CATALYTIC CONVERSION OF GLYCEROL AND SUGAR ALCOHOLS TO VALUE-ADDED PRODUCTS

A Dissertation presented to the Faculty of the Graduate School

University of Missouri-Columbia

In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy

by

MOHANPRASAD A. DASARI

Dr. Galen J. Suppes, Dissertation Supervisor

MAY 2006

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

CATALYTIC CONVERSION OF GLYCEROL AND SUGAR ALCOHOLS TO VALUE-ADDED PRODUCTS

Presented by Mohanprasad A. Dasari

a candidate for the degree of Doctor of Philosophy

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

Galen J Suppes

Thomas R. Marrero

Eric J. Doskocil

Rakesh Bajpai

Dedication

This dissertation is dedicated to my parents, Dasari Sambasiva Rao and Padmavathi, for instilling in me the values of hard work, a good attitude and persistence, and for stressing the value of education. Their love, concern and pride in my work were always a major source of strength to me and their encouragement, support and personal sacrifices made an everlasting impression on my life.

ACKNOWLEDGEMENTS

I would like to express my sincere gratitude and indebtedness to my advisor Dr. Galen J. Suppes for continuous support and advice through out these four vital years of my life. His invaluable guidance, suggestions, constructive criticism, and able supervision in all areas acted as the glue holding this dissertation together. I would like to thank him for being such a tremendous source of inspiration, and for having confidence in my abilities and me. I truly appreciate the freedom given to me to explore new ideas and his ability to keep me focused in the right direction.

I would like to express my sincere appreciation to the members of my dissertation committee: Drs. Fu-hung Hsieh, Rakesh Bajpai, Thomas R. Marrero, and Eric J. Doskocil for their valuable suggestions and critical reviews of the dissertation.

I owe deep debts of gratitude to Dr. “Rusty” Sutterlin, Dr. “Mike” Goff, Shaliesh, Roger, Aye, Kiran, Parag, Jason, Zuleica, Liza for being excellent co-workers, advising and helping me in crucial moments at all stages of my research. Moreover, their ideas and arguments added immeasurably to this work. I greatly appreciate the technical support provided by Leemer Cernohlavek from time to time on this project.

I gratefully acknowledge the financial support from National Science Foundation and Missouri Soybean Merchandising Council.

I would like to thank my friends Raman, Amit, Manish, Ajeet, Rajan, Shilpa, John for making my stay at Columbia a pleasant experience. Friends, thanks for everything, and I wish you the very best in your future endeavors.

Finally, I owe my love and respect to my mother Padmavathi, father Sambasiva Rao, sister Phanita, brother-in-law Ramanaji and my dearest Sandhya for always being on my side throughout my life and career. The sacrifices they made, love and patience they displayed and their constant support gave me the strength and courage to complete this project successfully.

TABLE OF CONTENTS

LIST OF TABLES

Page

LIST OF FIGURES

DISCLAIMER

This dissertation contains guidelines, procedure and protocols for performing reactions severe temperature and pressure conditions.

The author in no way implies that these procedures are described in complete details or are safe to reproduce. When performing chemical synthesis or analyzing products, there is no substitute for good judgment and thorough background research on hazards and toxicities.

A list of possible hazards and hazardous environments when performing these experiments include, but are not limited to:

- Mechanical failure
- High pressures
- High temperature
- High voltage
- Chemical toxicity
- Chemical reactivity
- Chemical explosion and
- Toxic vapors

The author assumes no responsibility for any incident that occurs when reproducing procedures similar to or the same as described in this dissertation.

DISSERTATION FORMAT

This dissertation is written as a series of six technical papers that have been submitted for publication in technical journals. Each paper has its own introduction, methods, materials, results and discussion as well as figures and tables.

Chapter 1 gives an overall introduction to glycerol and propylene glycol including their physical & chemical properties, market supply and uses.

Chapter 2 contains the first paper, which deals with conversion of glycerol to propylene glycol and low pressures.

Chapter 3 contains the second paper that deals with deactivation studies of copper chromium catalyst for hydrogenolysis of glycerol to propylene glycol.

Chapter 4 contains the third paper that deals with reactive distillation approach to produce acetol by dehydration of glycerol.

Chapter 5 contains the fourth paper that deals with production of propylene glycol by selective catalytic hydrogenation of acetol.

Chapter 6 contains the fifth paper that deals with solubility studies of hydrogen in acetol.

Chapter 7 contains the sixth paper that deals with kinetics and mass transfer analysis of hydrogenation of acetol to propylene glycol on copper chromium catalyst in a three-phase slurry reactor.

Chapter 8 contains the introduction to sugars and sugar alcohols & screening studies of conversion of sorbitol to propylene glycol.

Chapter 9 contains the summary and conclusions.

1 CHAPTER 1

INTRODUCTION TO GLYCEROL AND PROPYLENE GLYCOL

1.1 Introduction

The recent increases in crude oil prices have created unprecedented opportunities to displace petroleum-derived materials with biobased materials. Petroleum, a non-regenerative source, is an important feedstock of the modern society for its requirements of power, housing, clothing, agriculture and a host of synthetic materials and chemicals. Unfortunately, the available global stocks are depleting fast. Consequently, the current fuel crisis has influenced the economy of the oil-consuming countries adversely.

In view of the persistent shortages, there is an urgent need for the development of alternative processes for their production from agriculture-based regenerative type products. The world scientific community is focusing its attention on the use of renewable resources not only for energy supply but for synthetic chemicals as well.

In the above context, hydrogenolysis of glycerol to produce polyols such as 1,2 propanediol, 1,3 propanediol from a non-petroleum source is of topical interest.

1.2 Biodiesel Industry – Glycerol Market

Over the past couple of decades fatty acid methyl esters derived from vegetable oils and animal fats have assumed importance as a potential diesel fuel extender known as “biodiesel”. [1,2,3] with a worldwide production approaching one billion gallons per year.

$$\left.\begin{aligned}
\text{Triglycerides} + CH_3OH &\rightleftharpoons \text{Diglycerides} + R_1COOCH_3\\
\text{Diglycerides} + CH_3OH &\rightleftharpoons \text{Monoglycerides} + R_2COOCH_3\\
\text{Monoglycerides} + CH_3OH &\rightleftharpoons \text{Glycerol} + R_3COOCH_3
\end{aligned}\right\}\ \text{Biodiesel}$$

The production of biodiesel utilizes surplus vegetable oils, fats, and waste restaurant greases while reducing the US dependence on foreign crude oil. Biodiesel is a renewable, alternative fuel that reduces particulate matter and hydrocarbon emissions. Expansion of the world’s biodiesel industry is significantly limited by high capital costs for the biodiesel refineries. For every 9 kilograms of biodiesel produced, about 1 kilogram of a crude glycerol by-product is formed; and today, biodiesel production plants are in need of methods to realize increased income from this glycerol.

The U. S. annual production of biodiesel is 30-40 million gallons, which is expected to grow at a rate of 50-80% per year, with a target of 400 million gallons of production by the year 2012. The current production capacity, which includes dedicated biodiesel plants and oleochemical plants producing biodiesel, is estimated to be about 150 million gallons per year.[4] However, the major drawback on its commercialization is the poor economics (high cost of biodiesel as compared to petroleum diesel). Excluding capital depreciation, the production cost for biodiesel range from $0.65- $1.50 per gallon[5.] At this production capacity, ~3.5 million gallons of crude glycerol are produced every year. This crude glycerol can be purified by several steps to produce USP grade glycerol. However, refining the crude glycerol, which contains residual catalysts, water, and other organic impurities, is too complex and expensive to handle for small-scale producers in their available limited facilities. To take the crude glycerol described above to this level of purity requires either vacuum distillation or ion exchange refining. Vacuum distillation is capital intensive and not practical for small biodiesel plant operators. Ion exchange columns involve less capital but generate large volumes of wastewater during regeneration so they will involve additional wastewater treatment costs for large operators. About 50% of the biodiesel facilities (excluding P&G) pay for disposal of glycerol byproduct (waste) with the remaining drying the glycerol and either giving it away or selling the glycerol at a low price.

P&G estimated that refining costs to produce United States Pharmacopeia (USP) quality glycerol were less than 20 cents per pound using vegetable oil glycerol. Other grades of glycerol are discounted against USP grade prices. USP glycerol market prices are dropped from $1.00 per pound to roughly $0.50 per pound as the European biodiesel market expanded in the 1990s. Assuming 50 cent a pound value for USP glycerol and 20 cents per pound refining costs, the net credit to the biodiesel plant is 30 cents per pound. One gallon of biodiesel produces 0.735 pounds of glycerol theoretically (with yield losses the number is less). The maximum credit is 22 cents per gallon for large-scale biodiesel plants with glycerol refining capacity. Glycerol produced from dark fats and greases has a higher level of color and odor contaminants as well as other minor compounds. Refining costs for this type of glycerol are higher and the sale value is lower because markets are restricted to technical uses rather than food or pharmaceutical uses.

Another problem that results from refining crude glycerol is that the glycerol market cannot absorb it. In 1998, refined glycerol was abundant and production was declining. Nevertheless, by the end of 1999 and into 2000, the glycerol market was again tight. Today, with plenty of glycerol available to the world market, prices and U. S. exports have declined. Prices for pure glycerol have varied from $0.50 to $1.50/lb over the past several years. Prices in the glycerol market will continue to drop with an over saturated market and new supplies of glycerol coming into the market from the burgeoning biodiesel industry.

Current annual production of glycerol in the United States is about 400 million pounds per year. If biodiesel production in the U.S. reaches 250 million gallons per year, a relatively modest goal that would use only 10% of the U.S. production of soybean oil, the amount of additional glycerol produced from this source would be equal to 50% of the current glycerol production. The impact of this additional glycerol on prices is unclear but it is likely that if new uses for glycerol are not found, the glycerol price will drop to a level that is consistent with its value as a burner fuel, which is about 5 cents/lb.

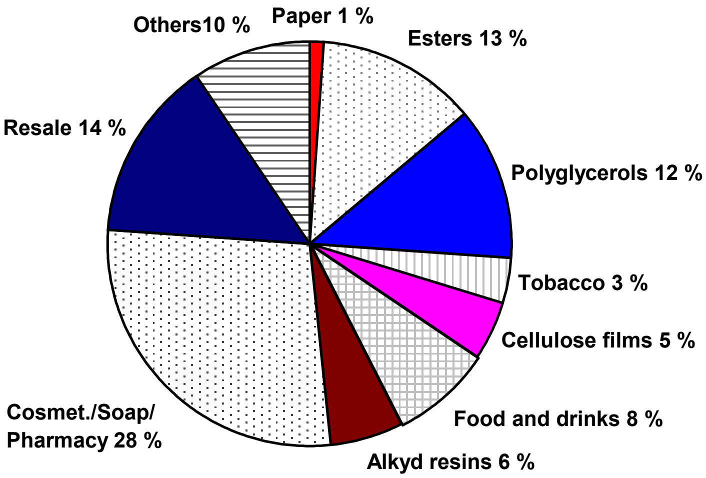
The proposed technology will make use of the crude glycerol to produce a propylene glycol based antifreeze product, which would sell for about $5.00 per gallon, thereby reducing the costs of the biodiesel by $0.25-$0.45 per gallon of biodiesel. This decrease in price of biodiesel would make it substantially more competitive with petroleum diesel to the extent that surplus oils, fats, and greases are available. Much of the biodiesel is and will be sold in regional economy markets—these same markets will be targeted for anti-freeze sales.

1.3 Uses of Glycerol

Glycerol is a commodity chemical with a multitude of uses. Jungermann makes the following comments about uses for glycerol: “Glycerol in is a versatile chemical. It is found in baby care products and in embalming fluids used by morticians, in glues that hold things together and in explosives to blow them apart; in throat lozenges and in suppositories.” Principle uses include: food products, cosmetics, toiletries, toothpaste, explosives, drugs, animal feed, plasticizers, tobacco, and emulsifiers.[6] Glycerol produced by transesterification is only about 50% pure. It contains a significant amount of contaminants including methanol, soap, and catalyst.

Although many uses have been developed for glycerol, most product markets are currently small and fragmented, reflecting glycerol’s relatively high price of $0.60 – 0.90/lb. However, development of a biodiesel market could have a huge impact on the availability and use of glycerol. Since glycerol is a key co product of biodiesel manufacture, increasing use of biodiesel will lead to much greater glycerol availability and lower cost. The lowest price that crude glycerol could fall to is $0.05/lb, because at that value steam reforming to hydrogen, animal feed, and other values will create large markets for crude glycerol. Glycerol prices could fall to $0.20/lb, which is the industry average cost for refining glycerol today although crude, unrefined glycerol, glycerol, may be available for a lower cost.[7]If prices drop into the $0.20 - $0.50/lb range, glycerol can become a major building block for the biorefinery. Small increases in fatty acid consumption for fuels and products can increase world glycerol production significantly. If the United States displaced 2% of the on-road diesel with biodiesel by 2012, almost 800 million pounds of new glycerol supplies would be produced. [8]

Figure 1.1: Distribution of glycerol uses (1995)[9] (Source: HBI)



1.4 Derivatives of Glycerol

Historically, the cost of glycerol has meant that it was either used directly, or subjected to simple structural modifications. Current derivatives include glycerol triacetate, glycerol esters (stearate, oleate), produced through chemical catalysis. At lower projected costs, there is a tremendous potential to develop a variety of new processes and product lines from glycerol, taking advantage of its unique structure and properties. As glycerol is a nontoxic, edible, biodegradable compound, it will provide important environmental benefits to the new platform products. Lower cost glycerol could open significant markets in polymers, ethers, and other compounds. From a technical standpoint, glycerol's multifunctional structure can be exploited by several different means. It is important to note that technology developed for glycerol would have broad crosscutting applications throughout the biorefinery. Since glycerol is structurally analogous to sugars, conversion processes developed for glycerol would also be applicable to inexpensive glucose, xylose, etc., greatly increasing the diversity of the biorefinery.

Selective oxidation of glycerol leads to a very broad family of derivatives that would serve as new chemical intermediates, or as components of new branched polyesters or nylons. These products would address very large chemical markets. Targeted polyesters have markets of 2-3 billion lb/yr, at values between $1.00 – 3.50/lb, while nylons are a 9 billion lb/yr market with values between $0.85 – 2.20/lb, depending on use. Technical barriers for production of these materials include the need to develop selective catalytic oxidation technology that can operate on a polyfunctional molecule such as glycerol. The processes will also need to use simple oxidants, such as oxygen or air, to carry out the required transformations.

New bond breaking (hydrogenolysis) technology will lead to the formation of a number of valuable intermediates. Propylene glycol and 1,3-propanediol are promising potential derivatives that could be produced from glycerol by development of appropriate catalytic systems. 1,3-propanediol can be produced through aerobic fermentation, however, a direct route from glucose to

1,3-propanediol (Dupont) is likely to be more cost effective. The conversion to propylene glycol would be via chemical catalysis. With the capacity to produce 1.5 billion lb/yr of propylene glycol in the US, propylene glycol offers a huge potential market for glycerol. A key barrier for this transformation is to make it cost competitive with the current petroleum route. Again, an important technical barrier is the need to develop selective catalysts to carry out these transformations, specifically, catalysts that can differentiate between C-C and C-O bonds.

1.5 Propylene Glycol Market and Production

To stall glycerol's bottoming prices, due to over supply from biodiesel industry, producers are keen to develop new applications for glycerol. Glycerol suppliers are taking advantage of this market situation to increase use of glycerol in industrial and consumer products. Glycerol is finding its way into antifreeze and deicing applications as substitute for propylene and ethylene glycol. However, due to its low freezing point (18°C), the use of glycerol as glycol substitute is limited. A better option is to economically synthesize propylene glycol from glycerol for use as antifreeze and coolant. Figure 1.2 shows the comparison of freezing point depression curves of propylene glycol and glycerol with commercially available brand of ethylene glycol antifreeze.

Glycols are aliphatic compounds that contain two hydroxyl groups in the molecule. They have a general chemical formula $C_nH_{2n}(OH)_2$. A considerable number of glycols are available commercially. The greatest industrially important glycols are ethylene glycol, propylene glycol, diethylene glycol and triethylene glycol. The lower glycols are neutral, viscous liquids whose physical properties are intermediate between those of monohydric alcohols and trihydric glycerols. Glycols are totally miscible with water and have higher boiling points than corresponding monohydric alcohols. Glycols have lower vapor pressures than water and higher boiling points due to which they are used in various applications as platicizers, coolants, and solubilizing agents

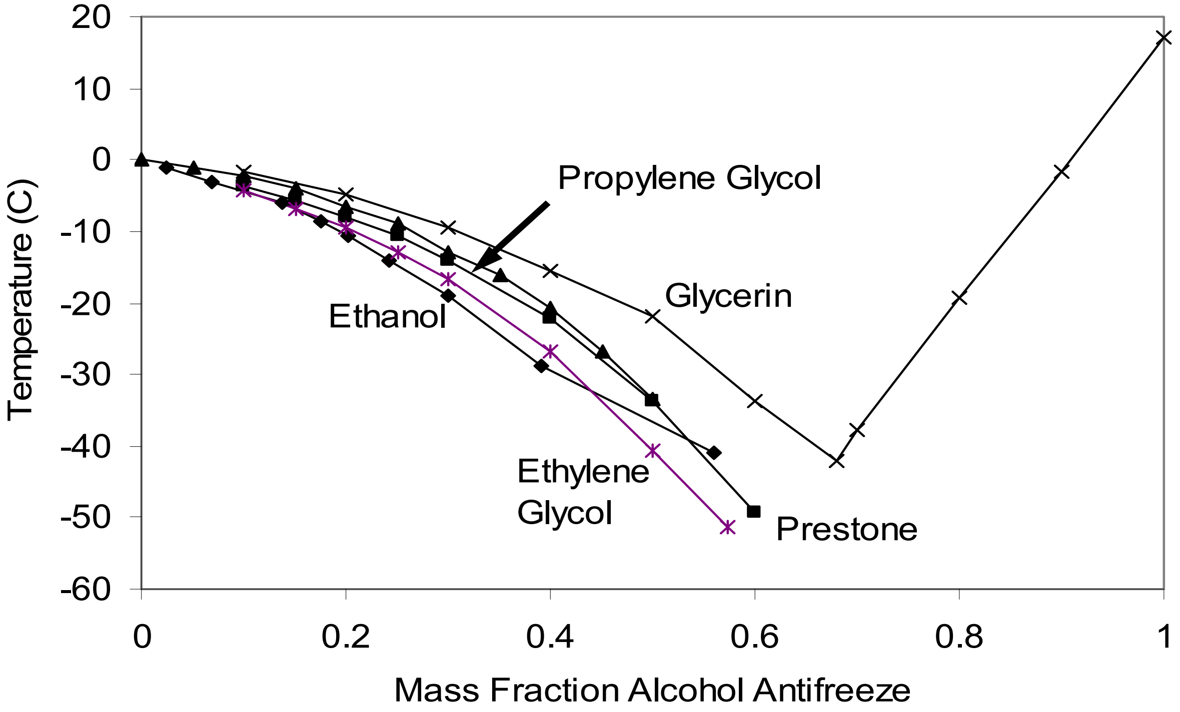


Figure 1.2: Freezing points of aqueous glycol solutions

1.6 Properties of Propylene Glycol

Propylene glycol or 1,2 Propanediol, ($CH_3CHOHCH_2OH$) is a clear, colorless, viscous, practically odorless and tasteless liquid. Propylene glycol is aliphatic organic compound having two hydroxyl groups per molecule and has intermediate properties between alcohols, with a single hydroxyl group and glycerol with its three hydroxyl groups. Likewise, the solubility characteristics of this glycol tend to be between those of the simple alcohols and glycerol. The physical properties of propylene glycol are given in

Table 1.1 below.

Table 1.1: Physical properties of propylene glycol[10]

Boiling point, ºC	187.3
Flash Point (Open Cup), ºC	107
Freezing Point, ºC	-60*
Heat of Vaporization at 1 atm, cal/g	165
Refractive Index, n_D^{20}	1.4329
Specific Gravity at 20/ 4 ºC	1.0363
Specific Heat at 25 ºC, cal/g	0.59
Surface Tension at 25 ºC, dynes/cm	0.37
Vapor Pressure at 20 ºC, mm Hg	0.05
Viscosity at 20 ºC, cps	60.5

* Sets to glass below this temperature

Several physical properties of propylene glycol are directly related to important industrial applications.

1.6.1.1 Freezing Point

The addition of water to a glycol yields a solution with a freezing point below that of water. This has led to the extensive use of glycol-water solutions as cooling media at temperatures appreciably below the freezing point of water. Instead of having sharp freezing points, glycol-water solutions become slushy during freezing. As the temperature is lowered, the slush becomes more and more viscous and finally fails to flow.

1.6.1.2 Burst Protection

Many liquids expand in volume upon cooling. This volume expansion may cause pipes and other enclosed systems containing a liquid to rupture or burst when exposed to low temperature conditions. Burst protection is needed to protect piping and other enclosed systems when they are inactive as they could rupture due to the expansion of an ice or slush mixture during low temperature conditions such as cold weather. Glycol-based fluids provide such burst protection in water solutions due to their low freezing points.

1.6.1.3 Solubility

Propylene glycol, like all low-molecular-weight alcohols, is soluble in all proportions in water. In addition, many water-immiscible materials can be carried into clear water solutions by means of the coupling action of glycols. As a general rule, propylene glycol is a better solvent for oils and organic chemicals than ethylene glycol.

1.6.1.4 Hygroscopicity

Propylene glycol is highly hygroscopic and in conjunction with low toxicity enjoys a unique position as humectant for food applications.

1.6.1.5 Viscosity

Viscosities of glycols vary inversely with temperature. Hot glycols flow freely, but their viscosities increase as they cool until they eventually set and fail to flow. Glycols are more fluid than many high boiling solvents and plasticizers. For this reason, they are often employed alone or with addition of various additives, to reduce the viscosities of composition.

1.6.1.6 Specific Heat

Specific heat is the amount of heat required to raise a unit weight of substance one degree in temperature. Addition of water to a glycol increases the specific heat. This is important whenever glycol solutions are considered for use as heat transfer media.

1.6.1.7 Toxicity

Propylene glycol is a considered practically non-toxic and is allowed as a food additive. Propylene glycol (PG) toxicity is especially low in this respect; studies in which rats were provided with drinking water containing as much as 10% propylene glycol over a period of 140 days showed no apparent ill effects. Other investigations have revealed that rats can tolerate up to 4.9% PG in the diet for 24 month periods without significant effect on growth rate. Most of the common glycols have low order of toxicity except for ethylene glycol. With respect to toxicity, as little as 2 fl. oz. of ethylene glycol can prove fatal to an adult human.

Ethylene glycol is more widely used antifreeze. However, concerns regarding its toxicity have lead to use of propylene glycol as a replacement. Currently, large scale propylene glycol is based on formation of propylene oxide followed by hydration to 1,2-propiondiol. This route uses propylene as a starting material to form propylene chlorohydrin intermediate, which is converted to propylene oxide.

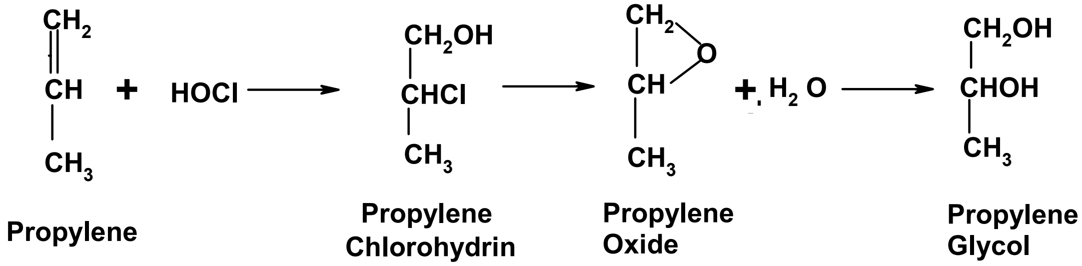


Figure 1.3: Reaction scheme for commercial synthesis of propylene glycol

Another commercial route is the direct oxidation of lower alkanes such as propane to form propylene oxide.

1.7 Uses of Propylene Glycol

Since propylene glycol can undergo chemical reactions on one or both hydroxyl groups, it is important as chemical intermediate. Propylene glycol plays a significant role in industry due to its wide range of practical applications. It is found in such diverse products and applications as thermo set plastics, clothing, latex paints, glass and enamel surface cleaners, automotive antifreeze/coolants, heat transfer fluids, aircraft deicing fluids, natural gas treatment, chemical process fluids, hydraulic fluids, paper and packaging, adhesives, plasticizers, pesticides, printing inks, cosmetics, pharmaceuticals, foods and electronics. All of these applications utilize propylene glycol, either as an integral part of the product or as a facilitator in their production. The major industrial applications of propylene glycol are shown in Figure 1.4.

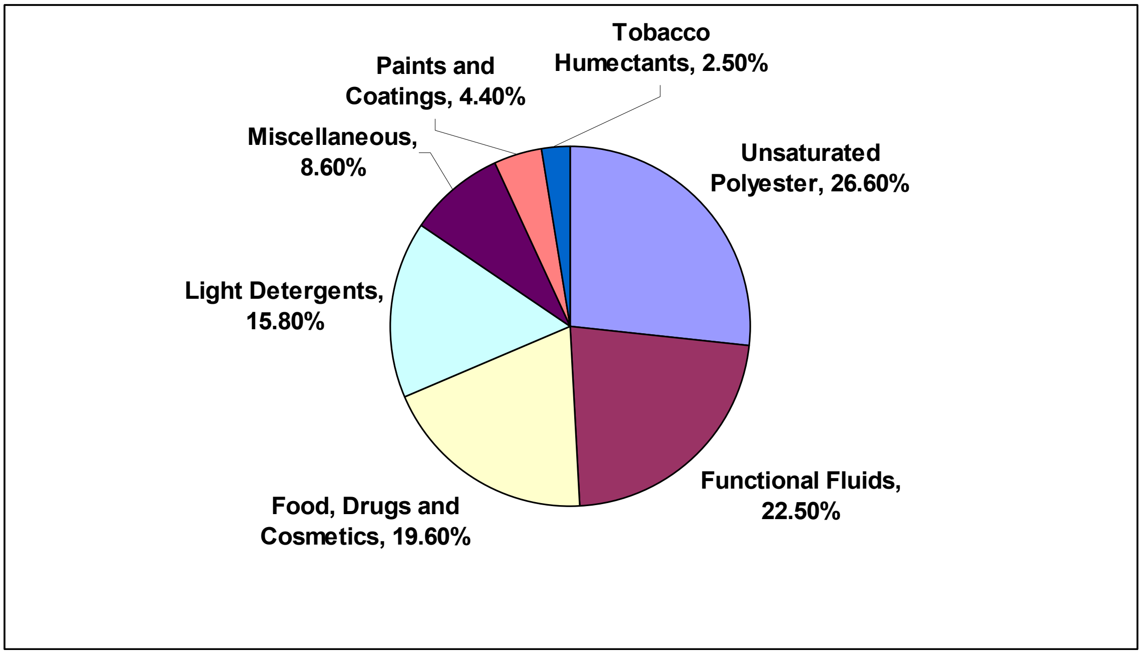


Figure 1.4: Distribution of various uses of propylene glycol.

The total production of propylene glycol in USA is about 1400 million pounds per year.[11] Domestic consumption of propylene glycol increased at rate of 4% from 1990 to 2000. However, it declined by about 3.5% in 2001 and 3% in 2002 due to economic downturn and is projected to increase at about 2% per year. The propylene glycol market is under severe pressure due to increase in oil and natural gas costs. Propylene, which is precursor to propylene oxide used to make propylene glycol has seen significant rise in price. Propylene is obtained by natural gas reforming by catalytic cracking of heavy fractions of crude petroleum. These sources are sensitive to natural gas and crude oil pricing. An alternate cost effective non-petroleum route using biodiesel glycerol as feedstock for making of propylene glycol is expected to prove to be commercially attractive.

This work has resulted in a technology that uses mild temperatures and pressures to synthesize propylene glycol from low cost glycerol feed stock. This route will add value to glycerol and biodiesel while giving consumer a low cost propylene glycol.

1.8 Background Literature

Catalytic processing of natural glycerol to propanediols uses a catalyst, for example, as reported in patents: US 5,616,817, US 4,642,394, US 5,214,219 and US 5,276,181 reporting the successful hydrogenation of glycerol to propanediols. In the patented processes, none provides a reaction product mixture that is suitable for use as antifreeze. The patents do not addresses optimal process conditions and reactions that provide an optimal reaction product mixture for direct use as antifreeze. None address the use of unrefined crude natural glycerol feed stock, and none of these processes are based on reactive distillation.

US 5,616,817 describe the catalytic hydrogenation of glycerol to produce propylene glycol in high yield, such as a 92% yield, with associated formation of n-propanol and lower alcohols. Conversion of glycerol is substantially complete using a mixed catalyst of cobalt, copper, manganese, and molybdenum. Hydrogenation conditions include a pressure of from 100 to 700 bar and a temperature ranging from 180°C to 270°C. Preferred process conditions include a pressure of from 200 to 325 bar and a temperature of from 200°C to 250°C. The lower pressures lead to incomplete reactions and the higher pressures increasingly form short chain alcohols. A crude glycerol feed may be used, such as is obtainable from the transesterification of fats and oils, but needs to be refined by short path distillation to remove contaminants, such as sulfuric acid that is commonly utilized in the transesterification process. The feed should contain glycerol in high purity with not more than 20% water by weight.

US 4,642,394 describeS a process for catalytic hydrogenation of glycerol using a catalyst that contains tungsten and a Group VIII metal. Process conditions include a pressure ranging from 100 to 15,000 psi and a temperature ranging from 75°C to 250°C. Preferred process conditions include a temperature ranging from 100°C to 200°C and a pressure ranging from 200 to 10,000 psi. The reaction uses basic reaction conditions, such as may be provided by an amine or amide solvent, a metal hydroxide, a metal carbonate, or a quaternary ammonium compound. The concentration of solvent may be from 5 to 100 mL solvent per gram of glycerol. Carbon monoxide is used to stabilize and activate the catalyst. The working examples show that process yields may be altered by using different catalysts, for example, where the yield of propanediols may be adjusted from 0% to 36% based upon the reported weight of glycerol reagent.

US 5,214,219 and US 5,266,181 describe the catalytic hydrogenation of glycerol using a copper/zinc catalyst. Process conditions include a pressure ranging from 5 MPa to 20 MPa and a temperature greater than 200°C. Preferred process conditions include a pressure ranging from 10 to 15 MPA and a temperature ranging form 220°C to 280°C. The concentration of glycerol may range from 20% to 60% by weight in water or alcohol, and this is preferably from 30% to 40% by weight. The reaction produces significant amounts of hydrocarbon gas and/or lactic acid in a situation where gas generation is high when lactic acid formation is low and lactic acid formation is high when gas generation is low. This difference is a function of base (sodium hydroxide) added to the solvent. Alcohol reaction products may range from 0% to 13% of hydrocarbon products in the reaction mixture by molar percentages, and propanediols from 27% to 80%. Glycerol conversion efficiency ranges from 6% to 100%.

2 CHAPTER 2

LOW PRESSURE HYDROGENOLYSIS OF GLYCEROL TO PROPYLENE GLYCOL

2.1 Abstract

Hydrogenolysis of glycerol to propylene glycol was performed using nickel, palladium, platinum, copper, and copper-chromite catalysts. The effects of temperature, hydrogen pressure, initial water content, choice of catalyst, catalyst reduction temperature, and the amount of catalyst were evaluated. At temperatures above 200°C and hydrogen pressure of 200 psi, the selectivity to propylene glycol decreased due to excessive hydrogenolysis of the propylene glycol. At 200 psi and 200°C the pressures and temperatures were significantly lower than those reported in the literature while maintaining high selectivities and good conversions. The yield of propylene glycol increased with decreasing water content. A new reaction pathway for converting glycerol to propylene glycol via an intermediate was validated by isolating the acetol intermediate.

KEY WORDS: Hydrogenolysis, Glycerol, Propylene Glycol, Copper-Chromite, Acetol.

2.2 Introduction and Background

Over the past couple of decades fatty acid methyl esters derived from vegetable oil and animal fat have assumed importance as potential diesel fuel extenders known as "biodiesel"[12, ,13 14, 15]. For every 9 kilograms of biodiesel produced, about 1 kilogram of a crude glycerol by-product is formed; and today, biodiesel production plants are in need of methods to realize increased income from this glycerol. If crude natural glycerol could be converted to propylene glycol, this technology could be used in biodiesel production plants to increase profitability. Preferred technology would convert crude natural glycerol at moderate temperatures and pressures.

Propylene glycol, i.e. 1, 2 propanediol, is a three-carbon diol with a steriogenic center at the central carbon atom. Propylene glycol is a major commodity chemical with an annual production of over 1 billion pounds in the United States[16] and sells for about $0.71[17] per pound with a 4% growth in the market size annually. The commercial route to produce propylene glycol is by the hydration of propylene oxide derived from propylene by either the chlorohydrin process or the hydroperoxide process.[18,19] There are several routes to propylene glycol from renewable feedstocks. The most common route of production is through hydrogenolysis of sugars or sugar alcohols at high temperatures and pressures in the presence of a metal catalyst producing propylene glycol and other lower polyols[20,21,22,23,24,25]. Some typical uses of propylene glycol are in unsaturated polyester resins, functional fluids (antifreeze, de-icing, and heat transfer), pharmaceuticals, foods, cosmetics, liquid detergents, tobacco humectants, flavors

& fragrances, personal care, paints and animal feed. The antifreeze and deicing market is growing because of concern over the toxicity of ethylene glycol-based products to humans and animals as well.

Figure 2.1 summarizes the overall reaction of converting glycerol to propylene glycols. In the presence of metallic catalysts and hydrogen, glycerol can be hydrogenated to propylene glycol, 1, 3 propanediol, or ethylene glycol. Several publications and patents document multiple schemes for hydrogenating glycerol to propylene glycol. Casale et al[21,22] described a method of hydrogenating glycerol using copper and zinc catalyst as well as sulfided ruthenium catalyst at a pressure of 2175 psi and temperature in the range of 240-270°C. Schuster et al[23] described a method of production of propanediols using a catalyst containing cobalt, copper, manganese, molybdenum, and an inorganic polyacid achieving a 95% yield of propylene glycol at pressures of 3625 psi and a temperature of 250°C. Che et al[24]describes a method of production of propanediols over homogeneous catalyst containing tungsten and Group VIII transition metals at a pressure of 4600 psi and a temperature of 200°C. Haas et al[25]described a process of simultaneous production of propylene glycol and 1, 3 propanediol from gaseous glycerol solutions at a temperature of 300°C using two stages. Cameron et al proposed a biocatalytic fermentation technique for production of propanediol from glycerol and sugars.[26,27]

In spite of several research efforts, this potentially important reaction was limited to a laboratory scale production because of common drawbacks of existing technologies. One drawback is use of high temperatures and pressures that would necessitate expensive high-pressure equipment, thereby increasing the capital cost of the process. Typical hydrogen pressures anywhere between 1450 – 4700 psi and temperatures in the range 200-350^{o}C were being used for this reaction.

An additional drawback is the use of dilute solutions of glycerol for this reaction. Typically, 10-30% (wt) glycerol solutions were predominantly used which will be further diluted through the water from the reaction. This will reduce the average space-time yield of the reaction increasing the energy consumption of the process and in turn decreasing the process profitability. However, not much has been reported about the positive effect of using dilute glycerol solutions instead of 100% glycerol.

A final drawback is the low selectivity towards propylene glycol. Most of the literature reports high selectivity towards ethylene glycol and other by products like lactic acid, acetol, acrolein, and degradation products like propanol, methanol, carbon dioxide, methane etc.

In an effort to overcome these drawbacks, our research focuses on developing a technology to perform the reaction at lower temperatures and pressures using concentrated glycerol while simultaneously achieving high selectivity towards propylene glycol and little or no selectivity towards ethylene glycol or other by-products. An additional objective of this paper is to validate our proposed novel reaction mechanism for converting glycerol to propylene glycol via a reactive intermediate.

2.3 Recommended Catalysts

Traditional practices of hydrogenating carbonyl groups to form alcohols along with the common practice of hydrogenating ester groups in fats and oils to form fatty alcohols indicate that the alcohol groups are stable and do not readily react at normal hydrogenating conditions. Moreover, the alcohols are also known as excellent solvents for the hydrogenation[28], which imply they very much resist reaction. Hence conventional hydrogenation catalysts such as nickel, ruthenium, and palladium are not very effective for hydrogenating glycerol. Copper is potentially a good catalyst for alcohol hydrogenation. It is known for its poor hydrogenolytic activity towards C-C bond and an efficient catalyst for C-O bond hydro-dehydrogenation[29,30].

2.4 Experimental Methods

2.4.1 Materials

Glycerol (99.9%), propylene glycol, acetol, and n-butanol were purchased from Sigma-Aldrich (Milwaukee, WI). High purity grade hydrogen and nitrogen were obtained from Praxair. Table 2.1 gives the description of various catalysts used in this study and their suppliers.

2.4.2 Experimental Setup

All reactions were carried out in a specially designed stainless steel multi-clave reactor capable of performing eight reactions simultaneously. Each reactor with a capacity of 150mL is equipped with stirrer, heater and a sample port for liquid sampling. The temperature of the reactors was controlled by CAMILE 2000 control and data acquisition system using TG 4.0 software. The reactors were flushed several times with nitrogen followed by hydrogen. Then the system was pressurized with hydrogen to the necessary pressure and heated to the desired reaction temperature. The speed of the stirrer was set constant at 100 rpm throughout the reaction. All the catalysts used in this study were reduced prior to the reaction in the same reactor by passing a stream of hydrogen over the catalyst bed at 300°C for 4 hours. The reactants were immediately transferred to the reactor without further delay.

2.4.3 Method of Analysis

The samples were taken at desired time intervals, cooled to room temperature and centrifuged using an IEC (Somerville, MA) Centra CL3R centrifuge to remove the catalyst. These samples were analyzed with a Hewlett-Packard 6890 (Wilmington, DE) gas chromatograph equipped with a flame ionization detector. Hewlett-Packard Chemstation software was used to collect and analyze the data. A Restek Corp (Bellefonte, PA) MXT® WAX 70624 GC column (30m x 250 μm x 0.5μm) was used for separation. A solution of n-butanol with a known amount of internal standard was prepared a priori and used for analysis. The samples were prepared for analysis by adding 100 μL of product sample to 1000 μL of stock solution into a 2mL glass vial. Figure 2.2 shows a typical gas chromatogram of the hydrogenolysis reaction product. Using the standard calibration curves that were prepared for all the components, the integrated areas were converted to weight percentages for each component present in the sample.

For each data point, selectivity of propylene glycol, conversion of glycerol, and yield of propylene glycol were calculated. Selectivity is defined as the ratio of the number of moles of the product formation to that of the glycerol consumed in the reaction, taking into account the stoichiometric coefficient. Conversion of glycerol is defined as the ratio of number of moles of glycerol consumed in the reaction to the total moles of glycerol initially present. Yield of propylene glycol is defined as the ratio of the number of moles of propylene glycol produced to the theoretical number of moles of the propylene glycol.

2.5 Results and Discussion

2.5.1 Reaction Mechanism

The primary goal of this study is to develop a technology that would allow production of propylene glycol from glycerol at milder hydrogenation conditions. To achieve this, it is necessary to understand the fundamental chemistry and mechanism behind the hydrogenolysis of crude glycerol to propylene glycol.

Preliminary investigations in our work indicated that hydroxyacetone (acetol) was formed and is possibly an intermediate of an alternative path for forming propylene glycol. GC analysis of the reaction product showed the presence of acetol in trace amounts. Acetol is formed by dehydration of a glycerol molecule, which further reacts with hydrogen to form propylene glycol with one mole of water by-product. The proposed mechanism is shown in Figure 2.4. Studies to investigate the effect of water on the hydrogenolysis reaction indicated that the reaction takes place even in absence of water with a 49.7% yield of propylene glycol. Moreover, since the copper-chromite catalyst is reduced in a stream of hydrogen prior to the reaction there will be no surface hydroxyl species taking part in the reaction.

Both the above observations contradict the mechanism proposed by Montassier et al[30] who proposed the reaction mechanism for the conversion of glycerol to propylene glycol shown in Figure 2.3. According to this mechanism, dehydrogenation of glycerol on copper can lead to glyceric aldehyde in equilibrium with its enolic tautomer. The formation of propylene glycol was explained by a nucleophilic reaction of water or adsorbed OH species, a dehydroxylation reaction, followed by hydrogenation of the intermediate unsaturated aldehyde. The Figure 2.3 mechanism supported by our data does not include water present in the form of surface hydroxyl species or as apart of reactants.

In order to validate the mechanism in Figure 2.4, preliminary reactions were conducted in two steps. In step-1, relatively pure acetol was isolated from glycerol at 200°C in absence of hydrogen at 9.4psi pressure in presence of copper-chromite catalyst. In step 2, the acetol formed in step-1 was further hydrogenated to propylene glycol at 200°C and 200 psi hydrogen pressure using similar catalyst that is used for the formation of acetol. The combination of these reactions gave high product yields and results were shown in Table 2.2. This mechanism was supported by the studies of Cameron et al[26,27] in which propanediols were made using biocatalytic routes from glycerol and sugars via formation of a reactive acetol intermediate. Optically active propylene glycol is currently prepared by the biocatalytic reduction of acetol.[31]

2.5.2 Catalyst Screening and Selection

Heterogeneous catalysts, including ruthenium, nickel, platinum, copper, raney copper, raney nickel, palladium, and copper-chromite in the form of metallic powders, metal oxides, and activated metals (metal sponge) were impregnated on an activated carbon support. Reactivities were tested at 200 psi hydrogen pressure and at a temperature of 200°C. Table 2.1 shows the performance comparision of these catalysts. Catalysts like ruthenium and palladium showed low selectivities, less than 50%, due to competitive hydrogenolysis of C-C and C-O bonds leading to excessive degradation of glycerol at lower pressures to form lower alcohols and gases. On the other hand, copper or copper based catalysts exhibited higher selectivity towards propanediols with little or no selectivity towards ethylene glycol and other degradation by-products. Copper-chromite catalyst was selected for further studies.

2.6 Parametric Studies

The effect of catalyst reduction temperature, reaction temperature, hydrogen pressure, initial water content and amount of catalyst for the hydrogenolysis reaction were determined using copper-chromite catalyst and the results are discussed in the following sections.

2.6.1 Effect of Catalyst Reduction Temperature

Copper-chromite catalyst obtained in an oxide form is partially or fully reduced in presence of hydrogen to increase its activity. Habaut et al[32] reports that the coordinately unsaturated sites of cuprous ions on the catalyst surface are the active sites for hydrogenation. Studies were performed in order to determine the activity of the catalyst as a function of catalyst prereduction temperature. The catalyst was reduced in an atmosphere of hydrogen at different temperatures: 150, 200, 250, 300, 350 and 400°C for 4 hours. Figure 2.5 provides the summary of the conversions of 80% glycerol solution at 200°C and 200 psi using copper-chromite catalyst reduced at different temperatures. The yield and selectivity of propylene glycol increase with catalyst reduction temperatures up to 300°C and decrease for temperatures greater than 300°C. Hence, reducing the catalyst at 300°C for 4 hours was detemined as the optimum conditon for the hydrogenolysis reaction and is used for further studies.

2.6.2 Effect of Catalyst Weight

It was observed that the activity of the copper-chromite catalyst is lost even before the reaction goes to completion. This catalyst can be regenerated by washing with a polar solvent and reducing it in a stream of hydrogen and in some cases has to be replaced with fresh catalyst. In order to minimize the high cost of catalyst replacement and addition of fresh catalyst, a minimum amount of fresh catalyst could be used in each batch, which can be discarded after use. Reactions were carried out to find the minimum weight of the catalyst required to achieve the necessary conversion. Table 2.3 shows the effect of catalyst weight on overall conversion of glycerol to propylene glycol. The glycerol conversion and the yield of propylene glycol increased with catalyst concentration. As the concentration of the catalyst increases, more surface area is available for the hydrogenolysis reaction to take place. The initial rates of conversion of glycerol and formation of propylene glycol have a proportional increase with the catalyst amount. However, as the reaction time increases, the excess catalyst further promotes excessive hydrogenolysis reaction converting propylene glycol to lower alcohols and gases. Hence, to get a good conversion of glycerol with high selectivity to propylene glycol an optimal amount of catalyst should be used depending on the reaction time.

2.6.3 Effect of Reaction Temperature

Temperature has a significant effect on the overall yield of the propylene glycol. Reactions were carried out at 150, 180, 200, 230, and 260^{o}C and at a pressure of 200 psi of hydrogen in the presence of a copper-chromite catalyst. Table 2.4 shows the effect of temperature on the conversion and yield of the reaction. As the temperarture of the reaction increases from 150 to 260^{o}C there is a uniform increase in the glycerol conversion from 7.2% to 87%. However, the overall yield of propylene glycol increased until 200^{o}C and began to decrease as the temperature was increased further. A similar trend is also observed in the case of the selectivity of the propylene glycol. This indicates that at a hydrogen pressure 200 psi, temperatures >200°C lead to excessive hydrogenolysis converting the propanediols into lower alcohols like methanol and ethanol, which upon further degradation form gaseous products like methane, ethane, propane, carbon dioxide, etc. Moreover, from our initial screening studies (data not presented) it was observed that it is necessary to operate at higher pressures to prevent degradation of glycerol at temperatures >200°C.

2.6.4 Effect of Hydrogen Pressure

Reactions were carried out at 50, 100, 150, 200 and 300 psi at a constant temperature of 200°C to determine the effect of hydrogen pressure on the overall reaction. Table 2.5 provides the summary of the conversions of 80% glycerol solution at 200°C under different hydrogen overhead pressures. As expected the conversion of the glycerol increased as the hydrogen pressure increased from 50 psi to 300 psi. The pressures were significantly lower than those reported in the literature. Lower pressure hydrogenolysis can be improtant to maximize the utility of existing equipment for performing hydrogenolysis.

2.6.5 Effect of Initial Water Content

Water is generated in this reaction and it is always preferable to eliminate the water from the initial reaction mixture to drive the equilibrium in the forward direction. Previous literature used very dilute glycerol solutions (10-30%), the reason being unknown. In order to isolate propylene glycol, it is therefore necessary to first remove large amounts of water by distillation, which means expenditure of large amounts of energy. In addition, as the concentration of glycerol decreases from 100% to 50%, the size of the reactor doubles to produce the same amount of product. Hence, reactions were performed using glycerol solutions made up of different water content to study the effect of initial water content on the overall reaction. Table 2.6 provides the summary of effect of initial water content on overall glycerol conversion at 200°C and 200 psi. As the initial water in the reaction increases, both the glycerol conversion and the yield of propylene glycol decreased. Morover, for glycerol solutions with concentration >80% a decrease in the selectivity was observed due to the degradation of reaction product due to polymerization. Hence it is essential to have atleast 10-20% of solvent (water, methanol) to minimise the degradation.

This demonstrates that high yields of propylene glycol can be achieved by using only 10-20% water in glycerol instead of 70-90% water as reported earlier. This would increase the space-time yield of the reaction (yield of propylene glycol product produced per unit volume per unit time) and reduce the size and pressure ratings of the reactor vessels. At these conditions, it is preferred to operate at low water contents to improve conversion and simultaneously reduce the reactor volumes. This was a valuable observation not previously reported in the literature.

2.7 Conclusion

Copper-chromite catalyst was identified as the most effective catalyst for the hydrogenolysis of glycerol to propylene glycol. The mild reaction conditions of 200°C and 200 psi used in these studies give the process based on copper-chromite catalyst distinctive competitive advantages over traditional processes using severe conditions of temperature and pressure. A novel mechanism to produce propylene glycol from glycerol via an acetol intermediate was proposed and validated. In a two-step reaction process, the first step of forming acetol can be performed at atmospheric pressure while the second requires a hydrogen partial pressure. Propylene glycol yields >73% were achieved at moderate reaction contions.

Table 2.1: Summary of conversion of glycerol, yield and selectivity of propylene glycol from glycerol over various metal catalysts and. Reactions were carried using 80% glycerol solution at 200°C and 200 psi hydrogen pressure for 24 hours

Supplier	Description	%Conversion	%Yield	%Selectivity
Johnson Matthey	5% Ru/C	43.7	17.5	40.0
Johnson Matthey	5% Ru/Alumina	23.1	13.8	59.7
Degussa	5% Pd/C	5	3.6	72.0
Degussa	5% Pt/C	34.6	28.6	82.7
PMC Chemicals	10% Pd/C	8.9	4.3	48.3
PMC Chemicals	20% Pd/C	11.2	6.4	57.1
Grace Davision	Raney Nickel	49.5	26.1	52.7
Grace Davision	Raney Copper	48.9	33.8	69.1
Sud-Chemie	Copper	53	21.1	39.8
Sud-Chemie	Copper-chromite	54.8	46.6	85.0
Johnson Matthey	Ni/C	39.8	27.3	68.6
Alfa-Aesar	Ni/Silica-Alumina	45.1	29.1	64.5

Table 2.2: Summary of reactions performed to validate the proposed reaction mechanism

Step 1: Formation and isolation of acetol intermediate from glycerol using copper-chromite catalyst

	Initial Loading (g)	Best Possible (g)	Final Product (g)
Glycerol	50	0	0
Acetol	0	40.22	30.72
Propylene glycol	0	0	2.23

Step 2: Formation and isolation of propylene glycol from acetol intermediate from Step 1using same catalyst

	Initial Loading (g)	Best Possible (g)	Final Product (g)
Acetol	20	0	0.8
Propylene glycol	0	20.5	18.3

Table 2.3: Effect of weight of catalyst on formation of propylene glycol from glycerol. All the reactions were performed using 80% glycerol solution at 200 psi hydrogen pressure for 24 hours

Wt % of Catalyst	%Conversion	%Yield	%Selectivity
1	28.3	17.9	63.3
2.5	33.5	26.2	78.2
5	54.8	46.6	85.0
10	58	45	77.6
15	70.1	45.2	64.5
20	78.5	48.7	62.0

Table 2.4: Effect of reaction temperature on formation of propylene glycol from glycerol. All the reactions were performed using 80% glycerol solution at 200 psi hydrogen pressure for 24 hours

Temperature (°C)	%Conversion	%Yield	%Selectivity
150	7.2	2.3	31.9
180	28	9.8	35.1
200	54.8	46.6	85.0
230	72	35.1	48.7
260	87	7.7	8.8

Table 2.5: Effect of hydrogen pressure on formation of propylene glycol from glycerol. All the reactions were performed using 80% glycerol solution at 200°C for 24 hours

Pressure (psi)	%Conversion	%Yield	%Selectivity
50	25	9.1	36.4
100	37	15.7	42.4
150	44	22.3	50.7
200	54.8	46.6	85.0
300	65.3	58.5	89.6

Table 2.6: Effect of initial water content in the reactants on formation of propylene glycol from glycerol. All the reactions were performed at 200°C and 200 psi hydrogen pressure for 24 hours

Water (wt%)	%Conversion	%Yield	%Selectivity
80	33.5	21.7	64.8
40	48	28.5	59.4
20	54.8	46.6	85.0
10	58.8	47.2	80.3
0	69.1	49.7	71.9

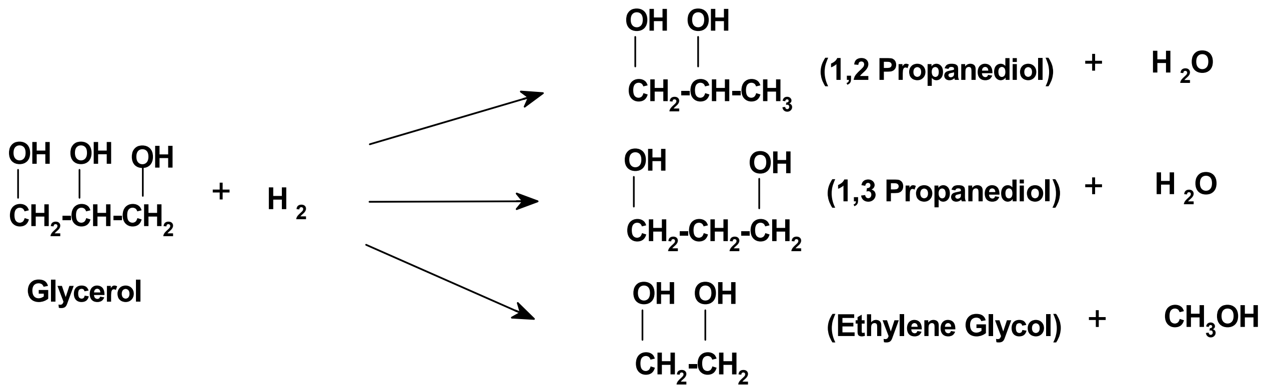


Figure 2.1: Summary of the overall reaction of converting glycerol to propylene and ethylene glycols

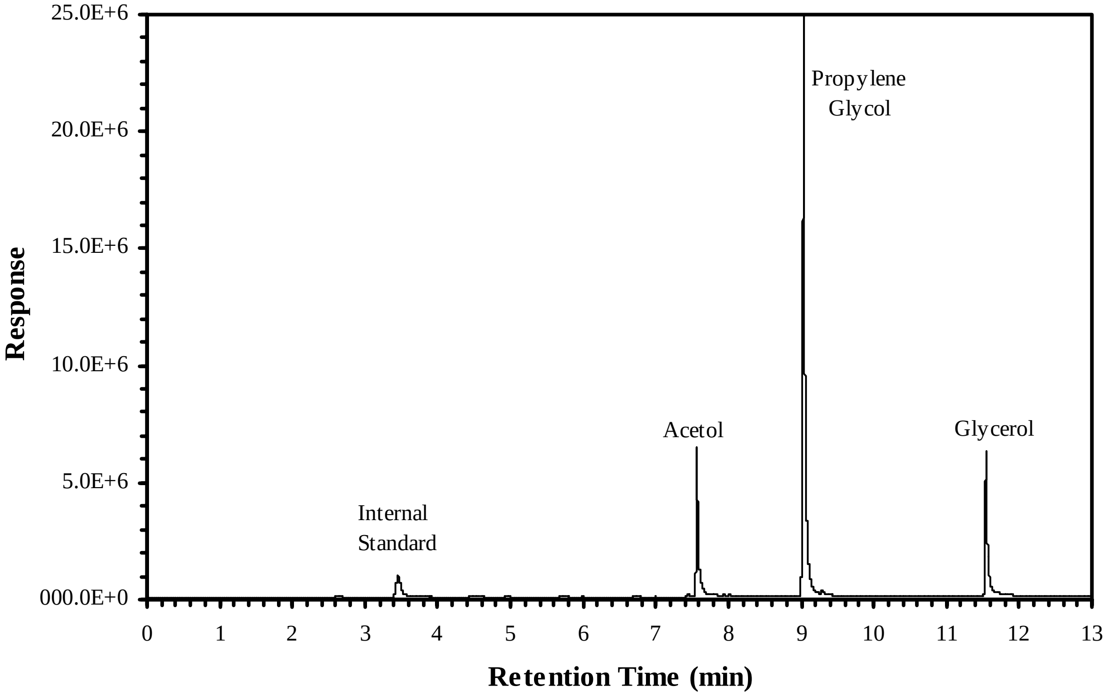


Figure 2.2: Gas chromatogram of the hydrogenolysis reaction product

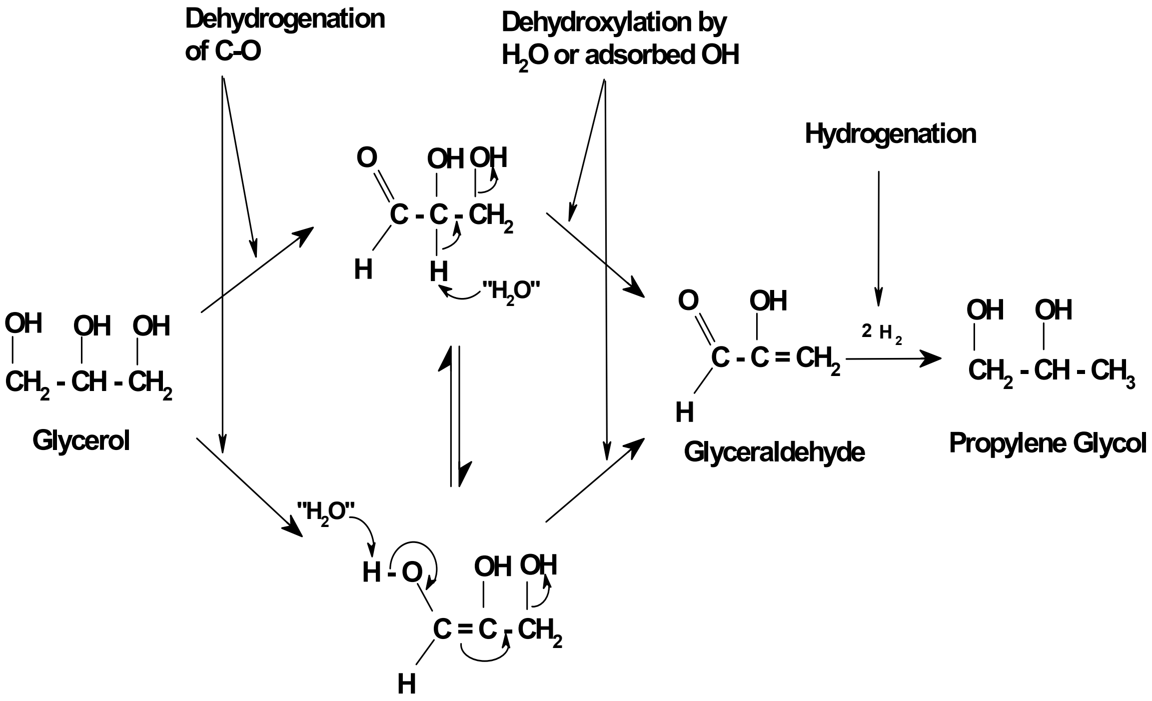


Figure 2.3: Reaction mechanism for conversion of glycerol to propylene glycol proposed by Montassier et al.[30]

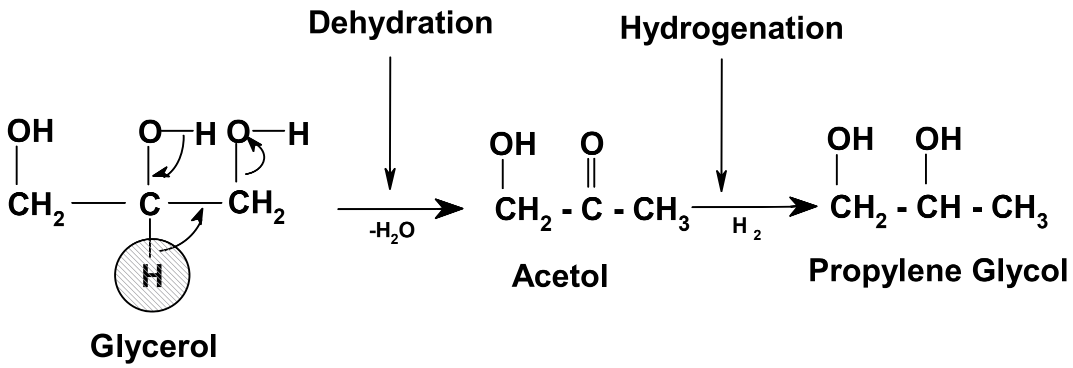


Figure 2.4: Proposed reaction mechanism for conversion of glycerol to propylene glycol

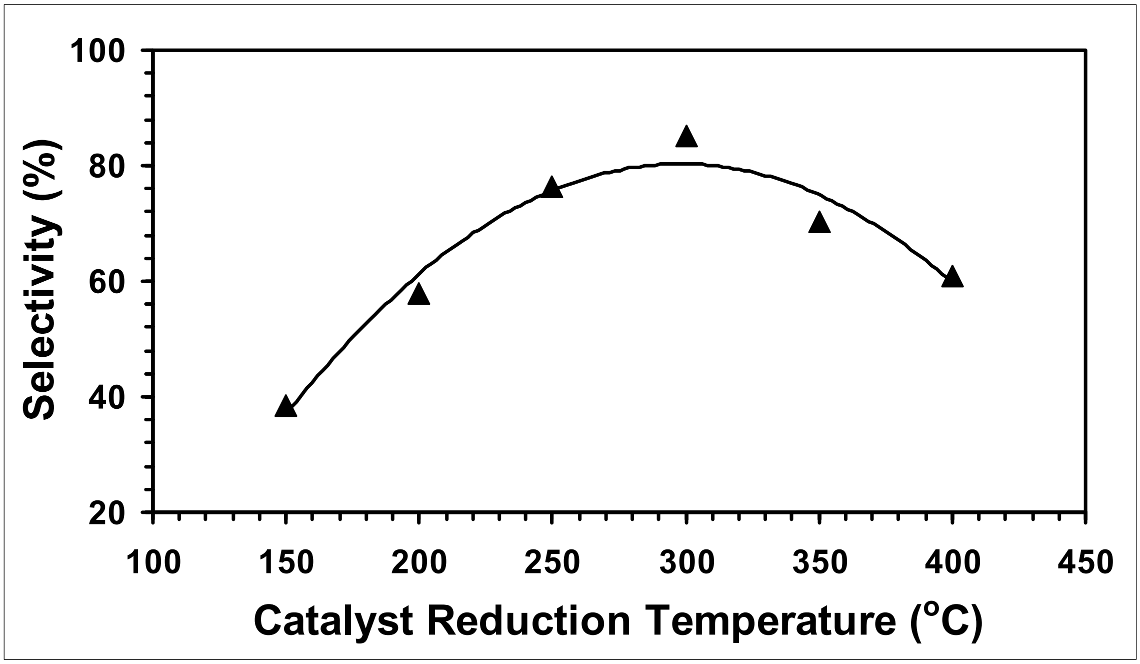


Figure 2.5: Effect of catalyst reduction temperature on formation of propylene glycol from glycerol. All the reactions were performed using 80% glycerol solution at 200°C and 200 psi hydrogen pressure for 24 hours

3 CHAPTER 3

DEACTIVATION OF COPPER CHROMIUM CATALYST FOR HYDROGENAOLYSIS OF GLYCEROL TO PORPYLENE GLYCOL

3.1 Abstract

Experimental studies were conducted to examine the deactivation mechanism of copper chromium catalyst used for hydrogenolysis of glycerol to propylene glycol in a laboratory scale batch reactor and optimum methods for catalyst regeneration were investigated. XPS, BET, XRD, TGA, TEM and AA were used to determine the nature of deactivation.

The main causes for the deactivation were reduction of the cuprous chromium active species into metallic copper species, metal leaching, and blocking of sites by strongly adsorbed inorganic and organic species present in the feed or generated during the reaction. An inorganic chlorine, sulfur and phosphorus poison, at a concentration of <3mmol, strongly and irreversibly deactivated the catalysts by forming corresponding copper salts depending on the nature of impurity. Catalyst deactivation was temporary due to blockage of active catalyst sites by physisorption of the polyol molecules. Catalyst was regenerated by washing the catalyst with methanol in reflux conditions for 6 hours and drying at 200°C for 2 hours. The propylene glycol yield using the regenerated catalyst was

44.1% when compared to 46.6% using the fresh catalyst.

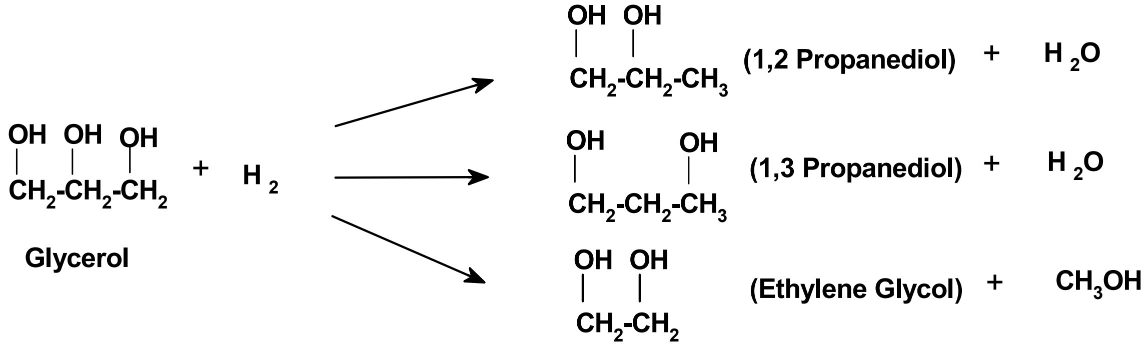
Key Words Catalyst deactivation, Glycerol, Propylene glycol, Copper chromium, X-ray Diffration, Hydrogenolysis

3.2 Introduction and Background

Catalytic hydrogenolysis of glycerol is an important process for the production of propylene glycol, a major commodity chemical with an annual production of over 1 billion pounds in the United States[33]. Propylene glycol sells for about $0. 71[34] per pound with a 4% growth in the market size annually. Some typical uses of propylene glycol include: functional fluids (antifreeze, de-icing, and heat transfer), pharmaceuticals, foods, cosmetics, liquid detergents, tobacco humectants, flavors & fragrances, personal care, paints and animal feed.

In spite of several research efforts, this potentially important reaction has not been commercialized due to low selectivity and relatively high production costs associated with product purification. In a recent publication the authors demonstrated the commercial feasibility of this technology by selectively converting glycerol to propylene glycol at low pressures in presence of copper chromium catalyst[35.] However, the deactivation of copper chromium catalyst at the reaction conditions cannot be neglected in long operation periods. This paper investigates the cause of deactivation and methods of regeneration of the copper chromium catalyst.

Equation 1 summarizes the overall reaction of converting glycerol to propylene glycols. In presence of metallic catalysts and at high temperatures, one mole of glycerol upon complete hydrogenolysis forms one mole of either propylene glycol, 1, 3 propanediol, ethylene glycol or a mixture of all the three along with a mole of water.



In any chemical reaction, that is catalyst dependent, inhibitors and catalyst poisons that deactivate the catalysts are of primary interest. Deactivation can be caused by chemical, thermal, and mechanical effects. The catalyst poisons may fall into two categories: those that temporarily reduce the catalyst activity and those that permanently reduce catalyst activity. Examples of temporary catalyst poisons may be organic compounds including water, soaps, glycerol, polyols etc. On the other hand, there are compounds that may irreversibly adsorb onto the catalyst surface to deactivate the catalyst permanently (eg., compounds containing halogens, sulfur, phosphorus). This paper focuses primarily on the effects these catalyst poisons on the hydrogenolysis reaction of glycerol to propylene glycol.

Depending upon the reaction conditions, other side reactions may take place due to excessive hydrogenolysis forming lower alcohols and gases. The use of an adequately selective catalyst, such as “Adkins” type of copper chromium catalyst[36] would selectively catalyze propylene glycol production with minimum byproduct[35] formation. Barium promoted copper chromium catalysts have excellent selectivity to propylene glycol and allow operation at less severe conditions where economically justified. They are less active but more selective than nickel catalysts. However, this specific copper chromium catalyst deactivates very quickly and brings an economical load on the process.

Organic acid impurities can cause rapid growth of copper crystallites and loss of activity. Barium promoted copper chromium provides resistance to such action as well as providing thermal stability.

Experimental studies indicate that the polyols effectively deactivate the copper chromium catalyst, limiting the rate of glycerol hydrogenolysis reaction[35]. However, the catalyst deactivation is not permanent, suggesting that the catalyst site blockage by physical adsorption of the polyhydroxyl compounds.

Previous studies show that addition of barium, calcium, or magnesium stabilizes the catalyst against reduction and consequent deactivation. This apparently enhances its activity by modifying the relative rates of competitive hydrogenation reactions[37].

Our previous mechanistic studies show that glycerol converts to propylene glycol via a reactive acetol intermediate and is shown in Figure 3.1.[35] This first step in the reaction is a dehydration reaction that is independent of any hydrogen overpressure. The net desired rate for the desired intermediate is influenced by the rate of transport of glycerol into the pore and the rate of transport of the product out of the pore. The opportunities for the intermediate to react further to the final state will increase when the transport of the intermediate is slow. This further reaction of acetol, especially to polyol oligomers, is hypothesized to be a primary cause for deactivation.

3.3 Modes of Deactivation in Copper Chromium Catalyst

Catalyst deactivation processes are generally divided into three general classes based on process characteristics:

3.3.1 Aging

Sintering of metal particles is an irreversible mode of catalyst deactivation that occurs due to agglomeration of the crystallites of the active phase resulting in loss of active surface area and, consequently, a decrease in the activity. Thermal sintering is the most prevalent sintering process. Apart from reduced dispersion, also ideally shaped crystallites are formed, which are generally less reactive. Unsupported metal particles can easily sinter even at temperatures lower than 100°C. Flynn et al have developed a model which describes the sintering phenomenon and tested the model with experimental data[38, 39]. Copper-based catalysts are more susceptible than other commonly used metallic catalysts, for example, nickel, palladium, iron and ruthenium catalysts. Sintering is expected to be happening at temperatures above 40% melting temperature of the solid[40] (Hüttig temperature) which in case of copper is less (325°C) when compared with, for example, that of ruthenium (484°C), iron (460°C) and nickel (437°C). Therefore, copper-based catalysts have to be operated at relatively low-temperatures, usually no higher than 300°C. Thermal sintering of metal particles is enhanced in presence of water. The catalytic activity of copper chromium catalyst was relatively high at an early stage[35], with good low-temperature activity, and better resistance to poisons than the unsupported copper metal [36]

Leaching of active metal into the reaction medium is a one of the main causes of deactivation in liquid phase reactions. Leaching of metal atoms depends upon the reaction medium (pH, oxidation potential, chelating properties of reactant and product molecules) and upon bulk and surface metal properties.

3.3.2 Poisoning of Catalyst

This deactivation mechanism occurs when the poison molecules become reversibly or irreversibly chemisorbed to active sites, there by reducing the number of sites available for the reaction. The poisoning molecule may be a reactant and/or product in the main reaction or it may be an impurity in the feed stream.

The ionic species are mainly from the neutralization of the residual catalyst after the biodiesel reaction. These ionic salts are dependant upon the type of catalyst and neutralization chemicals used. These impurities, in the form of acids (H_2SO_4, HCl, H_3PO_4) or their corresponding salts (K_2SO_4, Na_2SO_4, KCl, NaCl, $CaCl_2$, KH_2PO_4, K_2HPO_4 etc.,), accumulates by dissolving in the glycerol by- product and immediately deactivate the catalyst upon contact. Copper catalysts are extremely sensitive towards site-blocking poisons, and they are particularly sensitive to very low levels of poison such as sulphur, chlorine or phosphorus species. Therefore, it is very important to prevent very low levels of these impurities contacting the Cu catalysts during use.

Organic fatty materials will include relatively small amounts of fatty acid, mono and di glycerides, metallic soap (potassium soap, and calcium soap), trace amounts of triglycerides, and biodiesel. Because of the strong non-polar property of these organics against the strong polar property of glycerol, only trace amounts of organic impurities will dissolve in glycerol.

In a recent publication[41], it was identified that the distribution coefficient of potassium hydroxide catalyst is typically between 90 and 100—the concentration of catalyst in the glycerol phase toward the end of reaction is 90 to 100 times the concentration in the biodiesel phase. Hence, the crude glycerol of biodiesel production will typically have 4% to 16% base or salt. Likewise, soaps (base-neutralized fatty acid) are preferentially distributed into glycerol phases.

3.3.3 Catalyst Fouling

Coking generally occurs due to the excessive reaction bond breaking resulting in the formation of C_1 or C_2 products. Copper has a low activity for breaking the C-C bonds at the reaction conditions as a result coke formation is not a major problem in this reaction. This is supported from the fact that there is no formation of ethylene glycol during the reaction, which is a result of breaking C-C bond in glycerol molecule[35]. This potential problem is further reduced by operating the copper catalysts at fairly low temperatures to minimize thermal sintering and excessive reactions.

Reactant and product molecules or in some cases polymeric or oligomeric species formed in the liquid phase as a result of secondary reactions on reactant or impurities tend to deposit on the surface of the heterogeneous catalysts and restrict the reactant access to the active catalyst sites and product desorption from these sites. Even small molecular weight oligomers are able to block pore entrance or restrict considerably the reactant diffusion towards the metal particles. Preliminary studies performed in our lab indicated formation of polymeric/oligomeric species due to the reaction between acetol intermediate with unreacted glycerol species.[48]

3.3.4 Effect of solvents

Liquid phase hydrogenation reactions are frequently carried out in the presence of solvents. In most cases their adsorption is weak otherwise strong poisoning effect would occur due to high solvent concentration. Solvents play an important role in selectivity control either by their bonding with the metal surface or with the reactant molecules. It has been shown that the nature of the solvent employed also has a significant effect on the rate and selectivity of the reaction[42,43,44].

Several possible reasons have been proposed to explain the effect of solvents in a chemical reaction including: (a) Solubility of hydrogen in the reaction media (b) Competitive adsorption of solvent at active catalyst sites (c) Intermolecular interaction between the reactant and solvent molecules.

Favorable thermodynamic interaction of the solvent and the reactant is expected to decrease the adsorption of the reactant on to the catalyst surface while unfavorable interaction should aid the adsorption. In other words a polar solvent enhances the adsorption of non-polar reactant while the non-polar solvent enhances the adsorption of a polar reactant. Singh et al in their review on liquid phase hydrogenation indicated that the solvent effects can alter the surface coverage by hydrogen at a constant hydrogen partial pressure in the gas phase. Moreover, surface coverage of hydrogen is determined by the concentration of hydrogen in the liquid phase, thus increasing the liquid phase hydrogen solubility at a constant partial pressure of hydrogen would increase the surface coverage of hydrogen[45]. This study is consistent with the work of Cerveny et al who experimentally determined that the surface concentration of adsorbed hydrogen is proportional to the concentration in the bulk liquid phase over a 13-fold variation in hydrogen solubility[46].

3.4 Experimental Methods

3.4.1 Materials

Glycerol (99. 9%), propylene glycol, Acetol, n-butanol were purchased from Sigma-Aldrich (Milwaukee, WI). Copper Chromium catalyst was obtained from Sud Chemie Inc. High purity grade hydrogen and nitrogen were obtained from Praxair. Reactions were conducted in slurry of 5 to 10% copper chromium catalyst in different concentrations of glycerol where the catalyst had an average particle size of <0.05 cm.

3.4.2 Experimental Setup

All the reactions were carried out in a specially designed stainless steel multi-clave reactor system capable of performing eight reactions simultaneously. Each reactor with a capacity of 150ml is equipped with a stirrer, heater and a sample port for liquid samples. The temperature of the reactor was controlled by CAMILE 2000 control and data acquisition system using TG 4.0 software. The reactors were flushed several times with nitrogen followed by hydrogen. Then the system was pressurized with hydrogen and heated to desired reaction temperature. Hydrogen was added during the experiment to maintain a constant pressure. The speed of the stirrer was set constant at 100 rpm through out the reaction. All the catalysts used in this study were reduced prior to the reaction in a by passing a stream of hydrogen over the catalyst bed at a temperature of 400°C.

3.4.3 Product Analysis

Gas Chromatography The samples were taken at desired time intervals, cooled to room temperature and centrifuged using an IEC (Somerville, MA) Centra CL3R centrifuge to remove the catalyst. These samples were analyzed with a Hewlett-Packard 6890 (Wilmington, DE) gas chromatograph equipped with a flame ionization detector. Hewlett-Packard Chemstation software was used to collect and analyze the data. A Restek Corp (Bellefonte, PA) MXT® WAX 70624 GC column (30m x 250 μm x 0.5μm) was used for separation. A solution of n-butanol with a known amount of internal standard was prepared apriori and used for analysis. The samples were prepared for analysis by adding 100 μl of product sample to 1000 μl of stock solution into a 2ml glass vial. Using the standard calibration curves that were prepared for all the components, the integrated areas were converted to weight percentages for each component present in the sample.

For each data point, selectivity of propylene glycol, conversion of glycerol, and yield of propylene glycol were calculated as follows:

Selectivity is defined as the ratio of the number of moles of the product formation to that of the glycerol consumed in the reaction, taking into account the stoichiometric coefficient.

Conversion of glycerol is defined as the ratio of number of moles of glycerol consumed in the reaction to the total moles of glycerol initially present

3.4.4 Catalyst Characterization

X-Ray Diffraction In the present study x-ray diffraction analysis gave important information about the nature of the catalyst. The solid phase in the catalyst samples were identified by X-ray powder diffraction technique using the CuK_{α} radiation. A Scintag, Inc. X^2 automated powder diffractometer with Peltier detector (Cupertmo, CA) was used for all x-ray studies. Cu $K\alpha$ radiation was used as the source. The diffractometer is equipped with a liquid nitrogen cooling apparatus to control temperature of the sample to within +/- $0.1^{o}C$. DMSNT software was used to analyze the data and determine the degree of crystallinity.

BET Analysis Surface area and pore volume distribution information data of the catalysts are obtained by BET analysis. The catalysts in the form of powder were outgassed for 6 hours at $250^{o}C$ and the BET surface areas and the pore volumes for the catalysts were determined from N_2 adsorption isotherms at $-196^{o}C$ measured on a Porus Materials Incorporated gas sorption analyzer. The pore volumes are reported as the liquid volume associated with the nitrogen uptake at $P/P_o \sim 0.30$. High purity grade carbon dioxide, helium, hydrogen and nitrogen were obtained from Linweld gases.

Thermogravimetric Analysis A Q50 Series Thermogravimetric Analyzer (TGA) with TA5000 Advantage software was used to analyze the weight loss in the catalyst at different conditions. Samples were heated from room temperature to 500ºC @10ºCper minute.

X-ray Photoelectron Spectroscopy Surface analysis and chemical binding energy information of the catalysts used in the different reactions was done by

X-ray spectroscopy using KRATOS AXIS 165 at a base pressure of 10^{-9} Torr with a dual anode Al Kα X-ray source to excite the sample surface and hemispherical analyzer capable of 25mV resolution.

Transmission Electron Microscopy: TEM images were obtained JEOL 1200 EX microscope giving a resolution limit of 0.35nm and 500,000X magnification. Samples were prepared by mounting the specimen particles on a copper grid and were subjected to a beam of electrons and those transmitted are projected as a two dimensional image on film.

Atomic Absorption Spectroscopy: Quantitative measurements of the amount of copper and chromium metals, due to catalyst leaching into the product solutions, were performed by photon absorption of aqueous solution using Perkin-Elmer atomic absorption spectrometer.

3.5 Glycerol Hydrogenolysis Kinetics

Glycerol reacts with hydrogen and undergoes hydrogenolysis reaction in presence of copper chromium catalyst to selectively form propylene glycol. The reaction takes place at 200°C and 200 psi hydrogen pressure. Figure 3.2 shows typical concentration profiles of conversion of glycerol to propylene glycol using different feed concentrations. Preliminary kinetic studies showed that glycerol hydrogenolysis reaction follows a second order rate mechanism with a rate constant of k=0.023 mole/L. hr with a catalyst loading of 0.5g copper chromite catalyst per 10 grams of glycerol.

3.6 Results and Discussion

3.6.1 Catalyst Aging

Experiments are performed to evaluate catalyst aging due to catalyst sintering and leaching. Table 3.1 summarizes the stability of copper chromium catalyst in presence of water at different temperatures and pressures for a period of 24 hours. Sintering of the catalysts is enhanced by water. Results show that at temperatures < 200°C, copper chromium catalyst did not undergo sintering. A slight decrease in the surface area was observed at 50 psi hydrogen pressure and 250°C. However, this slight decrease in the surface area over a 24-hour period may not be a significant cause of catalyst deactivation.

Another potential deactivation taking place during this process is the leaching of copper into the liquid as soluble complexes. Analysis of these product samples by atomic absorption spectroscopy showed presence of both copper and chromium. Concentrations of copper and chromium in the product solutions at different reaction conditions are shown in Table 3.2 and Figure 3.4. At typical reaction conditions (200°C and 200psi), using 80% glycerol feed, the analysis of the product solution showed presence of 1.02 ppm copper and 7.8 ppm of chromium. Higher reaction temperatures led to maximum leaching of metals into the product solutions. At constant pressure of 200psi, the concentration of copper leached into the solution increased from 0.89 to 1.7 ppm and that of chromium increased from 5.6 to 9.4 ppm with increase in temperature from 150°C to 230°C. Similarly, at 200°C, decreasing hydrogen pressure from 300 to 50 psi increased the concentration of copper and chromium leaching into the solution.

Figure 3.4 shows variations of metal concentrations with repeated usage of the same catalyst using different feed concentrations. From the results it is evident that both copper and chromium leached from the catalyst at different rates. In the case of copper more leaching is observed in dilute (20%) glycerol solutions. On the contrary, the leaching of chromium is observed to be more predominant in concentrated (80%) glycerol solutions.

Reduced copper particles lose activity and gain mobility under hydrothermal conditions by forming oxide or hydroxide. At the experimental conditions the solublized Cu (+1) species may undergo disproportionation[47] as

$2Cu (+1) aq \rightarrow Cu (0) + Cu (+2)_{aq}$

Cu (+2) species thus formed would be drawn off into the water forming copper hydroxide (K_{sp}.= $4.8X10^{-20}$ at 25°C)

$2Cu (+2)aq + 2 H_2O \rightarrow 2Cu(OH)_2 + 2H^+$

Also, at sufficiently high pressures the Cu $(+2)_{aq}$ species may react with adsorbed hydrogen to form Cu (0) species. However, this reaction is rather slow at the pressures used in the reaction (200psi). Similarly, chromium can also be hydrated to form highly passive Cr $(OH)_3$ ($K_{sp} = 4x10^{-38}$ at 25°C). Chromium, on the other hand, can form organometallic complexes, which are more soluble in glycerol and propylene glycol solutions. The loss of the copper metal by this process seems to have a slight bearing on the loss of the activity. This conclusion is drawn from the observation that the regenerated catalyst after 7 successive runs which has already suffered some loss of metal showed activity similar to the freshly reduced catalyst.

3.6.2 Catalyst Poisoning

The catalyst underwent slow deactivation due to catalyst poisoning. The results listed in the Figure 3.3 pertain to the use of the same sample of the catalyst repeatedly in seven successive experiments without regeneration. After each experiment, the catalyst was filtered and used for the next experiment. Each time it took about six minutes to filter and transfer the catalyst to the reactor for the subsequent run. As can be seen, the activity of the catalyst rapidly decreased. The yield of propylene glycol decreased considerably from 46.6% in the first run to 11.1% after the seventh run. The possible reasons for this deactivation and optimal regeneration procedures are explained in the following sections.

The catalysts were regenerated by different treatments and the effectiveness of the regeneration procedure was determined by reusing the catalyst for hydrogenolysis reaction of glycerol. Table 3.7 shows the various procedures used to regenerate the used catalysts and the yield of propylene glycol obtained using these catalysts for hydrogenolysis of glycerol. The catalysts were washed with various solvents with different polarities under reflux conditions. Out of all the catalyst washed with methanol reflux for 6hrs had activity similar to the fresh catalyst and considered to be the best regeneration procedure in these studies.

The catalyst after the seventh experiment was regenerated in the following manner. The used catalyst was washed with methanol under reflux conditions for 6 hours, filtered and dried in a muffle furnace at 200°C for 2hrs, followed by reduction in a stream of hydrogen at 300°C for 4hours. The yield of propylene glycol using the regenerated catalyst is 39.6% compared to 46.6% using fresh catalyst. Catalyst refluxed in methanol for 4 hours showed a lower propylene glycol yield of 35.7%. Similar washing performed using less polar solvents like 2-propanol and hexane showed relatively lesser activity. This indicates that the pore blocking species are highly polar which in this case may be glycerol or propylene glycol.

Experiments were conducted to investigate the effect of the product propylene glycol on the glycerol hydrogenolysis. The glycerol feed solutions were prepared with different concentrations of propylene glycol instead of water. The results shown in Table 3.9 indicate that even at high loadings of propylene glycol glycerol is converted at the same rate as that of pure glycerol. Moreover, in some cases slightly higher yield of glycerol is obtained using propylene glycol as solvent. These results clearly show that the glycerol and propylene glycol are not competing for the same catalytic sites for reaction and desorption of propylene glycol did not effect the rate of glycerol hydrogenolysis.

Table 3.7 shows that used catalyst regenerated by heating the catalyst in presence of air at 300°C for 4hrs did not show a significant improvement in the activity. The reason for this phenomenon may be because of the decomposition of glycerol on prolonged heating leaving an insoluble deposit on the catalyst surface. In a separate experiment it was verified that the glycerol decomposes on prolonged heating at its boiling point (290°C), leaving a tarry polymeric material[48].

3.6.3 Thermogravimetric Analysis

The mass losses of various used and regenerated catalysts were determined by thermo gravimetric analysis. Figure 3.6 shows the overlay of the TGA spectra of these catalysts. Each sample had a different mass loss in the range of 100°C to 500°C. The fresh catalyst had nearly no mass loss, i.e. no accumulation of foreign material materials on it. The regenerated catalysts had a mass loss ranging from 4 to 30%, due to the deposition of the organic byproducts and some organic compounds from the working solution on the surface of the catalysts during the usage. The mass loss for the most optimal regenerated catalyst was similar to that of the fresh catalyst and the mass loss for the catalysts regenerated using the remaining procedures was much more than that of fresh catalyst.

It is also observed that the percentage mass loss was proportional to the decrease in the yields. The reduction in the yield suggested that glycerol or the by products formed due to its decomposition upon prolonged heating is deposited over the surface blocking the catalyst pores. Hence, it is concluded that a part of the reason for deactivation of the catalyst is the blocking of the active sites by the polar polyol molecules. Such poisoning of the active catalyst sites (believed to be coordinately unsaturated cuprous ion sites on the surface) by polar molecules was reported by the others[49, 50]. It was also observed that there was a substantial loss in the surface area of the used catalyst, which can be attributed to the blocking of the pores by the decomposed organic matter. The reduced surface area of the catalyst suggests some degree of texture change during the reaction.

3.6.4 TEM Analysis

TEM analysis of the catalyst samples was done to determine the change in the microtexture and microstructure of the deactivated used catalyst. Figure 3.9

shows the TEM micrographs of fresh and used catalyst samples captured at same magnification. TEM of the fresh sample show large number of bright spots ranging from 5-10 nm indicative of mesoporous structure of the catalyst. On the other hand, TEM of the used catalyst indicate presence of smaller micropores and almost complete absence of larger mesopores present in the fresh catalyst. In addition, large dark patches can be seen on the image of the used catalyst, which correspond to the dense areas that inhibit the transmission of the electrons. These dark patches may be due to the deposition of organic polyol molecules covering the pores of the catalyst. These conclusions are further supported by the pore-volume distribution data shown in

Figure 3.7.

3.6.5 X-ray Photoelectron Spectroscopy Analysis

XPS studies were done to study the electronic states of the catalysts at various conditions. Table 3.3 summarizes the binding energies relative to the $Cu2P_{3/2}$ transition of the fresh, activated, used and regenerated copper chromium catalysts. The $Cu^{2P}{}_{3/2}$ transition is characterized by a main peak with a BE of about 934ev and a satellite peak at about 942ev. Both the values of BEs and presence of satellite peaks are typical of copper in its +2 oxidation state[51,52]. The pretreated catalysts showed evidence of Cu^{+1} state and the deactivated catalyst shows BE lower than that of the fresh catalyst. This decrease in BE may due attributed to either due to the presence of Cu^{o} atoms formed due to the reduction of Cu^{+1} species in presence of hydrogen during the reaction or due to deposition of organic materials on the surface of the catalyst formed during the catalytic hydrogenolysis.

These organic compounds absorbed from the working solution as ligands of Cu^o, supply Cu with electrons decreasing the BE of the Cu. Decrease in the intensity of satellite peak also confirms these observations. In addition, comparison of the $C1^s$ spectra showed carbon accumulation which may deactivate the catalyst. Hence it can be concluded that the organic materials deposited on the surface of the catalyst is one of the reasons for catalyst poisoning, which is consistent with the results of the TGA analysis.

3.6.6 BET Surface Area and Porosimetric Analysis

The porosimetric data from the experiments are given in Table 3.8. The surface areas of the fresh, used and regenerated catalysts were found to be 62.89 m^2/g and 74.33 m^2/g, 64.61 m^2/g respectively. These show that the average micropore size of the used catalyst is smaller than the fresh catalyst while the average mesopore size is larger than the fresh catalyst. Although the total porosity of the used catalyst is smaller when compared to fresh catalyst, the microporosity is greater but the meso and macro porosity is smaller than that of the fresh catalyst. The pore volume distributions of fresh, used and regenerated catalyst samples were studied and the pore volume distribution curves are shown in

Figure 3.7. The pore distribution curve of the fresh catalyst indicates that the catalyst primarily consists of mesopores with an average pore diameter in the range of 35 to 75 Å along with some micropores (~20Å) and macropores (~110 Å). From

Figure 3.7 it can be seen that there is a significant decrease in the mesoporosity of the used catalyst and a slight increase in the microporosity along with the formation of new micropores. These results can be explained by the fouling action of some of the impurities or reaction components on the catalyst surface. During the reaction, some of the micro and mesopores of the fresh catalyst are plugged while some of them become narrower forming new smaller micropores. Similarly, the macro pores of the catalyst seem to be completely blocked by the formation of organic components. This formation of new micropores from macro and meso pores increases the surface area of the catalyst, at the same time deactivates the catalyst.

3.6.7 X-ray Diffraction Analysis

The X-ray diffractograms of the catalyst samples were shown in Figure 3.5. The XRD pattern of the fresh sample was in good agreement with that reported in the literature[53,54]. Upon preactivation, in presence of hydrogen, peaks predominantly appear at 2θ values of 50.7, 43.27, 42.33, and 36.5. The first two values were due to copper metal and the other two peaks were due to cuprous chromium. From our previous studies on conditions for catalyst reduction,[35] it was found that the catalyst reduced at 300°C for 4hours showed the maximum activity of 46.6% when compared to the fresh catalyst. XRD studies of the catalyst samples revealed that the fresh catalyst predominantly consists of Cu (II) species transform into Cu (I) and Cu (0) ions in presence of hydrogen. Moreover, as the reduction temperature increased, the intensity of the cuprous chromium peaks increased to reach a maximum at 300°C and then decreased. The intensity of the peak corresponding to copper metal steadily increased. Hence, Cu (I) and Cu (0) species are responsible for the increase in the catalyst activity. However, the activity of the catalyst pre-reduced at different temperatures was proportional to the cuprous chromium peak and the catalyst with more Cu (0) species showed a decrease in the activity. From these studies, it was inferred that the active sites of the copper chromium catalyst used for the hydrogenolysis of the glycerol to propylene glycol are the Cu (I) species and not Cu (II) and Cu (0) species.

These results agree with the previous studies done by Makarova et al and Pillai , who reported that the maximum activity of copper chromium catalyst for hydrogenation of acetone to isopropanol and for the reductive alkylation of aniline with acetone respectively was obtained at a reduction temperature of 573 K.[55, 56]

Figure 3.5 shows the overlay of XRD patterns of fresh reduced, used and regenerated catalysts. XRD of the fresh catalyst show presence of significant amount of Cu (I) and Cu (0) ions. XRD of the used catalyst show presence of more copper in metallic state. Hence, one reason for the deactivation of copper chromium catalyst is due to the further reduction of the active Cu (I) species to Cu (0) during the course of hydrogenolysis. Peak at $2\theta = 35.3°$ in the XRD of used catalyst, corresponding to Cu (II) species, indicate that some of the active Cu (I) species are being oxidized to Cu (II).

3.6.8 Effect of Ionic Species

Experiments were conducted to study the effect of the ionic species on the conversion of glycerol to propylene glycol and results are summarized in Figure

3.8. Copper catalysts are extremely sensitive towards site blocking poisons. Results in Figure 3.8 showed that even low levels of poisons such as chlorine, sulfur and phosphorus species have significant effect on the yield of propylene glycol. Under normal operating conditions, sulphur, chlorine, and phosphorus are powerful poisons for copper, as indicated by the change in enthalpies and gibbs free energies shown in Table 3.10.[57] For the same molar concentration, phosphorus impurities had the most poisoning effect over the catalyst followed by chlorine and sulfur. The yield of propylene glycol, at >3mmol concentration of impurity, is almost zero in case of chlorine and phosphorus impurities (in this case KCl and KH_2PO_4) and is about 16% in case of sulfur (in this case K_2SO_4). High ΔH^0 and ΔG^0 of these phosphorus compounds indicate these compounds are thermodynamically more favorable to form. In spite of higher enthalpy of formation, sulfate salts did not have significant poisoning impact on the glycerol conversion due to the presence of barium in the copper chromium catalyst, which acts as a sulfur scavenger. The operating conditions thermodynamically favor the adsorption of poisons, giving high surface coverage. These impurities can poison the copper chromium catalyst in several parallel mechanisms by direct adsorption on to the catalytic surface blocking or modifying the catalytic sites and in some cases reacting over the surface forming a monolayer on the catalyst surface causing them to deactivate.

Even though the formation of copper chloride is thermodynamically much less favorable than the copper sulfide, results indicate that, chlorides are stronger poisons for copper chromium catalysts. This can be explained by the lower melting point of copper chloride causing high surface mobility of copper chloride. Hence, due to the high surface mobility even extremely small amounts of copper chloride are sufficient to provide mobile species necessary to accelerate surface migration sintering of copper chromium catalysts. Moreover, the poisoning of the catalyst by adsorption of the impurities is exacerbated due the sintering process.

3.6.9 Effect of Organic Species

Experiments were conducted to study the effect of the organic species on the conversion of glycerol to propylene glycol. All the reactions were doped with 1wt% of organic material impurity. Results shown in Table 3.5 indicate that all the organic impurities, with an exception of free fatty acids, have relatively low impact in the conversion of glycerol. This can be explained by low solubility of the non-polar organic impurities in polar glycerol solution. With an exception of free fatty acid there is at most a 15% decrease in catalyst activity due to organic impurities in the glycerol. The relative solubilities of these impurities in glycerol based on polarity are:

Triglycerides<Methyl Esters<Free Fatty Acids<Monoglycerides<Alkali Soap

Based on the above trend it is expected that the triglyceride with lowest solubility will have least impact and alkali soap will have the highest poisoning effect. However, this trend did not seem to apply for free fatty acid and alkali soap. This deviation can be explained by the increase in the pH due to presence of alkali soap and slight decrease in the pH due to the presence of free fatty acids. From the studies to determine the effects of pH, it was found that the catalytic activity is higher in the pH range of 8-9 which can be related to the increase in the yield of propylene glycol due to the addition of alkali soap. Free fatty acids on the other hand bind to the copper surface forming cupric stearate surface film[58]. Also, free fatty acids in presence of copper chromium and hydrogen forms carboxyl alcohols. These carboxylate groups are very stable and create an inhibiting effect on the reaction rate.

These impurities physically adsorb on to the catalyst surface and due to the bulky nature of the molecules block the active catalyst sites. However, these impurities act as temporary poisons and the catalyst activity can be easily regenerated by washing the catalyst with selected solvents (based on polarity of impurities) and reducing it in a stream of hydrogen.

3.6.10 Effect of pH

A series of reactions were conducted to determine the impact of pH on the hydrogenolysis of glycerol. Table 3.4 shows the effect of reactant pH on the hydrogenolysis of glycerol to propylene glycol. Results of the pH screening studies indicated that selectivity towards propylene glycol is highest at a pH range of 7-9. Selectivity of propylene glycol starts to decrease at pH >9 or at pH<7 due to formation of byproducts by excessive hydrogenolysis of carbon-carbon π bonds in glycerol. Fouling action of these byproducts deactivate the catalyst by blocking the active catalytic sites due to coke formation at high temperatures.

The possible reactions that may hinder the conversion of glycerol to propanediols at hydrogenation conditions include:

At high pH (>10), glycerol tends to polymerize (in presence of alkali, such as sodium or potassium hydroxide, at high temperature >200^oC) to polyglycerol, which concentrates at the bottom of the reactor.

At low pH (<3), glycerol dehydrates to form acrolein and other lower alcohols like methanol. Acrolein readily self polymerizes in presence of heat to form polymeric species.[48]

Proper control of the pH of the glycerol solution is necessary to minimize these unwanted byproducts during glycerol hydrogenolysis which may deactivate the catalyst.

3.6.11 Studies on Crude Glycerol

Glycerol is mainly obtained as a byproduct from the transesterification of soybean oil (biodiesel process) and hydrolysis of animal fats (fat splitting process). This glycerol forms the bottom phase after the reaction and is typically separated by a simple settling process. However, this crude glycerol carries residual catalyst, dissolved solvents, reactants and products. The composition of glycerol, obtained by transesterification of soybean oil, before and after treatment, is shown in Table 3.6. The composition of crude glycerol is analyzed using different standard techniques shown in Table 3.6.

Experiments were conducted using treated and untreated crude glycerol as a feed stock. And the yield of propylene glycol after a 24 hour reaction is given in Table 3.6. The yield of propylene glycol using crude glycerol straight from the biodiesel process with out any treatment is 59.7% when compared to 46.6% using pure 80% glycerol solution. This increase in yield of propylene glycol can be attributed to: (a) presence of ~20% excess methanol which acts as a solvent. (b) high pH of crude glycerol feed.

The studies on solvent effects on glycerol hydrogenolysis (see Table 3.9) show that the presence of 20% solvent in place of water has a positive impact on yield of propylene glycol. Yield of propylene glycol using 20% methanol as a solvent is 58.8% which is consistent to that of untreated crude glycerol-1 (contains ~20% excess methanol). The reaction performed with crude glycerol-2 (excess methanol stripped out) has a propylene glycol yield of 53.6% which is less than that obtained from crude glycerol-1. On the other hand, high pH of the crude glycerol had a positive impact on the yield of propylene glycol. This is consistent with the results shown in Table 3.4 on effect of pH.

In a typical biodiesel process the residual base catalyst in biodiesel phase is neutralized using hydrochloric acid and then washed with water to remove salts and methanol. Studies done by our group indicated that these salts preferentially concentrate in the bottom glycerol phase along with methanol and water[41]. Methanol is generally stripped out from the glycerol phase and recycled back to the reactor. The treated glycerol in Table 3.6 is the crude glycerol, with chloride salts and water, obtained by the typical process described above. The yield of propylene glycol using this treated glycerol is 3.23%, and this low yield is attributed to the poisoning of catalysts by the chloride salts. This is consistent with the results shown in Figure 3.8 on effect of ionic impurities.

3.6.12 Effect of Solvents

Experiments were conducted at similar reaction conditions using 20% of different solvents in place of water. The results are summarized in Table 3.9. The results show that the solvents have a pronounced effect on the catalytic performance of copper chromium catalyst. With exceptions of acetone and THF, all the solvents showed a higher yield of propylene glycol when compared to 46.6% with water as a solvent. Among the organic solvents, there is little correlation between solvent power and reactivity. This is likely due to the dominating of the reaction by surface rather than solvent phenomena.

3.7 Conclusions

The deactivation mechanism of the catalyst was found to be mainly poisoning due to the reduction of the cuprous chromium active species into metallic copper species, metal leaching, and poisoning by strongly adsorbed inorganic and organic species present in the feed or generated during the reaction. X-ray photoelectron spectroscopy and X-ray diffraction studies indicate that the decrease in the catalytic activity is due to the formation of excess of inactive Cu (0) ions by reduction of active Cu (I) species. The results from BET porosimetric studies and transmission electron microscopy indicated that blockage of catalyst pores by glycerol or propylene glycol molecules or any intermediate species generated during the reaction.

Spent catalyst regenerated by refluxing in methanol for 6 hours followed by heating in the presence of air at 200°C for 2 hours showed a propylene glycol yield of 39.6 % when compared to 46.6% using the fresh catalyst. Regeneration using less polar solvents like 2-propanol and hexane showed relatively lesser activity. This indicates that the pore blocking species are highly polar species. Propylene glycol appeared to have a lower affinity for active sites on the metal catalyst compared to glycerol.

Leaching of copper and chromium metals into the final product solutions was observed. More leaching of metals occurred at higher reaction temperatures and low hydrogen pressures. For dilute glycerol solutions (20%), copper concentration in the product solution was greater (1.62 ppm) when compared to (1.02 ppm) in 80% glycerol solution. This may be due to dissolution of copper oxide species in the form of $Cu(OH)_2$. For concentrated glycerol solutions, the chromium concentration is higher (7.8 ppm), perhaps due to the formation of some organometallic chromium complexes which have a higher tendency to dissolve in the glycerol or propylene glycol.

Inorganic chloride and phosphorus impurities have significant poisoning effect on catalyst. The yield of propylene glycol is almost negligible with presence of 4mmol of impurity in the initial feed solution. Presence of sulfur impurities has relatively lesser impact due to the presence of barium in the catalyst which acts as a sulfur scavenger.

Organic impurities did not have a significant effect on the catalyst activity due to low solubilities of non-polar organic species in glycerol solution. The poisoning is temporary due to blockage of catalyst pores by the bulky organic molecules.

Solvents have a pronounced effect on the activity of copper chromium catalyst. With exceptions of acetone and THF all the solvents showed a higher yield of propylene glycol when compared to 46.6% with water as a solvent. The increase in the yield is attributed to the thermodynamic interaction between glycerol and the solvent and liquid phase concentration of hydrogen. The increase in propylene glycol yield to 80% with the use of limonene as a solvent can be attributed to the catalytic hydrogen transfer phenomena with limonene acting as a hydrogen donor.

The results of this study demonstrate the feasibility of copper chromium catalyst for production of propylene glycol by hydrogenolysis of glycerol.

Table 3.1: Stability of copper chromium catalyst in presence of water at different conditions of temperature and pressure after 24 hrs

Temperature (^oC)	**Pressure (psi)**	**Surface Area (m^2/g)**	**Pore volume (cm^3g^{-1})**
Initial Catalyst	-	62.89	0.11
200	300	63.03	0.11
150	200	64.75	0.13
200	200	64.09	0.12
250	200	61.44	0.10
200	100	62.38	0.11
200	50	61.17	0.10
250	50	60.94	0.09

Table 3.2: Temperature and pressure effects on selectivity copper chromium catalyst after 24 hours of glycerol conversion. Catalyst was reduced prior to the reaction in presence of hydrogen at 300°C for 4hours

Temperature (^oC)	**Pressure (psi)**	**Conversion (%)**	**Selectivity (%)**	**Surface Area (m^2/g)**	**Copper (ppm)**	**Chromium (ppm)**
Initial Catalyst	-	-	-	62.8		
230	50	83.1	29.3	63.8	1.7	9.4
230	200	72	48.7	65.9	1.2	8.8
200	50	25	36.4	64.4	1.35	8.9
200	200	54.8	85.0	64.1	1.02	7.8
200	300	65.3	89.6	62.9	0.38	5.3
150	50	4.8	52.8	64.3	0.92	6.8
150	200	7.2	31.9	67.5	0.89	5.6

Table 3.3: XPS data for the copper chromium catalysts

Catalyst Description	BE for Cu 2P (ev)	Description
Fresh CuCr Catalyst	934.9	Copper in its Cu^{+2} state
Pretreated with H_2 at 300°C	933.9	Copper in its Cu^{+1} state
After the reaction	932.8	Copper in its Cu^{0} state
Regenerated catalyst	933.7	Copper in its Cu^{+1} state

Table 3.4: Effect of pH on hydrogenolysis of glycerol to propylene glycol. All the reactions were performed using 80% glycerol solution at 200 psi hydrogen pressure for 24 hours

pH	% Conversion	% Selectivity
1	63.8	23.8
2.5	50.8	66.8
4.5	51.5	75.9
7	54.8	85.0
9	53.4	91.6
11	65.3	67.4

Table 3.5: Impact of 1 wt% organic impurities on formation of propylene glycol from glycerol. All the reactions were performed using 80% glycerol solution at 200 psi hydrogen pressure for 24 hours

Type of Impurity	Model Impurity	%Conversion	%Yield
Triglyceride	Tristearin	48.6	37.2
Methyl Ester	Methyl Stearate	45.3	30.6
Alkali Soap	Potassium Sterate	40.1	35.5
Free Fatty Acid	Stearic Acid	40.5	17.9
Monoglyceride	Monostearin	39.8	29.13
No Impurity	No Impurity	54.8	46.6

Table 3.6: Composition of crude glycerol in wt% obtained from biodiesel industry

Component	**Analysis Method**	**Crude Glycerol-1** [a]	**Crude Glycerol-2** [b]	**Treated Glycerol** [c]
Glycerol	ISO 2879-1975	58.25	72.86	80.8
Ash	ISO 2098-1972	9.86		6.71
MONG	ISO 2464-1973	8.36		1.47
Water	Karl Fischer	1.20	0.925	10.3
Methanol	GC	22.33	0	0.72
pH	pH meter	12.73		3.93
Yield (%)		59.47	53.58	3.23

[a] Crude glycerol obtained straight after the biodiesel reaction
[b] Crude glycerol from which methanol and some water was stripped out
[c] Crude glycerol in which the excess base catalyst is neutralized with hydrochloric acid and methanol is striped out

Table 3.7: Regeneration procedures of deactivated copper chromium catalysts

Catalyst Description*	% Yield
Fresh Catalyst	46.6
Fresh Catalyst Refluxed in methanol for 4hrs	45.1
Untreated used catalyst	11.1
Used Catalyst washed with water and dried in air at 300^oC for 4hrs (R1)	16.2
Used Catalyst Refluxed in methanol for 4hrs (R2)	35.7
Used Catalyst Refluxed in methanol for 6hrs (R3)	39.6
Used Catalyst Refluxed in 2-propanol for 4hrs (R4)	29.9
Used Catalyst Refluxed in water for 4hrs (R5)	32.4
Used Catalyst Refluxed in hexane for 4hrs (R6)	21.3

* All the catalysts were reduced before the reaction in presence of hydrogen for 4hrs at 300°C. Catalysts from R2-R6 are heated in presence of air at 200°C for 2 hours prior to reduction.

Table 3.8: Porosimetric Results for fresh, used and regenerated catalysts

Catalyst Property	Fresh	Used	Regenerated
Apparent Density (kg/l)	0.82	0.76	0.8
Average Micropore Radius (Å)	0.09	0.07	0.08
Average Mesopore Radius (Å)	0.36	0.42	0.38
Surface Area (m^2/g)	62.89	74.33	64.61
Micro porosity (<20 Å)	0.08	0.16	0.15
Meso porosity(20-100 Å)	0.48	0.25	0.45
Macro porosity(>100 Å)	0.28	0.06	0.17
Porosity	0.84	0.47	0.78

Table 3.9: Effect of solvents on hydrogenolysis of glycerol to propylene glycol. All the reactions were performed at 200psi and 200°C for 24hours

Solvent	Hildebrand Solubility Parameter	(%) Yield of Propylene Glycol
Water	23	46.6
Methanol	14.5	58.8
Isopropanol	11.5	52.2
n-Butanol	11.6	63.5
2-Butanol	10.8	54.9
Acetone	10	38.6
THF	9.1	39.9
Decane	7.8	50.8
Hexane	7.3	53.2
Clyclohexane	8.2	64.8
	Solvent Conc. (wt%)	
Propylene Glycol	20	48.9
	50	52.1
	80	58.9
Methanol	10	48.6
	20	58.8
	30	63.2
Limonene	5	58.3
	10	67.5
	20	73.9

Table 3.10: Heat of formation Gibbs free energy of some of the chlorine, sulfur, and phosphorus compounds of copper

	Oxidation State	**ΔH^0 (Kcal/mol)**	**ΔG^0 (Kcal/mol)**
CuCl	Cu^{+1}	-32.8	-28.65
$CuCl_2$	Cu^{+2}	-52.6	-42
CuS	Cu^{+2}	-12.7	-12.8
Cu_2S	Cu^{+1}	-19	-20.6
$CuSO_4$	Cu^{+2}	-184.36	-158.2
Cu_2SO_4	Cu^{+1}	179.6	
Cu_3P_2		-29	
$Cu_3(PO_4)_2$	Cu^{+2}		-490.3

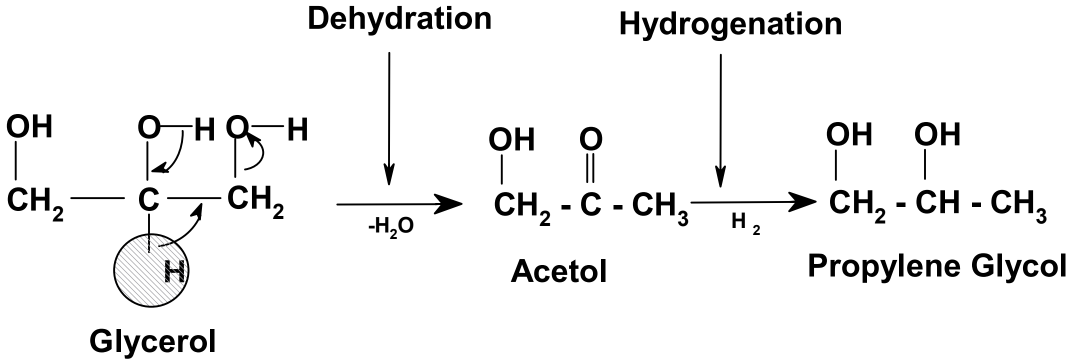


Figure 3.1: Proposed reaction mechanism to convert glycerol to propylene glycol

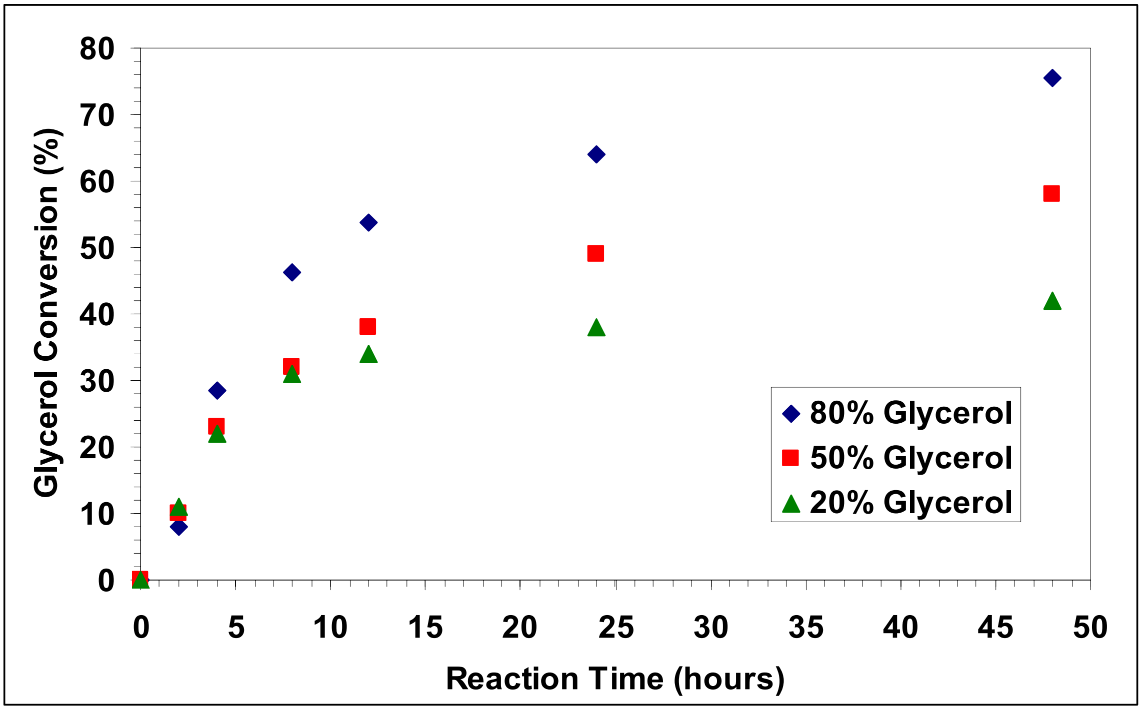


Figure 3.2: Reaction profile for the conversion of glycerol to propylene glycol using different feed concentrations using copper chromium catalyst. All the reactions were done at 200°C and 200psi

.

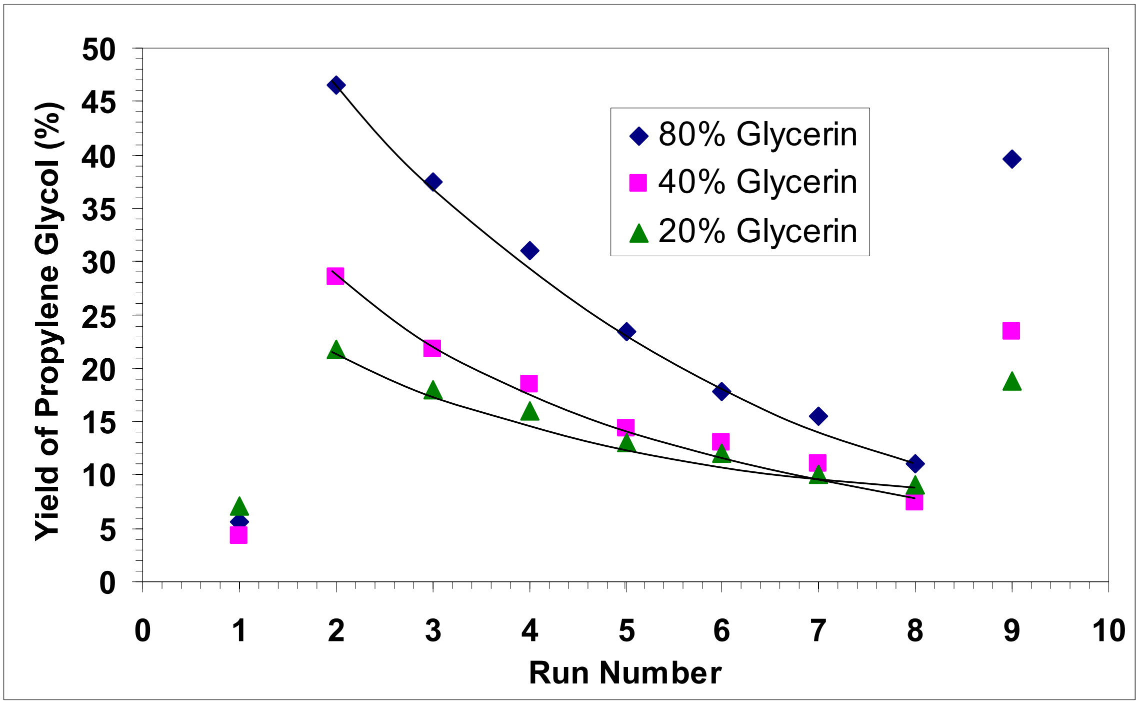


Figure 3.3: Deactivation of copper chromium catalyst with different feed concentrations. Run # 1 refers to fresh unreduced catalyst, Run # 2 refers to reduced fresh catalyst, Runs # 3 to 8 refers to repeated usage of the catalyst from Run # 2 in 24hr reactions without regeneration, Run # 9 refers to regenerated catalyst

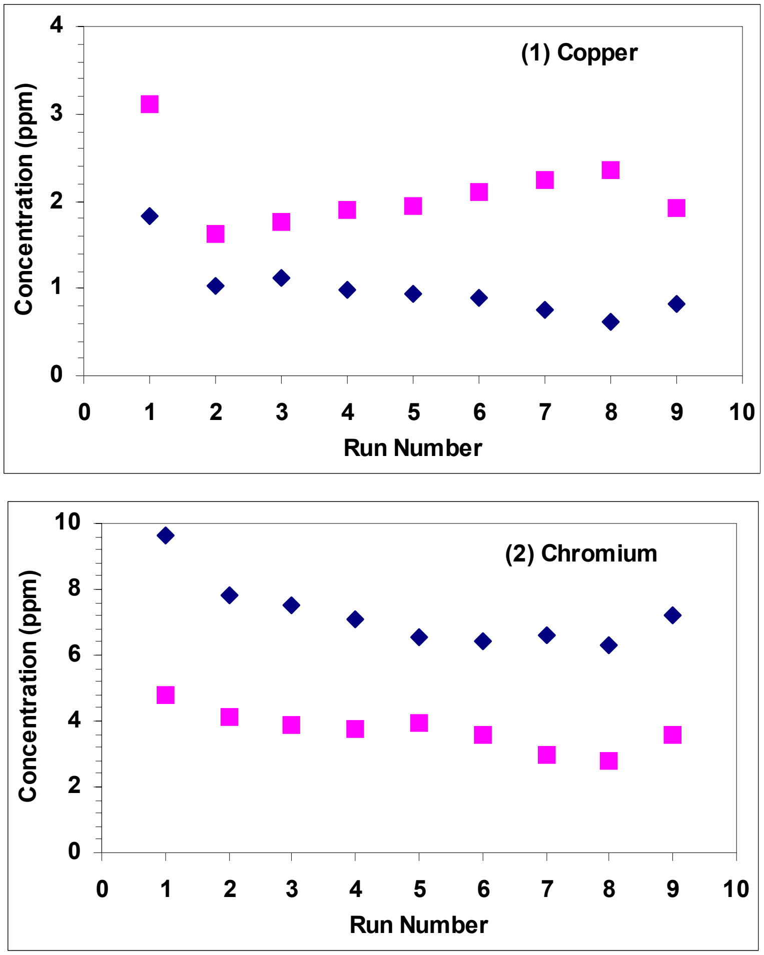


Figure 3.4: Variation of metal (1) copper and (2) chromium concentrations in the product solution with repeated usage of the same catalyst. Squares (■) represents reactions done with 80% glycerol solution and Diamonds (♦) represents reactions done with 20% glycerol solution Run # 1 refers to fresh unreduced catalyst, Run # 2 refers to reduced fresh catalyst, Runs # 3 to 8 refers to repeated usage of the catalyst from Run # 2 in 24hr reactions without regeneration, Run # 9 refers to regenerated catalyst

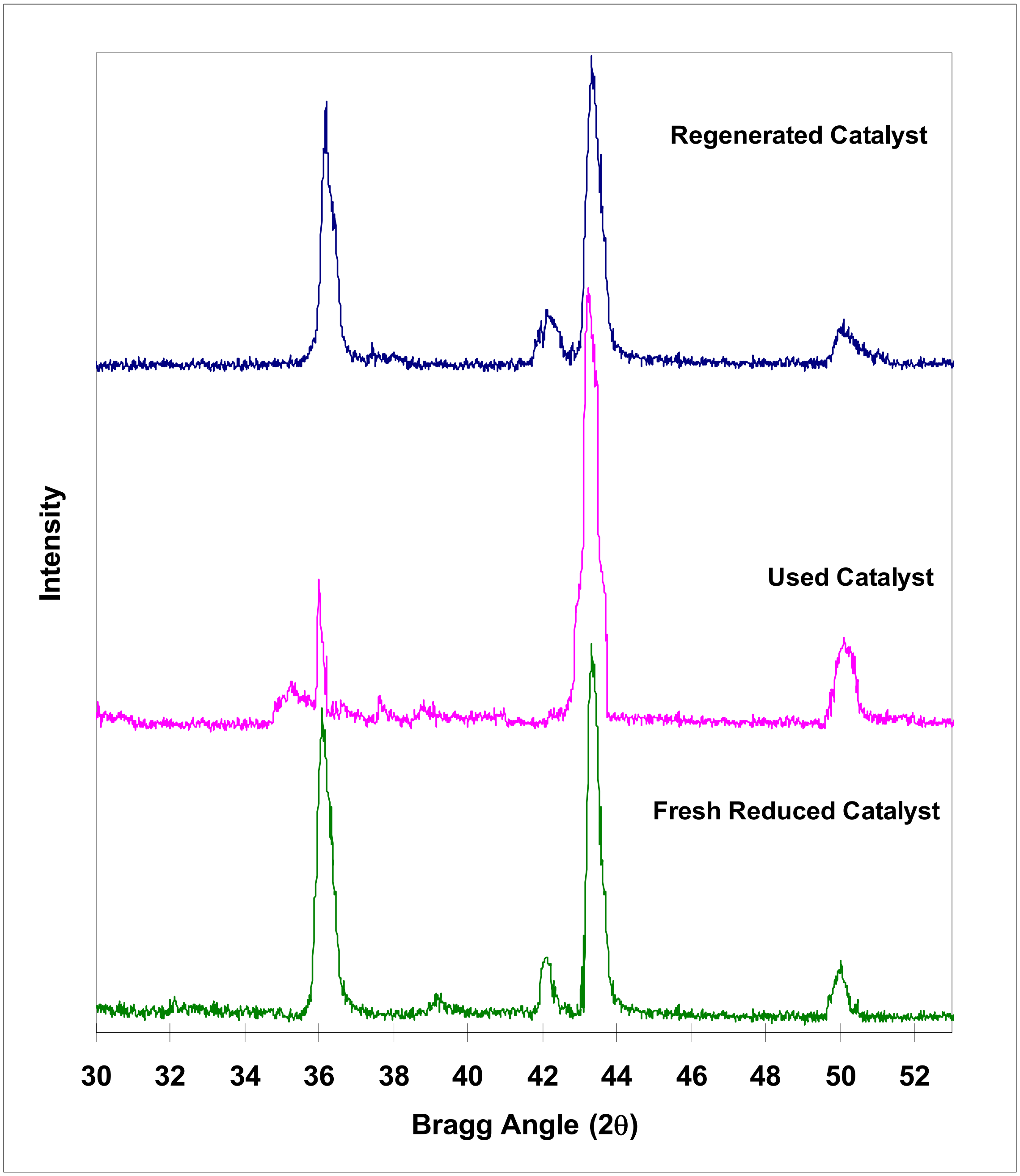


Figure 3.5: Overlay of X-ray diffractograms of different copper chromium catalysts

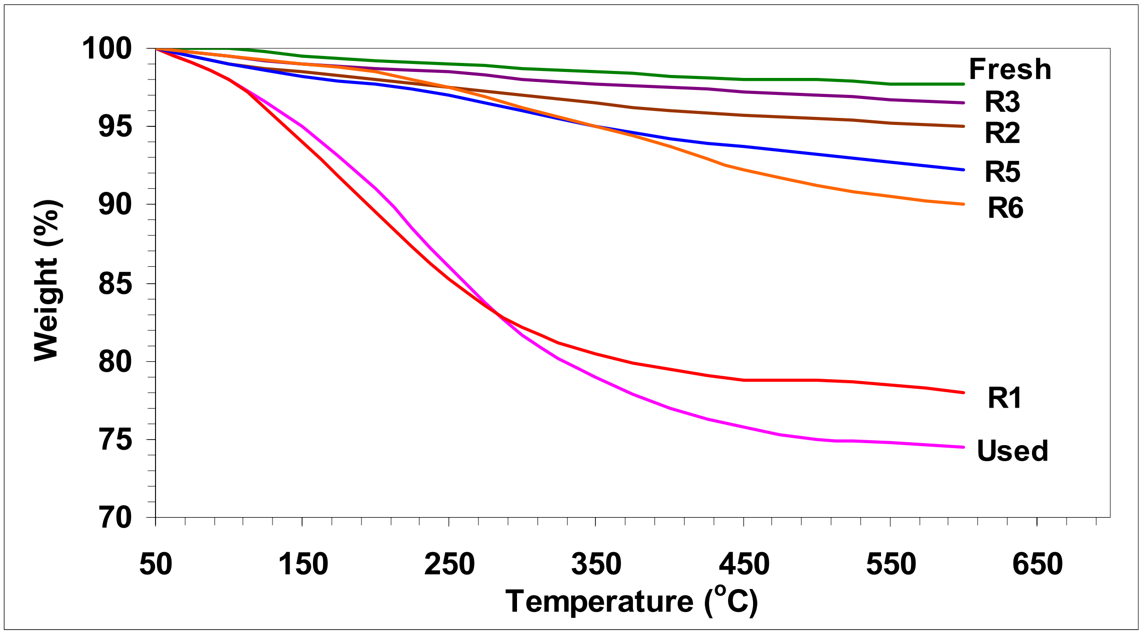


Figure 3.6: Overlay of TGA spectra for different catalysts

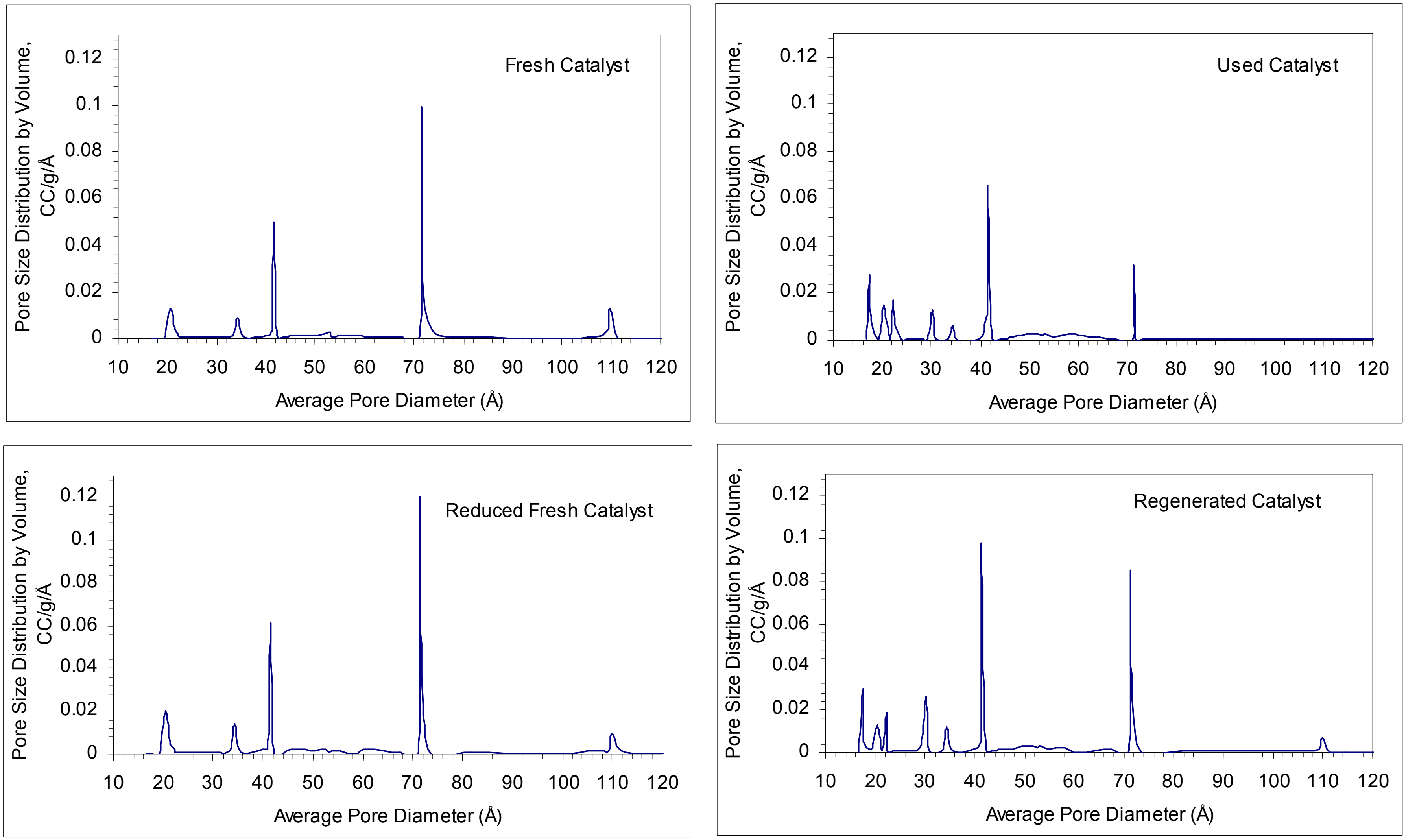


Figure 3.7: Pore-volume distribution of fresh, used and regenerated copper chromium catalyst

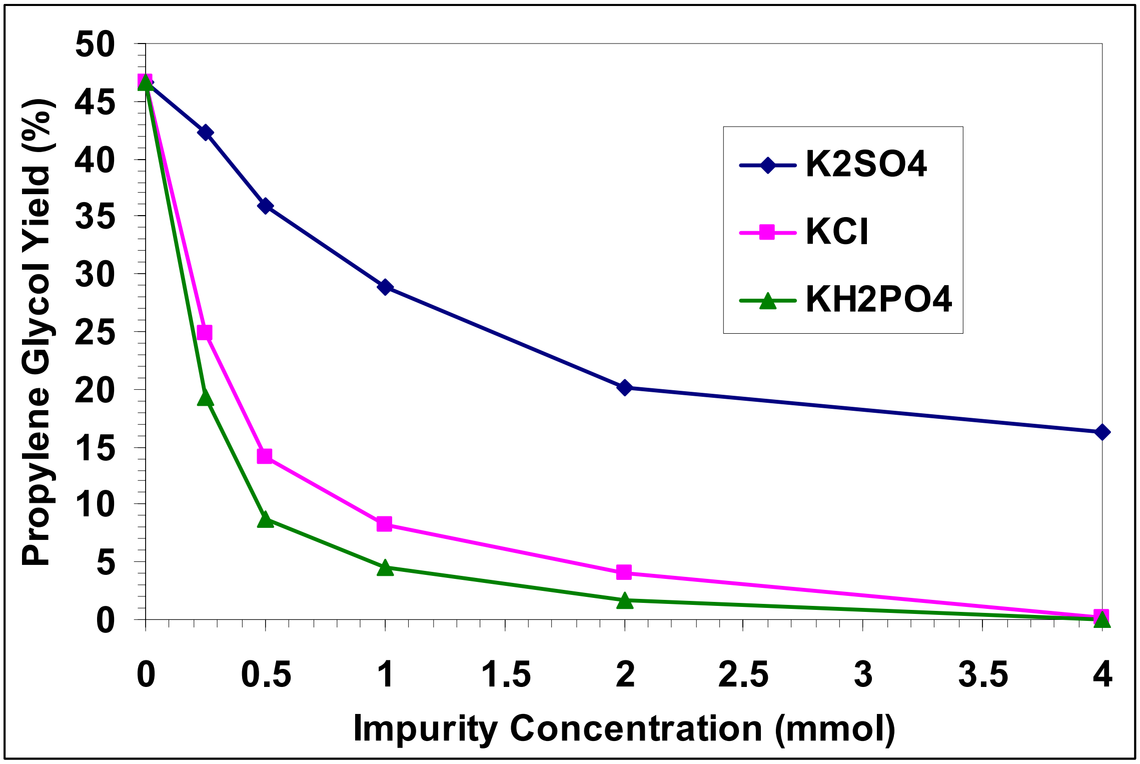


Figure 3.8: Impact of ionic impurities on formation of propylene glycol from glycerol

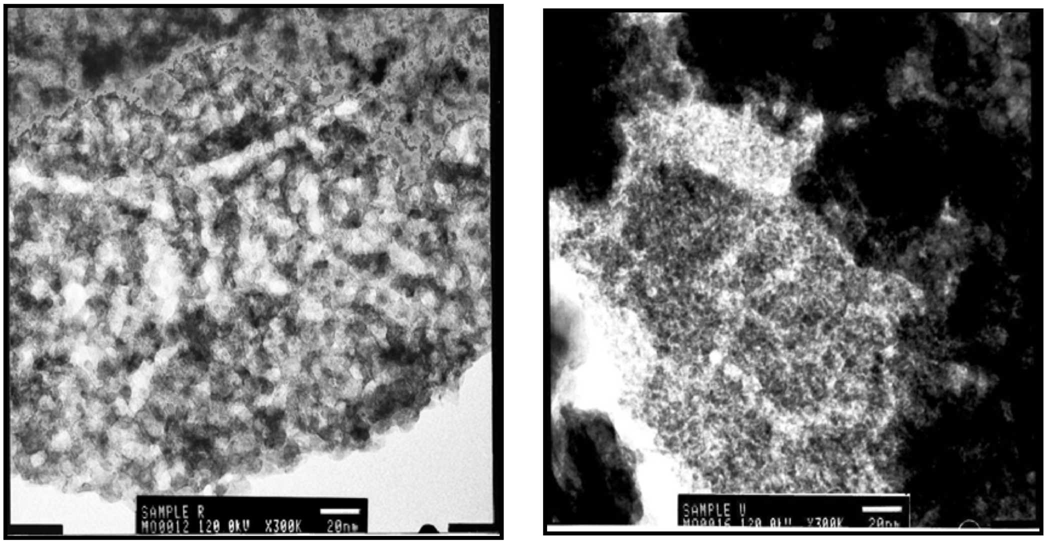


Figure 3.9: TEM images of fresh (left field view) and used (right field view) copper chromium catalysts. Both the images were captured at 300,000X magnification. The scale shown in the images is 20nm in size

4 CHAPTER 4

DEHYDRATION OF GLYCEROL TO ACETOL VIA CATALYTIC REACTIVE DISTILLATION

4.1 Abstract

Dehydration of glycerol was performed in the present of various metallic catalysts including alumina, magnesium, ruthenium, nickel, platinum, palladium, copper, raney nickel, and copper-chromite catalysts to obtain acetol in a single stage reactive distillation unit under mild conditions. The effects of operation mode, catalyst selection, glycerol feed flow rate, catalyst loading and initial water content were studied to arrive at optimum conditions.

High acetol selectivity levels (>90%) were achieved using copper-chromite catalyst and operating in semi-batch reactive distillation mode. A small amount of water content in glycerol feedstock was found to reduce the tendency for residue to form therein extending catalyst life. The acetol from this reaction readily hydrogenates to from propylene glycol providing an alternative route for converting glycerol to propylene glycol.

Keywords dehydration, glycerol, acetol, copper-chromite, reactive distillation, residue, propylene glycol.

4.2 Introduction

Use of fatty acid methyl esters (FAME) derived from vegetable oils and animal fats as diesel fuel extenders known as biodiesel has received considerable attention in recent years [59,60,61,62]. The U.S. production of biodiesel is 30-40 million gallons, which is expected to grow at a rate of 50-80% per year, with a projected 400 million gallons of production by the year 2012. A major drawback of biodiesel is its high cost when compared to diesel—the production costs for biodiesel range from $0.65- $1.50 per gallon.[63]

For every 9 kilograms of biodiesel produced, about 1 kilogram of a crude glycerol by-product is formed. Most of the larger biodiesel producers refine the glycerol for sale in the commodity glycerol market. However, the price of glycerol is already (2005) about half the price of past averages in Europe where biodiesel production exceeds 400 million gallons per year. Increased biodiesel production is expected to further suppress glycerol prices, and so, conversion of glycerol to other consumer products is desirable.

Propylene glycol is a major commodity chemical with an annual production of over 1 billion pounds in the United States [64] and sells for $0.71 [65] to over $1.00 per pound with a 4% growth in the market size annually. If crude glycerol could be used to produce propylene glycol, this technology could increase the profitability of biodiesel production plants and thereby reduce the costs of producing biodiesel.

The commercial petroleum-based propylene glycol is produced by either the chlorohydrin process or the hydroperoxide process that hydrates propylene oxide to propylene glycol. [66,67] Conventional processing of glycerol to propylene glycol uses metallic catalysts and hydrogen as reported in several United States patents.[68,69,70,71] These research efforts report the successful hydrogenation of glycerol to form propylene glycol. However, none of the processes that can suitably commercialize the resultant reaction products due to some common drawbacks of existing technologies, for example, high temperatures and high pressures, low production efficiency from using diluted solutions of glycerol, and low selectivity towards propylene glycerol.

In earlier work, we proposed the novel reaction mechanism for converting glycerol to propylene glycol via a reactive intermediate as shown in Figure 4.1. [72] Relatively pure hydroxyacetone (acetol) is isolated from dehydration of glycerol as the transient intermediate indicates that the reaction process for producing propylene glycerol with high selectivity can be done in two steps. In the broader sense, the present process may potentially advance the art and overcome those problems outlined above by the novel reaction mechanism to convert glycerol to acetol, and then acetol is hydrogenated in a further reaction step to produce propylene glycol.

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

Several prior works have been published on reactive distillation by Gaikar et al and Doherty et al.[73,74] Reactive distillation technique is now commercially exploited for the manufacture of methyl tert-butyl ether (MTBE), ethyl tert-butyl ether (ETBE), and tert-amylmethyl ether, which are used as octane number enhancers.[75] Reactive distillation is also used for esterificaiton of acetic acid with alcohols like methanol and ethanol, and hydrolysis reactions of esters like methyl acetate.

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

4.3 Experimental Methods

4.3.1 Materials

Glycerol (99.9%) and n-butanol were purchased from Sigma-Aldrich (Milwaukee, WI). Methanol (HPLC grade) was purchased from Fisher Scientific Co. (Fairlawn, NJ). Table 4.1 gives the description of various catalysts used in this study and their suppliers. All catalysts used in this study were used as delivered.

4.3.2 Experimental Setup

4.3.3 Batch Reactive Distillation

The experiments on batch reactive distillation were carried out in a fully agitated glass reactor of capacity 1.25 x 10^{-4} m^3. A magnetic stirrer at an agitation speed of 100 rpm was used to create a slurry reaction mixture. A condenser was attached to the top of glass reactor through which chilled water was circulated. The glass reactor was immersed in a constant temperature oil bath, the temperature of which was maintained within ±1 ^oC of the desired temperature. In the glass reactor, the catalyst was first heated to the reaction temperature of 240 °C, and then the amount of glycerol solution was charged immediately to the reactor. Complete addition of the glycerol solution was taken as zero time for the reaction. All experiments were conducted at a slight vacuum of 98 kPa by using an aspirator.

4.3.4 Semi-batch Reactive Distillation

The same reactive distillation setup was used as described in the section of batch reactive distillation. Experiments were carried out in a continuous mode of operation in the reactive distillation setup as shown in Figure 4.2. Glycerol solution was continuously introduced at the bottom of the glass reactor with different feed flow rates by a peristaltic pump. All experiments were conducted at a reduced pressure of 98 kPa (slight vacuum) by using an aspirator.

4.3.5 Method of Analysis

In the batch mode, the completion of reaction was considered when additional condensate ceased to collect. In the semi-batch mode, a digestion of the mixture was induced by stopping the feed and allowing the reaction to proceed for about 30 min to an hour. The residues in the glass reactor were weighed. The liquid samples in the distillate were weighed and analyzed with a Hewlett-Packard 6890 (Wilmington, DE) gas chromatograph equipped with a flame ionization detector. Hewlett-Packard Chemstation software was used to collect and analyze the data. A Restek Corp (Bellefonte, PA) MXT® WAX 70624 GC column (30m x 250 µm x 0.5µm) was used for separation.

For preparation of the GC samples, a solution of n-butanol with a known amount of internal standard was prepared a priori and used for analysis. The samples were prepared for analysis by adding 100 µL of product sample to 1000 µL of stock solution into a 2mL glass vial. Two micro liters of the sample was injected into the column. The oven temperature program consisted of: start at 45 °C (0 min), ramp at 0.2 °C /min to 46 °C (0 min), ramp at 30 °C /min to 220 °C (2.5 min). Figure 4.3 shows a typical gas chromatogram of the glycerol dehydration product. Using the standard calibration curves that were prepared for all the components, the integrated areas were converted to weight percentages for each component present in the sample.

For each data point, conversion of glycerol and selectivity of acetol were calculated. Conversion of glycerol is defined as the ratio of number of moles of glycerol consumed in the reaction to the total moles of glycerol initially present. Selectivity is defined as the ratio of the number of moles of product formation to the moles of glycerol consumed in the reaction, taking into account the stoichiometric coefficient.

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

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

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

4.4 Results and Discussion

4.4.1 Catalyst Selection

Heterogeneous catalysts, including alumina, magnesium, ruthenium, nickel, platinum, palladium, copper, raney nickel and copper-chromite in the form of metallic powders, metal oxides, and activated metals (metal sponge) were impregnated on an activated carbon support. Reactivities were tested in the batch mode of reactive distillation at a reaction temperature of 240 °C and a reduced pressure of 98 kPa.

Table 4.1 shows the performance comparison of these catalysts. Conventional dehydration catalysts like alumina were not effective for dehydrating glycerol to acetol since these catalysts with high acidic sites favor the dehydration of glycerol to acrolein.[76] Ruthenium catalysts showed low selectivities and high residue to initial glycerol ratios, greater than 30%, due to the polymerization (condensation) of hydrocarbon free radicals leading to further deactivation of catalyst. Low selectivities and low residue to initial glycerol ratios were observed in nickel and palladium based catalysts since they tend to be too active which results in excess reaction (degradation) of glycerol to form lower molecular alcohols and gases.

On the other hand, copper or copper-based catalysts are superior to the other catalysts studied here in both acetol selectivity and residue formation. The superiority is enhanced by mixing copper with chromite. A high acetol selectivity of 86.62% was obtained by using copper-chromite mixed oxide catalyst. Copper increases the intrinsic catalyst activity; however, copper favors sinterization leading to catalysts with low surface areas. Chromium acts as a stabilizer to preventing sintering (reduce the sintering rate) and thus maintains catalysts in high activity.[77] Copper-chromite catalyst was selected for further studies.

4.4.2 Batch versus Semi-batch Processing

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

In batch mode, glycerol and catalyst were loaded into the reactor at the start of the reaction. In semi-batch mode, the reactor was changed with catalyst and glycerol was continuously fed into the reactor at a uniform rate of 33.33 g/hr over a period of about 1.25 hours. Either process mode produced a residue which was a dark solid coated on the catalyst that was not soluble in water. Table 4.2 shows the semi-batch reactive-distillation exhibits higher yield and selectivity, and lower residue formation than batch due to the semi-batch operation having a higher catalyst loading to glycerol ratio in the reaction.

4.4.3 Glycerol Feed Flow Rate

Reactions were performed to study the effect of glycerol feed flow rate on semi-batch operation mode with 2.5% copper-chromite catalyst loading. It can be seen in Table 4.3 that increasing the flow rate decreases acetol selectivity and increases the residue to initial-glycerol ratio. As the amount of catalyst is fixed, an increase of the glycerol feed flow rate results in an accumulation of fed glycerol in the reaction mixture, hence reduces the catalyst loading to glycerol ratio during the reaction. This decrease in the catalyst loading to glycerol ratio results in lower acetol selectivity and higher reside formation reinforcing the afore-conclusion in the section of comparison of batch and semi-batch operation modes. It was also observed that decreasing the flow rate from 33.33 g/hr decreases the conversion of glycerol because the glycerol could be easily vaporized and appear in the distillate as an unconverted glycerol.

4.4.4 Catalyst Loading

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

In order to find the minimum catalyst loading required to achieve necessary conversion, lowering catalyst loadings from 5% to 0.83% was evaluated to determine the impact of catalyst loading on conversion of glycerol to acetol and residue formation. Reactions were carried out by reacting varying amounts of glycerol: 25g (5%), 50g (2.5%), 75g (1.67%), 100g (1.25%), 150g (0.83%) to 1.25g of copper-chromite catalyst in semi-batch reactive distillation mode. Table 4.4 summarizes the conversion results. These data illustrate that the formation of residue increased with increasing throughput of glycerol over the catalyst. Also, the acetol selectivity decreased with increasing throughput of glycerol over a fixed catalyst loading in the reactor due to residue increasing with reaction time leading to further deactivation of catalyst.

4.4.5 Water Content in Glycerol Feed

Reactions were performed to study the effect of initial water content on the overall reaction. Glycerol was reacted in presence of 2.5% copper-chromite catalyst to form acetol in a semi-batch reaction method. Water was added to the glycerol to evaluate if water would decrease the accumulation of the water-insoluble residue.

Table 4.5 summarizes the conversion results. As the initial water in the reaction increases, the residue to initial glycerol ratio decreased. The initial water content reduces the residue formation by stripping of the acetol along with water vapors from the reaction mixture before it can degrade/polymerize to form residue—water boils and provides the near-ideal diffusion of acetol in the reaction.

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

4.4.6 Residue Formation and Ability to Reuse Catalyst

The residue was taken as a solid form in room temperature and a slurry form at the reaction temperature during the long period of reaction time. The solid was soft and tacky in nature and readily dissolved in methanol to form slurry. Reactions were carried out to find the stability of the copper-chromite catalyst. After each run the catalyst was washed with methanol until the wash was clear and then the catalyst was dried in a furnace at 80 °C to remove the methanol for the subsequent runs (no catalyst reduction procedure was applied). The physical appearance of this catalyst after washing was similar to that of the fresh catalyst. The data of Figure 4.4 demonstrate the copper-chromite catalyst can be used repeatedly. The conversion of glycerol and the selectivity of acetol were slightly decreased over repeated usage.

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

4.5 Conclusions

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

Table 4.1: Summary of conversion of glycerol, selectivity of acetol and residue to initial glycerol ratio from glycerol over various metal catalysts

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

All reactions were performed in batch reactive distillation at 240 ^{o}C and 98 kPa (vac).

Table 4.2: Comparison of batch reactive distillation and semi-batch (continuous) reactive distillation on formation of acetol from glycerol

Mass balance details on batch reactive distillation using 5% copper-chromite catalyst loading. Initial loading of glycerol, 42.48; glycerol in distillate, 3.64; residue, 5.68; and amount of glycerol reacted, 38.84 all in grams. The glycerol reacted as described below

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

Mass balance details on semi-batch reactive distillation using 5% copper-chromite catalyst loading. Initial loading of glycerol, 54.29; glycerol in distillate, 4.91; residue, 3.80; and amount of glycerol reacted, 49.38 all in grams. The glycerol reacted as described below

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

Mass balance details on semi-batch reactive distillation using 2.5% copper-chromite catalyst loading. Initial loading of glycerol, 52.8; Glycerol in Distillate, 3.85; Residue, 4.91; and Amount of glycerol reacted, 48.95 all in grams. The glycerol reacted as described below

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

All reactions were performed at 240 ^{o}C and 98 kPa (vac). Glycerol feed rate was 33.33 g/hr for semi-batch reaction.

Table 4.3: Effect of glycerol feed flow rate on conversion of glycerol to acetol in semi-batch reactive distillation

Glycerol feed flow rate (g/hr)	Conversion (%)	Selectivity (%)	Residue Initial-Glycerol Ratio (%)
100	88.94	60.92	20.45
50	91.49	65.21	19.81
33.33	92.71	85.11	9.30
18.75	91.58	87.32	8.73
14.29	90.15	87.49	7.59

All reactions were performed in semi-batch reactive distillation at 240 ^{o}C and 98 kPa (vac).

Table 4.4: Effect of catalyst to glycerol throughput ratio on conversion of glycerol to acetol in semi-batch reactive distillation

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

All reactions were performed in semi-batch reactive distillation with glycerol feed rate of 33.33 g/hr at 240 ^{o}C and 98 kPa (vac).

Table 4.5: Effect of initial water content in the glycerol feedstock on residue formation

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

All reactions were performed in semi-batch reactive distillation with glycerol feed rate of 33.33 g/hr at 240 ^{o}C and 98 kPa (vac).

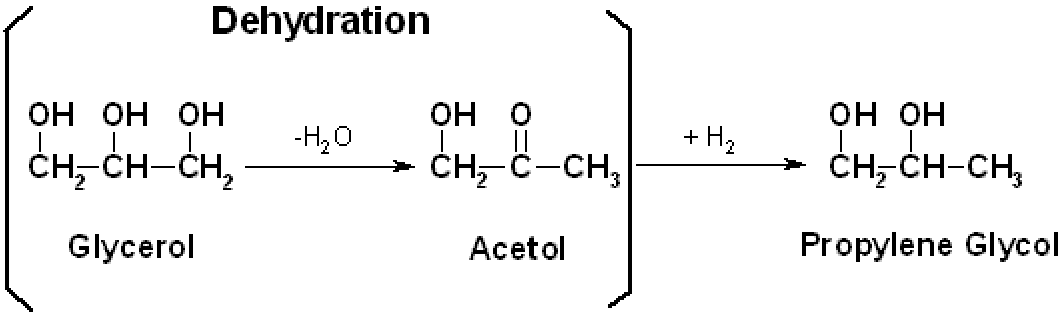


Figure 4.1: Proposed reaction mechanism for converting glycerol to acetol and then to propylene glycol.

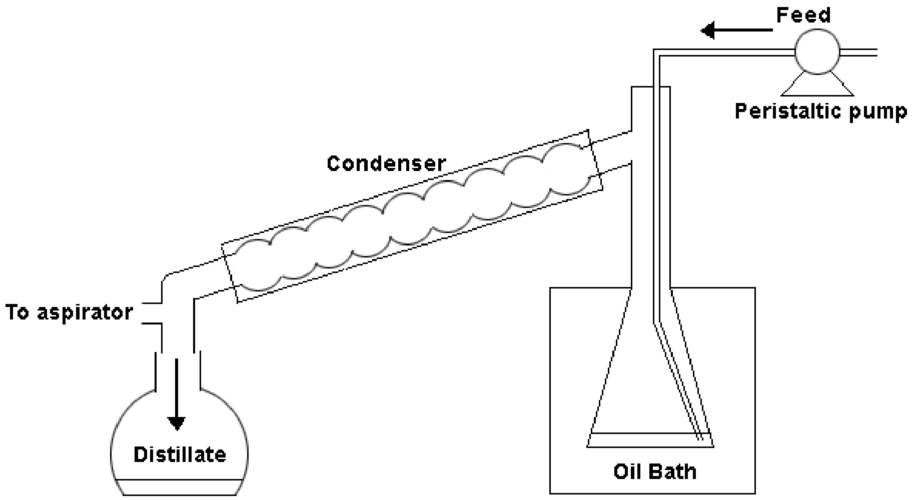


Figure 4.2: Diagram of semi-batch reactive distillation experimental setup

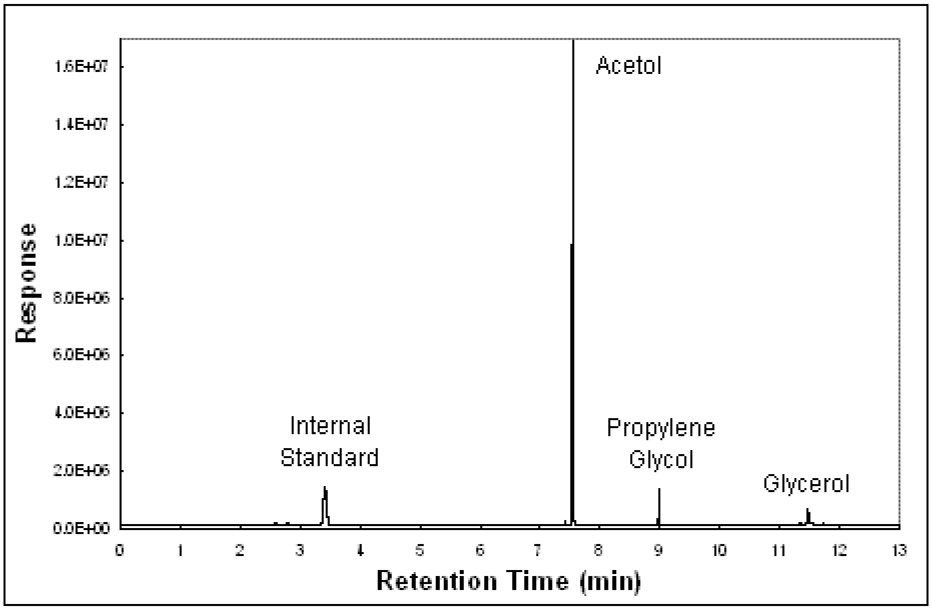


Figure 4.3: Gas chromatogram of the glycerol dehydration product

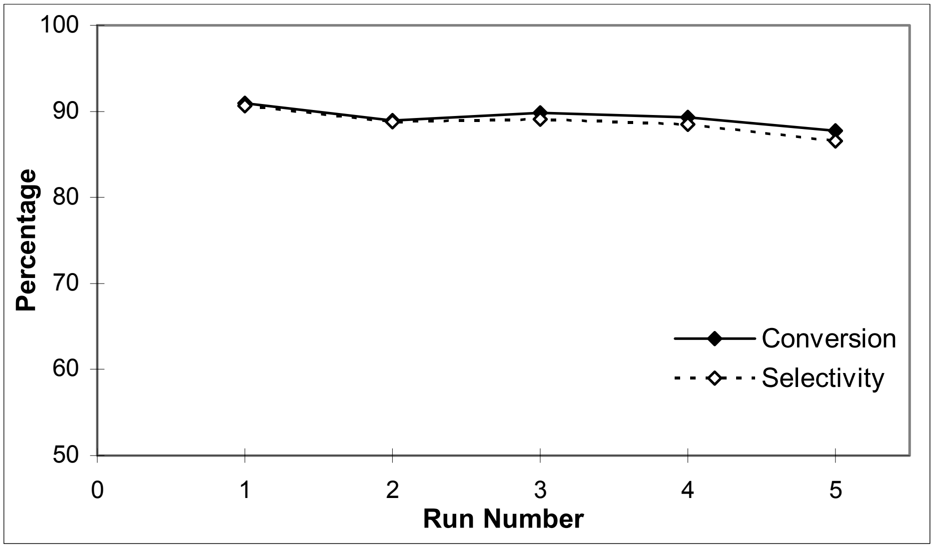


Figure 4.4: Copper-chromite catalyst reuse for conversion of glycerol to acetol. All reactions were performed using 5% copper-chromite catalyst loading in semi-batch reactive distillation with glycerol feed rate of 33.33 g/hr at 240°C and 98 kPa (vac)

5 CHAPTER 5

PRODUCTION OF PROPYLENE GLYCOL BY SELECTIVE CATALYTIC HYDROGENATION OF ACETOL

5.1 Abstract

Propylene glycol was produced in yields near 100% by liquid phase catalytic hydrogenation of acetol over metal catalysts. Hydrogenation was performed using nickel, ruthenium, palladium, platinum, copper, and copper chromium catalysts. The effects of temperature, hydrogen pressure, initial water content, choice of catalyst, and the amount of catalyst were evaluated. At temperature above 185°C and hydrogen pressure of 200 psi, complete conversion of acetol to propylene glycol was observed with a selectivity to propylene glycol greater than 97%. Seletivity to propylene glycol increased from 80.1 to 100% as the initial water conent increased from 0 to 70%. Yields of greater than 95% were attained with copper chromium, raney nickel and ruthenium catalysts.

At temperatures greater than 200°C and pressures less than 200 psi selectivity to propylene glycol decreased due to excessive reaction of propylene glycol or polymerization of acetol. Possible reaction pathways for polymerization of acetol are discussed. At lower reaction times and temperatures, an intermediate compound in the concentration profile was observed consistent with this compound being either an intermediate or an equilibrium-limited product that further hydrogenated to propylene glycol at longer reaction times. Little to no deactivation of the copper chromium catalyst was observed at the preferred reaction conditions.

KEY WORDS: Hydrogenation, Propylene Glycol, Copper Chromium, Acetol.

5.2 Introduction and Background

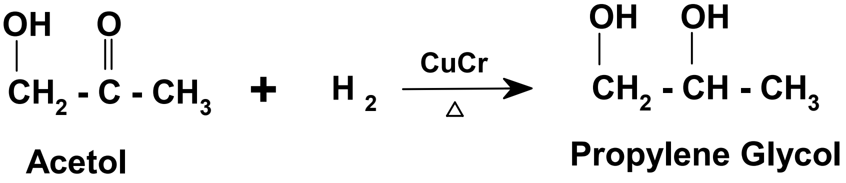
Over the past decade, there has been an increasing interest in production of value-added chemicals from renewable resources to displace petroleum consumption.[78] Catalytic processes that provide both a clean and economically competitive conversion of natural glycerol to products like propylene glycol are candidate processes for early commercialization to meet these increasing demands for green chemistry.

Propylene glycol is a major commodity chemical with an annual production of over 1 billion pounds in the United States [79] and sells for about $0.71 [80] per pound with a 4% growth in the market size annually. Some typical uses of propylene glycol are in unsaturated polyester resins, functional fluids (antifreeze, de-icing, and heat transfer), pharmaceuticals, foods, cosmetics, liquid detergents, tobacco humectants, flavors & fragrances, personal care, paints and animal feed. Use of propylene glycol in the antifreeze market is growing because of the concern over the toxicity of ethylene glycol-based products to humans and animals as well.

The commercial route to produce propylene glycol is by hydration of propylene oxide derived from propylene by either the chlorohydrin process or the hydroperoxide process. [81, 82] Alternative routes to propylene glycol synthesis are possible with renewable feedstocks. The most common alternative route of production is through hydrogenolysis of glycerol, sugars or sugar alcohols at high temperatures and pressures in the presence of a metal catalyst producing propylene glycol and other lower polyols. [83,84,85] However, the selectivities towards propylene glycol is compromised due to reactions at these severe reaction conditions. In a recent publication[86], the authors proposed a novel two-step process for a highly selective production of propylene glycol from glycerol via a reactive acetol intermediate.

Acetol has usually been prepared by the reaction between bromoacetone and sodium or potassium formate or acetate, followed by hydrolysis of the ester with methyl alcohol.[87, 88] Treatment of glycerol [89,86] or propylene glycol [90] at 200-300°C with a dehydrogenating catalyst leads to the formation of acetol, while the direct oxidation of acetone with Bayer and Villager's acetone-peroxide reagent furnishes acetol together with pyruvic acid. Acetol is extremely reactive as it contains both hydroxyl and carbonyl functional groups. Accordingly, acetol may undergo a variety of reactions including polymerization, condensation, dehydration, and oxidation reactions.

In the present work, selective hydrogenation of carbonyl group in acetol to form propylene glycol has been studied. Reaction scheme 1 shows conversion of acetol to propylene glycol as previously decribed by the authors.[86] In the presence of metallic catalysts and hydrogen, acetol can be hydrogenated to propylene glycol. A limited number of publications document schemes for converting acetol to propylene glycol.



$$\overset{\overset{\displaystyle OH}{|}}{CH_2} - \overset{\overset{\displaystyle O}{\|}}{C} - CH_3 + H_2 \xrightarrow[\Delta]{CuCr} \overset{\overset{\displaystyle OH}{|}}{CH_2} - \overset{\overset{\displaystyle OH}{|}}{CH} - CH_3 \qquad (1)$$

Kometani et al described a procedure to prepare (R) - and (S) - propylene glycol by reduction of acetol using baker's yeast.[91] Cameron et al proposed a biocatalytic fermentation technique for production of propylene glycol from glycerol and sugars with acetol being a reactive intermediate. [92, 93] Farber et al [94] demonstrated phytochemical reduction of acetol in the presence of top-yeast to form optically active propylene glycol. All the available literature only describes biochemical routes to produce propylene glycol from acetol. There is no available literature showing the chemical hydrogenation of acetol to propylene glycol.

The selective formation of propylene glycol requires hydrogenation of carbonyl group without effecting the terminal hydroxyl bond. The present study is focused on demonstrating the feasibility of producing propylene glycol by hydrogenation of acetol using heterogeneous metallic catalysts. The effect of various reaction parameters and the reaction kinetics were investigated.

5.3 Experimental Methods

5.3.1 Materials

Acetol, propylene glycol, and n-butanol were purchased from Sigma-Aldrich (Milwaukee, WI). High purity grade hydrogen and nitrogen were obtained from Praxair. Table 5.1 gives the description of various catalysts used in this study and their suppliers. A typical scanning electron micrograph of the copper chromium catayst is depicted in Figure 5.1 to provide a perspective on the surface topography. It is observed that the catalyst particles were not spherical. The catalyst was outgassed for 4 hours at 250°C and the BET surface areas and pore volumes were determined from nitrogen adsorption isotherms at -190°C measured on a Porus Materials Incorporated gas sorption analyzer. The copper chromium catalyst used in all the reactions had a BET surface area of 65.03 m^2 g^{-1}, a pore volume of 0.098 cm^3 g^{-1}, and a average pore diameter of 7.54 nm. A similar analysis was not performed on the other catalysts.

5.3.2 Experimental Setup

All the reactions were carried out in a specially designed stainless steel multi-clave reactor capable of performing eight reactions simultaneously. Each reactor with a capacity of 150ml is equipped with a magnetic stirrer, electric heater and a sample port for liquid samples. The temperature of the reactor was controlled by CAMILE 2000 control and data acquisition system using TG 4.0 software. The reactors were first charged with 10ml of reaction mixture and a parametric amount of catalyst. They were flushed several times with nitrogen to ensure inert atmosphere and then the nitrogen was purged out using hydrogen. Then the system was pressurized with hydrogen and heated to meet the pressure and temperature parameters of each experiment. The speed of the stirrer was set constant at 150 rpm through out the reaction. Control reactions performed utilizing an empty stainless steel reactor showed no formation of propylene glycol at the temperatures and pressures of our reaction. All the catalysts used in this study were reduced prior to the reaction in a by passing a stream of hydrogen over the catalyst bed at a temperature of 300°C for 4 hours.

5.3.3 Method of Analysis

Reaction product samples were cooled to room temperature and centrifuged using an IEC (Somerville, MA) Centra CL3R centrifuge to remove the catalyst. These samples were analyzed with a Hewlett-Packard 6890 (Wilmington, DE) gas chromatograph equipped with a flame ionization detector. Hewlett-Packard Chemstation software was used to collect and analyze the data. A Restek Corp (Bellefonte, PA) MXT® WAX 70624 GC column (30m x 250 μm x 0.5μm) was used for separation. A solution of n-butanol with a known amount of internal standard was prepared apriori and used for analysis. The samples were prepared for analysis by adding 100 μl of product sample to 1000 μl of stock solution into a 2ml glass vial.

Figure 5.2 shows a typical gas chromatogram of the hydrogenolysis reaction product. Using the standard calibration curves that were prepared for all the components, the integrated areas were converted to weight percentages for each component present in the sample.

For each data point, selectivity of propanediol and conversion of acetol to propanediol were calculated as follows:

Conversion of acetol is defined as the ratio of number of moles of acetol consumed in the reaction to the total moles of acetol initially present.

Selectivity defined as the ratio of the number of moles of the product formation to that of the acetol consumed in the reaction, taking into account the stoichiometric coefficient.

5.4 Results and Discussions

5.4.1 Catalyst Screening and Selection

Heterogeneous catalysts, including ruthenium, nickel, platinum, copper, raney copper, raney nickel, palladium, and copper chromium in the form of metallic powders, metal oxides, and activated metals (metal sponge) were impregnated on an activated carbon support. Reactivities were tested at 200 psi hydrogen pressure and at a temperature of 185°C. Table 5.1 shows the performance comparison of these catalysts.

Raney nickel, ruthenium and copper chromium based catalysts exhibited higher selectivity towards propylene glycol. In each case, essentially 100% of the product yield was accounted for propylene glycol. The table also shows the performance comparison of different copper chromium catalysts.

Under the hypothesis that the unknown product is converted to propylene glycol at higher reaction times, the primary distinguishing characteristic between the catalysts was reactivity with the more reactive catalysts having higher conversions. Barium and Manganese promoted copper chromium catalyst was selected for further studies.

5.4.2 Parametric Studies

The effect of reaction temperature, hydrogen pressure, initial water content and amount of catalyst for acetol hydrogenation reaction were determined using copper chromium catalyst and the results are discussed in the following sections.

5.4.3 Effect of Reaction Temperature

Table 5.2 shows the effect of temperature on the conversion and selectivity of the reaction. Temperature has a significant effect on the overall yield of the propylene glycol. Reactions were carried out at 50, 100, 150, 175, 185 and 210^{o}C and at a pressure of 200 psi of hydrogen in the presence of a copper chromium catalyst. As the temperature of the reaction increases from 50 to 210^{o}C there is a uniform increase in the acetol conversion from 19.4% to 93.8%. However, the selectivity of propylene glycol increased until 185^{o}C and began to decrease as the temperature increased. These trends in addition to the observation of the formation of a non-volatile oligomer at higher temperatures indicates that at a hydrogen pressure of 200 psi and temperatures >185°C excessive reaction or polymerization converts the acetol and propanediols into oligomers or degradation products like propanol and ethanol. Degradation gaseous products like methane, ethane, propane, carbon dioxide are also believed to be formed based on the inability to close the carbon balance for certain reactions. Moreover, from our initial screening studies (see, Figure 5.5) it was observed that it is necessary to operate at high pressures to prevent byproduct formation at temperatures >200°C.

Polymerization of Acetol Acetol tends to polymerize into dark gel at temperatures above 150°C. Figure 5.3 shows proposed reaction schemes for polymerization of acetol. In the absence of hydrogen, acetol undergoes dehydration to form acrolein. At the reaction conditions, in the absence of inhibitors, acrolein has high tendency to polymerize to highly cross linked solids which are infusible and insoluble in common solvents.[95] Also, acrolein may reduce to propanol in presence of hydrogen and copper chromium catalyst.

Studies were designed to elucidate the nature of acetol polymerization reaction. Acetol was heated in presence of hydrogen, nitrogen and air at different temperatures in sealed metal reactors for 6 hours without any catalyst. The extent of polymerization was determined by studying the degradation behavior of the reaction products using a TA Instruments (Newcastle, DE) Q50 Thermogravimateric Analyzer (TGA). The scans were taken at a heating rate of 10°C/min from room temperature to 500 °C. The results summarized in Figure 5.4, compares the TGA thermograms of pure acetol with the degradation curves of the reaction products from 40°C-500°C. Acetol completely degraded between 100°C and 150°C. All the other reaction products began to lose weight from the start but retained 7-22 % of their original weight even after 500°C depending on the extent of polymerization and stability of the polymer. Thermograms T1, T2, T3, and T4 show the formation of low boiling (higher molecular weight) compounds, which indicates that acetol polymerization, is self-catalytic and occurs even in the presence of an inert atmosphere like nitrogen. Presence of air or oxygen as a medium promotes the polymerization reaction forming thermally stable higher molecular weight polymers this is indicated by the relatively low loss in original weight in thermogram T4. Therefore, the reactor should be thoroughly purged with hydrogen before the temperature is increased. Moreover, as indicated by the data in Figure 5.5, polymerization has an increasingly adverse effect on propylene glycol yield at temepratures more than 185°C.

5.4.4 Effect of Hydrogen Pressure

Reactions were carried out at 50, 100, 200, and 300psi at temperatures of 100, 150, 185 and 210^{o}C to determine the effect of hydrogen pressure on the overall reaction. Figure 5.5 provides the summary of the conversions of 50% acetol solution at different temperatures and under different hydrogen overhead pressures.

The conversion of the acetol increased as the hydrogen pressure increased from 50 psi to 300 psi. Because of the low solubility of hydrogen in aqueous solutions, elevated pressures provide a means to increase the hydrogen concentration in liquid phase and thus achieve reasonable conversion rates. It was also observed that the reaction rates depended on the loading of liquid in the reactor suggesting that vapor-liquid contact is crucial with higher liquid levels reducing the efficacy of the mass transfer of hydrogen through the liquid to the slurried catalyst.

The optimal reaction temperature (producing a maximum yield of propylene glycol) was observed to be a function of the hydrogen over-pressure. Yields increased with temperature until undesirable side-reactions became more prevalent. Hence, at every pressure there exists an optimal temperature that maximizes the propylene glycol yield. Optimal operating pressures for hydrogenation of acetol to propylene glycol will balance the higher costs of high pressure equipment with decreased yields at lower pressures. .

5.4.5 Effect of Catalyst Weight

Reactions were performed to determine the impact of catalyst loading on conversion of acetol to propylene glycol. Table 5.3 summarizes the data on catalyst loading. The acetol conversion and selectivity increased with increase in the catalyst weight.

The catalyst was reduced at temperature of 300°C in hydrogen prior to reaction. Any copper oxide in the catalyst should be reduced to metallic copper, which is believed to be the primary reaction site for the conversion of acetol to propylene glycol.

Higher catalyst loading provides more active sites for the hydrogenolysis of acetol to propylene glycol. However, propylyene glycol in the presence of heat can undergo further hydrogenolysis to propanol and lower alcohols. The data of Table 3 illustrates high selectivities to propylene glcyol by copper chromium catalyst even at higher catalyst loadings—this is highly desirable for this reaction.

5.4.6 Effect of Feed Concentration

Qualitative observations during screening studies indicated that pure acetol readily polymerizes at temperatures near 200°C (see Figure 5.4). It was hypothesized that such polymerization is second order in acetol concentraiton, and as such, could be controlled with a diluent. Water is generated during the production of acetol from dehydration of glycerol, and so, it was selected for studies on the impact of diluents.

Reactions were performed using acetol solutions prepared with different water contents to study the effect of initial water content on the overall reaction. Table 5.4 provides the summary of effect of initial water content on overall acetol conversion at 185°C and 200 psi.

As the initial water in the reaction increases, the selectivity to propylene glycol increases. Addition of solvents like water or methanol reduces polymer formation. Moreover, for acetol solutions with concentrations >70% a decrease in the selectivity of propylene glycol was observed due to the degradation of reaction product due to polymerization. Results in Table 5.4 show that the product propylene glycol can also be used as solvent eliminating the cost of separating the water or methanol from the final product.

5.4.7 Kinetic Studies

Preliminary reaction kinetic studies of conversion of acetol to propylene glycol were conducted at 185°C and 200 psi hydrogen pressure. Figure 5.6 shows the conversion profile of the reaction system at these conditions. Propylene glycol conversion of ~97% is achieved in 4 hours. An intermediate product (identified as lactaldehyde) was generated initially during the reaction which further converts into propylene glycol. The reaction follows a first order model with an over rate constant of $k = 0.71\text{h}^{-1}$.

At higher concentrations of acetol (low water contents) formation of intermediate increases. Moreover, for acetol solutions with concentration >70% a decrease in the selectivity was observed due to possible side reactions and the degradation of reaction product due to polymerization. A water content of at least 30% minimizes the degradation and, also, minimizes the formation of the intermediate (which must be further reacted to maximize yield).

5.4.8 Catalyst Stability

Reactions were carried out to find the stability of the copper chromium catalyst. After each run the catalyst was filtered from the reaction product and used in the subsequent runs without any pretreatment. Figure 5.7 summarizes the acetol conversion for 12 cycles. No signs of deactivation of the copper chromium catalyst were observed. The conversion of acetol and the selectivity of 1,2 propanediol was essentially constant (>90%).

5.5 Conclusions

Hydrogenation of acetol to propylene glycol over copper chromium catalyst was studied and compared with other metal-based catalysts. High selectivities (>98%) for propylene glycol were achieved with acetol conversions nearing 97% for a 4 hour reaction time at moderate temperatures (185°C) and hydrogen pressures (200psi). The reaction kinetic results show that the reaction follows an overall first order rate model. Higher selectivities to propylene glycol were observed at higher hydrogen pressures. At temperatures of about 210°C excessive reaction takes place resulting in polymerization of acetol or formation of gaseous or liquid by-products. At least 30% diluent is recommended to reduce formation of byproducts from acetol.

Table 5.1: Summary of conversion of acetol and selectivity to propylene glycol over various metal catalysts. Reactions were carried at 185°C, 200 psi, and 4 hours

Supplier	**Description**	**Acetol conversion (%)**	**Propylene Glycol Selectivity (%)**
Grace Davison	Raney Copper	99.07	91.72
Degussa	5% Palladium/Carbon	76.22	74.26
Sud-Chemie	Copper-Zinc [a]	91.56	87.17
Sud-Chemie	Copper/Alumina [b]	82.67	96.91
Sud-Chemie	Copper Chromium [c] promoted by Ba and Mn	96.89	98.92
Sud-Chemie	Copper Chromium [d]	98.22	93.86
Sud-Chemie	Copper Chromium promoted by Ba [e]	74.22	95.97
Engelhard	Copper Chromium promoted by Mn [f]	98.00	96.08
In-house	Copper/Silica [g]	82.67	93.67
Grace Davison	Raney Nickel	99.56	98.90
Degussa	5% Platinum/Carbon	72.89	88.71
Johnson Matthey	5% Ruthenium/Carbon	100.00	100.00
Alfa Aesar	Nickel/silica-alumina	73.78	81.20
Johnson Matthey	Nickel/Carbon	90.22	89.16

Nominal Compositions (wt%):

[a] CuO (33), ZnO (65), Al_2O_3 (2)

[b] CuO (56), Al_2O_3 (34), MnO_2 (10)

[c] CuO (45), Cr_2O_3 (47), MnO_2 (3.5), BaO (2.7)

[d] CuO (50), Cr_2O_3 (38)

[e] CuO (41), Cr_2O_3 (46), BaO (13)

[f] CuO (36), Cr_2O_3 (33), MnO_2 (3)

[g] 23 wt% copper on silica support

Table 5.2: Effect of reaction temperature on formation of propylene glycol from acetol. All the reactions were performed using 50% acetol in water at 200psi for 4 hours

Temperature (°C)	**Acetol Conversion (%)**	**Propylene Glycol Selectivity (%)**
50	19.44	93.30
100	40.02	90.06
150	74.67	89.67
175	89.78	92.11
185	96.89	98.92
210	100.00	81.39

Table 5.3: Effect of copper chromium catalyst loading on formation of propylene glycol from acetol. All the reactions were performed using 50% acetol solution at 185°C and 200psi

Catalyst (Wt %)	Time (h)	Acetol conversion (%)	Propylene Glycol Selectivity (%)
10	4	98.31	99.04
5	4	96.89	98.92
2	4	91.56	95.41
1	4	70.67	92.06
0.5	4	65.33	90.53
1	6	87.11	93.64
0.5	6	71.78	90.66

Table 5.4: Effect of initial feed concentration on the formation of propylene glycol from acetol. All the reactions were performed at 185°C and 200psi for 4 hours

Feed Concentration (wt %)	**Acetol conversion (%)**	**Propylene Glycol Selectivity (%)**
100	99.44	74.98
70 [a]	95.33	89.29
50 [a]	96.89	98.92
30 [a]	100.00	100.00
10 [a]	100.00	100.00
70 [b]	95.79	91.38
50 [b]	97.26	99.02

[a] Water is used as solvent
[b] Propylene glycol used as solvent

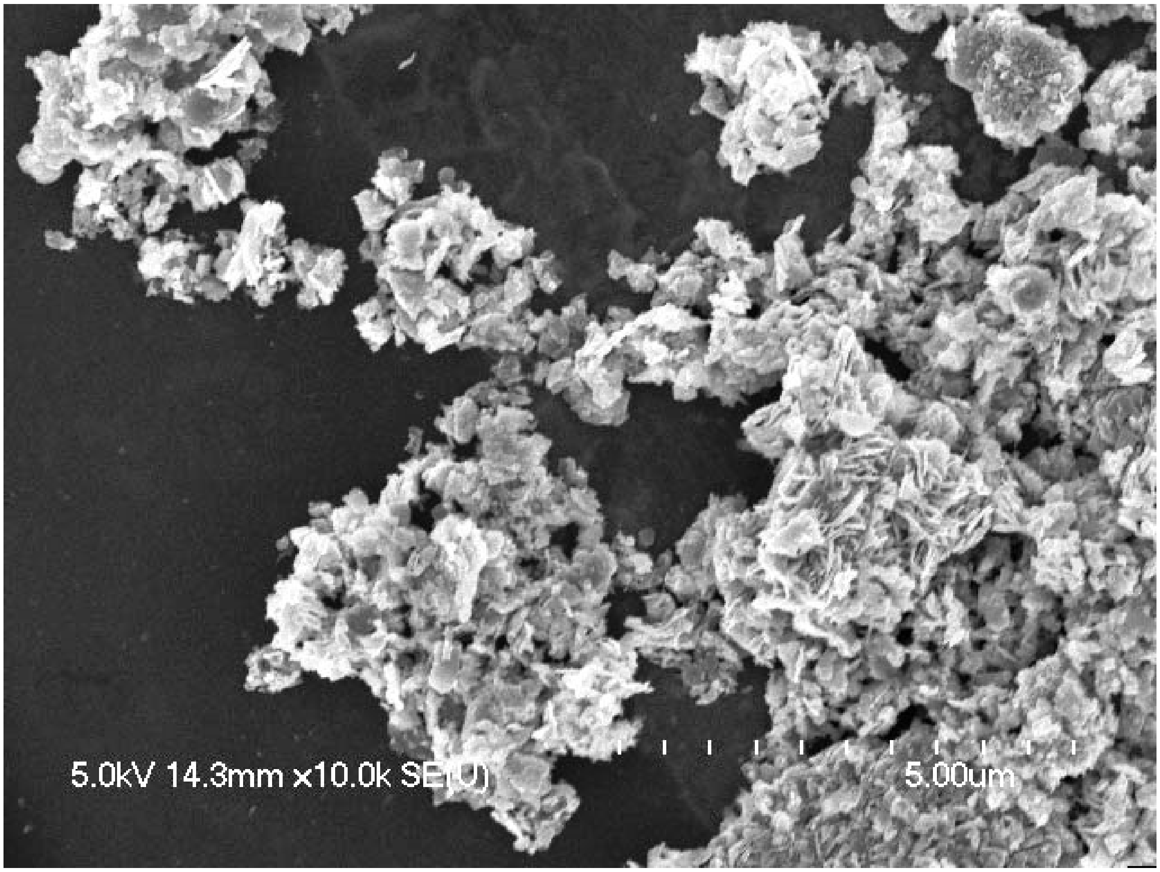


Figure 5.1: Scanning electron micrograph of the copper chromium catalyst

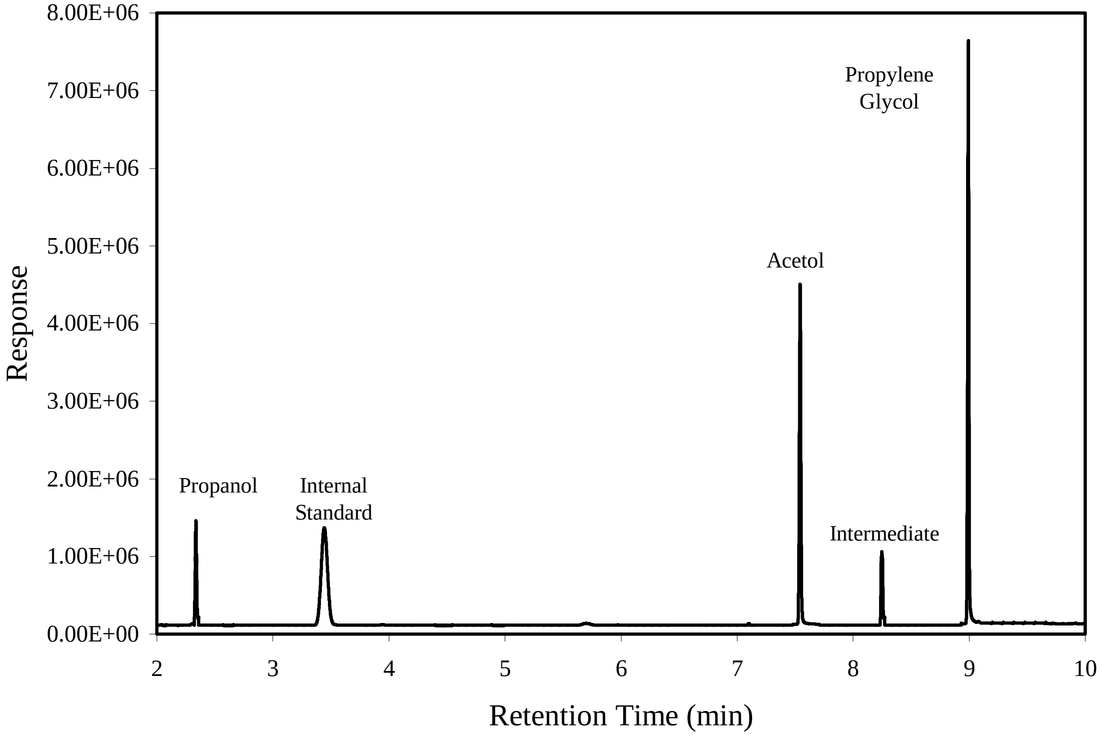


Figure 5.2: Gas chromatogram of the liquid hydrogenation reaction products

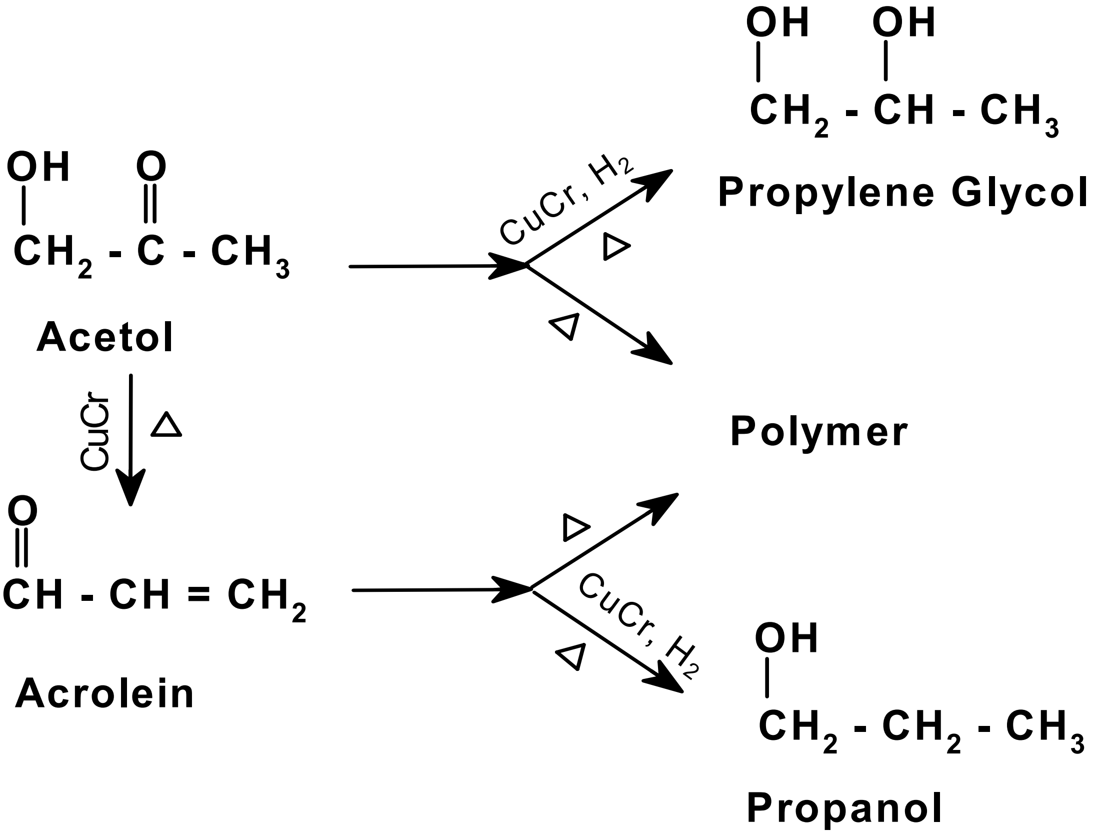


Figure 5.3: Reaction scheme of acetol polymerization

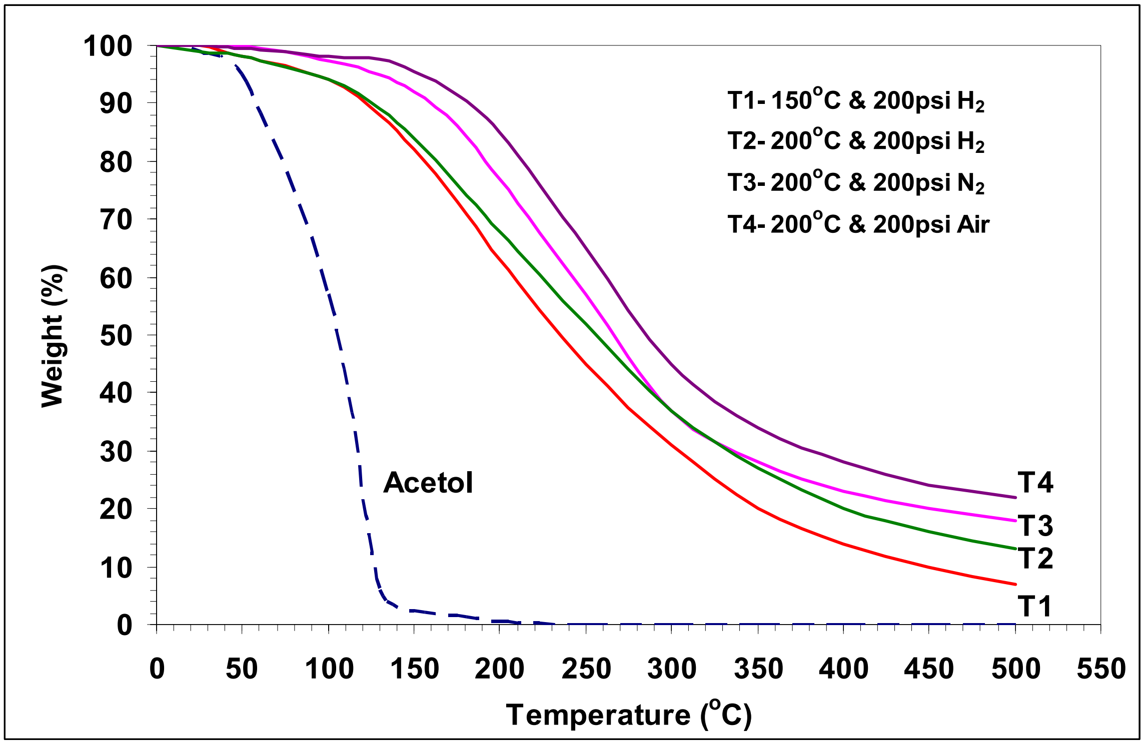


Figure 5.4: TGA thermograms of pure acetol and its polymerization products

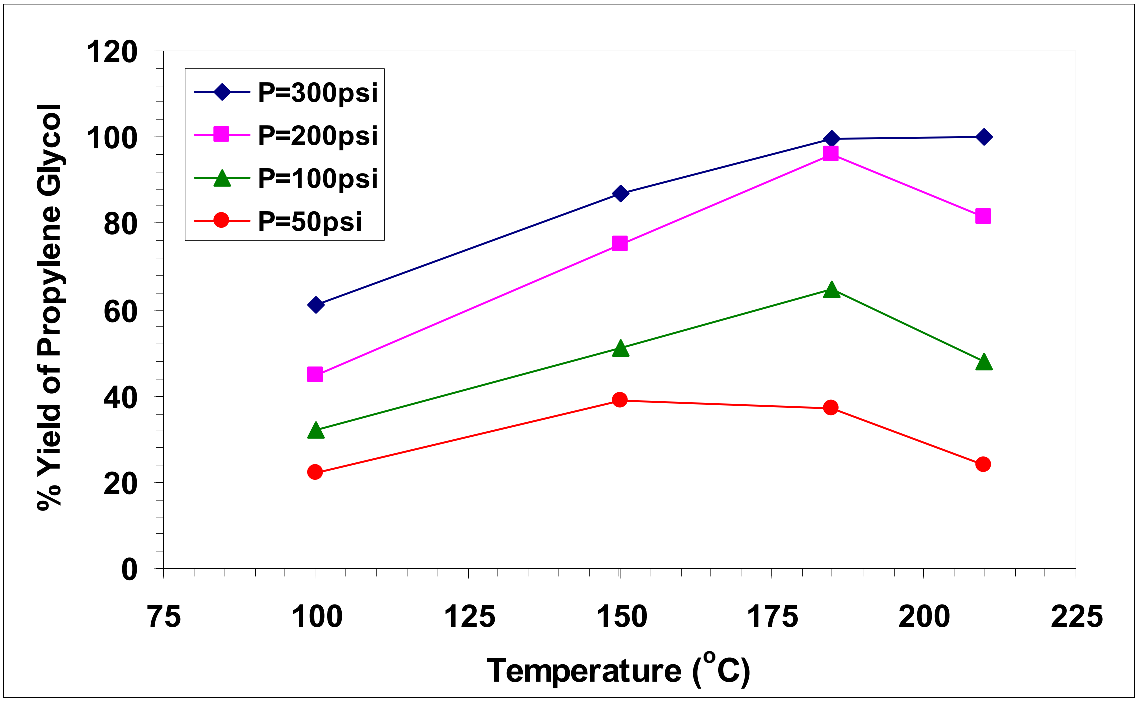


Figure 5.5: Effect of hydrogen pressure on the formation of propylene glycol from acetol. All the reactions were performed using 50% acetol in water for 4 hours

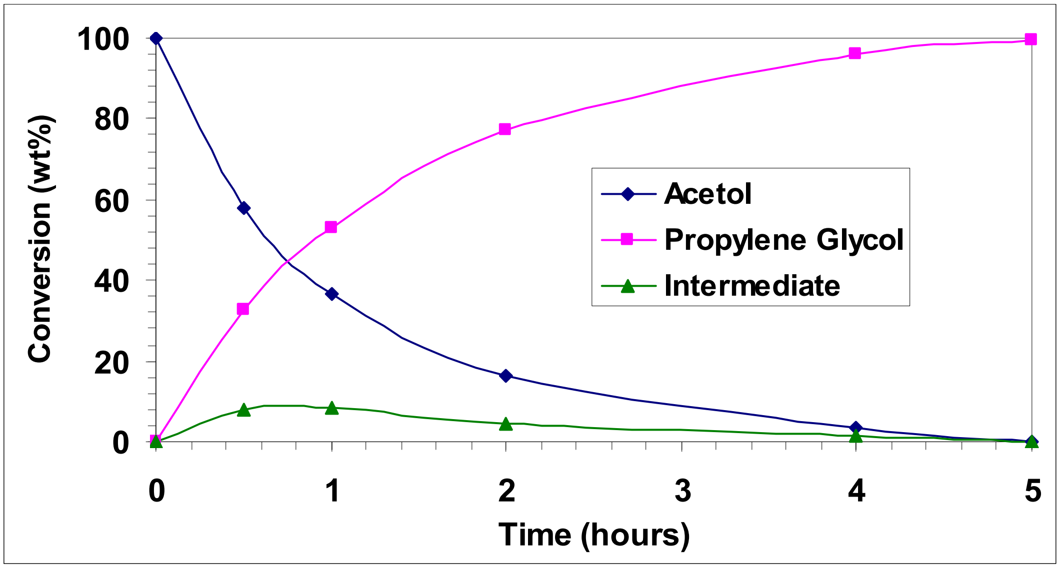


Figure 5.6: Reaction Profile for the conversion of acetol to propylene glycol at 185°C and 200psi

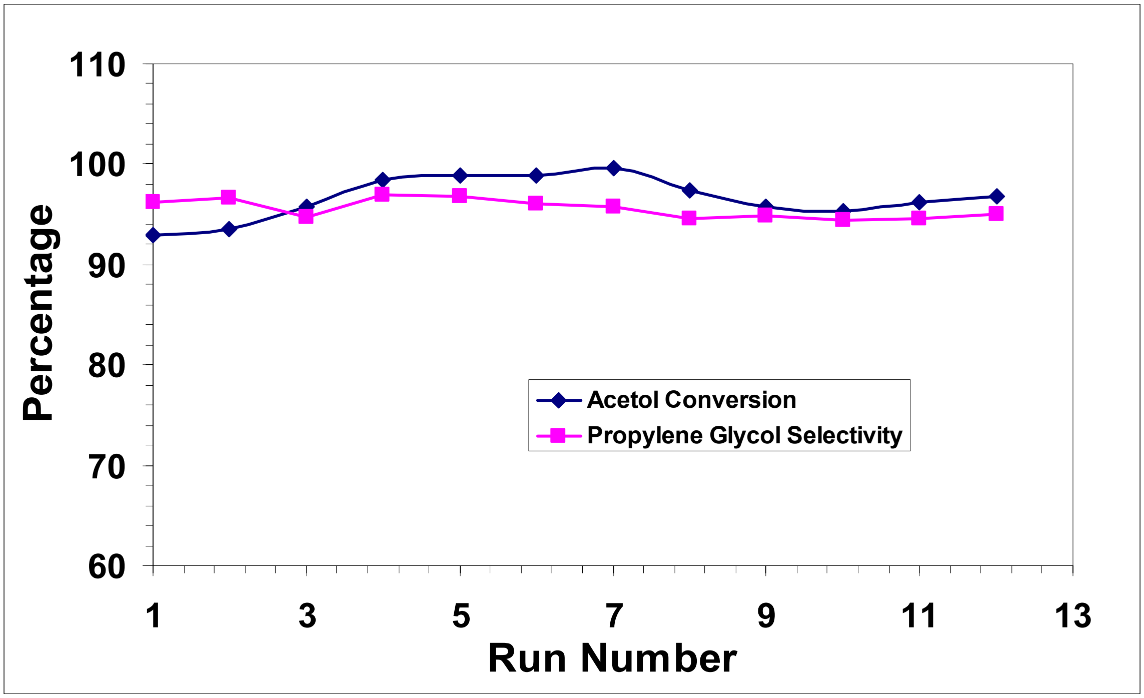


Figure 5.7: Stability of the copper chromium catalyst. Each of the reactions was carried at 185°C and 200 psi hydrogen pressure for 4 hours

6 CHAPTER 6

SOLUBILITY STUDIES OF HYDROGEN IN AQUEOUS SOLUTIONS OF ACETOL

6.1 Abstract

Solubility of hydrogen in aqueous solution of acetol was determined at temperatures between 50^o to 200^{o}C hydrogen pressures between 100 and 1000 psig and at molar concentrations between 1 and 10M. Henry's Law was observed in entire range of data, and the proper coefficients are reported.

6.2 Introduction

Precise data on the solubility of gaseous reactants is required in interpreting the kinetics of gas-liquid and gas-liquid-solid reactions. The purpose of this study is to determine the solubility of hydrogen in aqueous solutions of acetol (hydroxyacetone) under various conditions of temperature, pressure and solute concentrations. Selective hydrogenation of acetol is of a particular interest for producing propylene glycol in high yields and was not studied in greater detail.[96, 97] In this system a three-phase slurry hydrogenation is used to convert acetol to propylene glycol.[98]

No data have been reported in the literature for the solubility of hydrogen in acetol. Solubility of hydrogen in acetol was studied at 100° to 200°C, 100 to 1000psi and 1-10M concentration.

Because the dissociation of the gaseous hydrogen into atoms is endothermic (ΔH=104 Kcal/mole), its reactivity is very low. The solubility of hydrogen in aqueous phase is very low and not even measurable at high temperatures and atmospheric pressures. High pressures favor the dissolution of hydrogen, so high pressures will tend to increase the reaction rate. H_2 solubility or saturation concentration is a very important parameter in mass transfer analysis. However, no H_2 solubility data are available in the literature for high temperature and pressure. The measured solubility of H_2 at our reaction conditions will be reported in this section.

6.3 Experimental Methods

The solutions were prepared from distilled water and acetol at 90% purity obtained form Sigma-Aldrich (Milwaukee, WI). High purity grade hydrogen and nitrogen were obtained from Praxair.

The equipment used for solubility measurement is similar to that used by Radhakrishna et al[99]. It consists of a 300ml Parr stirred autoclave reactor equipped with automatic heating controls and an internal cooling coil used as a equilibrium cell, a burette with two port caps (for gas out and mixture in), and a water-bath with a glass cylinder for measuring the gas volume by water displacement. A needle valve was used in the liquid outlet to control the saturated liquid fluid rate. Coiled steel tubing was used after the needle valve to cool down the saturated liquid to minimize flash vaporization. By proper use of both heating elements and the cooling coil, it was possible to control the solution temperature to +/- 1^{o}C.

The first step was to fill the reactor with a known volume of solution mixture. The empty space in the reactor is flushed with hydrogen and is pressurized with hydrogen to a desired pressure. The gas burette is also flushed with hydrogen and kept at atmospheric pressure. Then the reactor was heated to the desired temperature and pressurized to the desired pressure at the same time. High stirring speed (1200 rpm) was used to ensure the gas and liquid reached equilibration within 15 minutes. After stopping stirring, another 30 minutes was allowed to let the liquid and gas fully separate. The saturated liquid was then collected from the dip tube to purge the liquid outlet line. Care was taken to prevent any gas pockets in the sampling lines. A hydrogen source with constant pressure (pressure regulator and a high-pressure cylinder tank) was connected to the reactor to maintain a constant pressure in the reactor. While the burette was empty and the glass cylinder was filled with water, the needle valve was carefully opened to let saturated liquid depressurize in the burette. The liquid was collected in the bottom and the gas displaced the water in the glass cylinder. When the liquid level in the burette reached about 20 ml or the gas volume in the glass cylinder was over 100 ml, the needle valve was closed and the liquid in the burette (weight and volume) and the gas volume in the cylinder were recorded.

6.3.1 Calculation

Hydrogen solubility's can be calculated as:

$$S(ml/g) = \frac{V_{gas}(ml) - \dfrac{W_1(g)}{d_1(g/ml)}}{W_1(g)}$$

V_{gas} is the total volume in mL (STP)

W_1 is the liquid weight (g)

d_1 is liquid density (g/mL)

6.4 Results and Discussion

6.4.1 Solubility of Hydrogen in Water

Table 6.1 is the hydrogen solubility in HPLC water. The solubility slightly increases with temperature at a given pressure. To verify the measurement, these data were compared to literature data[100] in Figure 6.2. The comparison shows that this measurement is accurate.

The reproducibility of the experimental measurements was checked by repeating a particular experiment 3 times. It was observed that the error in the solubility was within 3-4%. Thus indicating the accuracy of the method.

6.4.2 Solubility of Hydrogen in Acetol

In the same way, hydrogen solubility in acetol water solution was measured. Table 6.2 shows that H_2 solubility in acetol has the same trend as in water, but the solubility in acetol solution is smaller than that in pure water at all temperatures and pressures.

6.4.3 Effect of Pressure

The solubility data were found to follow the Henry's Law

$$S= \alpha p$$

Where S is the solubility of gas (ml/g), α is the Henry's constant (ml/g.psi), and p is the gas pressure in psi. The value of Henry's constant represents solubility of hydrogen at a pressure of 1kPa. The experimental data on solubility of hydrogen in aqueous solutions of acetol at different pressures are presented in the Figure 6.3. The Henry's constants were determined from least squares fit of data. Henry's law is satisfied in every case upto the highest pressure tested.

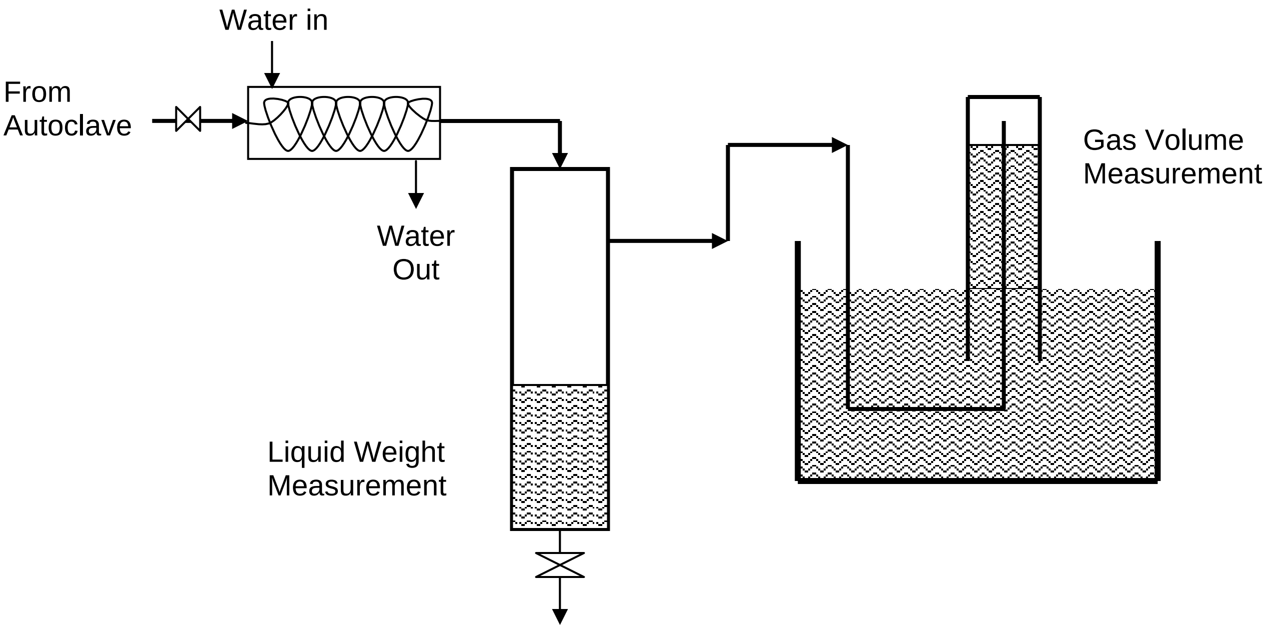
6.4.4 Effect of Temperature

From the data in Table 6.2, it is evident that for a given concentration of acetol hydrogen solubility increases linearly with increase in temperature. The effect of temperature on the solubility of hydrogen in acetol is shown in Figure 6.4 as a plot of α vs. 1/T according to the expression

$$\alpha = A \exp(-\Delta H/RT)$$

Where $-\Delta H$ is the heat of dissolution of the gas, R the gas constant, T the temperature and A is a constant. The solubility was found to be a mild function of temperature. The values of $-\Delta H$ and A, calculated as slope and intercept of linear plot of log α and 1/T (Figure 6.4), are 6.73 KJ/mol and 8.3x10-7 mol/ml.psi respectively. The values of heat of dissolution indicate that the dissolution of hydrogen is endothermic which is consistent with earlier observations.[101, 102]

Figure 6.1: Schematic of solubility apparatus



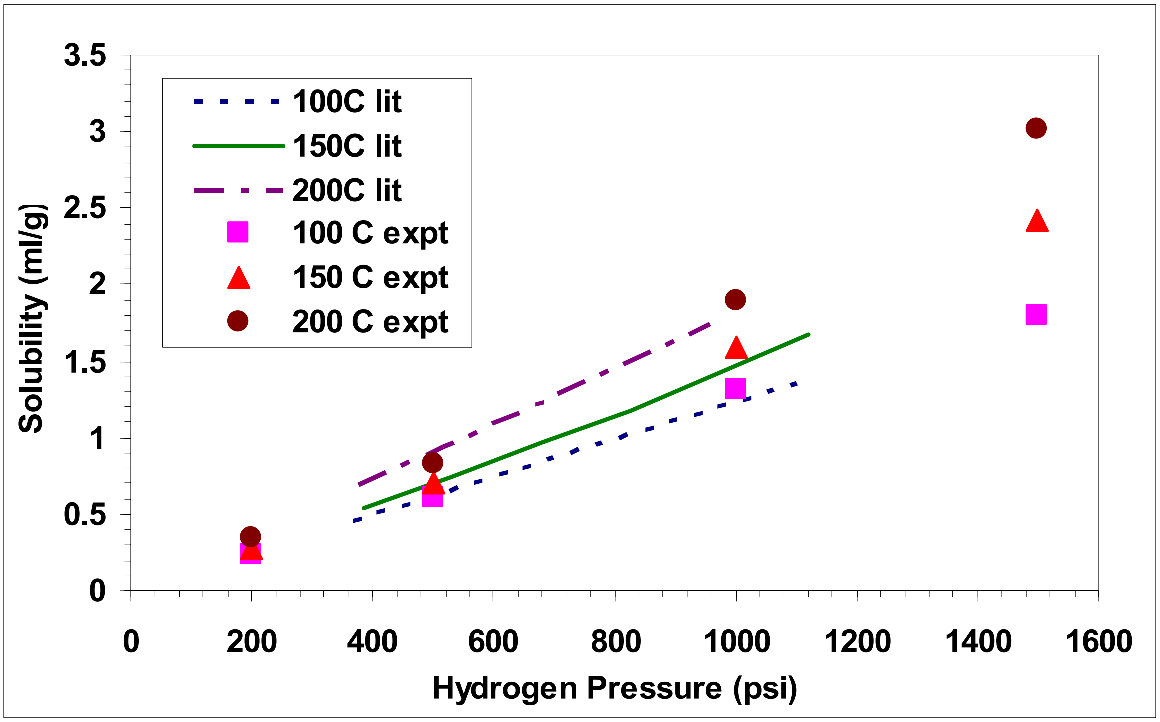


Figure 6.2: Comparison of measure solubility and literature data

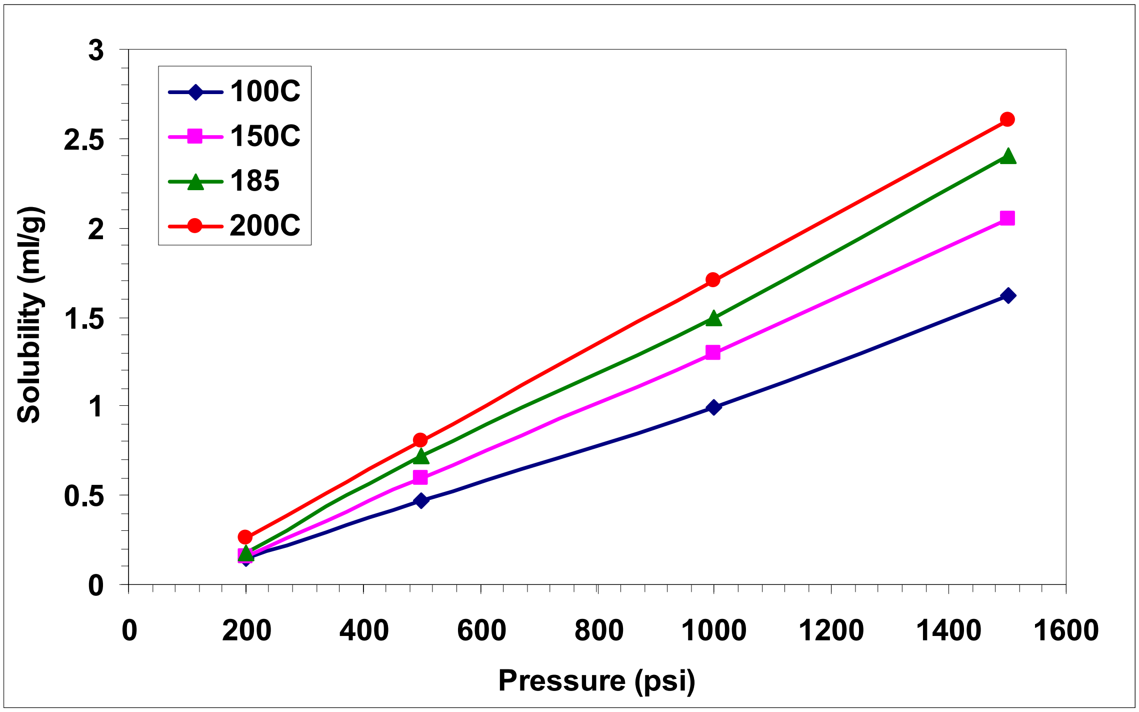


Figure 6.3: Effect of pressure on the solubility of hydrogen

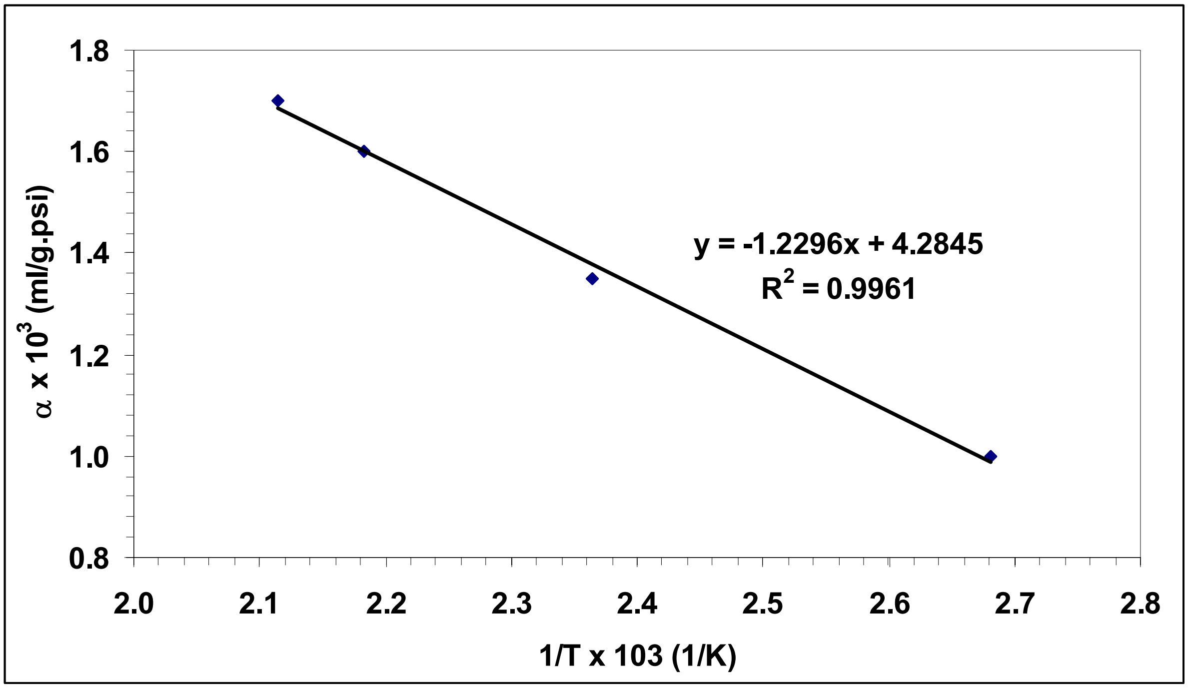


Figure 6.4: Temperature dependence of Henry's Law constant for 20% acetol solution (2.75M)

Table 6.1: Solubility of hydrogen in HPLC water (mL/g)

Pressure	**Temperature (^oC)**		
	100	**150**	**200**
200	0.24	0.28	0.34
500	0.61	0.7	0.83
1000	1.31	1.59	1.9
1500	1.8	2.42	3.01

Table 6.2: Solubility of hydrogen in 20% acetol solution (mL/g)

Pressure (psi)	**Temperature (°C)**			
	100	**150**	**185**	**200**
200	0.15	0.16	0.18	0.2
500	0.47	0.6	0.72	0.8
1000	0.99	1.3	1.5	1.7
1500	1.62	2.05	2.4	2.6

7 CHAPTER 7

KINETIC AND MASS TRANSFER ANALYSIS OF HYDROGENATION OF ACETOL TO PROPYLENE GLYCOL IN A THREE PHASE SLURRY REACTOR

7.1 Introduction

The selective catalytic hydrogenation of acetol, formed by dehydration of glycerol, is a novel and important process for the manufacture of propylene glycol reported by our group.[103, 104] The overall reaction mechanism is given in Figure 7.1. Preliminary results of catalyst screening, effect of reaction parameters like temperature, pressure, catalyst loading, feed concentrations were presented in the publication. Yields of propylene glycol as high as 95% with a selectivity of greater that 97% were achieved over a powder copper chromium catalyst at 185°C and 200psi hydrogen pressure in a stirred batch reactor. These studies demonstrated the feasibility of production of propylene glycol at high yields at mild reaction conditions. Propylene glycol is a major commodity chemical with an annual production of over 1 billion pounds in the United States[105] and sells for about $0.71[106] per pound with a 4% growth in the market size annually. Some typical uses of propylene glycol are in unsaturated polyester resins, functional fluids (antifreeze, de-icing, and heat transfer), pharmaceuticals, foods, cosmetics, liquid detergents, tobacco humectants, flavors & fragrances, personal care, paints and animal feed. The antifreeze and deicing markets are growing because of concern over the toxicity of ethylene glycol-based products to humans and animals as well. The commercial route to produce propylene glycol is by the hydration of propylene oxide derived from propylene by either the chlorohydrin process or the hydroperoxide process.[107,108] The proposed direct hydrogenation of acetol would provide a green chemical process for the production of propylene glycol.

The catalytic hydrogenation of acetol to propylene glycol is a three phase reaction with aqueous acetol solution and propylene glycol in liquid phase, hydrogen in gas phase and the solid copper chromium catalyst. In a three-phase slurry reactor the following process may limit the reaction rate:

1) Mass transfer of hydrogen in gas phase to acetol solution in liquid phase,

2) Mass transfer of hydrogen and acetol from liquid phase to solid catalyst surface,

3) Intra-particle diffusion of hydrogen and acetol within the catalyst, and

4) Chemical reaction of acetol to propylene glycol over the catalyst surface.[111]

A schematic of mass transfer resistances present in aqueous phase hydrogenation of acetol to propylene glycol is shown in Figure 7.2. Correlations in the literature have been used to calculate the mass-transfer coefficients across the phase boundaries.[111] To scale up the process, knowledge of intrinsic kinetics is essential. In three-phase hydrogenation, gas-liquid (G-L), liquid-solid (L-S) and intra-particle mass transfer will significantly influence the reaction rate. To investigate intrinsic kinetics, mass transfer effects must be eliminated by choosing suitable process parameters (catalyst particle size, stirring speed, catalyst loading, initial concentration, and reaction pressure and temperature). To establish intrinsic kinetic model, a reaction scheme should be setup and model parameters should be estimated by using regression techniques.

The present investigation was undertaken with the following objectives: 1) to perform a detailed analysis of the controlling regimes in hydrogenation of acetol to propyelene glycol on copper chromium catalyst in a three-phase slurry batch reactor and 2) to develop a Langmuir-Hinshelwood rate model, based on the kinetic data collected in a chemical control regime, which can be a basis for design of the catalytic reactor for hydrogenation process.

7.2 Experimental Methods

7.2.1 Materials

Acetol, propylene glycol, and n-butanol were purchased from Sigma-Aldrich (Milwaukee, WI). High purity grade hydrogen and nitrogen were obtained from Praxair. The catalyst was outgassed for 4 hours at 250°C and the BET surface areas and pore volumes were determined from nitrogen adsorption isotherms at -190°C measured on a Porus Materials Incorporated gas sorption analyzer. The copper chromium catalyst used in all the reactions had a BET surface area of 65.03 $m^2 g^{-1}$, a pore volume of 0.098 $cm^3 g^{-1}$, and a average pore diameter of 7.54 nm.

7.2.2 Experimental Setup

All the reactions were conducted in a 300ml stirred batch Parr autoclave reactor

(Model 4506, Parr Instrument Company) equipped with an electrically heated jacket, variable speed magnetic stirrer, temperature controller with internal cooling coil and liquid sampling ports. The gas inlet, gas release valve, cooling water feed line, pressure gauge and rupture disk were situated on top of the reaction vessel. The liquid sample line and the thermocouple were immersed in the reaction mixture. A chilled water condenser was fitted on the sample valve exit line to avoid flashing of the sample. The entire assembly was leak-proof.

7.2.3 Experimental Procedure

In a typical reaction, the catalyst was first loaded into the reactor and reduced by passing a stream of hydrogen over the catalyst bed at a temperature of 300°C for 4 hours. The reactor was charged with 100ml of 20% (2.75M) acetol solution and then flushed several times with nitrogen to ensure inert atmosphere and that the entire assembly is leak proof. The residual nitrogen was purged from the reactor using hydrogen. The system was then heated to meet the desired reaction temperature of each experiment.

The temperature was allowed to stabilize, stirring speed is set to 1000 rpm and the reactor was pressurized to the desired value to initiate the reaction. At this stage of the reaction, a sample was withdrawn and this was considered ‘zero’ time for the reaction. The conversion while achieving the desired temperature was was (<2%) and therefore neglected when calculating initial rates. Samples were withdrawn every 30min preceded by flushing of the sample line. The reaction was allowed to proceed for a prescribed amount of time after which the autoclave was allowed to cool and samples of the remaining reaction mixture were analyzed thereafter.

Control reactions performed without catalyst present showed no formation of propylene glycol at the temperatures and pressures of our reaction.

7.2.4 Method of Analysis

Reaction product samples were collected every 30min, cooled to room temperature and analyzed with a Hewlett-Packard 6890 (Wilmington, DE) gas chromatograph equipped with a flame ionization detector. Hewlett-Packard Chemstation software was used to collect and analyze the data. A Restek Corp (Bellefonte, PA) MXT® WAX 70624 GC column (30m x 250 μm x 0.5μm) was used for separation. A solution of n-butanol with a known amount of internal standard was prepared apriori and used for analysis. The samples were prepared for analysis by adding 100 μl of product sample to 1000 μl of stock solution into a 2ml glass vial.

7.3 Characterization of Mass Transfer in the Batch Reactor

Evaluating mass transfer limitation in the batch reactor was relatively straight forward because high stirring rates can be used to approach upper limits of operation where mass transfer from the gas to the liquid and to the catalyst surface is no longer the rate determining step. In addition, estimates of diffusion rates can be compared to observed reaction rates. Experiments and calculations from literature correlations were used to investigate mass transfer effects in the autoclave reactor. From comparison of the reaction rate with mass transfer rate, one can figure out the influence of mass transfer on conversion of acetol to propylene glycol.

7.3.1 Suspension of Catalyst

Catalyst suspension is not directly related to mass transfer, but the assumption for mass transfer study is that catalyst powder is evenly distributed in the liquid. Therefore, it is necessary to verify that the entire solid catalyst is suspended, or that no catalyst settles at the bottom of reactor. The minimum stirring speed requirement in the autoclave was given by Zwietering [109].

$$N_m = \frac{2(d_R / d_T)^{1.33} d_p^{\ 0.2} \mu_L^{\ 0.1} g^{0.45} (\rho_P - \rho_L)^{0.45} w^{0.13}}{\rho_L^{\ 0.55} d_T^{\ 0.85}}$$

where dR and dT are the reactor diameter and the stirrer diameter respectively and w is the catalyst loading (g/100g). Nm is the minimum speed needed to suspend all catalyst. Minimum speed requirement for different catalyst loadings is shown in Figure 7.3. It is clear that the stirring speeds we used (200~1200rpm) are much larger than the minimum suspension speed.

7.3.2 Maximum Reaction Rate

The highest reaction rate is needed for investigating the mass transfer effects. Reaction rate is defined as converted acetol mole per weight of catalyst and time. The fastest reaction happens at high temperature and high pressure. Therefore, the reaction rates are calculated only for the reaction at 185°C and 800psi. The initial reaction rate is the fastest because it is at the highest reactant concentration and with fresh catalyst. The maximum rate is about 0.195 mole/hr when the catalyst loading is 2g per 100g solution as shown in Table 7.1.

$$R_A\left[\frac{mole}{hr.g_{cat}}\right] = \frac{dC_A}{w\rho_L dt} = C_{Ao}\frac{d(1-x)}{\rho_L w dt} = -\frac{C_{Ao}(mole/ml)}{w(g_{cat}/100g_{liquid})\rho_L(g_{liquid}/ml)}\frac{dx}{dt}$$

7.3.3 Pseudo First Order Rate Constant

The concentration of the hydrogen in the reactor is much larger than the acetol concentration, and the concentration of hydrogen did not change appreciably during the course of the reaction. In this case, we consider the reaction to follow pseudo first order kinetics.

If the reaction is assumed as first order for acetol, we can calculate the rate constant.

$$-r_A = -\frac{dC_A}{w\rho_L dt} = kC_A \Rightarrow \frac{dC_A}{C_A} = wk\rho_L dt \Rightarrow \ln\left[\frac{C_{Ao}}{C_A}\right] = wk\rho_L t \Rightarrow \ln(1-x) = -wk\rho_L t$$

The calculation is shown in Table 7.2.and Figure 7.4. The reaction rates are calculated only for the reaction at 185°C and 800psi. The data from all catalyst loadings fall on the same line. Therefore, the same rate constant is obtained for all loadings. The effective rate constant for pseudo first order kinetics is k=0.5 1/hr.

7.3.4 Gas-Liquid Mass Transfer

A simple method was used to estimate the magnitude of the hydrogen-water mass transfer coefficient in batch reactor. The principle is to measure the pressure change in a sealed reactor after the beginning of stirring. From the pressure drop rate, the mass transfer coefficient can be calculated. Because the limit of the precision of pressure measurement and the speed of time recording, this method is only for the estimation of the magnitude of the mass transfer coefficient.

First, a certain amount of liquid (water) was charged into the sealed reactor, and then the reactor was heated with stirring to specified temperature (25°C). When the temperature stabilized, the stirring motor was stopped. The reactor was pressurized carefully to a desired pressure with hydrogen. To minimize the mass transfer during the pressurization, the hydrogen was introduced from the gas phase (not from dip tube). The mass transfer during pressurizing is assumed small enough to be neglected; this was confirmed by the very slow pressure drop observed without stirring. The stirrer was then turned on; reactor pressure drop with time was recorded immediately after the beginning of stirring at specified speed.

With S_o being the hydrogen solubility at temperature T and pressure P, S (ml/g) the hydrogen concentration in the liquid at time t, and $k_L\alpha$ the gas (G) liquid (L) mass transfer coefficient.   The rate of change of hydrogen concentration is:

$$\frac{dS}{dt} = (S_0 - S)k_L\alpha$$

Hydrogen solubility S_o will change during the experimental process because the pressure P will change. In the low-pressure range, we can estimate the change with Henry's law S_o = H*P (at 150°C, H=0.0218 ml/g.atm, from the hydrogen solubility measurement), from the hydrogen mass balance the instant hydrogen concentration in liquid phase S can be calculated.

$$S = \frac{22400 * V_G (P_0 - P)}{R * T * W_L}(ml/g)$$

Where, W_L is the liquid weight in reactor. V_G is gas phase volume at room temperature. P_o is the initial pressure in reactor and P is the pressure at time t.

$$\text{Let } \beta = \frac{22400 * V_G}{R * T * W_L} \quad \text{then } S = \beta(P_o - P)$$

$$\frac{dS}{dt} = \frac{-\beta dP}{dt} = k_L \alpha (S_o - S)$$

$$\text{Where } S_o = H * P \text{ and } S = \beta(P_o - P)$$

dS/dt is obtained by fitting S vs. t data to a fourth order polynomial and differentiating the polynomial. Plotting *dS/dt* vs. (*So-S)* and forcing a line to pass through the origin the mass transfer coefficient $k_L\alpha$ can be calculated from the slope.

The measured mass transfer coefficients at different liquid loading in the reactor are given in Table 7.3. The regression coefficients R^2 in most of the regressions are 0.85-0.98. That is reasonably good considering the very simple experimental equipment and method. It is seen that $k_L\alpha$ sharply increases after the stirring speed reaches 800rpm. Due to the limitation of equipment and experimental method, the reactor had to be filled to 70-80% of capacity to ensure measurable gas pressure drops. This leads to a very bad flow pattern in the reactor because the stirrer blades are on the bottom of the reactor. Therefore, the coefficients we measured are the mass transfer coefficient at the worst conditions and represent an estimate of the lower bound of G-L mass transfer.

Observations were made to evaluate the effects of stirring speed. A glass reactor with stirring capabilities was used and allowed gas-liquid interface to be observed. The experiments showed that gas bubbles were formed when the stirring speed reaching 200 rpm, and after 350 rpm, no clear liquid phase could be seen. This partially explains the mass transfer coefficient change with stirring speed. The comparison with literature data[110] is shown in Figure 7.5. The literature data come from a large (2L) Parr autoclave and the mass transfer coefficient is measured for hydrogen in methanol. The density of methanol is close to water and the hydrogen solubility in methanol is 1.4 *cc/g* at measurement conditions, so it is very close to our system. Relative differences related to the higher solubility of H_2 in water than in methanol and the bad flow pattern of our experimental system tended to cancel resulting in similar mass transfer coefficients. However, the liquid and gas contact pattern is much different in high stirring speed and fast mass transfer cannot be achieved with large liquid loading. This comparison verifies that this result is reasonably good.

At a stirring speed of 1000rpm, the G-L coefficient is about 3.2 l/min, which is equal to 192 l/hr. The solubility of hydrogen in 20% acetol at 800psi and 185°C is 1.21cc/g (0.061mole/L). Therefore, the maximum G-L mass transfer rate (when hydrogen concentration in solution is zero) will be 1.4 mole/hr (100g solution ~ 0.1L), which is much faster than the maximum observed reaction rate 0.195 mole/hr. Therefore, G-L mass transfer in batch reactor is negligible. Alternatively, the hydrogen concentration in liquid can be estimated as

$$R_G(mole/hr) = K_L a(S_o - S) * V_L \Rightarrow \frac{S}{S_o} = 1 - \frac{R_G}{K_L a V_L S_o} = 1 - \frac{0.195}{180 * 0.1 * 0.054} = 0.86$$

That means that the liquid hydrogen concentration is 86% of the solubility limit and gas liquid mass transfer will not control the autoclave hydrogenation of acetol to propylene glycol.

Gas-liquid mass transfer in mechanically stirred tank reactors has been investigated by a number of workers. Ramachandran[111] has given an extensive review. Among these investigators, Bern *et al* [112] correlation is relatively reliable, for it used data from different size reactors (include commercial reactor).

$$K_L a = 1.099 * 10^{-2} N^{1.16} d_I^{\ 1.979} u_g^{\ 0.32} V_L^{\ -0.521}$$

N is stirring speed (rpm)

d_I is the diameter of impeller (cm)

u_g is superficial gas velocity (cm/s) based on the reactor diameter

V_L is the liquid volume in reactor (ml)

With a fixed superficial gas velocity (0.001 cm/s), which was estimated from actual hydrogen consumption rate, the mass transfer coefficient was calculated at different stirring speeds. Figure 7.6, compares these mass transfer coefficients with those calculated from Bern's correlation, shows that the predicted value is very close to the measured value at both low and high speeds. However, the deviation in medium stirring speed is significant. This calculation also shows the measurement is consistent with published data.

As shown in previous section, the maximum rate for G-L mass transfer calculated using the measured coefficient is much larger than the maximum reaction rate, so we conclude that the G-L mass transfer resistance is negligible. This conclusion also is supported by the following propylene glycol reactions at different stirring speeds. These reactions were conducted at exactly the same temperature, pressure, catalyst loading and pre-reduction conditions [185°C, 800psi, 1gram 5%

CuCr powder]. The experimental results are summarized in Table 7.4. Virtually no relationship can be seen between the conversion and stirring speeds. That means the mass transfer does not control this reaction even at a stirrer speed of 300. The maximum difference in conversion is about 10%; this deviation may come from the uneven catalyst reduction.

7.3.5 Liquid-Solid Mass Transfer

It is well known that the coefficient of liquid-solid (L-S) mass transfer is very large compared to gas liquid mass transfer, so no actual measurement was conducted Only a creditable correlation from Sano *et al.*[113] was used.

$$Sh = \left[2 + 0.4 \left({ed_P}^4 \big/ \upsilon^3 \right)^{1/4} Sc^{1/3} \right] . \Phi_c$$

$$\frac{k_s d_P}{D \Phi_c} = 2 + 0.4 \left(\frac{{ed_P}^4 {\rho_L}^3}{{\mu_L}^3} \right)^{1/4} \left(\frac{\mu_L}{\rho_L D} \right)^{1/3}$$

Where $e = \dfrac{P}{\rho_L V_L}$

Φ_c is the shape factor of particles (=1)

$$a_P = \frac{6w(g) * \rho_B (ml/g)}{100(ml) * d_P (cm)}$$

a_P is the external area of particles per unit volume of the solution.

ρ_L is the Liquid density (1.02g/ml)

P is the power consumption in watts

We do not know the exact power consumption P, but it should be around 20-300 watt. The particle size used is *dp*=0.05cm as an upper limit. The L-S mass transfer coefficient of hydrogen ksap was calculated and shown in Figure 7.7. The calculation shows that L-S mass transfer is much faster than that at the G-L interface. Therefore, its resistance also can be neglected.

Another recommended correlation is from Boon-long et al[114]. Their equation does not need the power consumption, but it needs stirring speed.

$$Sh = 0.046\,\mathrm{Re}^{0.283}\,Ga^{0.173}\psi^{-0.011}(T/d)^{0.019}\,Sc^{0.461}$$

$$\frac{k_s d_p}{D} = 0.046\left(\frac{dT\omega\pi}{\mu}\right)^{0.283}\left(\frac{\rho^2 g d_p{}^3}{\mu^2}\right)^{0.283}\left(\frac{M_T}{\rho d_p{}^3}\right)^{-0.011}\left(\frac{T}{d_p}\right)^{0.019}\left(\frac{\mu}{\rho D_v}\right)^{0.461}$$

Figure 7.8 shows results from Boon-Long correlation. Comparing these results with Sano's correlation, the stirring power consumption of our autoclave at 1000 rpm is around 20W.

7.3.6 Intra-Particle Mass Transfer

Because we do not know the reaction order, the observable modulus (Weisz-Prater criterion) was calculated to estimate the effect of intra-particle mass transfer.

$$\eta\phi^2 = \frac{(-R_G)L^2}{\rho.C_A D_e}$$

$-R_G$ is the observed reaction rate (mole/g cat.sec)

The diffusivity of hydrogen and acetol are calculated from Wilke-Chang correlation.[115]

$$D = \frac{7.4x10^{-8}T(\theta M_w)^{0.5}}{\mu_L v_M{}^{0.6}}$$

The effective diffusivity $D_e = \varepsilon^2{}_B D$ is 3.4x10^{-5} cm^2/s at 100°C for hydrogen in water and 1.18x10^{-5} cm^2/s for acetol in water. Catalyst true density (ρ) is 0.8 g/ml for copper chromium catalyst given by the catalyst suppliers. Acetol consumption rate (mole/g cat.sec) was taken from Table 7.2. The modulus Characteristic length of catalyst is obtained by $L=D_p/6$, where D_p is the catalyst diameter. Figure 7.9 shows that if the catalyst particle size is smaller than 0.09 cm, the observable modulus will be less that 0.1, and then mass transfer can be neglected.

7.3.7 Summary of Mass Transfer in the Batch Reactor

The powder catalyst used in batch reactor is less than 0.05 cm diameter; therefore, the intra-particle mass transfer is negligible. The slowest mass transfer is gas to liquid. The maximum G-L mass transfer is significantly larger than the maximum reaction rate. Therefore, the calculations and experiments show that mass transfer in autoclave is unimportant, and the intrinsic reaction kinetics can be determined.

7.3.8 Batch Reactor Macro Kinetics

Since G-L, L-S and intra-particle mass transfer all can be neglected in batch reactor for acetol hydrogenation, the observed rate in batch should be the intrinsic surface reaction rate. The data used in the following analysis are from Figure 7.11 and Figure 7.12. Two temperatures (150 and 185°C), three pressures (400, 600, 800psi) and three different catalyst loading (1, 1.5 and 2 gram/l00g solution) were the variable parameters. The same catalyst and pre-reduction conditions were used. To avoid complications from possible active metal leaching and deactivation only initial rates will be considered here.

7.3.8.1 Initial Reaction Rate

The initial reaction rate was obtained by fitting the acetol concentration profile (CLA ~t) to a fourth order polynomial, differentiating the polynomial and setting the time to zero to get the initial reaction rate. This method is shown in Figure 7.13 and Figure 7.14 for experiment C9 (2 gram catalyst. 800psi and 185°C). All initial rates are summarized in Figure 7.15.

7.3.8.2 Activation Energy

From regressing the initial reaction rate by

$$R_{initial} = k_0 \exp\left(\frac{-E}{RT}\right) w^m {P_{H_2}}^n$$

One can get the macro activation energy, catalyst loading effect "m" and hydrogen pressure effect "n". First, the equation was rewritten as

$$\ln R_{initial} = \ln k_0 - \frac{-E}{RT} + m \ln w + n \ln p_{H2}$$

Then the multiple variable regressions were used to get energy E and constants m and n. The result is shown in Table 7.5. Then initial rate expression is

$$R_{initial} = 3361.02 \exp\left(\frac{-53162.09}{RT}\right) w^{0.32} {P_{H2}}^{0.81}$$

The activation energy (53.16 kJ/mole) shows that this is a chemical reaction control process, which also verifies that the mass transfer is negligible in the batch reactor which is consistent with the mass transfer analysis. This regression shows hydrogen pressure affects the initial rate (m=0.81), which indicates that acetol hydrogenation is not a simple surface reaction. The comparison of initial rate and predicted initial rate by the regressed expression is given in Figure 7.17

7.3.9 Effect of Reaction Temperature on Rate Constant

The reaction was carried at temperatures 120, 150 and 185°C. Results in Table 7.5 show that the reaction temperature had a strong effect on the initial rate of reaction and the initial rate is found to increase with increase in reaction temperature. Arrhenius plot in Figure 7.16 shows the temperature dependence of the apparent rate constant for hydrogenation of acetol at a constant acetol concentration of 2.75M. Normally, a reaction controlled by mass transport (either G-L or L-S mass transport or pore diffusion) has activation energy less than about 25 KJ/mol.[116] Therefore, the high value of the observed activation energy suggests that the influence of both G-L and L-S mass transport was negligible in this study.

7.4 Kinetic modeling

Even though the acetol hydrogenation reaction is relatively simple with high yields of propylene glycol and relatively insignificant byproducts, without the knowledge of surface reaction, it is still very difficult to get a reasonable kinetic model. Some insight into the reaction mechanism is given in a recent paper by our group.[104] Based on the main reaction mechanism, an H-W model is derived and fit to the low temperature reaction data.

The Hougen-Watson (H-W) model will be used to get a workable reaction model. First, we assume that all species molecularly adsorb on to single sites. The reaction consists of four steps, hydrogen and acetol adsorption, formation of propylene glycol and desorption of propylene glycol. Hydrogen and acetol adsorption are not likely the controlling steps because fast adsorption is seen from the literature and our experiments. The other surface reactions are the possible control step. Next, we assume that hydrogen is atomically adsorbed and all the other species are molecularly adsorbed on to single sites. The reaction consists of four steps, atomic adsorption of hydrogen, molecular adsorption of acetol adsorption, formation of propylene glycol and desorption of propylene glycol. And next, we assume that the acetol adsorbed on to the catalyst sites reacts with the hydrogen in the gas phase. The reaction consists of three steps, molecular adsorption of acetol, formation of propylene glycol and desorption of propylene glycol. In all the below calculations

S is active site

K is equilibrium constant

k is rate constant

C_v is the vacant active site concentration and

C_T is the total active site concentration.

7.4.1 Plausible Rate Models

7.4.1.1 Single Site Mechanism All Reaction Species Adsorbed Molecularly

$A + S \xleftrightarrow{K_1} S.A$ Acetol Adsorption

$H_2 + S \xleftrightarrow{K_2} S.H_2$ Hydrogen Adsorption

$S.H_2 + S.A \xleftrightarrow{K_3} S.P + S$ Formation of Propylene Glycol

$S.P \xleftrightarrow{K_4} P + S$ Propylene Glycol Desorption

Assume that the total active site density is constant and neglect the water adsorption.

$$K_1 = \frac{C_{S.A}}{C_A.C_v} \Rightarrow C_{S.A} = K_1 C_A C_v$$

$$K_2 = \frac{C_{S.H_2}}{P_{H_2}.C_v} \Rightarrow C_{S.H_2} = K_2 P_{H_2} C_v$$

$$K_3 = \frac{C_{S.P}.C_v}{C_{S.H_2}.C_{S.A}} \Rightarrow C_{S.P} = \frac{K_3 C_{S.H_2} C_{S.A}}{C_v} = K_3 K_2 K_1 C_A P_{H_2} C_v$$

$$K_4 = \frac{C_P.C_v}{C_{S.P}} \Rightarrow C_{S.P} = \frac{C_v C_P}{K_4}$$

$$R = k_3 C_{S.H_2} C_{S.A}$$

$$C_T = C_v + C_{S.H_2} + C_{S.A} + C_{S.P}$$

$$C_T = C_v + K_1 C_A C_v + K_2 P_{H_2} C_v + \frac{C_v C_P}{K_4}$$

$$C_T = C_v \left[1 + K_1 C_A + K_2 P_{H_2} + \frac{C_P}{K_4} \right]$$

$$C_v = \frac{C_T}{\left[1 + K_1 C_A + K_2 P_{H_2} + \frac{C_P}{K_4} \right]}$$

We assume that the formation of propylene glycol is the reversible rate controlling step and all the other reactions are in equilibrium.

$$R = k_3 C_{S.H_2} C_{S.A}$$

$$R = k_3 K_2 P_{H_2} C_v K_1 C_A C_v = k_3 K_2 P_{H_2} K_1 C_A \frac{C_T^{\,2}}{\left[1 + K_1 C_A + K_2 P_{H_2} + \frac{C_P}{K_4}\right]^2}$$

$$R = \frac{k K_1 K_2 P_{H_2} C_A}{\left[1 + K_1 C_A + K_2 P_{H_2} + \frac{C_P}{K_4}\right]^2}$$

The remaining rate models assuming various rate controlling steps are given in Table 7.6.

7.4.1.2 Single Site Mechanism Atomically Adsorbed Hydrogen and Molecularly Adsorbed Other Species

$A + S \xleftrightarrow{K_1} S.A$ Acetol Adsorption

$H_2 + 2S \xleftrightarrow{K_2} 2S.H$ Hydrogen Adsorption

$2S.H + S.A \xleftrightarrow{K_3} S.P + 2S$ Formation of Propylene Glycol

$S.P \xleftrightarrow{K_4} P + S$ Propylene Glycol Desorption

Assume that the total active site density is constant and neglect the water adsorption.

$$K_1 = \frac{C_{S.A}}{C_A.C_v} \Rightarrow C_{S.A} = K_1 C_A C_v$$

$$K_2 = \frac{C_{S.H}{}^2}{P_{H2}.C_v{}^2} \Rightarrow C_{S.H} = \sqrt{K_2 P_{H2} C_v{}^2}$$

$$K_3 = \frac{C_{S.P}.C_v{}^2}{C_{S.H}{}^2.C_{S.A}} \Rightarrow C_{S.P} = \frac{K_3 C_{S.H}{}^2 C_{S.A}}{C_v{}^2} = K_3 K_2 K_1 C_A P_{H2} C_v$$

$$K_4 = \frac{C_P.C_v}{C_{S.P}} \Rightarrow C_{S.P} = \frac{C_v C_P}{K_4}$$

$$R = k_3 C_{S.H}{}^2.C_{S.A}$$

$$C_T = C_v + C_{S.H} + C_{S.A} + C_{S.P}$$

$$C_T = C_v + K_1 C_A C_v + \sqrt{K_2 P_{H2} C_v{}^2} + \frac{C_v C_P}{K_4}$$

$$C_T = C_v \left[1 + K_1 C_A + \sqrt{K_2 P_{H2}} + \frac{C_P}{K_4} \right]$$

$$C_v = \frac{C_T}{\left[1 + K_1 C_A + \sqrt{K_2 P_{H2}} + \frac{C_P}{K_4} \right]}$$

We assume that the formation of propylene glycol is the reversible rate controlling step and all the other reactions are in equilibrium.

$$R = k_3 C_{S.H}{}^2.C_{S.A}$$

$$R = k_3 K_2 P_{H2} C_v{}^3 K_1 C_A = k_3 K_2 P_{H2} K_1 C_A \frac{C_T{}^3}{\left[1 + K_1 C_A + \sqrt{K_2 P_{H2}} + \frac{C_P}{K_4} \right]^3}$$

$$R = \frac{k K_1 K_2 P_{H2} C_A}{\left[1 + K_1 C_A + \sqrt{K_2 P_{H2}} + \frac{C_P}{K_4} \right]^3}$$

The remaining rate models assuming various rate controlling steps are given in Table 7.6.

7.4.1.3 Eley Rideal Mechanism Hydrogen in the Gas Phase and Other Species Molecularly Adsorbed

$A + S \xleftrightarrow{K_1} S.A$ Acetol Adsorption

$S.A + H_2(g) \xleftrightarrow{K_2} S.P$ Formation of Propylene Glycol

$S.P \xleftrightarrow{K_3} P + S$ Propylene Glycol Desorption

Assume that the total active site density is constant and neglect the water adsorption.

$$K_1 = \frac{C_{S.A}}{C_A.C_v} \Rightarrow C_{S.A} = K_1 C_A C_v$$

$$K_2 = \frac{C_{S.P}}{P_{H_2}.C_{S.A}} \Rightarrow C_{S.P} = K_2 P_{H_2}.C_{S.A} = K_2 K_1 C_A P_{H_2} C_v$$

$$K_3 = \frac{C_P.C_v}{C_{S.P}} \Rightarrow C_{S.P} = \frac{C_v C_P}{K_4}$$

$$R = k_2 P_{H_2} C_{S.A}$$

$$C_T = C_v + C_{S.A} + C_{S.P}$$

$$C_T = C_v + K_1 C_A C_v + \frac{C_v C_P}{K_3}$$

$$C_T = C_v\left[1 + K_1 C_A + \frac{C_P}{K_3}\right]$$

$$C_v = \frac{C_T}{\left[1 + K_1 C_A + \frac{C_P}{K_3}\right]}$$

We assume that the formation of propylene glycol is the reversible rate controlling step and all the other reactions are in equilibrium.

$$R = k_2 P_{H_2} C_{S.A}$$

$$R = k_2 K_1 P_{H_2} C_A C_v = k_2 K_1 P_{H_2} C_A \frac{C_T}{\left[1 + K_1 C_A + \frac{C_P}{K_3}\right]}$$

$$R = \frac{k K_1 P_{H_2} C_A}{\left[1 + K_1 C_A + \frac{C_P}{K_3}\right]}$$

The remaining rate models assuming various rate controlling steps are given in Table 7.6

7.4.2 Initial Choice of Models

All the plausible rate models were presented in Table 7.6. The parameters of all probable models were first estimated by linearizing them. The acceptable rival models selected by preliminary screening of all these models were then subjected to further discrimination among them to arrive at the final model. The initial selection of acceptable models from all the possible candidates was based on several now well known statistical criteria. These criteria have been summarized by many researchers in the literature and have demonstrated their application to a specific reaction[117, 118, 119]. These models were then subjected to nonlinear least-squares analysis by an iterative procedure involving a combination of the methods proposed in the literature[120, 121] which ensured fast rates of convergence from the initial estimates (obtained from the linear least-squares analysis) by putting restrictions on the changes in the parameters. The data were processed using Polymath software. The models for which the estimated parameters are negative are outrightly rejected. As a result of this preliminary screening, three models, based on surface reaction rate controlling, were found to merit consideration and are listed in Table 7.7. The values of the various constants along with their limits of confidence and residual sum of squares are included in Table 7.7. An initial comparison of the three models based on the RSS values indicates that model X does not give a good fit to the experimental data as compared to the other two models. Hence model X is eliminated. The RSS value of model VII (0.04) is less than RSS value of model III (0.07). However, from the Table 7.7, it can be seen that for model VII 95% confidence interval is greater than the value of the actual parameter itself thereby yielding negative values to the parameter $K_{A.}$ Hence, considering the physical realism of the parameters model VII is eliminated.

7.4.3 Effect of Propylene Glycol in Acetol Hydrogenation

Experiments were designed to investigate the effect of propylene glycol on acetol hydrogenation. The initial solutions were 20% acetol solutions with 10, 20% propylene glycol loadings. All the reactions were done at 185°C and 800psi and 2g catalyst loading. The conversion profiles were shown in Figure 7.10. The results show that even with high concentration of propylene glycol present in the reaction, acetol can be converted at a rate similar to pure acetol hydrogenation. It is clear that the acetol and propylene glycol are not competing for the same reaction sites. The slight decrease in the rates with increase in the propylene glycol concentration may be due to slow desorption of the propylene glycol product from the catalyst surface due to the high concentration of the propylene glycol in the reaction solution. Therefore, the propylene glycol term in the denominator of the proposed L-H rate model can be neglected. The final form of the L-H kinetic expression based on the above model is thus given by

$$R = \frac{kK_1K_2P_{H_2}C_A}{\left[1+K_1C_A+K_2P_{H_2}\right]^2}$$

The estimated parameter values for the above model at different temperatures and the fitted rate constants at each temperature and the R^2 are given in Table 7.8. The parity plot illustrating the agreement between experimental and predicted rates at 185°C is given in Figure 7.18. The fit of the data is good at both temperatures and, considering the simplifying assumptions made in deriving the L-H kinetic model and presence of any side reactions, which may consume 2-3% of acetol.

The reaction activation energy estimated from the Arrhenius plot in Figure 7.16 is found to be 53.16 KJ/mole. The effect of temperature on adsorption equilibrium constants are given by

$$K_A, K_H = A\exp(-\Delta H / RT)$$

The estimated heats of adsorption of acetol and hydrogen based on the adsorption constants at two temperatures are ΔH_A= 30.58 KJ/mol and ΔH_H=.38.98 KJ/mol. These are reasonable values for chemisorbed species. The comparison of the values of the adsorption constants K_A and K_H and heats of adsorption of the reactant species revealed that adsorption of hydrogen on the catalyst surface is higher than that of the acetol species. These above models estimated from the kinetic data may however be considered as semi-emperical ones, particularly useful only for reactor design purpose and not necessarily to understand the reaction mechanism of catalytic process.

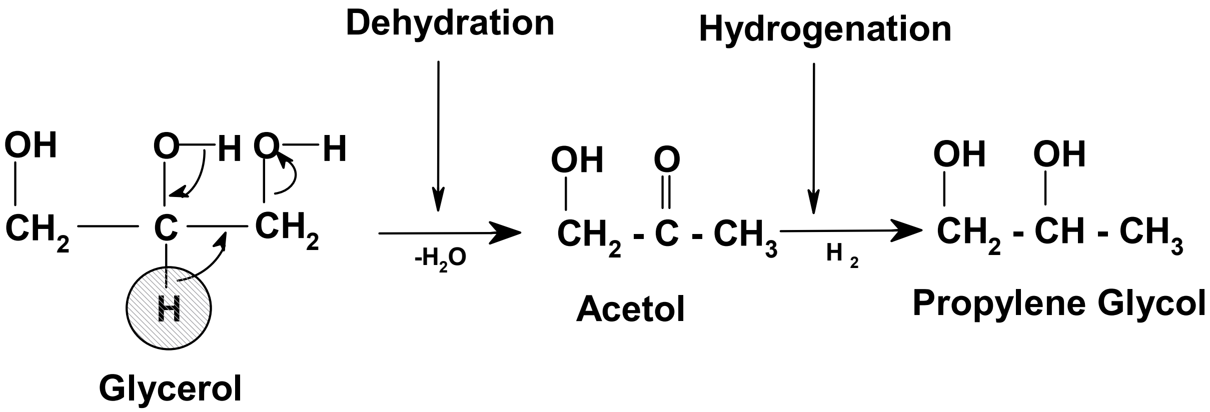


Figure 7.1: Reaction mechanism for conversion of glycerol to propylene glycol

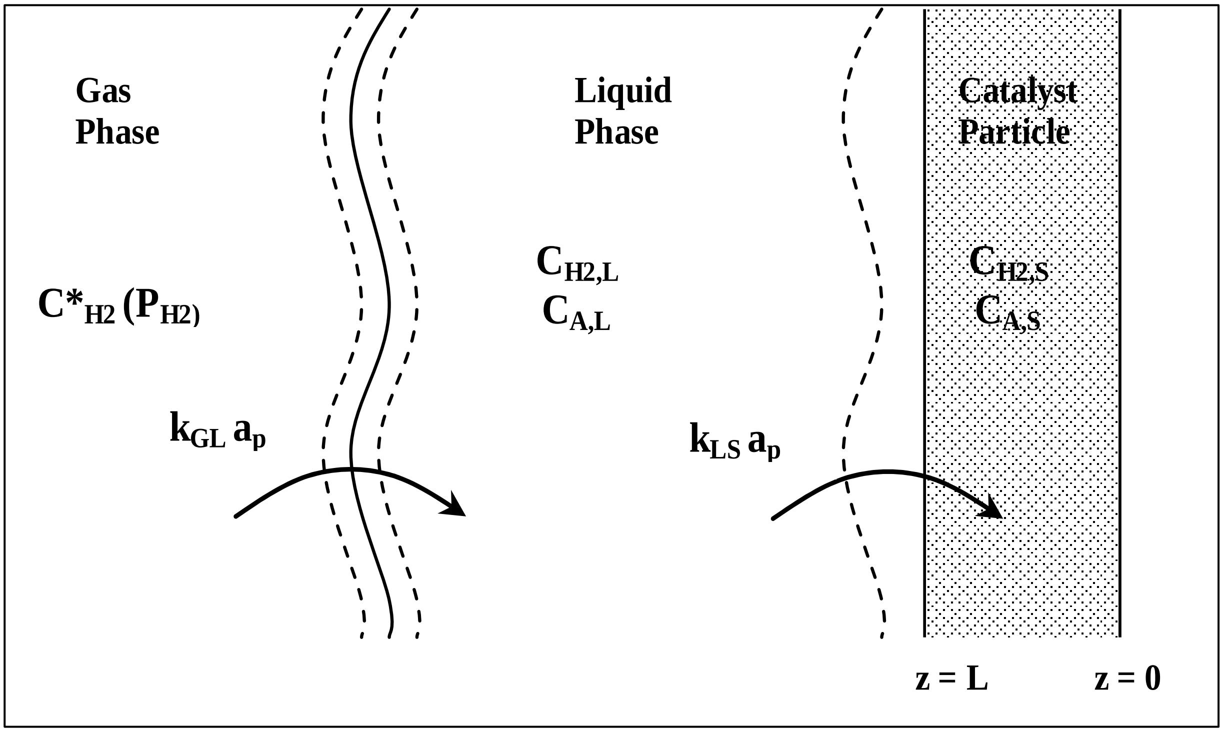


Figure 7.2: Schematic diagram of mass transfer in three phases

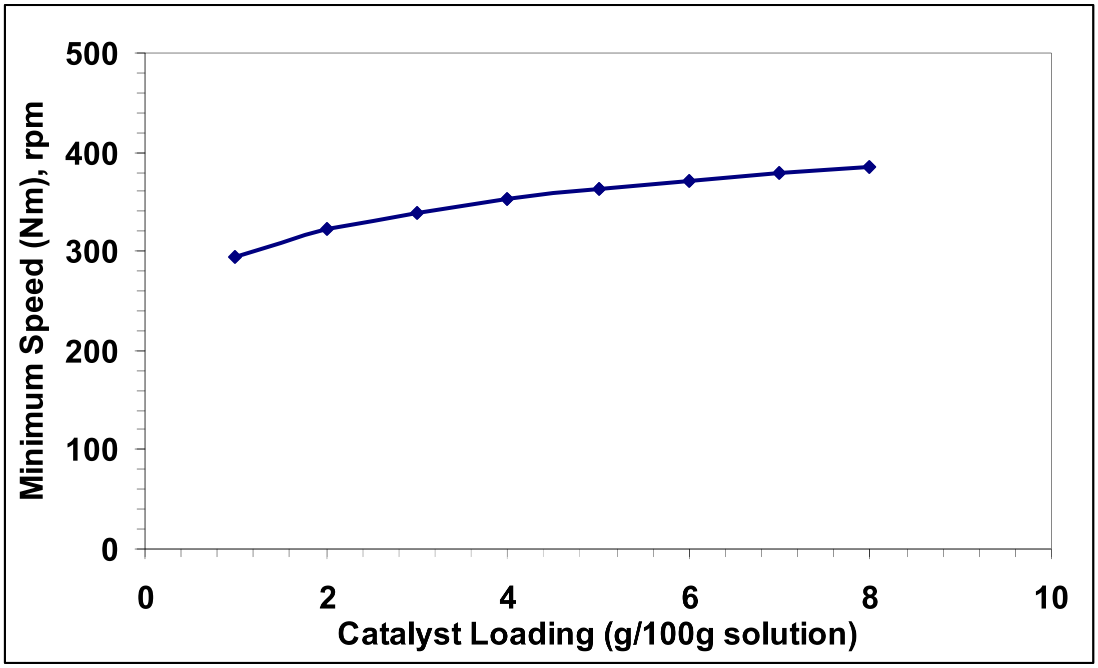


Figure 7.3: Minimum stirring speed for catalyst suspension

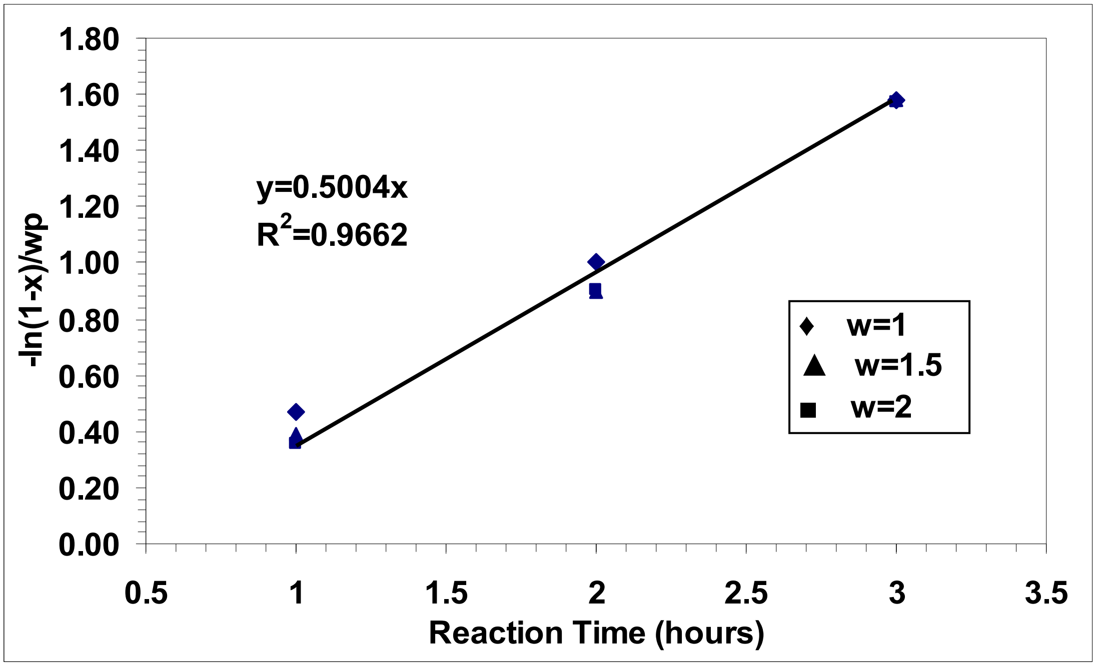


Figure 7.4: Calculation of pseudo first order rate from kinetic data

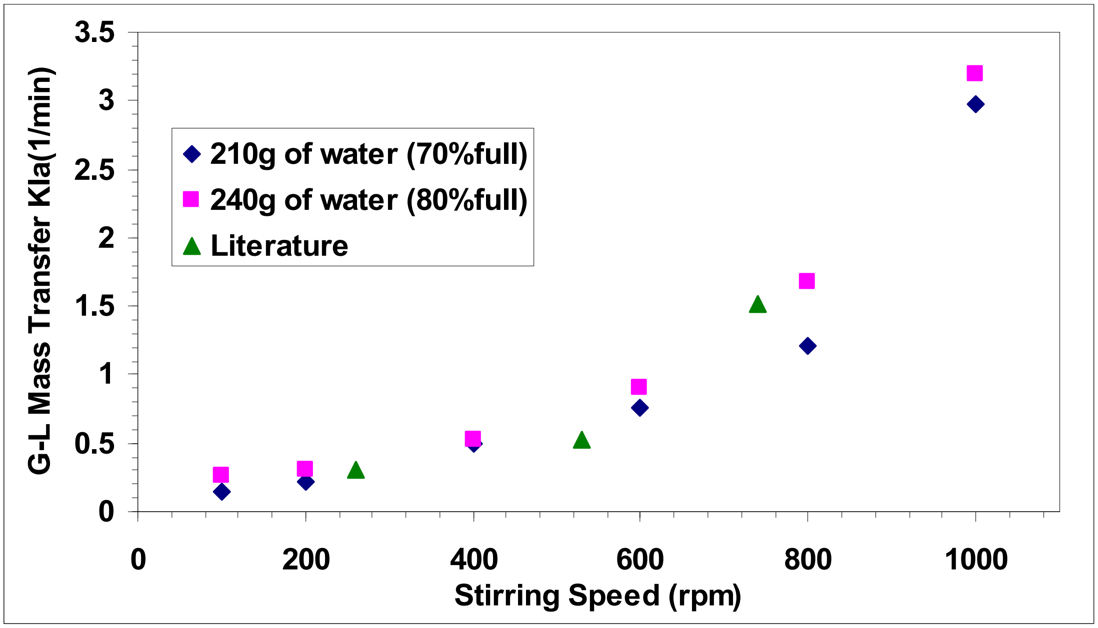


Figure 7.5: Hydrogen-water mass transfer coefficient in the autoclave

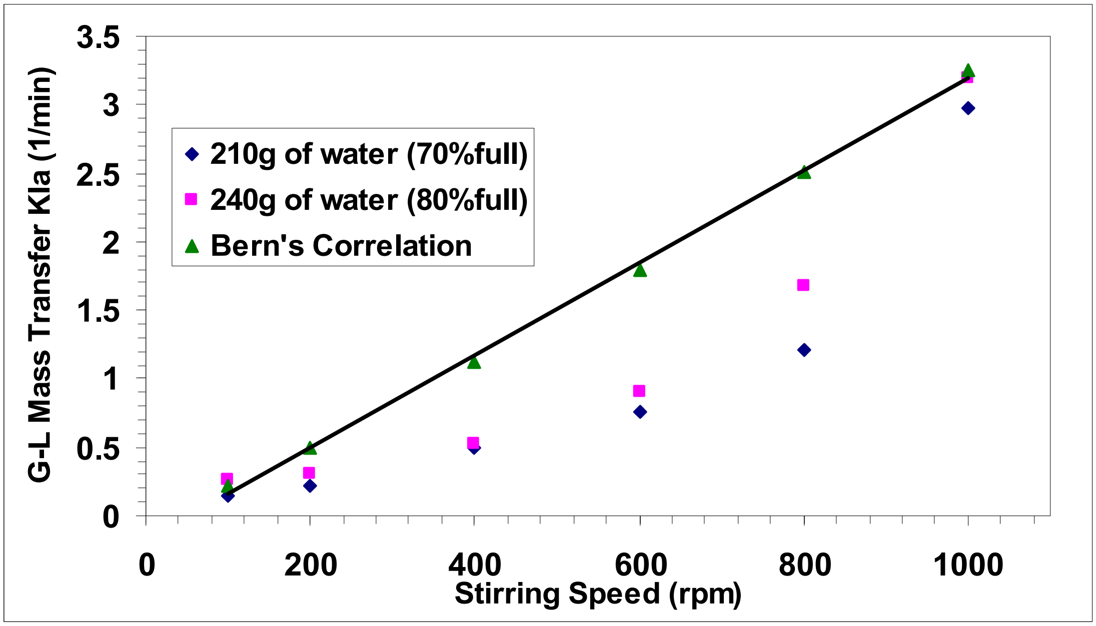


Figure 7.6: Comparison of Bern's correlation and measurement

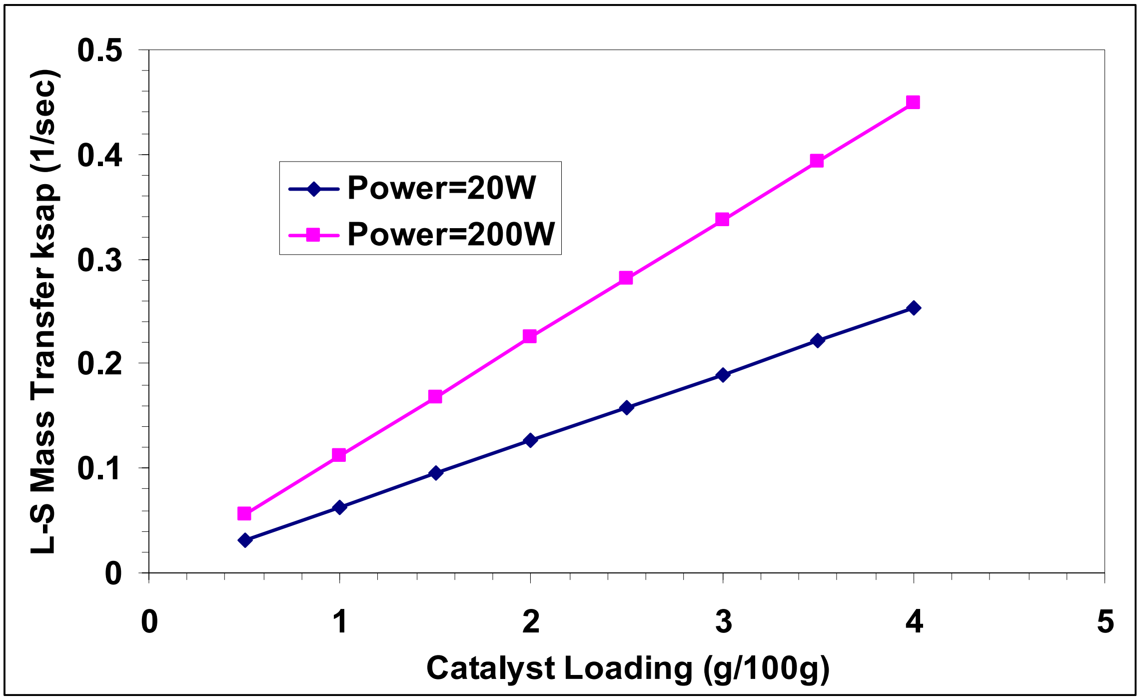


Figure 7.7: L-S mass transfer coefficient from Sano's correlation

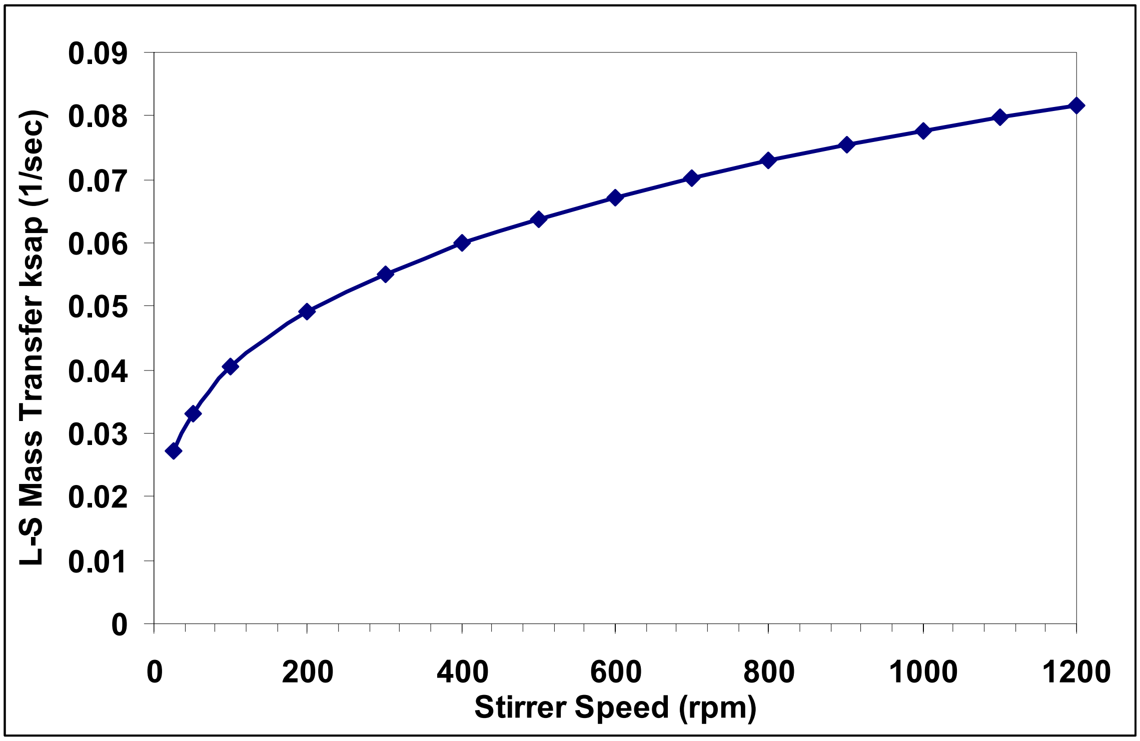


Figure 7.8: L-S mass transfer coefficient from Boon-long’s correlation

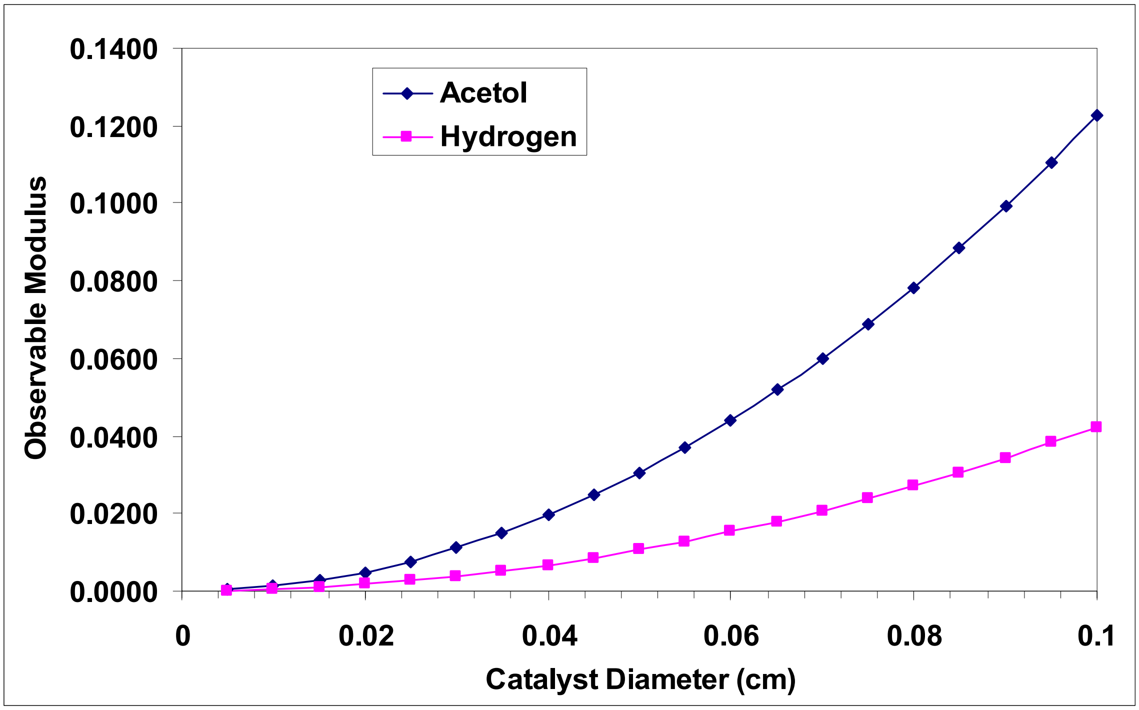


Figure 7.9: Observable modulus changes with catalyst diameter

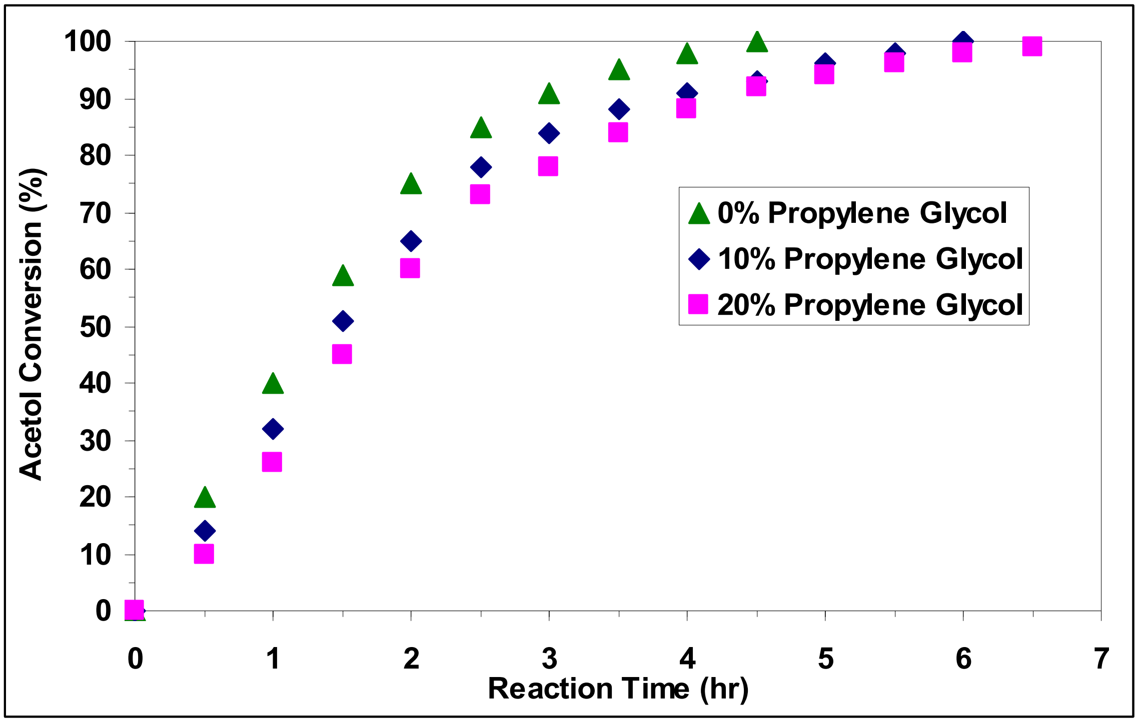


Figure 7.10: Effect of propylene glycol addition on acetol reaction rate

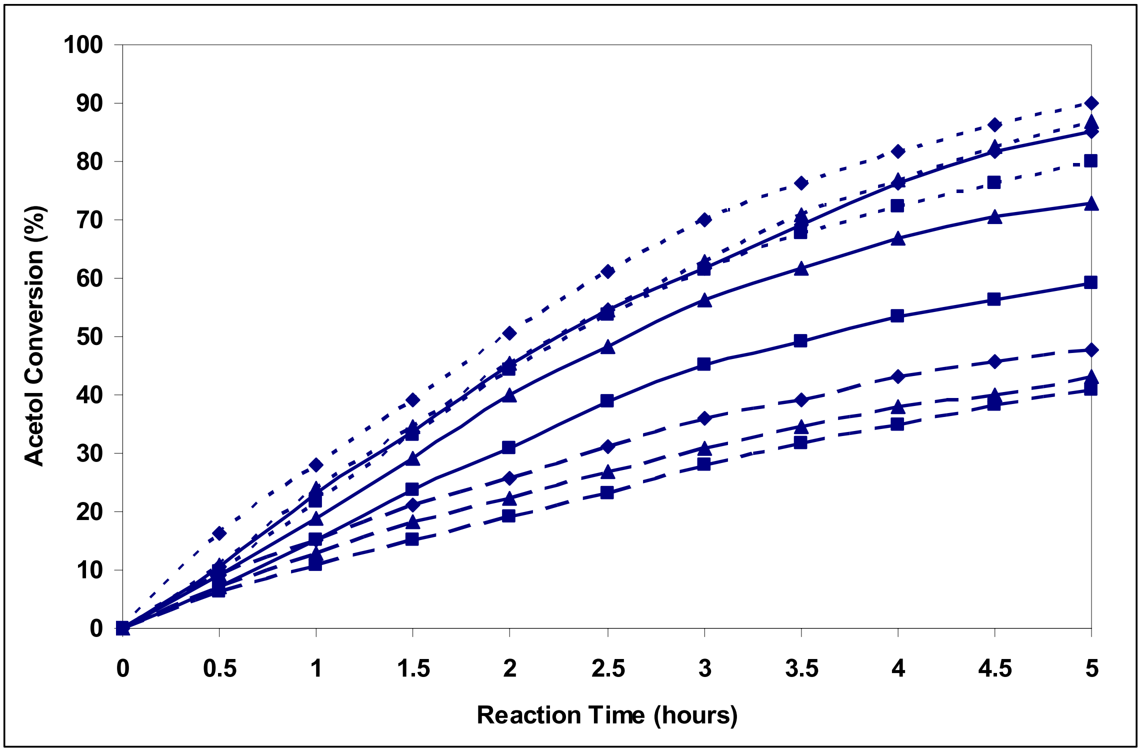


Figure 7.11: Conversion profile of acetol to propylene glycol at 150°C. Catalyst loading: (■) 1g, (▲) 1.5g, (♦) 2g; Hydrogen pressure: (– – –) 400psi, (- - - -)600psi, (——) 800psi

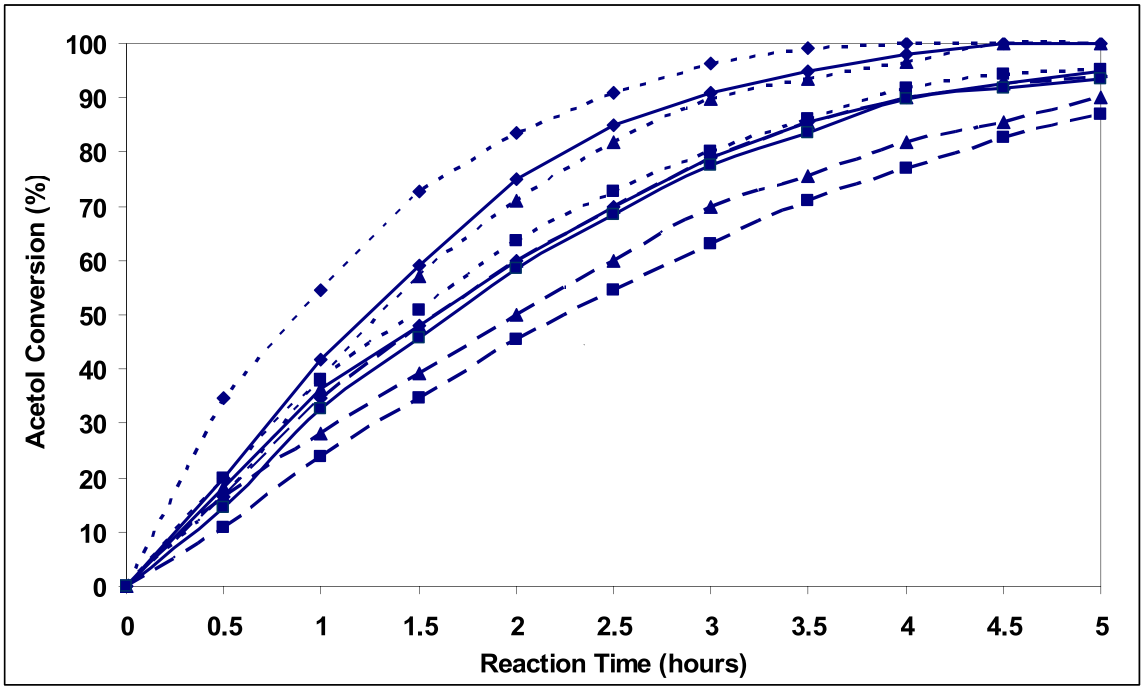


Figure 7.12: Conversion profile of acetol to propylene glycol at 185°C. Catalyst loading: (■) 1g, (▲) 1.5g, (♦) 2g; Hydrogen pressure: (– – –) 400psi, (- - - -)600psi, (——) 800psi

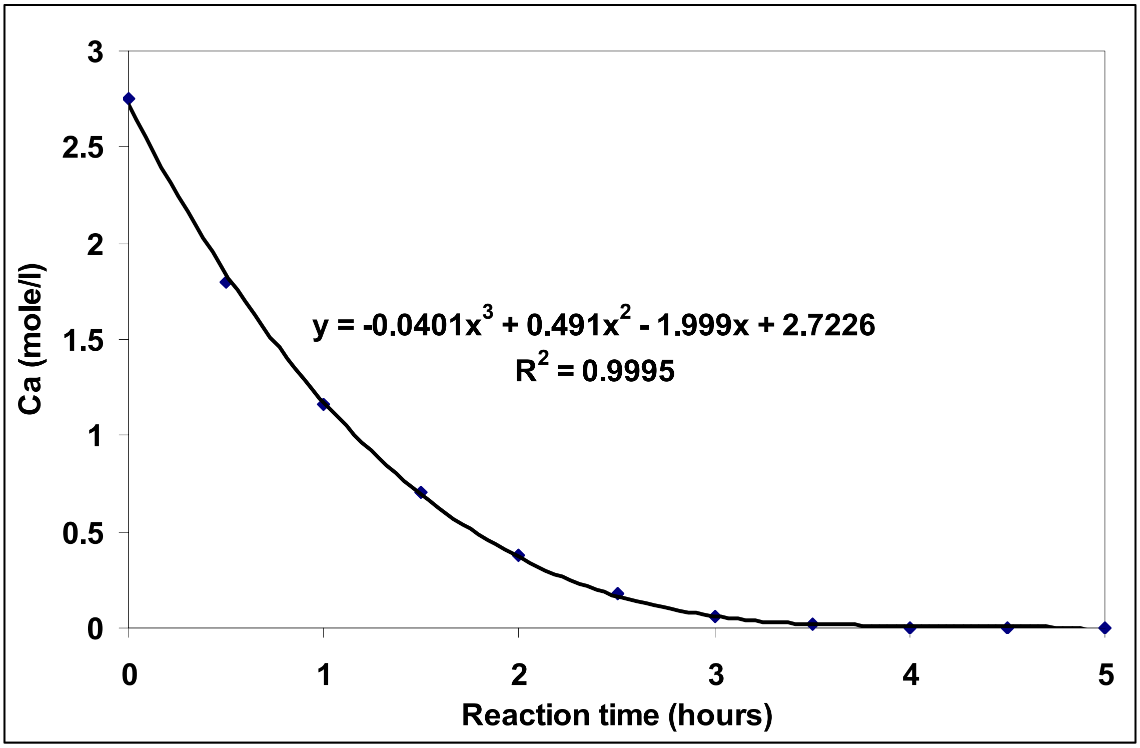


Figure 7.13: Polynomial fit for concentration profile of acetol

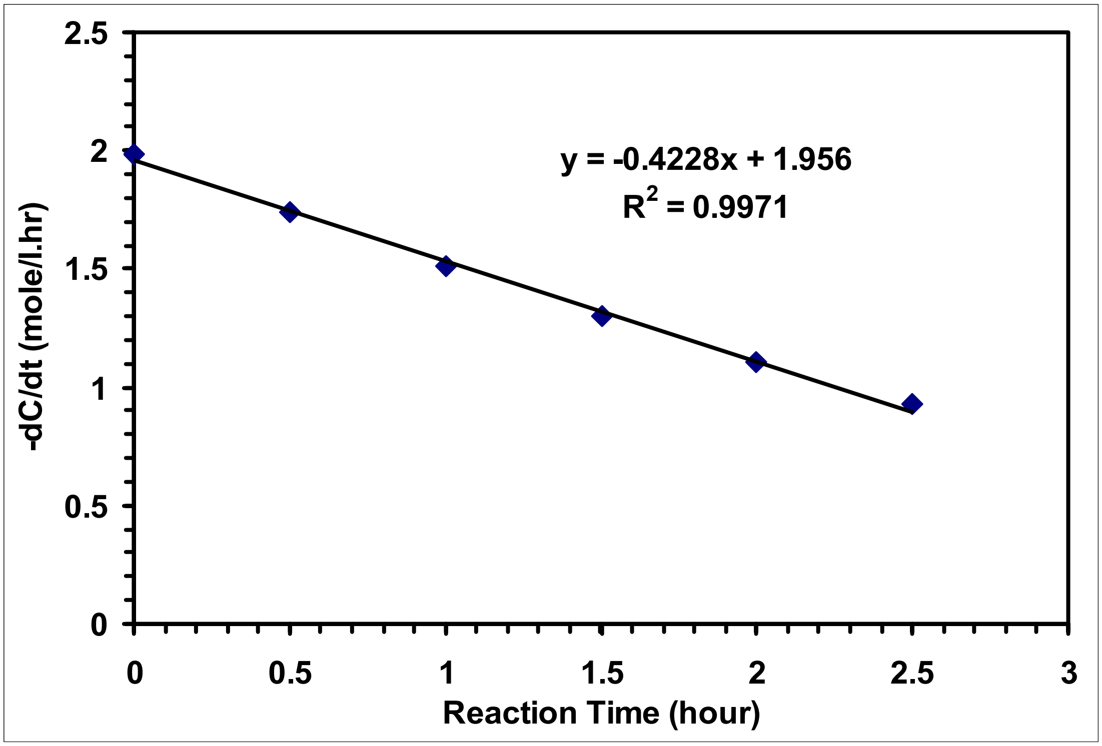


Figure 7.14: Initial reaction rate from extrapolating the rate curve

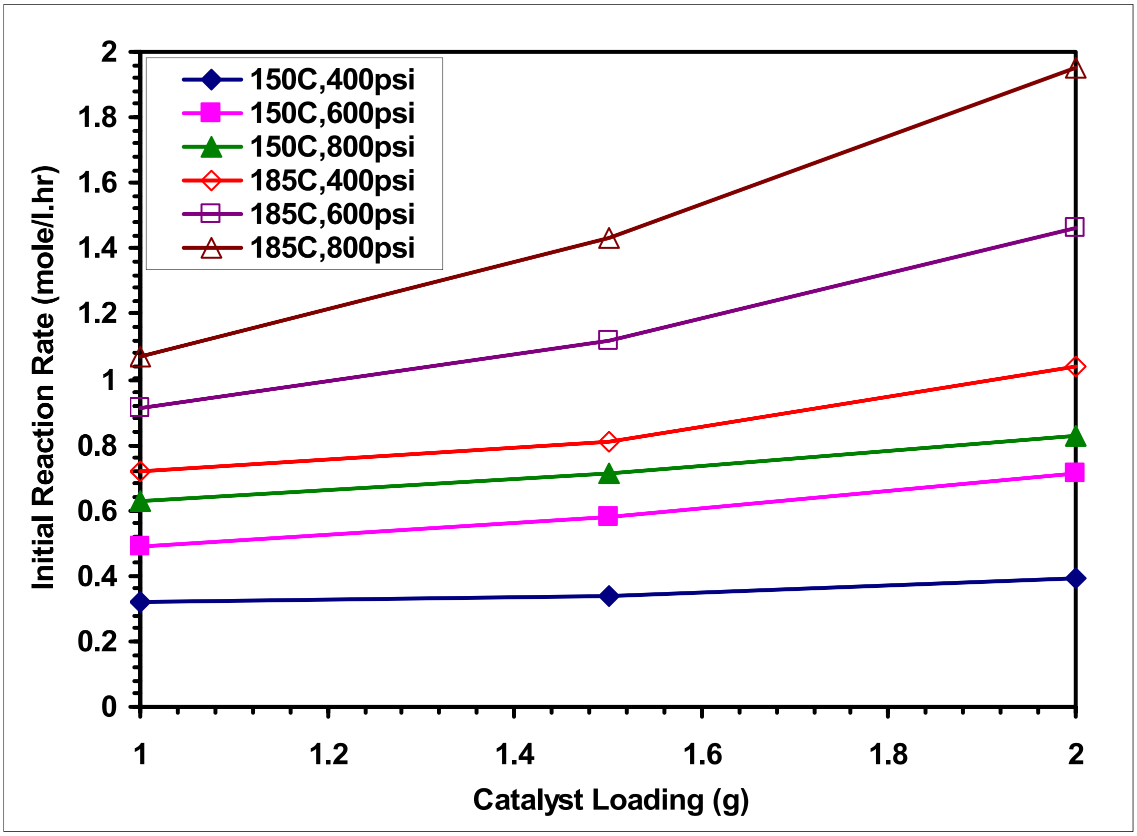


Figure 7.15: Initial reaction rates with catalyst loading

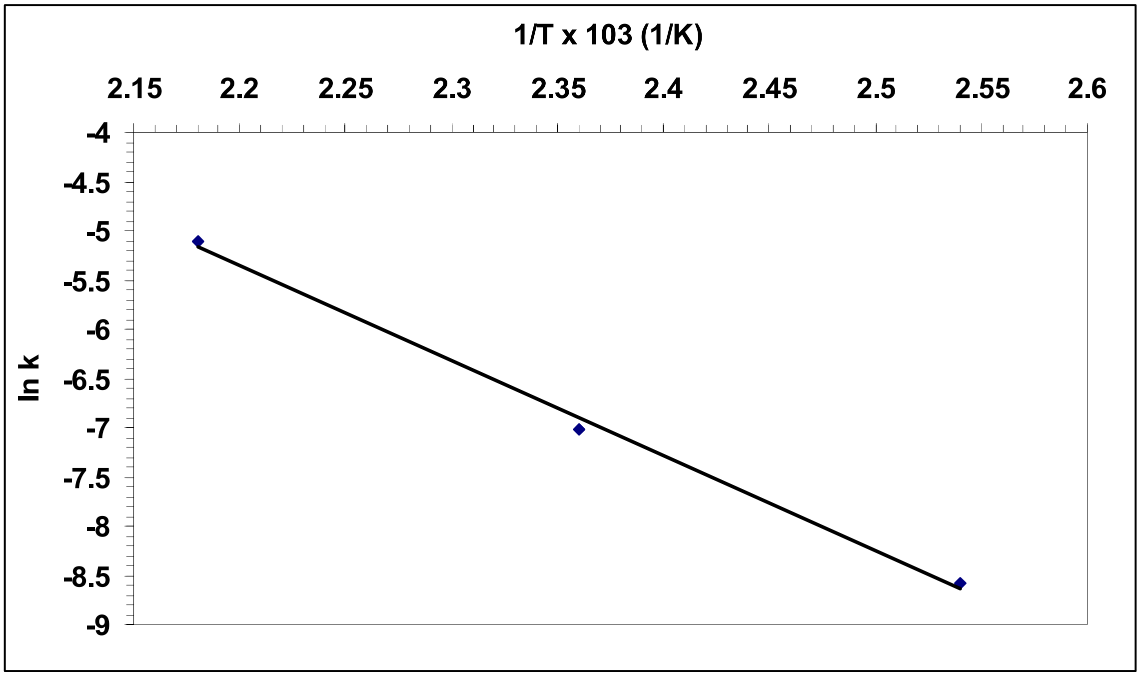


Figure 7.16: Temperature dependence of the apparent reaction rate constant for hydrogenation of acetol

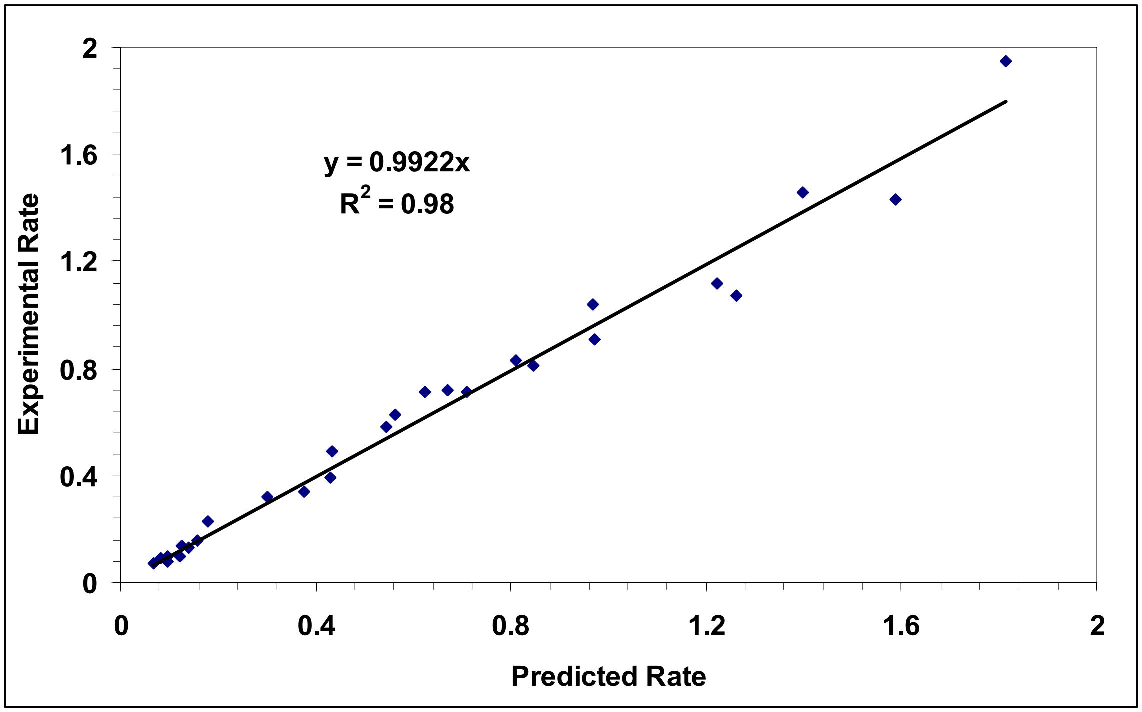


Figure 7.17: Comparison of experimental and predicted reaction rates

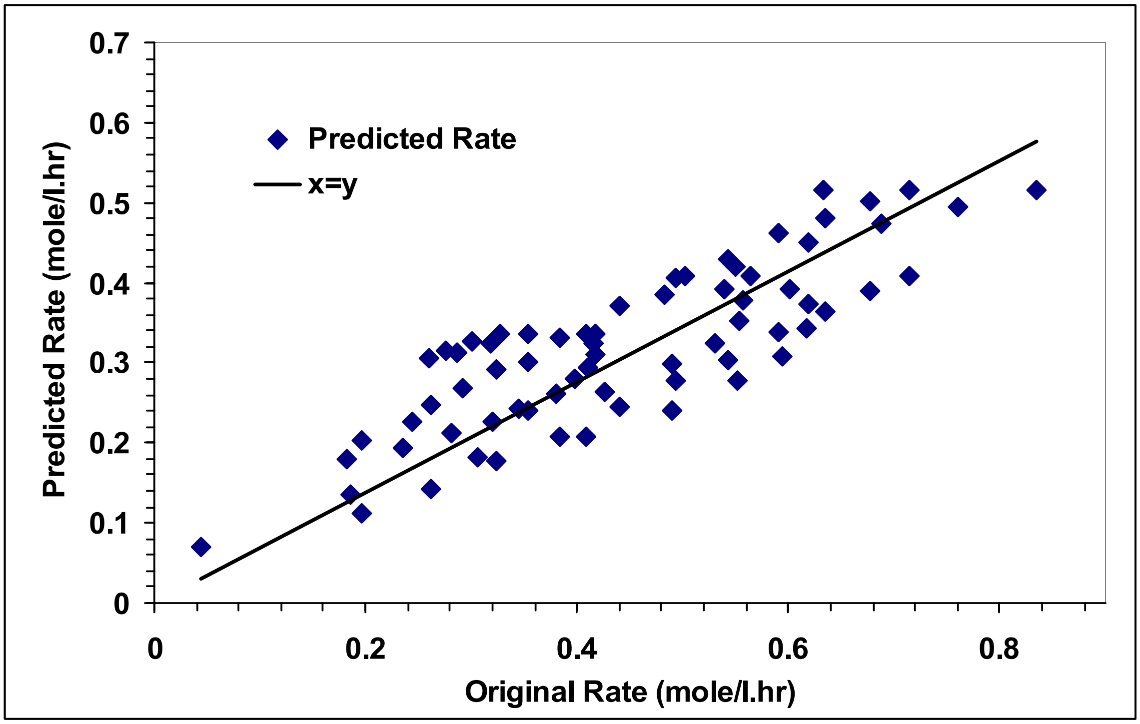


Figure 7.18: Comparison of experimental and predicted reaction rates for model III at 150°C

Table 7.1: Reaction rate for three catalyst loadings at 185°C and 800psi

Catalyst loading (g/100g)	1	1.5	2
C_{LAo} (mole/ml)	0.0028	0.0028	0.0028
Solution density (g/ml) ρ_L	1.02	1.02	1.02
		Conversion %	
1hr	38.2	41.8	54.5
2hr	63.6	75.0	83.6
3hr	80.0	91.0	96.4
4hr	91.1	96.7	100.0
Max dx/dt (at t=0) (l/hr)	0.93	1.20	1.62
Max rate (mole/hr)	0.112	0.143	0.195
Max rate (mole/hr.g)	0.112	0.095	0.098

Table 7.2: Pseudo first order kinetics

Loading	Time	Concentration	(-ln(1-x)) / wρ	k
1	1	0.38	0.47	0.47
	2	0.64	1.00	0.50
	3	0.8	1.58	0.53
1.5	1	0.42	0.36	0.36
	2	0.75	0.91	0.45
	3	0.91	1.57	0.52
2	1	0.55	0.39	0.39
	2	0.84	0.90	0.45
	3	0.96	1.58	0.53

Table 7.3: Summary of mass transfer coefficient

Water=210g		**Water=240g**	
R (rpm)	**k_La (min^{-1})**	**R (rpm)**	**k_La (min^{-1})**
100	0.14	100	0.28
200	0.22	200	0.
400	0.49	400	0.
600	0.76	600	0.91
800	1.21	800	1.67
1000	2.98	1000	3.2

Table 7.4: Stirring speed effects

Speed	**Conversion (%) at hour**				
	1	**2**	**3**	**4**	**5**
200	10	31	57	86	89
400	15	48	67	81	91
600	25	48	77	89	93
800	28	56	81	88	98
1000	27	54	83	90	100

Table 7.5: Regression results

Exp. No	Temperature (^oC)	Pressure (psi)	Rate (mole/l.hr)	Catalyst (g/100g)	ln (rate)
A1	120 ^oC	400	0.07	1	-2.66
A2		400	0.09	1.5	-2.41
A3		400	0.1	2	-2.30
A4		600	0.08	1	-2.53
A5		600	0.1	1.5	-2.30
A6		600	0.13	2	-2.04
A7		800	0.14	1	-1.97
A8		800	0.16	1.5	-1.83
A9		800	0.19	2	-1.66
B1	150 ^oC	400	0.32	1	-1.14
B2		400	0.34	1.5	-1.08
B3		400	0.39	2	-0.94
B4		600	0.49	1	-0.71
B5		600	0.58	1.5	-0.54
B6		600	0.71	2	-0.34
B7		800	0.63	1	-0.46
B8		800	0.71	1.5	-0.34
B9		800	0.83	2	-0.19
C1	185 ^oC	400	0.72	1	-0.33
C2		400	0.81	1.5	-0.21
C3		400	1.04	2	0.04
C4		600	0.91	1	-0.09
C5		600	1.07	1.5	0.07
C6		600	1.46	2	0.38
C7		800	1.12	1	0.11
C8		800	1.43	1.5	0.36
C9		800	1.95	2	0.67

Regression Statistics		Coefficients		Results	
Multiple R	1.00	Intercept	8.12	ko	3361.02
R^2	0.99	ln(P)	0.81	E	53.16 KJ/mole
Adjusted R^2	0.99	ln(w)	0.32	m	0.32
Standard Error	0.1	1/RT	-53162.1	n	0.81
Observations	27				

Table 7.6: Plausible Hougen-Watson models for the different controlling mechanisms for hydrogenation of acetol to propylene glycol

Model No.	Controlling Mechanism	Rate Model
Single Site Mechanism-All Reaction Species are Adsorbed Molecularly		
I	Adsorption of Acetol Controlling	$R = \dfrac{kC_A}{\left[1+K_1C_A+K_2P_{H2}+\dfrac{C_P}{K_4}\right]}$
II	Adsorption of Hydrogen Controlling	$R = \dfrac{kP_{H2}}{\left[1+K_1C_A+K_2P_{H2}+\dfrac{C_P}{K_4}\right]}$
III	Surface Reaction Controlling	$R = \dfrac{kK_1K_2P_{H2}C_A}{\left[1+K_1C_A+K_2P_{H2}+\dfrac{C_P}{K_4}\right]^2}$
IV	Desorption of PG Controlling	$R = \dfrac{kK_1K_2K_3P_{H2}C_A}{\left[1+K_1C_A+K_2P_{H2}+\dfrac{C_P}{K_4}\right]}$
Single Site Mechanism-Atomically Adsorbed Hydrogen and Other Species are Adsorbed Molecularly		

V	Adsorption of Acetol Controlling	$R = \dfrac{kC_A}{\left[1 + K_1 C_A + \sqrt{K_2 P_{H_2}} + \dfrac{C_P}{K_4}\right]}$
VI	Adsorption of Hydrogen Controlling	$R = \dfrac{kP_{H2}}{\left[1 + K_1 C_A + \sqrt{K_2 P_{H_2}} + \dfrac{C_P}{K_4}\right]^2}$
VII	Surface Reaction Controlling	$R = \dfrac{kK_1 K_2 P_{H_2} C_A}{\left[1 + K_1 C_A + \sqrt{K_2 P_{H_2}} + \dfrac{C_P}{K_4}\right]^3}$
VIII	Desorption of PG Controlling	$R = \dfrac{kK_1 K_2 K_3 P_{H_2} C_A}{\left[1 + K_1 C_A + \sqrt{K_2 P_{H_2}} + \dfrac{C_P}{K_4}\right]}$

Eley Rideal Mechanism-Hydrogen in gas phase and Other Species are Adsorbed Molecularly

IX	Adsorption of Acetol Controlling	$R = \dfrac{kC_A}{\left[1 + K_1 C_A + \dfrac{C_P}{K_3}\right]}$
X	Surface Reaction Controlling	$R = \dfrac{kK_1 P_{H_2} C_A}{\left[1 + K_1 C_A + \dfrac{C_P}{K_3}\right]}$
XI	Desorption of PG Controlling	$R = \dfrac{kK_1 K_2 P_{H_2} C_A}{\left[1 + K_1 C_A + \dfrac{C_P}{K_3}\right]}$

Table 7.7: Parameter estimates from non-linear linear least square analysis for the probable models with 95% confidence interval

Model No.	k	K_A	K_H	RSS
III	0.12±3E-04	11.09±0.28	0.02±5E-05	0.07
VII	0.003±0.05	0.9±1.2	0.07±0.2	0.041
X	24.6±12.9	133.8±59.2	-	1.02

Table 7.8: Parameters of the plausible rate model (model III) for hydrogenation of acetol

Temperature	**k**	**K_A**	**K_H**	**R^2**
120	0.12	11.09	2.3×10^{-2}	0.77
150	0.39	5.71	1.1×10^{-2}	0.82
185	0.58	2.37	0.4×10^{-2}	0.85

8 CHAPTER 8

CATALYTIC HYDROGENOLYSIS OF SUGARS AND SUGAR ALCOHOLS TO LOWER POLYOLS

8.1 Introduction & Background

Carbohydrates exhibit unusually rich chemical functionality but limited stability.[122] 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, like glycerol, ethylene glycol, and propylene glycol, in the presence of transition metal catalysts and enhanced by the addition of bases.[122] In the literature, sugar hydrogenolysis is dealt 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.

In the presence of a heterogeneous catalyst, it is believed that there are several stages in the interaction of a saturated polyol molecule with catalyst surfaces. The initial process, both in the presence and absence of hydrogen, is the loss of hydrogen atoms with the formation of radicals that may be held to the catalyst surface by multipoint adsorption. At temperatures higher than those required to affect this stage, and particularly in the presence of hydrogen, the dissociation of carbon-carbon bonds takes place and hydrocarbons of lower molecular weight are formed.

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; xylitol, 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.[122]

Due to poor selectivity, sugar hydrogenolysis is currently not an industrially important process. The process is un-economical 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.

Hydrogenolysis of sugars was first carried out on 1933 by Adkins et al. [123, 124]. Sucrose, glucose, maltose, sorbitol and mannitol were used as reactants in presence of copper chromium oxide as a catalyst. It was observed that the yield of higher boiling products increased substantially by interrupting the hydrogenolysis after absorption of 2-3 moles of hydrogen. This was followed by the work done by Lenth and Dupis who hydrogenolyzed of crude sugar and molasses with copper aluminum oxide and copper barium chromite as a catalyst at high pressure ranging form 64-286 atm[125].

However, research for the purpose of biomass conversion has only been carried out since the 1950's. Clark et. al. was the pioneer for this research at the U.S. Forestry Products Laboratory. In this early report of 1958, Clark claimed to obtain glycerol from sorbitol with yields as high as 40%.[126] 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.

Conradin et al.[127,128] reported that for increased production of propylene glycol, hydrogenolysis should be conducted over a Ni/Cu catalyst on a carrier such as magnesium oxide.

Conradin et al. also stated that hydrogen splitting of saccharose to glycerol and glycols can be carried out in the presence of practically any technically feasible catalyst, provided that sufficient alkali is added to ensure a pH of 11 to 12.5. In one example, it was reported that hydrogenolysis of an aqueous saccharose solution over a nickel-on-kieselguhr catalyst proceeded with an 83% conversion to a product containing 43% glycerol and 25% propylene glycol.

Boelhouwer et al in 1960 showed that greater yields (>75%) of distillable polyalcohols were attained by using beryllium oxide activated copper chromite catalyst to hydrogenate sucrose.[129] 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 and 2939 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.

Sirkar et al [130] reported sorbitol hydrogenolysis to produce glycerol over a nickel-on-kieselguhr catalyst in which an alkali promoter was added to the feed stream to control pH and prevent leaching of nickel from the catalyst.

Tanikella et al [131] described the hydrolysis of sorbitol and xylitol in nonaqueous solvents containing at least 10 mole% base. The catalyst used in the examples was nickel on silica/alumina. Distribution of ethylene glycol, propylene glycol and glycerol were reported.

Gubitosa et al.[132] discussed the hydrogenolysis of polyhydric alcohols, such as sorbitol, over a ruthenium-on-carbon catalyst. In the examples, Gubitosa et al. reported that 100% of the sorbitol can be converted, with 41 to 51% of the product carbon atoms in propylene glycol.

Chao et al[133] reported that 15-40 wt% sorbitol solution in water is catalytically hydrocracked in a fixed bed reaction process using a high activity nickel catalyst to produce at least about 30% conversion to glycerol and glycol products.

Huibers et al [134]described a multistage process of converting monosaccharides such as glucose and sorbitol to lower polyols. A 99.8% conversion of sorbitol was reported using high-activity supported nickel catalyst at temperatures in range of 130-180°C and pressures in range of 500-5000psi and pH in the range of 4.5 to 7 using a alkali solution to prevent acid leaching of the catalyst.

Innumerable patents and papers are available on production of lower polyols from sugars and sugar alcohols, but few are available on the kinetics of the reaction. Van ling et al[135] studied the hydrogenolysis of saccharides to find the optimum conditions for obtaining maximum yield of glycerol (cleavage selectivity, hydrogenation selectivity and cleavage percentage). They obtained best hydrogenation selectivity with the use of CuO-CeO_2-SiO_2 catalyst. And also found that small addition of $Ca(OH)_2$ could increase both the hydrogenation selectivity and cleavage percentage. After 1970, many investigators in the U.S.S.R. studied the reaction kinetics with particular emphasis on glycerol yield. Catalysts used were of Ni-series. The activation energy of sorbitol to glycerol was found to be 7.1×10^4 joule/mole.

Feng-Wen Chang et al also studied the reaction conditions (temperature, hydrogen pressure, catalyst amount, and agitation rate etc.) affecting the cracking of sorbitol and formation of glycerol.[136] They also came up with a rate equation for catalytic sorbitol hydrogenolysis as $-r_s=kC_sP^{-0.8}W^2$ ($P=5.62 \times 10^6$ to 1.04×10^7 Pa, $W=3.5$ to13.8 wt% based on sorbitol starting weight). They showed that the rate of sorbitol hydrolysis is first order with respect to sorbitol formation and second order with respect to catalyst amount. The activation energies of sorbitol hydrogenolysis and glycerol formation are 9.2×10^4 joule/mole and 9.9×10^4 joule/mole respectively.

8.1.1 Reaction Mechanism

The overall hydrogenolysis of sugars appears to be quite a complex reaction as there are many other products formed (such as xylitol, erythritol and ethylene glycol) the mechanism of their formation is not well established.

Montassier *et al.* subjected various sugar alcohols including sorbitol, xylitol, erythritol and even glycerol to hydrogenolysis conditions and proposed that the cleavage of C-O bonds occurs through dehydration of a β-hydroxyl carbonyl.**Error! Bookmark not defined.** 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, bases catalyze the dehydration step while transition metal complexes catalyze the dehydrogenation and hydrogenation steps.

The original mechanism proposed by Montassier *et al.* to explain the C-C cleavage in sugar and sugar alcohol hydrogenolysis is the retro-aldol reaction. **Error! Bookmark not defined.** The C-C cleavage precursor is again β-hydroxyl carbonyl. Cleavage of this β-hydroxyl carbonyl leads to an aldehyde and a ketone, which are subsequently hydrogenated to alcohols. Andrews et al suggested the same mechanism, based on their observation that the primary C-C cleavage site is β to the carbonyl group in sugar hydrogenolysis.[122]

Montassier *et al.* proposed another mechanism, namely, the retro-Claisen reaction for the C-C cleavage in glycerol hydrogenolysis.**Error! Bookmark not defined.** 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.* 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.[126, 137] This cleavage site selectivity along with the strong base catalysis further supports that a retro-aldol reaction may be involved. Furthermore, in a recent research on sugar hydrogenolysis conducted by Wang et al 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.**Error! Bookmark not defined.**

8.2 Results of Screening Studies

The main focus of this study is to understand the mechanisms controlling the hydrogenolysis of sugars and sugar alcohols. Glucose ($C_6H_{12}O_6$), sucrose ($C_{12}H_{22}O_{11}$) are used as sugar substrates and sorbitol ($C_6H_{14}O_6$) is used as a substrate for sugar alcohols. Hydrogenolysis can be described as cleavage of carbon-carbon or carbon-oxygen and addition of hydrogen molecule. Presence of a base promotes the C-C or C-O bond cleavage while presence of a transition metal catalyst promotes the hydrogenation. This cleavage of C-C, often termed as alkaline degradation, results in formation of organic carboxylic acids and other intermediates with lower carbon number. [138] These intermediates further hydrogenate into saturated product. This two-step mechanism is similar to the formation of acetol as a reactive intermediate by dehydration of glycerol which upon further hydrogenation forms propylene glycol.[139] From the survey of prior literature it is understood that both sugars and sugar alcohols follow similar hydrogenolysis reaction mechanism to form lower polyols like glycerol and propylene glycol. Hence, to avoid formation of complex reaction products all the screening studies, except catalyst selection, were performed using sorbitol as a substrate.

Main objective of these screening studies is to select a catalyst, which can give high yields of glycerol and propylene glycol with low selectivity to ethylene glycol. Formation of ethylene glycol is undesirable due to multiple reasons: a) formation of ethylene glycol is always accompanied by loss of carbon in the form of methanol or carbon dioxide gas b) ethylene glycol has a normal boiling point similar to that of propylene glycol- causing problems during separation and purification of propylene glycol c) finally, ethylene glycol is highly toxic to both animals and humans and is being replaced by environmentally safe propylene glycol.

8.2.1 Catalyst Screening & Selection

Efficacy of several commercially available heterogeneous catalysts, including nickel/silica-alumina, nickel/kieselguhr, ruthenium/carbon, raney nickel, palladium/carbon, and copper chromium in the form of metallic powders, metal oxides, and activated metals (metal sponge) in the conversion of glucose, sucrose and sorbitol was determined. Reactivities were tested at 250 psi hydrogen pressure and at a temperature of 230°C with a 5% catalyst loading for 12hours. Table 8.1, Table 8.2, and Table 8.3 shows the performance comparison of these catalysts for various substrates. It is evident that nickel based catalysts and ruthenium/carbon gave higher selectivity to glycerol and propylene glycol and palladium/carbon showed low selectivity to ethylene glycol. Among the two nickel catalysts, nickel/kieselguhr showed higher selectivity towards glycerol, propylene glycol and ethylene glycol. Due to its lower selectivity to ethylene glycol nickel/silica-alumina was selected for further screening studies.

8.3 Parametric Studies

The effect of reaction temperature, hydrogen pressure, feed concentration and amount of catalyst for hydrogenolysis of sorbitol were determined using nickel/silica-alumina catalyst and the results are discussed in the following sections.

8.3.1 Effect of Feed Concentration

Sorbitol is solid at room temperature and typical hydrogenolysis studies to date were performed using dilute solutions of sorbitol in water or other solvents like methanol or ethanol. Water is generated in this reaction and it is always preferable to eliminate the water from the initial reaction mixture to drive the equilibrium in the forward direction. In order to isolate propylene glycol, it is therefore necessary to first remove large amounts of water by distillation, which means expenditure of large amounts of energy. In addition, as the concentration of sorbitol decreases from 100% to 50%, the size of the reactor doubles to produce the same amount of product. Hence, reactions were performed using sorbitol solutions made up of different water content to study the effect of initial water content on the overall reaction. Table 8.6 provides the summary of effect of initial water content on overall sorbitol conversion at 230°C and 250 psi. As the sorbitol feed concentration in the reaction increases, both the glycerol conversion and the yield of propylene glycol increased. Moreover, the ratio total desired products (glycerol + propylene glycol) to the undesired ethylene glycol increases with increase in the feed concentration.

Studies were also done using glycerol as a solvent instead of water and the results were summarized in Table 8.7. Trends in the yields of glycerol and propylene glycol similar to that of sorbitol were observed. As expected, the ratio of the desired glycerol and propylene glycol products to that of the undesired ethylene glycol increased with decrease in the water content. Glycerol dissolves and stabilizes sorbitol in a manner much like water and allows reactions to be conducted without water being present. This creates improved opportunities to use reactive distillation for sorbitol conversion and to achieve higher yields. The absence of water in the sorbitol system reduces the pressure needed by up to

50%--from 400 to 200 psig and increases the average space-time yield of the reaction thus decreasing the energy consumption and eliminating the necessity of large high-pressure reactors. Due to this synergistic effect between glycerol and sorbitol a mixture of glycerol and sorbitol is used for the remaining parametric studies.

8.3.2 Effect of Reaction Temperature and Pressure

Table 8.4 shows the effect of reaction temperature and pressure on conversion of sorbitol-glycerol mixture. Reactions were carried at temperatures of 190 and 230°C and hydrogen pressures of 50, 100, 250psi. Both temperature and pressure showed significant effect on the overall yield of products. The conversion of the sorbitol increased as the hydrogen pressure increased from 50 psi to 250 psi. Because of the low solubility of hydrogen in aqueous solutions, elevated pressures provide a means to increase the hydrogen concentration in liquid phase and thus achieve reasonable conversion rates. It was also observed that the reaction rates depended on the loading of liquid in the reactor suggesting that vapor-liquid contact is crucial with higher liquid levels reducing the efficacy of the mass transfer of hydrogen through the liquid to the slurried catalyst surface.

The optimal reaction temperature (producing a maximum yield of propylene glycol and glycerol) was observed to be a function of the hydrogen over-pressure. With an exception for the reactions performed at 50psi, the yields of propylene glycol and glycerol increased with increase in temperature. Yields increased with temperature until undesirable side-reactions became more prevalent. Hence, at every pressure there exists an optimal temperature that maximizes the yield propylene glycol and glycerol. On the other hand, the results in Table 8.4 show that neither hydrogen pressure nor the reaction temperature showed any particular influence on yield of ethylene glycol. The yield of ethylene glycol essentially remained same in almost all the reactions. This indicates that the formation of ethylene glycol is influenced by the reaction parameters other than temperature and pressure of the reaction.

Optimal operating pressures for hydrogenation of sorbitol to propylene glycol will balance the higher costs of high-pressure equipment with decreased yields at lower pressures.

8.3.3 Effect of Catalyst Concentration

Reactions were performed to determine the impact of catalyst loading on conversion of sorbtiol to propylene glycol. Figure 8.5 summarizes the data on the effect of catalyst loading. The concentration of glycerol steadily decreases and concentration of propylene glycol steadily increases with increase in catalyst loading. The concentration of ethylene glycol essentially remains constant in all the runs. This is because, as the catalyst loading increases, the number of active sites available for hydrogenation reaction increases and hydrogenation of sorbitol and glycerol to propylene glycol preferentially occurs when compared to the base degradation of sorbitol and glycerol to ethylene glycol and other lower polyols. However, propylene glycol in the presence of heat excess and catalyst concentration can undergo further hydrogenolysis to propanol and lower alcohols.[140] The data of Figure 8.5 illustrates high yields to propylene glcyol by copper chromium catalyst even at higher catalyst loadings, which is highly desirable for this reaction.

8.3.4 Effect of Base Concentration

Reactions were performed to determine the impact of base loading on conversion of sorbtiol to propylene glycol and the results are summarized in Table 8.5. Results show that high yields of glycerol and propylene glycol products are formed at a very low base concentration of 0.05 M. At concentration above 0.05 M, a steady decrease in glycerol, propylene glycol and ethylene glycol is observed and at a base concentration of 1 M the yield of glycerol falls to zero. This indicates that as the base concentration increases the base catalyzed C-C cleavage dominates causing excessive degradation of both sorbitol and glycerol molecules to form lower alcohols like methanol, propanol and gases like methane and carbon dioxide.

Hence, for every catalyst loading, yields glycerol and propylene glycol increased with base concentration until undesirable side-reactions became more prevalent. Hence, for every catalyst concentration there exists an optimal amount of base that balances the extent of base degradation with hydrogenation thus maximizing the yield of the desired propylene glycol and glycerol.

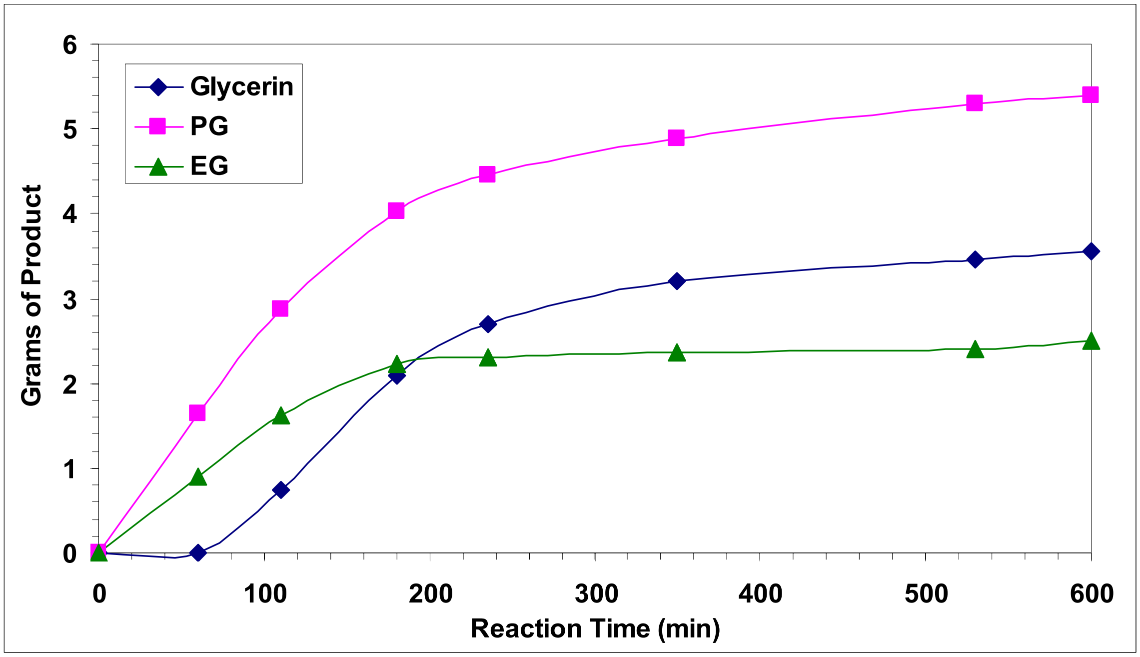


Figure 8.1: Reaction profile for the conversion of 20%sorbitol to propylene glycol, glycerol and ethylene glycol using 5% Ni/Silica-Alumina catalyst. Reaction is carried at 230°C and 600 psi. Feed: 20g sorbitol + 80g water, 0.2M KOH

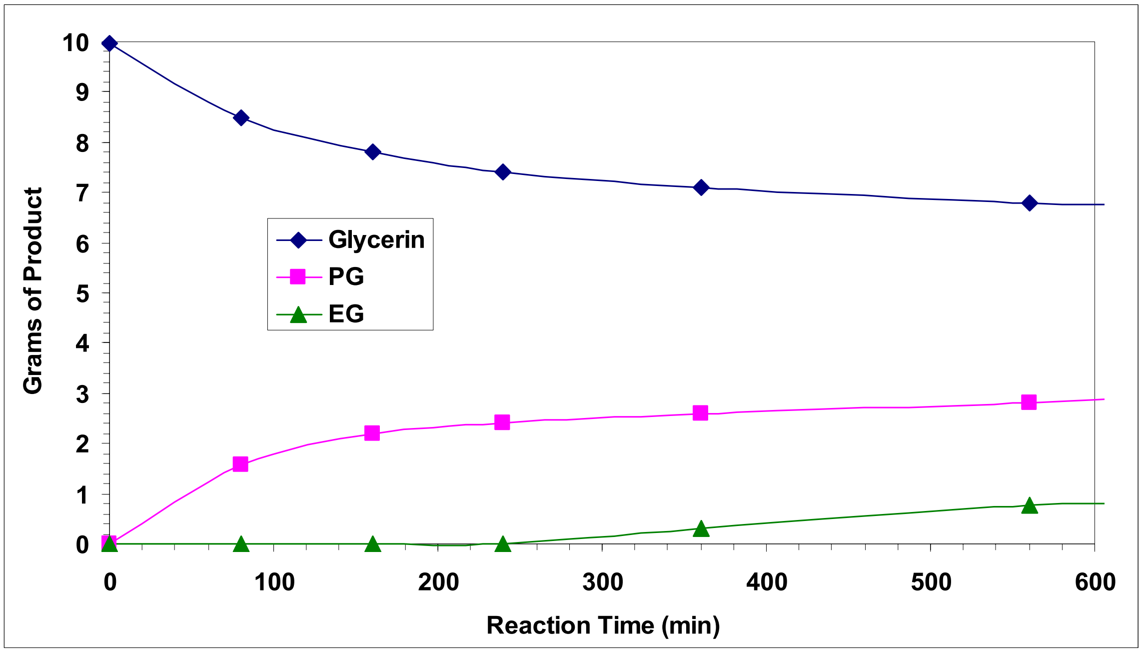


Figure 8.2: Reaction profile for the conversion of 20%sorbitol-glycerol mix to propylene glycol, glycerol and ethylene glycol using 5% Ni/Silica-Alumina catalyst. Reaction is carried at 230°C and 600 psi. Feed: 10g sorbitol + 10g glycerol+ 80g water, no base

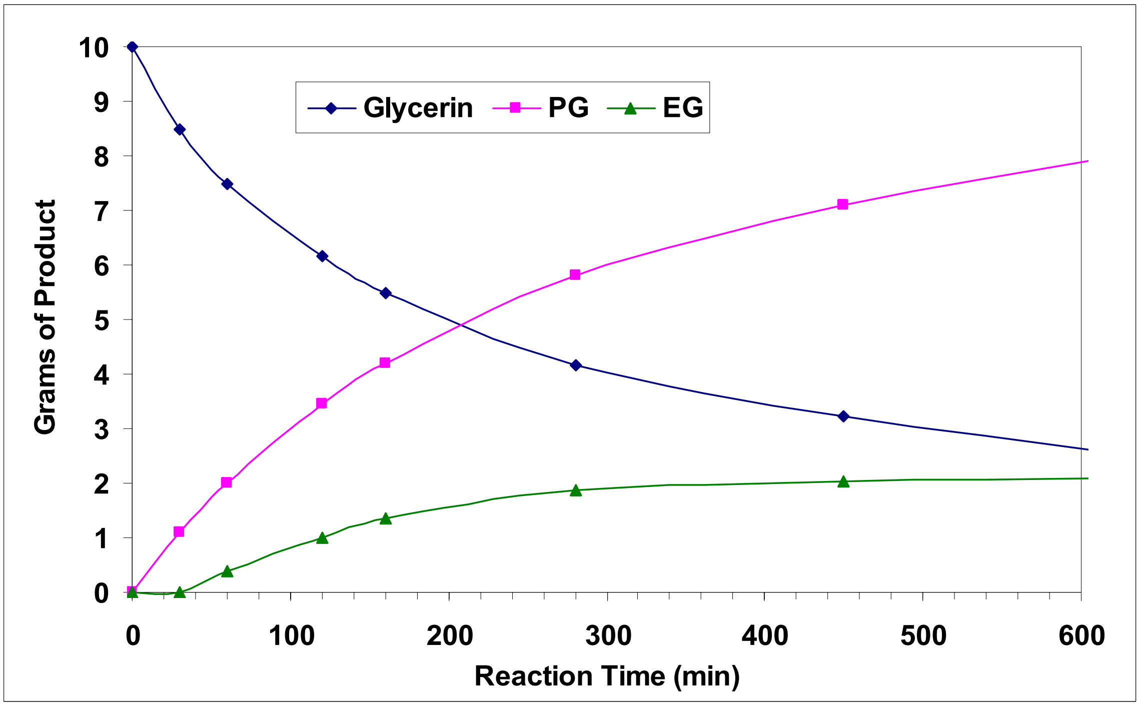


Figure 8.3: Reaction profile for the conversion of 20%sorbitol-glycerol mix to propylene glycol, glycerol and ethylene glycol using 5% Ni/Silica-Alumina catalyst. Reaction is carried at 230°C and 600 psi. Feed: 10g sorbitol + 10g glycerol+ 80g water, 0.2M KOH

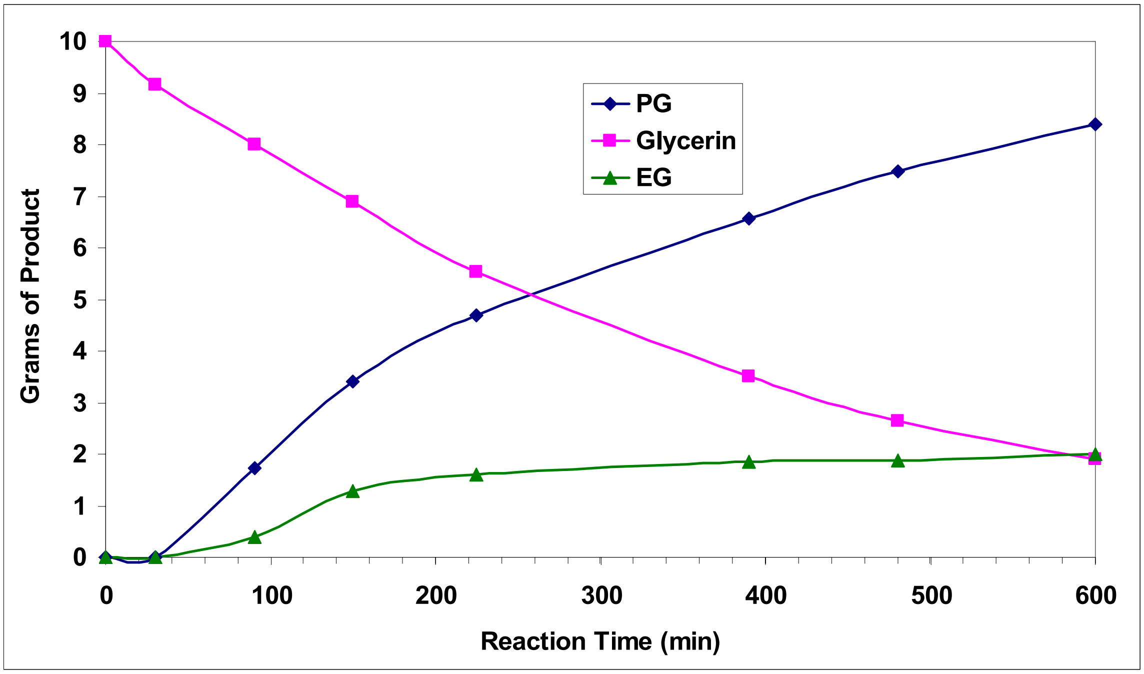


Figure 8.4: Reaction profile for the conversion of 20% sorbitol-glycerol mix to propylene glycol, glycerol and ethylene glycol using 5% Ni/Kieselguhr catalyst. Reaction is carried at 230°C and 600 psi. Feed: 10g sorbitol + 10g glycerol + 80g water, 0.2M KOH

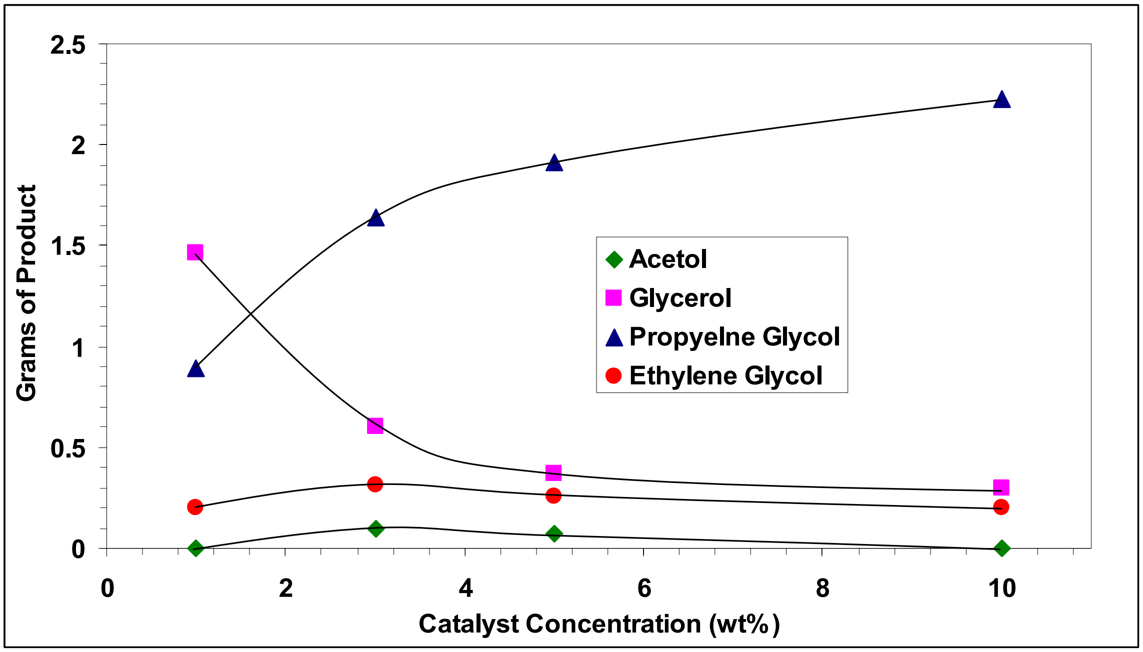


Figure 8.5: Effect of catalyst concentration on formation of glycerol, propylene glycol and ethylene glycol. All reactions were performed for 12 hours at 230°C and 250 psi. Feed: 2.5g sorbitol + 2.5g glycerol + 5g water.

Table 8.1: Summary of conversion of 25% sorbitol to glycerol, propylene glycol and ethylene glycol over various metal catalysts. Reactions were carried at 230°C, 250 psi, and 12 hours with 5% catalyst loading. Feed: 25g sorbitol in water. Base concentration: 0.2M

Catalyst	PG (g)	Glycerol (g)	EG (g)	Total (g)	% Selectivity (PG+Glycerol)
Copper Chromium	4.26	5.71	1.74	11.71	85.1%
Nickel/Silica-Alumina	6.5	3.67	1.7	11.87	85.7%
Nickel/Kieselguhr	7.8	4.52	2.1	14.42	85.4%
Palladium/Carbon	2.57	2.01	0.34	4.92	93.1%
Ruthenium/Carbon	3.83	6.45	1.3	11.58	88.8%
Nickel/Silica-Alumina +Copper Chromium	5.82	4.66	0.92	11.4	91.9%
Raney Nickel	1.86	4.61	1.38	7.85	82.4%

Table 8.2: Summary of conversion of 25% glucose to glycerol, propylene glycol and ethylene glycol over various metal catalysts. Reactions were carried at 230°C, 250 psi, and 12 hours with 5% catalyst loading. Feed: 25g glucose in water. Base concentration: 0.2M

Catalyst	PG (g)	Glycerol (g)	EG (g)	Total (g)	% Selectivity (PG+Glycerol)
Copper Chromium	1.2	2.6	0.52	4.32	88.0%
Nickel/Silica-Alumina	5.8	3.36	1.1	10.26	89.3%
Nickel/Kieselguhr	4.82	3.89	1.28	9.99	87.2%
Palladium/Carbon	1.73	3.95	0.23	5.91	96.1%
Ruthenium/Carbon	5.92	2.7	0.93	9.55	90.3%
Nickel/Silica-Alumina +Copper Chromium	5.46	4.06	1.14	10.66	89.3%
Raney Nickel	4.16	2.38	0.5	7.04	92.9%

Table 8.3: Summary of conversion of 25% sucrose to glycerol, propylene glycol and ethylene glycol over various metal catalysts. Reactions were carried at 230°C, 250 psi, and 12 hours with 5% catalyst loading. Feed: 25g sucrose in water: Base concentration: 0.2M

Catalyst	PG (g)	Glycerol (g)	EG (g)	Total (g)	% Selectivity (PG+Glycerol)
Copper Chromium	2.4	3.34	0.22	5.96	96.3%
Nickel/Silica-Alumina	6.2	2.7	1.03	9.93	89.6%
Nickel/Kieselguhr	5.1	2.3	2.11	9.51	77.8%
Palladium/Carbon	3.7	7.1	0.8	11.6	93.1%
Ruthenium/Carbon	8.8	2.66	1.3	12.76	89.8%
Nickel/Silica-Alumina +Copper Chromium	7.32	2.89	0.52	10.73	95.2%
Raney Nickel	8.08	2.72	1.83	12.63	85.5%

Table 8.4: Effect of reaction temperature and hydrogen pressure on formation of glycerol, propylene glycol and ethylene glycol. All reactions were performed for 12hours with 5% catalyst loading. Feed: 2.5g sorbitol + 2.5g glycerol + 5g water.

Pressure (psi)	**Temperature (°C)**	**Acetol (g)**	**PG (g)**	**Glycerol (g)**	**EG (g)**	**Total (g)**	**Selectivity (G + PG + Ac)**
50	190	0.15	0.86	0.25	0.17	1.43	88.1%
50	230	0.13	0.79	0.28	0.17	1.37	87.6%
100	190	0.1	0.75	0.24	0.18	1.27	85.8%
100	230	0.14	1.28	0.31	0.22	1.95	88.7%
250	190	0	0.98	0.29	0.18	1.45	87.6%
250	230	0	1.15	0.28	0.14	1.57	91.1%

Table 8.5: Effect of base (KOH) concentration on formation of glycerol, propylene glycol and ethylene glycol. All reactions were performed at 230°C and 250 psi hydrogen pressure for 12hours with 5% catalyst loading. Feed: 2.5g sorbitol + 2.5g glycerol + 5g water.

KOH Conc.	**Acetol (g)**	**PG (g)**	**Glycerol (g)**	**EG (g)**	**Total (g)**	**Selectivity (G + PG + Ac)**
Neutral	0.22	1.01	0.46	0.22	1.91	88.5%
0.05M	0.61	1.99	0.71	0.38	3.69	89.7%
0.1M	0.1	1.64	0.36	0.33	2.43	86.4%
0.2M	0	1.79	0.35	0.36	2.5	85.6%
0.5M	0	1.62	0.29	0.25	2.16	88.4%
1M	0	1.39	0	0.21	1.6	86.9%

Table 8.6: Effect of sorbitol feed concentration on formation of glycerol, propylene glycol and ethylene glycol. All reactions were performed at 230°C and 250 psi hydrogen pressure for 12hours with 5% catalyst loading.

% Sorbitol in Water	Sorbitol in Feed (g)	Acetol (g)	PG (g)	Glycerol (g)	EG (g)	Total (g)	Selectivity (G + PG + Ac)
10	1	0	0.22	0	0.09	0.31	71.0%
25	2.5	0	0.69	0.29	0.24	1.22	80.3%
50	5	0	1.52	0.57	0.54	2.63	79.5%
75	7.5	0.1	2.14	1.13	0.47	3.84	87.8%

Table 8.7: Effect of feed concentration on formation of glycerol, propylene glycol and ethylene glycol. All reactions were performed at 230°C and 250 psi hydrogen pressure for 12hours with 5% catalyst loading. Feed: 50:50 mixtures of sorbitol and glycerol.

% (Sorbitol+ Glycerol) in Water	(Sorbitol+ Glycerol) in Feed (g)	Acetol (g)	PG (g)	Glycerol (g)	EG (g)	Total (g)	Selectivity (G + PG + Ac)
25%	2.5	0	1.72	0.28	0.21	2.21	90.5%
50%	5	0	1.83	0.32	0.26	2.41	89.2%
75%	7.5	0.12	2.66	0.45	0.42	3.65	88.5%
100%	10	0.19	2.42	0.51	0.39	3.51	88.9%

9 CHAPTER 9

SUMMARY

Glycerol and other polyhydric alcohols like sorbitol were successfully converted to value added products like acetol and propylene glycol. It was identified that copper-chromite catalyst is the most effective catalyst for the hydrogenolysis of glycerol to propylene glycol and nickel based catalyst on silica-alumina or kiesulghur support was most effective for converting sorbitol and sugars to glycerol and propylene glycol. The mild reaction conditions of conditions (≤220 psig and ≤220°C) used in these studies give the process based on these heterogeneous catalysts distinctive competitive advantages over traditional processes using severe conditions of temperature and pressure. This catalytic process provided an alternative route for the production of propylene glycol from bio-renewable resources.

A novel mechanism to produce propylene glycol from glycerol via an acetol intermediate was proposed and validated. In a two-step reaction process, the first step of forming acetol can be performed at atmospheric pressure while the second requires a hydrogen partial pressure.

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

In the second step hydrogenation of acetol to propylene glycol over copper chromium catalyst was studied and compared with other metal-based catalysts. High selectivities (>98%) for propylene glycol were achieved with acetol conversions nearing 97% for a 4 hour reaction time at moderate temperatures (185°C) and hydrogen pressures (200psi). The reaction kinetic results show that the reaction follows an overall first order rate model. Higher selectivities to propylene glycol were observed at higher hydrogen pressures. At temperatures of about 210°C excessive reaction takes place resulting in polymerization of acetol or formation of gaseous or liquid by-products. At least 30% diluent is recommended to reduce formation of byproducts from acetol.

The kinetic and mass transfer calculations with creditable literature correlations and experiments show that G-L, L-S and intra particle mass transfer can be neglected in the batch reactor at our reaction conditions. The intrinsic kinetics is analyzed and the activation energy is 53.16 KJ/mol. The initial reaction rate for 20% acetol solution with copper chromite catalyst is well represented by:

$$R_{initial} = 3361.02\exp\left(\frac{-53162.09}{RT}\right)w^{0.32}{P_{H2}}^{0.81}$$

At 150°C, an Langmuir-Hinshelwood model was derived and the parameter fitting is reasonably good. The initial selection of acceptable models from all the possible candidates was based on several now well-known statistical criteria. It was found that the hydrogenation of acetol to propylene glycol follows a single site mechanism with molecular adsorption of both hydrogen and acetol on to the catalyst surface. The surface reaction of hydrogen and acetol is most likely the rate-controlling step.

$$R = \frac{kK_1K_2P_{H_2}C_A}{\left[1+K_1C_A+K_2P_{H_2}+\frac{C_P}{K_4}\right]^2}$$

The deactivation mechanism of the catalyst was found to be mainly poisoning due to the reduction of the cuprous chromium active species into metallic copper species, metal leaching, and poisoning by strongly adsorbed inorganic and organic species present in the feed or generated during the reaction. X-ray photoelectron spectroscopy and X-ray diffraction studies indicate that the decrease in the catalytic activity is due to the formation of excess of inactive Cu (0) ions by reduction of active Cu (I) species. The results from BET porosimetric studies and transmission electron microscopy indicated that blockage of catalyst pores by glycerol or propylene glycol molecules or any intermediate species generated during the reaction. Propylene glycol appeared to have a lower affinity for active sites on the metal catalyst compared to glycerol.

Leaching of copper and chromium metals into the final product solutions was observed. More leaching of metals occurred at higher reaction temperatures and low hydrogen pressures. This may be due to dissolution of copper oxide species in the form of $Cu(OH)_2$ or due to the formation of some organometallic chromium complexes which have a higher tendency to dissolve in the glycerol or propylene glycol.

Inorganic chloride and phosphorus impurities have significant poisoning effect on catalyst. The yield of propylene glycol is almost negligible with presence of 4mmol of impurity in the initial feed solution. Presence of sulfur impurities has relatively lesser impact due to the presence of barium in the catalyst, which acts as a sulfur scavenger. Organic impurities did not have a significant effect on the catalyst activity due to low solubilities of non-polar organic species in glycerol solution. The poisoning is temporary due to blockage of catalyst pores by the bulky organic molecules.

Sorbitol was converted to lower polyols with the selectivities of C3 derivatives (propylene glycol + glycerol + acetol) exceeding 80% using nickel-based catalysts. The reaction conditions used for these reactions are significantly less than that reported in the literature. Most importantly, the preliminary conversion data are far better than the starting point conversion data for the glycerol technology that has been developed to commercial viability. Conversions starting with glucose and sucrose are nearly as effective as the use of sorbitol. Glycerol dissolves and stabilizes sorbitol in a manner much like water and allows reactions to be conducted without water being present. The preliminary results of this study illustrate that high selectivity for conversions of C6 feedstocks can be maintained even at lower water contents. Yields remain high up to 75% sugar in water indicating more effective use of reactor volumes at 75% sugar relative to 25% sugar. This creates improved opportunities to use reactive distillation for sorbitol conversion and to achieve higher yields. The absence of water in the sorbitol system reduces the pressure needed by up to 50%--from 400 to 200 psig and increases the average space-time yield of the reaction thus decreasing the energy consumption and eliminating the necessity of large high-pressure reactors. Lastly, with the recycle of glycerin product, processes operating with zero water content are possible with C6 sugars. This is important when considering reactive distillation and provides a starting point for evaluating reactive distillation for these sugars.

Further work is required in finding other alternative uses for glycerol and sugar alcohols. Epoxide derivatives of these polyhydric alcohols like epichlorohydrin, glycidol, propylene oxide etc., will be of commercial interest in polymer industry. A thorough understanding of the fundamentals behind converting these polyhydric alcohols into value added derivatives paves the way for future work on finding more applications for these abundant bio-renewable resources.

REFERENCES

---

[1] Suppes, G. J, Dasari, M. A, Doskocil, E. J, Mankidy, P. J, Goff, M. J., Transesterification of Soybean Oil with Zeolite and Metal Catalysts, Applied Catalysis A: General, 257, 213-223, **2004**

[2] Chiu, C. W, Schumacher, L. G, Suppes, G. J, Impact of cold flow improvers on soybean biodiesel blend, Biomass and Bioenergy, 27 (5), 485, **2004**

[3] Dasari, M. A, Goff, M. J, Suppes, G. J, Non-Catalytic alcoholysis Kinetics of Soybean Oil. " J. Am. Oil. Chem. Soc, 80, 189, **2003**

[4] National biodiesel board , Tax Incentive Fact sheet, **2005**

[5] Higgins, J, On the Road to Fueling the Future. *Bioenergy '02*, Proceedings, Paper 2062, Published by Pacific Regional Biomass Energy Program, Boise, ID, Sep **2002**

[6] Jungermann, E, and Sonntag, N.O.V, Glycerine: A Key Cosmetic Ingredient, Marcel Dekker, Inc., New York, **1991**

[7] Glycerol refining costs for industry provided by Proctor & Gamble, July 17, **2003**

[8] Shaine, T. K. Oil Platform Analysis: A Scoping Study for Biorefineries, NREL Technical Report, **2004**

[9] HBI (Heming Boukris International). statistics, **1998**

[10] Monick, J. A, Alcohols, Their Chemistry, Properties and Manufacture' pp315,Reinhold Book Corporation,**1968**

[11] Chemical Market Reporter, Chemical Profile – Propylene Glycol October 25, **2005**

---

[12] Suppes, G. J, Dasari, M. A, Doskocil, E. J, Mankidy, P. J, Goff, M. J., Transesterification of Soybean Oil with Zeolite and Metal Catalysts, Applied Catalysis A: General, 257, 213-223, **2004**

[13] Canakci, M, Van Gerpen, J, Biodiesel Production from Oils and Fats with High FFAs, *Trans. ASAE* 44(6), 1429, **2001**

[14] Chiu, C. W, Schumacher, L. G, Suppes, G. J, Impact of cold flow improvers on soybean biodiesel blend, Biomass and Bioenergy, 27 (5), 485, **2004**

[15] Dasari, M. A, Goff, M. J, Suppes, G. J, Non-Catalytic alcoholysis Kinetics of Soybean Oil. " J. Am. Oil. Chem. Soc, 80, 189, **2003**

[16] Chemical Marketing Reporter, 1092-0110, Sept 24, **2001** v260 i11 p30

[17] Chemical Market Reporter , 1092-0110, April 26, **2004** v265 i17 p20(4)

[18] Martin, A. E, Murphy, F. H, Krik-Othmer Encyclopedia of Chemical Technology, 4th ed., John Wiley and Sons, New York, **1994**, Vol. 17, p. 715

[19] Trent, D. T. Krik-Othmer Encyclopedia of Chemical Technology, 4th ed., John Wiley and Sons, New York, **1996**, Vol. 20, p. 271

[20] Chopade, S, Miller, D, Jackson, J, Werpy, T, Frye Jr, J, Zacher, A. Catalysts and process for hydrogenolysis of sugar alcohols to polyols, US Patent 6,291,725, **2001**

[21] Casale, B, Gomez, A. M, Catalytic method of hydrogenating glycerol, US Patent 5, 276, 181, **1994**

[22] Casale, B, Gomez, A. M, Method of hydrogenating glycerol, US Patent 5, 214, 219, **1993**

[23] Ludwig, S, Manfred; E, Preparation of 1, 2 Propanediol, US Patent 5, 616, 817, **1997**

---

[24] Tessie, C, Production of propanediols, US Patent 4, 642,394, **1987**

[25] Haas, T, Neher, A , Arntz, D, Klenk, H, Girke; W, Process for the production of 1,2 and 1,3 propanediol, US Patent 5, 426, 249, **1995**

[26] Cameron, D. C, Cooney, C. L, Biotechnology, 4, **1986**, 651

[27] Cameron, D. C, Altaras, N. E, Hoffman, M. L, and Shaw, A. J,14, **1998**, 116

[28] Ullmann's Encyclopedia of Industrial Chemistry, 5th edition, Volume A13, VCH, **1985**

[29] J. Runberg, A. Baiker, J. Kijenski, J. Applied Catalysis, 17, **1985**, 309

[30] C. Montassier, D. Giraud, J. Barbier; Heterogeneous Catalysis and Fine Chemicals, **1988**, 165

[31] P. A. Levene, and A. Walti, Organic Syntheses, Vol. 2, 545-547, John Wiley and Sons, New York, **1943**

[32] R. Habaut, J. P. Bonnelle; J. Molecular Catalysis, 55 **1989**, 170

[33] Chemical Marketing Reporter 1092-0110, Sept 24, **2001** v260 i11 p30

[34] Chemical Market Reporter , 1092-0110, April 26, **2004** v265 i17 p20(4)

[35] Dasari, M. A., Kiatsimkul, P., Sutterlin, W. R., Suppes, G. J., Low-pressure Hydrogenolysis of Glycerol to Propylene Glycol. Applied Catalysis A:General, 281(1-2), 225-231, **2005**

[36] H. J. Adkins and R. J. Connor, American Chemical Society, 53 1931, 1091

[37] R.Connor, K. Fokers, and H. J. Adkins, American Chemical Society, 54, 1932,1138.

[38] P.C. Flynn, S. E. Wanke, Journal of Catalysis, 34 1974, 390

---

[39] P.C. Flynn, S. E. Wanke, Journal of Catalysis, 34 1974, 400

[40] R. Huges, Deactivation of Catalysts, Academic Press, San Diego, California, 1984

[41] Chiu, C. W., Goff, M. J., Suppes, G. J., Distribution of Methanol and Catalysts between Biodiesel and Glycerol. AIChE Journal, 51(4), 1274-1278, **2005**

[42] Iwamoto. I; Aonuma. T; Keil. T; Solvent effect on heterogeneous hydrogenation reactions. International Chemical Engineering, 11, 573-577, 1971

[43] Lo, H. S; Paulaitis, M. E; Estimation of solvent effects on chemical reaction rates using UNIFAC group contribution. AIChE Journal, 27, 842-844, 1981

[44] Rajadhyaksha. R. A; Karwa. S. L; Solvent effects in catalytic hydrogenation, Chemical Engineering Science, 41 (7), 1765-1770, 1986

[45] U. K Singh; M. A. Vannice, Kinetics of liquid phase hydrogenation reactions over supported metal catalysts-a review, Applied Catalysis A: General, 213, 1-24, 2001

[46] L. Cerveny; B. Vostry; V. Ruzicka, Collect. Czech Chem. Commun. 46, 1965, 1981

[47] Cubicciotti D, “Pourbaix Diagrams for Mixed Metal Oxides”, Chemistry of Copper in BWR Water,Corrosion, NACE, 44 (12) (1988) 875-880.

[48] M. A. Dasari, C. W. Chiu, W. R. Sutterlin, G. J. Suppes, Chemical Engineering Science (in review)

[49] Hubaut R and Bonnelle J P, Journal of Molecular Catalysis, 55 (1989), 170.

[50] R. B. C Pillai, K. K. Bhattacharyya, C. N. Pillai, Indian Journal of Chemistry, 29A, 1115, 1990

[51] Moretti. G, Fierro. G, Jacono. M, Lo Porta. P, Surf. Interf. Anal; 16, 352, 1990

---

[52] Cimino. A, De Angelis B. A, Minelli. G; Surf. Interf. Anal, 5, 150, 1983

[53] T. A. Krieger, L. M. Plyasova, T. M. Yurieva, Material Science Forum, Vols.321-324, 386, 2000

[54] J. D. Stroupe, Journal of American Chemical Society, 71, 569, 1949

[55] Pillai, R. B. C., *Catal. Lett.* **26**, 365 (1994).

[56] Makarova, O. V., Yur'eva, T. M., Kustova, G. N., Ziborov, A. V.,Plyasova, L. M., Miyukova, T. P., Davydora, L. P., and Zaikovskii,V. I., *Kinet. Catal.* **34**, 683 (1993)

[57] E. G. King, Alla D. Mah, and L. B. Pankratz., Thermodynamic properties of copper and its inorganic compounds, International Copper Research Association, New York, 1973

[58] Hu. Z. S, S. M. Hsu and P. S. Wang Surface Science Investigations in Tribology, A. C. S Symposium series, 485, 1992, 195

[59] Canakci, M., Gerpen, J. V., (2001). Biodiesel Production from Oils and Fats with High FFAs. Transactions of the ASAE, 44(6), 1429-1436.

[60] Dasari, M. A, Goff, M. J, Suppes, G. J, Non-Catalytic alcoholysis Kinetics of Soybean Oil. " J. Am. Oil. Chem. Soc, 80, 189, **2003**

[61] Suppes, G. J, Dasari, M. A, Doskocil, E. J, Mankidy, P. J, Goff, M. J., Transesterification of Soybean Oil with Zeolite and Metal Catalysts, Applied Catalysis A: General, 257, 213-223, **2004**

[62] Chiu, C. W., Goff, M. J., Suppes, G. J., Distribution of Methanol and Catalysts between Biodiesel and Glycerol. AIChE Journal, 51(4), 1274-1278, **2005**

[63] Higgins, J., On the Road to Fueling the Future. Bioenergy '02, Proceedings Paper 2062, Pacific Regional Biomass Energy Program, Boise, ID, **2002**

---

[64] Chemical Market Reporter, vol. 260 i11, p. 30, **2001**

[65] Chemical Market Reporter, vol. 265 i17, p. 20(4), **2001**

[66] Martin, A. E., Murphy, F. H, Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed., Volume 17, John Wiley, New York, p. 715, **1994**

[67] Trent, D. T, Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed., Volume 20, John Wiley, New York, p. 271, **1996**

[68] Casale, B., Gomez, A. M., Method of hydrogenating glycerol. US Patent 5,214,219, **1993**

[69] Casale, B., Gomez, A. M., Catalytic method of hydrogenating glycerol. US Patent 5,276,181, **1994**

[70] Ludwig, S., Manfred, E., Preparation of 1, 2 Propanediol. US Patent 5,616,817, **1997**

[71] Tessie, C., Production of propanediols. US Patent 4,642,394, **1987**

[72] Dasari, M. A., Kiatsimkul, P., Sutterlin, W. R., Suppes, G. J., Low-pressure Hydrogenolysis of Glycerol to Propylene Glycol. Applied Catalysis A:General, 281(1-2), 225-231, **2005**

[73] Gaikar, V. G., Sharma, M. M., Separations through Reactions and over Novel Strategies. Separation and Purification Methods, 18(2), 111-176, **2001**

[74] Doherty, M. F., Buzad, G., Reactive Distillation by Design. Chemical Engineering Research and Design, 70(A5), 448-458, **1992**

[75] DeGarmo, J. L., Parulekar, V. N., Pinjala, V., Consider Reactive Distillation. Chemical Engineering Progress, 88(3), 43-50, **1992**

---

[76] Clacens, J.-M., Pouilloux, Y., Barrault, J., Selective etherification of glycerol to polyglycerols over impregnated basic MCM-41 type mesoporous catalysts. Applied Catalysis A:General, 227(1-2), 181-190, **2002**

[77] Newsome, D. S., The water-gas shift reaction. Catalysis Reviews-Science and Engineering, 21(2), 275-318, **1980**

[78] Research to develop both fuels and value-added chemicals from corn and other renewable resources, NREL report, **2003**

[79] Chemical Market Reporter, vol. 260 i11, p. 30, **2001**

[80] Chemical Market Reporter, vol. 265 i17, p. 20(4), **2001**

[81] Martin, A. E., Murphy, F. H, Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed., Volume 17, John Wiley, New York, p. 715, **1994**

[82] Trent, D. T, Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed., Volume 20, John Wiley, New York, p. 271, **1996**

[83] Ludwig, S., Manfred, E., Preparation of 1, 2 Propanediol. US Patent 5,616,817, **1997**

[84] Tessie, C., Production of propanediols. US Patent 4,642,394, **1987**

[85] Haas, T, Neher, A , Arntz, D, Klenk, H, Girke; W, Process for the production of 1,2 and 1,3 propanediol, US Patent 5, 426, 249, **1995**

[86] Dasari, M. A., Kiatsimkul, P., Sutterlin, W. R., Suppes, G. J., Low-pressure Hydrogenolysis of Glycerol to Propylene Glycol. Applied Catalysis A:General, 281(1-2), 225-231, **2005**

[87] Nef, Ann. 335, 247, 260,**1904**

[88] Urion, Catalytic decompositions of several complex alcohols, Ann. chim. (11) 1, 78 , **1934**

---

[89] Holmes, Brit. pat. 428,462 C. A. 29, 6908, **1935**

[90] Carbide and Carbon Chemicals Corporation, U. S. pat. 2,143,383, **1939**

[91] Preparation of (R) - and (S)-propylene glycol with baker's yeast. Kometani T; Matsuno R, Annals of the New York Academy of Sciences , 750 421-4, **1995**

[92] D. C. Cameron, C. L, Cooney, Biotechnology, 4, 651, **1986**

[93] D. C. Cameron, N. E. Altaras, M. L. Hoffman, and A. J. Shaw, 14, 116, **1998**

[94] Farber, E, Nord, F. F., The phytochemical reduction of acetol to optically active propylene glycol. Biochemische Zeitschrift, 112, 313-23, **1920**

[95] Ohara, T; T. Sato; N. Shimizu; G. Prescher; H. Schwind; and O. Weiberg, Acrolein and Methacrolein, in Ullman’s Encyclopedia of Industrial Chemistry, Fifth Edition, VCH publishers, NY, **1985**, Vol A1

[96] Dasari, M. A., Kiatsimkul, P., Sutterlin, W. R., Suppes, G. J., Low-pressure Hydrogenolysis of Glycerol to Propylene Glycol. Applied Catalysis A:General, 281(1-2), 225-231, **2005**

[97] Dasari, M. A, Chiu, C. W, Sutterlin, W. R, Suppes, G. J, Production of propylene glycol by selective hydrogenation of acetol, Applied Catalysis A: General (in review)

[98] Dasari, M. A, Suppes, G. J, Kinetic Modeling of Aqueous Phase Hydrogenation of Acetol to Propylene Glycol, Chemical Engineering Science, (in review)

[99] Radhakrishnan, K, Ramachandran, P. A, Brahme , P. H, and Chaudhari, R. V, Solubility of Hydrogen in Methanol, Nitrobenzene, and Their Mixtures. Experimental Data and Correlation, Journal of Chemical & Engineering Data, 28, 1-4, **1983**

---

[100] Stephen H and Stephen T, “Solubility of inorganic and organic compounds”, vol 1, The Macmillan Company, NewYork, **1963**

[101] Brahme, P.H, Vadgaonkar, H. G, Ozarde, P. S, Parande, M. G, Solubility of Hydrogen in Aqueous Solution of 2-Butyne-1,4-diol and 2-Butene-1,4-diol, Journal of Chemical Engineering Data, 26, 416-417, **1981**

[102] Radhakrishna. K, Ramachandran. P. A, Brahme. P. H, Chaudhari. R. V, Journal of Chemical Engineering Data, 28, 1-4, **1983**

[103] Dasari, M. A., Kiatsimkul, P., Sutterlin, W. R., Suppes, G. J., Low-pressure Hydrogenolysis of Glycerol to Propylene Glycol. Applied Catalysis A:General, 281(1-2), 225-231, **2005**

[104] Dasari, M. A, Suppes, G. J, Kinetic Modeling of Aqueous Phase Hydrogenation of Acetol to Propylene Glycol, Chemical Engineering Science, (in review)

[105] Chemical Marketing Reporter, 1092-0110, Sept 24, **2001** v260 i11 p30

[106] Chemical Market Reporter , 1092-0110, April 26, **2004** v265 i17 p20(4)

[107] Martin, A. E., Murphy, F. H, Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed., Volume 17, John Wiley, New York, p. 715, **1994**

[108] Trent, D. T, Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed., Volume 20, John Wiley, New York, p. 271, **1996**

[109] Zwietering, T.N. “ Suspending of solid particles in liquid by agitators” Chemical Engineering Science, 8, 244,**1958**

[110] Vasant R. et.al Ind. Eng Chem Res; **1998**, 37, 3879-3887

[111] Ramachandran, P.A and R. V. Chaudhari, “Three Phase catalytic reactors”, Gordon and Breach Science

---

[112] Bern, L; Lidefelt, J.O and Shoon, N. H; Journal of American Oil Chemists Society, 53,463, **1976**

[113] Sano, Y et al Mass transfer from suspended particles in agitated vessels. J.Chem. Eng. Japan, 255, **1974**

[114] Boon-Long, S et al. “ Mass Transfer from suspended solids to a liquid in agitated vessels” Chem. Eng. Sci, 33,813, **1978**

[115] Wilke, C. R, Chang, P. C, AIChE Journal, 1,264,**1955**

[116] Satterfield, C. N, Mass Transfer in Heterogeneous Catalysts, Cambridge, England, **1970**

[117] Kittrell, J. R; Advances in Chemical engineering, 8, 110-147, **1970**

[118] Choudhary, V. R, Doraiswamy, L. K, Ind Eng. Chem. Proc. Des. Dev, 14, 227, **1975**

[119] Brahme P. H, Doraiswamy, L. K, Ind Eng. Chem. Proc. Des. Dev, 15, 130, **1976**

[120] Law, V. J, Bailey. R. V, Chem. Eng. Sci, 18, 189, **1963**

[121] Rubin, D. I, Chem. Eng. Prog. Symp. Ser. 59 (42), 90, **1963**

[122] Andrews, M. A and Klaeren, S. A, Selective hydrocracking of monosaccharide carbon-carbon single bonds under mild conditions. Ruthenium Hydride Catalyzed formation of glycols. Journal of American Chemical Society, 111, 4131-4133, **1989**

[123] Connor, R, Adkins. H, Hydrogenolysis of Oxygenated Organic Compounds, Journal of American Chemical Society, 54, 4678-4690, 54.

[124] Zartman, W. H and Adkins, H, J. Am. Chem. Soc, 55, 4559, **1933**

---

[125] Lenth, C. W; Dupuis R. N; U. S patent 2190439, **1943**

[126] Clark, I. T, Hydrogenolysis of Sorbitol, Industrial & Engineering Chemistry Research, 50, 1125-1126, **1958**

[127] Conradin et al. U.S. Pat. No. 2,852,270

[128] Conradin et al. U.S. Pat. No. 3,030,429,

[129] Boelhouwer, C, Korf. D, Waterman. H. I, Catalytic Hydrogenation of Sugars. Journal of Applied Chemistry, 10, 292-296, **1960**

[130] Sirkar et al Catalytic Hydrogenolysis of Alditols to Produce Polyols, U.S. Pat. No. 4,338,472, **1981**

[131] Tanikella et al, Hydrogenolysis of Polyols to Ethylene Glycolin Nonaqueous Solvents, U.S. Pat. No. 4,404,411, **1983**

[132] Gubitosa et al. U.S. Pat. No. 5,600,028

[133] Chao, J, Catalytic Hydrogenolysis of Alditols to Product Glycerol and Polyols, US Patent 4366332, **1982**

[134] Huibers, D, Chao, J, Shah R, Multistage catalytic conversion of aldoses to alditols, US Patent 4433184, **1984**

[135] Vang Ling et al., Ind. Eng. Chem., Prod. Res. Dev., 9(2), 210, **1970**

[136] Feng-wen chang et al, A kinetic study on the hydrogenolysis of sorbitol over Raney Nickel catalysts, J. of the Chin. I. Ch.E., 16, 17-23, **1985**

[137] Dasari, M. A., Kiatsimkul, P., Sutterlin, W. R., Suppes, G. J., Low-pressure Hydrogenolysis of Glycerol to Propylene Glycol. Applied Catalysis A:General, 281(1-2), 225-231, **2005**

---

[138] De Bruijn, J. M, Kieboom, A. P. G, Van Bekkum, H, Reactions of monosaccharides in aqueous alkaline solutions, Sugar Technology Reviews, 13,21-52,**1986**

[139] Dasari, M. A, Chiu, C. W, Sutterlin, W. R, Suppes, G. J, Production of propylene glycol by selective hydrogenation of acetol, Applied Catalysis A: General, **2006**, (in review)

[140] Dasari, M. A., Kiatsimkul, P., Sutterlin, W. R., Suppes, G. J., Low-pressure Hydrogenolysis of Glycerol to Propylene Glycol. Applied Catalysis A:General, 281(1-2), 225-231, **2005**

VITA

Mohanprasad A. Dasari was born on the July 28, 1979, in Visakhapatnam, India. He attended private elementary and high schools in Visakhapatnam. In May 2001, he received his Bachelors of Technology degree in Chemical Engineering with a minor in Petroleum Engineering from Andhra University, Visakhapatnam, India. Since August 2001, he initiated his graduate studies in Chemical Engineering at University of Missouri, Columbia, MO under the supervision of Dr. Galen J. Suppes. He received his Master of Science degree in August 2003 and Doctor of Philosophy degree with doctoral minor in Material Science in May 2006.