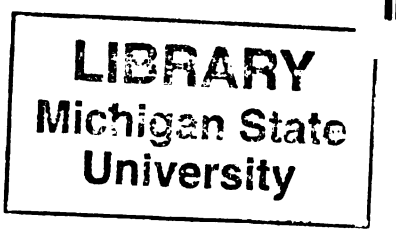

This is to certify that the

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Catalytic Conversion of Glucose, Fructose, and Sucrose to High-Valued Chemicals

presented by

Jennifer Elizabeth Jacobs

has been accepted towards fulfillment
of the requirements for

Master of Science degree in Chemical Engineering

Matt C Hawley

Major professor

Date 5/10/2000

CATALYTIC CONVERSION OF GLUCOSE, FRUCTOSE, AND SUCROSE TO HIGH-VALUED CHEMICALS

By

Jennifer Elizabeth Jacobs

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
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ABSTRACT

CATALYTIC CONVERSION OF GLUCOSE, FRUCTOSE, AND SUCROSE TO HIGH-VALUED CHEMICALS

By

Jennifer Elizabeth Jacobs

Many industrially important chemicals are currently produced using petroleum and natural gas as feedstocks. These fossil fuel resources are finite and nonrenewable. Development of new technology for the conversion of sugars to major industrial chemicals namely glycerol, propylene glycol, and ethylene glycol may replace the current petroleum or fermentation based processes. Selectivity-controlled hydrogenolysis is a promising pathway for conversion of sugars to polyhydric alcohols with no carbon atom loss. In this research with substrates glucose, fructose, and sucrose, I examine the efficacy of nine different catalysts and two solvents in the sugar hydrogenolysis process. Catalysts or catalyst combinations that favored the desired reaction pathway included 5% ruthenium on carbon; nickel on kieselguhr; palladium 1% on carbon and boron oxide; and nickel on alumina/silica and iron (III) oxide. Yields as high as 39%, 33%, and 12% were attained for propylene glycol, glycerol, and ethylene glycol, respectively. Also, a total selectivity of 63% for the products propylene glycol, glycerol, and ethylene glycol was achieved under the studied reaction conditions. Barium promoted copper chromite yielded 100% conversions for substrates glucose, fructose, and sucrose. The catalytic conversion of glucose, fructose, and sucrose in this work has demonstrated that further development of an efficient selectivity-controlled sugar hydrogenolysis process would inevitably lead to an industrially, economically, and environmentally significant process.

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CHAPTER 1

GENERAL INTRODUCTION

Many industrially important chemicals are currently produced using petroleum and natural gas as feedstocks. These fossil fuel resources are finite and nonrenewable; thus their depletion is an enduring concern. Due to the diminishing reserves of petroleum and natural gas, the chemical process industry may eventually face feedstock problems. Alternative sources and pathways will need to be developed in order to continue production of our many synthetic chemicals, which are largely responsible for our current standard of living. In this research, I explored the development of a biomass catalytic conversion process, namely sugar hydrogenolysis, that will produce high-valued chemicals such as glycerol, propylene glycol, and ethylene glycol, from renewable biomass resources. The term "biomass" refers to organic matter, which can be converted to energy. It is a complex material made up of three major organic fractions with representative compositions on a dry-weight basis being as follows: 35-50% cellulose, 20-35% hemicellulose, and 12-20% lignin (Wyman, 1999). Some of the most common organic materials include wood, agricultural residues, solid waste, animal waste, sewage, corn, sugarcane, and crops grown specifically for energy (Wyman, 1999). Biomass is made up mainly of the elements carbon and hydrogen, and technologies exist that can free the energy from the chemical compounds which consist of these elements.

Currently, glycerol, ethylene glycol and propylene glycol are all produced from petroleum-based processes. Sugar hydrogenolysis is potentially an economically viable process to produce these chemicals from renewable biomass resources. The development

and application of this process is significant because there are both considerable economic and environmental incentive. A selective sugar hydrogenolysis process will address the petroleum depletion concern as well as potentially eliminate the environmentally unfriendly chlorohydrin intermediates that result from the current production methods. Another process to produce these high-valued chemicals is fermentation. However, fermentation causes loss of carbons from the starting material by producing carbon dioxide. The hydrogenolysis of sugars to useful chemicals while preserving all the carbon atoms in the starting material supercedes fermentation processes.

Biomass is a copious material and it is estimated that the U.S. generates about 1 billion dry tons of it each year (Barrier and Bulls, 1992). The annual production of biomass in the world is estimated to be as high as 10^{11} to 10^{12} dry tons (Grohman *et al.*, 1993). Development of a selective conversion process can enhance utilization of the abundant biomass by converting the biomass into a variety of value-added chemicals. Current glucose hydrogenation technology involves either a batch or continuous–slurry process (Arena, 1992). One important result of biomass use is likely to be development of a compatible set of products, such as organic acids, alcohols, and natural polymers, where these products could integrate with one another in a similar way that the complex infrastructure of fuels, solvents, plastics, etc have evolved (Wyman, 1999).

1.1 Literature Survey on Sugar Hydrogenolysis

Sugar hydrogenolysis is a chemical process that selectively converts simple sugars to glycerol, ethylene glycol, and propylene glycol, which have extensive uses and

large markets at the present time. Carbohydrates exhibit unusually rich chemical functionality but limited stability (Andrews and Klaeren, 1989). Hydrogenolysis refers to the cleavage of a molecule under conditions of catalytic hydrogenation. Under high hydrogen pressure and high temperature, sugars and sugar alcohols can be catalytically hydrocracked into lower polyhydric alcohols in the presence of transition metal catalysts and enhanced by the addition of bases (Andrews and Klaeren, 1989). In the literature, sugar hydrogenolysis is discussed indistinguishably from sugar alcohol hydrogenolysis, because of the close relationship between these two reactions. In this process, both C-C and C-O bonds are susceptible to cleavage:

$$R_3C\text{-}CR'_3 + H_2 \longrightarrow R_3CH + HCR'_3$$

$$R_3C\text{-}OH + H_2 \longrightarrow R_3CH + H_2O$$

The reaction mechanism described in Figure 1 can explain all of the reaction products found so far in the hydrogenolysis of sugars and sugar alcohols (Furney, 1995). The products which have been reported for the hydrogenolysis of glucose, fructose, and sucrose, and sugar alcohols include glycerol, ethylene glycol, propylene glycol, 1,4-butanediol, 2,3-butanediol, erythritol, threitol, xylitol, 3,4-dideoxygenated hexitol, ethanol, methanol, and sometimes hydrocarbons and carboxylic acids, depending on the process. Selectivity is the main shortcoming with sugar hydrogenolysis and of the compounds listed above, glycerol, ethylene glycol, and propylene glycol are the most industrially important. However, homogenous transition-metal catalysts offer the unique combination of high selectivity and reactivity needed to effectively manipulate these important substrates (Andrews and Klaeren, 1989).

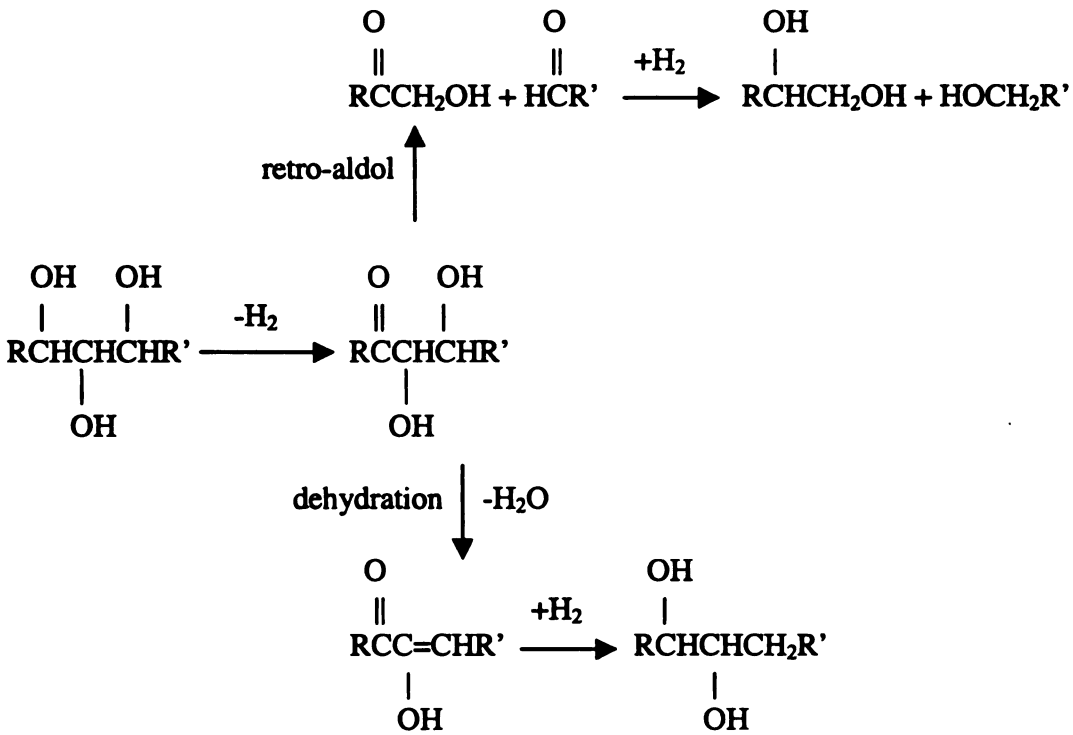


Figure 1. Mechanism of Sugar and Sugar Alcohol Hydrogenolysis

Currently, glycerol is produced from the chlorination and subsequent hydrolysis of propylene (Furney, 1995). Several commercial processes exist to produce glycerol from propylene and the predominant pathway includes the environmentally harmful intermediates ally chloride, dichlorhydrin and epichlorohydrin. A small portion of glycerol is also produced from fatty material as a by-product of soap production. Glycerol is often used in food and personal hygiene industries and can be found in liqueurs, inks, lubricants, alkyd resin, ester gums, polyethers, pharmaceuticals and humectants. Additionally, glycerol is a valued intermediate in many industrial chemical processes.

Ethylene glycol is a highly valuable chemical in industry and is currently produced by the hydration of ethylene oxide (Furney, 1995), a petroleum based process. Ethylene glycol is used as an antifreeze, and used in hydraulic fluids, paints, deicers and alkyd and polyester resins.

Propylene glycol is produced from propylene with propylene chlorohydrin and propylene oxide as intermediates. Propylene glycol and ethylene glycol have similar uses and applications, and propylene glycol is often used as a substitute for the more toxic ethylene glycol. Propylene glycol is used as a biodegradable antifreeze. Additionally propylene glycol is used in food additives, tobacco humectants, cosmetic softening agents, lotions, and sunscreens.

Due to poor selectivity, sugar hydrogenolysis is currently not an industrially important process. The process is uneconomical due to a wide distribution of products from sugar molecules under hydrogenolysis conditions. A sugar molecule contains many C-C and C-O bonds that are susceptible to cleavage. Knowledge of the bond cleavage

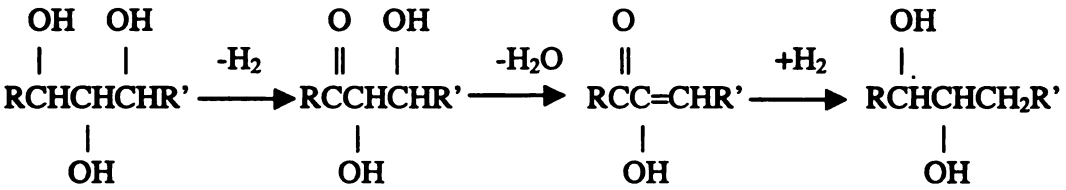
mechanism governing sugar and sugar alcohol hydrogenolysis is important in order to control the selectivity and greatly increase production of the most highly valued compounds.

1.2 Mechanism and Selectivity Development

Sugar hydrogenolysis reactions have been studied since the 1930's (Conner and Adkins, 1932). However, research for the purpose of biomass conversion has only been carried out since the 1950's. Clark (1958) was the pioneer for this research at the U.S. Forestry Products Laboratory. In this early report, Clark claimed to obtain glycerol from sorbitol with yields as high as 40%. In his experiments sorbitol was reacted under the hydrogenolysis conditions in the presence of a nickel on kieselguhr catalyst. Reactions were carried out in the aqueous phase at temperatures between 215 and 240 C, and hydrogen pressures between 2000 and 5600 psi. The identified products included glycerol, propylene glycol, ethylene glycol, erythritol and xylitol.

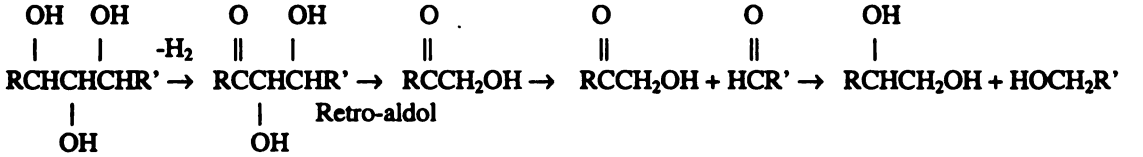
Greater yields (75%) of distillable polyalcohols were attained by using beryllium oxide activated copper chromite catalyst to hydrogenate sucrose (Boelhouwer *et al.* 1960). The reaction was performed in a rotating autoclave with methanol being used as the solvent. Experiments were run between a temperature range of 195 and 250 C, and the hydrogen pressure range was between 2204.4 and 2939.3 psi (150 and 200 atm). The reaction products were separated by distillation. In one experiment, the glycerol fraction was reported to account for 61% of the product. However, since this fraction covers a wide range of boiling points, exact products were not determined. Glycerol, propylene glycol, and ethylene glycol were believed to be included in the products.

Since these early reports, the body of literature on sugar hydrogenolysis has been steadily increasing. In the mid-to late-1970's many biomass conversion projects experienced an "explosion" in the amount of research being conducted. In the United States the government initiated major programs to fund the development of new energy sources in response to tightening petroleum supplies and high energy costs. The oil crisis in the 1970's may have stimulated this general interest in biomass conversion. As energy prices dropped, interest and development of new energy sources declined, thus petroleum remains the largest single source of energy in the United States, providing about 40% of the total energy use (Wyman, 1999). Various sugar alcohols including sorbitol, xylitol, erythritol and even glycerol, were subjected to hydrogenolysis conditions (Montassier *et al.* 1988). Montassier *et al.* (1988) proposed that the cleavage of C-O bonds occurs through dehydration of a β-hydroxyl carbonyl:



The structure of the β-hydroxyl carbonyl is already contained in an open-chain sugar molecule, and may be generated from a sugar alcohol by dehydrogenation. In this reaction scheme, the dehydration step is catalyzed by bases while the dehydrogenation and hydrogenation steps are catalyzed by transition metal complexes.

The original mechanism proposed by Montassier *et al.* (1988) to explain the C-C cleavage in sugar and sugar alcohol hydrogenolysis is the retro-aldol reaction:



The C-C cleavage precursor is again a β-hydroxyl carbonyl. Cleavage of this β-hydroxyl carbonyl leads to an aldehyde and a ketone, which are subsequently hydrogenated to alcohols. Andrews and Klaren (1989) suggested the same mechanism, based on their observation that the primary C-C cleavage site is β to the carbonyl group in sugar hydrogenolysis.

Montassier *et al.* (1988) proposed another mechanism, namely, the retro-Claisen reaction for the C-C cleavage in glycerol hydrogenolysis. This mechanism was proposed in order to explain the absence of methanol and the presence of carbon dioxide in the hydrogenolysis products of glycerol and sugar alcohols. The formation of formaldehyde and its subsequent hydrogenation to methanol can be predicted from the retro-aldol reaction. The retro-Claisen mechanism allows for formation of formic acid rather than formaldehyde, which decomposes under hydrogenolysis conditions to form CO_2. The retro-Claisen was proposed to better explain the experimental hydrogenolysis products obtained from sugar and sugar alcohols. Montassier *et al.* (1988) also proposed the retro-Michael reaction, which requires a δ-dicarbonyl as the bond cleavage precursor, to explain the C-C cleavage in the hydrogenolysis of xylitol and sorbitol.

The reaction mechanisms just reviewed are all consistent with the products obtained in sugar hydrogenolysis. The major product of fructose cleavage is glycerol and for glucose cleavage the major product is ethylene glycol and erythritol. Propylene glycol is formed by the hydrogenation of glycerol (Clark, 1958). This cleavage site selectivity along with the strong base catalysis further supports that a retro-aldol reaction may be involved. Furthermore, recent research on sugar hydrogenolysis conducted by our group (Wang *et al.*, 1996) identified the retro-aldol reaction of a β-hydroxyl carbonyl

precursor as the C-C cleavage mechanism, and excluded the other mechanisms due to two theoretical considerations and experimental results (Figure 1).

1.3 Project Background

The previous researchers on this project at Michigan State University (Wang *et al.*, 1996) performed a mechanism study of sugar and sugar alcohol hydrogenolysis using 1,3-Diols. Based on the possible bond cleavage mechanisms governing sugar and sugar alcohol hydrogenolysis they were able to conclude that cleavage of the C-C bonds and C-O bonds in hydrogenolysis is through retro-aldolization and dehydration of a β-hydroxyl carbonyl, respectively. Their results prevented them from believing that either retro-Claisen or retro-Michael is a dominating C-C cleavage mechanism over the retro-aldol in hydrogenolysis.

Twigg (1998) continued research on this project and investigated use of a 1, 3-diol, specifically, 2,4-pentanediol (2,4-PD). The focus was on developing a catalyst to increase the selectivity of the hydrogenolysis process. Numerous metals, in the presence of hydrogen, can hydrogenate aldehyde groups of carbohydrate molecules in aqueous solution (Montassier *et al.*, 1991). Two types of catalysts, namely metal oxides and nickel on alumina/silica, were found to have desirable effects on the hydrogenolysis reaction and it were these catalysts that were chosen for study in the current research. Barium promoted copper chromite; copper (II) oxide; palladium 1% on carbon and boron oxide; and nickel on alumina/silica and copper (II) oxide were found to promote highest selectivity toward C-C cleavage. Twigg (1998) also examined the effects of temperature

and pressure and found limited effects from temperature change (above 190 °C) and pressure inversely affects the reaction rate and 3.5MPa is adequate.

1.4 Objectives and Scope of Current Research

Our focus is to understand the mechanisms controlling the hydrogenolysis of sugars. Our hypothesis is that sugars and sugar alcohols will hydrolyze similarly to the simpler 1,3-diol model compounds. Based on the mechanisms of selective sugar hydrogenolysis, a large scale process can be optimized to compete economically and environmentally with our existing petroleum based processes.

Specific Aims

1) develop analytical methods for detecting the various products produced in the hydrogenolysis of D-glucose, fructose, and sucrose; 2) determine the efficacy of nine different catalysts or catalyst combinations and two different solvents in the conversion of D-glucose, fructose, and sucrose into propylene glycol, ethylene glycol and glycerol; and 3) explore the mechanism of sugar hydrogenolysis by identifying some of the many intermediates and products of sugar hydrogenolysis.

CHAPTER 2

EXPERIMENTAL SYSTEM AND METHODS

2.1 Description of Apparatus

A specially designed, stainless steel continuously stirred steady-state batch reactor with a 50 ml capacity and capable of withstanding high pressures and temperatures was used for all hydrogenolysis reactions. The detailed design of this reactor is shown in Figure 2.

Compressed hydrogen from a cylinder equipped with a pressure regulator was used to maintain a constant pressure of 3.5 MPa during the course of the reaction. An additional pressure gauge was added to the hydrogen supply line to monitor the pressure near the reactor. A vacuum line connected to the reactor was used to purge the system before the experiment. The desired reaction temperature was maintained by a 1000W electric coil immersed in a silicone oil bath and controlled with a proportional temperature controller and platinum RTD probe. A uniform temperature distribution of 210 ± 3 °C was sustained by stirring the oil bath with nitrogen bubbles.

The continuously stirred batch reactor was equipped with one sampling port that was composed of a sampling valve, 1/16-in. stainless steel tubing and a 0.45 μm pore size stainless filter at the inlet immersed in the reaction medium. The filter prevented the contamination of the samples with solid catalyst particles, which could interfere with the high pressure liquid chromatograph (HPLC) and gas chromatograph (GC) analyses. The total hold volume was several microliters which allowed for an accurate representation of the mixture components at the time of sampling. A magnetic stirring bar was used to

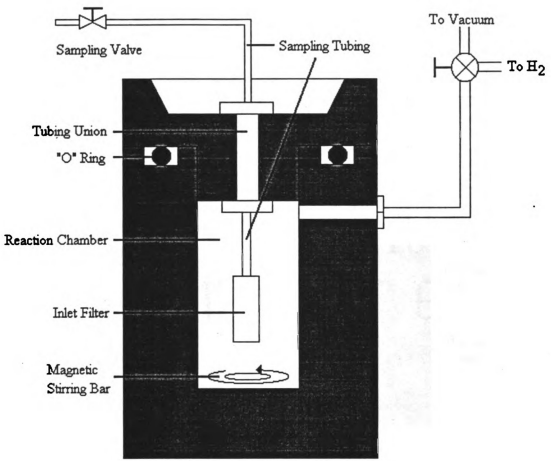


Figure 2. Illustration of Hydrogenolysis Reactor

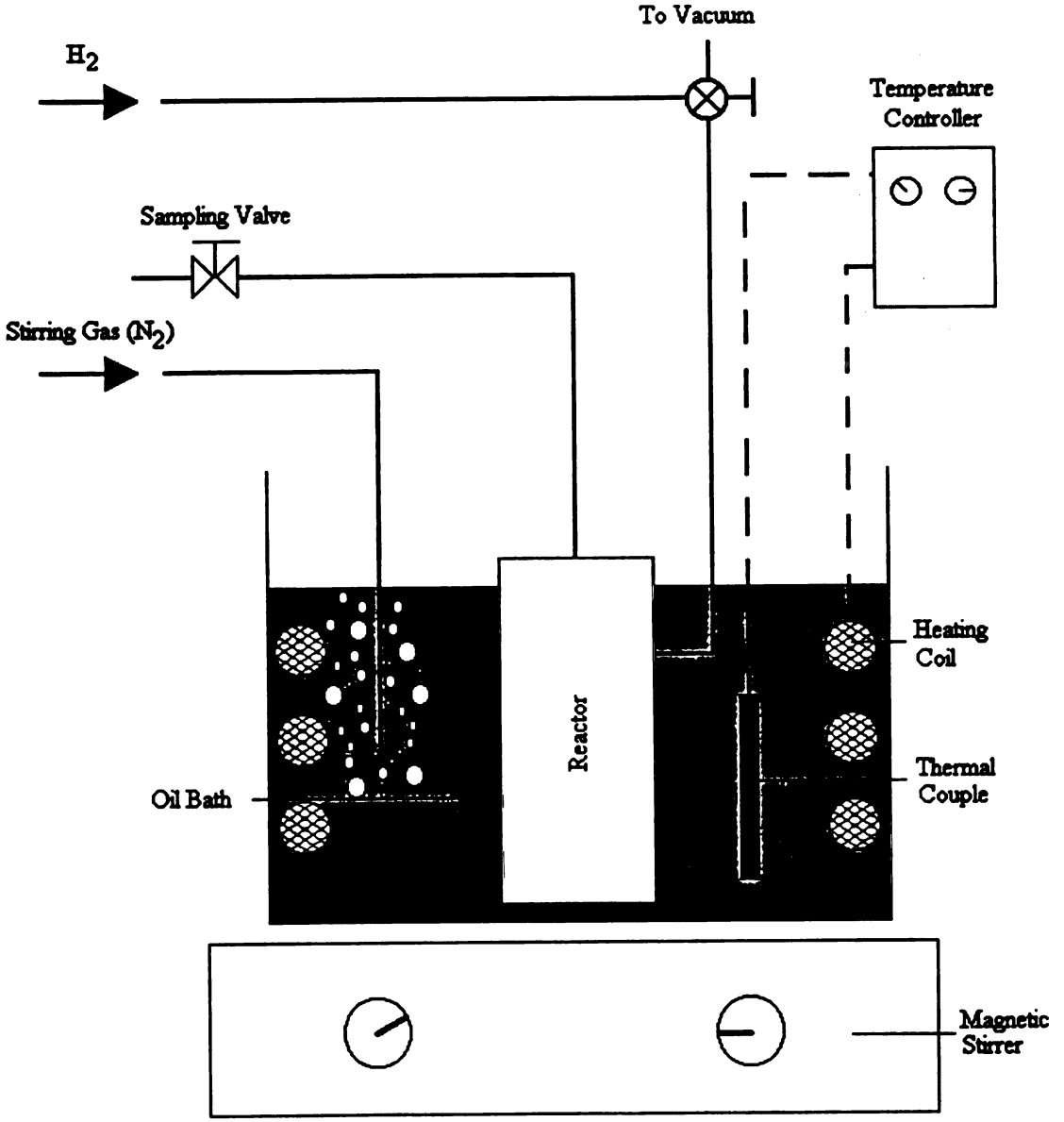


Figure 3. Schematic Illustration of Experimental System

blend the mixture in the reactor. The entire reactor assembly was placed on a magnetic stir plate. A schematic illustration of the whole experimental system is provided in Figure 3.

2.2 Experimental Procedure

To carry out the reaction, about 0.5 g of starting sugar, 0.05 g of selected catalyst, 1 ml of 1N sodium hydroxide, and proper amounts of solvent were placed in the reactor, giving a total volume of about 40 ml. The reactor was purged by alternately connecting it to nitrogen and a vacuum, and then was heated until the reactor reached 210 °C. Hydrogen pressure was applied to the reactor and maintained at 3.5 MPa. During the reaction course, the reaction medium was constantly stirred and its composition was monitored using gas chromatography (GC) and high pressure liquid chromatography (HPLC).

2.3 Chemical Components

The following chemicals are from Aldrich Chemical Co. (Milwaukee, WI): copper (II) oxide (99.9999%); copper chromite, barium promoted; palladium, 1 wt. % on carbon; boron oxide (99.999%); iron (III) oxide (99.998%); Ruthenium, 5 wt. % on carbon; nickel on kieselguhr (60-62% Ni); sodium hydroxide (97 + %); 1,4-butandiol; ethyl alcohol-d (99%); and α-D-glucose (96%). D-fructose, sucrose (99.9%), and methyl alcohol were purchased from Fisher Scientific (Fair Lawn, NJ), Boehringer Mannheim (Indianapolis, IN) and Mallinckrodt, respectively. The water used came from a reverse osmosis system (DA-15, Filterchem, Alhambra, CA). The hydrogen (99.9%) and

nitrogen was obtained from Purity Cylinder Gases (Lansing, MI) and AGA Gas Products (Lansing, MI).

2.4 Sample Analysis

Prior to each collection about 0.5 ml of sample was discarded due to dead space volume. Following this, a 1 ml sample was collected every 30 minutes for a total of 240 minutes from the reaction vessel and placed into a small vial.

Internal Standards For analysis an internal standard (IS) calibration method was performed. The internal standard used must be well resolved from the other peaks, elute close to the peaks of interest, and have a structural similarity to the unknown. For HPLC analysis with starting substrate glucose and fructose the internal standard used was sucrose, and with starting substrate sucrose the internal standard used was fructose. The final concentration of either of the internal standards for HPLC analysis in solution was 4.72 mM sucrose or 8.97 mM fructose. For GC analysis the internal standard used for all experiments was 1,4-butanediol. The final concentration of 1,4-butanediol in solution was 10.47 mM.

Liquid Chromatography The starting sugar and glycerol were separated in a Shodex Asahipak NH2P-50 packed column, 4.6 mm i.d. x 150 mmL, particle size 5 μm (Keystone Scientific Inc., Bellefonte, PA) and maintained at 30 °C. The HPLC system consisted of a Dionex gradient pump, a Waters injector, and a Sedex Model 55 evaporative light scattering detector (Richard Scientific, Novato, CA). The detector was operated at 46 °C and pressure was held at 2.2 MPa with nitrogen. A 75/25 acetonitrile/water mixture was used as the mobile phase at a flow rate of 1.0 ml/min, and

10 µl portions of the solution were injected into the HPLC chromatographic system in order to calculate the concentrations. The approximate HPLC retention times for glycerol, fructose, glucose, and sucrose were 3.0, 5.7, 6.8 and 9.1 min, respectively. The liquid chromatography results were entered into a spreadsheet which automatically calculated the selectivity and overall conversion of the starting sugar and the yield of glycerol.

Gas Chromatography A 3.0 µl aliquot of solution was injected into a Hewlett Packard Model 5890 Series II gas chromatograph (Hewlett Packard, Avondale, PA), equipped with a 30 m x 0.53 mm i.d., 0.50 micron megabore Supelco capillary column (Supelco, Bellefonte, PA) and flame ionization detector for separation of ethylene glycol and propylene glycol. The column temperature was programmed for a 1-min hold at 100 °C followed by a 12.5-min ramp at 4 °C/min up to 150 °C. The injector and detector temperatures were 250 and 350 °C, respectively. The approximate retention times for propylene glycol, ethylene glycol, and 1,4-butanediol were 5.7, 6.3 and 12.4 min, respectively. The gas chromatography results were entered into a spreadsheet which automatically calculated the yields of propylene glycol and ethylene glycol.

Standard Preparation The HPLC and GC were calibrated for each individual compound using an internal standard (IS) calibration method. The internal standard calibration method helps to standardize the amount of sample manually injected. This is very important due to the small amounts of sample injected, namely 3 µl for GC and 10 µl for HPLC analysis. The HPLC and GC calibration curves are listed in Appendix A and B, respectively. An internal calibration verification (ICV) was prepared for both instruments. The ICV was performed by preparing a standard and injecting it three

consecutive times into either the HPLC or GC. Using the reported area and the prepared calibration curves, the concentration of each compound in the standard was calculated. The standard deviation for each compound was calculated for the three consecutive runs, and it is desired to receive a RSD value of less than 5%. Relative standard deviation (RSD) values of 0.51, 1.58, 3.65 and 18.4% were obtained for propylene glycol, ethylene glycol, glucose and glycerol, respectively. It was found that glycerol has a much higher RSD value. The RSD value is higher because glycerol is a very viscous material and it is difficult to prepare samples and inject accurate amounts into the HPLC due to its tendency to retain to glass, therefore causing the accuracy of measurement to be less.

Error Estimation Error is present due to both the small volumes used in sample analysis and associated instrumental error. In order to better measure the amount of instrumental error, the ICV standard was run prior to using the instruments for each individual experiment. This enabled an instrumental error to be calculated over the entire course of using these instruments. For the experiments in which D-glucose was the substrate a relative standard deviation (RSD) of 11%, 18%, 14% and 20% was calculated for D-glucose, glycerol, propylene glycol, and ethylene glycol, respectively. The instruments were recalibrated after these experiments with fructose as the substrate and RSD values of 21%, 32%, 20% and 22%, were calculated for fructose, glycerol, propylene glycol and ethylene glycol, respectively. Again the instruments were recalibrated for the final set experiments with sucrose as the substrate and RSD values of 5% and 16% were calculated for sucrose and glycerol, respectively. Although instrumental error is present it is estimated that the average error was not more than 15%

between experiments. Although this may seem high, the results are qualitatively correct and can be used to identify general efficacy of the nine catalysts or catalyst combinations.

CHAPTER 3

RESULTS AND DISCUSSION

The focus of this research was to understand the mechanisms controlling the hydrogenolysis of sugars, namely glucose, fructose, and sucrose. Hydrogenolysis can be described as the cleavage of carbon to carbon or carbon to oxygen bonds, accompanied by the addition of hydrogen (Connor and Adkins, 1932). In order to examine the hydrogenolysis reaction of glucose, fructose, and sucrose, I developed analytical methods to detect for the various intermediates and products. Additionally, the efficacy of nine different catalysts and two different solvents in the conversion and selectivity of glucose, fructose, and sucrose into propylene glycol, ethylene glycol, and glycerol was determined.

In sugar hydrogenolysis it has been determined that catalyst is essential in order to convert the starting sugar (Tronconi *et al.*, 1992). Extensive studies have been done on developing effective catalysts for the hydrogenolysis of carbohydrates. Two types of catalysts promoted the desired results, favoring retro-aldolization over the dehydration reaction pathway: the first type was a series of metal oxides, most notably copper oxide, which promoted high selectivities, and the second type was nickel on alumina/silica, which promoted high conversions (Twigg, 1998).

A total of 36 experiments (Tables 1-4, details in Appendix D) were run during the current phase of the project, resulting in valuable catalytic hydrogenolysis data for various combinations of substrates, solvents, and catalysts. Several catalysts were studied in addition to those previously investigated by Wang and Furney (1995). The

catalysts used in the current study included palladium 1% on carbon, nickel on alumina/silica, copper (II) oxide, iron (III) oxide, boron oxide, aluminum oxide, nickel on kieselguhr, 5% ruthenium on carbon, and barium promoted copper chromite. Catalysts were studied individually, and in some cases up to three were combined to determine their effectiveness in obtaining both a high conversion of the starting sugar chain and a high selectivity toward C-C cleavage versus C-O cleavage (Figure 1).

A number of physical parameters are important to this type of process, including temperature, hydrogen partial pressure, and base. Twigg (1998) used a model compound, 2,4-pentanediol (2,4-PD) to establish a set of optimal reactor conditions that were selected for this study. The conditions chosen included a reactor temperature of 210 °C, 3.5 MPa hydrogen partial pressure, and NaOH as base. Two variables, solvents and catalysts, were studied during the current phase of the project. For these reaction conditions and the two variables, data were collected and catalysts or catalyst combinations most effective in sugar hydrogenolysis were identified. Table 5 presents a summary of the best catalytic results. However, it should be noted that each catalyst may have different optimum reaction conditions, thus further optimization will need to be explored.

Table 1. Summary of Experiments with Substrate D-Glucose, Solvent Water, 210 °C, and 3.5 MPa

CATALYST	TOTAL SELECTIVITY[a]	FINAL CONVERSION[b] (%)	YIELD[c] (%):		
			Propylene Glycol	Ethylene Glycol	Glycerol
Copper (II) Oxide	0.2026	97.46	8.02	2.18	9.54
Ba prom Cu-Chromite	0.1660	99.26	4.39	1.81	10.28
Nickel on Alumina/Silica	0.4397	90.44	22.07	4.25	13.45
Nickel on Alumina/Silica Copper (II) Oxide	0.3507	97.67	18.80	3.16	12.30
Palladium 1% on Carbon Boron Oxide	0.2420	97.52	6.90	0.92	15.78
Nickel on Alumina/Silica Iron (III)oxide	0.2857	99.16	16.64	2.17	9.53
Nickel on Alumina/Silica Aluminum Oxide Copper (II) Oxide	0.4489	95.56	21.84	4.80	16.25
5% Ruthenium on Carbon	0.3876	99.06	23.70	3.74	10.95
Nickel on Kieselguhr	0.4962	79.70	18.88	5.08	15.59

Highlighting indicates the catalyst which was most effective for selectivity, conversion, and yield of desired product.

[a] Selectivity = carbon moles of total desired products/carbon moles of substrate reacted

[b] Conversion = carbon moles of substrate reacted/carbon moles of substrate fed

[c] Yield = carbon moles of desired product/carbon moles of substrate fed

Table 2. Summary of Experiments with Substrate D-Glucose, Solvent 1M Ethanol, 210 °C, and 3.5 MPa

CATALYST	TOTAL SELECTIVITY	FINAL CONVERSION (%)	YIELD (%):		
			Propylene Glycol	Ethylene Glycol	Glycerol
Copper (II) Oxide	0.2704	86.48	10.08	3.51	9.79
Ba prom Cu-Chromite	0.1886	97.34	7.15	2.24	8.97
Nickel on Alumina/Silica	0.3732	93.03	18.07	4.60	12.04
Nickel on Alumina/Silica Copper (II) Oxide	0.3064	93.25	15.14	3.09	10.34
Palladium 1% on Carbon Boron Oxide	0.3401	91.50	8.47	2.04	20.61
Nickel on Alumina/Silica Iron (III)oxide	0.4893	93.11	23.53	6.16	15.87
Nickel on Alumina/Silica Aluminum Oxide Copper (II) Oxide	0.3146	94.47	17.57	2.25	9.90
5% Ruthenium on Carbon	0.4442	95.35	25.73	4.56	12.06
Nickel on Kieselguhr	0.3531	95.94	15.63	6.23	12.03

Table 3. Summary of Experiments with Substrate Fructose, Solvent 1M Ethanol, 210 °C, and 3.5 MPa

CATALYST	TOTAL SELECTIVITY	FINAL CONVERSION (%)	YIELD (%)		
			Propylene Glycol	Ethylene Glycol	Glycerol
Copper (II) Oxide	0.3819	100.00	21.14	4.80	12.26
Ba prom Cu-Chromite	0.1915	100.00	6.92	2.15	10.08
Nickel on Alumina/Silica	0.2732	100.00	13.50	1.84	11.98
Nickel on Alumina/Silica Copper (II) Oxide	0.4171	99.55	19.49	5.53	16.50
Palladium 1% on Carbon Boron Oxide	0.4559	99.97	13.49	1.95	30.14
Nickel on Alumina/Silica Iron (III)oxide	0.4369	100.00	19.90	6.30	17.48
Nickel on Alumina/Silica Aluminum Oxide Copper (II) Oxide	0.4292	100.00	22.31	5.71	14.90
5% Ruthenium on Carbon	0.4494	99.97	24.49	6.70	13.74
Nickel on Kieselguhr	0.4529	100.00	21.91	5.86	17.52

Table 4. Summary of Experiments with Substrate Sucrose, Solvent 1M Ethanol, 210 °C, and 3.5 MPa

CATALYST	TOTAL SELECTIVITY	FINAL CONVERSION (%)	YIELD (%)		
			Propylene Glycol	Ethylene Glycol	Glycerol
Copper (II) Oxide	0.4802	87.58	24.68	5.79	11.60
Ba prom Cu-Chromite	0.3617	99.83	13.85	4.90	17.36
Nickel on Alumina/Silica	0.5552	97.36	31.22	8.10	14.73
Nickel on Alumina/Silica Copper (II) Oxide	0.5273	98.30	28.00	9.08	14.74
Palladium 1% on Carbon Boron Oxide	0.5871	99.94	18.82	7.31	32.54
Nickel on Alumina/Silica Iron (III)oxide	0.6339	99.89	36.35	11.37	15.60
Nickel on Alumina/Silica Aluminum Oxide Copper (II) Oxide	0.5567	100.00	33.23	6.48	15.96
5% Ruthenium on Carbon	0.6330	100.00	39.41	9.24	14.65
Nickel on Kieselguhr	0.5120	99.96	25.51	12.44	13.23

Table 5. Summary of Results for Substrates Glucose, Fructose, and Sucrose and Solvents Water and 1M EtOH over Nine Catalysts or Catalyst Combinations.

Substrate/Solvent	TOTAL SELECTIVITY	FINAL CONVERSION (%)	YIELD (%)		
			Propylene Glycol	Ethylene Glycol	Glycerol
Glucose/Water	0.4962: Nickel on Kieselguhr	99.26: Ba prom. Cu-Chrom.	23.70: 5% Ruthenium on Carbon	5.08: Nickel on Kiesleguhr	16.25: Nickel on Alumina/Silica, Aluminum Oxide, Copper (II) Oxide
Glucose/1M EtOH	0.4893: Nickel on Alumina/Silica, Iron (III) Oxide	97.34: Ba prom. Cu-Chrom.	25.73: 5% Ruthenium on Carbon	6.23: Nickel on Kieselguhr	20.61: Palladium 1% on Carbon, Boron Oxide
Fructose/1M EtOH	0.4559: Palladium 1% on Carbon, Boron Oxide	100*	24.49: 5% Ruthenium on Carbon	6.70: 5% Ruthenium on Carbon	30.14: Palladium 1% on Carbon, Boron Oxide
Sucrose/1M EtOH	0.6339: Nickel on Alumina/Silica, Iron (III) Oxide	100**	39.41: 5% Ruthenium on Carbon	12.44: Nickel on Kieselguhr	32.54: Palladium 1% on Carbon, Boron Oxide

note: All calculations were performed on a per mole carbon basis

*100% conversion was obtained with six of the nine catalysts including Copper (II) Oxide; Ba. Prom. Cu-Chrom.; Nickel on Alumina/Silica; Nickel on Alumina/Silica and Iron (III) Oxide, Nickel on Alumina Silica, Aluminum Oxide, and Copper (II) Oxide; and Nickel on Kieselguhr.

**100% conversion was obtained with both Nickel on Alumina/Silica, Aluminum Oxide, and Copper Oxide; and 5% Ruthenium on Carbon.

3.1 Solvent Comparison

Two solvents, 1M EtOH and water, were studied with substrate D-glucose. The preferred solvent was determined to be 1M EtOH. In determining the better solvent for sugar hydrogenolysis at these conditions, final conversion, total selectivity, and yields of the desired products were considered.

FINAL CONVERSION

When comparing the efficiency of both solvents in converting D-glucose in sugar hydrogenolysis, the best result indicated almost 100% final conversion for both with the same catalyst, barium promoted Cu-chromite. For water and 1M EtOH, final conversion of D-glucose was 99.26% and 97.34%, respectively (Figures 4 and 5). Conversions were comparable with both solvents for each catalyst or catalyst combination.

TOTAL SELECTIVITY

For 1M EtOH five of the nine catalysts or catalyst combinations yielded a greater total selectivity than water. The greatest total selectivity calculated for water was 0.4962 with nickel on kieselguhr, and for 1M EtOH, 0.4893 for the catalyst combination nickel on alumina/silica and iron (III) oxide. Figure 6 illustrates the compiled selectivity results.

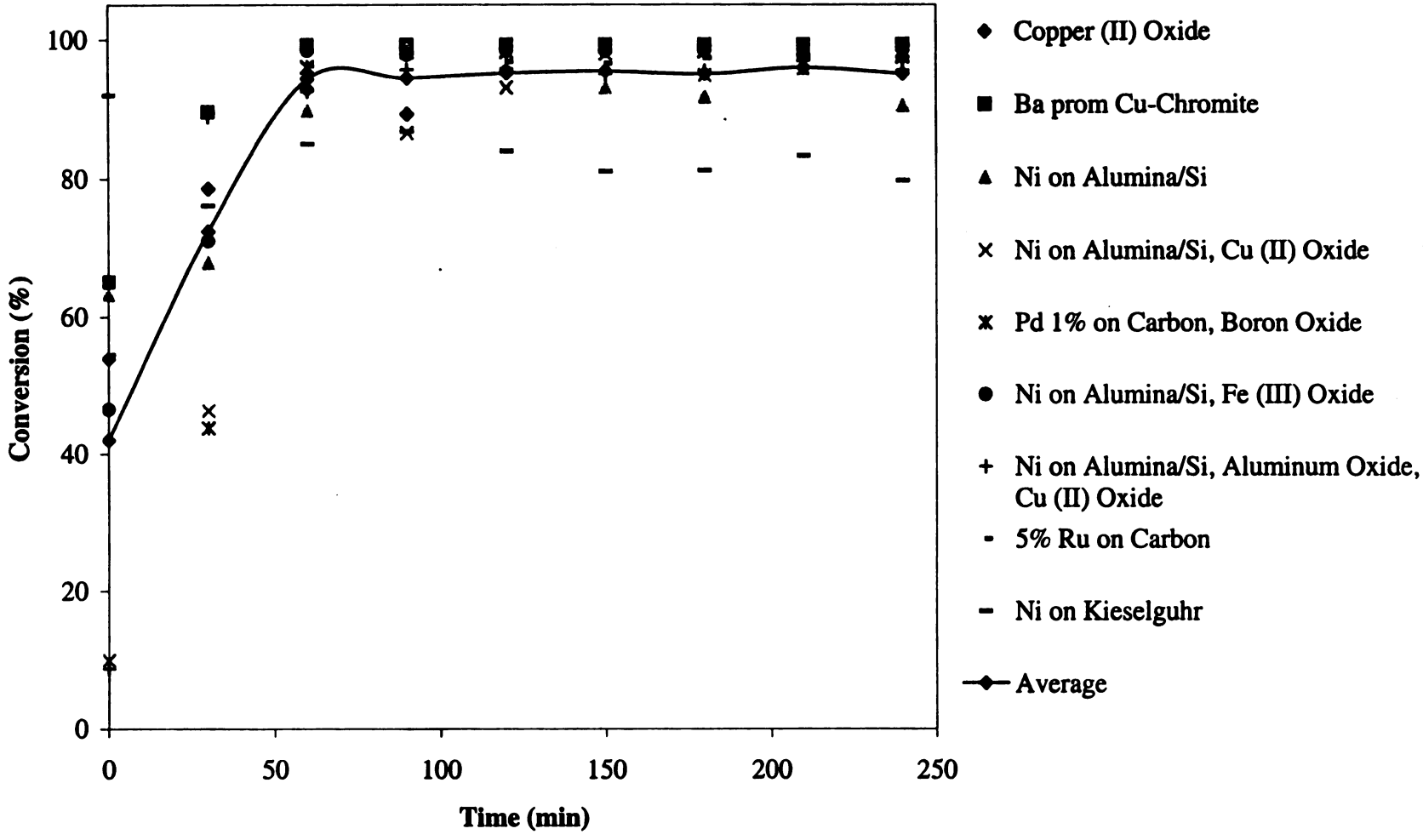


Figure 4. Conversion (%) versus reaction time (min) for substrate D-glucose, solvent water, 210 C reactor temperature, and 3.5 MPa hydrogen partial pressure

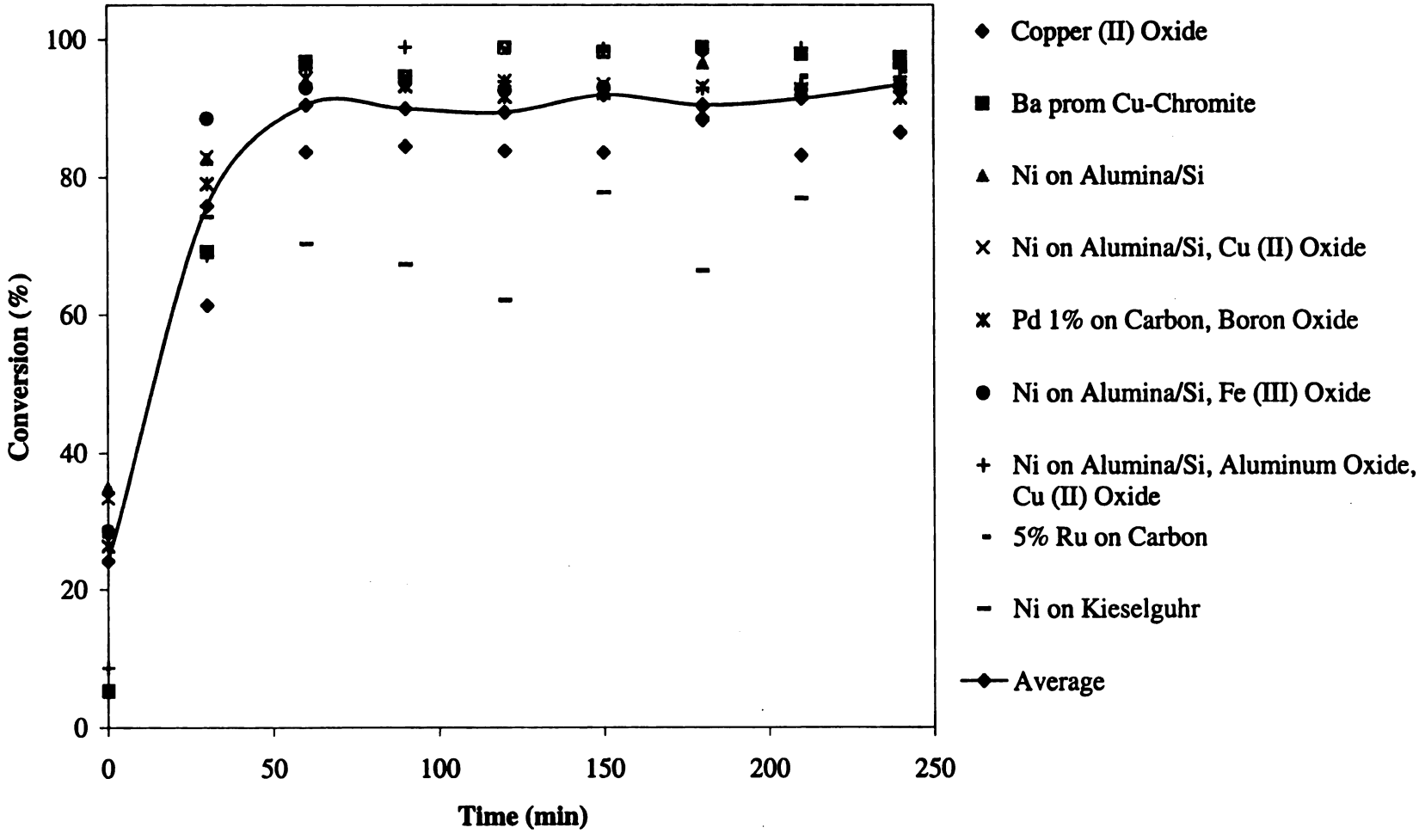


Figure 5. Conversion (%) versus reaction time (min) for substrate D-glucose, solvent 1M EtOH, 210 C reactor temperature, and 3.5 MPa hydrogen partial pressure

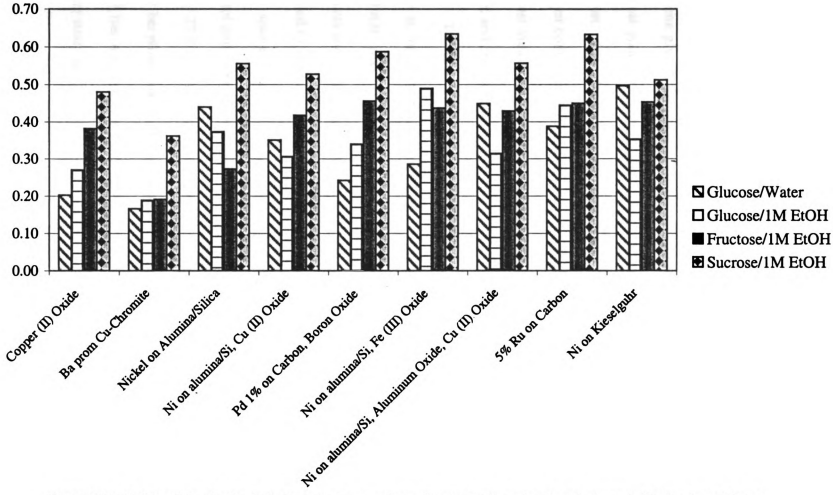


Figure 6. Total Selectivity for the desired products, propylene glycol, ethylene glycol, and glycerol, for the nine different catalysts or catalyst combinations at 210 C reactor temperature, and 3.5 Mpa hydrogen partial pressure.

YIELD

catal

solver

yield

ethyl

greate

catal

catal

greate

oxide

EtOH

1M I

produ

oppo

batch

sorbi

near-

using

EtOH

surfa

YIELD OF DESIRED PRODUCT

1M EtOH proved to give higher yields of the desired products for the same five catalysts or catalyst combinations. The greatest yield of propylene glycol obtained with solvent 1M EtOH was 25.73%, where, as with solvent water the greatest propylene glycol yield was 23.70%. Both these yields are for the catalyst 5% ruthenium on carbon. For ethylene glycol, the greatest yield with solvent 1M EtOH was 6.23%, and for water, the greatest yield was 5.08%. These yields were obtained using nickel on kieselguhr as the catalyst. For glycerol, using solvent 1M EtOH, the greatest yield was 20.61% with catalyst combination palladium 1% on carbon and boron oxide, and for solvent water, the greatest yield was 16.25% with catalyst combination nickel on alumina/silica, aluminum oxide, and copper (II) oxide (Figures 7 and 8).

Tables 1 and 2 present the above results for D-glucose with either water or 1M EtOH as the solvent. Although some of the best results are similar for the two solvents, 1M EtOH may be preferred over water because it is easier to separate from the end products and could thereby reduce separation costs. Some studies have used methanol as opposed to water as a solvent, but the results are contradictory. Tronconi *et al.* (1992) in batch studies concluded that methanol as a solvent led to low conversion of the sugar sorbitol and a very low selectivity. However, Boelhouwer et al. (1960) attained yields of nearly 75% of distillable polyalcohols, in a rotating autoclave with methanol as solvent, using beryllium oxide activated copper chromite catalyst to hydrogenate sucrose. 1M EtOH has not received much attention. However, from the current results it warrants further study as a possible solvent choice.

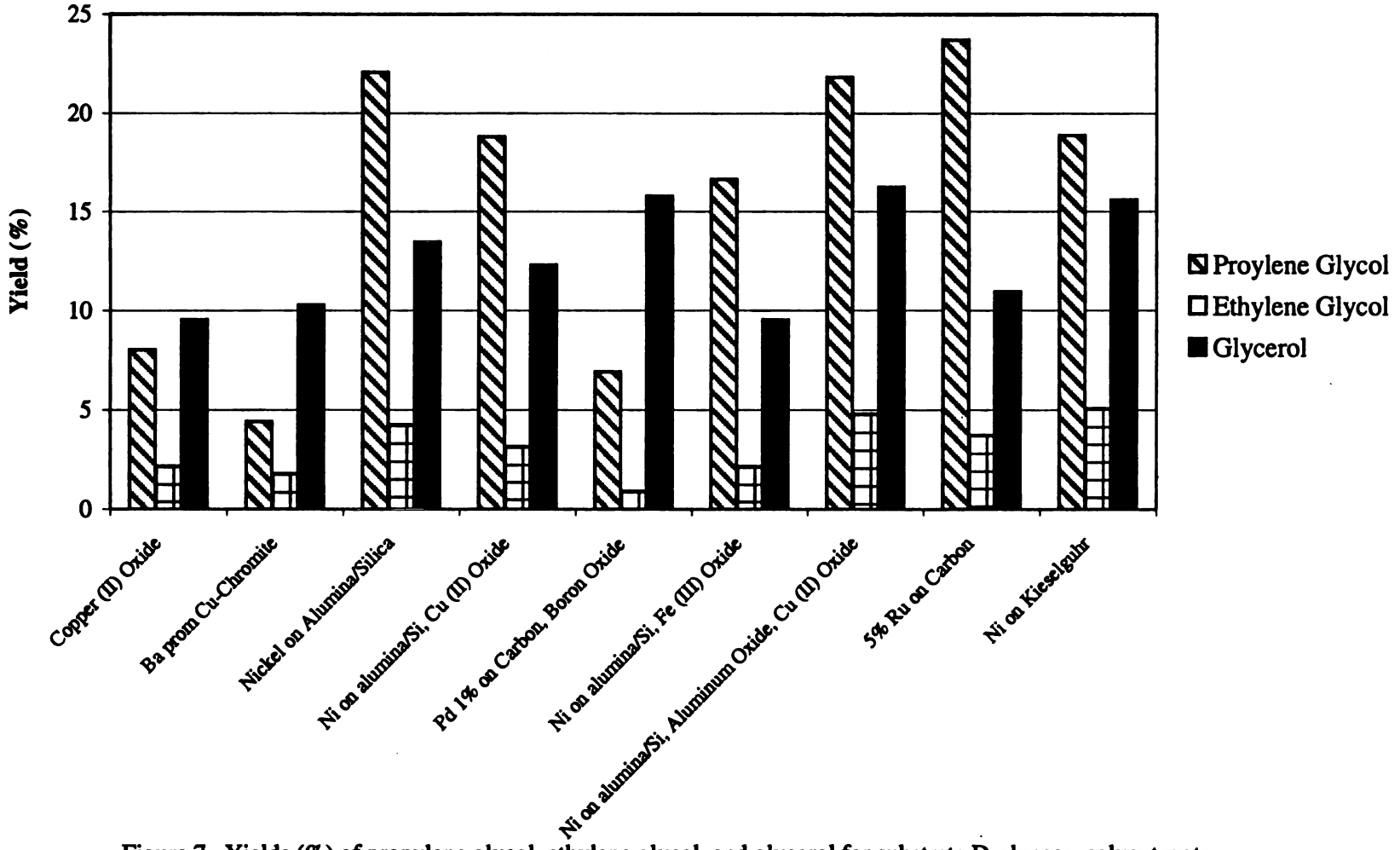


Figure 7. Yields (%) of propylene glycol, ethylene glycol, and glycerol for substrate D-glucose, solvent water, 210 C reactor temperature, and 3.5 MPa hydrogen partial pressure for the nine different catalysts or catalyst combinations.

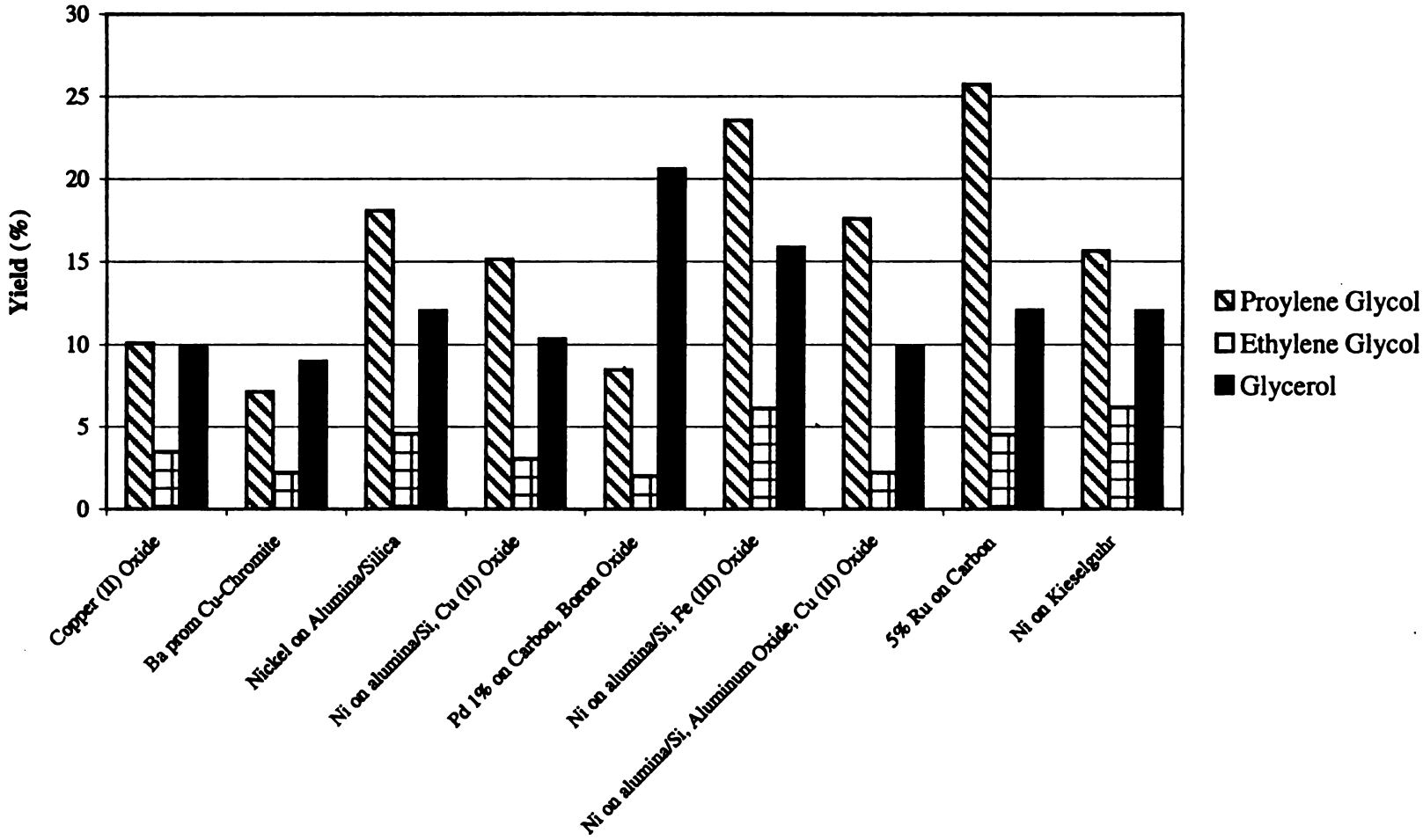


Figure 8. Yields (%) of propylene glycol, ethylene glycol, and glycerol for substrate D-glucose, solvent 1M EtOH, 210 C reactor temperature, and 3.5 MPa hydrogen partial pressure for the nine different catalysts or catalyst combinations.

3.2 Analysis of Nine Catalysts and their Efficacy in Sugar Hydrogenolysis

The ultimate goal of the current phase of the project was to identify catalysts that would promote C-C cleavage, and thus the production of propylene glycol, ethylene glycol, and glycerol, in sugar hydrogenolysis. The two main parameters used to determine the effectiveness of a given catalyst were the selectivity towards C-C cleavage and the overall conversion of the starting sugar chain.

As mentioned, Twigg (1998) established a set of optimum reactor conditions for a model compound, 2,4-pentanediol, and these conditions were adopted for this project. Reactor temperature was maintained at 210°C because Twigg (1998) determined that an increase in temperature resulted in greater C-C selectivity and overall 2,4-pentanediol conversion. Twigg (1998) indicated that the hydrogenolysis reaction is not occurring to any great extent at 150°C, and that the optimum operating temperature was between 190°C and 220°C. From a computer simulation study using model compound 2,4-pentanediol, conducted by Wang *et al.* (1999), increased temperature was found to greatly enhance the reaction rate; however it had little effect on selectivity.

In the current work, hydrogen partial pressure was held constant in the reactor at 3.5 MPa because it was in the optimum range determined by Twigg (1998). The effect of hydrogen partial pressure varies with the catalyst used. For a given catalyst, selectivity increases with the hydrogen pressure at low pressures (hydrogen concentration less than 110 mM, at medium pressures (hydrogen concentration greater than 110 mM and less than 150 mM) selectivity appears to be unaffected, and for high hydrogen pressure (hydrogen concentration greater than 150 mM) selectivity decreases (Wang *et al.*, 1999). Twigg (1998) concluded hydrogen partial pressure was inversely related to C-C

selectivity. Tronconi *et al.* (1992) observed with ruthenium on carbon catalyst in batch experiments, that a high hydrogen partial pressure was not required for sorbitol (feed 30% w/w) conversion; however, the use of low partial pressure gives rise to the formation of condensation products. Montassier *et al.* (1991) found when studying hydrogen partial pressures between 0-7 MPa, with substrate glucitol over Cu-Ru at 493K, that in the absence of hydrogen partial pressure, cyclodehydration was accompanied by the production of large quantities of degradation products (namely, carbon dioxide). Final optimization might benefit from a redesign of the current specifications of the reaction vessel, thereby allowing lower pressure systems to be studied (< 3.0MPa).

The base selected to promote the hydrogenolysis reaction was 1N NaOH. Tronconi *et al.* (1992) found in the absence of base, NaOH, low conversion of sugar sorbitol and a low selectivity of desired products resulted. Sorbitol is formed via hydrogenolysis of fructose (Andrews and Klaeren, 1989). Muller *et al.* (1991) noted that base promotes selectivity to propylene glycol with substrate saccharose, catalyst 5% ruthenium on carbon, 220°C, and 5.5 MPa. The role of NaOH seems associated with the cleavage of C-C bonds, the desired pathway in sugar hydrogenolysis (Tronconi *et al.*, 1992, Wang *et al.*, 1999).

All results were calculated on a per mole carbon basis. Multiplying the calculated concentrations of each compound by the number of carbons in the compound serves to normalize the results. Thus, for each of the reported yields, selectivities, and for conversion of starting substrate, a per mole carbon basis was used.

FINAL CONVERSION

Conversion is defined as the number of carbon moles of substrate reacted per carbon moles of starting substrate. The same number of carbon moles for glucose, fructose, and sucrose was provided for each experiment. However, the number of starting moles for D-glucose and fructose was twice the amount of sucrose. The catalyst that resulted in the greatest overall conversion of each of the three starting sugar chains was determined (Figures 5, 9, 10). In the experiments with D-glucose and 1M EtOH as the solvent, conversion of 97.34% was obtained with catalyst barium promoted copper chromite. Fructose and sucrose reached conversions of 100% for several different catalysts or catalyst combinations. Fructose reached 100% conversion over six of the nine catalysts or catalyst combinations and a conversion greater than 99.5% for all nine studied. The six were copper (II) oxide; barium promoted copper chromite; nickel on alumina/silica; nickel on alumina/silica and iron (III) oxide; nickel on alumina/silica, aluminum oxide, and copper (II) oxide; and nickel on kieselguhr. For sucrose 100% conversion was reached with two of the nine catalysts or combinations. The two catalyst combinations were nickel on alumina/silica, aluminum oxide, and copper (II) oxide; and 5% ruthenium on carbon. Tables 2-4 present the results of conversion for each starting substrate, D-glucose, fructose, and sucrose with solvent 1M EtOH. Figures 5, 9, and 10 illustrate the conversion data for each starting substrate over the nine catalysts or catalyst combinations. For detailed results of the amount of converted starting substrate at each 30 minute sample time interval refer to Appendix D. At this point, because conversion is so high, it is not the main issue or focus in determining the most effective catalyst or

catalyst combination for this reaction optimization. If conversion less than 100% is achieved, separation and recycle technologies can be employed.

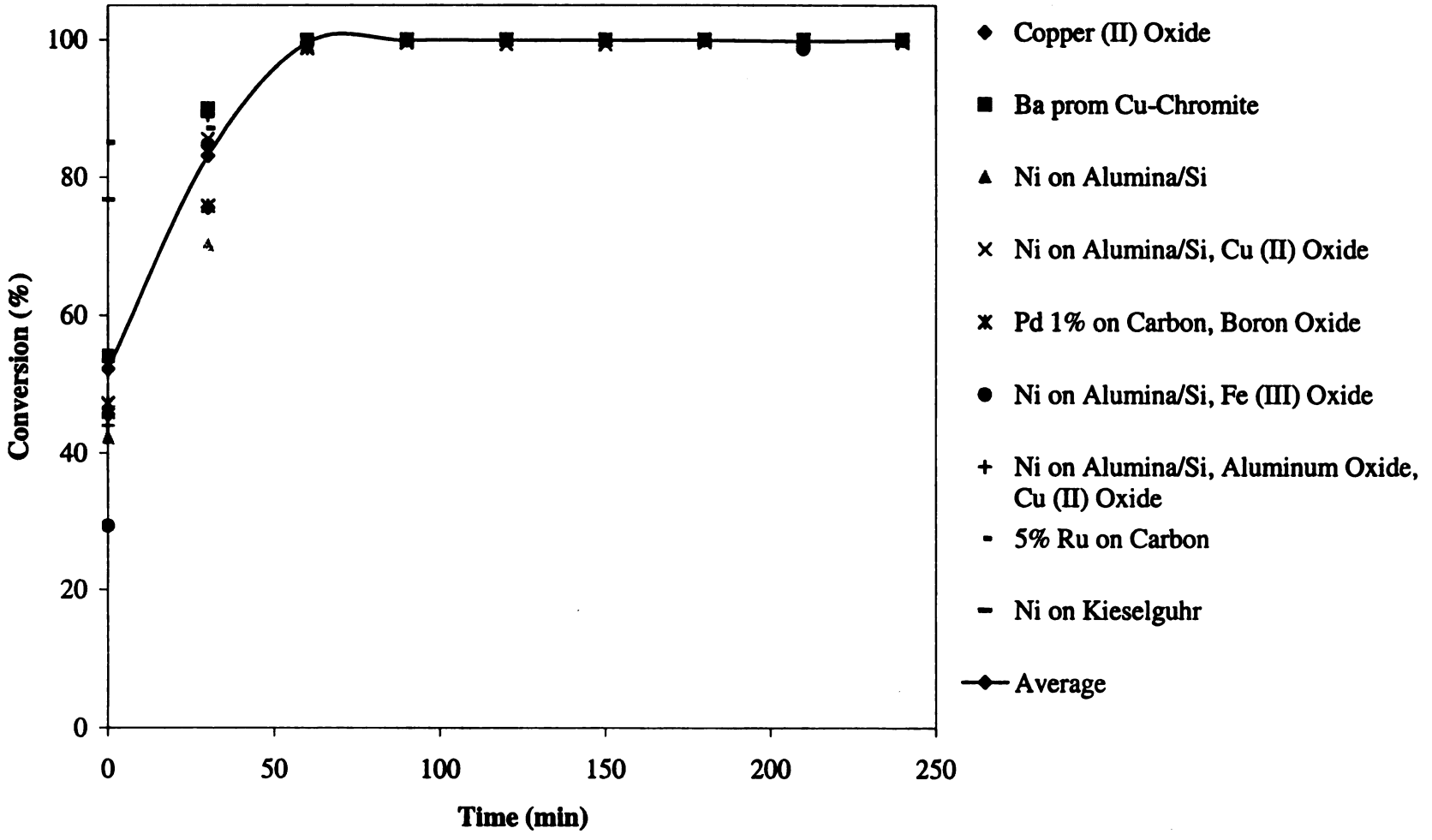


Figure 9. Conversion (%) versus reaction time (min) for substrate fructose, solvent water, 210 C reactor temperature, and 3.5 MPa hydrogen partial pressure

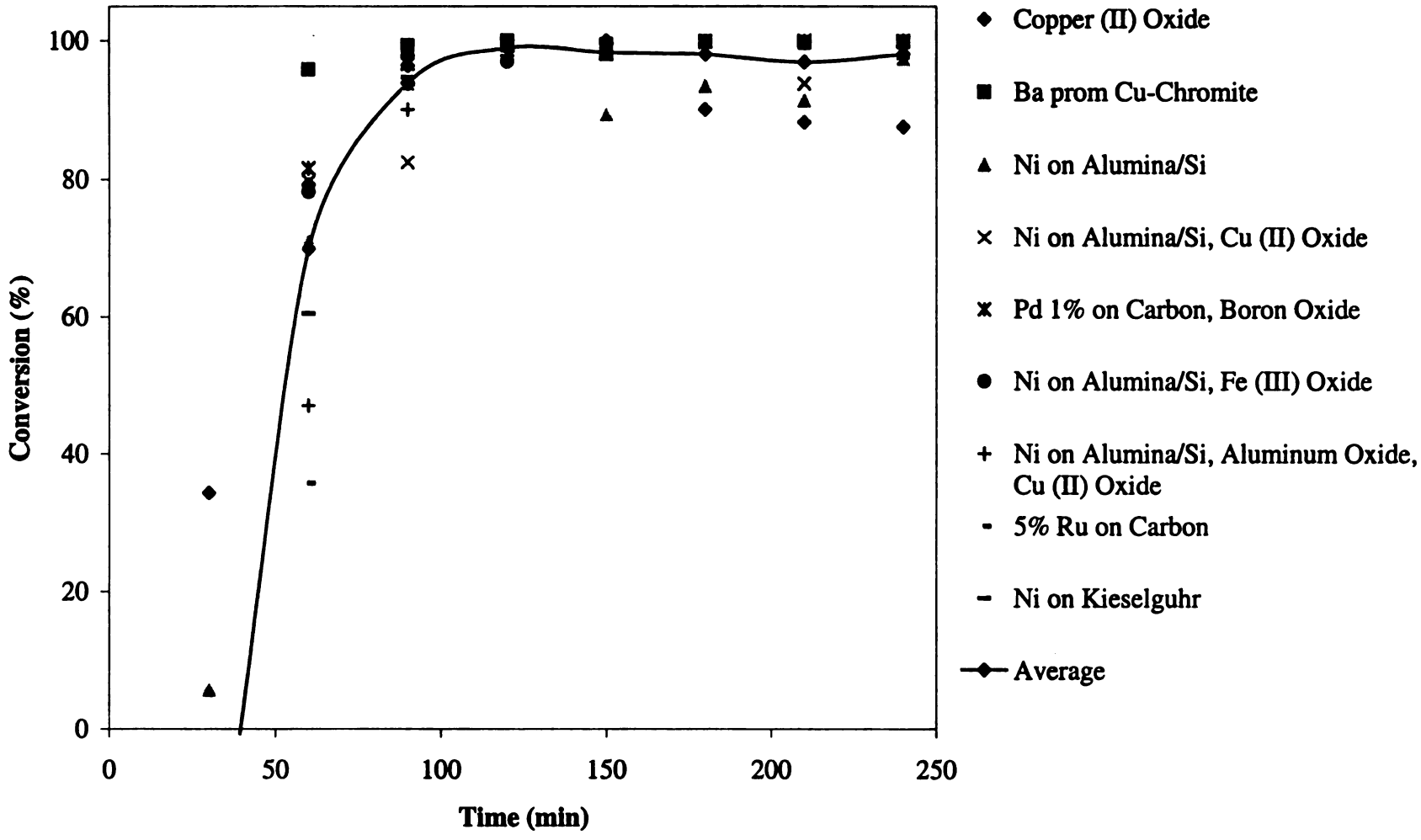


Figure 10. Conversion (%) versus reaction time (min) for substrate sucrose, solvent 1M EtOH, 210 C reactor temperature, and 3.5 MPa hydrogen partial pressure

TOTAL SELECTIVITY

Selectivity is defined as the ratio of carbon moles of desired products formed per carbon moles of starting substrate reacted. Again, the desired products are formed via C-C cleavage opposed to C-O cleavage and are propylene glycol, ethylene glycol, and glycerol. Sucrose yielded the highest total selectivity, 0.6339, with nickel on alumina/silica and iron (III) oxide as the catalyst. A total selectivity of 0.6339 achieved for substrate sucrose indicates that the desired products comprised more than 63% of the total products. This is promising because when comparing these results to fermentation we find the yield of desired products to be about 43%, with nearly 40% of the other remaining products going to CO_2. This is an important result because the selective conversion of sugars to useful chemicals while preserving all the carbon atoms in the starting material supercedes fermentation processes. Fermentation, which can also produce these high valued chemicals, causes loss of carbons from the starting material by producing carbon dioxide. For glucose with 1 M EtOH as the solvent a total selectivity of 0.4893 resulted with nickel on alumina/silica and iron (III) oxide as the catalyst combination. Using fructose as the starting sugar chain, a total selectivity of 0.4559 with palladium 1% on carbon and boron oxide was achieved. Again, refer to Tables 2-4 and Figure 6 for a summary of total selectivity results. For detailed results of the total selectivity at each 30 minute sample time interval refer to Appendix D.

YIELD OF DESIRED PRODUCT

Yield of desired product is defined as the carbon moles of the desired product divided by the carbon moles of starting substrate and is equivalent to conversion multiplied by the selectivity. The yields of the desired products propylene glycol,

ethylene glycol, and glycerol were calculated at each 30 minute sample time interval and detailed results can be found in Appendix D.

a) Propylene Glycol

For D-glucose with 1M EtOH as the solvent, the greatest yield of propylene glycol was 25.73% with 5% ruthenium on carbon as the catalyst. For experiments with fructose as the starting substrate a yield of 24.49% was obtained with 5% ruthenium on carbon. Using sucrose as the starting substrate a yield of 39.41% also resulted with 5% ruthenium on carbon. It can be concluded that 5% ruthenium on carbon promotes the production of propylene glycol for starting substrates D-glucose, fructose, and sucrose. This supports previous research in sugar hydrogenolysis preformed with catalyst 5% ruthenium on carbon. The role of 5% ruthenium on carbon catalyst consists in promoting the hydrogenation and dehydrogenation reactions. Both the conversion of D-glucose, fructose, and glycerol involve a first dehydration step to give a reactive aldehydic species. Thus, the reactions can not proceed in the absence of the catalyst, which also diminishes the selectivities to the most reduced products (glycols) (Tronconi *et al.*, 1992).

Propylene glycol is primarily formed by the hydrogenation of glycerol (Clark, 1958). If the reaction proceeds for too long, the glycols could degrade to alcohols or hydrocarbons. If glycerol was hydrated alone a 2:1 ratio of propylene glycol to ethylene glycol resulted (Clark, 1958). The current work illustrated a ratio greater than 3:1 for propylene glycol to ethylene glycol in the hydrogenolysis of D-glucose, fructose, or sucrose. Refer to Figures 8, 11, and 12 for a summary of the compiled results.

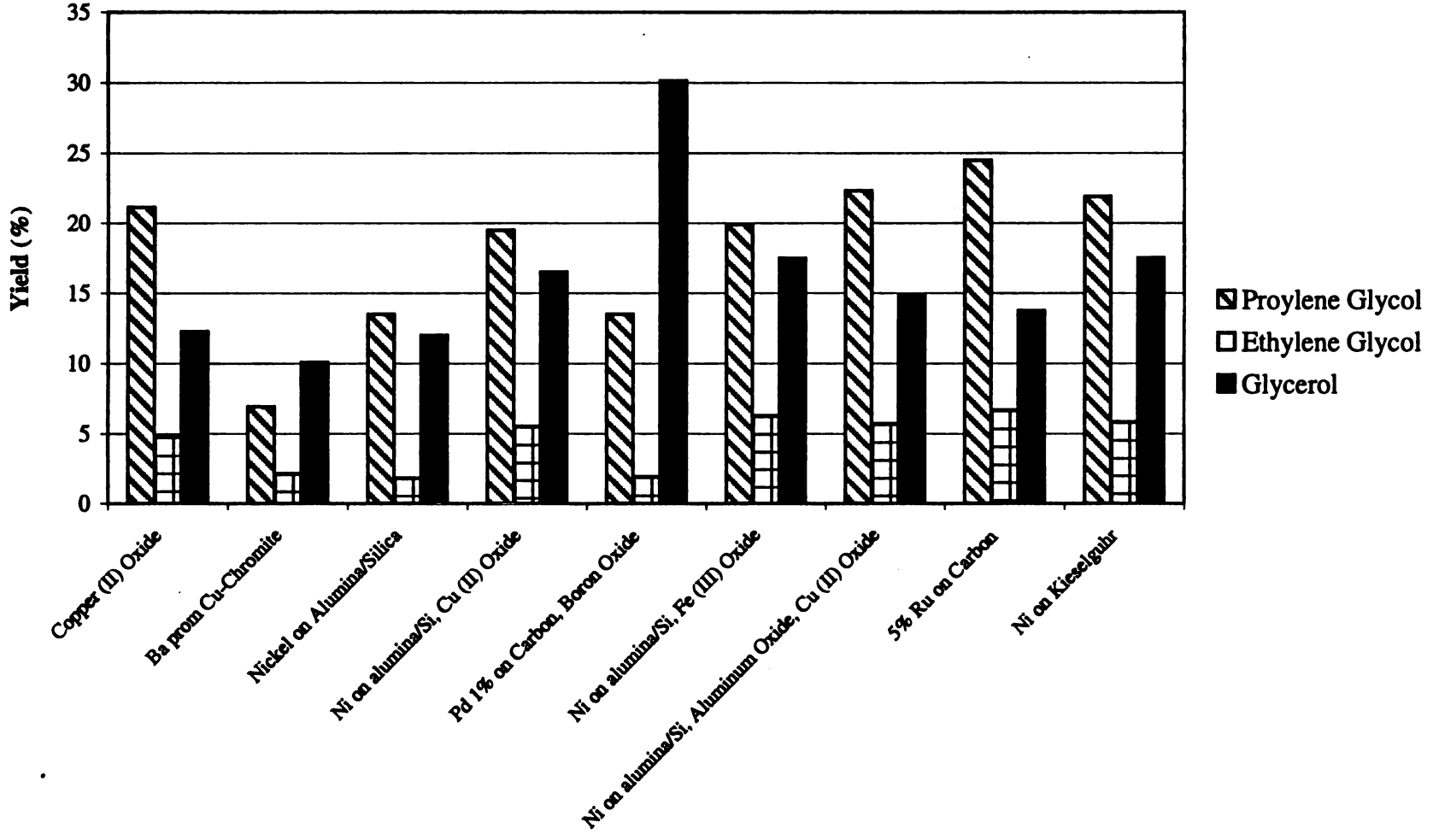


Figure 11. Yields (%) of propylene glycol, ethylene glycol, and glycerol for substrate fructose, solvent 1M EtOH, 210 C reactor temperature, and 3.5 MPa hydrogen partial pressure for the nine different catalysts or catalyst combinations.

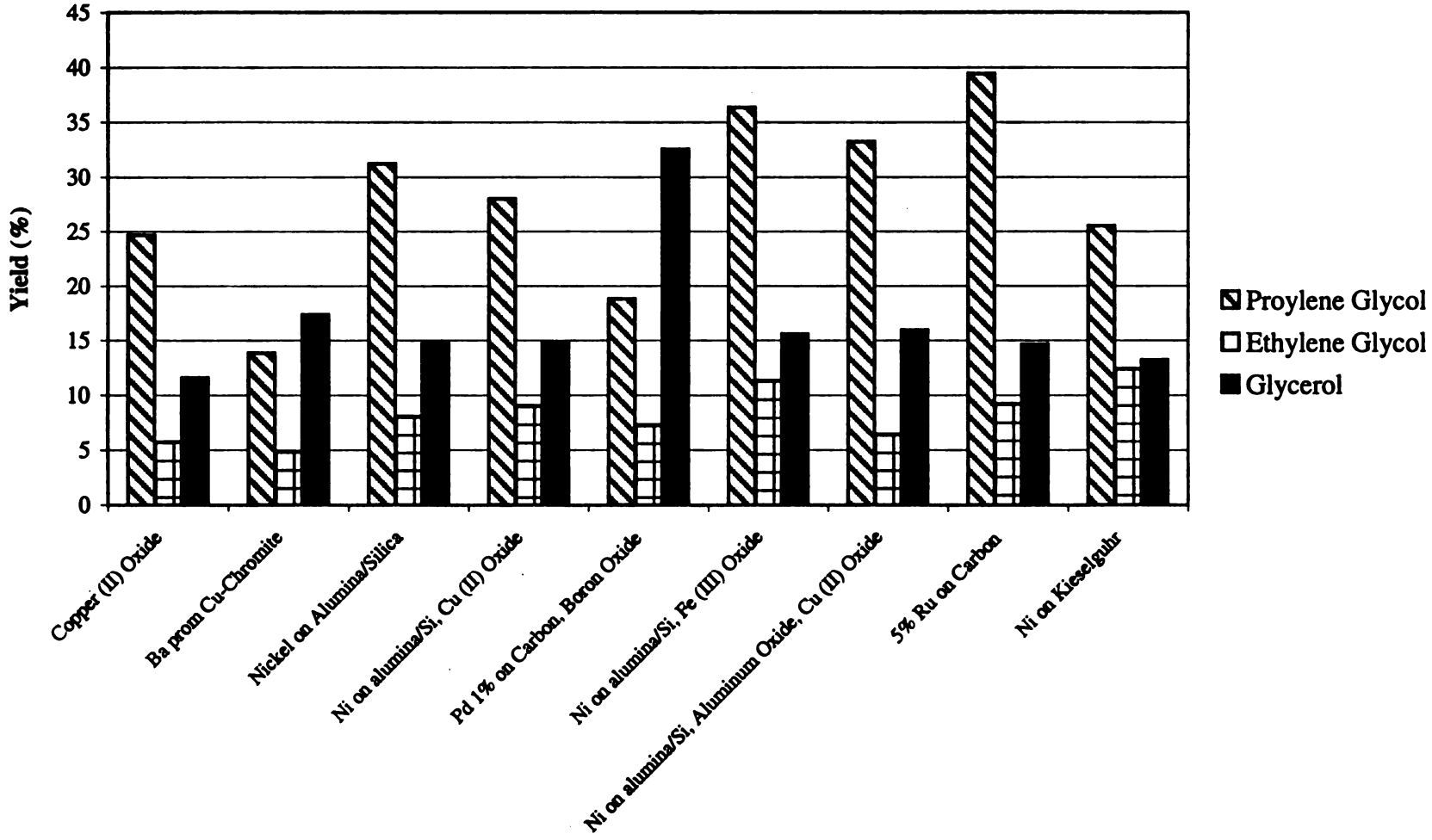


Figure 12. Yields (%) of propylene glycol, ethylene glycol, and glycerol for substrate sucrose, solvent 1M EtOH, 210 C reactor temperature, and 3.5 MPa hydrogen partial pressure for the nine different catalysts or catalyst combinations.

b) Ethylene Glycol

For D-glucose with 1M EtOH as the solvent, the greatest yield of ethylene glycol achieved was 6.23% with nickel on kieselguhr as the catalyst. For fructose as the substrate the greatest yield was 6.70% and was obtained with 5% ruthenium on carbon. Using sucrose as the substrate a yield of 12.44% resulted with nickel on kieselguhr as the catalyst. Again, refer to Figures 8, 11, and 12 for a summary of the results.

c) Glycerol

For D-glucose with 1M EtOH as the solvent, the greatest yield of glycerol was 20.61% with palladium 1% carbon and boron oxide catalyst combination. For experiments with fructose as the substrate a yield of 30.14% was obtained with palladium 1% on carbon and boron oxide. Using sucrose as the substrate a yield of 32.54% resulted with palladium 1% on carbon and boron oxide as the catalyst combination. Refer to Figures 8, 11, 12 for a summary of the complete results.

Montassier et al. (1991) found at temperatures near 373K, hydrogenolysis of glucose yields sorbitol and hydrogenolysis of xylose yields xylitol. For higher temperatures, 423K or greater, these compounds react further resulting in dehydration products. These reactions are generally considered to be the result of C-C and C-O bonds, therefore sorbitol can be converted into glycerol, 1,2-propanediol and ethylene glycol in a mixture with numerous other alcohols and polyols but the yield of glycerol remains below 40% of the initial sorbitol (Montassier *et al.*, 1991).

Again, results for the specific yields for each of the three desired compounds, propylene glycol, ethylene glycol, and glycerol, at each 30 minute time interval for each experiment can be found in Appendix D.

These results are competitive and supercede many of the other reported yields for these commercially viable compounds. Tronconi *et al.* (1992) reported yields between 7.3-36.2 wt % for propylene glycol and 5-18.1 wt % for ethylene glycol with starting substrate sorbitol and 5% ruthenium on carbon as the catalyst in a continuous reactor. VanLing *et al.* (1967) reported a yield of 10 wt % for ethylene glycol and 35.1 wt % for glycerol with sucrose as the starting substrate and catalyst $CuO\text{-}CeO_2\text{-}SiO_2$ in a batch reactor. At very mild conditions, temperature 100 °C and pressure 2.0 MPa with catalyst $H_2Ru(PPh_3)_4$ catalyst in N-methyl-2-pyrrolidinone and starting sugar fructose, Andrews and Klaeren (1989) obtained yields of 8 wt % ethylene glycol and 26 wt % glycerol. Our preliminary results with substrates glucose, fructose, and sucrose compare well with the optimized systems and scale-up of others, as illustrated.

3.3 Analysis of the Reaction Products formed During Catalytic Hydrogenolysis of D-glucose, Fructose and Sucrose

Hydrogenolysis sugars yield a complex mix of products because of the multiple C-C and C-O bonds of sugar available for cleavage. It is very difficult to tie the various reaction products of sugar hydrogenolysis to a specific bond cleavage reaction due to the existence of more than one pathway to the same product. In this work, to examine and explore the mechanism of sugar hydrogenolysis, gas chromatography/mass spectrometry and liquid chromatography/mass spectrometry were employed. Products that were identified included ethylene glycol, propylene glycol, lactic acid, glycolic acid, glycerol, glyceraldehyde, glyceric acid, 3-deoxy-tetronic acid, erythritol, threitol, erythronic, threonic, deoxy hexons lactonic, 3-deoxyhexonic, methanol, ethanol, acetone, 3-methyl-2-butanone, 2-methyl pentane, 3-buten-2-one, and 1-hydroxy-2-propanone. This is in agreement with the findings of VanLing et al. (1967) who reported glycerol, ethylene glycol, and propane-1,2-diol composed 58.2 wt % of the products and the remaining products included tetritols, pentitols, hexitols, dehydrated hexitols, butane-2,3-diol, methyl D-glucopyranosides, and dehydrated hexitols.

It is desirable to make the hydrogenolysis of sugars more selective. The C-O cleavage is to a great extent responsible for the complication of sugar hydrogenolysis products; therefore minimizing the C-O cleavage is expected to make the reaction more selective. Reduction of C-O cleavage is expected to increase the yield of glycerol, the highest valued major product of sugar hydrogenolysis. Glycerol preserves all the oxygen atoms in the starting sugar molecule. Muller *et al.* (1991) observed that the hydrogenolysis of fructose yields an enediol as a reaction intermediate and the formation of polyols in the presence of less catalyst. More specifically, hydrogenolysis of fructose

yields a combination of mannitol and glucitol (sorbitol) and glycerol, where glycerol is 15% of the product (Andrews and Klaeren, 1989). It also has an intermediate selectivity between glucose and mannose. The glycerol is produced from the hydrocracking of the single C(3)-C(4) bond. The glucitol can continue to react under the conditions of base, NaOH, and ruthenium catalyst and produce an aldehydic intermediate which further yields either glycerol or lactic acid. The production of lactic acid facilitated by base produces 1,2-propanediol. 1,2-ethanediol is a by-product of glycerol production (Tronconi *et al.*, 1992).

Most of the work reported in the literature has focused on hydrogenolysis of D-glucitol; however some studies have included xylitol as a feedstock. With xylitol as a feedstock, 25% of the products were unidentified and the remaining 75% consisted of 1,2-propanediol and glycerol, with an equal amount of ethylene glycol and ethanol (Montassier *et al.*, 1991). It was concluded that the retro-Claisen reaction dominated over the retro-Michael with this substrate. Erythritol is converted mainly into dehydroxylation products. The majority, 80%, is 1,2-butanediol and small amounts of 2,3-butanediol are formed. The other 20% are retro-Claisen products, namely glycerol, 1,2-propanediol, CO_2, and ethylene glycol. Initially the presence of 1,2,3 and 1,2,4-butanetriols were observed (Montassier *et al.*, 1991). Some experiments on the hydrogenation of glycerol show that it is not converted into 1,2-propanediol; however, glyceraldehyde is converted to a mixture of 1,2-propanediol and glycerol. Glyceraldehyde was detected and can be considered a reaction intermediate.

Referring to Figure 1, the proposed mechanism of sugar and sugar alcohol hydrogenolysis, we can identify numerous reactions. The dehydration and retro-

aldolization of the β-hydroxy carbonyl are reversible reactions catalyzed by the base catalyst (hydroxide ion). This base catalyst is also directly involved in the rate limiting step of dehydrogenation of the substrate and activation of hydrogen. The dehydrogenation of the open chain sugar chain is promoted by a transition metal catalyst, which also is responsible for activating the hydrogen. This activation is required in order to reduce any unsaturated compounds and hydrogenate ketones and aldehydes. The reaction of hydrogen with the metal catalyst forms a metal hydride species which has the ability to hydrogenate both C-C and C-O double bonds (Collman *et al.*, 1987; Masters, 1981; Pignolet, 1983). The hydrogenation reaction between the metal hydride and the unsaturated species must regenerate the metal catalyst, so that it can be re-used in the next cycle of catalysis. The metal hydride works as a hydrogen carrier to transport hydrogen from the substrate and the molecular hydrogen to those unsaturated intermediate products. Hydrogenation of ketones and aldehydes and dehydrogenation of alcohols are both reversible reactions (Wang *et al.*, 1991). The hydrogenation of alkene species is irreversible because the reaction equilibrium lies far to the product end (Collman *et al.*, 1987, Masters, 1981).

Head space sampling was used in addition to mass spectrometry for the further identification and quantification of the intermediates and products of sugar hydrogenolysis. The products that were quantified included acetone, ethanol, butyraldehyde, 2-pentanone, isobutanol, monomethyl ether, 2-pentanol, 3-pentanol, 3-penten-2-one, and 2-hexanol. The reaction pathway was studied and possible intermediates identified, then using headspace sampling the samples could be spiked in order to conclusively determine if a compound was present. In brief, the method of

analysis included bringing our sample volume up to a volume of 10 ml, followed by heating in a hot water bath to 80 °C. An internal standard was used and 0.6 ml of gas were injected into a gas chromatograph with a capillary column and flame ionizing detector. This preliminary work may serve as a foundation for further quantification of the many intermediates and products of sugar hydrogenolysis.

The knowledge surrounding this complex sugar hydrogenolysis process continues to increase through concentrated research studies. The findings presented in this paper lend insight on effective catalysts in the hydrogenolysis of D-glucose, fructose, and sucrose and support the proposed mechanism described in Figure 1 (Wang *et al.*, 1991). Preliminary work in identifying some of the various products and intermediates is a first step in furthering our understanding of the mechanisms involved and controlling the C-O selectivity.

CHAPTER 4

CONCLUSIONS AND IMPLICATIONS

Development of new technology is required for the economic conversion of sugars to industrial chemicals including glycerol, propylene glycol, and ethylene glycol. Selectivity controlled hydrogenolysis is a promising approach for conversion of sugars to polyhydric alcohols with no carbon atom loss. In this research with substrates D-glucose, fructose, and sucrose I examined the efficacy of nine different catalysts and two solvents in the sugar hydrogenolysis process. The reaction conditions chosen for this study were an isothermal batch reactor held at temperature 210°C, 3.5 MPa hydrogen partial pressure, and NaOH as base catalyst.

Catalysts or catalyst combinations which favored the desired reaction pathway included 5% ruthenium on carbon; nickel on kieselguhr; palladium 1% on carbon and boron oxide; and nickel on alumina/silica and iron (III) oxide. Yields as high as 39%, 33%, and 12% were attained for propylene glycol, glycerol, and ethylene glycol, respectively. Also, a total selectivity of 63% for the desired products was achieved under the studied reaction conditions. Barium promoted copper chromite yielded 100% conversions for substrates D-glucose, fructose, and sucrose.

This work supports previous findings (Wang et al., 1999; Furney, 1995; Twigg, 1998) suggesting that carbon-carbon cleavage occurs through retro-aldolization and that carbon-oxygen cleavage occurs through dehydration. Using model compound, 2,4-pentanediol, Twigg (1998) concluded that barium promoted copper chromitel; copper (II) oxide; palladium 1% on carbon and boron oxide; and nickel on alumina/silica and copper

(II) oxide promoted high selectivities. Through this work we have identified possible catalysts or catalyst combinations that favor the retro-aldolization reaction of sugars. However, it should be noted that each catalyst may have different optimum reaction conditions, and when a sole catalyst or catalyst combination is selected for optimization further reaction conditions will have to be explored. Our research thus far has been centered about developing a detailed understanding of the mechanism governing sugar hydrogenolysis, understanding the role of reaction conditions in selectivity control, and experimentation with a variety of catalysts to determine their selectivity. We have defined a set of reaction conditions which favor the retro-aldolization reaction pathway in sugar hydrogenolysis, determined effective catalysts or catalyst combinations, and identified many of the products in the sugar hydrogenolysis process.

As optimization of this process continues, a developed biomass conversion process to produce the afromentioned high valued chemicals will potentially replace current petroleum and fermentation based processes. Our process will have several advantages over the current industrial processes. These include potentially lower production costs, renewable feedstocks versus depleting fossil fuel feedstocks, and better environmental conditions – less toxic substances are used in the process. If this process can become highly selective, this process may have an immediate impact on the industrial production of propylene glycol, ethylene glycol, and glycerol.

CHAPTER 5

FUTURE WORK

As the process continues to be developed it is important to further study the industrial technologies of this process. Three recycle and separation technologies, namely distillation (evaporation), solvent extraction, and crystallization have been considered and reviewed to separate the sugar hydrogenolysis products. Distillation or evaporation may be employed to address the problems arising from separating any unconverted sugar from the products. However, we have seen that nearly 100% conversion for substrates D-glucose, fructose, and sucrose can be achieved. Examining the many byproducts of sugar hydrogenolysis reveals that their different boiling points may allow a distillation or evaporation technology to be used for effective separation. If some of the products were not separated completely, unconverted sugar and sugar alcohols could be recycled back to the reactor. An evaporation column may be more effective than a distillation column because it is less likely to accumulate sugar residue.

Solvent extraction is a possibility, but not likely to be a promising technology to pursue. It poses numerous problems including finding a suitable leachate that would selectively remove the byproducts and leave behind the sugar water. Crystallization is another technology that could be further studied; however, a non-aqueous environment is desired and a chemical to aid the crystallization process would need to be sought.

On the subjects of recycle and separation technologies, further study on possible solvents should be considered. In the current work ethanol was selected and compared with water. Ethanol proved to be effective. It may aid the separation technology and also

favor the desired selectivity. Other solvents such as propylene glycol and ethylene glycol should also be considered.

Reaction conditions used in this study were based on previous results using model compound, 2,4-pentanedio, on this project (Twigg, 1998). Temperature, hydrogen partial pressure, base concentration, and catalyst amount were constant for each experiment. However, now that catalyst testing has begun on actual sugar chains more studies need to be done. Optimum conditions may be different for each catalyst or catalyst combination. From literature and previous research on this project a reaction vessel which allows for a wider range of temperatures and pressures may result in greater yields of desired products and a higher selectivity. A reaction vessel should be constructed which would allow lower pressures (< 3.0 MPa) and higher temperatures (> 240°C) to be studied. A redesign of the reactor, including greatly increasing the diameter and reducing the height, would increase the surface area thereby allowing more of the reactants to be in contact with the hydrogen partial pressure. This increased contact may greatly enhance the reactions. A larger reaction vessel or scale-up should be developed that would better model an industrial batch study.

Another point which requires further study is the pH during the reaction. Hydrogenolysis produces an enediol as a reaction intermediate which is unfavored in acidic media, and hydrogenation occurs at acidic pH (pH 5 to 6) (Muller *et al.*, 1991). Therefore, separation between hydrogenation and hydrogenolysis could be obtained by modification of the pH during the reaction. If the reaction starts at an acidic pH, namely pH 6, then after the hydrogenation step base can be added up to pH 10 and this may result in an increased yield of the desired products. It can be assumed that when the reaction

begins the pH of the solution drops during the first hour, as acidic compounds are produced. A reaction vessel which would allow for the testing of the pH during the reaction and the later addition of the base catalyst, NaOH, could prove to enhance the desired selectivity.

Future research on the mechanisms controlling the selectivity of sugar hydrogenolysis will focus on understanding the chemistry involved in the complex reaction. If some of the other byproducts can be quantified and tied to one of the reaction pathways, then the effects of different reaction parameters on the process can be more readily understood. From this work using a one step sugar hydrogenolysis reaction process, we have been able to produce the high valued chemicals propylene glycol, ethylene glycol, and glycerol. Using this current catalyst research with sugar chain substrates, further development of an efficient selectivity-controlled sugar hydrogenolysis process should be sought which would inevitably lead to an industrially, economically, and environmentally significant process.

APPENDIX ITEMS

Appendix A: HPLC Calibration Curves

Appendix B: GC – glycols Calibration Curves

Appendix C: Error Estimation

Appendix D: Detailed Experimental Data

Appendix E: Intermediate Calculations

APPENDIX A

Calibration for D-Glucose

Concentration IS (sucrose) ppm = 1615.38

Standard	Glucose (ppm)	Area Glucose	Area IS	y = area/areaIS	x = conc./conc.IS
1	500	28079.74	171713.72	0.1635	0.3095
2	1010	48917.90	192038.81	0.2547	0.6252
3	2980	206036.19	154865.52	1.3304	1.8448
4	5020	413425.50	173660.02	2.3807	3.1076
5	7010	555957.99	159709.72	3.4811	4.3395
6	9030	770005.09	156563.25	4.9182	5.5900
7	11980	1089054.20	161569.91	6.7405	7.4162

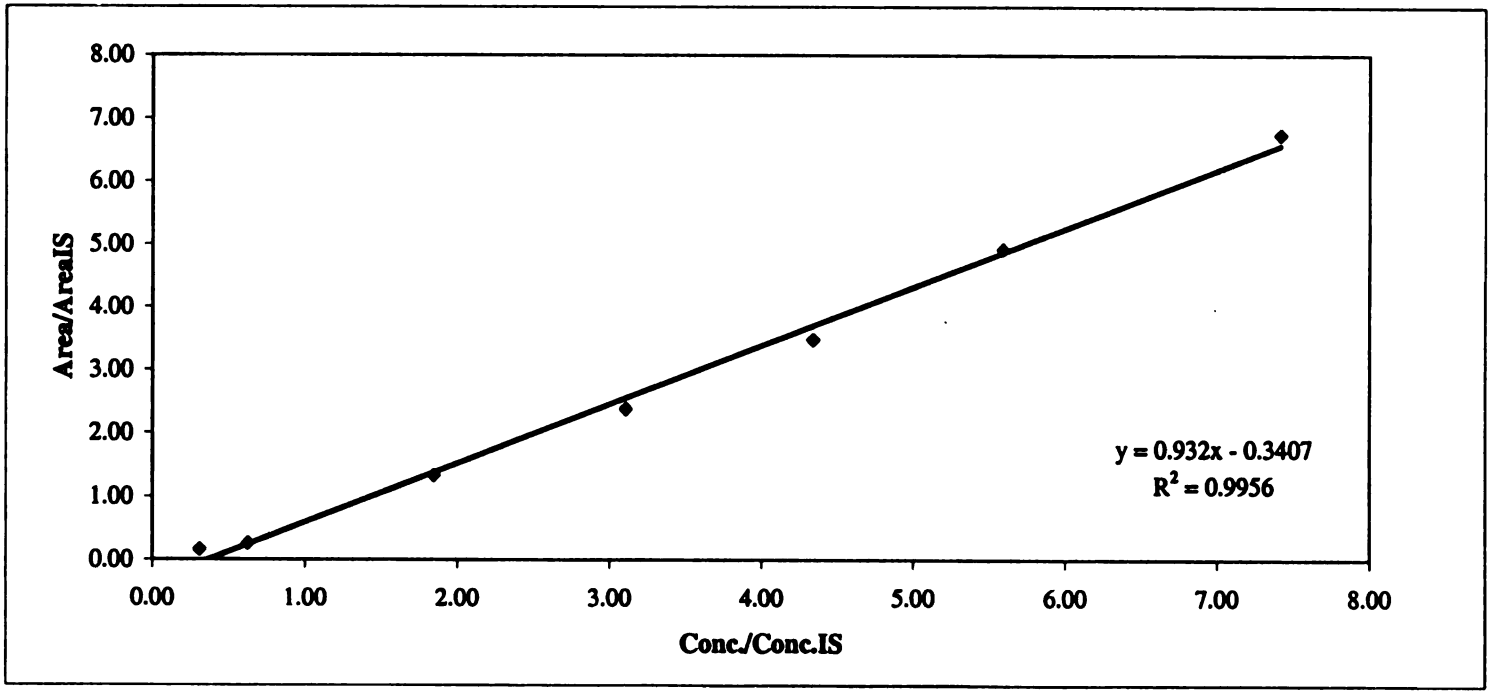


Figure A-1. Calibration Curve for D-Glucose

Calibration for Fructose | **Concentration IS (sucrose) ppm =** | **1614.69**

Standard	Fructose (ppm)	Area Fructose	Area IS	y = area/areaIS	x = conc./conc.IS
1	570	34630.75	169101.20	0.2048	0.3530
2	1020	77595.91	168159.51	0.4614	0.6317
3	3010	219061.26	204609.86	1.0706	1.8641
4	4980	431223.41	170140.22	2.5345	3.0842
5	7000	635018.59	166923.44	3.8043	4.3352
6	8980	830836.23	166088.08	5.0024	5.5614
7	12070	1182577.23	164675.74	7.1812	7.4751

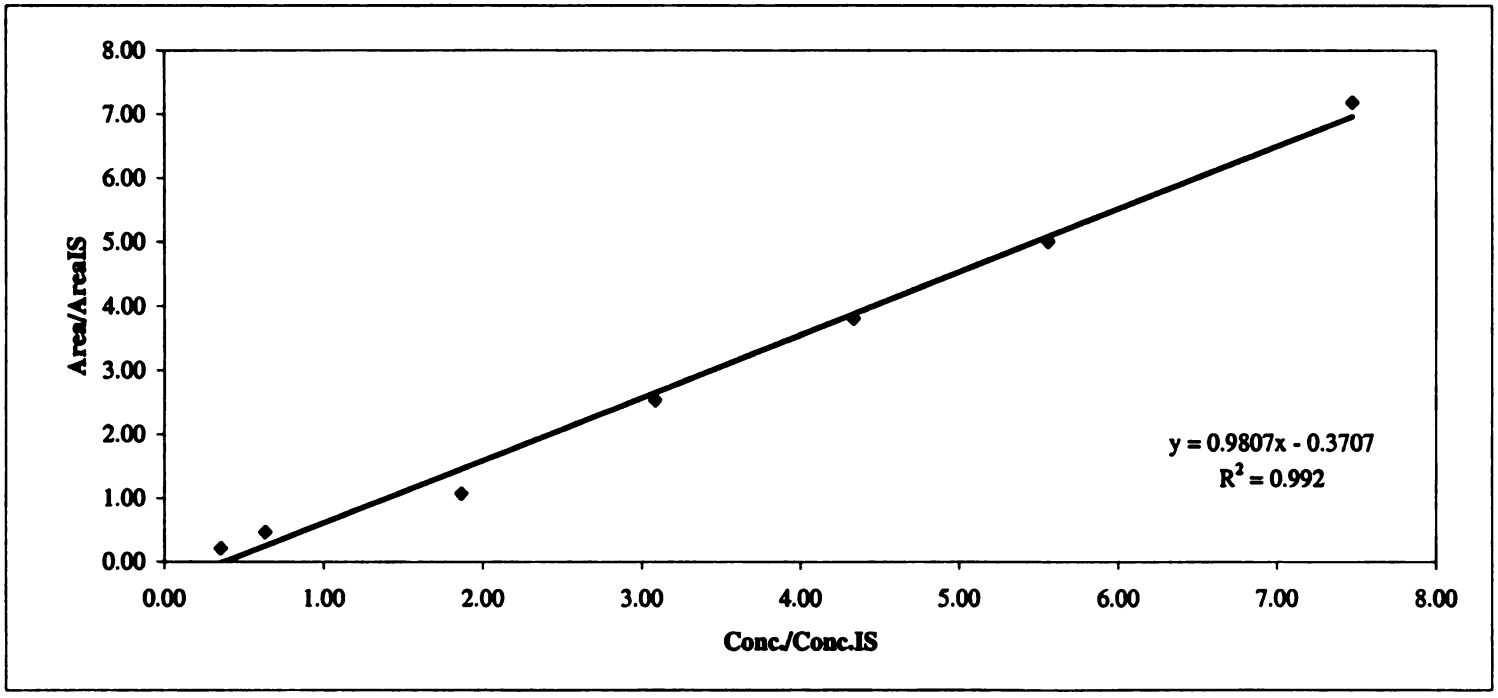


Figure A-2. Calibration Curve for Fructose

Calibration for Sucrose				Concentration IS (fructose) ppm =	1613.54
Standard	Sucrose (ppm)	Area Sucrose	Area IS	y = area/areaIS	x = conc./conc.IS
1	510	30935.81	158294.94	0.1954	0.3161
2	980	82780.96	190781.63	0.4339	0.6074
3	3010	250460.61	179972.55	1.3917	1.8655
4	4980	400533.96	207972.10	1.9259	3.0864
5	7010	636463.39	176387.32	3.6083	4.3445
6	8990	840763.00	176697.06	4.7582	5.5716

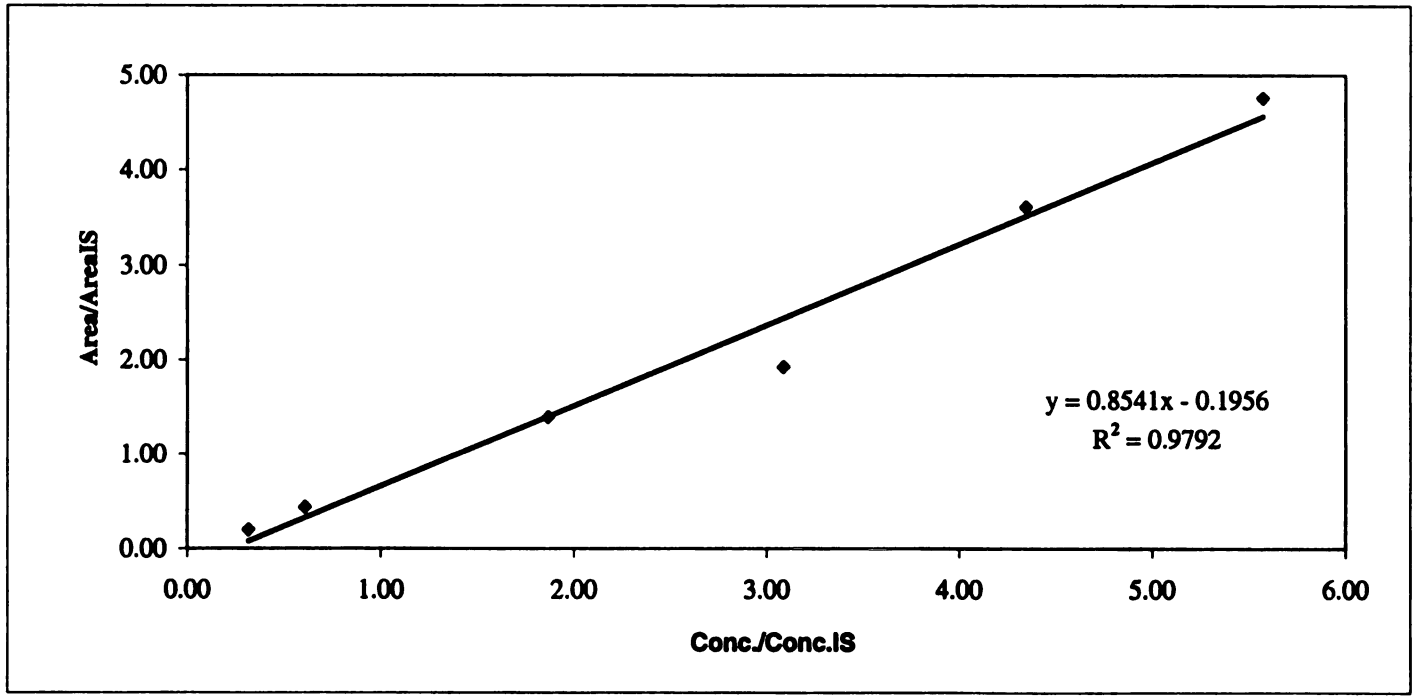


Figure A-3. Calibration Curve for Sucrose

Calibration for Glycerol | **Concentration IS (sucrose) ppm =** | **1615.38**

Standard	Glycerol (ppm)	Area Glycerol	Area IS	y = area/areaIS	x = conc./conc.IS
1	799	8151.80	171713.72	0.0475	0.4946
2	1371	17025.30	192038.81	0.0887	0.8487
3	1536	27717.46	173660.02	0.1596	0.9509
4	1832	26762.98	154865.52	0.1728	1.1341
5	1963	34844.21	159709.72	0.2182	1.2152
6	2140	48893.48	156563.25	0.3123	1.3248
7	2607	81744.34	161569.91	0.5059	1.6139

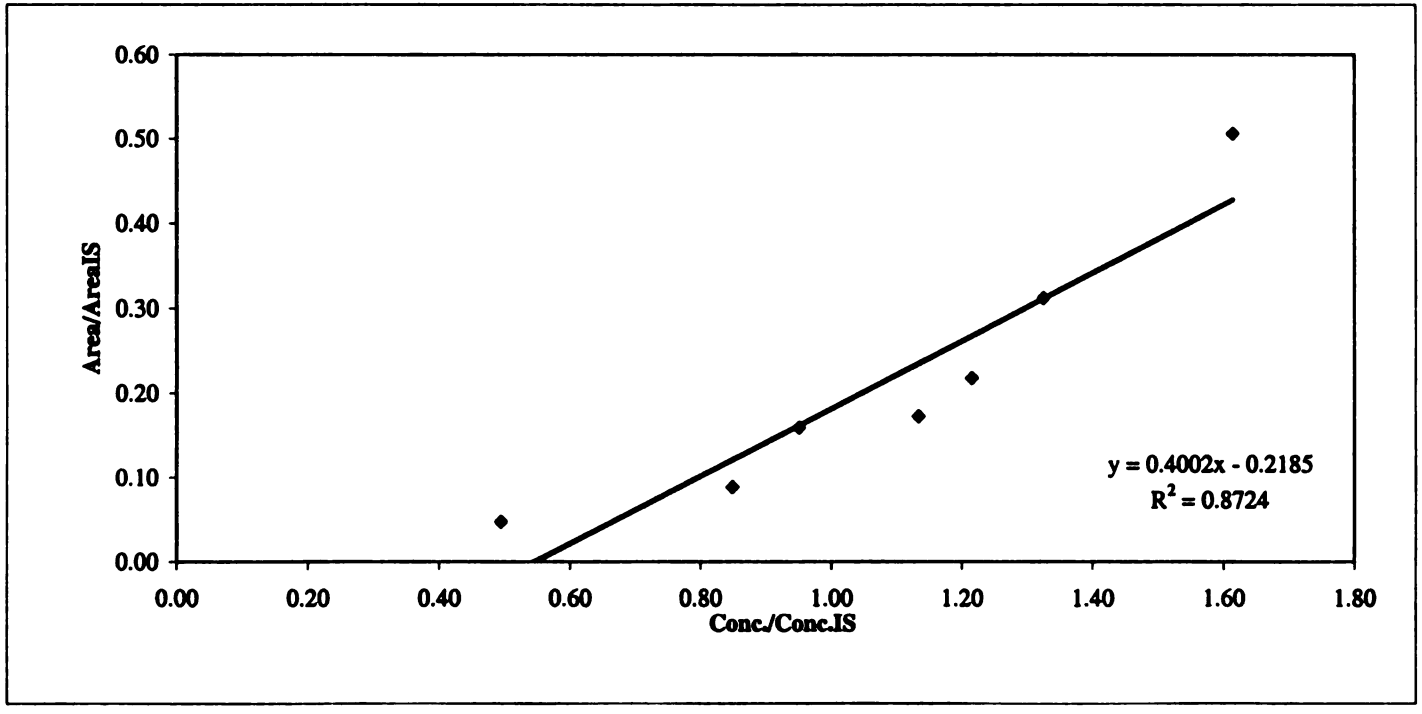


Figure A-4. Calibration Curve for Glycerol

APPENDIX B

Calibration for Propylene Glycol | **Concentration IS (1,4-butanediol) ppm =** 943.50

Standard	PG (ppm)	Area PG	Area IS	y = area/areaIS	x = conc./conc.IS
1	25.15	55720.12	593450.17	0.0939	0.0267
2	301.8	125796.30	628366.78	0.2002	0.3199
3	603.6	231790.12	534684.26	0.4335	0.6397
4	905.4	345203.51	543608.41	0.6350	0.9596
5	1207.2	548928.23	621353.51	0.8834	1.2795
6	1509	636746.83	565678.18	1.1256	1.5994
7	2012	830495.17	560714.79	1.4811	2.1325

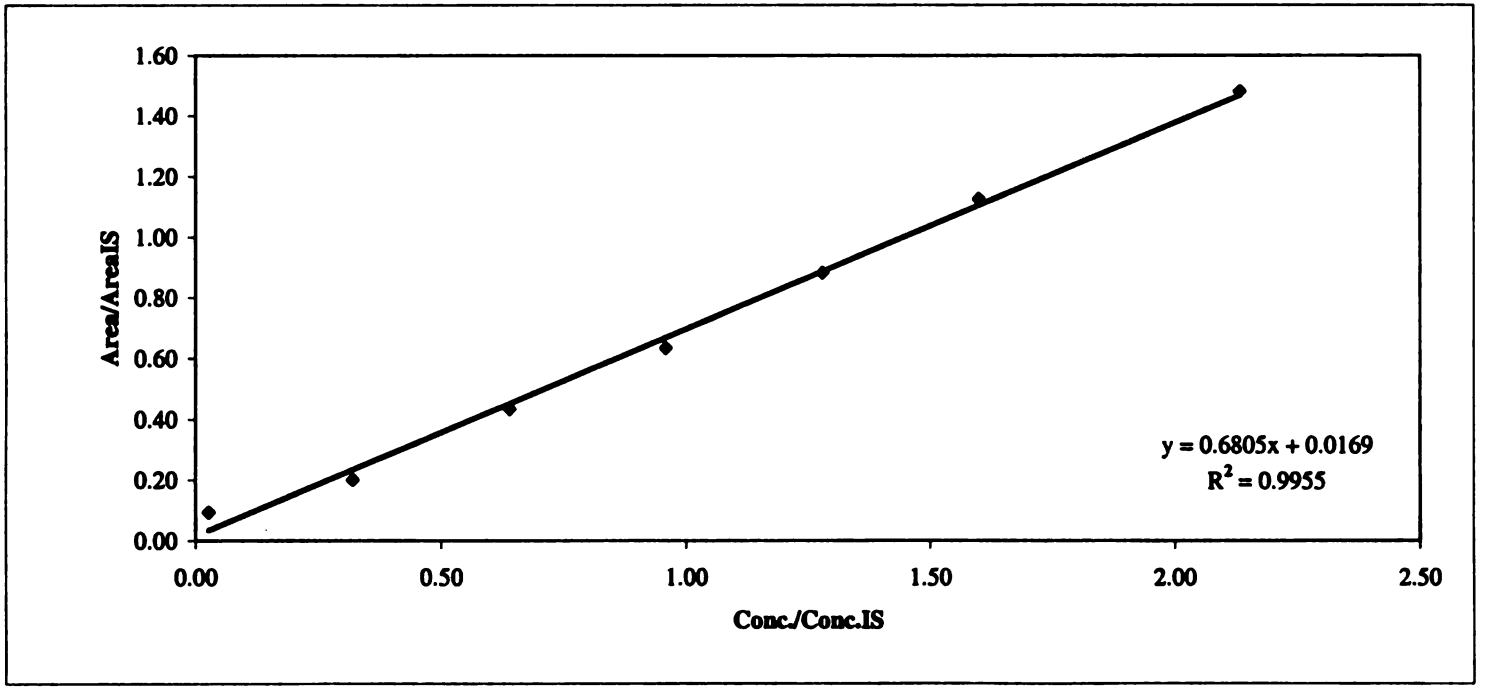


Figure B-1. Calibration Curve for Propylene Glycol

Calibration for Ethylene Glycol

Concentration IS (1,4-butanediol) ppm = 943.50

Standard	EG (ppm)	Area EG	Area IS	y = area/areaIS	x = conc./conc.IS
1	25.07	13150.68	439368.92	0.0299	0.0266
2	100.22	33170.56	512852.18	0.0647	0.1062
3	200.38	60406.90	511481.48	0.1181	0.2124
4	300.60	95698.94	458224.34	0.2088	0.3186
5	400.82	126403.84	429361.92	0.2944	0.4248
6	500.98	163914.82	445823.00	0.3677	0.5310
7	600.20	192635.41	458026.61	0.4206	0.6361

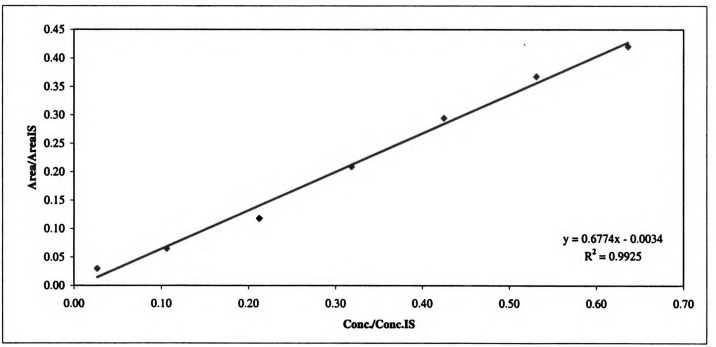


Figure B-2. Calibration Curve for Ethylene Glycol

APPENDIX C

ERROR ANALYSIS

ICV Preparation

Internal Calibration Verification

Ethylene Glycol

Area	Conc.IS (ppm)	Area IS	y = Area/AreaIS	x = Conc./Conc.IS	Conc.		
112769	943.5	562045.32	0.2006	0.3012	454.7	Std. Dev.	2.3
125965.39	943.5	624087.89	0.2018	0.3030	457.4	mean	455.0
92677.54	943.5	463927.64	0.1998	0.2999	452.8		

Relative Standard Deviation (%) **0.51**

Propylene Glycol

Area	Conc.IS (ppm)	Area IS	y = Area/AreaIS	x = Conc./Conc.IS	Conc.		
270198.5	943.5	562045.32	0.4807	0.6816	1029.0	Std. Dev.	16.5
300510.55	943.5	624087.89	0.4815	0.6828	1030.7	mean	1039.3
229176.98	943.5	463927.64	0.4940	0.7011	1058.4		

IS = 1,4-butanediol

Relative Standard Deviation (%) **1.59**

Internal Calibration Verification

Glycerol

Area	Conc.IS (ppm)	Area IS	y = Area/AreaIS	x = Conc./Conc.IS	Conc.		
180450.07	1615.4	142344.2	1.268	3.714	7799	Std.Dev.	1800
282045.28	1615.4	163237.9	1.728	4.863	10213	mean	9777
317187.09	1615.4	163626.5	1.938	5.390	11319		

Relative Standard Deviation (%) **18.41**

Glucose

Area	Conc.IS (ppm)	Area IS	y = Area/AreaIS	x = Conc./Conc.IS	Conc.		
499750.71	1615.385	142344.2	3.511	4.133	8678	Std.Dev.	322.6
567524.64	1615.385	163237.9	3.477	4.096	8601	mean	8824.8
611963.59	1615.385	163626.5	3.740	4.378	9195		

IS = sucrose

Relative Standard Deviation (%) **3.66**

Internal Calibration Verification

Glycerol

Area	Conc.IS (ppm)	Area IS	y = Area/AreaIS	x = Conc./Conc.IS	Conc.		
578624.25	1615.4	151699.66	3.814	10.077	21161	Std.Dev.	1982
532393.72	1615.4	141464.32	3.763	9.950	20895	mean	22170
658379.6	1615.4	148235.7	4.441	11.644	24452		

Relative Standard Deviation (%) **8.94**

Fructose

Area	Conc.IS (ppm)	Area IS	y = Area/AreaIS	x = Conc./Conc.IS	Conc.		
617039.16	1615.4	151699.66	4.068	4.526	9504	Std.Dev.	128
592353.16	1615.4	141464.32	4.187	4.648	9760	mean	9629
611226.38	1615.4	148235.7	4.123	4.582	9623		

IS = sucrose

Relative Standard Deviation (%) **1.33**

Internal Calibration Verification

Glycerol

Area	Conc.IS (ppm)	Area IS	y = Area/AreaIS	x = Conc./Conc.IS	Conc.		
470808.31	1613.5	166051.01	2.835	7.631	16006	Std.Dev.	513
497010.63	1613.5	164007.99	3.030	8.118	17029	mean	16490
491663.12	1613.5	168550.31	2.917	7.835	16434		

Relative Standard Deviation (%) **3.11**

Sucrose

Area	Conc.IS (ppm)	Area IS	y = Area/AreaIS	x = Conc./Conc.IS			
579707.07	1613.5	166051.01	3.491	4.317	9054	Std.Dev.	48
575747.01	1613.5	164007.99	3.510	4.339	9102	mean	9102
594978.55	1613.5	168550.31	3.530	4.362	9150		

IS = fructose **Relative Standard Deviation (%)** **0.52**

APPENDIX D

Exp #1 Date 7/21/99

Reaction Components:		
	Type	Amount
Substrate	D-Glucose	0.5 g
Solvent	Water	40 ml
Base	1N NaOH	1 ml
Catalyst	Copper (II) oxide	0.05 g

Reaction Conditions

	HPLC Run	GC Run
Temperature	Injection Amount	Injection Amount
210 °C	10 ml	3 ml
Pressure	Internal Standard	Internal Standard
3.5 Mpa	0.231 ml sucrose/ml	0.1875 ml 1,4-but./ml
	1615.385 ppm sucrose	943.5 ppm 1,4-but.

TIME (min)	HPLC Response Area:		
	Glucose	Glycerol	Sucrose (IS)
0	429231.59	0.00	170313.98
30	190045.56	0.00	165519.18
60	56108.68	0.00	158672.77
90	84619.39	5351.53	152565.66
120	30784.29	462.43	149964.9
150	684.92	637.82	154725.7
180	2055.26	583.22	153358.33
210	3489.35	423.88	144183.76
240	14934.29	2073.24	149174.44

TIME (min)	GC Response Area:		
	Propylene Glycol	Ethylene Glycol	1,4-butanediol (IS)
0	23967.80	18486.76	650033.16
30	15562.96	27779.24	665469.25
60	46299.71	55313.65	623255.12
90	67464.63	72497.73	652433.9
120	96584.66	70635.03	684861.56
150	116939.09	60980.95	645565.2
180	163810.25	68543.16	548257.34
210	211726.04	67600.80	676663.92
240	254743.41	78628.53	638829.14

Conversion (%)	YIELDS (%)			Total Selectivity
	Glycerol	Propylene Glycol	Ethylene Glycol	
53.83	8.97	0.42	0.55	0.1846
78.56	8.97	0.14	0.78	0.1258
92.89	8.97	1.21	1.59	0.1267
89.26	10.41	1.82	1.98	0.1591
95.56	9.10	2.61	1.84	0.1417
99.18	9.14	3.45	1.69	0.1440
99.02	9.13	5.92	2.22	0.1743
98.83	9.09	6.22	1.78	0.1730
97.46	9.54	8.02	2.18	0.2026

Exp #2 Date 7/22/99

Reaction Components:		
	Type	Amount
Substrate	D-Glucose	0.5 g
Solvent	Water	40 ml
Base	1N NaOH	1 ml
Catalyst	Ba prom. Cu-Chromite	0.05 g

Reaction Conditions

	HPLC Run	GC Run
Temperature	Injection Amount	Injection Amount
210 °C	10 ml	3 ml
Pressure	Internal Standard	Internal Standard
3.5 Mpa	0.231 ml sucrose/ml	0.1875 ml 1,4-but./ml
	1615.385 ppm sucrose	943.5 ppm 1,4-but.

TIME (min)	HPLC Response Area:		
	Glucose	Glycerol	Sucrose (IS)
0	316954.85	610.43	167239.61
30	84609.99	681.76	157639.29
60	529.13	2019.87	153133.03
90	144.47	1123.78	150452.46
120	173.10	3422.39	146985.36
150	308.92	2913.21	152865.02
180	351.79	699.88	147439.42
210	191.21	3063.21	155446.5
240	0.00	4754.90	149452.89

TIME (min)	GC Response Area:		
	Propylene Glycol	Ethylene Glycol	1,4-butanediol (IS)
0	27079.84	14361.09	639740.76
30	12501.92	33492.85	648791.42
60	32461.76	50957.85	602155.14
90	38563.42	46210.86	593410.20
120	63376.94	54891.11	620894.49
150	83176.09	65876.22	727633.16
180	98981.61	48203.82	675961.42
210	136800.54	61349.96	704980.91
240	155395.30	69693.84	687256.75

Conversion (%)	YIELDS (%)			Total Selectivity
	Glycerol	Propylene Glycol	Ethylene Glycol	
65.10	9.12	0.53	0.45	0.1552
89.59	9.15	0.05	0.95	0.1133
99.20	9.51	0.78	1.52	0.1190
99.24	9.28	1.01	1.40	0.1178
99.24	9.93	1.79	1.58	0.1340
99.23	9.75	2.05	1.62	0.1353
99.22	9.17	2.72	1.29	0.1328
99.24	9.78	3.72	1.56	0.1518
99.26	10.28	4.39	1.81	0.1660

Exp #3 Date 7/27/99

Reaction Components:		
	Type	Amount
Substrate	D-Glucose	0.5 g
Solvent	Water	40 ml
Base	1N NaOH	1 ml
Catalyst	Nickel on Alumina/Silica	0.05 g

Reaction Conditions

	HPLC Run	GC Run
Temperature	Injection Amount	Injection Amount
210 °C	10 ml	3 ml
Pressure	Internal Standard	Internal Standard
3.5 Mpa	0.231 ml sucrose/ml	0.1875 ml 1,4-but./ml
	1615.385 ppm sucrose	943.5 ppm 1,4-but.

TIME (min)	HPLC Response Area:		
	Glucose	Glycerol	Sucrose (IS)
0	310052.71	588.55	155094.3
30	272258.82	385.82	156319.58
60	86626.61	1984.54	164228.68
90	4805.99	2089.21	156896.14
120	30803.07	7285.83	155018.77
150	56299.93	10564.35	163865.65
180	65814.50	11010.85	157399.27
210	30352.18	8226.36	160031.96
240	70618.87	15749.07	144320.35

TIME (min)	GC Response Area:		
	Propylene Glycol	Ethylene Glycol	1,4-butanediol (IS)
0	31929.75	35707.50	677540.99
30	40659.34	70532.37	546476.97
60	102061.51	126924.23	641620.73
90	288061.02	134424.06	618194.00
120	606239.75	163765.40	697706.61
150	614056.21	156289.05	642979.67
180	659130.33	167312.81	662146.16
210	736905.87	166341.87	759853.02
240	743468.53	169146.24	696494.35

Conversion (%)	YIELDS (%)			Total Selectivity
	Glycerol	Propylene Glycol	Ethylene Glycol	
63.23	9.13	0.63	0.97	0.1697
67.87	9.07	1.21	2.28	0.1851
89.75	9.47	2.99	3.47	0.1774
98.71	9.52	9.43	3.81	0.2306
95.68	10.90	17.90	4.11	0.3439
93.07	11.62	19.71	4.25	0.3823
91.72	11.84	20.56	4.42	0.4014
95.84	11.08	20.02	3.83	0.3645
90.44	13.45	22.07	4.25	0.4397

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Exp #4 Date 7/28/99

Reaction Components:		
	Type	Amount
Substrate	D-Glucose	0.5 g
Solvent	Water	40 ml
Base	1N NaOH	1 ml
Catalyst	Nickel on Alumina/Silica	0.05 g
	Copper (II) Oxide	.05g

Reaction Conditions

	HPLC Run	GC Run
Temperature	Injection Amount	Injection Amount
210 °C	10 ml	3 ml
Pressure	Internal Standard	Internal Standard
3.5 Mpa	0.231 ml sucrose/ml	0.1875 ml 1,4-but./ml
	1615.385 ppm sucrose	943.5 ppm 1,4-but.

TIME (min)	HPLC Response Area:		
	Glucose	Glycerol	Sucrose (IS)
0	658996.51	1339.55	132988.91
30	385654.50	1907.31	131133.16
60	2751.29	172.77	153029.96
90	98457.69	0.00	139878.83
120	50070.33	7751.24	145880.83
150	10426.28	5434.09	145880.83
180	34632.68	5545.94	142804.19
210	9732.35	5494.01	152094.54
240	11979.18	11014.23	136056.53

TIME (min)	GC Response Area:		
	Propylene Glycol	Ethylene Glycol	1,4-butanediol (IS)
0	22715.54	25313.10	565434.22
30	11477.28	30260.93	647410.74
60	57251.73	61934.73	617303.94
90	151014.61	63352.32	600200.22
120	328249.51	75981.04	712313.27
150	697148.27	169992.51	712313.27
180	518884.67	107222.64	642247.11
210	492299.68	89939.11	583796.47
240	561294.24	110597.23	615596.82

Conversion (%)	YIELDS (%)			
	Glycerol	Propylene Glycol	Ethylene Glycol	Selectivity
9.94	9.38	0.49	0.83	1.0770
46.25	9.57	0.02	0.86	0.2260
98.94	9.02	1.59	1.79	0.1253
86.57	8.97	4.93	1.88	0.1823
93.07	11.15	9.33	1.90	0.2404
97.97	10.50	20.20	4.18	0.3560
94.89	10.57	16.62	2.94	0.3174
98.11	10.45	17.36	2.72	0.3112
97.67	12.30	18.80	3.16	0.3507

Exp #5 Date 7/29/99

Reaction Components:		
	Type	Amount
Substrate	D-Glucose	0.5 g
Solvent	Water	40 ml
Base	1N NaOH	1 ml
Catalyst	Palladium 1% on Carbon	0.05 g
	Boron Oxide	0.05g

Reaction Conditions

	HPLC Run	GC Run
Temperature	Injection Amount	Injection Amount
210 °C	10 ml	3 ml
Pressure	Internal Standard	Internal Standard
3.5 Mpa	0.231 ml sucrose/ml	0.1875 ml 1,4-but./ml
	1615.385 ppm sucrose	943.5 ppm 1,4-but.

TIME (min)	HPLC Response Area:		
	Glucose	Glycerol	Sucrose (IS)
0	925941.88	1266.76	144581.89
30	539098.13	7950.05	174944.56
60	45258.32	5139.81	252954.51
90	16866.84	5342.56	286530.55
120	16098.54	7014.65	285346.28
150	3358.48	8389.21	187987.09
180	9185.08	10834.26	173238.45
210	20677.34	16205.58	148842.47
240	11412.72	19549.45	117972.04

TIME (min)	GC Response Area:		
	Propylene Glycol	Ethylene Glycol	1,4-butanediol (IS)
0	16391.67	11848.67	496186.41
30	13073.64	7297.08	437646.03
60	13511.22	13444.98	412861.45
90	33988.30	24071.62	451727.59
120	50716.09	21135.45	393922.58
150	98999.70	24062.81	456730.32
180	139854.52	29186.69	498561.19
210	157299.52	24062.85	513980.94
240	163485.57	23511.65	473143.34

Conversion (%)	YIELDS (%)			Total Selectivity
	Glycerol	Propylene Glycol	Ethylene Glycol	
-16.18	9.33	0.34	0.47	-0.6267
43.71	10.84	0.27	0.35	0.2621
96.04	9.81	0.33	0.62	0.1120
98.20	9.74	1.23	0.98	0.1216
98.24	9.98	2.35	0.98	0.1355
98.94	10.80	4.20	0.97	0.1614
98.31	11.54	5.54	1.07	0.1846
96.76	13.44	6.07	0.87	0.2106
97.52	15.78	6.90	0.92	0.2420

Exp #6 Date 8/2/99

Reaction Components:		
	Type	Amount
Substrate	D-Glucose	0.5 g
Solvent	Water	40 ml
Base	1N NaOH	1 ml
Catalyst	Nickel on Alumina/Silica	0.05 g
	Iron (III) oxide	0.05g

Reaction Conditions

	HPLC Run	GC Run
Temperature	Injection Amount	Injection Amount
210 °C	10 ml	3 ml
Pressure	Internal Standard	Internal Standard
3.5 Mpa	0.231 ml sucrose/ml	0.1875 ml 1,4-but./ml
	1615.385 ppm sucrose	943.5 ppm 1,4-but.

TIME (min)	HPLC Response Area:		
	Glucose	Glycerol	Sucrose (IS)
0	335389.88	0.00	114463.38
30	226087.09	261.65	144564.58
60	6446.93	806.92	142675.86
90	11348.80	4619.38	141705.73
120	5283.63	6794.18	118256.33
150	5791.37	2874.83	119893.48
180	5699.07	6456.25	125184.35
210	12514.90	5100.53	147912.36
240	769.54	1822.33	135111.6

TIME (min)	GC Response Area:		
	Propylene Glycol	Ethylene Glycol	1,4-butanediol (IS)
0	41656.87	23834.33	450034.55
30	26018.46	25534.50	572965.89
60	104656.74	52773.45	506894.91
90	382459.74	85580.01	624228.75
120	475289.67	81506.00	522126.11
150	552048.06	67778.43	617849.27
180	505584.03	60028.99	501719.84
210	627705.87	85259.02	686536.86
240	593888.80	89747.79	734303.65

Conversion (%)	YIELDS (%)			Total Selectivity
	Glycerol	Propylene Glycol	Ethylene Glycol	
46.44	8.97	1.59	0.97	0.2483
71.07	9.05	0.60	0.83	0.1473
98.45	9.20	3.98	1.85	0.1528
97.82	10.31	12.52	2.42	0.2581
98.46	11.33	18.77	2.75	0.3336
98.39	9.96	18.41	1.95	0.3082
98.44	11.09	20.81	2.12	0.3456
97.74	10.39	18.85	2.20	0.3217
99.16	9.53	16.64	2.17	0.2857

Exp #7 Date 8/3/99

Reaction Components:		
	Type	Amount
Substrate	D-Glucose	0.5 g
Solvent	Water	40 ml
Base	1N NaOH	1 ml
Catalyst	Nickel on Alumina/Silica	0.05 g
	Aluminum Oxide	0.05 g
	Copper (II) Oxide	0.05 g

Reaction Conditions

	HPLC Run	GC Run
Temperature	Injection Amount	Injection Amount
210 °C	10 ml	3 ml
Pressure	Internal Standard	Internal Standard
3.5 Mpa	0.231 ml sucrose/ml	0.1875 ml 1,4-but./ml
	1615.385 ppm sucrose	943.5 ppm 1,4-but.

TIME (min)	HPLC Response Area:		
	Glucose	Glycerol	Sucrose (IS)
0	652442.96	0.00	129923.16
30	78599.42	78.56	137026.63
60	47370.18	189.08	126149.14
90	24705.34	3964.54	124686.17
120	27318.47	18990.01	143149.14
150	28825.11	21425.47	123255.19
180	29624.59	21627.16	141372.84
210	18442.07	20291.04	142055.51
240	29800.24	25733.44	145162.63

TIME (min)	GC Response Area:		
	Propylene Glycol	Ethylene Glycol	1,4-butanediol (IS)
0	50439.86	32431.61	562013.80
30	47820.30	80089.24	634828.53
60	46662.97	88099.10	496281.02
90	200440.10	103915.71	498419.80
120	562076.99	158456.42	615171.31
150	481921.35	149431.06	513825.32
180	650965.49	164180.33	638023.31
210	683877.81	170414.94	612968.17
240	671083.89	174645.83	635060.58

Conversion (%)	YIELDS (%)			Total Selectivity
	Glycerol	Propylene Glycol	Ethylene Glycol	
8.74	8.97	1.53	1.05	1.3221
88.92	8.99	1.23	2.23	0.1401
92.49	9.03	1.62	3.12	0.1489
95.69	10.28	8.09	3.65	0.2302
95.82	14.42	18.84	4.50	0.3941
95.05	16.11	19.35	5.07	0.4264
95.48	15.25	21.08	4.50	0.4276
96.92	14.84	23.08	4.85	0.4413
95.56	16.25	21.84	4.80	0.4489

Exp #8 Date 8/9/99

Reaction Components:		
	Type	Amount
Substrate	D-Glucose	0.5 g
Solvent	Water	40 ml
Base	1N NaOH	1 ml
Catalyst	5% Ruthenium on Carbon	0.05 g

Reaction Conditions

	HPLC Run	GC Run
Temperature	Injection Amount	Injection Amount
210 °C	10 ml	3 ml
Pressure	Internal Standard	Internal Standard
3.5 Mpa	0.231 ml sucrose/ml	0.1875 ml 1,4-but./ml
	1615.385 ppm sucrose	943.5 ppm 1,4-but.

TIME (min)	HPLC Response Area:		
	Glucose	Glycerol	Sucrose (IS)
0	284923.28	0.00	114459.39
30	74822.07	102.30	137873.35
60	22233.69	3748.34	132327.57
90	8806.92	1820.24	134662.63
120	16056.78	3138.57	118466.32
150	16048.36	8321.60	107172.44
180	12638.76	5410.12	119105.5
210	13281.01	7722.31	119332.88
240	1380.83	5838.63	121078.98

TIME (min)	GC Response Area:		
	Propylene Glycol	Ethylene Glycol	1,4-butanediol (IS)
0	140351.16	76509.88	495788.03
30	44990.23	43863.39	497180.73
60	109358.77	87079.13	531743.54
90	450323.01	58316.38	515655.79
120	645793.75	116222.64	674200.26
150	711697.11	114958.98	672165.35
180	706936.05	129920.02	698134.92
210	671055.27	101973.19	625607.11
240	745824.40	138835.06	651216.47

Conversion (%)	YIELDS (%)			Total Selectivity
	Glycerol	Propylene Glycol	Ethylene Glycol	
54.39	8.97	5.59	2.72	0.3178
89.48	9.00	1.55	1.58	0.1355
96.23	10.13	3.97	2.88	0.1765
98.08	9.53	17.99	2.01	0.3010
96.82	10.06	19.77	3.03	0.3394
96.56	12.16	21.89	3.01	0.3837
97.35	10.84	20.92	3.27	0.3598
97.26	11.63	22.18	2.87	0.3771
99.06	10.95	23.70	3.74	0.3876

Exp #9 Date 8/10/99

Reaction Components:		
	Type	Amount
Substrate	D-Glucose	0.5 g
Solvent	Water	40 ml
Base	1N NaOH	1 ml
Catalyst	Nickel on Kieselguhr	0.05 g

Reaction Conditions

	HPLC Run	GC Run
Temperature	Injection Amount	Injection Amount
210 °C	10 ml	3 ml
Pressure	Internal Standard	Internal Standard
3.5 Mpa	0.231 ml sucrose/ml	0.1875 ml 1,4-but./ml
	1615.385 ppm sucrose	943.5 ppm 1,4-but.

TIME (min)	HPLC Response Area:		
	Glucose	Glycerol	Sucrose (IS)
0	49433.83	374.83	122020.42
30	151716.09	0.00	118231.69
60	92542.33	0.00	116772.11
90	82075.90	5607.19	118627.47
120	80368.89	16175.11	94734.67
150	137343.31	18476.03	135908.19
180	143726.65	20712.38	143245.15
210	112976.60	15525.64	127773.01
240	126663.97	18812.25	116715.74

TIME (min)	GC Response Area:		
	Propylene Glycol	Ethylene Glycol	1,4-butanediol (IS)
0	40349.82	78278.44	507044.18
30	22526.02	50597.27	558217.74
60	68988.26	105861.13	477852.97
90	280513.94	103625.24	543873.10
120	437715.39	134363.09	599258.80
150	395100.62	169965.01	454539.54
180	564389.95	154676.51	482304.86
210	585959.36	141296.19	572098.09
240	601488.85	191398.66	657048.16

Conversion (%)	YIELDS (%)			Total Selectivity
	Glycerol	Propylene Glycol	Ethylene Glycol	
91.96	9.10	1.32	2.72	0.1428
76.13	8.97	0.49	1.62	0.1456
84.98	8.97	2.68	3.88	0.1827
86.79	10.91	10.48	3.35	0.2850
83.97	15.98	14.99	3.93	0.4156
81.05	14.55	17.91	6.51	0.4808
81.18	14.91	24.23	5.59	0.5510
83.32	13.96	21.16	4.32	0.4733
79.70	15.59	18.88	5.08	0.4962

Exp #10 Date 8/10/99

Reaction Components:		
	Type	Amount
Substrate	D-Glucose	0.5 g
Solvent	1 M EtOH	40 ml
Base	1N NaOH	1 ml
Catalyst	Copper (II) Oxide	0.05 g

Reaction Conditions

	HPLC Run	GC Run
Temperature	Injection Amount	Injection Amount
210 °C	10 ml	3 ml
Pressure	Internal Standard	Internal Standard
3.5 Mpa	0.231 ml sucrose/ml	0.1875 ml 1,4-but./ml
	1615.385 ppm sucrose	943.5 ppm 1,4-but.

TIME (min)	HPLC Response Area:		
	Glucose	Glycerol	Sucrose (IS)
0	496999.83	346.65	126072
30	257554.82	266.12	122382.83
60	107638.55	0.00	124171.1
90	105248.06	854.15	128044.05
120	119736.85	314.25	139295.61
150	105354.26	1727.03	120900.14
180	75528.63	1525.92	124012.4
210	106607.61	2001.33	119102.53
240	88244.87	2467.53	124456.56

TIME (min)	GC Response Area:		
	Propylene Glycol	Ethylene Glycol	1,4-butanediol (IS)
0	20639.92	36390.63	426892.29
30	15847.60	29366.27	556045.59
60	20883.24	57532.30	615701.01
90	61985.13	89022.92	629574.33
120	96047.84	82441.12	556929.94
150	190169.90	114413.10	703623.99
180	231805.86	103117.67	600726.97
210	262573.68	107136.61	585838.05
240	323766.67	130555.20	651728.18

Conversion (%)	YIELDS (%)			Total Selectivity
	Glycerol	Propylene Glycol	Ethylene Glycol	
28.20	9.08	0.66	1.53	0.3998
61.33	9.06	0.24	0.97	0.1675
83.64	8.97	0.36	1.67	0.1315
84.44	9.25	1.71	2.50	0.1593
83.77	9.06	3.27	2.61	0.1784
83.55	9.56	5.32	2.86	0.2124
88.28	9.48	7.75	3.02	0.2293
83.13	9.66	9.06	3.21	0.2639
86.48	9.79	10.08	3.51	0.2704

Exp #11 Date 8/11/99

Reaction Components:		
	Type	Amount
Substrate	D-Glucose	0.5 g
Solvent	1 M EtOH	40 ml
Base	1N NaOH	1 ml
Catalyst	Ba prom. Cu-Chromite	0.05 g

Reaction Conditions

	HPLC Run	GC Run
Temperature	Injection Amount	Injection Amount
210 °C	10 ml	3 ml
Pressure	Internal Standard	Internal Standard
3.5 Mpa	0.231 ml sucrose/ml	0.1875 ml 1,4-but./ml
	1615.385 ppm sucrose	943.5 ppm 1,4-but.

TIME (min)	HPLC Response Area:		
	Glucose	Glycerol	Sucrose (IS)
0	684511.05	78.30	131258.32
30	216791.14	37.28	129401.02
60	18607.19	94.54	131872.62
90	31017.31	60.81	120055.26
120	3221.37	104.13	127049.77
150	7681.09	872.17	131511.94
180	3171.11	0.00	131115.18
210	9734.37	1817.29	126528.65
240	13921.17	0.00	130282.92

TIME (min)	GC Response Area:		
	Propylene Glycol	Ethylene Glycol	1,4-butanediol (IS)
0	0.00	0.00	465355.44
30	2680.40	21010.37	648368.58
60	5297.84	47145.56	620688.68
90	9456.12	53847.79	652382.91
120	82771.04	62938.86	647945.34
150	128133.24	62187.30	617222.87
180	142926.13	72383.43	656558.12
210	86928.61	55946.35	588946.91
240	216402.76	76502.19	605593.69

Conversion (%)	YIELDS (%)			Total Selectivity
	Glycerol	Propylene Glycol	Ethylene Glycol	
5.26	9.00	-0.36	0.06	1.6547
69.06	8.98	-0.27	0.62	0.1351
96.72	9.00	-0.18	1.37	0.1054
94.60	8.99	-0.05	1.48	0.1102
98.80	9.00	2.33	1.73	0.1323
98.21	9.24	4.01	1.80	0.1532
98.83	8.97	4.22	1.96	0.1533
97.87	9.56	2.75	1.70	0.1431
97.34	8.97	7.15	2.24	0.1886

Exp #12 Date 8/15/99

Reaction Components:		
	Type	Amount
Substrate	D-Glucose	0.5 g
Solvent	1 M EtOH	40 ml
Base	1N NaOH	1 ml
Catalyst	Nickel on Alumina/Silica	0.05 g

Reaction Conditions

	HPLC Run	GC Run
Temperature	Injection Amount	Injection Amount
210 °C	10 ml	3 ml
Pressure	Internal Standard	Internal Standard
3.5 Mpa	0.231 ml sucrose/ml	0.1875 ml 1,4-but./ml
	1615.385 ppm sucrose	943.5 ppm 1,4-but.

TIME (min)	HPLC Response Area:		
	Glucose	Glycerol	Sucrose (IS)
0	496989.47	0.00	139381.07
30	126542.33	0.00	137295.42
60	41125.17	537.28	139941.17
90	39391.71	4025.97	139597.28
120	4802.93	8081.41	146260.51
150	4995.41	7790.95	142608.18
180	23365.04	12286.67	157331.79
210	45319.70	8186.42	145108.43
240	51870.84	11229.03	150059.92

TIME (min)	GC Response Area:		
	Propylene Glycol	Ethylene Glycol	1,4-butanediol (IS)
0	35165.85	36181.43	387068.11
30	35435.64	35723.33	458943.53
60	79054.59	75809.13	530111.43
90	154534.32	72573.01	506538.42
120	433536.76	159416.82	555033.97
150	414952.01	153923.36	508345.45
180	407246.80	131310.35	500338.99
210	563079.16	160312.57	659706.24
240	585579.05	175893.81	667619.76

Conversion (%)	YIELDS (%)			Total Selectivity
	Glycerol	Propylene Glycol	Ethylene Glycol	
34.99	8.97	1.55	1.67	0.3486
82.65	8.97	1.27	1.40	0.1408
93.96	9.13	2.78	2.53	0.1536
94.18	10.16	6.05	2.53	0.1990
98.67	11.24	16.05	5.01	0.3274
98.63	11.21	16.79	5.28	0.3375
96.58	12.18	16.74	4.59	0.3469
93.63	11.29	17.58	4.25	0.3537
93.03	12.04	18.07	4.60	0.3732

Exp #13 Date 8/16/99

Reaction Components:		
	Type	Amount
Substrate	D-Glucose	0.5 g
Solvent	1 M EtOH	40 ml
Base	1N NaOH	1 ml
Catalyst	Nickel on Alumina/Silica	0.05 g
	Copper (II) Oxide	0.05 g

Reaction Conditions

	HPLC Run	GC Run
Temperature	Injection Amount	Injection Amount
210 °C	10 ml	3 ml
Pressure	Internal Standard	Internal Standard
3.5 Mpa	0.231 ml sucrose/ml	0.1875 ml 1,4-but./ml
	1615.385 ppm sucrose	943.5 ppm 1,4-but.

TIME (min)	HPLC Response Area:		
	Glucose	Glycerol	Sucrose (IS)
0	576021.32	983.78	157597.27
30	127162.96	1222.10	140345.36
60	36774.96	1097.20	135119.66
90	52730.11	3592.54	156222.84
120	41633.46	3314.25	141704.02
150	54698.40	6665.32	169582.23
180	59586.01	5702.40	175461.49
210	62448.07	5885.49	161882.16
240	56506.61	5644.47	169461.4

TIME (min)	GC Response Area:		
	Propylene Glycol	Ethylene Glycol	1,4-butanediol (IS)
0	29101.28	33562.01	446857.80
30	18230.17	43957.57	527553.93
60	135011.06	87701.11	543418.03
90	271573.99	101360.01	648300.02
120	321421.04	112242.49	588749.12
150	361411.10	120709.60	604643.15
180	517330.90	150783.63	768801.54
210	422592.05	130041.16	553729.92
240	433485.20	103252.04	587580.16

Conversion (%)	YIELDS (%)			Total Selectivity
	Glycerol	Propylene Glycol	Ethylene Glycol	
33.38	9.23	1.01	1.35	0.3474
82.93	9.33	0.37	1.50	0.1350
94.36	9.30	4.86	2.84	0.1803
93.18	9.92	8.44	2.76	0.2266
93.97	9.93	11.11	3.35	0.2596
93.45	10.59	12.20	3.50	0.2813
93.14	10.31	13.78	3.44	0.2956
92.31	10.46	15.68	4.11	0.3277
93.25	10.34	15.14	3.09	0.3064

Exp #14 Date 8/17/99

Reaction Components:		
	Type	Amount
Substrate	D-Glucose	0.5 g
Solvent	1 M EtOH	40 ml
Base	1N NaOH	1 ml
Catalyst	Palladium 1% on Carbon	0.05 g
	Boron Oxide	0.05 g

Reaction Conditions

	HPLC Run	GC Run
Temperature	Injection Amount	Injection Amount
210 °C	10 ml	3 ml
Pressure	Internal Standard	Internal Standard
3.5 Mpa	0.231 ml sucrose/ml	0.1875 ml 1,4-but./ml
	1615.385 ppm sucrose	943.5 ppm 1,4-but.

TIME (min)	HPLC Response Area:		
	Glucose	Glycerol	Sucrose (IS)
0	522334.23	716.38	129190.41
30	141686.64	539.28	126300.27
60	23340.88	1018.54	134850.1
90	42368.18	7677.76	127898.72
120	49113.18	18047.94	116375.5
150	49191.74	23948.07	124490.02
180	82301.49	48463.61	150494.27
210	46103.81	27334.22	127019.98
240	55802.93	36720.71	129575.9

TIME (min)	GC Response Area:		
	Propylene Glycol	Ethylene Glycol	1,4-butanediol (IS)
0	14443.75	8993.82	285124.71
30	7577.94	10995.92	276965.29
60	34277.84	26923.26	386333.55
90	43143.46	20764.08	316984.08
120	92576.38	41366.92	335955.85
150	117668.40	68004.83	348878.20
180	127639.66	55732.97	323567.98
210	164870.32	57636.95	400128.74
240	158814.89	43473.03	378006.30

Conversion (%)	YIELDS (%)			
	Glycerol	Propylene Glycol	Ethylene Glycol	Selectivity
26.38	9.20	0.71	0.60	0.3984
79.04	9.15	0.22	0.74	0.1279
96.14	9.28	1.51	1.26	0.1253
93.29	11.44	2.50	1.19	0.1622
91.65	15.34	5.43	2.18	0.2505
92.14	16.87	6.73	3.42	0.2933
89.40	22.19	7.93	3.03	0.3708
92.72	17.81	8.30	2.54	0.3090
91.50	20.61	8.47	2.04	0.3401

Exp #15 Date 8/23/99

Reaction Components:		
	Type	Amount
Substrate	D-Glucose	0.5 g
Solvent	1 M EtOH	40 ml
Base	1N NaOH	1 ml
Catalyst	Nickel on Alumina/Silica	0.05 g
	Iron (III) Oxide	0.05 g

Reaction Conditions

	HPLC Run	GC Run
Temperature	Injection Amount	Injection Amount
210 °C	10 ml	3 ml
Pressure	Internal Standard	Internal Standard
3.5 Mpa	0.231 ml sucrose/ml	0.1875 ml 1,4-but./ml
	1615.385 ppm sucrose	943.5 ppm 1,4-but.

TIME (min)	HPLC Response Area:		
	Glucose	Glycerol	Sucrose (IS)
0	584322.76	0.00	149054.6
30	92974.70	182.42	155824.93
60	51752.92	8424.10	148253.24
90	48160.65	21029.29	159995.63
120	67883.94	25222.37	181979.27
150	63472.23	29242.34	183487.01
180	8451.76	31709.06	193828.23
210	56591.16	25858.86	154596.54
240	57587.83	28372.84	168879.13

TIME (min)	GC Response Area:		
	Propylene Glycol	Ethylene Glycol	1,4-butanediol (IS)
0	67124.62	42220.91	360862.62
30	56365.36	104030.75	516592.19
60	302266.20	189154.97	628539.01
90	575993.37	235847.32	583063.92
120	645677.08	176665.70	590911.78
150	658602.40	221788.78	589153.76
180	638042.32	237172.26	607910.06
210	717618.36	224299.00	606096.53
240	725672.35	225803.44	638160.45

Conversion (%)	YIELDS (%)			Total Selectivity
	Glycerol	Propylene Glycol	Ethylene Glycol	
28.60	8.97	3.55	2.08	0.5106
88.51	9.02	1.94	3.53	0.1637
92.97	11.30	9.75	5.25	0.2829
93.84	14.37	20.40	7.04	0.4455
92.54	14.66	22.60	5.22	0.4590
93.03	15.51	23.13	6.55	0.4858
98.48	15.69	21.69	6.79	0.4485
92.66	15.84	24.52	6.44	0.5050
93.11	15.87	23.53	6.16	0.4893

Exp #16 Date 8/24/99

Reaction Components:		
	Type	Amount
Substrate	D-Glucose	0.5 g
Solvent	1 M EtOH	40 ml
Base	1N NaOH	1 ml
Catalyst	Nickel on Alumina/Silica	0.05 g
	Aluminum Oxide	0.05 g
	Copper (II) Oxide	0.05 g

Reaction Conditions

	HPLC Run	GC Run
Temperature	Injection Amount	Injection Amount
210 °C	10 ml	3 ml
Pressure	Internal Standard	Internal Standard
3.5 Mpa	0.231 ml sucrose/ml	0.1875 ml 1,4-but./ml
	1615.385 ppm sucrose	943.5 ppm 1,4-but.

TIME (min)	HPLC Response Area:		
	Glucose	Glycerol	Sucrose (IS)
0	659292.16	69.94	131060.72
30	227286.13	129.62	133501.33
60	34118.41	1420.77	178655.47
90	3616.30	2827.56	172544.85
120	46626.54	3744.34	154517.98
150	5332.27	3606.52	158198.8
180	65751.83	6247.67	185302.55
210	5564.29	5189.75	171552.49
240	39887.22	3384.82	150017.88

TIME (min)	GC Response Area:		
	Propylene Glycol	Ethylene Glycol	1,4-butanediol (IS)
0	69179.81	56568.68	444807.23
30	44702.97	30924.56	469267.22
60	91367.80	38267.83	534960.41
90	233973.31	128428.22	573449.32
120	297671.32	107274.95	619800.69
150	433485.20	103252.04	587580.16
180	346465.77	109156.54	608791.43
210	490076.70	115736.61	660586.06
240	475719.29	70904.90	557434.89

Conversion (%)	YIELDS (%)			Total Selectivity
	Glycerol	Propylene Glycol	Ethylene Glycol	
8.58	8.99	2.91	2.25	1.6493
68.57	9.01	1.65	1.20	0.1728
95.82	9.30	3.23	1.29	0.1443
98.88	9.64	8.22	3.92	0.2203
93.82	9.97	9.73	3.04	0.2424
98.65	9.91	15.14	3.09	0.2852
92.87	10.36	11.60	3.15	0.2704
98.68	10.21	15.23	3.08	0.2891
94.47	9.90	17.57	2.25	0.3146

Exp #17 Date 8/25/99

Reaction Components:		
	Type	Amount
Substrate	D-Glucose	0.5 g
Solvent	1 M EtOH	40 ml
Base	1N NaOH	1 ml
Catalyst	5% Ruthenium on Carbon	0.05 g

Reaction Conditions

	HPLC Run	GC Run
Temperature	Injection Amount	Injection Amount
210 °C	10 ml	3 ml
Pressure	Internal Standard	Internal Standard
3.5 Mpa	0.231 ml sucrose/ml	0.1875 ml 1,4-but./ml
	1615.385 ppm sucrose	943.5 ppm 1,4-but.

TIME (min)	HPLC Response Area:		
	Glucose	Glycerol	Sucrose (IS)
0	0.00	0.00	0
30	0.00	0.00	0
60	0.00	0.00	0
90	0.00	0.00	0
120	0.00	0.00	0
150	0.00	0.00	0
180	0.00	0.00	0
210	36140.79	10121.17	138960.18
240	33944.08	11783.81	156592.46

TIME (min)	GC Response Area:		
	Propylene Glycol	Ethylene Glycol	1,4-butanediol (IS)
0	0.00	0.00	0.00
30	0.00	0.00	0.00
60	0.00	0.00	0.00
90	0.00	0.00	0.00
120	0.00	0.00	0.00
150	0.00	0.00	0.00
180	0.00	0.00	0.00
210	782195.59	208159.23	686085.23
240	850787.71	178987.21	685112.83

Conversion (%)	YIELDS (%)			Total Selectivity
	Glycerol	Propylene Glycol	Ethylene Glycol	
#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
94.57	11.96	23.59	5.29	0.4319
95.35	12.06	25.73	4.56	0.4442

Exp #18 Date 8/26/99

Reaction Components:		
	Type	Amount
Substrate	D-Glucose	0.5 g
Solvent	1 M EtOH	40 ml
Base	1N NaOH	1 ml
Catalyst	Nickel on Kieselguhr	0.05 g

Reaction Conditions

Temperature	HPLC Run	GC Run
	Injection Amount	Injection Amount
210 °C	10 ml	3 ml
Pressure	Internal Standard	Internal Standard
3.5 Mpa	0.231 ml sucrose/ml	0.1875 ml 1,4-but./ml
	1615.385 ppm sucrose	943.5 ppm 1,4-but.

TIME (min)	HPLC Response Area:		
	Glucose	Glycerol	Sucrose (IS)
0	539424.78	341.46	136101.2
30	167788.72	261.65	120507.69
60	192907.75	4069.81	119680.43
90	199323.70	8164.67	112092.87
120	281090.65	15484.25	136108.52
150	141869.15	6468.27	118687.55
180	267211.91	10457.76	146087.79
210	154405.91	9170.05	123921.9
240	22588.52	9130.53	122705.85

TIME (min)	GC Response Area:		
	Propylene Glycol	Ethylene Glycol	1,4-butanediol (IS)
0	41246.40	18163.90	424306.63
30	60277.33	130360.58	531292.54
60	138746.13	39664.75	482468.97
90	296078.63	202652.84	580533.98
120	174985.77	11325.24	402412.44
150	372264.06	161070.58	502897.89
180	437092.99	203784.74	591598.50
210	454624.65	208351.28	659537.22
240	447423.55	210370.33	588167.58

Conversion (%)	YIELDS (%)			Total
	Glycerol	Propylene Glycol	Ethylene Glycol	Selectivity
27.82	9.07	1.69	0.80	0.4155
74.16	9.06	2.03	4.29	0.2074
70.21	10.37	5.69	1.48	0.2497
67.21	11.96	10.36	6.08	0.4226
62.03	13.64	8.78	0.54	0.3702
77.72	11.21	15.20	5.58	0.4116
66.29	11.91	15.17	6.00	0.4990
76.80	12.01	14.13	5.51	0.4120
95.94	12.03	15.63	6.23	0.3531

Exp #19 Date 9/21/99

Reaction Components:		
	Type	Amount
Substrate	Fructose	0.5 g
Solvent	1M EtOH	40 ml
Base	1N NaOH	1 ml
Catalyst	Copper (II) Oxide	0.05 g

Reaction Conditions

	HPLC Run	GC Run
Temperature	Injection Amount	Injection Amount
210 °C	10 ml	3 ml
Pressure	Internal Standard	Internal Standard
3.5 Mpa	0.231 ml sucrose/ml	0.1875 ml 1,4-but./ml
	1615.385 ppm sucrose	943.5 ppm 1,4-but.

TIME (min)	HPLC Response Area:		
	Fructose	Glycerol	Sucrose (IS)
0	405135.08	0.00	127699.97
30	190318.52	0.00	133203.59
60	2472.70	0.00	129434.28
90	177.10	1941.64	134014.65
120	0.00	3437.00	127706.91
150	0.00	5907.36	120107.05
180	0.00	7259.65	128577.23
210	0.00	7417.44	129860.19
240	0.00	9928.10	124108.14

TIME (min)	GC Response Area:		
	Propylene Glycol	Ethylene Glycol	1,4-butanediol (IS)
0	0.00	40505.43	331951.70
30	16254.16	38272.84	570311.89
60	32290.83	94158.11	609692.56
90	119451.25	83068.02	582590.24
120	279747.78	97206.46	710034.76
150	384657.41	112350.02	515366.24
180	553874.16	120439.03	646987.20
210	535391.80	118064.99	681645.31
240	660921.43	177496.99	645955.72

Conversion (%)	YIELDS (%)			Total Selectivity
	Glycerol	Propylene Glycol	Ethylene Glycol	
45.65	8.97	-0.36	2.16	0.2361
75.52	8.97	0.24	1.22	0.1381
99.67	8.97	0.76	2.72	0.1249
99.98	9.57	3.95	2.52	0.1604
100.00	10.08	7.92	2.42	0.2042
100.00	10.99	15.32	3.82	0.3013
100.00	11.29	17.63	3.27	0.3219
100.00	11.32	16.14	3.05	0.3051
100.00	12.26	21.14	4.80	0.3819

Exp #20 Date 12/10/1999

Reaction Components:		
	Type	Amount
Substrate	Fructose	0.5 g
Solvent	1M EtOH	40 ml
Base	1N NaOH	1 ml
Catalyst	Ba prom. Cu-Chromite	0.05 g

Reaction Conditions

	HPLC Run	GC Run
Temperature	Injection Amount	Injection Amount
210 °C	10 ml	3 ml
Pressure	Internal Standard	Internal Standard
3.5 Mpa	0.231 ml sucrose/ml	0.1875 ml 1,4-but./ml
	1615.385 ppm sucrose	943.5 ppm 1,4-but.

TIME (min)	HPLC Response Area:		
	Fructose	Glycerol	Sucrose (IS)
0	456013.58	900.92	170093.83
30	99181.93	961.33	162490.56
60	835.55	0.00	168127.73
90	349.13	192.12	136988.02
120	362.54	661.79	154986.69
150	460.26	2383.49	184142.37
180	0.00	2785.14	155394.14
210	0.00	1002.45	189601.48
240	0.00	4861.53	180041.28

TIME (min)	GC Response Area:		
	Propylene Glycol	Ethylene Glycol	1,4-butanediol (IS)
0	47061.63	20950.12	264140.24
30	48285.85	31018.97	347104.31
60	35967.84	8057.13	503885.04
90	26860.83	33217.01	559886.29
120	26806.32	6947.12	439198.92
150	78487.92	63748.12	472460.61
180	113884.23	64283.80	467118.02
210	172249.35	73441.20	609532.05
240	208318.66	72932.46	601449.35

Conversion (%)	YIELDS (%)			Total Selectivity
	Glycerol	Propylene Glycol	Ethylene Glycol	
54.07	9.19	3.39	1.43	0.2590
89.54	9.21	2.57	1.60	0.1494
99.91	8.97	1.14	0.33	0.1046
99.96	9.03	0.65	1.08	0.1077
99.96	9.15	0.93	0.33	0.1041
99.96	9.50	3.13	2.39	0.1503
100.00	9.71	4.77	2.43	0.1691
100.00	9.19	5.58	2.14	0.1691
100.00	10.08	6.92	2.15	0.1915

Exp #21 Date 9/28/99

Reaction Components:		
	Type	Amount
Substrate	Fructose	0.5 g
Solvent	1M EtOH	40 ml
Base	1N NaOH	1 ml
Catalyst	Nickel on Alumina/Silica	0.05 g

Reaction Conditions

	HPLC Run	GC Run
Temperature	Injection Amount	Injection Amount
210 °C	10 ml	3 ml
Pressure	Internal Standard	Internal Standard
3.5 Mpa	0.231 ml sucrose/ml	0.1875 ml 1,4-but./ml
	1615.385 ppm sucrose	943.5 ppm 1,4-but.

TIME (min)	HPLC Response Area:		
	Fructose	Glycerol	Sucrose (IS)
0	439827.79	0.00	130364.85
30	293269.16	189.08	168490.02
60	1518.04	37.28	139478.04
90	544.64	3368.18	148335.57
120	195.18	6418.78	136324.9
150	342.22	5890.81	142856.5
180	0.00	5589.88	124256.33
210	0.00	8410.79	126093.48
240	0.00	10125.36	138049.27

TIME (min)	GC Response Area:		
	Propylene Glycol	Ethylene Glycol	1,4-butanediol (IS)
0	17856.47	13715.68	338315.37
30	18013.11	24410.57	641545.72
60	101607.94	113186.19	548570.52
90	270327.93	84694.81	513458.70
120	329748.66	112218.67	510442.12
150	444839.99	116527.96	579318.53
180	491334.57	106301.44	575962.63
210	475697.44	69949.05	608690.10
240	428486.49	67198.34	649741.65

Conversion (%)	YIELDS (%)			Total Selectivity
	Glycerol	Propylene Glycol	Ethylene Glycol	
42.20	8.97	0.75	0.76	0.2484
70.18	9.02	0.23	0.71	0.1420
99.81	8.98	3.54	3.62	0.1617
99.94	9.90	10.70	2.90	0.2353
99.98	10.90	13.22	3.85	0.2798
99.96	10.66	15.78	3.53	0.2998
100.00	10.82	17.57	3.24	0.3163
100.00	11.71	16.06	2.04	0.2981
100.00	11.98	13.50	1.84	0.2732

Exp #22 Date 10/5/99

Reaction Components:		
	Type	Amount
Substrate	Fructose	0.5 g
Solvent	1M EtOH	40 ml
Base	1N NaOH	1 ml
Catalyst	Nickel on Alumina/Silica	0.05 g
	Copper (II) Oxide	0.05 g

Reaction Conditions

	HPLC Run	GC Run
Temperature	Injection Amount	Injection Amount
210 °C	10 ml	3 ml
Pressure	Internal Standard	Internal Standard
3.5 Mpa	0.231 ml sucrose/ml	0.1875 ml 1,4-but./ml
	1615.385 ppm sucrose	943.5 ppm 1,4-but.

TIME (min)	HPLC Response Area:		
	Fructose	Glycerol	Sucrose (IS)
0	475169.92	0.00	150509.99
30	129057.06	188.42	153076.13
60	7192.25	11219.35	160291.64
90	3787.94	8346.21	146098.54
120	5618.87	25604.38	142314.25
150	6082.02	22466.05	142334.14
180	3472.70	13919.21	153000.89
210	2226.12	12882.82	138875.37
240	3878.71	27218.00	148370.9

TIME (min)	GC Response Area:		
	Propylene Glycol	Ethylene Glycol	1,4-butanediol (IS)
0	5970.28	8610.44	564759.60
30	48580.35	64828.95	370887.50
60	223875.93	179365.62	488344.34
90	436056.32	214758.10	616063.43
120	535785.51	256677.11	615283.18
150	615438.34	267847.91	680728.26
180	453195.64	134716.46	600263.57
210	513260.88	199628.36	545259.60
240	641195.46	215266.42	678766.55

Conversion (%)	YIELDS (%)			Total Selectivity
	Glycerol	Propylene Glycol	Ethylene Glycol	
45.92	8.97	-0.13	0.32	0.1995
85.56	9.02	2.40	3.07	0.1694
99.23	11.85	9.28	6.39	0.2773
99.56	11.32	14.51	6.07	0.3204
99.32	16.36	17.94	7.25	0.4183
99.27	15.45	18.64	6.85	0.4124
99.61	12.71	15.51	3.93	0.3227
99.73	12.78	19.42	6.37	0.3868
99.55	16.50	19.49	5.53	0.4171

Exp #23 Date 9/21/99

Reaction Components:		
	Type	Amount
Substrate	Fructose	0.5 g
Solvent	1M EtOH	40 ml
Base	1N NaOH	1 ml
Catalyst	Boron Oxide	0.05 g
	Palladium 1% on Carbon	0.05 g

Reaction Conditions

	HPLC Run	GC Run
Temperature	Injection Amount	Injection Amount
210 °C	10 ml	3 ml
Pressure	Internal Standard	Internal Standard
3.5 Mpa	0.231 ml sucrose/ml	0.1875 ml 1,4-but./ml
	1615.385 ppm sucrose	943.5 ppm 1,4-but.

TIME (min)	HPLC Response Area:		
	Fructose	Glycerol	Sucrose (IS)
0	478617.05	0.00	155374.17
30	286356.12	0.00	202550.8
60	14601.60	0.00	203908.41
90	542.57	35871.19	203568.36
120	177.76	68727.48	168562.59
150	206.39	67439.04	218771.37
180	159.76	65791.38	214314.06
210	213.72	87623.15	199347.52
240	239.68	75360.18	146190.42

TIME (min)	GC Response Area:		
	Propylene Glycol	Ethylene Glycol	1,4-butanediol (IS)
0	33055.82	29562.61	294773.63
30	5337.14	5796.30	244856.36
60	33129.99	20068.87	383585.03
90	100707.42	33956.10	415532.90
120	217865.96	55813.53	501729.20
150	289800.01	78271.17	456995.10
180	291678.53	89131.46	410776.76
210	304118.18	39182.43	467451.51
240	343930.71	57157.53	521802.32

Conversion (%)	YIELDS (%)			Total Selectivity
	Glycerol	Propylene Glycol	Ethylene Glycol	
47.23	8.97	2.00	1.79	0.2702
75.78	8.97	0.10	0.47	0.1259
98.77	8.97	1.46	0.96	0.1153
99.95	16.21	4.74	1.47	0.2242
99.98	25.71	8.77	1.98	0.3646
99.98	21.63	12.97	3.01	0.3761
99.99	21.58	14.56	3.80	0.3994
99.98	27.02	13.31	1.50	0.4184
99.97	30.14	13.49	1.95	0.4559

Exp #24 Date 12/11/1999

Reaction Components:		
	Type	Amount
Substrate	Fructose	0.5 g
Solvent	1M EtOH	40 ml
Base	1N NaOH	1 ml
Catalyst	Nickel on Alumina/Silica	0.05 g
	Iron (III) Oxide	0.05 g

Reaction Conditions

	HPLC Run	GC Run
Temperature	Injection Amount	Injection Amount
210 °C	10 ml	3 ml
Pressure	Internal Standard	Internal Standard
3.5 Mpa	0.231 ml sucrose/ml	0.1875 ml 1,4-but./ml
	1615.385 ppm sucrose	939.1875 ppm 1,4-but.

TIME (min)	HPLC Response Area:		
	Fructose	Glycerol	Sucrose (IS)
0	516331.84	190.14	125117.85
30	129853.34	0.00	145276.97
60	6956.50	7596.54	198341.49
90	86.01	14418.11	153161.12
120	0.00	30047.27	193138.55
150	0.00	23352.86	189641.43
180	103.86	32634.23	177302.46
210	14437.94	30466.71	185737.69
240	0.00	36989.35	178425.47

TIME (min)	GC Response Area:		
	Propylene Glycol	Ethylene Glycol	1,4-butanediol (IS)
0	60220.92	30883.31	539347.54
30	60252.39	71402.36	329089.46
60	85349.68	146046.94	367860.58
90	441541.07	216665.74	646100.18
120	503172.27	190080.07	518223.69
150	525364.36	171241.84	564593.57
180	636194.18	179522.65	651307.67
210	517385.54	146379.82	467659.30
240	587968.15	220728.61	606946.28

Conversion (%)	YIELDS (%)			Total Selectivity
	Glycerol	Propylene Glycol	Ethylene Glycol	
29.31	9.03	1.98	1.04	0.4114
84.69	8.97	3.48	3.78	0.1916
99.40	10.54	4.50	6.88	0.2205
99.99	12.84	13.94	5.82	0.3259
100.00	15.36	19.95	6.36	0.4167
100.00	14.03	19.10	5.27	0.3840
99.99	16.53	20.07	4.79	0.4140
98.67	15.71	22.78	5.43	0.4451
100.00	17.48	19.90	6.30	0.4369

Exp #25 Date 12/13/1999

Reaction Components:		
	Type	Amount
Substrate	Fructose	0.5 g
Solvent	1M EtOH	40 ml
Base	1N NaOH	1 ml
Catalyst	Nickel on Alumina/Silica	0.05 g
	Aluminum Oxide	0.05 g
	Copper (II) Oxide	0.05 g

Reaction Conditions

	HPLC Run	GC Run
Temperature	Injection Amount	Injection Amount
210 °C	10 ml	3 ml
Pressure	Internal Standard	Internal Standard
3.5 Mpa	0.231 ml sucrose/ml	0.1875 ml 1,4-but./ml
	1615.385 ppm sucrose	939.1875 ppm 1,4-but.

TIME (min)	HPLC Response Area:		
	Fructose	Glycerol	Sucrose (IS)
0	513362.53	1740.08	157057.93
30	112279.63	1072.83	175190.52
60	5490.32	11594.96	159386.82
90	0.00	19875.80	149648.47
120	0.00	22595.87	191668.26
150	0.00	24584.55	166136.49
180	0.00	21341.36	167412.41
210	0.00	23683.81	201580.11
240	0.00	24998.67	173128.17

TIME (min)	GC Response Area:		
	Propylene Glycol	Ethylene Glycol	1,4-butanediol (IS)
0	59310.16	46643.14	468008.29
30	43925.57	60814.23	682169.23
60	240230.58	219516.13	665587.57
90	522609.12	186482.15	646447.27
120	600469.10	192977.48	701007.57
150	506621.42	130032.46	381226.35
180	489961.08	201692.39	469614.73
210	547791.52	242915.01	452228.46
240	686042.46	208408.08	633074.83

Conversion (%)	YIELDS (%)			Total Selectivity
	Glycerol	Propylene Glycol	Ethylene Glycol	
44.01	9.43	2.30	1.77	0.3066
89.02	9.22	0.99	1.59	0.1326
99.41	11.96	7.19	5.72	0.2502
100.00	14.42	16.55	5.01	0.3599
100.00	13.81	17.56	4.79	0.3616
100.00	15.05	27.44	5.91	0.4840
100.00	14.21	21.46	7.43	0.4310
100.00	13.80	24.98	9.28	0.4805
100.00	14.90	22.31	5.71	0.4292

Exp #26 Date 12/14/1999

Reaction Components:		
	Type	Amount
Substrate	Fructose	0.5 g
Solvent	1M EtOH	40 ml
Base	1N NaOH	1 ml
Catalyst	5 % Ruthenium on Carbon	0.05 g

Reaction Conditions

	HPLC Run	GC Run
Temperature	Injection Amount	Injection Amount
210 °C	10 ml	3 ml
Pressure	Internal Standard	Internal Standard
3.5 Mpa	0.231 ml sucrose/ml	0.1875 ml 1,4-but./ml
	1615.385 ppm sucrose	939.1875 ppm 1,4-but.

TIME (min)	HPLC Response Area:		
	Fructose	Glycerol	Sucrose (IS)
0	135762.99	2503.33	155428.76
30	117440.41	0.00	156191.08
60	488.68	2171.77	157952.39
90	126.78	9459.39	156010.66
120	291.57	14599.20	156061.92
150	38.62	18824.23	197389.86
180	15.98	20274.30	197855.65
210	720.17	27782.92	210708.98
240	249.22	17025.30	146500.91

TIME (min)	GC Response Area:		
	Propylene Glycol	Ethylene Glycol	1,4-butanediol (IS)
0	75088.06	53585.82	368811.98
30	40852.42	52005.27	391622.28
60	61658.33	149056.77	519575.94
90	359927.35	170536.56	561307.95
120	448280.96	205300.49	443231.19
150	695704.08	238539.18	652977.86
180	694540.44	172760.59	627906.98
210	697493.32	197570.60	568820.64
240	763642.35	248694.93	642887.90

Conversion (%)	YIELDS (%)			Total Selectivity
	Glycerol	Propylene Glycol	Ethylene Glycol	
85.04	9.63	3.90	2.55	0.1892
87.12	8.97	1.83	2.34	0.1508
99.95	9.54	2.13	4.98	0.1666
99.99	11.46	13.06	5.27	0.2980
99.97	12.81	20.80	8.01	0.4163
100.00	12.89	21.93	6.33	0.4114
100.00	13.18	22.78	4.78	0.4074
99.94	14.38	25.29	6.02	0.4572
99.97	13.74	24.49	6.70	0.4494

Exp #27 Date 1/7/2000

Reaction Components:		
	Type	Amount
Substrate	Fructose	0.5 g
Solvent	1M EtOH	40 ml
Base	1N NaOH	1 ml
Catalyst	Nickel on Kieselguhr	0.05 g

Reaction Conditions

	HPLC Run	GC Run
Temperature	Injection Amount	Injection Amount
210 °C	10 ml	3 ml
Pressure	Internal Standard	Internal Standard
3.5 Mpa	0.231 ml sucrose/ml	0.1875 ml 1,4-but./ml
	1615.385 ppm sucrose	939.1875 ppm 1,4-but.

TIME (min)	HPLC Response Area:		
	Fructose	Glycerol	Sucrose (IS)
0	271837.47	959.39	199803.13
30	91516.75	0.00	166999.34
60	1687.53	1740.35	150904.13
90	180.95	12596.84	225015.6
120	116.51	29204.98	198371.62
150	22.64	35659.19	151126.5
180	0.00	30882.22	165624.5
210	68.35	30266.31	157445.41
240	0.00	32225.70	154721.04

TIME (min)	GC Response Area:		
	Propylene Glycol	Ethylene Glycol	1,4-butanediol (IS)
0	75088.06	53585.82	368811.98
30	36763.03	34480.30	599377.09
60	71400.52	140792.74	475473.01
90	141871.80	43758.67	471112.30
120	557077.60	151012.40	572458.70
150	599506.14	202296.71	533803.98
180	533288.78	194337.27	498984.00
210	657128.44	191185.32	599029.90
240	595529.80	188860.55	559244.44

Conversion (%)	YIELDS (%)			Total Selectivity
	Glycerol	Propylene Glycol	Ethylene Glycol	
76.69	9.17	3.90	2.55	0.2037
90.61	8.97	0.93	1.05	0.1208
99.81	9.44	2.79	5.14	0.1741
99.99	11.27	5.94	1.65	0.1887
99.99	15.02	20.00	4.59	0.3960
100.00	18.66	23.13	6.57	0.4836
100.00	16.63	22.00	6.75	0.4537
99.99	16.86	22.59	5.54	0.4499
100.00	17.52	21.91	5.86	0.4529

Exp #28 Date 1/10/2000

Reaction Components:		
	Type	Amount
Substrate	Type	0.5 g
Solvent	Sucrose	40 ml
Base	1N NaOH	1 ml
Catalyst	Copper (II) Oxide	0.05 g

Reaction Conditions

	HPLC Run	GC Run
Temperature	Injection Amount	Injection Amount
210 °C	10 ml	3 ml
Pressure	Internal Standard	Internal Standard
3.5 Mpa	0.231 ml sucrose/ml	0.1875 ml 1,4-but./ml
	1615.385 ppm suc.	939.1875 ppm 1,4-but.

TIME (min)	HPLC Response Area:		
	Fructose	Glycerol	Sucrose (IS)
0	976880.01	0.00	130442.47
30	660368.13	434.09	197544.61
60	357961.30	817.58	338693.6
90	30998.55	449.67	171125.84
120	4093.21	1949.52	151113.62
150	0.00	6780.13	194683.92
180	87207.11	16214.38	173004.61
210	110734.53	14400.80	185610.72
240	134178.80	16793.48	212271.2

TIME (min)	GC Response Area:		
	Propylene Glycol	Ethylene Glycol	1,4-butanediol (IS)
0	79743.37	47704.01	424943.88
30	71185.65	70830.14	555045.82
60	59129.61	67895.15	553955.39
90	57589.11	52241.93	503404.12
120	124631.71	136617.21	568498.24
150	515009.52	226586.66	628054.47
180	653091.87	158418.30	631578.55
210	593347.64	136659.98	435553.61
240	841719.27	234833.18	668490.62

Conversion (%)	YIELDS (%)			Total Selectivity
	Glycerol	Propylene Glycol	Ethylene Glycol	
-47.14	8.51	3.39	1.89	-0.2926
34.32	8.60	2.21	2.14	0.3772
79.23	8.61	1.78	2.05	0.1571
96.44	8.62	1.94	1.75	0.1275
99.47	9.02	4.02	3.98	0.1710
100.00	9.87	15.95	5.94	0.3176
90.10	12.16	20.21	4.15	0.4053
88.28	11.54	26.73	5.17	0.4920
87.58	11.60	24.68	5.79	0.4802

Exp #29 Date 2/7/2000

Reaction Components:		
	Type	Amount
Substrate	Sucrose	0.5 g
Solvent	1M EtOH	40 ml
Base	1N NaOH	1 ml
Catalyst	Ba prom. Cu-Chromite	0.05 g

Reaction Conditions

	HPLC Run	GC Run
Temperature	Injection Amount	Injection Amount
210 °C	10 ml	3 ml
Pressure	Internal Standard	Internal Standard
3.5 Mpa	0.231 ml sucrose/ml	0.1875 ml 1,4-but./ml
	1615.385 ppm suc.	939.1875 ppm 1,4-but.

TIME (min)	HPLC Response Area:		
	Fructose	Glycerol	Sucrose (IS)
0	937361.58	0.00	95009.52
30	983881.58	131.16	86424.14
60	31307.59	29974.18	147770.97
90	4976.20	31693.51	136933.24
120	295.61	26656.54	144935.42
150	17805.59	41230.03	181705.73
180	513.98	30987.93	153998.67
210	1883.87	28935.39	157094.71
240	1135.82	30373.49	133691.19

TIME (min)	GC Response Area:		
	Propylene Glycol	Ethylene Glycol	1,4-butanediol (IS)
0	88219.35	49005.84	473221.57
30	64056.67	46765.42	346159.96
60	79898.94	69213.92	360622.08
90	103779.12	103326.00	547787.46
120	65137.33	133692.55	495848.74
150	94720.85	160990.35	538375.30
180	154970.76	150013.86	655517.39
210	254598.71	140825.93	451838.68
240	373916.58	155384.06	523511.35

Conversion (%)	YIELDS (%)			Total Selectivity
	Glycerol	Propylene Glycol	Ethylene Glycol	
-93.84	8.51	3.37	1.74	-0.1452
-123.67	8.57	3.34	2.26	-0.1146
95.84	16.42	4.07	3.19	0.2470
99.29	17.53	3.43	3.13	0.2426
99.96	15.68	2.27	4.45	0.2241
98.07	17.35	3.16	4.93	0.2595
99.93	16.35	4.36	3.79	0.2452
99.76	15.69	10.86	5.14	0.3176
99.83	17.36	13.85	4.90	0.3617

Exp #30 Date 1/20/2000

Reaction Components:		
	Type	Amount
Substrate	Sucrose	0.5 g
Solvent	1M EtOH	40 ml
Base	1N NaOH	1 ml
Catalyst	Nickel on Alumina/Silica	0.05 g

Reaction Conditions

	HPLC Run	GC Run
Temperature	Injection Amount	Injection Amount
210 °C	10 ml	3 ml
Pressure	Internal Standard	Internal Standard
3.5 Mpa	0.231 ml sucrose/ml	0.1875 ml 1,4-but./ml
	1615.385 ppm suc.	939.1875 ppm 1,4-but.

TIME (min)	HPLC Response Area:		
	Fructose	Glycerol	Sucrose (IS)
0	875093.22	1432.42	165966.71
30	955758.76	1056.81	199041.56
60	288958.42	1667.11	195210.39
90	56601.98	482.69	177717.05
120	2426.10	20079.19	154968.94
150	93244.03	19126.53	171788.86
180	51521.49	34235.01	154006.22
210	66318.53	33497.36	151162.45
240	19596.79	23274.89	145758.06

TIME (min)	GC Response Area:		
	Propylene Glycol	Ethylene Glycol	1,4-butanediol (IS)
0	112055.82	44774.62	567067.27
30	71691.41	67190.94	514490.65
60	93493.09	131680.42	555502.44
90	241323.20	216560.40	580931.16
120	424890.04	277332.28	615450.68
150	689377.14	319329.22	585484.98
180	927299.84	368688.76	659054.73
210	915242.10	281306.99	566735.23
240	1048081.36	325563.43	659817.04

Conversion (%)	YIELDS (%)			Total Selectivity
	Glycerol	Propylene Glycol	Ethylene Glycol	
-3.59	8.85	3.59	1.34	-3.8340
5.66	8.72	2.43	2.19	2.3577
70.92	8.85	3.01	3.92	0.2224
93.74	8.62	7.92	6.14	0.2418
99.69	13.56	13.38	7.41	0.3445
89.34	12.85	23.05	8.95	0.5021
93.43	17.17	27.62	9.18	0.5777
91.38	17.15	31.75	8.15	0.6242
97.36	14.73	31.22	8.10	0.5552

Exp #31 Date 1/20/2000

Reaction Components:		
	Type	Amount
Substrate	Sucrose	0.5 g
Solvent	1M EtOH	40 ml
Base	1N NaOH	1 ml
Catalyst	Nickel on Alumina/Silica	0.05 g
	Copper (II) Oxide	0.05 g

Reaction Conditions

	HPLC Run	GC Run
Temperature	Injection Amount	Injection Amount
210 °C	10 ml	3 ml
Pressure	Internal Standard	Internal Standard
3.5 Mpa	0.231 ml sucrose/ml	0.1875 ml 1,4-but./ml
	1615.385 ppm suc.	939.1875 ppm 1,4-but.

TIME (min)	HPLC Response Area:		
	Fructose	Glycerol	Sucrose (IS)
0	872047.95	2293.53	147921.44
30	917497.18	2031.63	138288.67
60	179688.78	2170.19	173915.79
90	10802.35	5454.06	12113.18
120	n/a	n/a	n/a
150	3676.25	6892.14	155605.86
180	1402.34	22254.71	140334.89
210	52994.73	23918.78	168655.02
240	12348.88	22747.00	142324.64

TIME (min)	GC Response Area:		
	Propylene Glycol	Ethylene Glycol	1,4-butanediol (IS)
0	n/a	n/a	n/a
30	85428.15	67755.80	704951.60
60	100999.09	139429.19	643737.29
90	241626.76	217465.95	539915.57
120	485312.97	307727.03	695151.93
150	627016.31	310918.50	632069.59
180	752373.02	302908.89	526448.64
210	919238.75	296586.49	660941.20
240	892227.42	346205.00	625438.42

Conversion (%)	YIELDS (%)			Total Selectivity
	Glycerol	Propylene Glycol	Ethylene Glycol	
-15.83	9.12	#VALUE!	#VALUE!	#VALUE!
-30.35	9.09	2.07	1.62	-0.4210
79.70	9.00	2.78	3.59	0.1928
82.48	26.06	8.55	6.63	0.4999
#VALUE!	#VALUE!	13.53	7.28	#VALUE!
99.54	10.24	19.37	8.08	0.3786
99.80	14.69	28.05	9.44	0.5229
93.83	14.04	27.29	7.37	0.5191
98.30	14.74	28.00	9.08	0.5273

Exp #32 Date 2/4/2000

Reaction Components:		
	Type	Amount
Substrate	Sucrose	0.5 g
Solvent	1M EtOH	40 ml
Base	1N NaOH	1 ml
Catalyst	Palladium 1% on Carbon	0.05 g
	Boron Oxide	0.05 g

Reaction Conditions

	HPLC Run	GC Run
Temperature	Injection Amount	Injection Amount
210 °C	10 ml	3 ml
Pressure	Internal Standard	Internal Standard
3.5 Mpa	0.231 ml sucrose/ml	0.1875 ml 1,4-but./ml
	1615.385 ppm suc.	939.1875 ppm 1,4-but.

TIME (min)	HPLC Response Area:		
	Fructose	Glycerol	Sucrose (IS)
0	1100663.16	669.77	119780.96
30	654099.88	195.95	126392.81
60	157154.96	3432.34	167754.82
90	24605.86	16846.79	144899.33
120	3702.27	43298.30	120871.64
150	4187.44	55326.94	124971.37
180	224.25	101489.28	146369.69
210	370.17	108940.53	131920.28
240	452.73	89438.03	145022.08

TIME (min)	GC Response Area:		
	Propylene Glycol	Ethylene Glycol	1,4-butanediol (IS)
0	66674.47	51072.53	274322.98
30	50441.09	40460.20	315531.95
60	34895.59	20803.99	399776.44
90	108113.60	129608.47	351887.41
120	297514.24	218889.85	482978.32
150	381527.68	225817.15	474812.92
180	550965.54	283855.34	491167.35
210	582274.41	276463.55	523779.00
240	577241.71	266301.03	598576.97

Conversion (%)	YIELDS (%)			Total Selectivity
	Glycerol	Propylene Glycol	Ethylene Glycol	
-80.54	8.73	4.49	3.09	-0.2026
-1.68	8.57	2.84	2.15	-8.0822
81.59	9.31	1.40	0.90	0.1423
96.66	13.04	5.77	6.06	0.2573
99.40	22.47	11.90	7.45	0.4207
99.34	25.76	15.63	7.81	0.4953
99.97	35.53	21.95	9.48	0.6698
99.94	40.69	21.75	8.67	0.7114
99.94	32.54	18.82	7.31	0.5871

Exp #33 Date 2/10/2000

Reaction Components:		
	Type	Amount
Substrate	Sucrose	0.5 g
Solvent	1M EtOH	40 ml
Base	1N NaOH	1 ml
Catalyst	Nickel on Alumina/Silica	0.05 g
	Iron (III) Oxide	0.05 g

Reaction Conditions

	HPLC Run	GC Run
Temperature	Injection Amount	Injection Amount
210 °C	10 ml	3 ml
Pressure	Internal Standard	Internal Standard
3.5 Mpa	0.231 ml sucrose/ml	0.1875 ml 1,4-but./ml
	1615.385 ppm suc.	939.1875 ppm 1,4-but.

TIME (min)	HPLC Response Area:		
	Fructose	Glycerol	Sucrose (IS)
0	952810.34	687.08	164024.64
30	1066394.16	96.15	146372.15
60	178159.12	1000.67	160406.91
90	21805.59	1669.77	194212.16
120	28073.90	14402.80	183202.4
150	2878.19	22134.82	160172.78
180	2163.37	26262.18	161312.92
210	2115.18	29518.64	159361.07
240	752.64	24655.08	135575.24

TIME (min)	GC Response Area:		
	Propylene Glycol	Ethylene Glycol	1,4-butanediol (IS)
0	64223.51	46168.22	351342.82
30	34328.12	29338.26	406251.71
60	111387.34	132149.08	597059.89
90	96921.38	159587.95	411846.98
120	480712.57	257405.38	567796.09
150	795338.61	277171.44	641031.09
180	967410.56	285212.43	555871.09
210	932648.21	309552.77	611939.88
240	1041780.08	391245.40	564110.11

Conversion (%)	YIELDS (%)			Total Selectivity
	Glycerol	Propylene Glycol	Ethylene Glycol	
-14.13	8.68	3.30	2.20	-1.0028
-43.14	8.54	1.34	1.23	-0.2576
78.18	8.76	3.37	3.67	0.2020
97.79	8.85	4.34	6.38	0.2000
96.99	11.58	16.48	7.45	0.3661
99.65	13.90	24.31	7.11	0.4548
99.74	14.86	34.24	8.42	0.5767
99.74	15.73	29.94	8.31	0.5412
99.89	15.60	36.35	11.37	0.6339

Exp #34 Date 2/10/2000

Reaction Components:		
	Type	Amount
Substrate	Sucrose	0.5 g
Solvent	1M EtOH	40 ml
Base	1N NaOH	1 ml
Catalyst	Nickel on Alumina/Silica	0.05 g
	Aluminum Oxide	0.05 g
	Copper (II) Oxide	0.05 g

Reaction Conditions

	HPLC Run	GC Run
Temperature	Injection Amount	Injection Amount
210 °C	10 ml	3 ml
Pressure	Internal Standard	Internal Standard
3.5 Mpa	0.231 ml sucrose/ml	0.1875 ml 1,4-but./ml
	1615.385 ppm suc.	939.1875 ppm 1,4-but.

TIME (min)	HPLC Response Area:		
	Fructose	Glycerol	Sucrose (IS)
0	955929.48	1097.20	159818.91
30	887229.30	0.00	137474.7
60	396587.02	15220.28	147103.86
90	77340.88	3192.57	153398.8
120	14289.37	6734.94	129338.88
150	2430.76	11803.60	149387.13
180	553.93	21491.24	142717.71
210	952.06	32749.33	133055.26
240	0.00	28349.92	148315.46

TIME (min)	GC Response Area:		
	Propylene Glycol	Ethylene Glycol	1,4-butanediol (IS)
0	85205.17	110134.98	342144.31
30	58189.07	60387.41	461936.79
60	142192.23	190659.88	687369.50
90	217795.59	270322.83	668528.61
120	371960.07	361608.53	611035.59
150	597130.55	385490.04	519332.08
180	859053.32	407725.12	569208.16
210	928717.75	458883.55	532283.48
240	1046691.70	244157.81	619539.37

Conversion (%)	YIELDS (%)			Total Selectivity
	Glycerol	Propylene Glycol	Ethylene Glycol	
-17.52	8.78	4.61	5.31	-1.0674
-26.80	8.51	2.17	2.19	-0.4801
47.03	12.54	3.77	4.58	0.4443
90.09	9.32	6.14	6.65	0.2454
97.83	10.54	11.76	9.71	0.3272
99.68	11.59	22.51	12.16	0.4641
99.92	14.38	29.65	11.74	0.5581
99.86	18.10	34.32	14.12	0.6664
100.00	15.96	33.23	6.48	0.5567

Exp #35 Date 2/17/2000

Reaction Components:		
	Type	Amount
Substrate	Sucrose	0.5 g
Solvent	1M EtOH	40 ml
Base	1N NaOH	1 ml
Catalyst	5% Ruthenium on Carbon	0.05 g

Reaction Conditions

	HPLC Run	GC Run
Temperature	Injection Amount	Injection Amount
210 °C	10 ml	3 ml
Pressure	Internal Standard	Internal Standard
3.5 Mpa	0.231 ml sucrose/ml	0.1875 ml 1,4-but./ml
	1615.385 ppm suc.	939.1875 ppm 1,4-but.

TIME (min)	HPLC Response Area:		
	Fructose	Glycerol	Sucrose (IS)
0	968775.65	827.73	131300.81
30	1095956.08	2342.72	152887.69
60	543856.20	14472.31	166382.16
90	49916.58	2854.97	157194.39
120	9599.20	9162.12	132031.96
150	1723.04	15723.88	127507.33
180	187.92	18752.23	117597.87
210	335.71	17008.76	134999.19
240	0.00	18817.64	119543.28

TIME (min)	GC Response Area:		
	Propylene Glycol	Ethylene Glycol	1,4-butanediol (IS)
0	67349.55	112501.27	345816.98
30	50000.00	76449.28	343581.27
60	96105.19	180875.35	486699.27
90	232681.03	311224.83	665184.37
120	443023.26	290887.01	470994.87
150	784259.34	424104.32	601951.05
180	954310.97	379745.47	541960.48
210	985961.43	405109.42	559719.52
240	1531789.78	431148.88	765588.33

Conversion (%)	YIELDS (%)			Total
	Glycerol	Propylene Glycol	Ethylene Glycol	Selectivity
-44.96	8.76	3.53	5.36	-0.3926
-40.84	9.11	2.56	3.68	-0.3759
35.78	11.90	3.59	6.12	0.6039
93.76	9.22	6.61	7.69	0.2509
98.57	11.22	18.35	10.13	0.4027
99.73	13.32	25.55	11.55	0.5055
99.97	14.73	34.64	11.48	0.6087
99.95	13.42	34.66	11.86	0.5997
100.00	14.65	39.41	9.24	0.6330

Exp #36 Date 2/17/2000

Reaction Components:		
	Type	Amount
Substrate	Sucrose	0.5 g
Solvent	1M EtOH	40 ml
Base	1N NaOH	1 ml
Catalyst	Nickel on Kieselguhr	0.05 g

Reaction Conditions

	HPLC Run	GC Run
Temperature	Injection Amount	Injection Amount
210 °C	10 ml	3 ml
Pressure	Internal Standard	Internal Standard
3.5 Mpa	0.231 ml sucrose/ml	0.1875 ml 1,4-but./ml
	1615.385 ppm suc.	939.1875 ppm 1,4-but.

TIME (min)	HPLC Response Area:		
	Fructose	Glycerol	Sucrose (IS)
0	891025.31	840.21	101594.54
30	767229.71	737.62	124251.67
60	325611.19	5000.18	161824.65
90	35187.10	1245.01	129874.84
120	1765.28	898.80	119255.66
150	287.62	4489.41	121936.75
180	108.95	7248.56	117972.04
210	514.65	13883.68	133733.69
240	301.69	16327.13	134754.33

TIME (min)	GC Response Area:		
	Propylene Glycol	Ethylene Glycol	1,4-butanediol (IS)
0	0.00	0.00	168517.49
30	46602.95	77507.89	421207.70
60	75116.31	136199.75	600470.42
90	104920.68	186213.49	440069.69
120	175694.89	20540.22	572539.08
150	299803.92	231701.00	678628.37
180	463005.07	291130.57	523442.40
210	382311.35	288721.57	340493.75
240	628483.56	366633.17	483055.20

Conversion (%)	YIELDS (%)			Total Selectivity
	Glycerol	Propylene Glycol	Ethylene Glycol	
-72.32	8.84	-0.34	0.06	-0.1183
-21.32	8.74	1.86	3.06	-0.6409
60.47	9.72	2.15	3.76	0.2583
94.68	8.89	4.40	6.96	0.2138
99.71	8.81	5.76	0.64	0.1525
99.95	9.95	8.44	5.62	0.2402
99.98	10.91	17.24	9.13	0.3728
99.92	12.56	21.97	13.89	0.4845
99.96	13.23	25.51	12.44	0.5120

APPENDIX E

Intermediate Calculations

Substrate: Sucrose
Solvent: 1 M EtOH
Base: 1 N NaOH
Catalyst: Nickel on Alumina/Silica and Iron (III) Oxide

1) Obtain response areas

HPLC Response Area	
sucrose	752.64
glycerol	24655.08
fructose (IS)	135575.24

GC Response Area	
propylene glycol	1041780.08
ethylene glycol	391245.4
1,4-butanediol (IS)	564110.11

2) Using calibration curves, determine concentration (ppm)
ie. Sucrose: $y = 0.8541x - 0.1956$ $y = \text{area}/\text{area}_{IS}$
$x = \text{conc.}/\text{conc.}_{IS}$

$([(752.64/135575.24)+0.1956]/8541)*1613.54 = \text{conc. of sucrose}$
$= 380.01$

3) Adjust the calculated concentration (due to the addition of IS)
$C_1V_1 = C_2V_2$

HPLC	GC
sucrose: C_1*(0.5ml) = (380.01ppm)[a]*(0.65ml)	C_1*(0.5ml) = C_2[a]*(0.80ml)
[a] Concentration was obtained from step 2 also calculate C_1 for glycerol and fructose (IS)	calculate C_1 for propylene glycol, ethylene glycol, and 1,4-butanediol (IS)

4) Calculate Conversion
Conversion = substrate reacted/substrate fed (per mole carbon basis)

ie. sucrose fed:
(12500 µg/ml)*(g/10^6 µg)*(mol sucrose/342.3 g)*(12 mol C/1 mol sucrose) =
0.000438 mol C sucrose/ml

sucrose left:
(494.01 µg/ml)*(g/10^6 µg)*(mol sucrose/342.3 g)*(12 mol C/1 mol sucrose) =
0.0000173 mol C sucrose/ml

sucrose reacted:
sucrose reacted = sucrose fed - sucrose left
= (0.000438-0.0000173) mol C sucrose/ml
= 0.0004207 mol C sucrose/ml

conversion = 0.0004207/0.000438 = .9605*100 = 96.05%

5) Calculate Yield of desired product

Yield = mole desired product formed/mol substrate fed (per mole carbon basis)

ie. Propylene glycol (pg)
(4040.77 μg/ml)[a]*(g/10^6 μg)*(mol pg/76.1 g)*(3 mol C/1 mol pg)/(0.000438 mol C sucrose fed)
= 0.3637 mol C pg produced/ mol C sucrose fed
[a]: concentration was calculated from steps 1, 2 and 3

same procedure for ethylene glycol and glycerol yields

6) Calculate Total Selectivity
Total Selectivity = Sum of Yields of all desired products/Final Conversion (per mole carbon basis)

ie. ((36.37 + 11.37 + 15.60)/96.05) = 0.6594

Yield = (Yield)PG + (Yield)EG + (Yield)Glycerol

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