
221	2	16.60	56.51	3.40	494	2.02	0.53
220	2	12.74	51.20	4.02	493	2.03	0.60
221	2	14.88	49.38	3.32	494	2.02	0.52
237	2	23.35	35.53	1.52	510	1.96	0.18
236	2	19.91	40.56	2.04	509	1.96	0.31
240	2	18.85	31.80	1.69	513	1.95	0.23
220	4	10.50	69.47	6.62	493	2.03	0.82
220	4	12.55	65.83	5.25	493	2.03	0.72
240	4	6.95	30.91	4.45	513	1.95	0.65
240	4	12.12	51.36	4.24	513	1.95	0.63

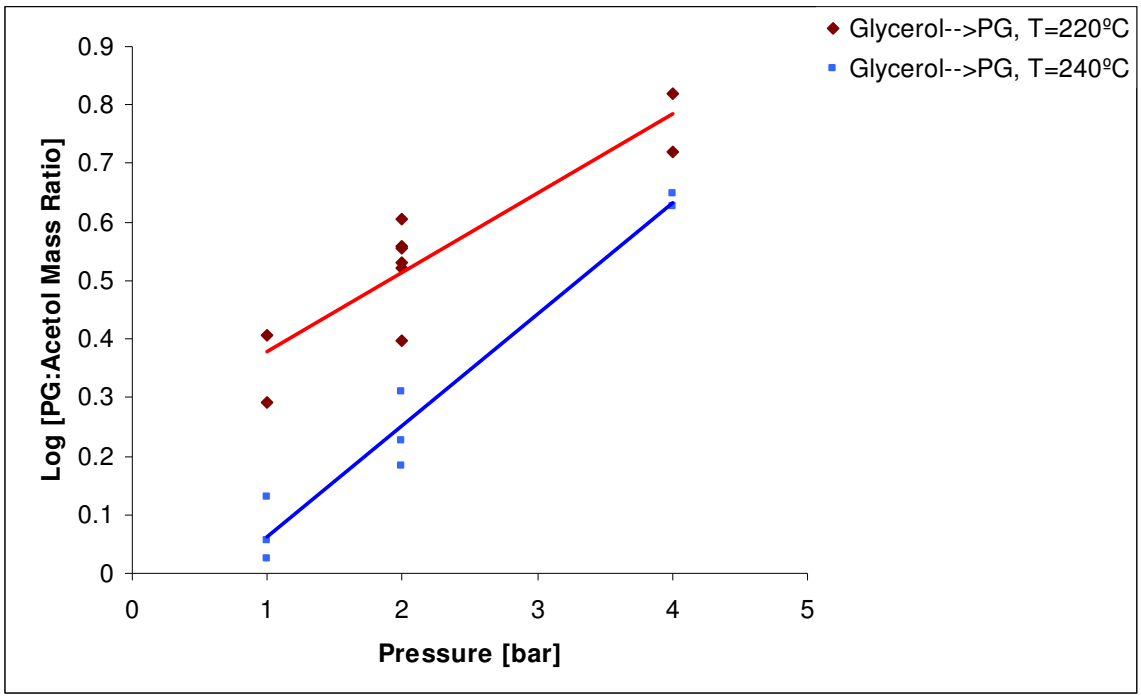

Figure 3.2. Pressure Dependence of the Glycerol to Propylene Glycol Reaction, at temperatures of 220ºC, and 240ºC.

The effect of pressure from 1 to 4 bars on the Log [PG: Acetol Mass Ratio] values for the glycerol to propylene glycol reaction was determined at 220ºC, and 240ºC; this effect is presented in Figure 3.2. This figure indicates that increasing the pressure of the system results in an increase of the mass ratio of propylene glycol to acetol. This effect is evident at each of the two temperatures. At the lower temperatures the conversion of propylene glycol increases. In agreement with Figure 3.1, this result for the conversion of glycerol to propylene glycol indicates that the preferred reaction operating conditions are higher pressure and lower temperature. Table 3-1 lists the experimental values plotted in Figure 3.2.

Table 3-1 lists the Log [PG: Acetol Mass Ratio] values for each system pressure of the glycerol to propylene glycol reaction. Table 3-1 indicates that at

higher pressures more propylene glycol can be produced and also indicates that at lower temperature the weight percent values of propylene glycol increases.

In summary, these results for the conversion of glycerol to propylene glycol indicate that the preferred reaction operating conditions are lower temperature and higher pressure.

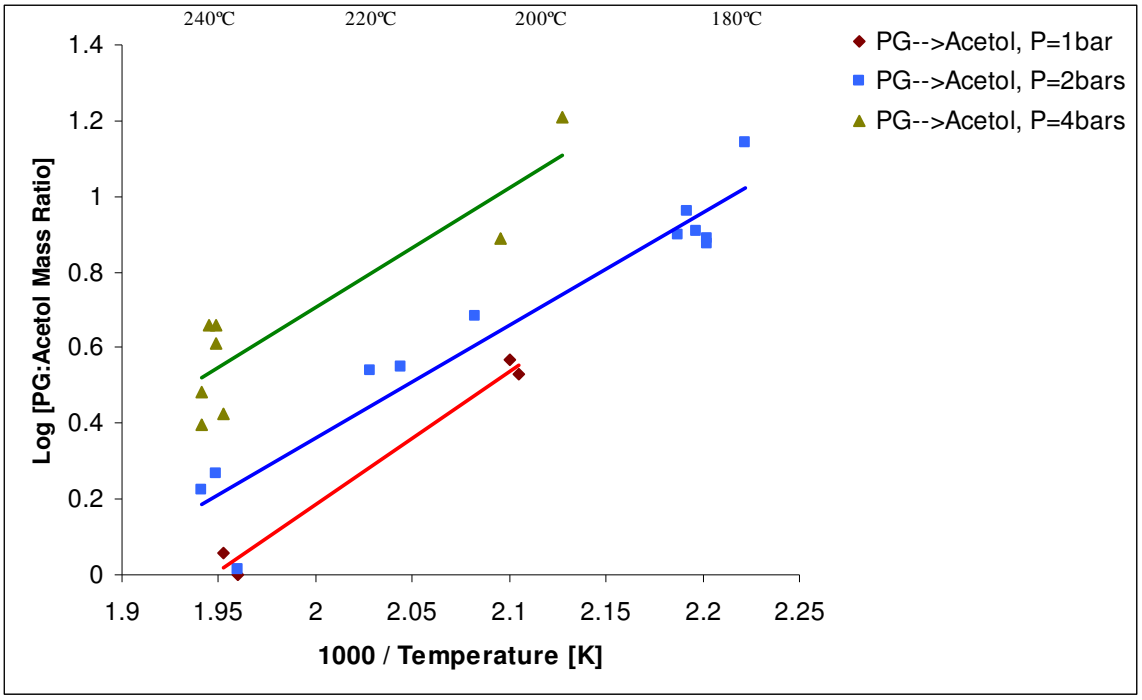

Figure 3.3. Temperature Dependence of the Propylene Glycol to Acetol Reaction, at system pressures of 1, 2 and 4 bar.

3.2 Reaction of Propylene Glycol to Acetol

Figure 3.3 shows the behavior of the propylene glycol to acetol reaction at different temperatures, 180 ºC to 240 ºC; and pressures of 1, 2, and 4 bar. This figure indicates that, for a specific pressure, at lower temperature more propylene

glycol is produced. Figure 3.3 also shows that higher pressures cause more propylene glycol to be produced from acetol at a given temperature.

In summary, more propylene glycol is produced at lower temperature and higher pressure. This result is similar to the conversion of glycerol to propylene glycol as presented in Figure 3.1. Table 3-2 list the experimental data plotted in Figure 3.3.

Table 3-2 lists the Log [PG: Acetol Mass Ratio] values to each temperature of reaction of the propylene glycol to acetol reaction. Table 3-2 indicates that at lower reaction temperatures more desired product (propylene glycol) is produced.

Table 3-2 Effect of Temperature and Pressure on the Formation of Acetol from Propylene Glycol.

Reactor Temperature [ºC]	Pressure of Discharge [bar]	Acetol [wt%]	PG [wt%]	[PG:Acetol Mass Ratio]	Reactor Temperature [K]	1000 / Temperature [K]	Log [PG:Acetol Mass Ratio]
203	1	17.36	64.31	3.70	476.15	2.10	0.57
239	1	34.27	39.16	1.14	512.15	1.95	0.06
202	1	21.33	72.40	3.39	475.15	2.10	0.53
237	1	34.56	34.67	1.00	510.15	1.96	0.00
177	2	6.39	88.90	13.91	450.15	2.22	1.14
181	2	11.07	85.55	7.73	454.15	2.20	0.89
184	2	11.06	87.84	7.94	457.15	2.19	0.90
181	2	11.6	87.06	7.51	454.15	2.20	0.88
182	2	11.03	89.24	8.09	455.15	2.20	0.91
183	2	10.15	92.22	9.09	456.15	2.19	0.96
207	2	15.58	75.00	4.81	480.15	2.08	0.68
220	2	18.19	63.25	3.48	493.15	2.03	0.54
216	2	17.25	61.20	3.55	489.15	2.04	0.55
237	2	35.1	36.08	1.03	510.15	1.96	0.01
240	2	23.61	43.64	1.85	513.15	1.95	0.27
242	2	21.77	36.54	1.68	515.15	1.94	0.22
204	4	10.35	80.10	7.74	477.15	2.10	0.89
239	4	21.91	58.34	2.66	512.15	1.95	0.43
197	4	5.8	94.01	16.21	470.15	2.13	1.21
242	4	11.29	34.45	3.05	515.15	1.94	0.48
242	4	20.96	52.45	2.50	515.15	1.94	0.40
241	4	9.15	41.65	4.55	514.15	1.94	0.66
240	4	13.02	59.51	4.57	513.15	1.95	0.66
240	4	13.63	55.59	4.08	513.15	1.95	0.61

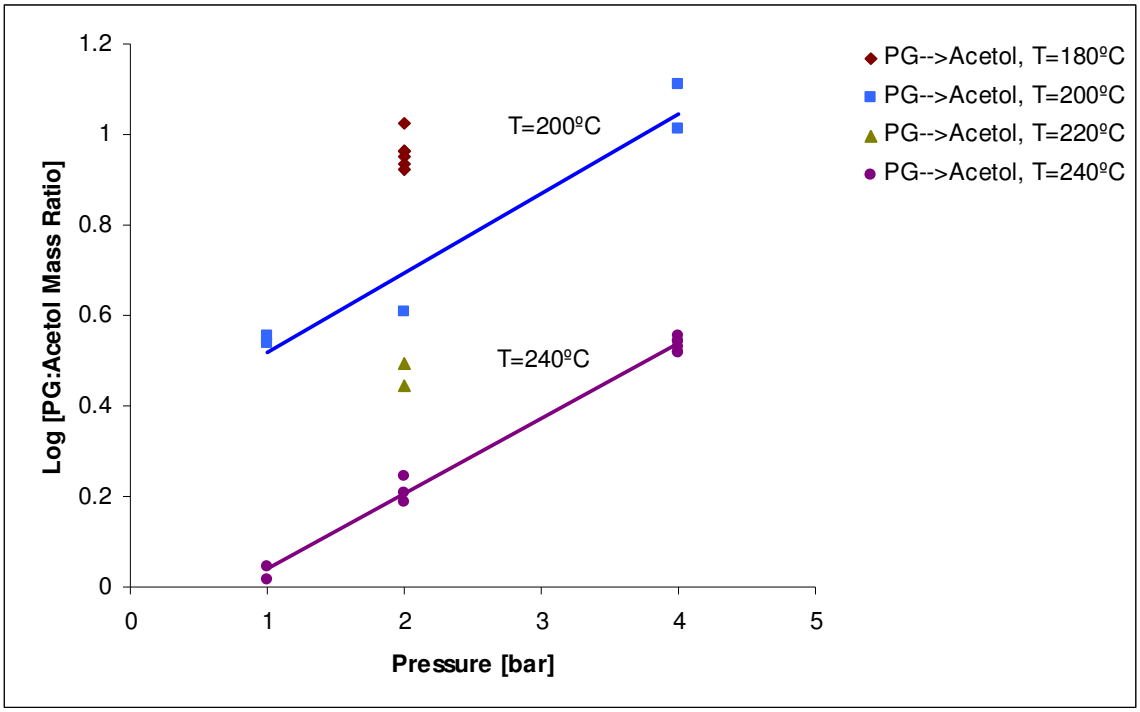

Figure 3.4. Pressure Dependence of the Propylene Glycol to Acetol Reaction, at temperatures of 180ºC, 200ºC, 220ºC and 240ºC.

Figure 3.4 shows the change of the Log [PG: Acetol Mass Ratio] values as a function of pressure of the propylene glycol to acetol reaction at four different values of temperatures (180ºC, 200ºC, 220ºC and 240ºC). It is possible to study this reaction at a lower temperature than the glycerol reagent studies because both the propylene glycol and acetol have higher vapor pressures than glycerol.

Similar to data with glycerol as a reagent, these data show that increasing the pressure of the system at a fixed temperature increases the mass ratio of propylene glycol to acetol. This behavior was reflected in each of the four temperatures. Also, decreasing the temperature of the reaction resulted in more propylene glycol in the product stream.

In summary, the results plotted in Figure 3.4 for the conversion of

propylene glycol to acetol indicate that the preferred reaction operating conditions are higher pressure and lower temperature. The results plotted on Figure 3.4 are tabulated in Table 3-2.

Table 3-2 lists the Log [PG: Acetol Mass Ratio] values of the propylene glycol to acetol reaction.

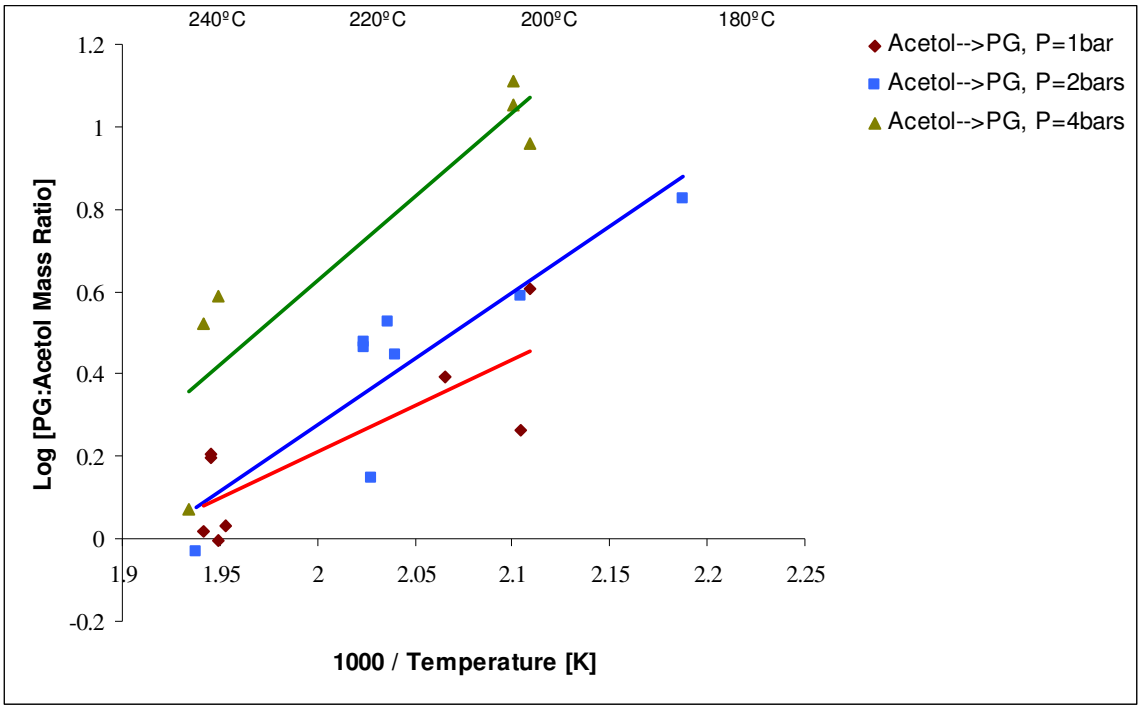

Figure 3.5. Temperature Dependence of the Acetol to Propylene Glycol Reaction, at system pressures of 1, 2 and 4 bar.

3.4 Reaction of Acetol to Propylene Glycol

The effect of temperature (180 ºC to 240 ºC) on the Log [PG: Acetol Mass Ratio] values for the acetol to propylene glycol reaction at three different pressures (1, 2, and 4 bar) is presented in Figure 3.5. This figure indicates that

more propylene glycol is produced at lower reaction temperatures. This effect was evident at each of the three pressures. At the higher pressures the conversion of propylene glycol increased.

In summary, the result for the conversion of acetol to propylene glycol indicate that more formation of propylene glycol exist at lower temperature and higher pressure. This behavior is in agreement with results obtained for the conversion of glycerol to propylene glycol reaction and propylene glycol to acetol reaction as presented in Figures 3.1 and 3.3. Table 3-3 presents the experimental values plotted in Figure 3.5.

Table 3-3 lists the Log [PG: Acetol Mass Ratio] values of the acetol to propylene glycol reaction. The data in Table 3-3 indicates that at higher pressures more propylene glycol can be produced at a given value of temperature.

Table 3-3 Effect of Temperature and Pressure on the Formation of Propylene Glycol from Acetol.

Reactor Temperature [ºC]	Pressure of Discharge [bar]	Acetol [wt%]	PG [wt%]	[PG:Acetol Mass Ratio]	Reactor Temperature [K]	1000/ T(K)	Log [PG:Acetol Mass Ratio]
202	1	20.14	36.94	1.83	475.15	2.10	0.26
211	1	14.88	36.83	2.48	484.15	2.07	0.39
241	1	13.43	21.1	1.57	514.15	1.94	0.20
241	1	12.74	20.37	1.60	514.15	1.94	0.20
201	1	13.17	53.15	4.04	474.15	2.11	0.61
240	1	30.18	29.81	0.99	513.15	1.95	-0.01
242	1	31.76	33.19	1.05	515.15	1.94	0.02
239	1	24.54	26.38	1.07	512.15	1.95	0.03
184	2	8.56	57.3	6.69	457.15	2.19	0.83
202	2	11.12	43.14	3.88	475.15	2.10	0.59
217	2	14.32	39.91	2.79	490.15	2.04	0.45
220	2	21.64	30.28	1.40	493.15	2.03	0.15
221	2	14.92	43.51	2.92	494.15	2.02	0.46
218	2	13.86	46.82	3.38	491.15	2.04	0.53
221	2	12.91	38.95	3.02	494.15	2.02	0.48
243	2	44.84	41.83	0.93	516.15	1.94	-0.03
201	4	6.03	55.15	9.15	474.15	2.11	0.96
203	4	4.68	60.46	12.92	476.15	2.10	1.11
244	4	19.14	22.64	1.18	517.15	1.93	0.07
203	4	5.29	59.89	11.32	476.15	2.10	1.05
242	4	10.3	34.33	3.33	515.15	1.94	0.52
240	4	11.34	43.86	3.87	513.15	1.95	0.59

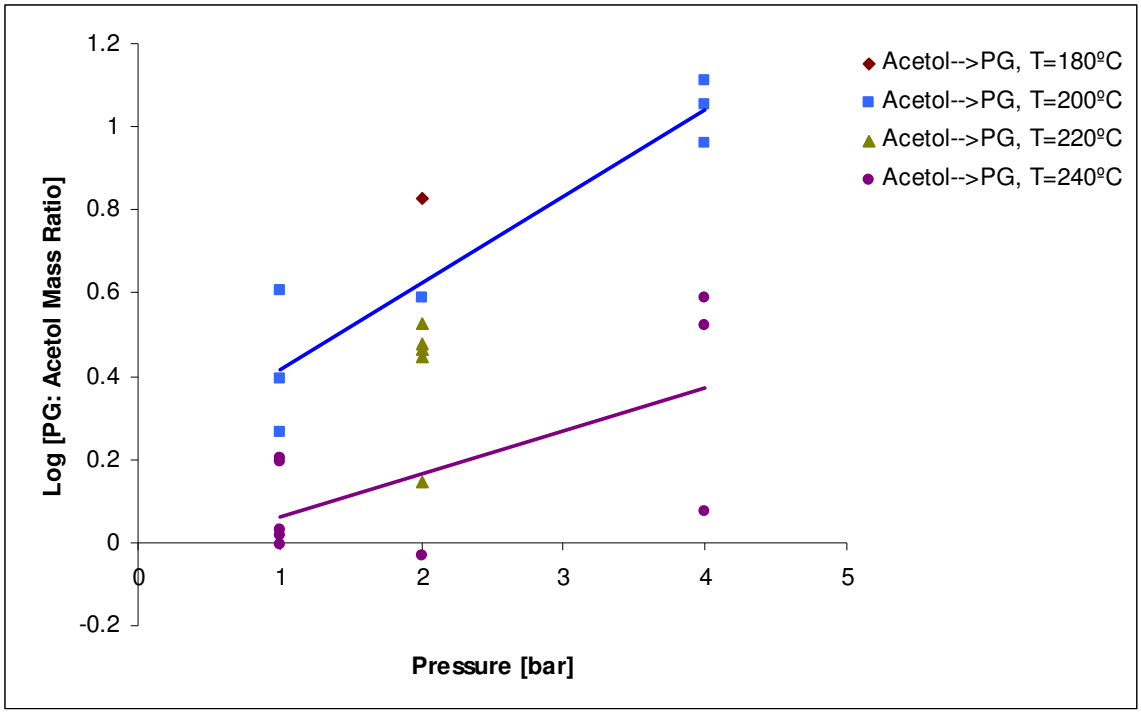

Figure 3.6. Pressure Dependence of the Acetol to Propylene Glycol Reaction, at temperatures of 180ºC, 200ºC, 220ºC, and 240ºC.

Figure 3.6 presents the change of the Log [PG: Acetol Mass Ratio] values as a function of pressure of the acetol to propylene glycol reaction at four different values of temperatures (180ºC, 200ºC, 220ºC, and 240ºC). This figure indicates that, for a specific pressure, at lower temperature more propylene glycol is produced. Figure 3.6 also indicates that higher pressures produce more propylene glycol at a given temperature. This behavior was reflected at each of the four temperatures.

Accorded to previous reactions, this reaction of acetol to propylene glycol indicates that the preferred reaction operating conditions are lower temperature and higher pressure. The values plotted in Figure 3.6 are tabulated in Table 3-3.

Table 3-3 lists the Log [PG: Acetol Mass Ratio] values of each acetol to propylene glycol samples. Table 3-3 indicates that increasing the system pressure increases the propylene glycol production.

3.5 Equilibrium Constant and Gibbs Free Energy

Previously discussed in Chapter 2 the reaction of acetol to propylene glycol is expected to be under equilibrium conditions. This hypothesis was tested, and the results are shown in Figure 3.7.

Figure 3.7 superposed the data (Figures 3.4 and 3.6) of propylene glycol to acetol reaction and acetol to propylene glycol reaction at the same temperatures and pressures.

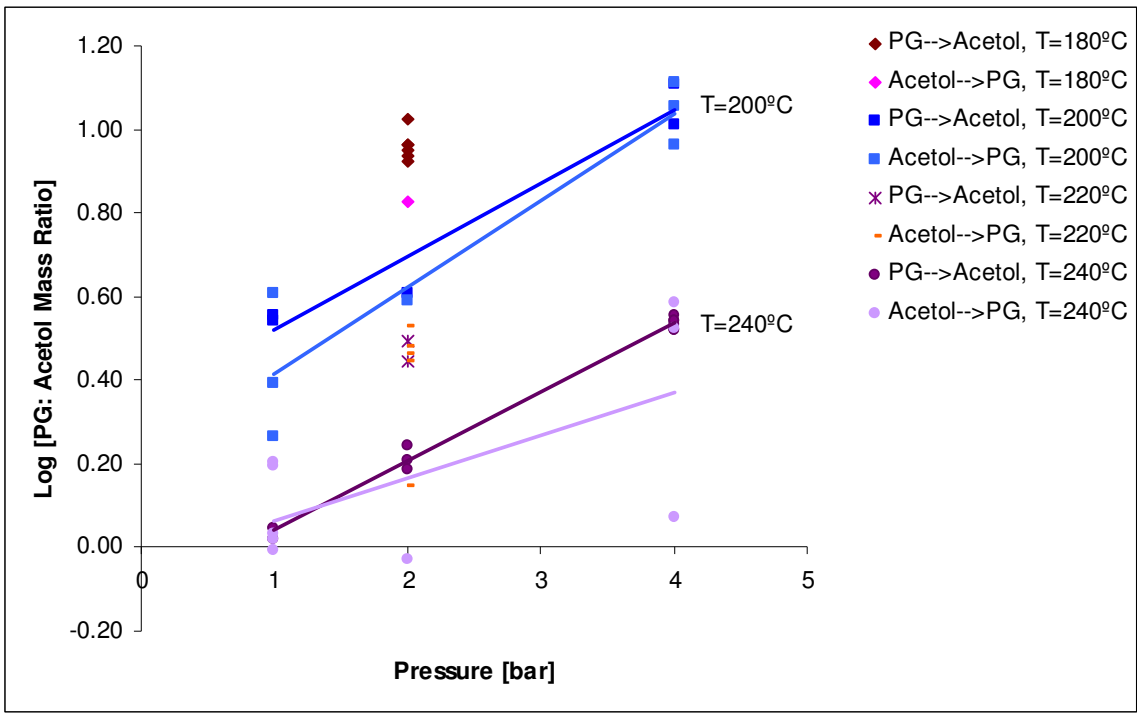

Figure 3.7. Equilibrium Reaction: Propylene Glycol to Acetol and Acetol to Propylene Glycol.

Since the data of similar temperature substantially superimpose, Figure 3.7 established that the reaction of acetol to propylene glycol is equilibrium limited. Since the data represent approaches to this equilibrium from both directions (producing propylene glycol and using propylene glycol) the results are definitive. The data further indicate that kinetic limited reaction conditions are likely at temperatures lower than 180℃.

Table 3-4 Equilibrium constant and Gibbs free energy values for the Propylene Glycol to Acetol Reaction.

Reactor Temperature [K]	P_{TOTAL} [bar]	YAC	YPG	YPG / YAC	Y H_2	YPG / (YAC*YH2)	K eq, YPG / (YAC*YH2*P)	ΔG [J/gmol]
450	2	0.06	0.85	13.55	0.89	17.84	7.58	-7579.35
454	2	0.11	0.80	7.52	0.89	10.58	4.21	-5430.3
457	2	0.11	0.82	7.73	0.89	10.59	4.33	-5572.69
454	2	0.11	0.81	7.31	0.89	10.08	4.09	-5319.77
453	2	0.11	0.83	7.88	0.89	10.61	4.41	-5590.19
456	2	0.10	0.84	8.85	0.86	12.18	5.13	-6197.74
480	2	0.15	0.72	4.69	0.86	7.63	2.74	-4020.2
476	1	0.18	0.64	3.61	0.74	7.68	4.91	-6296.26
475	1	0.21	0.68	3.30	0.74	6.52	4.44	-5887.31
477	4	0.09	0.70	7.54	0.93	11.58	2.03	-2812.42
470	4	0.05	0.83	15.78	0.92	20.60	4.27	-5675.43
493	2	0.18	0.60	3.39	0.85	6.58	1.99	-2811.27
489	2	0.17	0.59	3.45	0.85	6.89	2.02	-2865.41
510	1	0.34	0.33	0.98	0.74	4.00	1.32	-1188.67
510	2	0.33	0.33	1.00	0.85	3.55	0.59	2243.48
513	2	0.22	0.40	1.80	0.85	5.31	1.06	-250.565
515	2	0.21	0.34	1.63	0.85	5.61	0.96	158.9529
512	1	0.30	0.34	1.11	0.73	4.51	1.52	-1779.86
515	4	0.06	0.18	2.97	0.85	19.69	0.87	577.815
515	4	0.18	0.44	2.44	0.85	6.46	0.72	1427.368
514	4	0.08	0.36	4.43	0.92	13.55	1.21	-805.754
513	4	0.12	0.52	4.45	0.92	9.34	1.21	-814.523
513	4	0.13	0.51	3.97	0.91	8.47	1.09	-362.552
512	4	0.22	0.57	2.59	0.92	4.94	0.71	1478.77

Table 3-4 list the equilibrium constant and Gibbs free energy values of the propylene glycol to acetol reaction. The tabulated data is presented in Figure 3.8 to Figure 3.10.

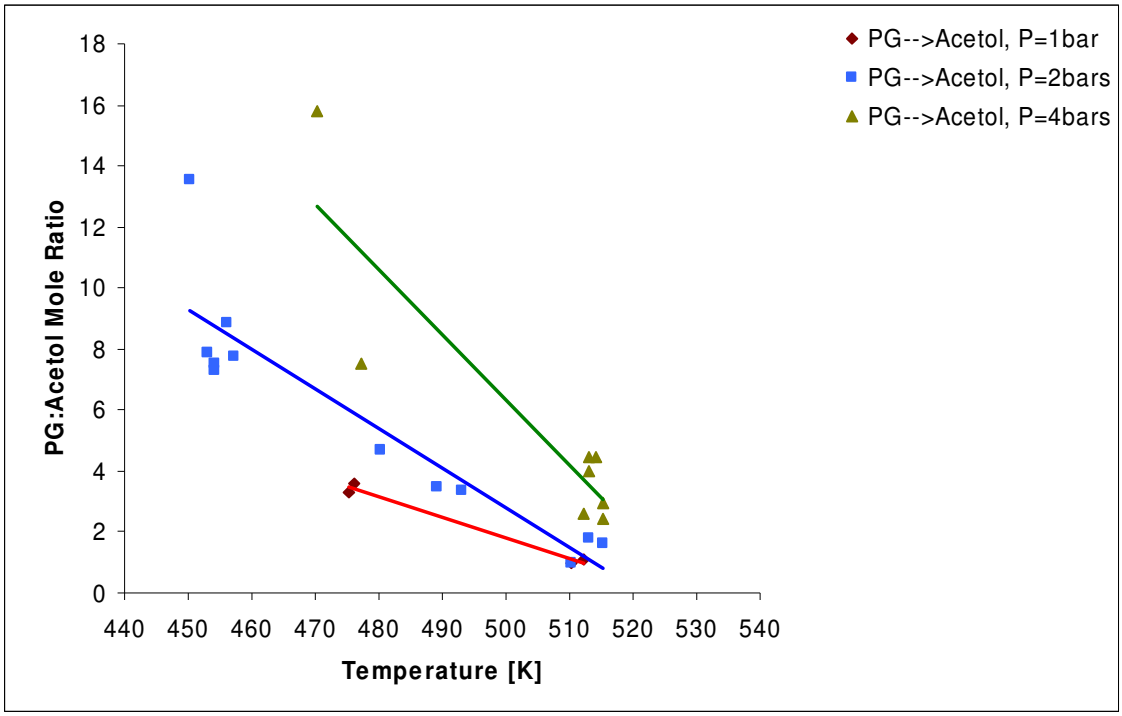

Figure 3.8. Effect of temperature on the propylene glycol to acetol mole ratio of the propylene glycol to acetol reaction, at system pressures of 1, 2, and 4 bars.

Figure 3.8 presents the effect of temperature (180 ºC to 240 ºC) on the PG: Acetol Mole Ratio values of the propylene glycol to acetol reaction at three different pressures (1, 2, and 4 bar). This figure indicates that less propylene glycol is converted to acetol at lower reaction temperatures. This effect was evident at each of the three pressures.

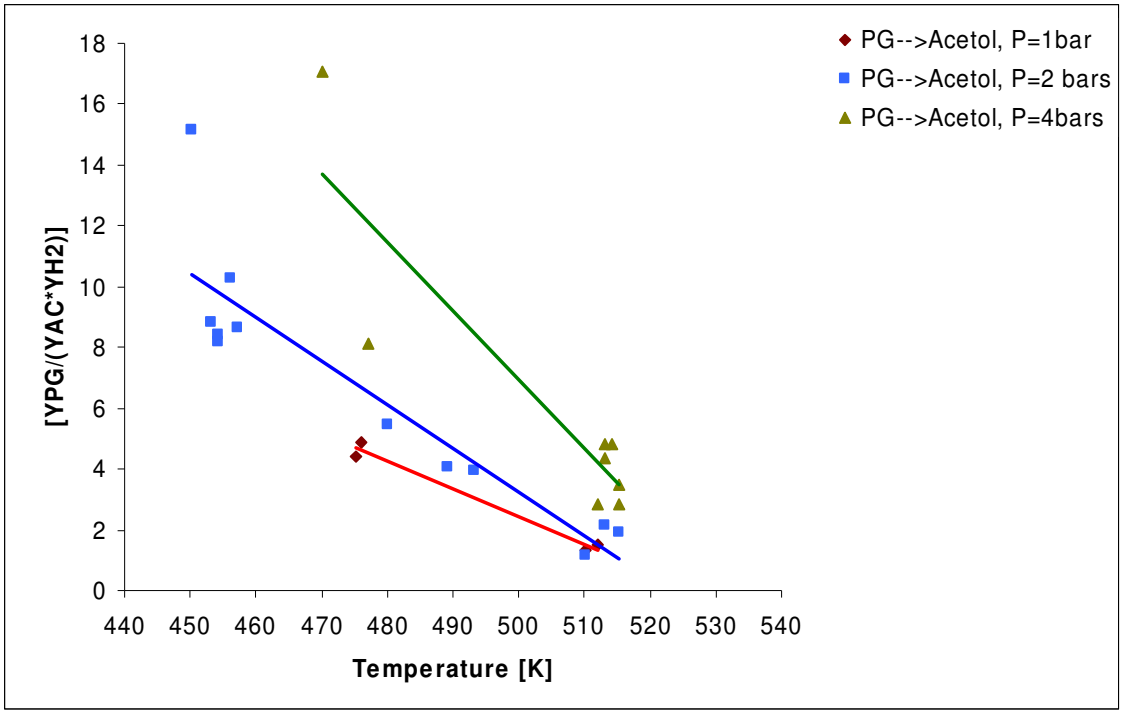

Figure 3.9. Temperature dependence on the propylene glycol to acetol and hydrogen mole ratio of the propylene glycol to acetol reaction, at pressures of 1, 2, and 4 bars.

Figure 3.9 presents the effect of temperature (180 ºC to 240 ºC) on the $YPG/(YAC*YH_2)$ values of the propylene glycol to acetol reaction at three different pressures (1, 2, and 4 bar). This figure indicates that the conversion of propylene glycol to acetol decreases at lower reaction temperatures. This effect was evident at each of the three pressures.

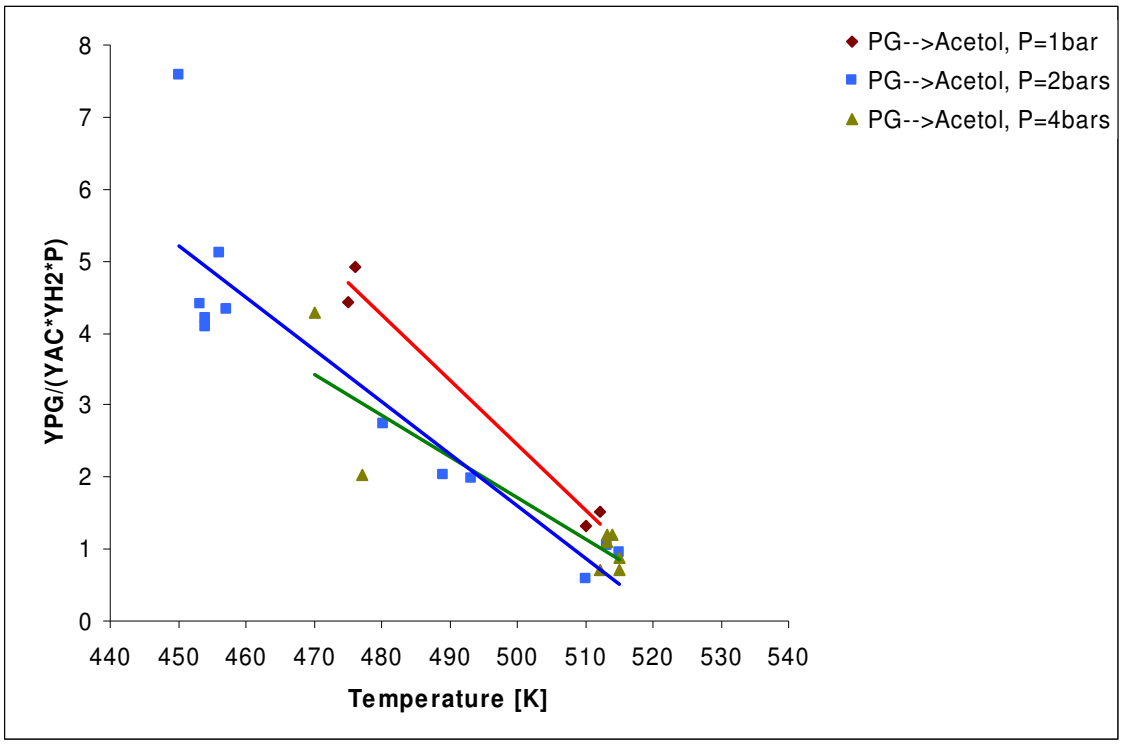

Figure 3.10. Effect of temperature on the equilibrium constant of the propylene glycol to acetol reaction, at system pressures of 1, 2, and 4 bars.

Figure 3.10 presents the effect of temperature (180 ºC to 240 ºC) on the equilibrium constant values of the propylene glycol to acetol reaction at three different pressures (1, 2, and 4 bar). This figure indicates that the equilibrium constant values increases at lower temperatures where more moles of propylene glycol are present.

Table 3-5 Equilibrium constant and Gibbs free energy values for the Acetol to Propylene Glycol Reaction.

Reactor Temperature [K]	P_{TOTAL} [bar]	YAC	YPG	YPG / YAC	Y H_2	YPG / (YAC*YH2)	K eq, YPG / (YAC*YH2*P)	∆G [J/gmol]
457	2	0.05	0.30	6.52	0.86	25.62	3.79	-5059.54
475	1	0.10	0.17	1.79	0.48	21.56	3.70	-5171.55
475	2	0.05	0.21	3.78	0.85	21.74	2.23	-3172.27
474	1	0.07	0.28	3.93	0.75	18.54	5.25	-6534.36
476	4	0.03	0.31	11.02	0.92	39.06	2.99	-4333.03
474	4	0.03	0.27	8.91	0.92	35.93	2.43	-3496.03
476	4	0.02	0.31	12.58	0.92	44.10	3.43	-4879.46
484	1	0.07	0.18	2.41	0.72	19.24	3.37	-4888.07
490	2	0.06	0.17	2.71	0.87	18.49	1.56	-1817.34
493	2	0.10	0.14	1.36	0.87	11.56	0.78	993.421
494	2	0.07	0.20	2.84	0.87	16.25	1.64	-2022.76
491	2	0.06	0.21	3.29	0.87	18.02	1.89	-2607.56
494	2	0.06	0.18	2.94	0.84	19.18	1.74	-2272.33
516	2	0.18	0.16	0.91	0.84	6.72	0.54	2634.137
513	1	0.14	0.13	0.96	0.64	11.44	1.50	-1725.2
515	1	0.13	0.14	1.02	0.71	10.53	1.43	-1536.74
514	1	0.06	0.09	1.53	0.71	22.71	2.15	-3267.45
514	1	0.06	0.10	1.56	0.71	22.91	2.19	-3342.4
512	1	0.12	0.12	1.05	0.72	11.85	1.45	-1576.73
515	4	0.05	0.16	3.25	0.91	22.41	0.90	472.8089
513	4	0.06	0.21	3.77	0.92	19.43	1.03	-110.795
517	4	0.12	0.14	1.15	0.92	9.05	0.31	4975.326

Table 3-5 list the equilibrium constant and Gibbs free energy values of the acetol to propylene glycol reaction. The tabulated data is presented in Figure 3.11 to Figure 3.13.

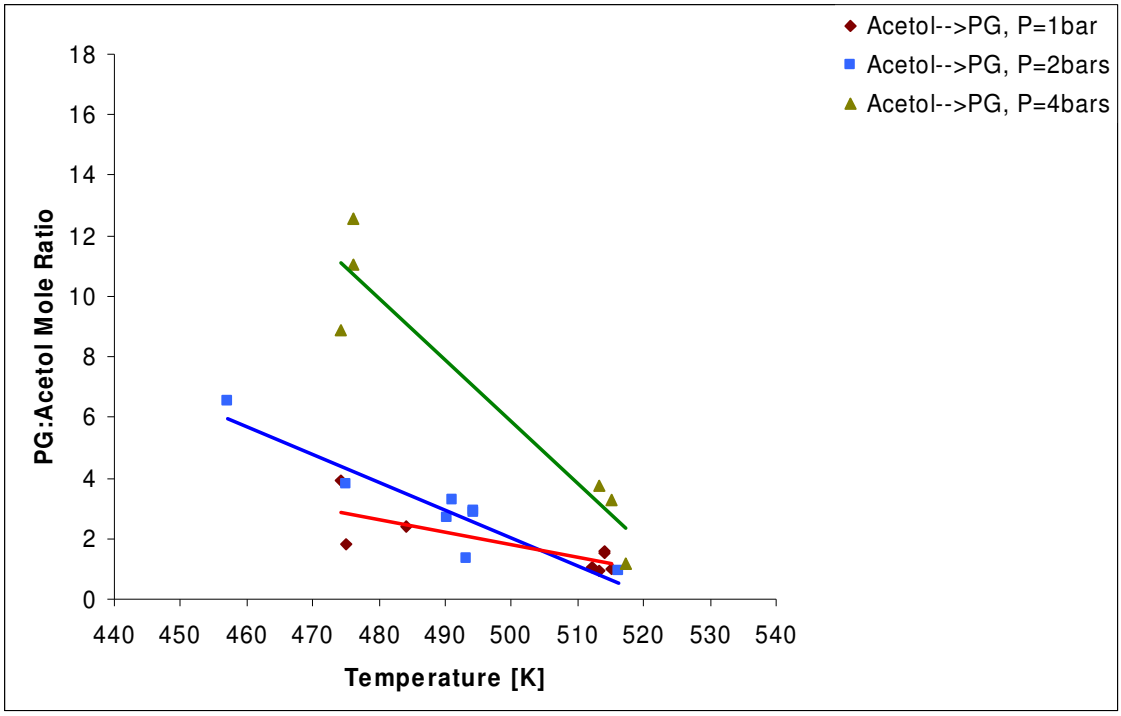

Figure 3.11. Effect of temperature on the propylene glycol to acetol mole ratio of the acetol to propylene glycol reaction, at system pressure of 1, 2, and 4 bars.

Figure 3.11 presents the effect of temperature (180 ºC to 240 ºC) on the PG: Acetol Mole Ratio values of the acetol to propylene glycol reaction at three different pressures (1, 2, and 4 bar). This figure indicates that more propylene glycol is produced at lower reaction temperatures. This effect was evident at each of the three pressures.

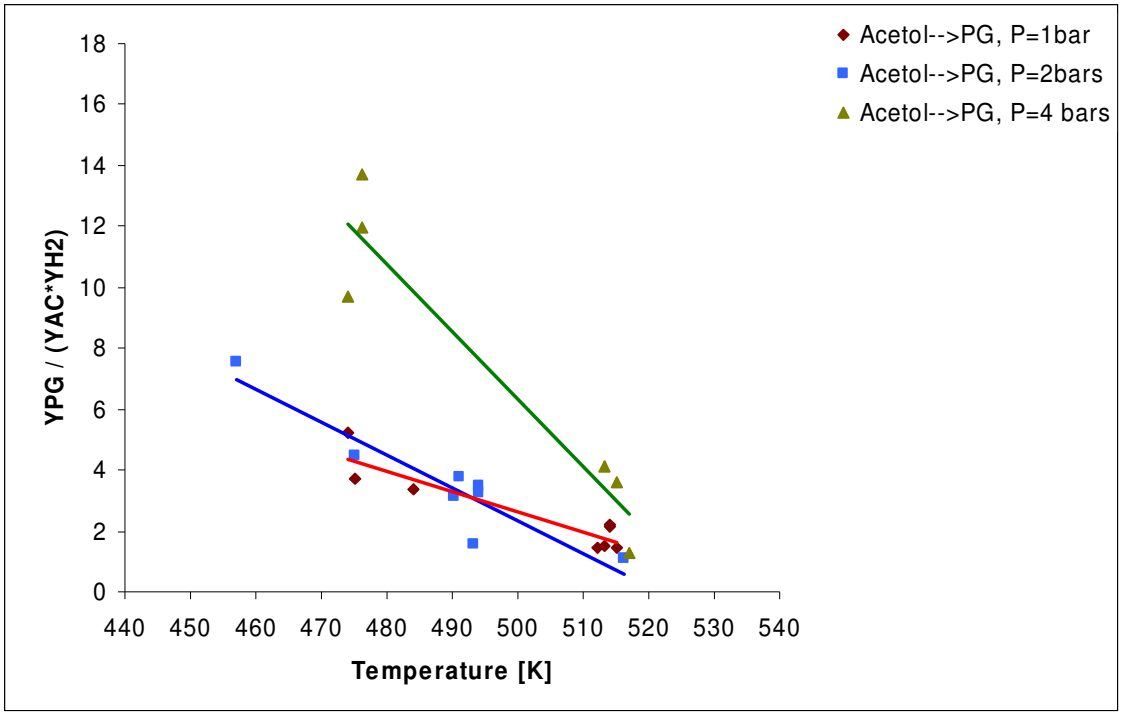

Figure 3.12. Temperature dependence on the propylene glycol to acetol and hydrogen mole ratio of the acetol to propylene glycol reaction, at pressures of 1, 2, and 4 bars.

Figure 3.12 shows the effect of temperature (180 ºC to 240 ºC) on the YPG/(YAC*YH_2) values of the acetol to propylene glycol reaction at three different pressures (1, 2, and 4 bar). This figure indicates that the production of propylene glycol increase at lower reaction temperatures. This effect was evident at each of the three pressures.

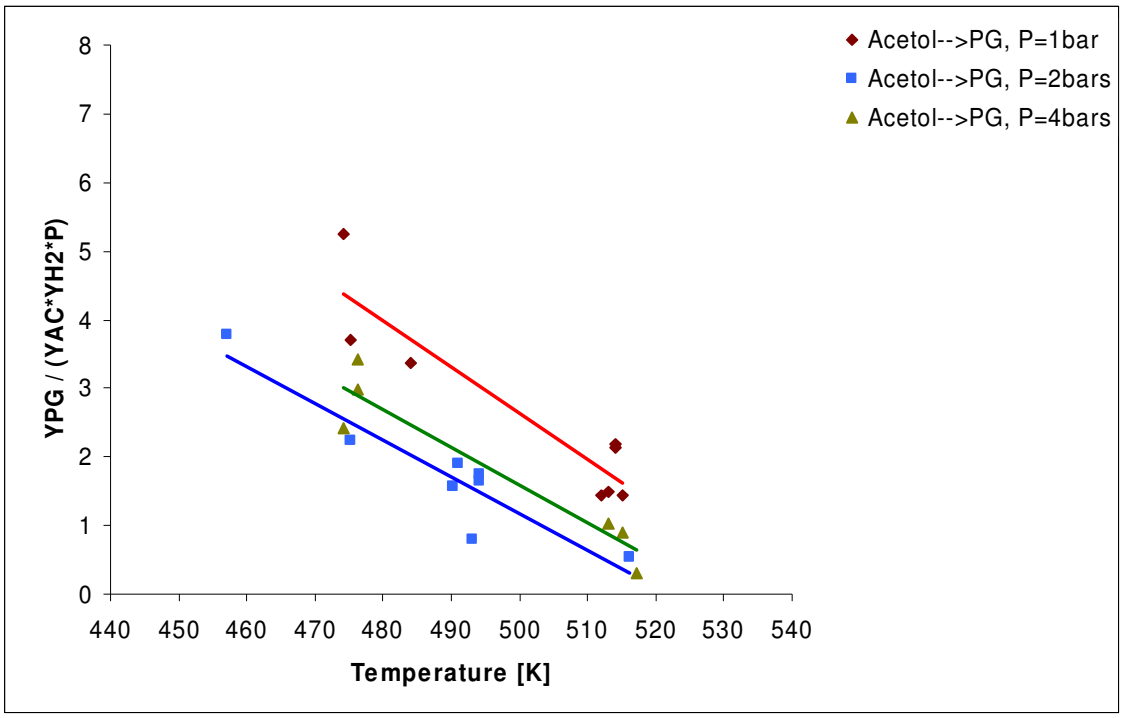

Figure 3.13. Effect of temperature on the equilibrium constant of the propylene glycol to acetol reaction, at system pressures of 1, 2, and 4 bars.

Figure 3.13 presents the effect of temperature (180 ºC to 240 ºC) on the equilibrium constant values of the propylene glycol to acetol reaction at three different pressures (1, 2, and 4 bar). This figure indicates that the equilibrium constant values increases at lower temperatures where more propylene glycol is produced.

CHAPTER 4

4. TRENDS IN BYPRODUCTS

In order to decrease the amount of byproducts formed in the reaction, identification of trends on byproducts was evaluated. The selectivity on conversion of glycerol to propylene glycol decrease as side reactions become prominent. The effect of temperature, pressure, residence time and water content on total byproducts was evaluated. Figure 4.1 presents the effect of temperature (220 ºC to 240 ºC) on byproducts of the glycerol to propylene glycol reaction at three different pressures (1, 2, and 4 bars).

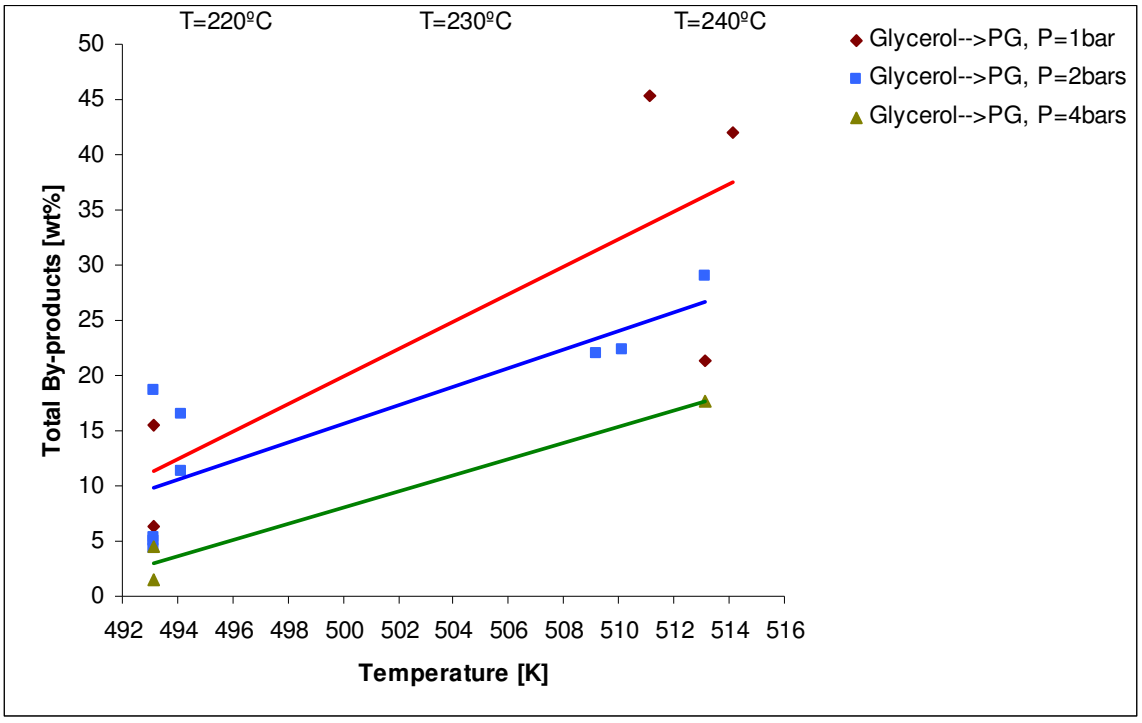

Figure 4.1. Byproducts of glycerol conversion to propylene glycol: effect of temperature.

4.1 Reaction of Glycerol to Propylene Glycol

Figure 4.1 indicates that increasing the temperature of reaction results in more byproducts. In other words at lower temperatures less byproducts are produced. This trend was repeated at each of the three pressures.

At a given temperature, Figure 4.1 indicates that higher pressures produce fewer by products. In summary, these results for the conversion of glycerol to propylene glycol indicate that the preferred reaction operating conditions are lower temperature and higher pressure.

Table 4-1 shows the experimental data plotted in Figure 4.1. Table 4-1 indicates that increasing the temperature of reaction more weight percent of total by products can be formed.

Table 4-1 Effect of temperature and pressure on total byproducts of the glycerol to propylene glycol reaction.

Reactor Temperature [ºC]	Pressure of Discharge [bar]	Reactor Temperature [K]	Total Byproducts [wt%]
220	1	493	6.29
220	1	493	15.50
238	1	511	45.29
241	1	514	42.06
240	1	513	21.31
220	2	493	4.27
220	2	493	4.98
220	2	493	5.37
221	2	494	11.36
220	2	493	18.65
221	2	494	16.46
237	2	510	22.32
236	2	509	22.01
240	2	513	29.03
220	4	493	4.54
220	4	493	1.58
240	4	513	17.59

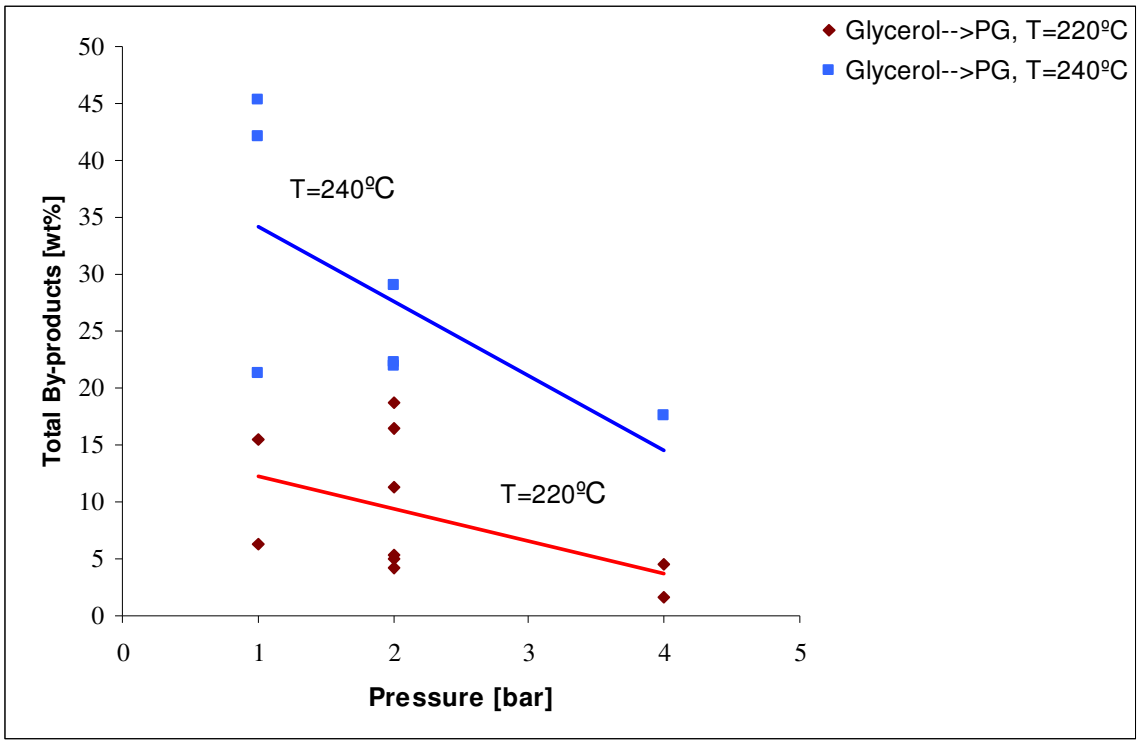

Figure 4.2. Byproducts of glycerol conversion to propylene glycol: effect of pressure.

Pressure has a significant effect in the glycerol to propylene glycol reaction. From the literature (see Chapter 2) operating conditions at higher pressures are necessary to minimize the degradation of glycerol.

Figure 4.2 presents the change of total byproducts as a function of pressure of the glycerol to propylene glycol reaction at different values of temperatures (220ºC, and 240ºC). This figure indicates that, for a specific pressure, at lower temperature fewer byproducts are produced. Figure 4.2 also indicates that higher pressures lead to fewer byproducts at a given temperature.

This behavior was repeated at each temperature.

In summary, these results for the conversion of glycerol to propylene glycol exhibit that the preferred reaction operating conditions are higher pressure and lower temperature. Table 4-1 shows the data plotted in Figure 4.2.

Table 4-1 indicates that higher pressures result in formation of fewer byproducts.

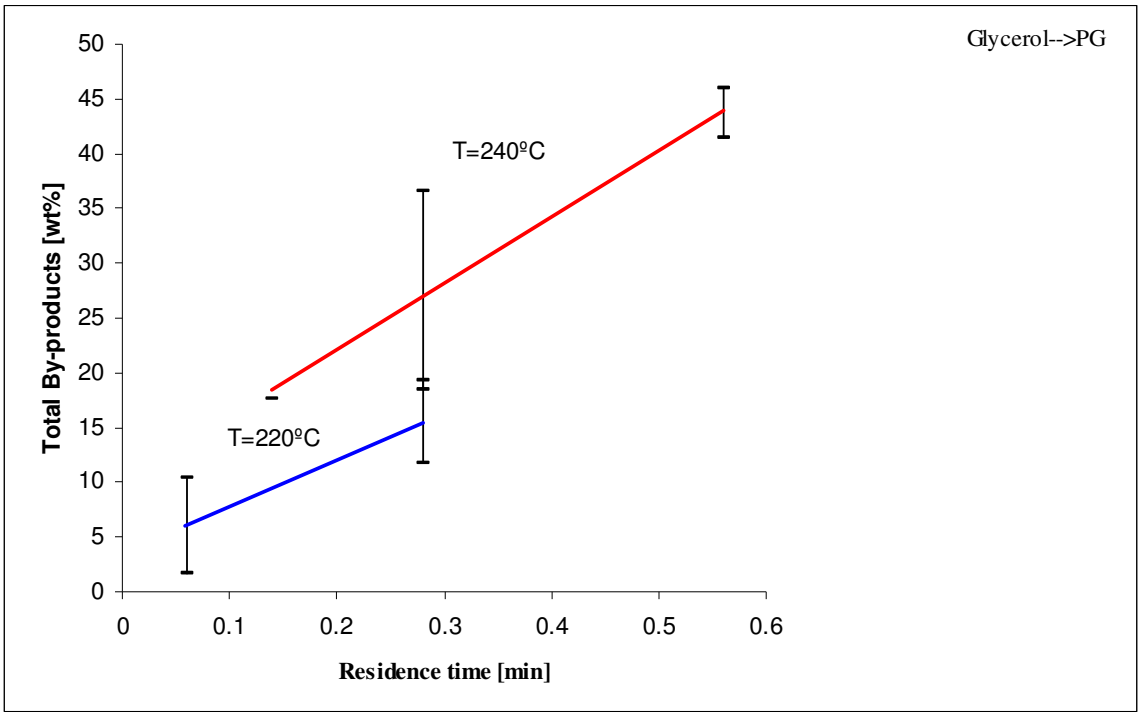

Figure 4.3. Byproducts of glycerol conversion to propylene glycol: effect of residence time.

The effect of residence time in by products at two different temperatures (220ºC, and 240ºC) is presented in Figure 4.3. This figure indicates that with an increase in residence time, the total byproducts increase. This effect was repeated at each temperature of reaction.

Figure 4.3 also indicates that at lower temperatures, fewer byproducts are formed. For this reaction less residence time and lower temperature reduce the formation of byproducts in glycerol to propylene glycol reaction. Table 4-2 presents the data plotted in Figure 4.3.

Table 4-2 lists the total byproducts to each residence time of the glycerol to propylene glycol reaction. Table 4-2 data indicates that for glycerol to propylene glycol reaction, a decrease of residence time reduces significantly the byproducts formation.

Table 4-2 Effect of the residence time on byproducts of the glycerol to propylene glycol reaction.

Reactor Temperature [ºC]	Pressure of Discharge [bar]	Hydrogen flowrate [(ft^3)/min]	Reactor Volume [ft^3]	Residence time [min]	Total Byproducts [wt%]	Water Content [wt%]
220	1	0.59	0.05	0.08	6.29	18.52
220	1	0.78	0.05	0.06	15.5	21.96
220	2	1.28	0.05	0.04	4.27	18.93
220	2	0.87	0.05	0.06	4.98	13.71
220	2	0.87	0.05	0.06	5.37	13.30
221	2	0.18	0.05	0.28	11.36	20.74
220	2	0.18	0.05	0.28	18.65	21.01
221	2	0.18	0.05	0.28	16.46	23.29
220	4	1.06	0.05	0.05	4.54	17.16
220	4	0.78	0.05	0.06	1.58	15.73
238	1	0.09	0.05	0.56	45.29	15.72
241	1	0.09	0.05	0.56	42.06	14.02
240	1	0.18	0.05	0.28	21.31	25.70
237	2	0.18	0.05	0.28	22.32	24.01
236	2	0.18	0.05	0.28	22.01	24.09
240	2	0.18	0.05	0.28	29.03	26.63
240	4	0.18	0.05	0.28	42.86	28.78
240	4	0.35	0.05	0.14	17.59	26.51

Water is generated in this reaction and it is always preferable to eliminate the water from the initial reaction mixture to drive the equilibrium in the forward direction. As the initial water in the reaction increases, both the glycerol conversion of the propylene glycol decreased. The decrease in the selectivity is due to the degradation of the reaction product.

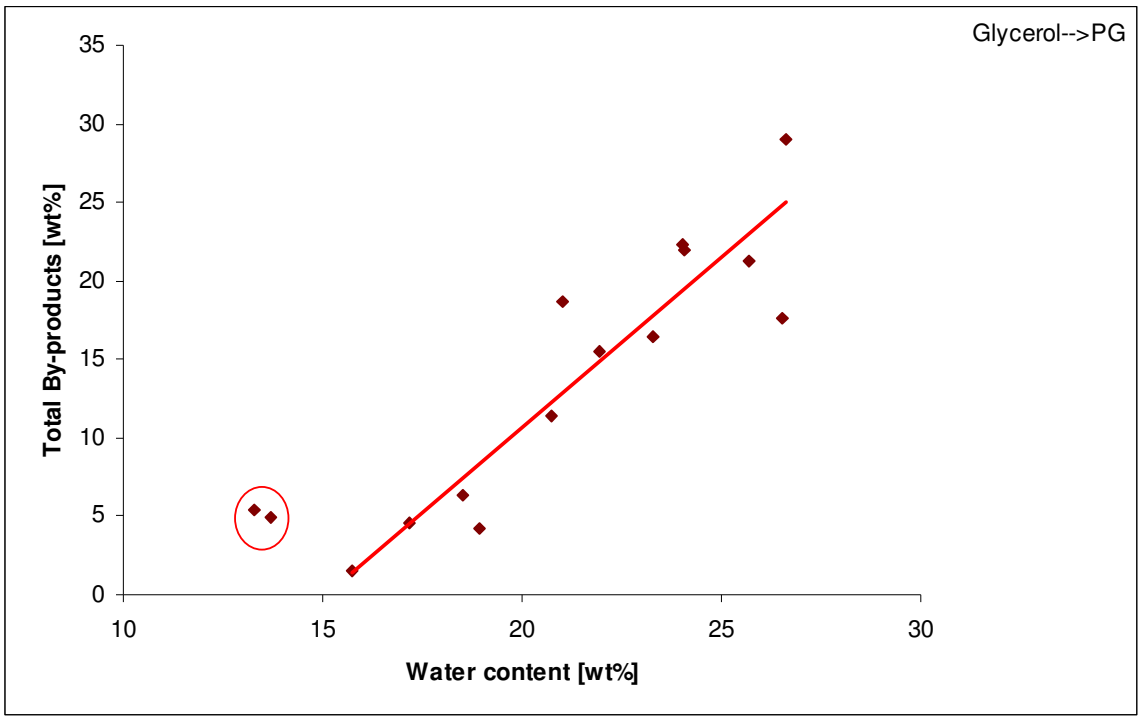

Figure 4.4. Byproducts of glycerol conversion to propylene glycol: effect of water content.

Figure 4.4 presents the impact of water content on byproducts of the glycerol to propylene glycol reaction. This reaction was carried out at 220ºC and 240ºC at system pressures of 1, 2, and 4 bars in the presence of a pre-reduced copper-chromite catalyst. Pure glycerol was used as a reagent to each experimental run.

From stoichiometric calculations, about 20% of the glycerin mass becomes water in this reaction. Because of these theoretical calculations, the values on a circle were not considered. It is hypothesized that for the circled data, sampling errors due to inadequate condensation of the chemicals from the hydrogen in the product gas caused erroneous results.

The impact of water content was evaluated in Figure 4.4. This figure indicates that with an increase in water content from de-hydrolysis of glycerol more byproducts are produced.

In summary, low water contents improve the conversion of glycerol to propylene glycol. The data plotted in Figure 4.4 is tabulated in Table 4-3. The water content in the final product is a good indicator of the quality of the product.

Table 4-3 indicates that with an increase of temperature more water content can be obtained. Also, Figure 4-3 indicates that an increase in water content produces more byproducts.

Table 4-3 Effect of the water content on byproducts of the glycerol to propylene glycol reaction

Reactor Temperature [ºC]	Pressure of Discharge [bar]	Water content [wt%]	Total Byproducts [wt%]
220	1	18.52	6.29
220	1	21.96	15.5
240	1	25.7	21.31
220	2	18.93	4.27
220	2	13.71	4.98
220	2	13.3	5.37
221	2	20.74	11.36
220	2	21.01	18.65
221	2	23.29	16.46
237	2	24.01	22.32
236	2	24.09	22.01
240	2	26.63	29.03
220	4	17.16	4.54
220	4	15.73	1.58
240	4	26.51	17.59

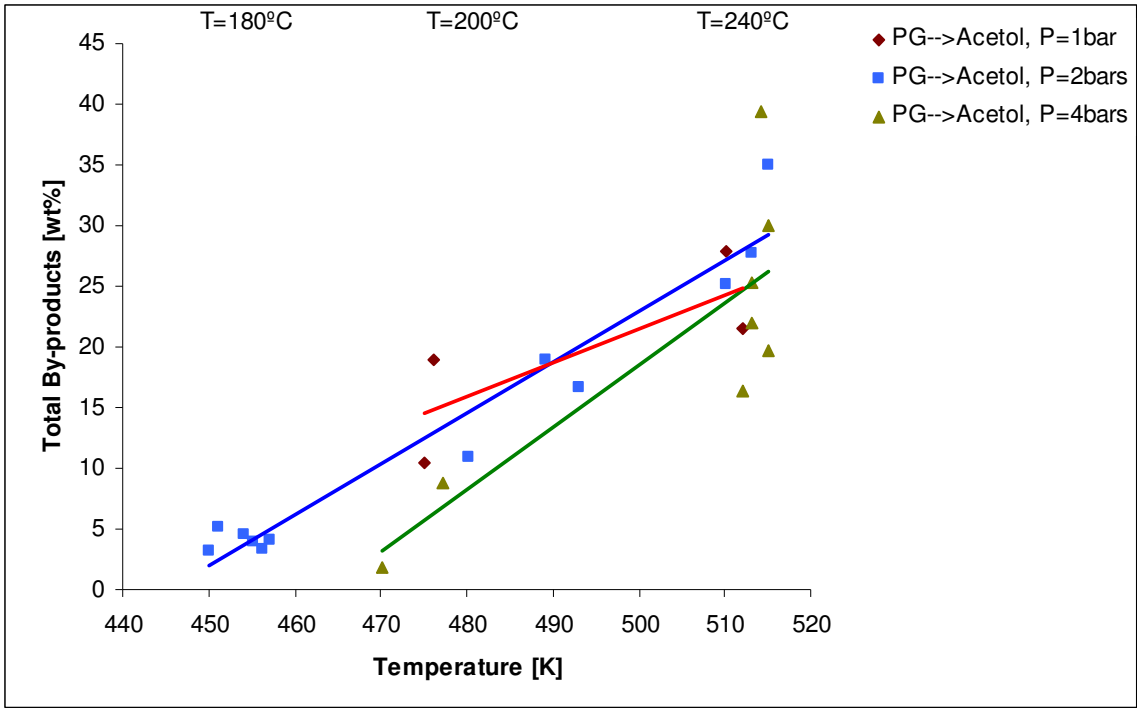

Figure 4.5. Byproducts of propylene glycol conversion to acetol: effect of temperature.

4.2 Reaction of Propylene Glycol to Acetol

The effect of temperature (180 ºC to 240 ºC) on byproduct formation for the propylene glycol to acetol reaction at three different pressures (1, 2 and 4 bar) is presented in Figure 4.5. This figure indicates that more byproducts are produced at increasing temperatures of reaction. The same effect was also observed at each of the three pressures.

At a given temperature, Figure 4.5, indicates that higher pressures produce fewer by products.

Figure 4.5 demonstrates that at lower temperatures the byproducts has

more dependence of pressure. In contrast, at higher temperatures the dependence of byproducts in pressure decreases.

In summary, this result for the conversion of propylene glycol to acetol shows that fewer byproducts are present in the product at lower temperatures and higher pressures. This result is similar to the conversion of glycerol to propylene glycol presented in Figure 4.1. Table 4-4 summarized the results plotted in Figure 4.5. Table 4-4 presents the effect of temperature on byproducts of the propylene glycol to acetol reaction and indicates that at lower temperature fewer byproducts are formed.

Table 4-4 Effect of temperature and pressure on byproducts of the propylene glycol to acetol reaction.

Reactor Temperature [ºC]	Pressure of Discharge [bar]	Reactor Temperature [K]	Total Byproducts [wt%]
203	1	476	18.94
202	1	475	10.41
237	1	510	27.84
239	1	512	21.51
177	2	450	3.13
178	2	451	5.11
184	2	457	4.02
181	2	454	4.53
182	2	455	3.99
183	2	456	3.35
207	2	480	10.84
220	2	493	16.62
216	2	489	18.99
237	2	510	25.22
240	2	513	27.74
242	2	515	35.03
204	4	477	8.79
197	4	470	1.82
242	4	515	30.03
242	4	515	19.7
241	4	514	39.39
240	4	513	21.98
240	4	513	25.35

239	4	512	16.43

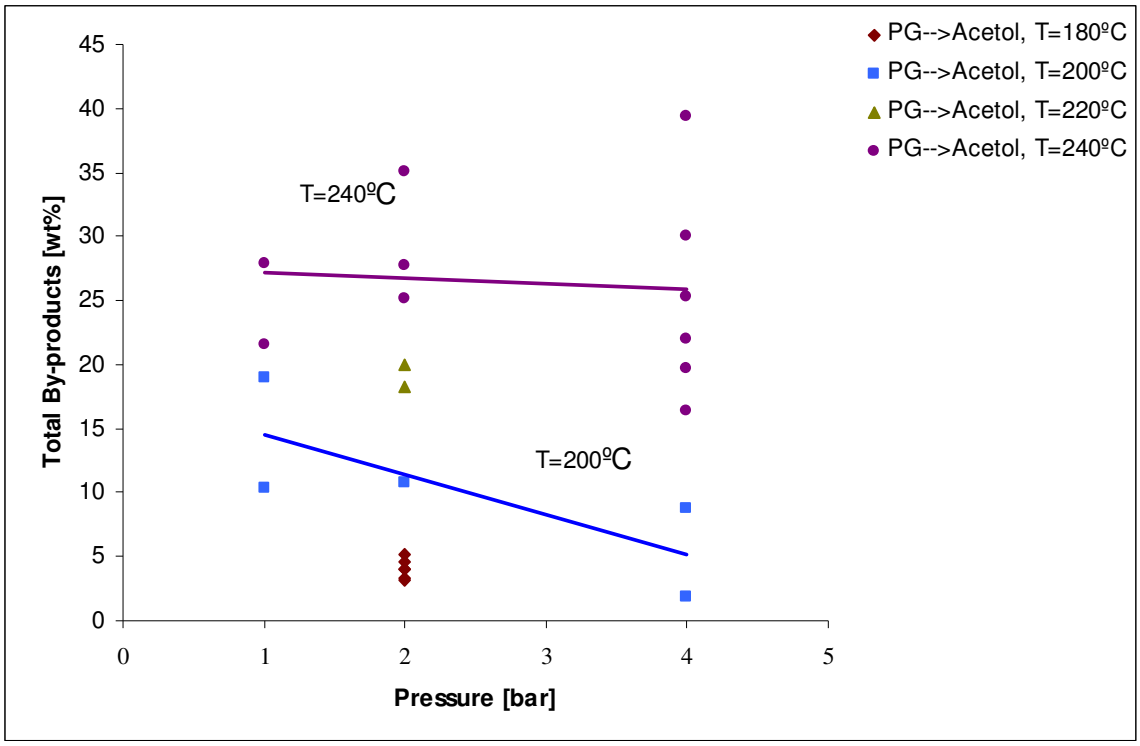

Figure 4.6. Byproducts of propylene glycol conversion to acetol: effect of pressure.

The effect of pressure in byproducts of the propylene glycol to acetol reaction is presented in Figure 4.6 at 180ºC, 200ºC, 220ºC and 240ºC. This figure indicates that, for a specific pressure, at lower temperatures fewer byproducts are produced. The effect of pressure at low temperature (200 ºC) indicates that the ratio of pressure from 1 to 4 bars (factor of four), decrease byproducts by 3 whereas at high temperature (240 ºC) the ratio of pressure from 1 to 4 bars (factor of four) there is no significant change in byproducts. Thus, if system operates at low temperature then pressure should be as high as possible.

In summary, these results for the conversion of propylene glycol to acetol indicate that the favored reaction operating conditions are higher pressures and lower temperatures. Table 4-4 presents the data plotted in Figure 4.6.

Table 4-4 lists the byproducts values to each system pressure of the propylene glycol to acetol reaction. Table 4-4 indicates that increasing the pressure of reaction produces less byproducts.

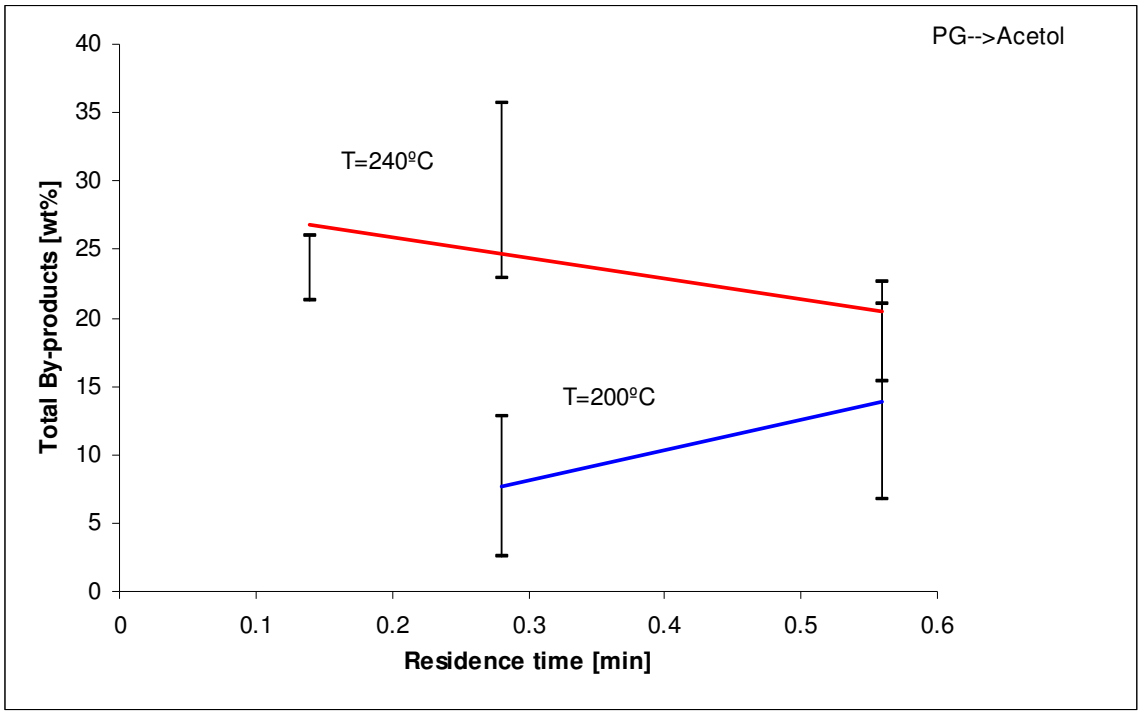

Figure 4.7. Byproducts of propylene glycol conversion to acetol: effect of residence time.

Figure 4.7 presents the effect of residence time in by products of the propylene glycol to acetol reaction at 180ºC, 200ºC, 220ºC and 240ºC. This figure indicates that at lower temperatures with an increase in residence time more total byproducts can be formed. The trends in data at 240ºC are anomalous

and are expected to be due to experimental error—further investigation is required.

An explanation of this difference in trends at different temperatures can be the impact of pressure of the system in the reaction. The impact of pressure at the same temperature can be the cause to this discrepancy in trends.

The effect of residence time on byproducts data plotted in Figure 4.7 are tabulated in Table 4-5. Table 4-5 lists the values of total byproducts and residence time of the propylene glycol to acetol reaction.

Table 4-5 presents the effect of residence time on by products of the propylene glycol to acetol reaction as function of temperature and pressure.

Table 4-5 Effect of the residence time on byproducts of the propylene glycol to acetol reaction.

Reactor Temperature [ºC]	Pressure of Discharge [bar]	Hydrogen flowrate [L/min]	Hydrogen flowrate[(ft^3)/min]	Reactor Volume [ft^3]	Residence time [min]	Total Byproducts [wt%]
177	2	5.0	0.2	0.05	0.28	3.13
178	2	5.0	0.2	0.05	0.28	5.11
184	2	5.0	0.2	0.05	0.28	4.02
181	2	5.0	0.2	0.05	0.28	4.53
182	2	5.0	0.2	0.05	0.28	3.99
183	2	5.0	0.2	0.05	0.28	3.35
203	1	2.5	0.1	0.05	0.56	18.94
202	1	5.0	0.2	0.05	0.28	10.41
207	2	5.0	0.2	0.05	0.28	10.84
204	4	2.5	0.1	0.05	0.56	8.79
197	4	5.0	0.2	0.05	0.28	1.82
220	2	5.0	0.2	0.05	0.28	16.62
216	2	5.0	0.2	0.05	0.28	18.99
239	1	2.5	0.1	0.05	0.56	21.51
237	1	5.0	0.2	0.05	0.28	27.84
237	2	5.0	0.2	0.05	0.28	25.22
240	2	5.0	0.2	0.05	0.28	27.74
242	2	5.0	0.2	0.05	0.28	35.03
242	4	5.0	0.2	0.05	0.28	30.03
242	4	5.0	0.2	0.05	0.28	19.7
241	4	5.0	0.2	0.05	0.28	39.39
240	4	10.0	0.4	0.05	0.14	21.98
240	4	10.0	0.4	0.05	0.14	25.35
239	4	2.5	0.1	0.05	0.56	16.43

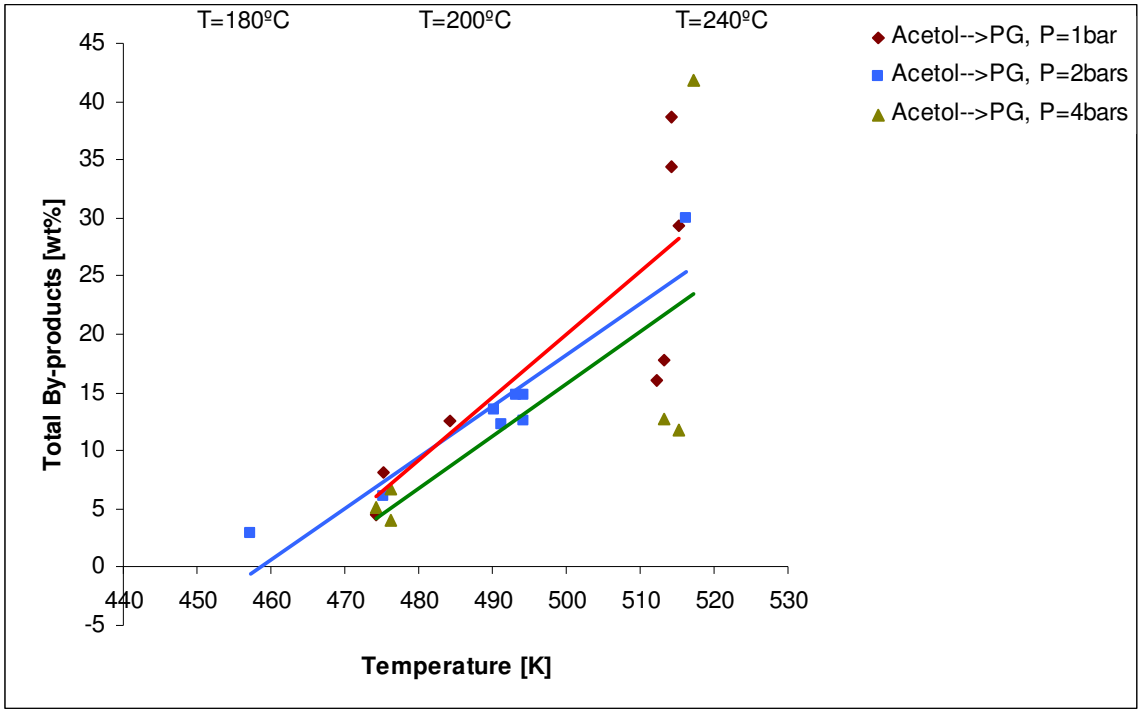

Figure 4.8. Byproducts of acetol conversion to propylene glycol: effect of temperature.

4.4 Reaction of Acetol to Propylene Glycol

Figure 4.8 presents the effect of temperature on byproducts of the acetol to propylene glycol reaction at three different pressures (1, 2, and 4 bars). This figure indicates that with an increase in temperature more byproducts are present in the product. This figure also shows that fewer byproducts are produced with an increase in pressure at a given temperature.

Figure 4.8 demonstrates that for this reaction at lower temperatures the byproducts have less dependence of the system pressure. By contrast, at higher temperatures there is notable the pressure dependence of byproducts.

In summary, these results for the conversion of acetol to propylene glycol indicate that the preferred reaction operating conditions are higher pressure and lower temperature. This result is similar to the conversion of glycerol to propylene glycol reaction and propylene glycol to acetol reaction as presented in Figure 4.1 and 4.5. The values plotted in Figure 4.8 are tabulated in Table 4-6.

Table 4-6 lists the byproducts of the acetol to propylene glycol reaction at different temperatures and pressures. Table 4-6 indicates that at higher pressures fewer byproducts are formed in the reaction.

Table 4-6 Effect temperature and pressure on byproducts of the acetol to propylene glycol reaction.

Reactor Temperature [ºC]	Pressure of Discharge [bar]	Reactor Temperature [K]	Total Byproducts [wt%]
202	1	475	8.12
211	1	484	12.63
241	1	514	34.39
241	1	514	38.74
201	1	474	4.48
240	1	513	17.74
242	1	515	29.39
239	1	512	16.08
184	2	457	2.94
202	2	475	6.11
217	2	490	13.58
220	2	493	14.83
221	2	494	12.56
218	2	491	12.27
221	2	494	14.79
243	2	516	29.96
201	4	474	5.2
203	4	476	4.04
244	4	517	41.81
203	4	476	6.63
242	4	515	11.84
240	4	513	12.77

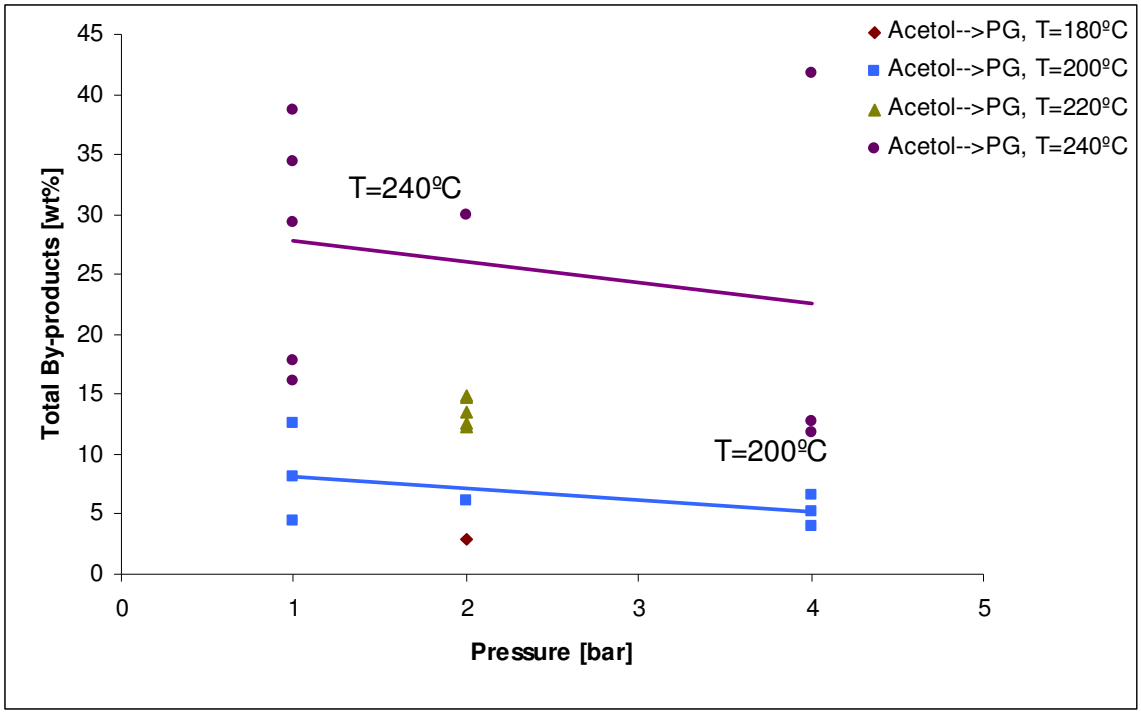

Figure 4.9. Byproducts of acetol conversion to propylene glycol: effect of pressure.

The effect of pressure (1, 2, and 4 bars) in byproducts of the acetol to propylene glycol reaction at 180º C, 200ºC, 220ºC, and 240ºC was evaluated in Figure 4.9. Similar to Figure 4.6, with an increase in pressure, less byproducts are formed at a given temperature. This figure also shows that with an increase in temperature more byproducts can be produced.

The results in Figure 4.9 for the conversion of propylene glycol to acetol show that fewer byproducts are present in the product formation at lower temperature and higher pressure. This result is consistent with Figure 4.9. The data presented in Figure 4.9 is tabulated in Table 4-6.

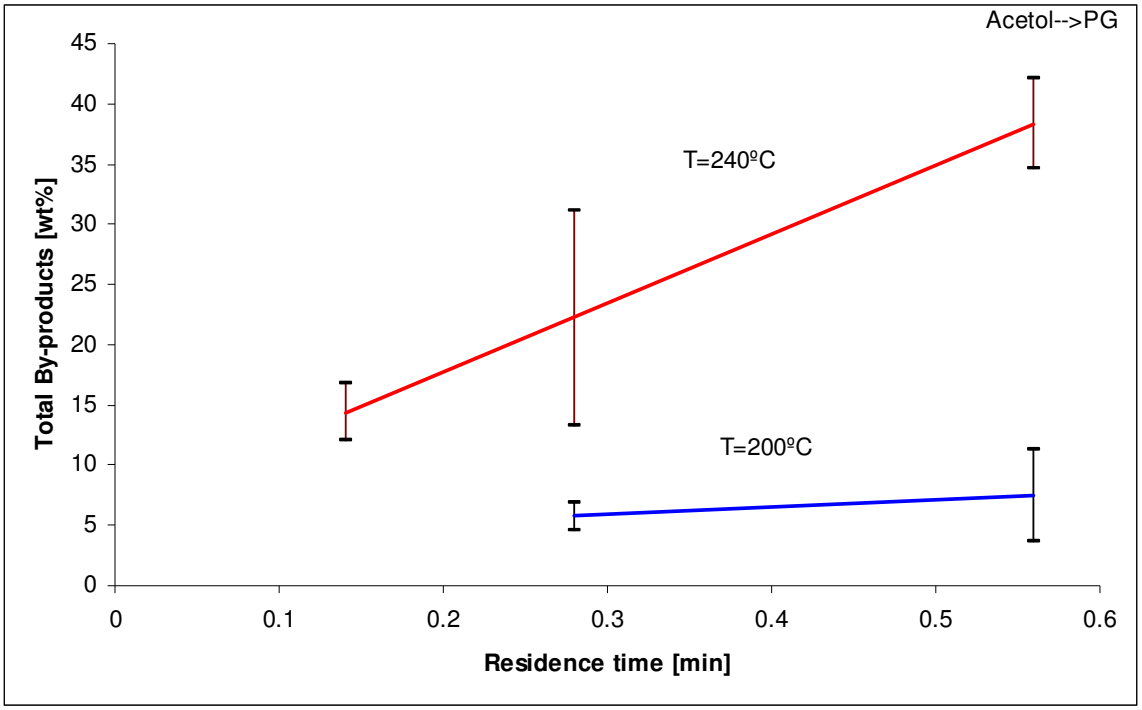

Figure 4.10. Byproducts of acetol conversion to propylene glycol: effect of residence time.

Data of Table 4-6 indicates that at higher pressure fewer byproducts are present in the acetol to propylene glycol reaction. A lower value of 4 percent of byproducts can be obtained at 4 bars and 200ºC.

The effect of residence time on the acetol to propylene glycol reaction at two different temperatures is presented in Figure 4.10. This figure indicates that with an increment of resident time, more byproducts can be obtained. This effect was repeated at each of the two temperatures.

Figure 4.10 also indicates that at lower temperatures the change in byproducts is insignificant but at higher temperatures the change in total byproducts increases twice. In summary, these results of the acetol to propylene

glycol reaction indicates that lower temperatures and less residence time are the preferred operating conditions to reduce the total byproducts in the reaction.

Table 4-7 lists the residence time and total by product of each experimental run as function of temperature and pressure. Table 4-7 indicates that with an increment of residence time more total byproducts can be produced.

Table 4-7 Effect of the residence time on byproducts of the acetol to propylene glycol reaction.

Reactor Temperature [ºC]	Pressure of Discharge [bar]	Hydrogen flowrate [L/min]	Hydrogen flowrate [(ft^3)/min]	Reactor Volume [ft^3]	Residence time [min]	Total Byproducts [wt%]
184	2	5.0	0.18	0.05	0.28	2.94
202	1	2.5	0.09	0.05	0.56	8.12
201	1	5.0	0.18	0.05	0.28	4.48
202	2	5.0	0.18	0.05	0.28	6.11
201	4	2.5	0.09	0.05	0.56	5.20
203	4	2.5	0.09	0.05	0.56	4.04
203	4	5.0	0.18	0.05	0.28	6.63
211	1	2.5	0.09	0.05	0.56	12.63
217	2	5.0	0.18	0.05	0.28	13.58
220	2	5.0	0.18	0.05	0.28	14.83
221	2	5.0	0.18	0.05	0.28	12.56
218	2	5.0	0.18	0.05	0.28	12.27
221	2	5.0	0.18	0.05	0.28	14.79
241	1	2.5	0.09	0.05	0.56	34.39
241	1	2.5	0.09	0.05	0.56	38.74
240	1	5.0	0.18	0.05	0.28	17.74
242	1	5.0	0.18	0.05	0.28	29.39
239	1	10.0	0.35	0.05	0.14	16.08
243	2	5.0	0.18	0.05	0.28	29.96
244	4	2.5	0.09	0.05	0.56	41.81
242	4	5.0	0.18	0.05	0.28	11.84
240	4	10.0	0.35	0.05	0.14	12.77

CHAPTER 5

5. CATALYST PRODUCTIVITY

Traditional practices of hydrogenating carbonyl groups to form alcohols along with the common practice of hydrogenating ester groups in fats and oils to form fatty alcohols indicate that the alcohols groups are stable and do not readily react at normal hydrogenating conditions[16].

Copper is potentially a good catalyst for alcohol hydrogenation. It is known for its poor hydrogenolytic activity towards C-C bond and an efficient catalyst for C-O bond hydro-dehydrogenation[7]. Copper-chromite catalyst was used in this research for the hydrogenolysis of all reactions.

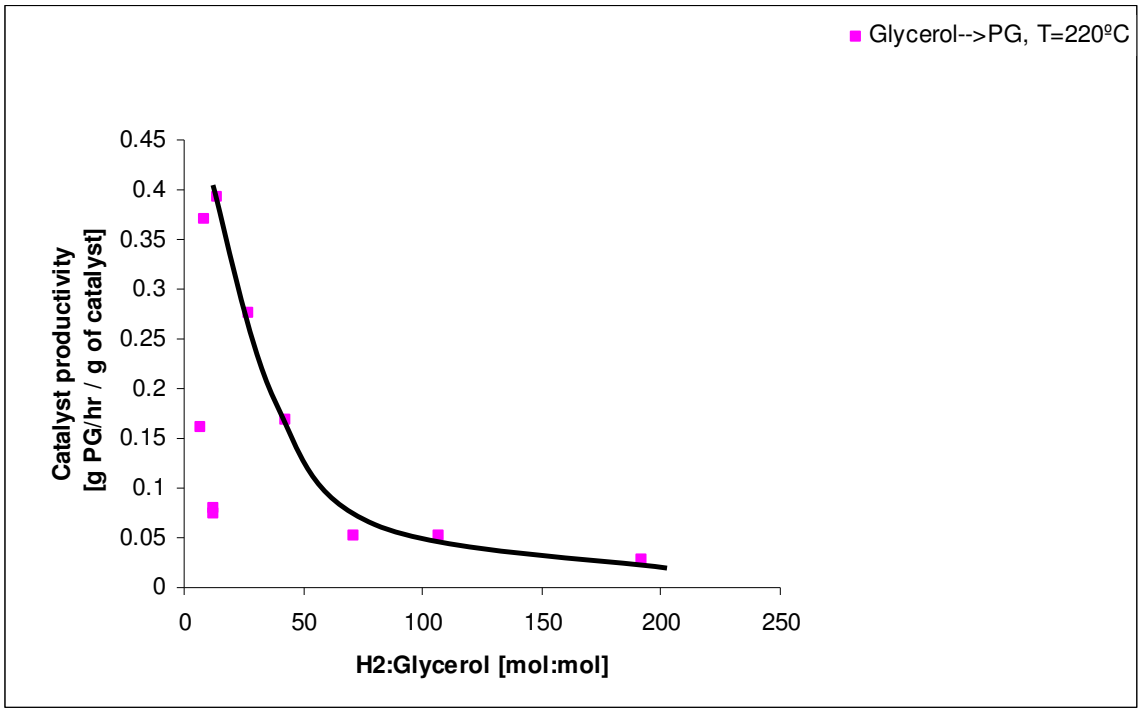

Figure 5.1. Glycerol to propylene glycol reaction: effect of H_2: Glycerol mole ratio on catalyst productivity at 220ºC.

5.1 Reaction of Glycerol to Propylene Glycol

The effect of H_2: Glycerol mole ratio on catalyst productivity of the glycerol to propylene glycol at 220ºC was evaluated and presented in Figure 5.1. The units or productivity are grams of propylene glycol produced per hour per gram of catalyst in the packed bed.

Figure 5.1 indicates that the catalyst productivity increases with a decrease in H_2: Glycerol mole ratio. Figure 5.1 demonstrates that large amount of glycerol increase the catalyst productivity. In contrast, smaller amounts of glycerol the catalyst activity decreases and less propylene glycol can be produced.

Figure 5.1 shows that at a value of 50 of H_2: Glycerol mole ratio the production of propylene glycol start to increase. At 220ºC, this reaction needs to operate with large amounts of glycerol without exceeding the solubility limits of glycerol in hydrogen.

Table 5-1 lists the catalyst productivity to each experimental run of the glycerol to propylene glycol reaction.

A possible explanation of the trends in the data of Figure 5.1 consists of two components. First, at high ratios of hydrogen to glycerol, the hydrogen simply pushes the glycerol through the reactor before it is able to react—the glycerol residence time is too low. At low ratios of hydrogen to glycerol, the propylene glycol can degrade due to residence times that are too low. An optimal ratio is near 15:1.

Table 5-1 Effect of H_2: Glycerol mole ratio on catalyst productivity for the glycerol to propylene glycol reaction.

Reactor Temperature [ºC]	Pressure of Discharge [bar]	Hydrogen flowrate [L/min]	Glycerin flow rate [g/hr]	H2:Glyc [mol:mol]	Product flow rate [g/hr]	PG [wt%]	Catalyst Productivity [g PG / g cat]
220	1	16.7	500.0	8.83	473.88	50.84	0.37
220	1	22.1	90.0	70.98	70.20	47.29	0.05
220	2	36.2	226.2	42.26	195.43	56.31	0.17
220	2	24.7	90.0	192.17	28.74	63.71	0.03
220	2	24.7	90.0	106.82	51.92	65.75	0.05
221	2	5.0	201.6	7.02	185.00	56.51	0.16
220	2	5.0	127.2	12.14	99.96	51.20	0.08
221	2	5.0	127.2	12.40	97.68	49.38	0.07
220	4	29.9	226.2	26.72	258.84	69.47	0.28
220	4	22.1	500.0	13.70	386.76	65.83	0.39
238	1	2.5	99.5	8.78	71.56	27.31	0.03
241	1	2.5	99.5	6.58	99.90	27.73	0.04
240	1	5.0	198.0	6.83	191.23	31.35	0.09
237	2	5.0	198.0	9.91	125.00	35.53	0.07
236	2	5.0	198.0	9.79	126.80	40.56	0.08
240	2	5.0	198.0	7.52	170.80	31.80	0.08
240	4	5.0	198.0	12.70	95.23	30.91	0.05
240	4	10.0	390.6	7.63	336.24	51.36	0.27

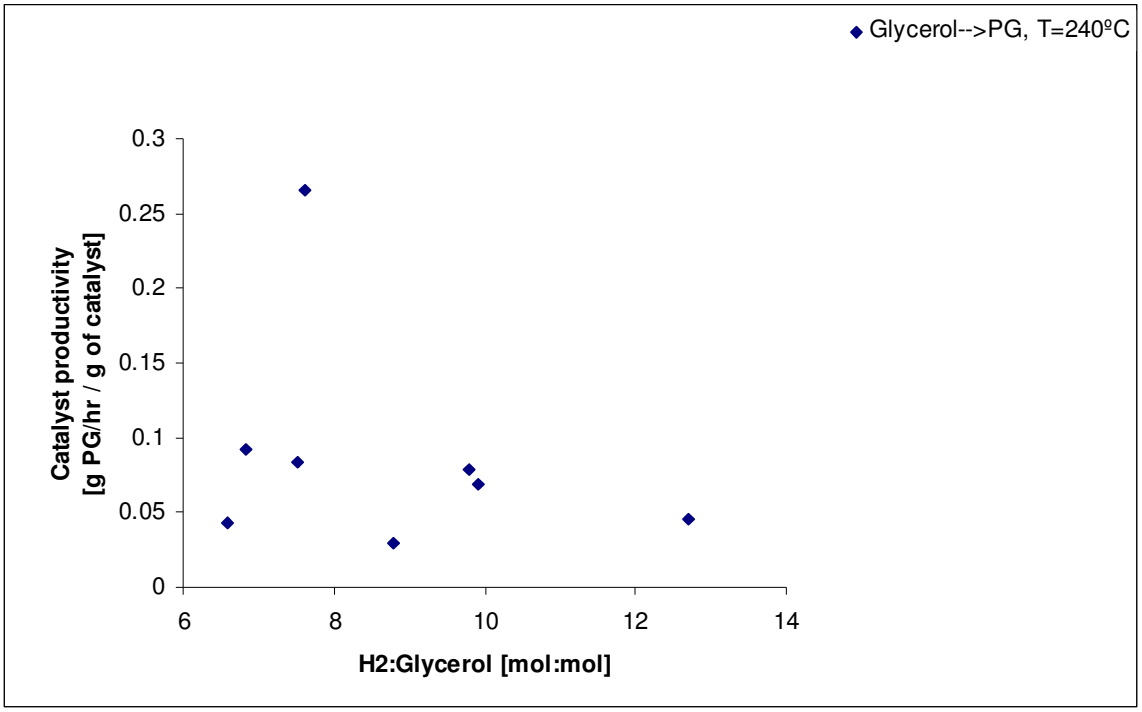

Figure 5.2. Glycerol to propylene glycol reaction: effect of H_2: Glycerol mole ratio on catalyst productivity at 240ºC.

Figure 5.2 presents the effect of H_2: Glycerol mole ratio on catalyst productivity of the glycerol to propylene glycol at 240ºC. In contrast to Figure 5.1, this figure indicates that at 240ºC lower values of catalyst productivity were obtained at different values of H_2: Glycerol mole ratio.

Comparing Figure 5.1 and 5.2 can be observed that lower temperatures are the preferred operated conditions to increase the catalyst productivity. For the data of Figure 5.2, the degradation reaction biases results (and perhaps non-optimal residence times) and makes it difficult to determine the best ratio for producing propylene glycol.

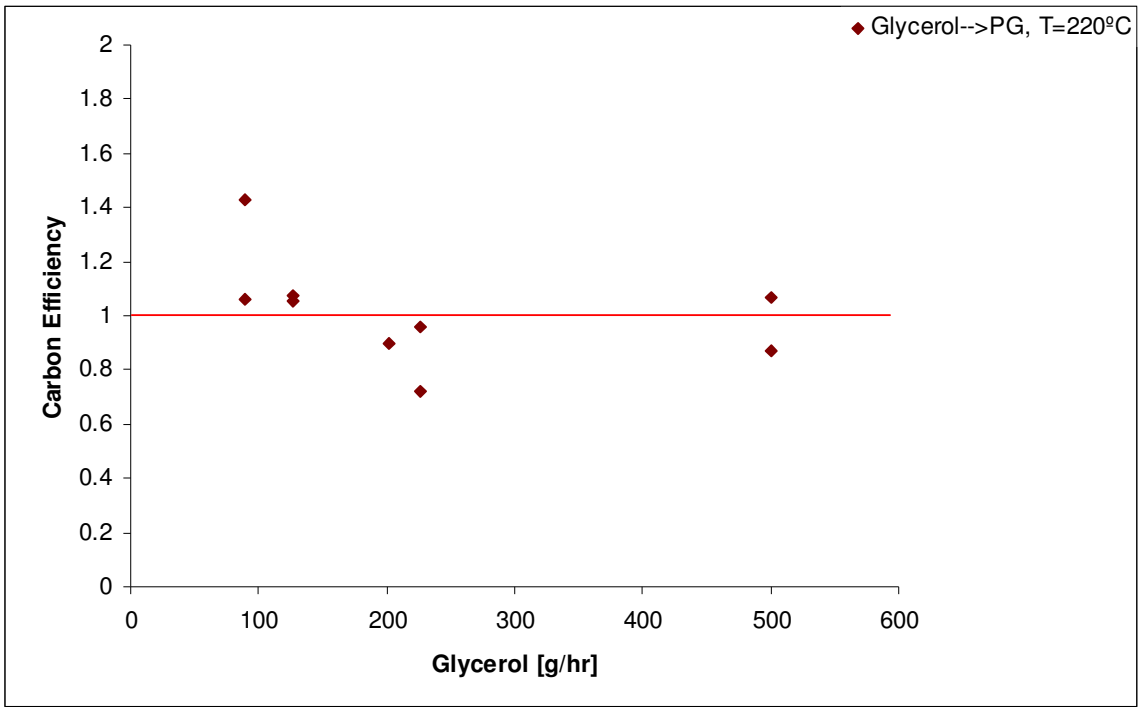

Figure 5.3. Carbon efficiency versus glycerol flow rate of the glycerol to pPropylene glycol reaction at temperature of 220ºC.

Figure 5.3 presents the carbon efficiency as a function of glycerol flow rate of the glycerol to propylene glycol reaction. Carbon efficiency is defined as the percentage of carbon in the reactants that remain in the final product.

This figure indicates that at 220ºC, the reaction was moving forward and the conversion of reactants to the products was close to 100 percent.

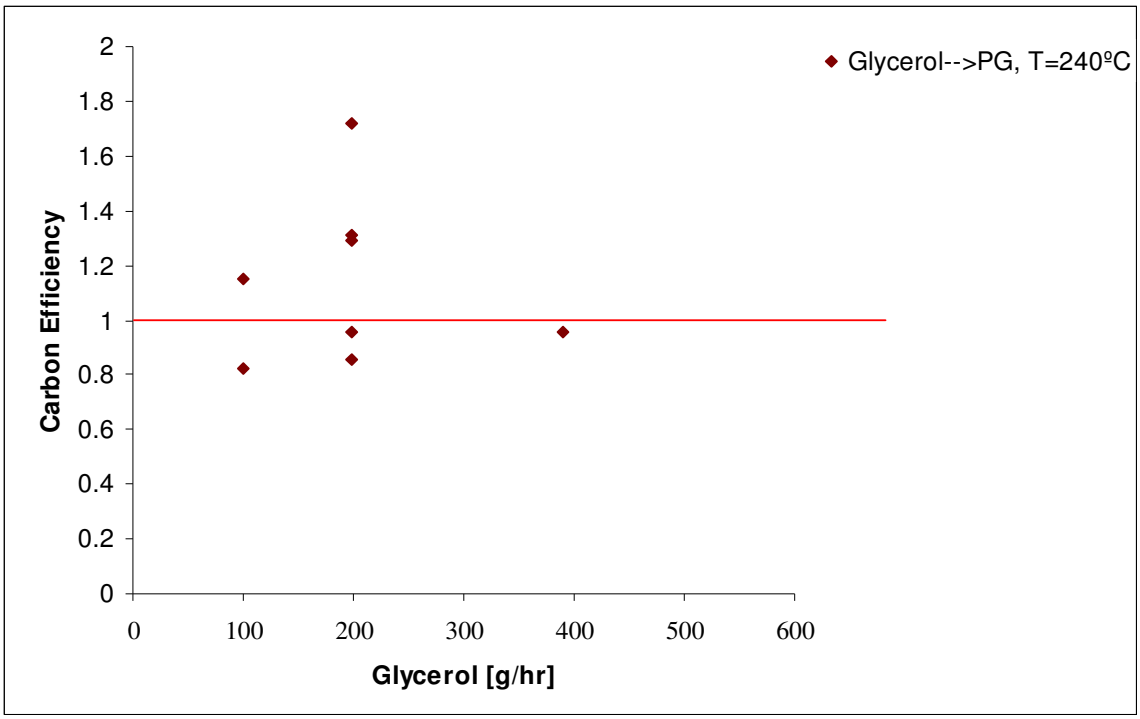

Figure 5.4. Carbon efficiency versus glycerol flow rate of the glycerol to propylene glycol reaction at temperature of 240ºC.

Figure 5.4 present the carbon efficiency as a function of glycerol flow rate of the glycerol to propylene glycol reaction. This figure indicates that at 240ºC exist a lower conversion of reactants to products.

Comparing with Figure 5.3, lower temperatures help the total conversion of reactant to products.

Values of carbon efficiency greater than 1.0 could be due to sampling errors due to inadequate condensation of water.

Table 5-2 Carbon efficiency values of the glycerol to propylene glycol reaction.

Reactor Temperature [ºC]	Glycerin flow rate [g/hr]	Product flow rate[g/hr]	Carbon Efficiency
220	500	473.88	0.87
220	90	70.2	1.06
238	99.5	71.56	1.15
241	99.5	99.9	0.82
240	198	191.23	0.86
220	226.2	195.43	0.96
220	90	28.74	2.59
220	90	51.92	1.43
221	201.6	185	0.90
220	127.2	99.96	1.05
221	127.2	97.68	1.08
237	198	125	1.31
236	198	126.8	1.29
240	198	170.8	0.96
220	226.2	258.84	0.72
220	500	386.76	1.07
240	198	95.23	1.72
240	390.6	336.24	0.96

CHAPTER 6

6. CONCLUSIONS

On the bases of the experimental tests, the following conclusions are made with respect to the effect of operating conditions on propylene glycol formation from glycerol.

6.1 Effect of Reaction Temperature

Temperature has a significant effect on the overall yield of propylene glycol. Reactions were carried out at 180, 200, 220, and 240ºC and at a system pressure of 1, 2, and 4 bars in the presence of a copper-chromite catalyst.

6.1.1 Reaction of Glycerol to Propylene Glycol

The results of the effect of temperature for the glycerol to propylene glycol indicate that as the temperature of the reaction decreases from 240 to 220ºC there is an increase in conversion of glycerol to propylene glycol.

The results of the effect of temperature on byproducts indicate that at lower temperatures (220ºC) the weight percent of byproducts decrease.

6.1.2 Reaction of Propylene glycol to Acetol

The results of the effect of temperature for the propylene glycol to acetol reaction indicate that as the temperature of the reaction decreases from 240 to

180ºC more propylene glycol can be produced.

The results of the effect of temperature on byproducts indicate that at lower temperatures (180ºC) the weight percent of byproducts decrease.

6.1.3 Reaction of Acetol to Propylene Glycol

The results of the effect of temperature for the acetol to propylene glycol reaction indicate that as the temperature of the reaction decrease from 240 to 180ºC the conversion of acetol to propylene glycol increase.

The results of the effect of temperature on byproducts indicate that at lower temperatures (180ºC) the weight percent of byproducts decrease.

6.2 Effect of System Pressure

6.2.1. Reaction of Glycerol to Propylene Glycol

The results of the effect of system pressure on the glycerol to propylene glycol reaction indicate that at higher pressures (4 bars) the conversion of propylene glycol from glycerol increases.

The results of the effect of pressure on byproducts indicate that at higher pressures (4 bars) fewer byproducts are formed in the reaction.

6.2.2. Reaction of Propylene Glycol to Acetol

The results of the effect of system pressure of the propylene glycol to acetol reaction indicate that at higher pressures (4 bars) the conversion of acetol from propylene glycol decreases.

The results of the effect of pressure on byproducts indicate that at higher pressures (4 bars) fewer byproducts are formed in the reaction.

6.2.3. Reaction of Acetol to Propylene Glycol

The results of the effect of system pressure of the acetol to propylene glycol reaction indicate that at higher pressures (4 bars) the conversion of acetol to propylene glycol increases.

The results of the effect of pressure on byproducts indicate that at higher pressures (4 bars) fewer byproducts are formed in the reaction.

6.3 Effect of Residence Time

6.3.1. Reaction of Glycerol to Propylene Glycol

The results of the effect of residence time at different temperatures (220ºC and 240ºC) of the glycerol to propylene glycol reaction indicate that increasing the residence time forms more byproducts. At lower temperature, the formation of byproducts decreases.

6.3.2. Reaction of Propylene Glycol to Acetol

The results of the effect of the residence time on byproducts at different temperatures (180ºC, 200ºC, 220ºC and 240ºC) of the propylene glycol to acetol reaction indicates that at lower temperatures increasing the residence time forms more byproducts. In contrast, with an increment in temperature the total byproducts decrease with an increase in residence time. The impact of pressure

of the system in the reaction can be the cause of this difference in trends.

6.3.3. Reaction of Acetol to Propylene Glycol

The results of the effect of the residence time on byproducts at different temperatures indicate that increasing the residence time forms more byproducts.

6.4. Effect of H_2: Glycerol Mole Ratio

The results for the effect of H_2: Glycerol Mole Ratio on catalyst productivity of the glycerol to propylene glycol reaction at different temperatures (220ºC and 240ºC) indicates that 220ºC is the preferred temperature to produce more propylene glycol. It can be inferred that near-optimal conditions are near the solubility limit of glycerol in hydrogen without exceeding that limit.

At 240ºC, the results for the catalyst productivity at different H_2: Glycerol Mole Ratio was lower than the results obtained at 220ºC. These results may be indicative of a non-optimal residence time. At higher temperatures, optimal conditions are more strongly dependent on operating at the best possible residence time.

The research emphasis of this project was fulfilled. Results indicate that temperature, pressure, residence time, H_2: Glycerol mole ratio and water content have a significant impact in the reaction and consequently in the propylene glycol production. All results indicate that lower temperatures and higher pressures promote the selectivity on conversion of glycerol to propylene glycol.

The results are also fully consistent with a two-step reaction in which the

second step of conversion of acetol to propylene glycol is equilibrium limited. This equilibrium has an exothermic heat of reaction, and so, lower temperatures lead to more-favorable conversions.

6.5. Effect of Water Content

6.5.1. Reaction of Glycerol to Propylene Glycol

The results of the effect of water content of the glycerol to propylene glycol reaction indicate that product quality correlates with lower water content. Another way of stating this is that water is at typical byproduct of reactions forming byproducts.

6.6 Carbon Efficiency

6.6.1 Reaction of Glycerol to Propylene Glycol

The results of the carbon efficiency of the glycerol to propylene glycol reaction indicates that at lower temperatures (220ºC) a better efficiency can be obtained compared with higher temperatures (240ºC) where results indicate that the glycerol can be degraded.

6.7 Recommendations

In this research is demonstrated that at a 4 bars of pressure the amount of byproducts can decrease to a 4%. Further studies could use higher pressures to possibly further decrease by-product formation.

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APPENDIX

A. ADITIONAL GRAPHS AND TABLES

B. SAMPLE CALCULATIONS

C. EQUIPMENT PHOTOGRAPHS

D. PHYSICAL AND CHEMICAL PROPERTIES, MSDS

i. 1,2-Propanediol (Propylene Glycol, PG)

ii. Hydroxyacetone (Acetol)

iii. Glycerol

APPENDIX A

ADDITIONAL GRAPHS AND TABLES

A.1 Reaction of Glycerol to Propylene Glycol

Table A. 1 Low, Medium, and High Volatile Byproducts Values as a Function of Reaction Temperature of the Glycerol to Propylene Glycol Reaction.

Reactor Temperature [°C]	Byproducts before solvent [wt%]	Byproducts between PG and solvent [wt%]	Byproducts after PG [wt%]
220	1.56	0	2.71
220	1.21	1.89	3.19
220	2.44	0	2.1
220	8.46	3.38	3.66
220	0	0	1.58
220	2.33	0	2.65
220	2.04	0.38	2.95
221	4.05	2.12	5.19
220	9.98	2.67	6
221	8.53	2.45	5.48
238	20.32	12.86	12.11
241	14.37	14.41	13.28
240	8.12	7.57	5.62
237	11.69	3.83	6.8
236	10.2	3.75	8.06
240	16.34	5.08	7.61
240	33.33	3.7	5.83
240	10.29	1.92	5.38

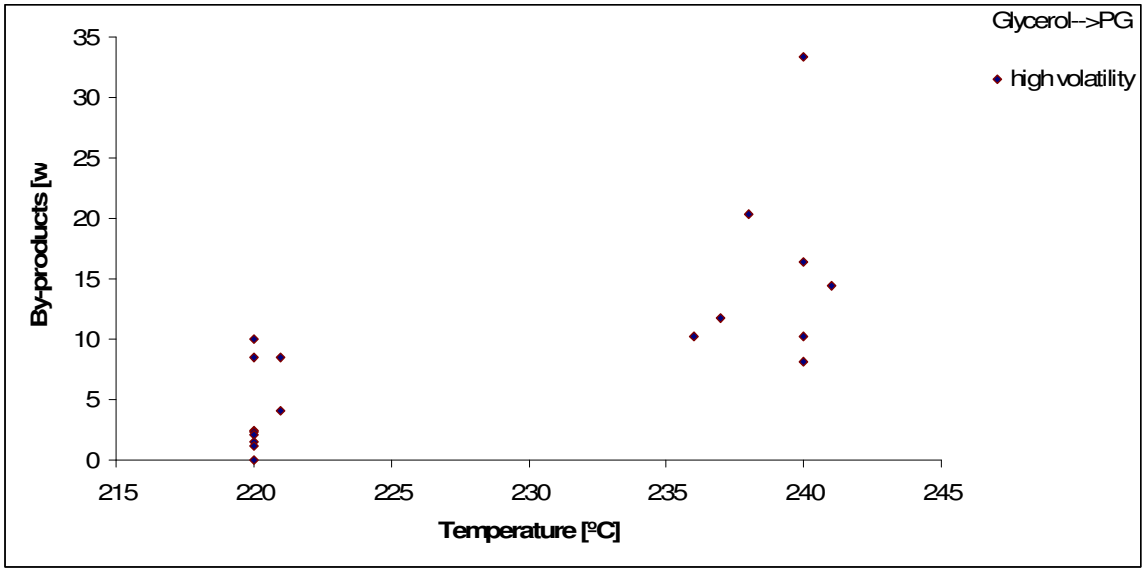

Figure A. 1. Effect of Reaction Temperature on High Volatile Byproducts of the Glycerol to Propylene Glycol Reaction.

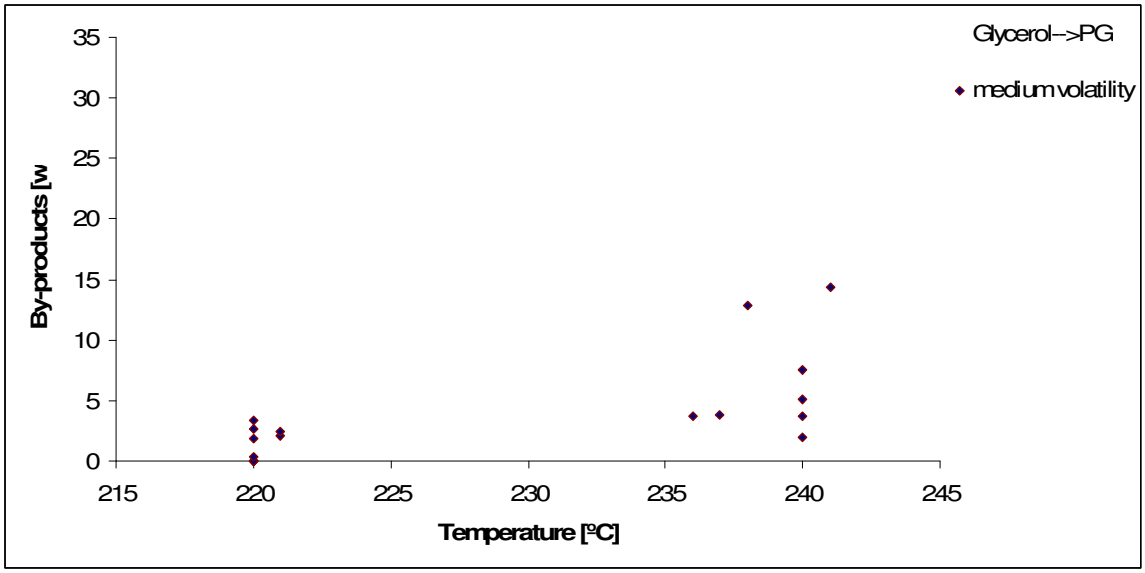

Figure A. 2. Effect of Reaction Temperature on Medium Volatile Byproducts of the Glycerol to Propylene Glycol Reaction.

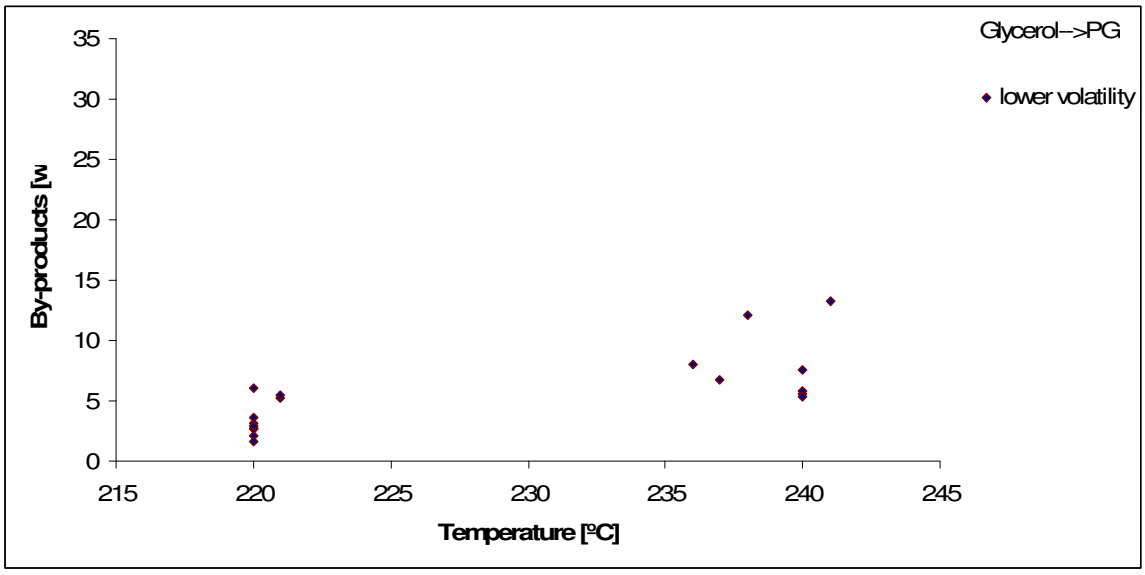

Figure A. 3. Effect of Reaction Temperature on Low Volatile Byproducts of the Glycerol to Propylene Glycol Reaction.

A.2 Reaction of Acetol to Propylene Glycol

Table A. 2 Low, Medium, and High Volatile Byproducts Values as a Function of Reaction Temperature of the Acetol to Propylene Glycol Reaction.

Reactor Temperature [°C]	Byproducts before solvent [wt%]	Byproducts between PG and solvent [wt%]	Byproducts after PG [wt%]
184	0	1.8	1.14
202	3.22	4.9	0
202	1.2	3.28	1.63
201	0	2.61	1.87
203	0	2.01	2.03
201	0	2.85	2.35
203	1.72	2.27	2.64
211	4.45	5.06	3.12
217	5.89	4.05	3.64
220	4.03	8.14	2.66
221	4.45	4.86	3.25
218	4.48	3.87	3.92
221	6.31	4.21	4.27
243	9.96	14.03	5.97
240	5.78	8.88	3.08
242	11.51	13.1	4.78
241	18.58	10.03	5.78
241	19.99	12.17	6.58
239	5.45	7.63	3
242	0	4.59	7.25
240	6.15	3.62	3
244	22.43	14.56	4.82

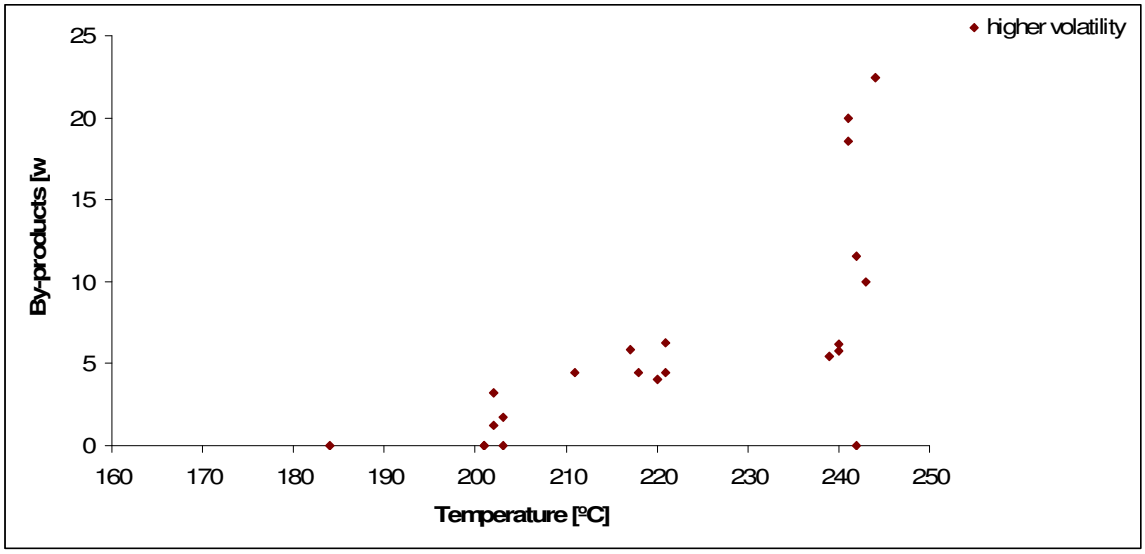

Figure A. 4. Effect of Reaction Temperature on High Volatile Byproducts of the Acetol to Propylene Glycol Reaction

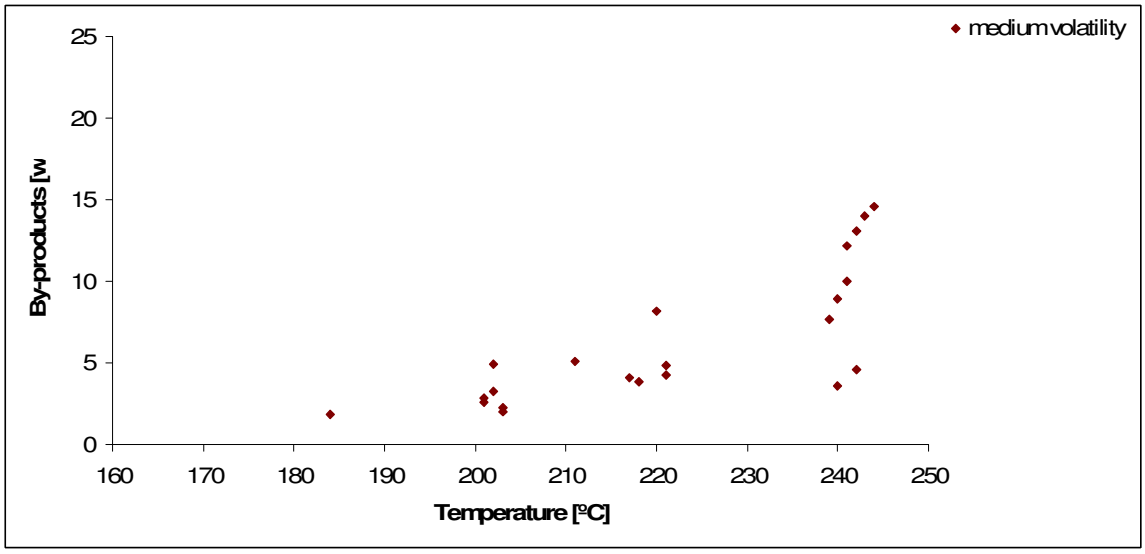

Figure A. 5. Effect of Reaction Temperature on Medium Volatile Byproducts of the Acetol to Propylene Glycol Reaction

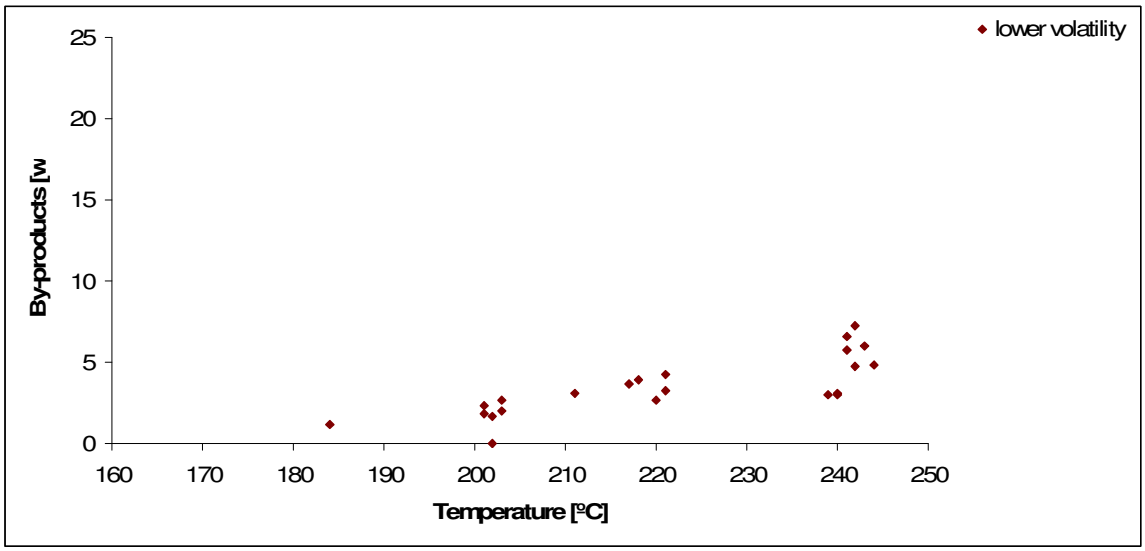

Figure A. 6. Effect of Reaction Temperature on Low Volatile Byproducts of the Acetol to Propylene Glycol Reaction

A.3 Reaction of Propylene Glycol to Acetol

Table A. 3 Low, Medium, and High Volatile Byproducts values as a function of temperature of the Propylene Glycol to Acetol Reaction.

Reactor Temperature [°C]	Byproducts before solvent [wt%]	Byproducts between PG and solvent [wt%]	Byproducts after PG [wt%]
177	0	0	3.13
178	1.37	0.69	3.05
184	0.83	0.61	2.58
181	0.83	0.72	2.98
182	0.71	0.6	2.68
183	0.65	0.49	2.21
207	4.04	2.18	4.62
203	6.51	6.17	6.26
202	2.7	2.67	5.04
204	4.8	0.3	3.69
197	0	0	1.82
220	6.47	3.5	6.65
216	9.1	3.49	6.4
237	11.85	8.98	7.01
237	10.3	8.27	6.65
240	17.47	4.74	5.53
242	19.84	7.22	7.97
239	10.35	5.2	5.96
242	13.83	7.24	8.96
242	5.39	5.46	8.85
241	26.31	5.21	7.87
240	14.95	3.52	3.51
240	16.68	3.98	4.69
239	7.02	3.19	6.22

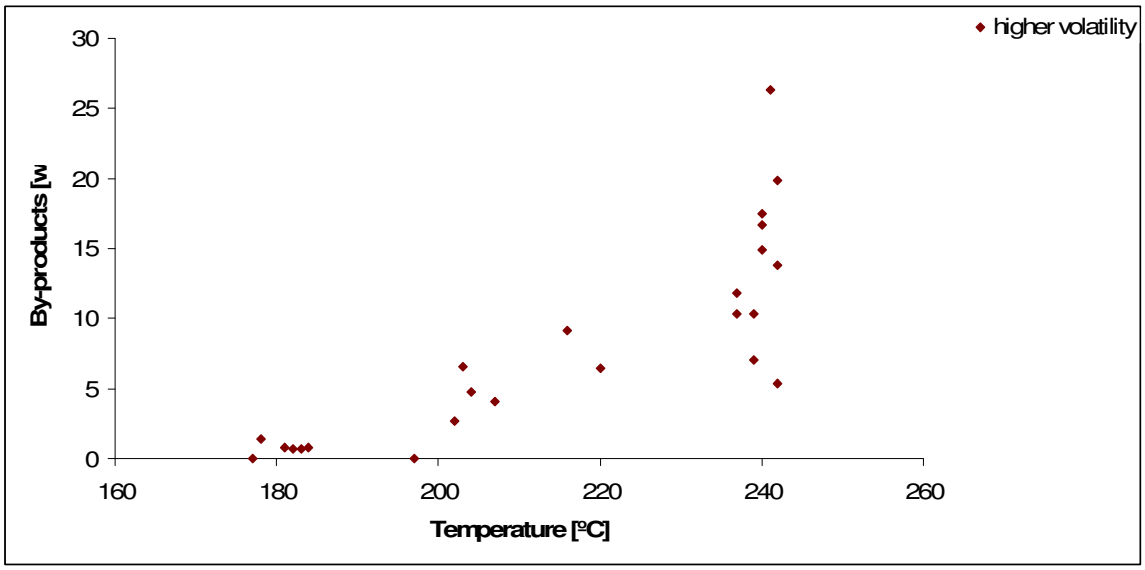

Figure A. 7. Effect of Reaction Temperature on High Volatile Byproducts of the Propylene Glycol to Acetol Reaction.

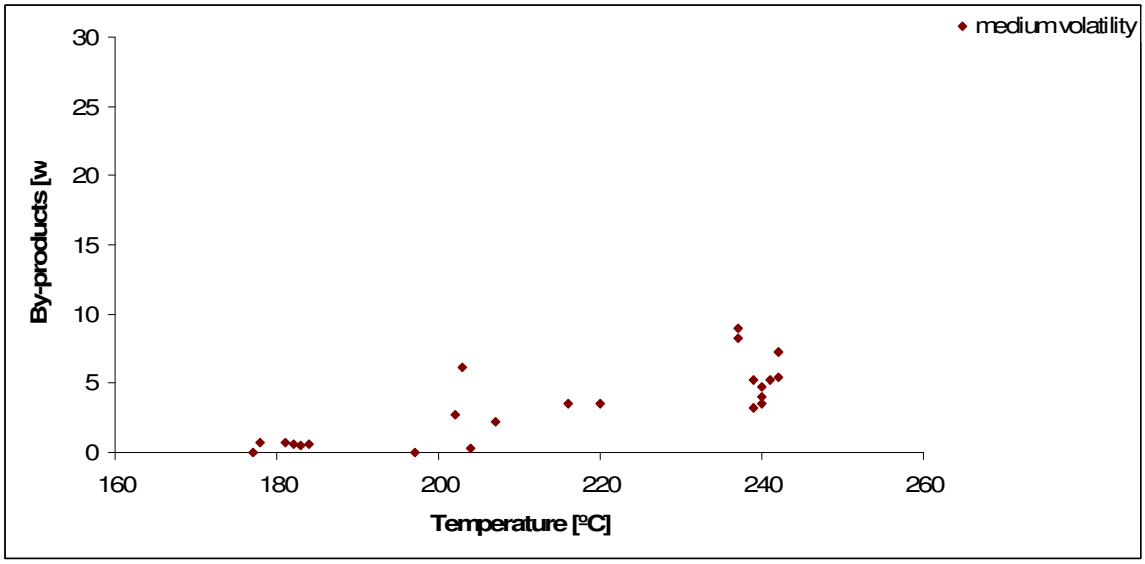

Figure A. 8. Effect of Reaction Temperature on Medium Volatile Byproducts of the Propylene Glycol to Acetol Reaction.

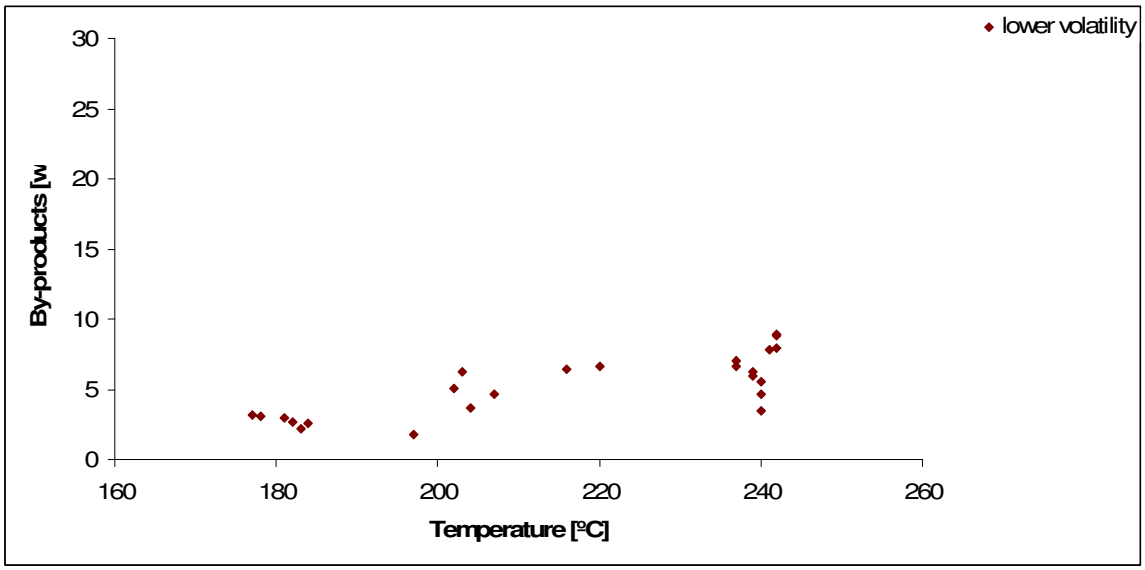

Figure A. 9. Effect of Reaction Temperature on Low Volatile Byproducts of the Propylene Glycol to Acetol Reaction.

APPENDIX B

SAMPLE CALCULATIONS

EQUILIBRIUM CONSTANT CALCULATION

The equilibrium constants shown in Tables 3-4 and 3-5 were calculated using the partial vapor pressure of the components in the reaction.

The equilibrium constant used was,

$$K = \frac{[P_V\ products]}{[P_V\ reac\tan ts]} * P_{TOTAL}$$

Where P_v, is the partial vapor pressure, and P_{TOTAL} is the total pressure of the system. For a mixture,

$$P_V = y * (P_{TOTAL})$$

Assuming total condensation of vapor to sample y was calculated on basis of sample weights.

Example:

If the total pressure of the system is 2 bars, and the composition in the mixture is

	Molecular weight [g/mol]
acetol (wt%) = 8.56%	74g/mol
propylene glycol (wt%)= 57.30%	76g/mol
water (wt%) = 30.28%	18g/mol

others = 3.89% (neglected for calculation)

Then, taking a basis of 100 grams of sample

$$y_{acetol} = \frac{8.56/74}{\left(\left(\frac{8.56}{74}\right)+\left(\frac{57.3}{76}\right)+\left(\frac{30.28}{18}\right)\right)} = 0.05$$

$$y_{PG} = \frac{57.3/76}{\left(\left(\frac{8.56}{74}\right)+\left(\frac{57.3}{76}\right)+\left(\frac{30.28}{18}\right)\right)} = 0.30$$

$$y_{H_2} = 0.86$$

$$K = \frac{[0.30]}{((0.05)(0.86))} * 2 = 3.79$$

GIBBS FREE ENERGY CALCULATION

The Gibbs free energy values shown in Tables 3-4 and 3-5 were calculated using the following equation:

$$\Delta G = -RT * LN(K)$$

Where R is the universal gas constant in J/mol, T is the temperature of reaction in Kelvin, and K is the equilibrium constant of the reaction.

Example:

Using the following values of R and T and using the previous result for K=3.79

$$R = \frac{8.3144J}{molK}$$

$$T = 457K$$

Substituting into the Gibbs free energy equation

$$\Delta G = -5059.54\frac{J}{mol}$$

REACTOR VOLUME CALCULATION

The volume of the reactor shown in Tables 4-2, 4-5, and 4-7 were calculated using the following equation

$$V_R = \frac{\pi}{4} D^2 h$$

Where V_R is the volume of the reactor, D is is the diameter of a cylinder and *h* is the height of the cylinder.

Example:

If the diameter of the reactor *D* is equal to 0.062 ft and the height *h* is equal to 16 ft then, the volume of the reactor is

$$V_R = 0.05 ft^3$$

RESIDENCE TIME CALCULATION

The residence time values shown in Tables 4-2, 4-5, and 4-7 were calculated using the following equation

$$\tau = \frac{V_R}{H_2 \, flowrate}$$

Where τ is the residence time, and V_R is the volume of the reactor.

Example:

Using previous result of V_R, and using a value of 0.08 ft3/min for the H2: Glycerol flow rate, the residence time is

$$\tau = 0.55 \min$$

CARBON EFFICIENCY CALCULATION

The carbon efficiency values shown in Table 5-2 were calculated using the stoichiometric moles in the glycerol to propylene glycol reaction and the molecular weigh of the compound.

glycerol molecular weight = 92 grams/hour

propylene glycol molecular weight = 76 grams/hour

Example:

For a glycerol flow rate of 500 grams/hour and a product flow rate (propylene glycol) of 473.88 grams, the carbon efficiency is

$$C_{efficiency} = \left(500\frac{gG}{hr}\right)\left(\frac{molG}{92gG}\right)\left(\frac{molPG}{molG}\right)\left(\frac{76gPG}{molPG}\right)\left(\frac{hr}{473.88gPG}\right) = 0.087$$

APPENDIX C

EQUIPMENT PICTURES

Figure C. 10. FMI Metering Lab Pump – Model RP-SY

Figure C. 11. Reactor

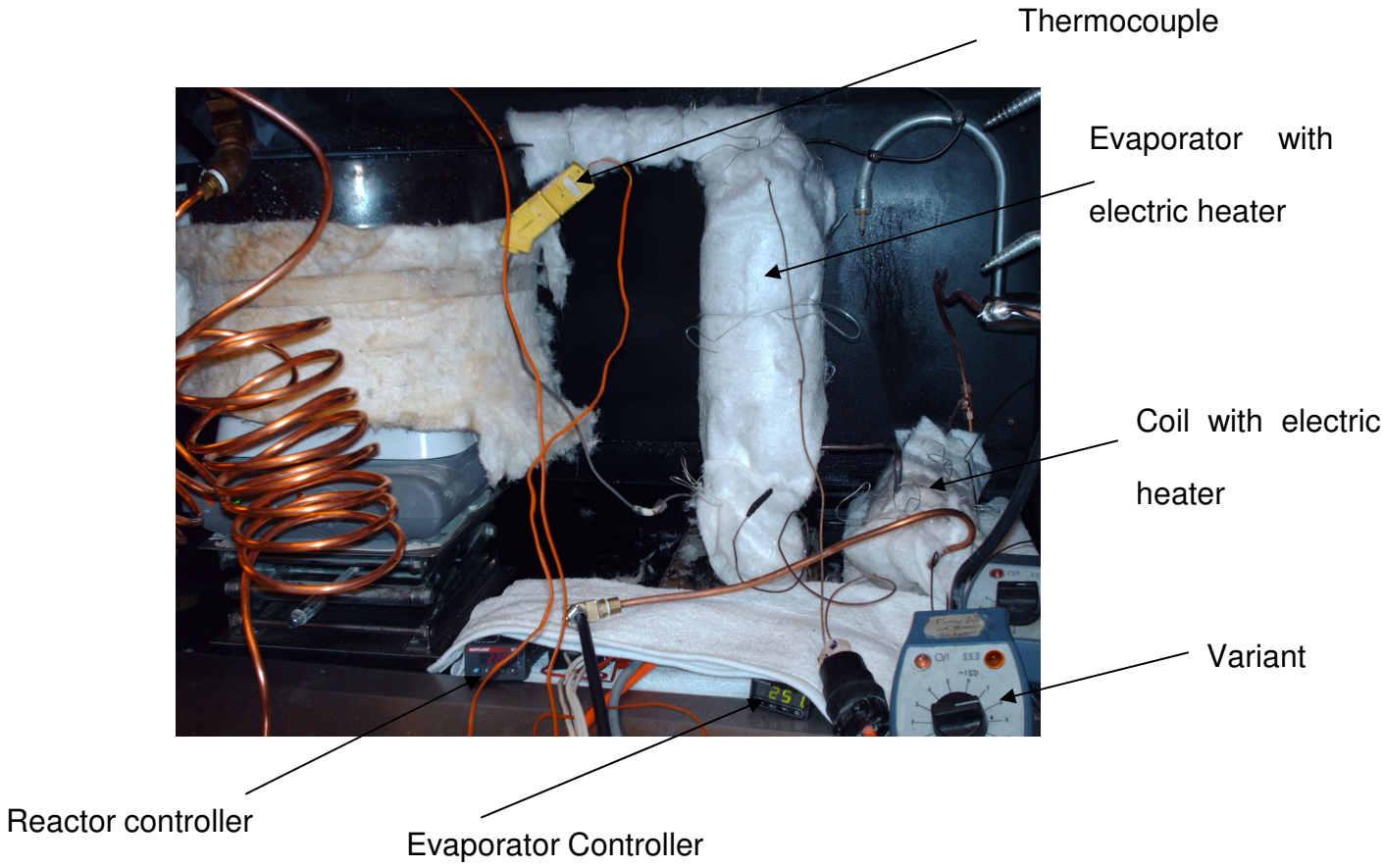

Figure C. 12. Pre-heated and Evaporator System

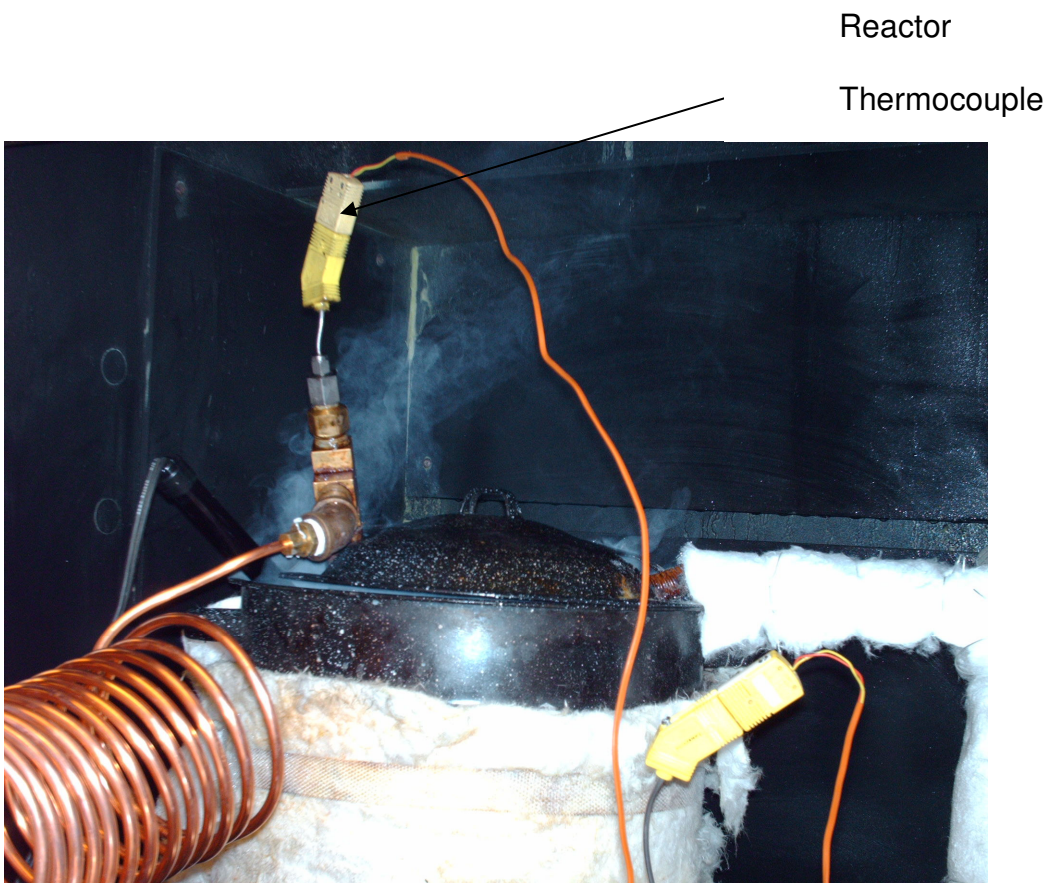

Figure C. 13. Reactor thermocouple

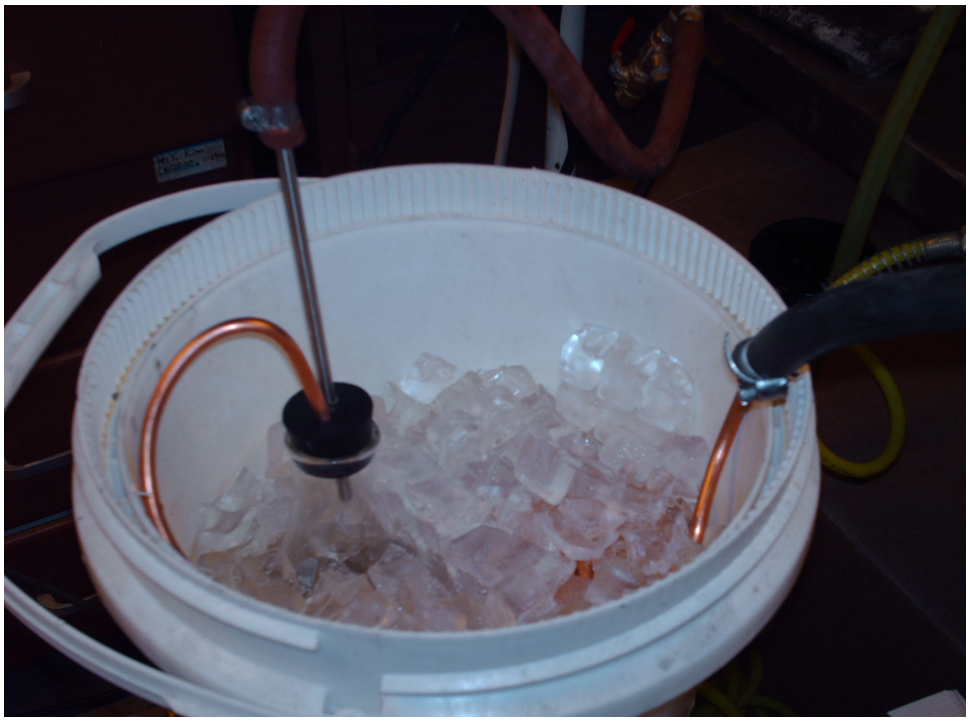

Figure C. 14. Cold Trap

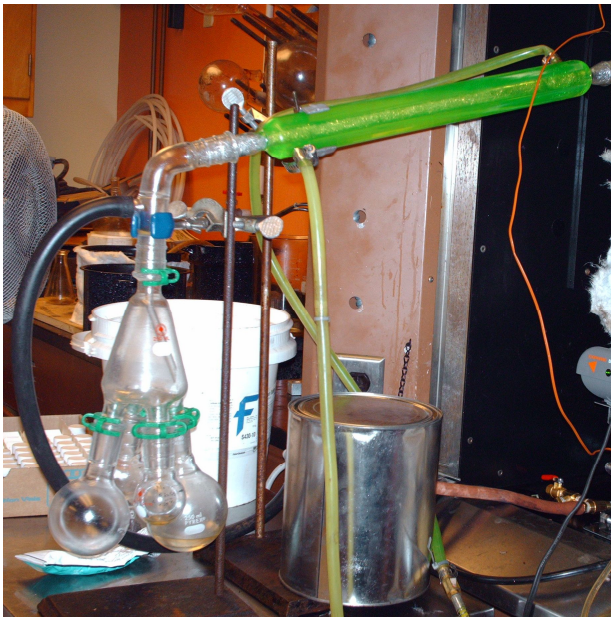

Figure C. 15. Condenser and sample collector

Figure C. 16. Recirculator VWR by PolyScience

Figure C. 17. Hewlett-Packard 6890 Gas Chromatograph

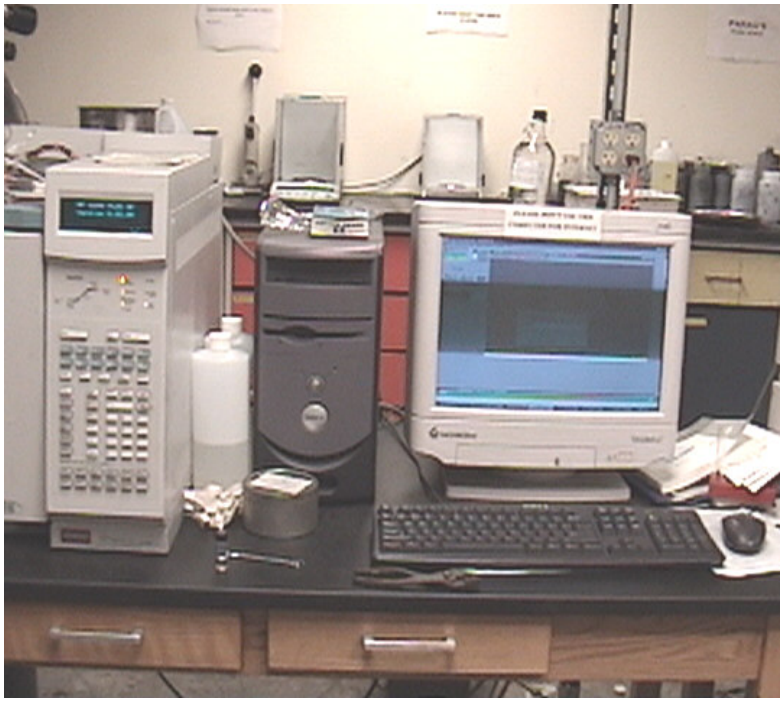

Figure C. 18. Hewlett-Packard ChemStation software used to collect and analyze the data.

Figure C. 19. 758 Karl Fisher Tritation by Metrohm (KFD tritino)

Figure C. 20. Example of product samples

APPENDIX D

PHYSICAL AND CHEMICAL PROPERTIES

i. Propylene Glycol

Molecular Weight:	76.10
Melting Point:	-60 deg C (-76 deg F) (35,39); supercools (11)
Boiling Point:	187.6 deg C (369.7 deg F) (35,39)
Relative Density (Specific Gravity):	1.036 at 20 deg C (36,39); 1.033 at 25 deg C (39) (water = 1)
Solubility in Water:	Soluble in all proportions (35,36)
Solubility in Other Liquids:	Soluble in all proportions in ethanol, acetone and chloroform; soluble in diethyl ether and benzene; sparingly soluble in petroleum ethers and carbon tetrachloride.(16,35,36)
Coefficient of Oil/Water Distribution (Partition Coefficient):	Log P(oct) = -0.92 (experimental) (40)
pH Value:	Not available
Acidity:	Very weak acid.
Dissociation Constant:	pKa = 14.8 at 25 deg C (39)
Viscosity-Dynamic:	56 mPa.s (56 centipoises) at 20 deg C (39); 48.6 mPa.s (48.6 centipoises) at 25 deg C (11)
Viscosity-Kinematic:	54.05 mm2/s (54.05 centistokes) at 20 deg C; 47.09 mm2/s (47.09 centistokes) at 25 deg C (calculated)
Saybolt Universal Viscosity:	Approximately 220-250 Saybolt Universal Seconds at 37.8 deg C (100 deg F) (calculated)
Surface Tension:	38 mN/m (38 dynes/cm) at 20 deg C (16); 36.51 mN/m (36.51 dynes/cm) at 25 deg C (39)
Vapour Density:	Not applicable
Vapour Pressure:	0.011 kPa (0.08 mm Hg) at 20 deg C (7); 0.017 kPa (0.129 mm Hg) at 25 deg C (calculated from experimentally derived coefficients) (38)
Saturation Vapour Concentration:	Approximately 105 ppm (0.01%) at 20 deg C; approximately 170 ppm (0.02%) at 25 deg C (calculated)

Evaporation Rate: 0.01 (n-butyl acetate = 1) (39)

Propylene Glycol MSDS

SECTION 1. CHEMICAL IDENTIFICATION

CHEMINFO Record Number: 501

CCOHS Chemical Name: 1,2-Propylene glycol

Chemical Name French: 1,2-Propylène glycol

Chemical Name Spanish: 1,2-Propilenglicol

CAS Registry Number: 57-55-6

RTECS Number(s): TY2000000

EU EINECS/ELINCS Number: 200-338-0

Chemical Family: Aliphatic polyhydric alcohol / aliphatic dihydric alcohol / aliphatic diol / glycol

Molecular Formula: C3-H8-O2

Structural Formula: CH3-CH(OH)-CH2-OH

SECTION 2. DESCRIPTION

Appearance and Odour:
Clear, colourless, viscous, practically odourless liquid.(11) Strongly hygroscopic (absorbs moisture from the air).(16,33)

Odour Threshold:
Not applicable; practically odourless.

Warning Properties:
NONE - 1,2-propylene glycol is essentially odourless and non-irritating.

Composition/Purity:
1,2-Propylene glycol is available commercially in two high purity grades, Industrial grade and "super pure" or USP grade, which have at least 99.5% purity. Impurities include chlorides (1-10 ppm max), iron (0.5-1.0 ppm max), heavy metals (5 ppm max), arsenic (3 ppm max), sulfate (0.006 wt% max) and water (0.2 wt% max).(16) Lower grades may contain small amounts of dipropylene glycol.

Uses and Occurrences:
1,2-Propylene glycol is used to manufacture unsaturated polyester resins, polyether polyols and low molecular mass polyethers; to produce alkyd resins for paints and varnishes, ester lubricants, emulsifiers, polymeric plasticizers and a polyester-type fluorescent resin matrix; as an intermediate in the synthesis of organic compounds, such as 1,2-propylene diamine and polypropylene glycol; as a solvent and plasticizer in printing inks; as a humectant (moisture-retaining agent), solvent and preservative in food products; as a humectant in tobacco and cosmetics; as a preservative in floral arrangements; as a stabilizer in hydraulic fluids; in the formulation of heat-transfer fluids that contain corrosion inhibitors; as an automotive coolant; as an airplane and runway deicing agent; as a substitute for ethylene glycol and glycerol; as a solvent for aromatics in the flavour concentrate industry; as a wetting agent for natural gums; in cosmetics, personal hygiene and pharmaceutical preparations; and as a lubricant.(11,16)
1,2-Propylene glycol is a component of special effect fog/smoke used during theatrical events and in fire training programs to simulate fire-training conditions.(20) Water solutions of 1,2-propylene glycol containing a corrosion inhibitor are used for low-temperature protection of fresh-water plumbing in recreational vehicles and boats.(12)

SECTION 3. HAZARDS IDENTIFICATION

EMERGENCY OVERVIEW:
Clear, colourless, viscous, practically odourless liquid. Strongly hygroscopic. Not combustible, but can burn if strongly heated. No unusual hazard in a fire situation. Essentially non-toxic.

POTENTIAL HEALTH EFFECTS

Effects of Short-Term (Acute) Exposure

Inhalation:

1,2-Propylene glycol does not readily form a vapour at room temperature. Therefore, it must be heated or misted before inhalation exposure would occur. Exposure to the vapour or mist is unlikely to cause significant health effects. Humans exposed to saturated and supersaturated atmospheres have not reported harmful effects.(4, unconfirmed)

NOTE: 1,2-Propylene glycol may be a component of a mixture of glycols used to generate a special effect fog/smoke during theatrical performances and in fire training programs. Information on the potential health effects of this fog/smoke is not reviewed here, since exposure is to a mixture of chemicals, which is heated to a high temperature (releasing thermal decomposition products).

Skin Contact:

1,2-Propylene glycol is not considered a skin irritant, based on human and animal evidence. However, 1,2-propylene glycol may cause irritation if sealed to the skin for a prolonged period by gloves, shoes or tight clothing.
Irritation was seen in 16% of 866 dermatitis patients, 48 hours after application of undiluted 1,2-propylene glycol to covered skin. Excessive dehydration of the skin by 1,2-propylene glycol may have been an important predisposing factor to the reactions.(1) Patches containing 0.05 mL of 100% 1,2-propylene glycol were applied to the backs of 50 men for 48 hours, open or under cover. Severe irritation was observed in the covered test, while no irritation was observed in the open test. The skin reaction disappeared rapidly.(8) Application of 100% 1,2-propylene glycol to the forearms of 10 men for 48 hours did not produce significant irritation.(24) Application of 200 microL of 30% 1,2-propylene glycol under cover to the backs of 9 women for 4 days was judged to be non-irritating.(26)
A detailed review has examined numerous studies of humans dermally exposed to 1,2-propylene glycol. Irritant contact dermatitis was determined to be the most commonly observed effect, although it appears to be related to prolonged exposure to very high concentrations of 1,2-propylene glycol. The possibility of an allergic reaction or hives developing is considered rare. Subjective or sensory irritation, with itching, burning or stinging sensations, but no signs of inflammation, is considered to be a fairly common reaction among users of cosmetics containing propylene glycol or in volunteers following application of 1,2-propylene glycol.(30)
1,2-Propylene glycol is not absorbed through the skin to a significant extent.

Eye Contact:

The undiluted liquid causes no to mild irritation, based on animal and limited human information. A drop applied to the human eye caused stinging, twitching of the eyelid and tearing which subsided after a few seconds. This was followed by mild, temporary congestion of the inner eyelid, with no residual discomfort or injury.(3, personal observation)

Ingestion:

1,2-Propylene glycol is not expected to produce harmful effects if ingested, based on animal toxicity information. Ingestion is not a typical route of occupational exposure.

Effects of Long-Term (Chronic) Exposure

Exposure to the vapour or mist is unlikely to pose a health hazard. Animals exposed on a long-term basis to high vapour/mist mixtures did not develop any adverse health effects.

NOTE: 1,2-Propylene glycol may be a component of a mixture of glycols used to generate a special effect fog/smoke during theatrical performances and in fire training programs. Information on the potential health effects of this fog/smoke is not reviewed here since exposure is to a mixture of chemicals, which is heated to a high temperature (releasing thermal decomposition products).

Skin:

Repeated or prolonged contact with the concentrated liquid can cause drying and irritation.(8,19,20,30)
In a 21-day patch test with 24 men, 1,2-propylene glycol caused a skin reaction which peaked on days 15-17 and then gradually decreased. It was concluded that the reaction

was due to primary irritation rather than an allergic response.(8)

Skin Sensitization:

1,2-Propylene glycol is not considered an occupational skin sensitizer.
No occupational case reports were located and negative results have been obtained in animal tests. Sensitization reactions have been reported in cosmetics users, volunteers, and dermatology patients exposed to 1,2-propylene glycol. Controversy exists regarding the incidence of 1,2-propylene glycol allergy. However, high concentrations (10% and greater) may be capable of producing skin sensitization, especially in sensitive populations (individuals with pre-existing skin disorders).(19,20,30,32)

Carcinogenicity:

There is no human information available. 1,2-Propylene glycol is not considered carcinogenic based on animal information.
The International Agency for Research on Cancer (IARC) has not evaluated the carcinogenicity of this chemical.
The American Conference of Governmental Industrial Hygienists (ACGIH) has no listing for this chemical.
The US National Toxicology Program (NTP) has not listed this chemical in its report on carcinogens.

Teratogenicity and Embryotoxicity:

There is no human information available. Animal information indicates that 1,2-propylene glycol does not cause developmental effects.

Reproductive Toxicity:

There is no human information available. Animal information indicates that 1,2-propylene glycol does not cause reproductive effects.

Mutagenicity:

There is no human information available. Animal information indicates that 1,2-propylene glycol is not mutagenic. Negative results are reported for 3 tests (host-mediated, dominant lethal and bone marrow chromosomal aberration) using rats and mice exposed to 1,2-propylene glycol orally.(12, unconfirmed) These unpublished studies were reviewed by an expert panel and determined to be well conducted. Other animal studies report positive and negative results, but the route of exposure (intraperitoneal administration) is not considered relevant to occupational situations.

Toxicologically Synergistic Materials:

There is no information available.

Potential for Accumulation:

1,2-Propylene glycol does not accumulate. It is rapidly absorbed from the gastrointestinal tract. In most mammals, part of the absorbed 1,2-propylene glycol is eliminated unchanged by the kidneys, while another portion is excreted by the kidneys as a glucuronic acid conjugate. Metabolism, primarily in the liver and kidney, commences within 2-4 hours after exposure. 1,2-Propylene glycol is oxidized to lactic acid, which is then converted to pyruvic acid. Both of these chemicals are normal constituents of the energy-generating process for humans. Pyruvic acid can be further metabolized to carbon dioxide and water. The majority of 1,2-propylene glycol and its breakdown products are excreted within 48 hours.(20,32)

SECTION 4. FIRST AID MEASURES

Inhalation:

If symptoms are experienced, remove source of contamination or move victim to fresh air. If symptoms persist, obtain medical advice.

Skin Contact:

Flush with lukewarm, gently flowing water for at least 5 minutes or until the chemical is removed. Under running water, remove contaminated clothing, shoes and leather goods (e.g. watchbands, belts). Completely decontaminate clothing, shoes and leather goods before re-use or discard.

Eye Contact:

Immediately flush the contaminated eye(s) with lukewarm, gently flowing water for 5 minutes, or until the chemical is removed, while holding the eyelid(s) open. If irritation persists, obtain medical advice.

Ingestion:

If irritation or discomfort occur, obtain medical advice immediately.

First Aid Comments:

All first aid procedures should be periodically reviewed by a doctor familiar with the material and its conditions of use in the workplace.

SECTION 5. FIRE FIGHTING MEASURES

Flash Point:

99 deg C (210 deg F) (closed cup).(34,35) Also reported as 103-104 deg C (217.4-219.2 deg F) (closed cup) (11,16)

Lower Flammable (Explosive) Limit (LFL/LEL):

2.6% (16,34)

Upper Flammable (Explosive) Limit (UFL/UEL):

12.5% (34,36)

Autoignition (Ignition) Temperature:

371 deg C (700 deg F) (34,36); also reported as 410 deg C (770 deg F) (16)

Sensitivity to Mechanical Impact:

Probably not sensitive. Stable material.

Sensitivity to Static Charge:

1,2-Propylene glycol will not accumulate static charge, since it has a high electrical conductivity.(16) Mixtures of 1,2-propylene glycol vapour and air at concentrations in the flammable range will not be ignited by a static discharge, since it has a high flash point.

Electrical Conductivity:

4.4 X 10(6) pS/m at 20 deg C (16)

Minimum Ignition Energy:

Not available

Combustion and Thermal Decomposition Products:

Carbon monoxide and carbon dioxide. Incomplete combustion may also produce toxic and irritating fumes and acrid smoke.

Fire Hazard Summary:

1,2-Propylene glycol is not combustible, but can burn if strongly heated. During a fire, irritating fumes and acrid smoke may be generated. Closed containers may rupture violently and suddenly release large amounts of product when exposed to fire or excessive heat for a sufficient period of time.

Extinguishing Media:

Carbon dioxide, dry chemical powder, "alcohol" foam, water spray or fog. Water or foam may cause frothing. Special "alcohol-resistant fire fighting foams" are recommended for use with any polar flammable liquid that is soluble in water, such as 1,2-propylene glycol.(34) Fire fighting foam manufacturers should be consulted for recommendations regarding types of foams and application rates.

NATIONAL FIRE PROTECTION ASSOCIATION (NFPA) HAZARD IDENTIFICATION

NFPA - Health:	0 - Exposure, under fire conditions, would be no more hazardous than an ordinary combustible material.
NFPA - Flammability:	1 - Must be preheated before ignition can occur.
NFPA - Instability:	0 - Normally stable, even under fire conditions, and not reactive with water.

ii. Acetol

General

Synonyms: acetone alcohol, acetylmethanol, hydroxymethyl methyl ketone, 2-oxopropanol, hydroxypropanone, acetol, acetylcarbinol, alpha-hydroxyacetone, Rongal 5242

Molecular formula: $C_3H_6O_2$

CAS No: 116-09-6

EINECS No: 204-124-8

Physical data

Appearance: colourless to yellow liquid

Melting point: -17 C

Boiling point: 145 - 146 C

Vapour pressure: 5 mm Hg at 20 C

Density (g cm^{-3}): 1.08

Explosion limits: 3.0 - 14.9%

Acetol MSDS

1-Hydroxy-2-propanone

- Acetone alcohol
- Hydroxyacetone
- Acetylcarbinol
- 2-Oxopropanol
- Hydroxymethyl methyl ketone
- Hydroxypropanone

Formula CH_3COCH_2OH

Structure 

Description Colorless to yellow liquid.

Registry Numbers and Inventories.

CAS	116-09-6
EC (EINECS/ELINCS)	204-124-8
EC Safety Phrase	S 23 24/25
RTECS	UC2800000
RTECS class	Mutagen
UN (DOT)	1993
Merck	13,66
Beilstein/Gmelin	605368

Beilstein Reference	4-01-00-03977
Swiss Giftliste 1	G-1764
Canada DSL/NDSL	DSL
US TSCA	Listed
Austrailia AICS	Listed
Japan ENCS (MITI)	Listed
Korea ECL	Listed

Properties.

Formula	C3H6O2
Formula mass	74.08
Melting point, ℃	-17
Boiling point, ℃	145
Vapor pressure, mm_{Hg}	56 (20 C)
Vapor density (air=1)	2.55
Density	1.0928 g/cm3 (20 C)
Solubility in water	Very soluble

Refractive index	1.425 (20 C)
pKa/pKb	13.14 (pKa)

Hazards and Protection.

Storage	Keep away from heat, sparks, and flame. Keep away from sources of ignition. Store in a cool, dry, well-ventilated area away from incompatible substances. Flammables-area. Keep containers tightly closed.
Handling	Wash thoroughly after handling. Use with adequate ventilation. Ground and bond containers when transferring material. Use spark-proof tools and explosion proof equipment. Avoid contact with eyes, skin, and clothing. Empty containers retain product residue, (liquid and/or vapor), and can be dangerous. Avoid contact with heat, sparks and flame. Avoid ingestion and inhalation. Do not pressurize, cut, weld, braze, solder, drill, grind, or expose empty containers to heat, sparks or open flames.
Protection	Eyes: Wear appropriate protective eyeglasses or chemical safety goggles as described by OSHA's

	eye and face protection regulations in 29 CFR 1910.133 or European Standard EN166. Skin: Wear appropriate protective gloves to prevent skin exposure. Clothing: Wear appropriate protective clothing to prevent skin exposure.
Respirators	Follow the OSHA respirator regulations found in 29CFR 1910.134 or European Standard EN 149. Always use a NIOSH or European Standard EN 149 approved respirator when necessary.
Small spills/leaks	Absorb spill with inert material, (e.g., dry sand or earth), then place into a chemical waste container. Avoid runoff into storm sewers and ditches which lead to waterways. Clean up spills immediately, using the appropriate protective equipment. Remove all sources of ignition. Use a spark-proof tool. Provide ventilation. A vapor suppressing foam may be used to reduce vapors. Water spray may reduce vapor but may not prevent ignition in closed spaces.
Stability	Stable under normal temperatures and pressures.
Incompatibilities	Strong oxidizing agents.

Decomposition	Carbon monoxide, irritating and toxic fumes and gases, carbon dioxide.

Fire.

Flash Point, ℃	56
Autoignition, ℃	275
Upper exp. limit, %	14.9
Lower exp. limit, %	3.0
Fire fighting	Wear a self-contained breathing apparatus in pressure-demand, MSHA/NIOSH (approved or equivalent), and full protective gear. Will burn if involved in a fire. Use water spray to keep fire-exposed containers cool. Containers may explode in the heat of a fire. May be ignited by heat, sparks, and flame. Extinguishing media: For small fires, use dry chemical, carbon dioxide, water spray or alcohol-resistant foam. For large fires, use water spray, fog, or alcohol-resistant foam. Use water spray to cool fire-exposed containers.

		Water may be ineffective. Do NOT use straight streams of water.
Fire potential		HIGHLY FLAMMABLE: Will be easily ignited by heat, sparks or flames.
Hazards		Vapors may form explosive mixtures with air. Vapors may travel to source of ignition and flash back. Most vapors are heavier than air. They will spread along ground and collect in low or confined areas (sewers, basements, tanks). Vapor explosion hazard indoors, outdoors or in sewers.
Combustion products		Fire may produce irritating, corrosive and/or toxic gases.
NFPA	**Health**	1
	Flammability	2
	Reactivity	0

Health.

Poison_Class	4
Exposure effects	
Ingestion	May cause irritation of the digestive tract.
Inhalation	May cause respiratory tract irritation. Vapors may cause dizziness or suffocation.
Skin	May cause skin irritation.
Eyes	May cause eye irritation.

First aid

Ingestion	If victim is conscious and alert, give 2-4 cupfuls of milk or water. Never give anything by mouth to an unconscious person. Get medical aid immediately.
Inhalation	Remove from exposure to fresh air immediately. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical aid.
Skin	Get medical aid. Flush skin with plenty of soap and water for at least 15 minutes while

	removing contaminated clothing and shoes. Wash clothing before reuse.
Eyes	Immediately flush eyes with plenty of water for at least 15 minutes, occasionally lifting the upper and lower eyelids. Get medical aid immediately.

Transport.	
UN number	1993
Response guide	128
Hazard class	3
Packing Group	I; II; III
HS Code	2914 40 90

iii. Glycerol MSDS

Common synonyms	1,2,3-propanetriol, glycerine, glycerin, glycyl alcohol, glycerol USP
Formula	$C_3H_8O_3$
Physical properties	Form: viscous colourless liquid Stability: Stable Melting point: 17.8 C Boiling point: 290 C Specific gravity: 1.26 Flash point: 160 C Critical temperature: 492.2 C Critical pressure: 42.5 atm
Principal hazards	Glycerol is generally regarded as a safe material for which no special handling precautions are required. However, it is flammable. It also feels oily, so may be a slipping hazard if spilled on the floor.
Safe handling	Wear safety glasses if required by local rules. Clear up spills promptly.
Emergency	Eye contact: Immediately flush the eye with water. If irritation persists, call for medical help. Skin contact: Wash off with water. If swallowed: Call for medical help if the amount swallowed is large. Glycerol is widely used in foods, so accidental consumption of a small amount is unlikely to be harmful.
Disposal	Small amounts of glycerol may be flushed down the sink unless local rules prohibit this. Glycerol is viscous, so unless care is taken to wash all liquid away, some may remain in the sink and pose a fire risk.
Protective equipment	Safety glasses if required by local rules.
Further information	Glycerol Chemicals in the HSci database More extensive safety data