Gas Phase Conversion of Sugars to C3 Chemicals

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By

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DEDICATION

This dissertation is dedicated to my parents, Xiaoguang Yan and Jin Liu, my dear wife Liang Zhu and sister Hua Yan 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 in my life.

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THESIS FORMAT

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

Chapter 1 gives an overall introduction and background to conversion of biorenewable sources, especially sugars or sugar alcohols, to produce valuable chemicals.

Chapter 2 contains the first paper, which deals with vapor pressure estimation by thermogravimetric analysis (TGA) method and experimental evaporation studies of C6 sugars and sugar alcohols in continuous operation.

Chapter 3 contains the second paper, which deals with production of value-added C3 chemicals (e.g. acetol) by gas phase heterogeneous hydrogenolysis of C6 sugars or sugar alcohols.

Chapter 4 contains the third paper, which deals with gas phase dehydration of glycerol to acrolein in the presence of solid acid catalysts (phosphoric acid supported on activated carbon).

Chapter 5 summarizes the results of three research projects and presents some suggestions for future investigations.

DISCLAIMER

This dissertation contains guidelines, procedures and protocols for performing reactions at severe temperatures and pressures.

The authors in no way implied 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 dangerous environments when performing these experiments include, but are not limited to:

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

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

Gas Phase Conversion of Sugars to C3 Chemicals

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ABSTRACT

The limited fossil oil reserve, fast-rising crude oil price and increasing environmental concerns make scientists and researchers give a serious look at biomass as feed stocks to produce chemicals and fuels. Five chapters in this dissertation focused on various methodologies to convert biomass into value-added chemicals.

The vapor pressure estimation and evaporation of sugars and sugar alcohols was first discussed. The purpose of this study is to overcome the drawbacks of liquid phase hydrogenolysis (low selectivities to desired products and high cost of catalyst recovery) and identify potential conditions for gas phase hydrogenolysis. A thermogravimetric analysis (TGA) method was used to estimate a boiling point of 362 °C for sorbitol with sorbitol's vapor pressure following a Clausius-Clapeyron model behavior. In addition, evaporation studies demonstrated sobitol evaporation and condensation on a practical level. The evaporation of sorbitol was experimentally validated with no decomposition at 0.1 bar and 294 °C and

2.5 % (mass fraction) in water. The evaporation of high-concentration sorbitol feed can be achieved by mixing with a high-temperature gas. Glucose evaporated with partial decomposition at temperatures as low as 220 ℃.

Gas phase catalytic hydrogenolysis was secondly demonstrated to be a means to produce valuable chemicals from sugars and sugar alcohols. Copper-chromite, palladium, and nickel beads catalysts were investigated for gas phase hydrogenolysis of sorbitol. Complete conversion was attained at reaction pressures of 0.3 to 1 bars. The highest selectivities favored acetol. The advantages over liquid phase hydrogeonolysis are mild reaction conditions (low temperatures and pressures), high selectivity to acetol and continuous operation in packed bed reactor.

In addition, gas phase dehydration of glycerol was studied in the presence of solid acid catalyst. The reaction mechanism of producing acroelin from glycerol was proposed and validated. At mild condition of 260℃ and 0.85 bar, up to 84% selectivity to acrolein can be achieved. Compared with other processes, this technology showed more advantages, e.g. higher selectivity, milder reaction conditions and long catalyst life. This process was considered as an alternative process for industry-scale production of acrolein.

1 CHAPTER 1
INTRODUCTION

1.1 Introduction

Petroleum continues to supply most of the world demand for transportation fuels and commodity chemicals. With the development of global economy, the available petroleum stocks are expensive and the supply is limited in a few decades[1,2,3,4]. The increases in crude oil prices have adverse effects on the economy of all the counties. Coal is plentiful but introduces burdens on the environment, such as acid rain and mercury poisoning. There are needs to develop reliable renewable resources that have fewer environmental impacts than fossil resources.

Currently, economics do not favor bioenergy and biobased products. However, other factors increase the attractiveness of biorenewable resource utilization. These include improved environmental quality and concerns for national security by reliance on foreign sources of fossil fuels.

The production and use of fossil fuels lead to increasing concern about environmental pollution. Local impacts can arise from solid waste disposal sites, ash from coal combustion, coke and sulfur from petroleum refineries. Combustion of coal or petroleum-based motor fuel produces carbon dioxide, fine particulate matter, and smog as local environmental problems. Regional impacts of fossil fuel energy use come from acid rain from sulfur dioxide and nitrogen oxides released during the combustion. Global impacts from nitrogen oxides that can react with ozone molecules in the upper atmosphere. The greatest concern is the possible role of carbon dioxide produced during the combustion in leading to global warning.

Although bioenergy and biobased products cannot solve all environmental problems, the environmental burden from the use of biorenewable resources is less than from the use of fossil resources.

Secondly, the lesson learned from the "1973 Energy Crisis" was that effective national security incorporates an energy policy that reduces reliance on foreign energy sources. Petroleum imported to the United States of America currently exceeds 60% and will easily grow up to 65% by 2020[5]. Two-thirds of world petroleum reserves are located in the Middle East. Increasing reliance on imported energy sources is inevitable and adversely affects national security unless domestic biorenewable energy sources are developed.

It is estimated that if all the reasonably harvestable biomass in the U.S. were converted to liquid fuels, these fuels would displace about 25 % of liquid petroleum fuel consumption[6]. Biomass is not the answer to energy problems related to fossil fuel consumption; however, in combination with technologies like plug-in hybrid electric vehicle technology and electric trains, biomass fuels and bio-based chemicals will be a vital component of future sustainable fuels and chemicals.

1.2 Biomass for sugar

Biomass is organic material of recent biological origin. Biomass comes from crops, forests, prairies, marshes and fisheries. Solar energy collected by green plants is converted into organic chemicals to produce proteins, oils and carbohydrates. This stored chemical energy can be used as a resource for heat and stationary power, transportation fuels and commodity chemicals. Sugar production from sugar crops, starch and inulin crops, and lignocellulosic materials are widely used as feed stocks for chemicals and fuels.

1.2.1 Sugar crops

Traditional sugar crops used for fermentation include fruits, sugar cane, sugar beets, corn and sweet sorghum. Molasses (the residual syrup from crystallization of sugar from sugar cane and sugar beets) is a common feedstock. Pulp and paper-mill sludges contain as much as 40-50 % (mass fraction) glucose. Preparing these feed stocks for sugar is relatively simple. For example, sugar cane contains 20-30 % (mass fraction) sugar. The cane stalks are chopped, crushed and washed with hot water to extract the sugar.

1.2.2 Starch and inulin crops

Starch is a polymer that accumulates in most plant cells where they serve as storage for carbohydrate. Mechanical grinding liberates the starch granules. Starch is a glucose polymer with two main components: amylase, a liner polymer of glucose with an α-1,4 linkage, and amylopectin, a branched chain including an α-1,6 linkages at the branch points. Enzymatic hydrolysis of starch requires two enzymes. The enzyme amylase hydrolyzes starch to maltose in a process known as liquefaction. The enzyme maltase hydrolyzes maltose into glucose in a process known as saccharification. Cereal grains (e.g. corn, wheat, and barley) are the most widely used sources of starch for sugars. Grain starch consists of 10-20 % (mass fraction) amylase and 80-90 % (mass fraction) amylopetin, both of which yield glucose or maltose on hydrolysis.

Inulin is a storage carbohydrate, but its basic unit is fructose rather than glucose. It is commonly found in tuber crops such as dahlias and Jerusalem antichokes. It is also easily depolymerized by both acid- and enzyme-catalyzed hydrolysis.

1.2.3 Lignocellulosic feedstocks to sugar

Much of the carbohydrate in plant materials is structural polysaccharides, providing shape and strength to the plant. The hydrolysis of polysaccharides in cell walls is more difficult than the hydrolysis of storage polysaccharides such as starch. This structural material, known as lignocellulose, is a composite of cellulose fibers embedded in a cross-linked lignin-hemicellulose matrix. Depolymerization of basic plant components is difficult because lignocellulose is resistant to both chemical and biological attack.

A variety of physical, chemical and enzymatic processes have been developed to fractionate lignocellulose into the major components of hemicellulose, cellulose, and lignin. The hemicellulose fraction is readily hydrolyzed to pentoses (five-carbon sugars). The cellulose exists in amorphous and crystalline forms, both of which hydrolyze to hexoses (six-carbon sugars). Lignin, which is not susceptible to biological reduction but can be chemically upgraded or used as fuel.

1.3 Sugar production

On September 12, 2007, the United States Department of Agriculture (USDA) released its latest supply and use estimates for 2007 and projections for 2008 in the World Agricultural Supply and Demand Estimates (WASDE) report. Sugar production in 2008 is projected to be 8.342 million short tons, raw value (STRV), a decrease of about 152,000 STRV from 2007. Beet sugar is forecast at 4.657 million STRV (371,000 STRV, or 7.4 percent, lower than 2007), and cane sugar is forecast at 3.684 million STRV (219,000 STRV, or 6.3 percent, higher than 2007). The USDA estimates sugar in 2007 deliveries for food and beverage use at 9.850 million STRV and sugar in 2008 deliveries at 10.000 million STRV. Table 1.1[7] and Table 1.2[8] shows sugars supply and price.

From the comparison of the costs of feed stocks[9] summarized in Table 1.3, it is clear that sugar-type feed stocks appear to be sustainably available at prices equal to or less than petroleum feed stocks. Now it is time to replace petroleum with biorenewable resources as the primary source of feedstock to the chemical industry.

1.4 Methods for sugar conversion

1.4.1 Fermentation

Fermentation can produce a wide variety of chemicals (e.g. organic acids and alcohols). Most microorganisms used in commercial fermentations require hexoses (six-carbon sugars, e.g. glucose) or disaccharides (e.g. sucrose) as substrates. Recent technological advances have made possible the fermentation of pentoses (five-carbon sugars, e.g. xylose). As indicated in Table 1.4, a variety of value-added chemicals can be produced by fermentation[10].

However, several factors greatly limit the use of fermentation technology in the industrial production of chemicals. Production rates by microorganisms in aqueous media of low solids volume are inherently low. The microorganisms are sensitive to both inhibitors and operating conditions, especially temperature and pH. Most of fermentations require aseptic conditions, which can be difficult to achieve in large-scale operations. Recovery of water-soluble products from dilute solutions can be expensive. Effluent usually contains high biological oxygen demand (BOD) and requires waste water treatment before discharge.

1.4.2 Chemical reactions

1.4.2.1 Hydrogenolysis

Hydrogenolysis is defined as the splitting of a bond to each of the fragments. Based on commercial production, the major uses of this reaction occur in the petroleum and natural fatty-oil industries. Hydrotreating of petroleum stocks includes the hydrogenolysis of organo-sulfur, -nitrogen, -oxygen and -metallic compounds. Hydrogenolysis of fatty acids and fatty esters produced from natural oils is a significant pathway to fatty alcohols. Several successful applications of hydrogenolysis are described below.

Fatty alcohols are aliphatic alcohols of carbon chain lengths from C_6-C_{22}. They are usually produced from natural fats or oils or synthesized by Ziegler polymerization of ethylene with subsequent oxidation and hydrolysis [11]. If unsaturation is desired for syntheses of other useful compounds, only natural sources can be used. The production procedure of fatty alcohols from natural sources includes three steps. The first step is the splitting out the fatty acids from natural oils by hydrolysis or by transesterification using methanol to form the methyl ester directly. If the first step is hydrolysis, the second step involves the formation of a fatty acid ester. The third step is the hydrogenolysis of the ester to two moles of alcohol. The most frequently used commercial catalysts are summarized in Table 1.5 along with typical applications. Improvements of the copper chromite and zinc chromite catalysts have been made by several suppliers. For instance, the use of zinc to enhance the activity of copper chromite catalysts and improvement of zinc chromite performance by the addition of alumina. Ruthenium-tin and ruthenium-tin boride catalysts have also been reported to improve the activity for catalysts and the selectivity of hydrogenolysis. The operation conditions are in the range of 200-250 bar and 230-250 ℃. Yields are 99 % alcohol[12].

Another application of hydrogenolysis is production of 1, 4-dimethylcyclohexane from dimethyl terephthalate (DMT) using a two-step hydrogenation-hydrogenolysis of DMT. 1,4-dimethylcyclohexane is used as the diol in producing amorphous polyesters with high clarity for products such as films and bottles. The first step involves selective hydrogenation of the aromatic ring in the presence of palladium catalysts. The second step is a standard ester hydrogenolysis in the presence of copper-chromite catalysts. The operation conditions are in the range of 300-400 bar and 160-180 ℃[13].

Hydrogenolysis is also called hydrodealkylation in the production of benzene from toluene since the C-C bond is cleaved instead of the C-O bond. The major building blocks of aromatic chemistry (benzene, toluene, ethylbenzene and xylene) are obtained almost exclusively from catalytic reformate and pyrolysis. In the steam cracking of the naphtha, there often is produced an oversupply of toluene and undersupply of benzene. In that situation, hydrodealkylation is an economical process for changing this imbalance. Two practical routes for hydrodealkylation of toluene are both used commercially. Thermal free-radical hydrodealkylation was the initial process used and continues to be used. It required a higher temperature than the catalytic process. For catalytic process, the catalysts used include Cr_2O_3/alumina, Mo_2O_3/alumina or CoO/alumina. The chromium-on-alumina catalyst (3-12 % Cr_2O_3, spheres or tablets) has been the most widely used. The operating conditions are in the range of 35-70 bar and 550-650 ℃[14,15].

Hydrogenolysis can be applied in sugar/sugar alcohol conversion for production of valuable chemicals. The catalysts for hydrogenolysis are summarized in Table

1.6. Hydrogenolysis of sugars or sugar alcohols will be reviewed in detail in the next section.

1.4.2.2 Hydrogenation

Hydrogenation is the most widespread reaction in the commercial organic chemical industry. Both heterogeneous and homogeneous catalysts are used but heterogeneous catalysts dominate commercial practice, especially for large-scale production [16]. Hydrogenation catalysts most frequently used in commercial practice are base metals (Ni, Cu, Co, and Ca) and precious metals (Pt, Pd, Rh, Ru). The platinum metals are in most cases more active than base metals and thus require milder conditions and smaller amounts of catalyst. Nickel is the preferred catalyst for hydrogenating a wide variety of functional groups in instances where higher temperature and pressure present no physical and chemical disadvantages.

Of course, hydrogenation is also applied for sugar conversion for production of sugar alcohols. Although conversion of sugars to sugar alcohols can be achieved with various methods (e.g. enzymatic conversions, fermentation, electrolytic reduction etc), catalytic hydrogenation is most widely used for sugar alcohol production. The basic chemistry for sugar hydrogenation is shown below.

$$\underset{\text{Sugar}}{HOCH_2(CHOH)_n\text{-}CHO} + \underset{\text{Hydrogen}}{H_2} \xrightarrow[\text{Heat}]{\text{Cat}} \underset{\text{Sugar alcohol}}{HOCH_2(CHOH)_n\text{-}CH_2OH}$$

The most common sugar alcohol, sorbitol is commercially produced in large volume from glucose using batch hydrogenation processes in the presence of nickel catalyst. The operation conditions are in the range of 150-200 bar and 160-170 ℃ in the presence of Raney Nickel catalyst. Yield of sorbitol can be achieved in the range of 65 % to 75 %[17]. Another important sweetener, xylitol is also hydrogenated from xylose in the presence of nickel catalysts.

1.4.2.3 Dehydration

Dehydration of alcohols is used in certain fine chemical productions as a convenient procedure for introducing a double bond in a compound. Several large-scale commercial applications of dehydration are described below. One involves the production of tetrahydrofuran from 1,4-butanediol. This acid catalyzed reaction usually employs liquid acids in a homogeneous reaction. The other large-scale process dehydrates 1-phenylethanol to produce styrene using heterogeneous catalyst. The catalysts used in this process are TiO_2/alumina and TiO_2/silica. The dehydration reaction is carried out in the vapor phase in the range of 1-2 bar and 180-190 ℃. Conversions of 97 % and selectitivies of 89-95 % have been reported[18,19].

It is known that glycerol can be dehydrated in the presence of acid substances. The processes for the production of acrolein from glycerol have been widely investigated since the 1960's. The dehydration reaction of glycerol could be carried out in the liquid phase or in the gas phase. Ramayya et al.[20] described that dehydration of glycerol was performed in a homogeneous phase above the critical pressure of water with low concentration of acidic catalyst (e.g. sulfuric acid) as catalyst. Under the conditions of 350 ℃ and 345 bar, glycerol conversion was reported between 39 % and 55 %, and the weight ratio of acrolein and acetaldehyde (two major products) was 3:1 to 4:1. The drawbacks of this process are the considerable technical costs of working in the supercritical range and the recycling or treatment of the sulfuric acid.

To overcome the drawbacks of homogeneous catalysis, heterogeneous catalysis was proposed in the dehydration process of glycerol. It was reported in Organic Synthesis I[21], acrolein can be produced by treating a mixture of powdered potassium hydrogen sulphate, potassium sulphate and glycerol at the temperature of 190 ℃ to 200 ℃. This process required high ratio of dehydrating salts to glycerol. However, the yield of acrolein was not satisfactory. Hence, researchers searched for suitable acidic substances as catalysts. A process for production of acrolein from glycerol was performed by French scientists. The glycerol vapors were passed over a packed bed catalyst at a temperature, ranging from 350 ℃ to 420 ℃[22]. The catalysts used in this process are salts of tribasic acids or mixtures of such salts which may be on a catalyst support. For example, pumice coated with 1 % lithium phosphate or 1 % iron phosphate could be used. The acrolein yield of this process could be achieved up to the range of 30 to 35 % at 400 ℃. Allyl alcohol, acetaldehyde and propionaldehyde were also formed as secondary products. This process is considered unsuitable for industrial production owing to its low yield and selectivity to acrolein.

H-ZSM5 zeolites were also studied as the dehydrating catalysts for acrolein production. The reactions were carried out from 350 ℃ to 500 ℃[23]. The process possessed the same problems as previous process: low selectivity and yield of acrolein. Moreover, catalyst service life was limited to a few hours.

In an effort to overcome these drawbacks, our research focuses at developing a technology to perform the reaction at lower temperatures and in proper vacuum environment and achieving high acrolein selectivity, little or no formation of acetol, allyl alcohol or other by-products. The detailed research results are shown in chapter 3.

1.5 Hydrogenolysis of sugars or sugar alcohols

1.5.1 Literature review

Carbohydrates exhibit unusually rich chemical functionality with limited stability. Hydrogenolysis refers to the cleavage of a molecule under conditions of catalytic hydrogenation. Under high hydrogen pressure and high temperature, sugars and sugar alcohols can be catalytically hydrocracked into lower polyhydric alcohols in the presence of transition metal catalysts and could be enhanced by the addition of bases[24]. In the literature, sugar hydrogenolysis is dealt indistinguishably from sugar alcohol hydrogenolysis. In this process, both C-C and C-O bonds are susceptible to cleavage.

In the hydrogenolysis of sugars (e.g. glucose, fructose, and sucrose) and sugar alcohols (e.g. sorbitol, mannitol and xylitiol), the products 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 major shortcoming with hydrogenolysis of sugars and sugar alcohols. Among the compounds listed, glycerol, ethylene glycol, and propylene glycol are commercially interesting products.

Adkins et al.[25,26] reported hydrogenolysis of sugars in 1933. 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 consumption of 2-3 moles of hydrogen. In the research work done by Lenth and Dupis[27], hydrogenolysis of crude sugar and molasses was performed with copper aluminum oxide and copper barium chromite as a catalyst and at high pressure in the range of 64-286 bar.

Since the 1950's, hydrogenolysis of sugars or sugar alcohols using nickel on a variety of supports has been widely investigated. Clark et al.[28] was the pioneer for this research at the U.S. Forestry Products Laboratory. In his studies, aqueous solution containing 40 % of 99 % D-sorbitol were used with 1% calcium hydroxide as a promoter and 50 % nickel on kieselguhr catalyst suspended in a slurry with the feed in a stirred reactor. Conditions used were 138-386 bar hydrogen partial pressure, (215 to 245) °C temperature and reaction times up to 400 min to produce glycerol, ethylene glycol, propylene glycol, and other minor products.

Conradin et al.[29] reported that in order to increase the production of propylene glycol, hydrogenolysis should be conducted over a nickel catalyst on a carrier such as magnesium oxide. Conradin et al.[30] also stated that hydrogen splitting of saccharose to glycerol and glycols could be carried out in the presence of a broad range of catalysts, 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.

Sirkar et al.[31] 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.

Other than nickel catalyst, other transition metal catalysts were also applied for hydrogenolysis of sugars or sugar alcohols. Gubitosa et al.[32] discussed the hydrogenolysis of polyhydric alcohols, such as sorbitol, over a ruthenium-on-carbon catalyst. In the examples, he demonstrated that 100 % of the sorbitol was converted, with 41 to 51 % of the product carbon atoms in propylene glycol.

Chopade et al.[33] presented the process for production of glycerol, propylene glycol, and ethylene glycol from sorbitol or xylitol. A preferred process used ruthenium deposited on an alumina, titania, or carbon support. The dispersion of the ruthenium on the support increases during the hydrogenolysis reaction. The reaction was carried out in the vessel, where the reaction mixture containing the base with the catalyst and hydrogen. The operation conditions were in the range of 180 to 250 °C and 34 to140 bar to produce the ethylene glycol and propylene glycol in the reaction mixture.

Werpy et al.[34] reported that methods using a Re-containing multimetallic catalyst for hydrogenolysis of both C-O and C-C bonds. Methods and compositions for reactions of hydrogen over a Re-containing catalyst with compositions containing a 6-carbon sugar, sugar alcohol, or glycerol were described. It has been discovered that reaction with hydrogen over a Re-containing multimetallic catalyst resulted in superior conversion and selectivity to desired products such as propylene glycol.

All sources stated that the aqueous sugar or sugar alcohol reagent was hydrogenolyzed in the presence of various transition metal catalysts. Some hydrogeonlysis also were performed using non-aqueous sugar or sugar alcohol solution. Boelhouwer et al.[35] showed that greater yields (>75 %) of distillable polyalcohols were achieved by using beryllium oxide activated copper chromite catalyst to hydrogenolyze sucrose. The reaction was performed in a rotating autoclave with methanol as the solvent. Experiments were run at a temperature in the range of 195 to 250 ℃, and the hydrogen pressure ranging from 150 to 200 bar. The reaction products were separated by distillation. In one experiment, the glycerol fraction was reported to be 61 % of the product. Glycerol, propylene glycol, and ethylene glycol were included in the products.

Tanikella et al.[36] described the hydrolysis of sorbitol and xylitol in nonaqueous solvents containing at least 10 % (mole fraction) base. The catalyst used in the examples was nickel on silica/alumina. Distribution of ethylene glycol, propylene glycol and glycerol were reported.

Multiple-stage catalytic reaction processes were also proposed for hydrogenolysis of sugar (e.g. glucose, mannose, and sucrose) to produce sugar alcohols and polyols such as glycerol and other polyol products. Huibers et al.[37]

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 to 180 °C and pressures in range of 35 to 345 bar and pH in the range of 4.5 to 7 using an alkali solution as a promoter.

Hellwig et al.[38] disclosed that by using a single or multi-stage upflow ebullated bed catalytic reactor at 90-290 °C temperature and 48-240 bar hydrogen partial pressure, glycerol and glycols can be produced from saccharides. Examples of the conditions used for converting a sorbitol type feed to glycerol in a single stage reaction were about 190 °C temperature, 117 bar hydrogen partial pressure, 1.2 liquid hourly space velocity (LHSV), and using nickel on alumina catalyst to produce roughly 50 % (mass fraction) glycerol and 20 % (mass fraction) ethylene glycol and propylene glycol, with the remainder being methanol, ethanol, isopropanol, and other products.

Chao et al.[39] reported that 15-40 % (mass fraction) sorbitol in water is catalytically hydrocracked in a packed bed reaction process using a high-activity nickel catalyst to produce at least about 30 % conversion to glycerol and glycol products.

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.[40] 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 hydrogenolysis 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 hydrogenolysis selectivity and cleavage percentage. After 1970's, 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.[41] also studied the reaction conditions (temperature, hydrogen pressure, catalyst amount, and agitation rate etc.) affecting the hydrogenolysis of sorbitol and formation of glycerol. They also came up with a rate equation for catalytic sorbitol hydrogenolysis as $-r_s = kC_sP^{-0.8}W^2$ (P=56.2 to 104 bar, W=3.5 to13.8 % (mass fraction) based on sorbitol starting weight). They showed that the rate of sorbitol hydrolysis is first order with respect to sorbitol concentration 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.

1.5.2 Reaction Mechanism

Until recently, hydrogenolysis of sugars or sugar alcohols has not been an industrially important process. The process is not 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. The overall hydrogenolysis of sugars is complex and thus mechanisms for their formation is not well established. 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.

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 were 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.

Montassier et al.[42] 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. 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.

To explain the C-C cleavage in sugar and sugar alcohol hydrogenolysis, Montassier et al. proposed the original mechanism, which is the retro-aldol reaction. 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.[43] suggested the same mechanism, based on their observation that the primary C-C cleavage site is β to the carbonyl group in sugar hydrogenolysis.

Montassier et al. proposed another mechanism, the retro-Claisen reaction for the C-C cleavage in glycerol hydrogenolysis. This mechanism was proposed in order to explain the absence of methanol and the presence of carbon dioxide in the hydrogenolysis products of glycerol and sugar alcohols. The formation of formaldehyde and its subsequent hydrogenation to methanol can be predicted from the retro-aldol reaction. The retro-claisen mechanism allows for formation of formic acid rather than formaldehyde, which decomposes under hydrogenolysis conditions to form CO_2. The retro-claisen was proposed to better explain the experimental hydrogenolysis products obtained from sugars 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 products are ethylene glycol and erythritol. Propylene glycol is formed by the hydrogenation of glycerol. 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.[44] identified the retro-aldol reaction of a β-hydroxyl carbonyl precursor as the C-C cleavage mechanism and excluded the other mechanisms.

Table 1.1 Sugar supply and use in the United States of America.

Item	2005/2006	2006-2007	2007/2008	
			October	November
	1,000 short tons, raw value			
Beginning stocks	1,332	1,698	1,750	1,787
Production	7,399	8,435	8,446	8,450
Beet sugar	4,444	5,002	4,764	4,791
Cane sugar	2,955	3,433	3,682	3,659
Imports	3,443	2,080	2,123	2,193
Total supply	12,174	12,213	12,319	12,430
Exports	203	422	250	250
Deliveries	10,341	10,125	10,170	10,300
Total use	10,478	10,426	10,420	10,550
Ending stocks	1,698	1,787	1,899	1,880

Table 1.2 Average costs of producing raw cane sugar, beet sugar, and high fructose syrup, by categories of world producers, 2000/01-2005/06.

Category	2001/02	2002/03	2003/04	2004/05	2005/06
	Cents/pound				
	Raw cane sugar				
Low-cost producers 1/	7.23	6.59	7.01	7.52	8.69
Major exporter 2/	7.73	7.07	7.50	8.08	9.20
Cane sugar, White value equivalent					
Low-cost producers 1/	10.80	10.11	10.56	11.12	12.39
Major exporter 2/	11.35	10.63	11.10	11.72	12.94
Beet sugar, refined value					
Low-cost producer 3/	20.89	18.51	21.01	20.71	21.22
High fructose corn syrup					
Low-cost producers 4/	10.90	11.07	11.38	11.52	11.50

1/ Average of 10 producing regions: Australia, Brazil, Columbia, Ethiopia, Guatemala, Malawi, Sudan, Swaziland, Zambia, and Zimbabwe 2/ Average of 6 countries: Australia, Brazil, Columbia, Guatemala, South Africa, and Thailand 3/ Average of 7 countries: Chile, China, Czech Republic, France, United Kingdom, Red river valley(US), and Pacific Northwest(US) 4/ Average of 6 countries: Argentina, Bularia, Canada, Egypt, Hungary, and United States.

Table 1.3 Costs of feed stocks for chemical industry.

Feed Stock	Approximate price	Approximate price in $/lb
Petroleum	$90/barrel	$0.26
Corn	$5 per cwt	$0.05
Soybeans	$10 per cwt	$0.10
Crude glycerin	-	$0.05-$0.20
Sugars from corn	-	$0.20 or less

Table 1.4 Examples of chemical products from fermentation of carbohydrates.

Chemical	Substrate(s)	Microorganism(s)
Aceticacid	Various sugars	Acetobacter aceti Clostridium Thermoaceticum Pachysolen tannophius
Acetone	Various sugars	Clostridium sp.
2,3-Butanediol	Various sugars and acids	Aerobacter aerogenes Bacillus polymyxa Klebsiella oxytoca K. pneuminiae
n-Butanol	Various sugars and organics	Clostridium sp.
Butyraldehyde	Glucose	Clstridium acetobutrylium
Butyric acid	Various sugars	Clostridium sp.
Citric acid	Various sugars	Aspergillus niger Saccharomycopsis lipolytica
Ethanol	Various sugars	Kluyberomyces sp. Candida utilis Saccharomyces cerevisiae Zymomonas mobilis
C12-C20 fatty acids	Sucrose	Bacteria, mold, yeast
Gluconic	Glucose	Aspergillus niger Gluconobacter suboxydans
Isopropyl alcohol	Various sugars	Clostridium sp.
Itaconic acid	Glucose, sucrose	Aspergillus itaconicus Ustiago zeae A. terreus
Linoleic acid	Glucose, lactose	C, curvata
Linolenic acid	Various sugars	Mortierella ramammiana
Oleic acid	Glucose, lactose	C. curvata
Palmitic acid	Glucose, Lactose	C. curvata
Propanediol	Algal biomass, glucose	Clostridium pasteurianum C. thermosaccharolyticum

n-Propanol	Glucose	Clostridium fallax
Propoinic acid	Various sugars	Clostridium sp. Propionibacterium shermanii
Pyruvic acid	Glucose	Pseudomonas aeruginosa
Stearic acid	Glucose, lactose	C. curvata
Succinic acid	Various sugars	Many species

Table 1.5 Fatty ester hydrogenolysis catalysts.

General Type	Typical Atomic Weight Percentages					Application
	Cu	Cr	Ba	Mn	Zn	
Unpromoted copper chromite	40	26				Resistant to free fatty acid
	38	30				
Ba-promoted copper chromite	37	32	11			Ba provides better thermal resistance and hinders agglomeration of Cu
	33	30	8			
	34	27	7			
Ba and Mn promoted copper chromite	37	32	3	3		Mn retards complete reduction of CuO assuring active double bond isomerization and hydrogenation.
Mn-promoted copper chromite	39	37		3		Mn retards complete reduction of CuO assuring active double-bond isomerization and hydrogenation.
	28	34		25		
	36	33		3		
Unpromoted copper chromite	Low ratio of Cu/Cr=0.7					Lower activity but higher resistance to acid attack
Zinc chromite		23			48	Highly selective. Will not hydrogenate double bonds, but less active
Raney/sponge copper	1-6% residual aluminum					Used in slurry system

Table 1.6 Summary of catalysts for hydrogenolysis reaction.

Supplier	**Description**
Johnson Matthey	5% Ru/C
Johnson Matthey	5% Ru/Alumina
Degussa	5% Pd/C
Degussa	10% Pd/C
PMC Chemicals	10% Pd/C
PMC Chemicals	20% Pd/C
Grace Davision	Raney Nickel
Grace Davision	Raney Copper
Sud-Chemie	Copper
Sud-Chemie	Copper-chromite
Johnson Matthey	Ni/C
Alfa-Aesar	Ni/Silica-Alumina

2 CHAPTER 2

VAPOR PRESSURES ESTIMATION AND EVAPORATION STUDIES OF SUGAR/SUGAR ALCOHOL

Abstract

The use of heterogeneous catalysts for conversion of sugars and sugar alcohols to value-added chemicals has been widely studied in liquid phases. Low selectivities and high costs associated with catalyst recovery have substantially limited commercialization of these processes. Gas phase packed-bed catalysis has recently been successful in overcoming these obstacles for the hydrogenolysis of glycerol to propylene glycol. In this paper, the evaporation of glucose and sorbitol was investigated to identify potential conditions for gas phase conversions of these sugars. In our studies, vapor pressures of sorbitol were estimated in a wider temperature range of (250 to 350) °C than work done by Guido et al. (J. Chem. Soc. Faraday Trans. 1990, 86, 75-79.) at (177 to 227) °C. A thermogravimetric analysis (TGA) method was used to estimate a boiling point of 362 °C for sorbitol with sorbitol's vapor pressure following a Clausius-Clapeyron model behavior. In addition, evaporation studies demonstrated sobitol evaporation and condensation on a practical level. The evaporation of sorbitol was experimentally validated with no decomposition at 0.1 bar and 294 °C and 2.5 % (mass fraction) in water. The evaporation of high-concentration sorbitol feed can be achieved by mixing with a high-temperature gas (e.g. steam).

Glucose evaporated with partial decomposition at temperatures as low as 220 °C.

Keywords: Evaporation, Glucose, Sorbitol, Vapor pressure, Thermogravimetric analysis

2.1 Introduction and background

Sugars and sugar alcohols have been considered as bio-based feedstocks to produce many of the chemicals in common use, which are derived from petroleum feedstocks. Utilization of bio-based materials will help overcome energy shortage and prevent serious environmental pollution. Heterogeneous hydrogenolysis is one means to convert sugars to value-added chemicals[45].

Conradin et al.[46,47,48], Clack et al.[49] and Sirkar et al.[50] reported that hydrogenolysis of aqueous sorbitol solution to glycerol and propylene glycol can be carried out in the presence of a broad range of catalyst (e.g. Ni/Cu catalyst) and enhanced by the addition of base. The product distribution by mass was about 43 % glycerol and 25 % propylene glycol with 83 % conversion at (80 to 140) bar and (200 to 260) °C.

Tanikella et al.[51] and Van Ling et al.[52] described the hydrogenolysis of sorbitol and xylitol in non-aqueous solvents containing a mole fraction of 10 % of base (e.g. KOH). The catalyst used was nickel on silica/alumina. Distribution of ethylene glycol, propylene glycol and glycerol were reported.

Gubitosa et al.[53] discussed the hydrogenolysis of polyhydric alcohols, such as sorbitol, over a ruthenium-on-carbon catalyst. In the examples, it was reported that 100 % of the sorbitol can be converted, with (41 to 51) % of the product carbon atoms in propylene glycol.

Usually, these batch hydrogenolysis reactions usually were carried out at (140 to 350) bar in the presence of hydrogen, at temperatures of (200 to 250) °C, with residence times in excess of 1.5 h and in the presence of a slurry of catalyst.

Liquid-phase packed-bed reactions were performed by Hellwig et al. [54] Hydrogenolysis reactions were performed in a single or multi-stage packed bed catalytic reactor at (100 to 300) °C temperature and (50 to 240) bar hydrogen partial pressure, 1.2 liquid hourly space velocity and using nickel on alumina catalyst to produce 50 % mass fraction glycerol and 20 % mass fraction propylene glycol from sorbitol type feed.

To date, low selectivities, high pressure, and catalyst recovery has limited the potential of these technologies. Thus, there is a need for new methods of converting sugars and sugar alcohols to high value chemicals such as propylene glycol and 1,3-propanediol. Gas phase catalytic hydrogenolysis may be one feasible way in sugar conversion for achieving continuous operations and reduced reaction conditions, particularly using improved catalysts in packed-bed reactors. To achieve this, it is necessary to understand how to evaporate sugars and sugar alcohols with minimal degradation prior to gas phase catalytic hydrogenolysis in packed-bed reactor. Traditional methods used to evaluate vapor pressures and determine boiling points cannot be used due to decomposition of C4 and higher sugars.

Guido et al.[55] reported that the vaporization of sorbitol was determined from the temperature dependence of its vapor pressure, as measured by torsion-effusion method. In Guido's study, the vapor pressures were estimated in the temperature range of (177 to 227) °C. This paper evaluates vapor pressures at higher temperatures and uses an experimental system to validate the ability to evaporate and recover/condense sorbitol vapors. A Thermogravimetric analysis (TGA) technique was adopted for vapor pressure estimation. Goodrum et al.[56] discussed the estimation of vapor pressure and boiling points using TGA method. A TGA laser-drilled capsule method provided a method of obtaining vapor pressures and boiling points. However, the diameter of laser-drilled hole had significant influence on the accuracy of this method. The laser-drilled hole must be small enough to restrict diffusion out of the sample container to a rate less than the vaporization rate inside the container, yet have sufficient diameter to prevent any self-pressurization. An alternative method was reported by Guckel et al.[57] In this method, an open sample tray instead of a laser-drilled container was evaluated using isothermal thermogravimetry to the measurement of evaporation rates. These evaporation rates correlated well with vapor pressures. This method provides rapid, simple and accurate measurement.

Guckel et al.[57] suggested that the logarithm of the evaporation rate at a given temperature was linearly proportional to the logarithm of vapor pressure, as shown in eq 1. This linearly relationship is independent of the sample and the temperature range of analysis.

The constants, a and b, are dependent on the instrument, operational parameters (e.g. gas purge rate), and sample containment procedure[58].

$$\ln(p/\mathrm{bar}) = a \ln(k/\%\cdot\mathrm{min}^{-1}) + b \tag{1}$$

where p is the vapor pressure at a given temperature, and k is the corresponding evaporation rate. This equation and method were adopted in this paper. Rapid evaluation, as possible with mg samples in thermogravimetric analysis (TGA) methods, and analysis at lower temperatures reduces sugar degradation during this method.

Compared with glycerol and ethylene glycol, sugars and sugar alcohols are more difficult to evaporate since they have higher boiling points than glycerol and ethylene glycol (290 °C and 197.3 °C, respectively); sugars and sugar alcohols tend to decompose at temperature lower than their boiling points during the evaporation process. For practical applications, degradation during evaporation can be reduced by dilution (e.g. with water or hydrogen) or by the reducing system pressure. Another means to prevent the degradation or side reactions is direct contact heating by mixing the sugars with high-temperature steam. Both of these "practical" methods were evaluated in this paper to correlate with TGA-based vapor pressure estimates.

2.2 Experimental methods

2.2.1 Materials

Glucose (99.9 %), sorbitol (99.9 %), sucrose (99.9 %), glycerol (99.9 %) and methanol (HPLC grade) were purchased from Sigma-Aldrich (Milwaukee, WI). High purity grade nitrogen and helium were obtained from Praxair (Dunbury, CT).

2.2.2 Experimental setup

Figure 2.1 provides a schematic of Evaporation System I, including the evaporator, trap, air-cooled condenser and ice-water condenser, for sugar and sugar alcohol evaporation studies. The trap was for gas-liquid separation. Two condensers were used to achieve better condensation at lower pressures. The temperatures of evaporator and trap were controlled using a Single Display Proportional-Integral-Derivative (PID) Controller (Winona, MN). The pressure was indicated and controlled by a GAST vacuum pump (Benton Harbor, MI). While the system reached the desired conditions, the aqueous feed (initial sugar or sugar alcohol mass fraction in solution was 2.5 %) was pumped into the evaporation system by a micro-pump at 200 $g \cdot h^{-1}$. The evaporation samples were collected from the ice-water condenser and analyzed by thermogravimetric analysis (TGA), high performance liquid chromatography (HPLC) and gas chromatography (GC) without further delay. In this study, sugar or sugar alcohol was recovered in the condenser, accumulated in the trap, or decomposed. The recovered portion was reported, evidence of decomposition was reported if observed in GC results, and/ or the amount remaining in the trap was quantified.

Figure 2.2 shows a schematic of Evaporation System II, in which sorbitol was evaporated by mixing with high-temperature steam. The aim of this system was to reduce sugar degradation that can result for prolonged exposure of concentrated sugar on hot surfaces. In addition, the use of fine sprays can significantly reduce the time the sugar exists as a liquid before evaporating. The flow rate of steam was controlled by a valve. The steam temperature and sorbitol feed (mass fraction is 67 %) pre-heated temperature were controlled using a Single Display Proportional-Integral-Derivative Controller. The temperature after mixing was recorded as were the feed temperatures (as controlled). The vapors were condensed after passing through the trap and the sugar content of the condensate was evaluated as previously described.

2.2.3 Thermogravimetric methodology

Condensate samples were taken at regular time intervals and analyzed with a Q50 Series Thermogravimetric Analyzer (TGA) with TA5000 Advantage software to determine the mass concentration of non-volatiles in the samples. Samples were first equilibrated at 25 °C, heated up to 400 °C at the rate of 10 $°C \cdot min^{-1}$, and maintained 400 °C for 10 min. Thermogravimetric analysis was carried out under a nitrogen purge at a constant rate of 50 $mL \cdot min^{-1}$ to prevent any oxidation of samples. The mass fraction of non-volatiles was determined from TGA. Recovery of non-volatiles was calculated assuming all the water fed to the system condensed in the condenser and was defined as the ratio of the mass of non-volatile matter in the condensate divided by the mass of sugar or sugar alcohol fed to the system (based on measured flow rates and mass fractions in each stream).

To estimate vapor pressure using the isothermal TGA method, the sample was heated from 25 °C to the desired temperature at a heating rate of 50 °C·min^{-1} and held at the desired temperature for 30 min. The sample mass fraction loss was monitored with time throughout the experiment. The evaporation rate at a given temperature was obtained by calculating the rate of mass fraction loss with time.

2.2.3.1 Chromatographic analysis

For sugar analysis, the samples were analyzed with a Hewlett-Packard 1100 high performance liquid chromatography with an Alltech ELSD 500 evaporative light-scattering detector (Alltech Associates Inc. Deerfield, IL). An Alltech HPLC silica based column (Apollo, 250 mm × 4.6 mm, 5 μm) was used for separation. The ELSD drift tube temperature was set at 75 °C. The nitrogen gas flow rate of the nebulizer was set at 4.97 L·min^{-1} and a pressure of 0.56 bar. Autoinjection was in a 30 μL loop. The eluent flow rate was 1 mL·min^{-1} at room temperature. The eluent mixture had a volume fraction of 97 % methanol and 3 % water. The samples were placed in the oven at 80 °C for (12 to 24) h to remove water and dissolved in methanol prior to analysis. The calibration curves of sugar and sugar alcohol were prepared and the mass fractions of sugar or sugar alcohol were determined from calibration curves. Recovery of sugar or sugar alcohol is defined as the ratio of numbers of grams of sugar or sugar alcohol from the condenser to the number of grams of sugar or sugar alcohol initially present.

The samples were also analyzed with a Hewlett-Packard 6890 (Wilmington, DE) gas chromatograph equipped with a flame ionization detector and mass spectra detector. A J&W Scientific Inc. (Folsom, CA) DB-WAX 123-7033 GC column (30 m × 320 µm × 0.5 µm) was used for separation. The detector and injector temperatures were 250 ℃ and 230 ℃, respectively; and the oven temperature was programmed at 10 ℃·min^{-1} from 45 ℃ to 200 ℃ and 15 ℃·min^{-1} to final temperature of 225 ℃, which was held for 10 min. Helium was used as carrier gas at a flow rate of 1.0 mL·min^{-1}, the split ratio was 1:120.

2.3 Results and discussion

2.3.1 Evaporation study of sorbitol

Sorbitol, a 6-carbon sugar alcohol exists as a white powder at room temperature with a melting point of 95 ℃. Preliminary studies showed that evaporation at 1 bar and (270 to 300) ℃ could not achieve good recovery of sorbitol. Therefore, lower pressures were applied at 294 ℃. As summarized by Table 2.1, pressure played a significant role in the evaporation of sorbitol in water.

The highest sorbitol recovery was 88.6 %, corresponding to the lowest pressure of 0.1 bar. Recovery decreased to 26.9 % when pressure increased up to 1 bar. The sorbitol, which can not be evaporated, accumulated in the trap. With increasing pressure, the amount of residual sorbitol in the trap increased correspondingly. This observation confirmed that lower pressure could achieve better sorbitol evaporation.

To investigate the effect of temperature on sorbitol evaporation, evaporation experiment was performed at the pressure of 0.1 bar and the range of temperatures as summarized in Table 2.2. Recovery of sorbitol dropped from 88.6 % at 294 °C and 51.1 % at 280 °C. No degradation by GC analysis or discolorization was observed over this temperature range. Increased evaporation with increasing temperatures qualitatively agrees with theory.

Figure 2.3 shows the GC analysis of the effluent condensate. The GC will not pick up the sorbitol and verifies the absence of more-volatile decomposition products. HPLC analysis of the condensate confirmed a high yield of sorbitol. No discoloration of the condensate was observed at the lower pressures.

Evaporation System II was used to evaluate direct contact evaporation for comparison to the Table 2.1 and Table 2.2 results. In this study, the flow rate of steam was maintained at 318 $g \cdot h^{-1}$ and the temperature of the preheated 67 % mass fraction of sorbitol feed was maintained 120 °C. The evaporation experiments were performed at different sorbitol feed flow rates of (54 to 120) $g \cdot h^{-1}$ and steam temperatures of (210 to 250) °C. Tables 2.3 and 2.4 summarize the sorbitol recoveries. When the feed flow rate increased (Table 2.3), the sorbitol mass fraction in the effluent decreased from 10.4 % to 1.4 % and the recovery of sorbitol decreased from 91.2 % to 5.3 %, which was due to higher flow rates causing lower temperatures after the mixing of the steam with the sorbitol. The mixture temperature and pressure are the intensive properties that specify the vapor-liquid equilibrium in the trap.

Increasing steam temperatures caused the sorbitol fraction in the effluent to increase dramatically (Table 2.4). The GC analysis verified the absence of decomposition products. The condensate from Evaporation System II contained up to 10 % mass fraction of sorbitol, which is considerably greater than the maximum of 2.3 % for Evaporation System I.

Sorbitol evaporation in the Evaporation System II would be characterized as direct contact heating with steam followed by adiabatic flash separation. This process was simulated using ChemCad simulation software. Simulation results for evaporation of 67 % mass fraction of sorbitol feed with high-temperature steam are summarized in Table 2.5, Table 2.6 and Figure 2.4. This simulation confirmed the significant effect of feed flow rate and steam temperature. The simulations were performed prior to experimentation to confirm that experiments were being conducted at temperatures and pressures that would produce a vapor containing up to 10 % mass fraction of sorbitol.

The simulated recoveries and adiabatic mixing temperatures were higher than with the experimental data. Lower experimental temperatures were likely due to heat losses from the tubing. Tables 2.3 and 2.4 include simulation results adjacent to the experimental results where the simulation was modified to provide the same adiabatic mixing (effluent) temperature as was observed in the experimental system.

2.3.2 Evaporation study of glucose

The evaporation of glucose was evaluated at (280 to 290) °C and at (0.1 to 0.5) bar. The results are summarized in Table 2.7. Figure 2.3 compares the gas chromatography of the glucose condensate to the sorbitol condensate. The presence of decomposition products (e.g. acetol, furfural), a dark tint to the condensate, and smell of burnt sugar all substantiate that the glucose underwent decomposition. Increasing decomposition of glucose to non-volatiles components at higher temperatures was qualitatively observed as would be expected.

The glucose studies were repeated with a 1 % mass fraction of aqueous glucose feed at (220 to 280) °C and pressure of 0.1 bar. Less than 10 % of glucose was recovered in the condensate.

Based on the data of Tables 2.1 through 2.4, sorbitol can be successfully evaporated at mass fraction up to 10 %, while glucose degraded at pressures as low as 0.1 bar. This did confirm that sorbitol was undergoing a true evaporation as opposed to entrainment in the vapor. If the experimental system promoted entrainment, sorbitol and glucose should have experienced similar degrees of entrainment.

2.3.3 Vapor studies

TGA analysis of glycerol, sorbitol, glucose and sucrose was performed at a constant heating rate of 10 $°C\cdot min^{-1}$. As the results (Figure 2.5) indicate, the thermograms of glycerol and sorbitol exhibit a rapidly increasing rate of mass fraction loss with increasing temperatures until no sample remains—

characteristic of an evaporation process. However, the thermograms for glucose and sucrose have multiple inflection points and do not proceed to zero mass at the temperature range of the study—characteristic of decomposition with eventual formation of char.

These results are consistent with the evaporation studies in two evaporator systems. Since the sorbitol appeared to evaporate, an isothermal TGA method was used for vapor pressure estimation.

Glycerol was used as a reference compound to calibrate the TGA instrument and experimental conditions by the method prescribed by Wiedemann.[59] Figure 2.6 showed a set of representative experimental time constants (TGA thermograms) depicting mass loss from 190 °C to 270 °C for glycerol. Figure 2.7 illustrates similar TGA thermograms from 250 °C to 350 °C for sorbitol.

The thermograms are nearly linear indicating that the evaporation followed apparent zero-order kinetics. This is consistent with an evaporation mechanism in the method developed by Guckel et al.[57] The respective zero-order rate constants for evaporation are equal to the slope of each isothermal as reported in Table 2.8. The slopes were estimated using linear regression. Glycerol's vapor pressure data[60] were used to obtain the constants for the characteristic equation for this TGA (see eq 1).

Figure 2.8 illustrates the nice correlation of glycerol's evaporation rates versus vapor pressure. The characteristic eq 1 constants were: a at 1.43 with standard deviation of 0.09 and b at -5.73 with standard deviation of 0.25 (see eq 2). As indicated earlier, these constants are instrument specific and are valid for any chemicals evaluated at the same conditions. Eq 2 was thus used to convert sorbitol evaporation rates to vapor pressures as reported in Table 2.9.

$$\ln(p/\text{bar}) = 1.43 \ln(k/\%\cdot\text{min}^{-1}) - 5.73 \tag{2}$$

2.3.4 Clausius-Clapeyron relation

The isothermal TGA analysis of sorbitol were also carried out at (250 to 350) °C. The thermograms over this range of temperatures were consistent with evaporation without degradation.

The Clausius-Clapeyron relation is widely used in chemistry and chemical engineering to model vapor pressures of pure substances. The equation is as follows:

$$\ln(p/\text{bar}) = A/(T/K) + B \tag{3}$$

where p is the vapor pressure and T is the absolute temperature. A and B are constants fundamentally related to the enthalpy and entropy of vaporization.[61, 62] Linear regression of the Table 2.9 vapor pressure for sorbitol estimated A at -12703 with a standard deviation of 292 and B at 20.01 with standard deviation of 0.51. Figure 2.9 illustrates the correlation of sorbitol's vapor pressure with temperature. The vapor pressures correlate well with the Clausius-Clapeyron model.

The TGA method for vapor pressure estimation is consistent with the previous work done by Guido et al[55] (Figure 2.4). These regression results predict sorbitol's boiling point at 362 °C. Based on the previous work done by Guido et al[55], the predicted boiling point of sorbitol is 624 °C. The difference is due to greater extrapolation needed to project a boiling point based on Guido's data that are at lower temperatures. The results from the present TGA studies are extrapolated by about 12 °C, and so, are expected to be accurate to within about 2 °C.

Based on these results, sorbitol can be successfully evaporated either at low pressures or by mixing with high-temperature steam. This provides a possible operating window for gas phase catalytic conversion of sorbitol to value-added chemicals.

2.4 Conclusion

Vapor pressures of sorbitol were estimated by an isothermal TGA method and modeled using the Clausius-Clapeyron equation. The results provided an improved estimate for sorbitol's boiling point at 362 °C. Evaporation studies validated that low-concentration sorbitol feed could be evaporated at high temperatures and low pressures. High pressure steam was able to evaporate concentration sorbitol feed to produce vapors of up to 10 % mass fraction sorbitol with no noticeable decomposition of the sorbitol. Experimental data accurately followed process simulation based on the estimated vapor pressures. The combined use of the TGA method, fitting to a theory-based model, process simulation of anticipated performance, and experimental validation of the process simulation provide great certainty on the ability to produce vapor-phase sorbitol at concentrations which are sufficiently high for practical packed-bed catalysis. While only 10 % mass fraction vapor phase were validated, staged evaporation-reaction approaches would allow for much higher “effective” sorbitol concentrations to be used in the gas phase catalytic processes.

Table 2.1 Evaporation of 2.5 % (mass fraction) sorbitol feed at different pressures p with evaporation system I. Recovery* denotes the recovery of non-volatiles from TGA analysis. Recovery denotes the recovery of sorbitol from HPLC analysis.

t/(℃)	p/(bar)	Recovery*/(%)	Recovery/(%)
294	0.1	90.8±0.4	88.6±0.3
294	0.2	75.2±0.6	74.3±0.5
294	0.3	55.1±0.5	53.9±0.6
294	0.5	41.5±0.3	40.2±0.4
294	0.7	35.7±0.6	34.3±0.5
294	1.0	28.1±0.5	26.9±0.6

Table 2.2 Evaporation of 2.5 % (mass fraction) sorbitol feed at different temperatures t with evaporation system I. Recovery* denotes the recovery of non-volatiles from TGA analysis. Recovery denotes the recovery of sorbitol from HPLC analysis.

t/(℃)	p/(bar)	Recovery*/(%)	Recovery/(%)
280	0.1	51.8±0.5	51.1±0.6
285	0.1	64.5±0.4	63.3±0.4
290	0.1	77.9±0.6	75.6±0.5
292	0.1	83.9±0.7	81.7±0.5
294	0.1	90.8±0.3	88.6±0.7

Table 2.3 Evaporation of 67 % (mass fraction) sorbitol feed at different feed flow rates Q with evaporation system II. Feed flow rate, Q; Steam temperature, t1, Sorbitol feed temperature, t2; Mixing temperature, t3; Sorbitol mass fraction in effluents, C; Recovery denotes the recovery of sorbitol from HPLC analysis. C† denotes the simulated sorbitol mass fraction in effluents at same mixing temperature.

$Q/(g\cdot h^{-1})$	t1/(℃)	t2/(℃)	t3/(℃)	C/(%)	Recovery/(%)	C†/(%)
54	250	120	243	10.4±0.3	91.2±0.5	9.7
84	250	120	229	5.1±0.2	28.5±0.3	4.9
120	250	120	210	1.4±0.2	5.3±0.2	1.9

Table 2.4 Evaporation of 67 % (mass fraction) sorbitol feed at different steam temperatures t with evaporation system II. Feed flow rate Q, Steam temperature, t1; Sorbitol feed temperature, t2; Mixing temperature, t3; Sorbitol mass fraction in effluents, C; Recovery denotes the recovery of sorbitol from HPLC analysis. C† denotes the simulated sorbitol mass fraction in effluents at same mixing temperature.

$Q/(g \cdot h^{-1})$	t1/(℃)	t2/(℃)	t3/(℃)	C/(%)	Recovery/(%)	C†/(%)
54	210	120	206	0.2±0.1	1.7±0.2	1.0
54	230	120	221	3.4±0.2	29.7±0.3	3.2
54	250	120	243	10.4±0.3	91.2±0.5	9.7

Table 2.5 Simulation results of evaporation of 67 % (mass fraction) sorbitol feed at different MFR. Steam temperature, t1; Sorbitol feed temperature, t2; Mixing temperature, t3; Mass flow ratio of feed over steam, MFR; Sorbitol mass fraction in effluents, C; Recovery denotes the recovery of sorbitol from HPLC analysis.

t1/(℃)	t2/(℃)	t3/(℃)	MFR/(%)	C/(%)	Recovery/(%)
250	120	254	0.17	9.7	100
250	120	242	0.26	7.9	52.9
250	120	232	0.38	5.0	23.5

Table 2.6 Simulation results of evaporation of 67 % (mass fraction) sorbitol feed at different steam temperatures. Steam temperature, t1; Sorbitol feed temperature, t2; Mixing temperature, t3; Mass flow ratio of feed over steam, MFR; Sorbitol mass fraction in effluents, C; Recovery denotes the recovery of sorbitol from HPLC analysis.

t1/(℃)	t2/(℃)	t3/(℃)	MFR/(%)	C/(%)	Recovery/(%)
210	120	237	0.17	6.1	60.7
230	120	243	0.17	8.4	85.4
250	120	254	0.17	9.7	100

Table 2.7 Evaporation of 2.5 % (mass fraction) glucose feed at different temperatures t and pressures p. Recovery* denotes the recovery of non-volatiles from TGA analysis. Recovery denotes the recovery of glucose from HPLC analysis.

t/(℃)	p/(bar)	Recovery*/(%)	Recovery/(%)
280	0.1	1.1±0.2	1.2±0.1
285	0.1	2.0±0.2	1.8±0.2
290	0.1	4.5±0.3	3.5±0.3
290	0.3	2.5±0.2	2.7±0.3
290	0.5	1.9±0.2	1.8±0.2

Table 2.8 Glycerol evaporation rates k and vapor pressures p

t/(°C)	k/(%·min^{-1})	10^2 ·p/(bar)
190	5.89±0.15	3.85±0.02
210	9.08±0.17	8.64±0.03
230	16.7±0.20	17.9±0.03
250	28.9±0.35	34.5±0.07
270	36.5±0.40	62.6±0.09

Table 2.9 Sorbitol evaporation rates k and estimated vapor pressures p

t/(°C)	k/(%·min^{-1})	10^2 ·p/(bar)
250	2.65±0.08	1.31±0.01
275	6.27±0.11	4.49±0.01
300	12.7±0.15	12.3±0.02
325	23.6±0.32	30.0±0.06
350	40.5±0.45	65.0±0.10

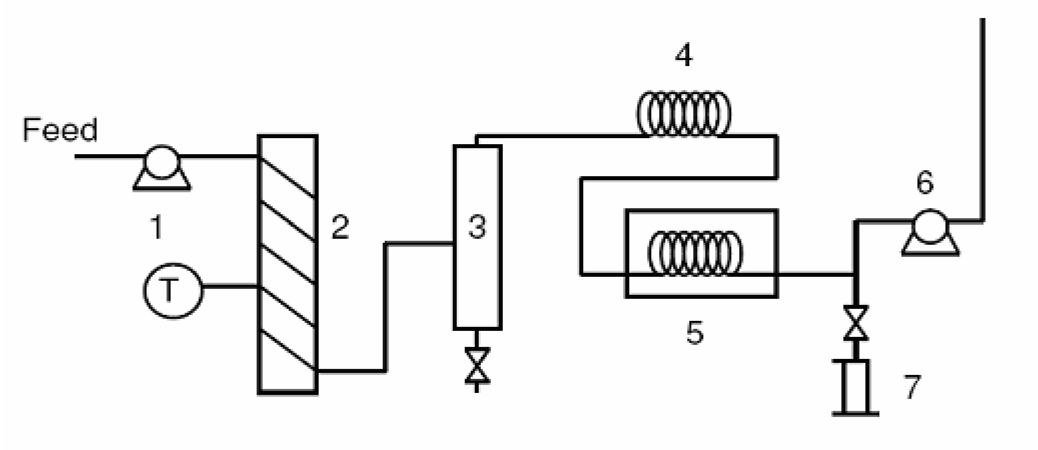


Figure 2.1 Evaporation System I. The different components are: 1, Feed pump; 2, Evaporator; 3, Trap; 4, Air-cooled condenser; 5, Ice-water condenser; 6, Vacuum pump; 7, Product collector.

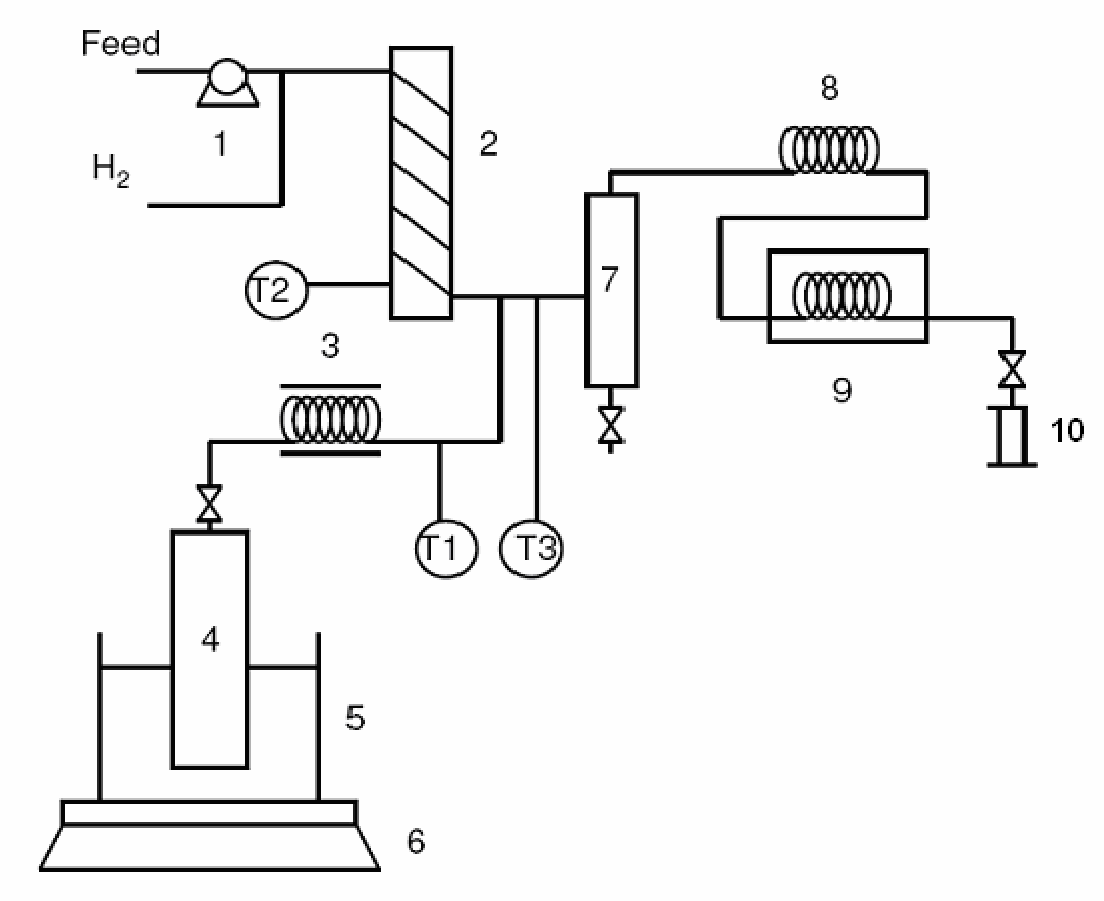


Figure 2.2 Evaporation System II. The different components are: 1, Feed pump; 2, Pre-heater; 3, Heater; 4, Steam vessel; 5, Oil bath; 6, Hot plate; 7, Trap; 8, Air-cooled condenser; 9, Ice-water condenser; 10, Product collector.

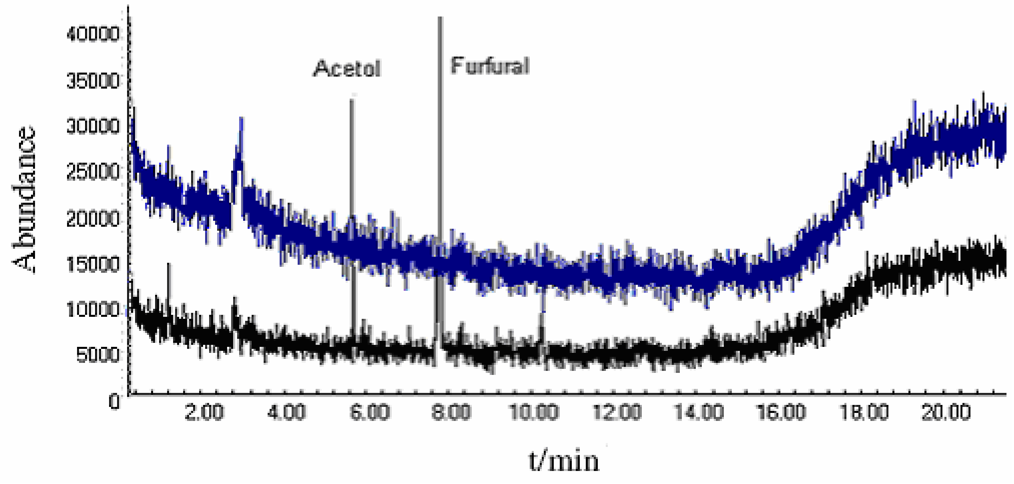
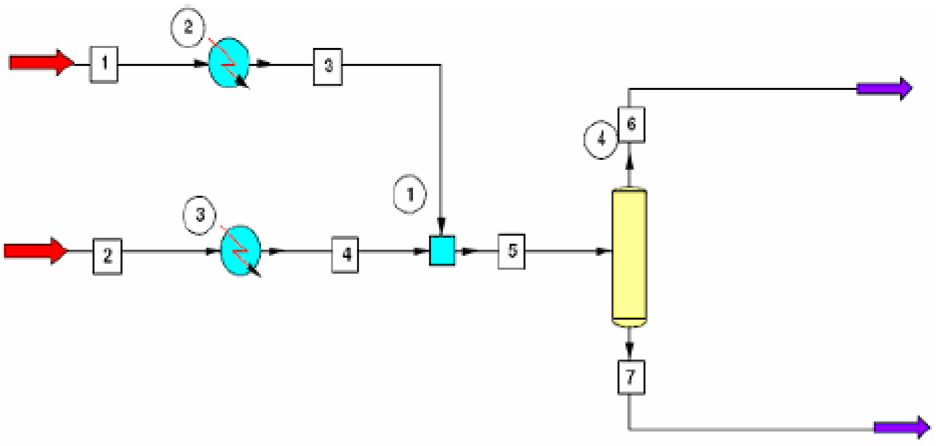


Figure 2.3 **Gas chromatography of evaporation samples of sorbitol and glucose. The upper curve is for sorbitol evaporation sample. The lower curve is for glucose evaporation sample.**



Stream No	1	2	3	4	5	6	7
Mass flow, g/h	318	54	318	54	372	372	0
Temp, °C	25	25	349.6	120	254.2	254.4	0
Vapor mass fraction	0	0	1	0.196	1	1	0
Vapor mass flow, g/h	0	0	318	10.6	372	372	0
Liquid mass flow, g/h	318	54	0	43.4	0	0	0
Flow rates in g/h							
Water	318	17.8	318	17.8	335.8	335.8	0
Sorbitol	0	36.2	0	36.2	36.2	36.2	0

Figure 2.4 Simulation results of evaporation of 67 % (mass fraction) sorbitol feed at the conditions shown below. Steam temperature *t1*: 250 °C, Sorbitol feed temperature *t2*: 120 °C, Mass flow ratio of feed over steam MFR: 0.17.

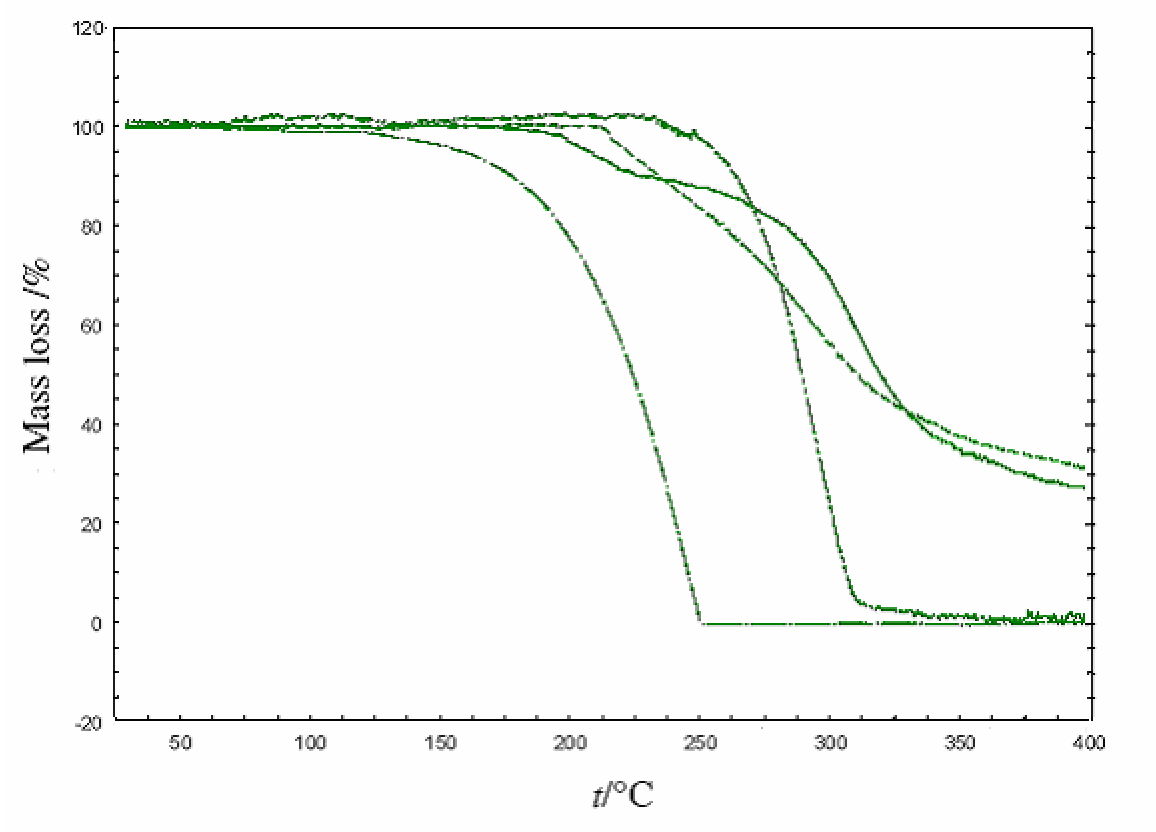


Figure 2.5 Mass fraction loss analysis of glycerol, sorbitol, glucose and sucrose. ——— , glucose; - - - - , sucrose; —— - · , glycerol; —— - - , sorbitol.

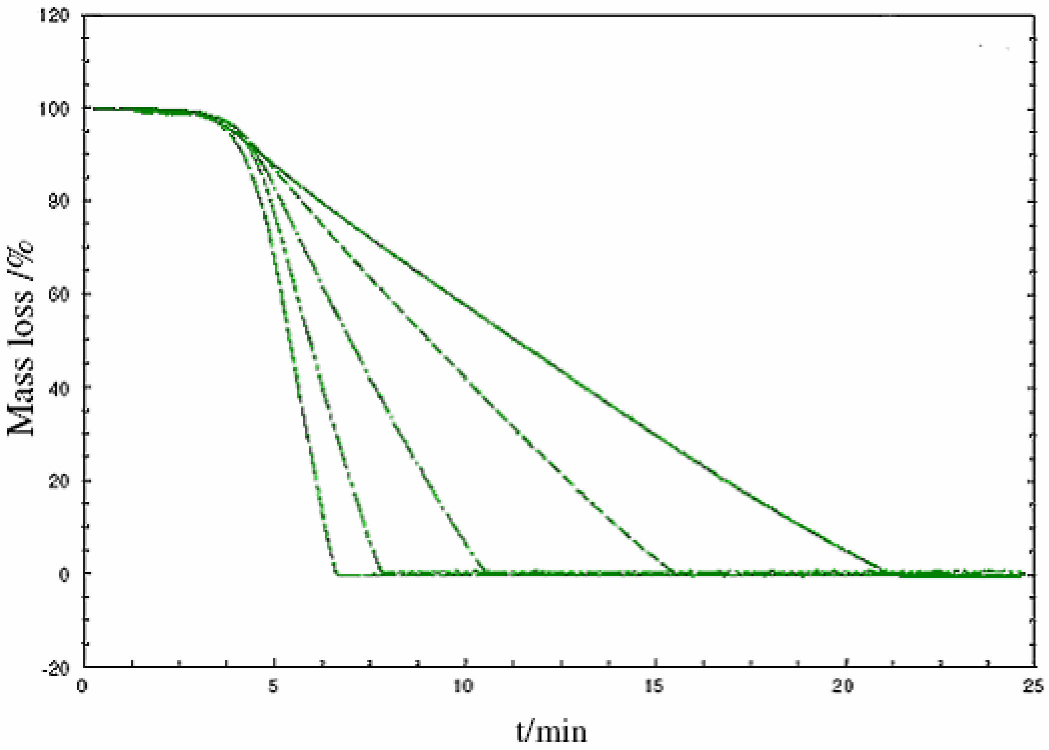


Figure 2.6 The mass fraction loss from isothermal thermogravimetric analysis of glycerol. ——, 190 °C; ---- , 210 °C; —-·, 230 °C; —-- , 250 °C; — —, 270 °C.

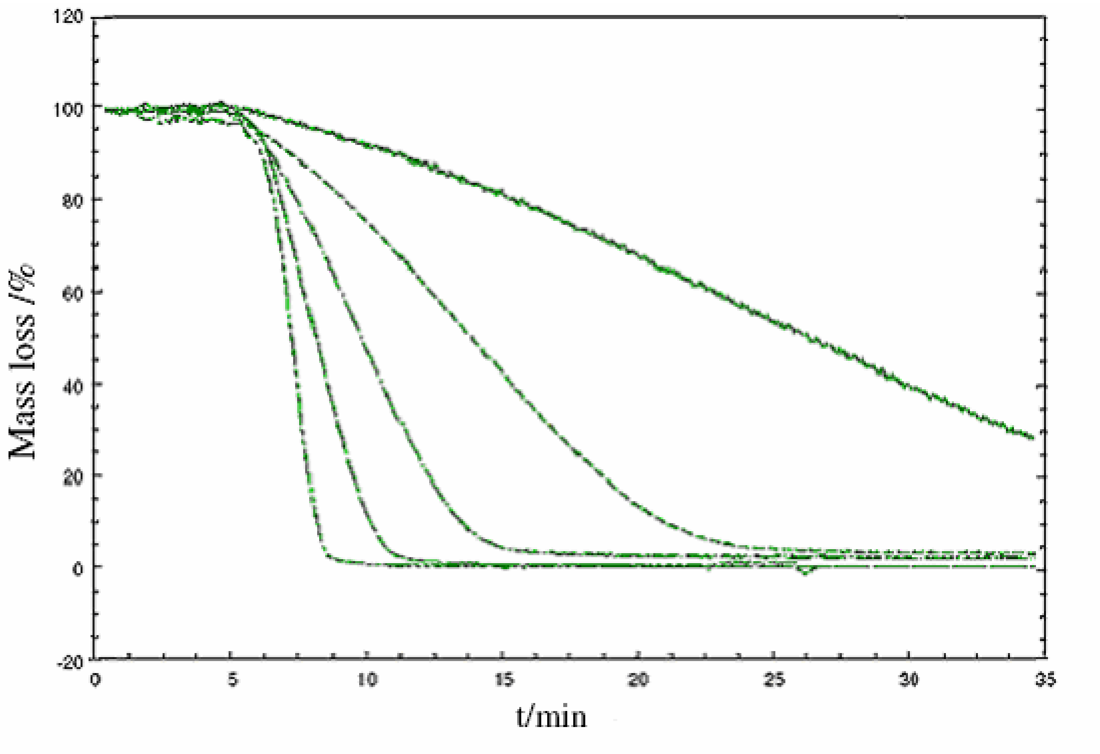


Figure 2.7 The mass fraction loss from isothermal thermogravimetric analysis of sorbitol.
——, 250 °C; ---- , 275 °C; —-·, 300 °C; —-- , 325 °C; — —, 350 °C.

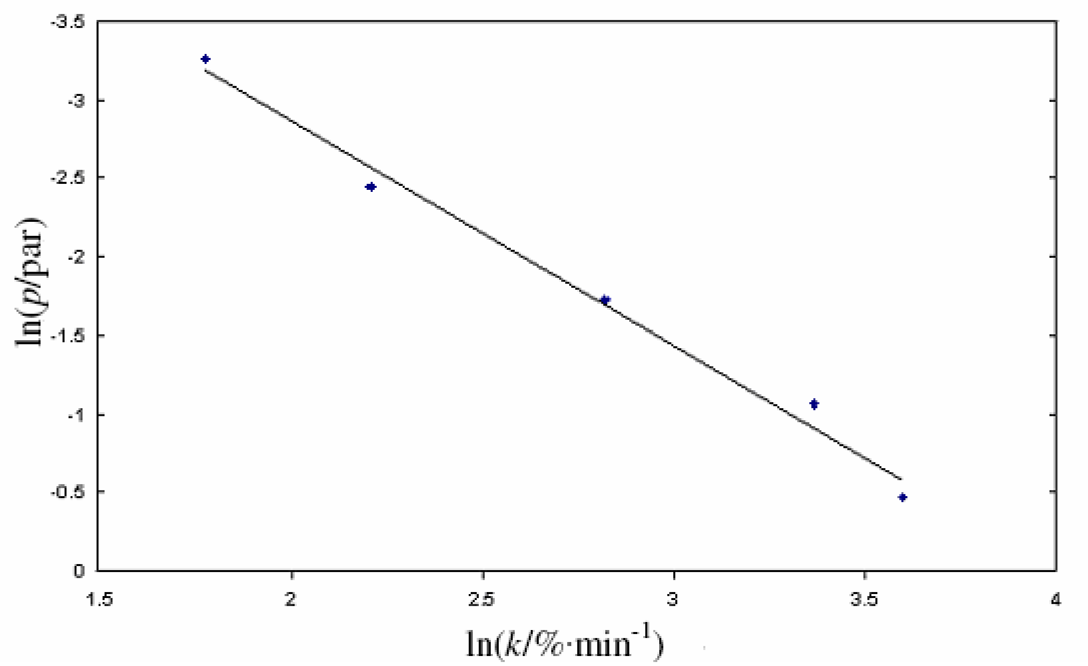


Figure 2.8 The linear logarithmic relationship between the evaporation rates of glycerol and the corresponding vapor pressures. The theoretical line is obtained by fitting to eq 1 using linear regression.

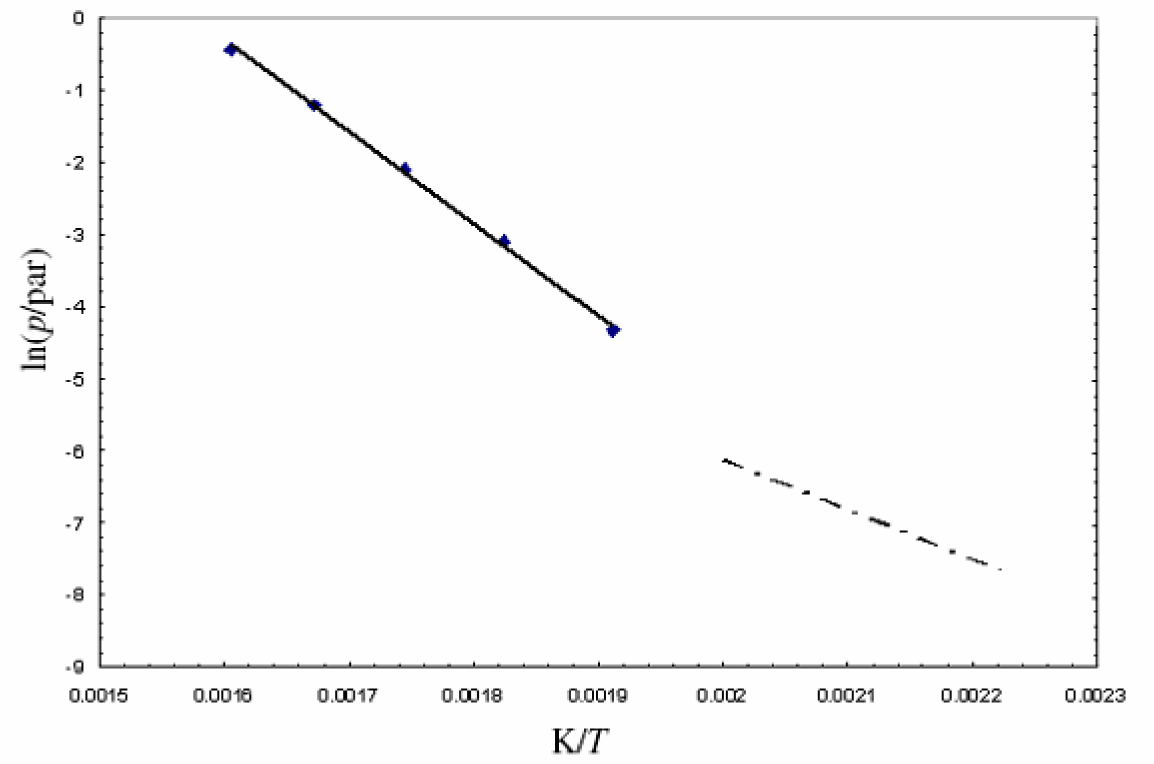


Figure 2.9 Temperature dependence of vapor pressure for sorbitol. Solid line denotes the regression line of vapor pressure data obtained from isothermal TGA method. Dash line denotes the temperature dependence of vapor pressure of sorbitol in the temperature range shown in Guido's work.

3 CHAPTER 3
GAS PHASE CONVERSION OF SUGAR AND SUGAR ALCOHOL TO VALUABLE C3 CHEMICALS

Abstract

Conversion of sugar/sugar alcohol to value-added chemicals had been widely studied. Especially for higher sugars, research has been widely exclusively on liquid phase reactions with emphasis on catalytic hydrogenolysis. The hydrogenolysis reactions are performed at high hydrogen pressure to achieve high conversion and selectivity. In this paper, gas phase catalytic hydrogenolysis is evaluated as a means to overcome liquid phase hydrogenolysis barriers associated with high pressures and catalyst deactivation. Copper-chromite, palladium, and nickel beads catalysts were screened in gas phase hydrogenolysis and of sorbitol and glucose. Complete conversions were attained at reaction pressures of 0.3 to 1 bars. The highest selectivities were to acetol.

Keywords: Gas phase, Catalytic conversion, Sugar, Sugar alcohol, C3 chemicals, Acetol

3.1 Introduction and background

Many chemicals in common use are derived from petroleum feed stocks. The limited petroleum reserves and rapidly increasing petroleum cost motivate researchers to focus on the utilization of biomass to replace petroleum as chemical feedstock. For instance, biodiesel and bioethanol have been widely used as alternative fuels in many countries. Bio-based feedstocks can be converted into other chemicals that can be used in a variety of processes and products, such as propylene glycol and acetol by gas phase hydrogenolysis of glycerol, which is obtained as a major by-product from biodiesel industry[63].

Hydrogenolysis processes were widely applied for cleavage of C-C and C-O bonds. Since the 1930's, sugar/sugar alcohol hydrogenolysis has been widely studied[64,65] with most of publications and patents related to hydrogenolysis of C6 sugar/sugar alcohol such as glucose and sorbitol[66,67,68]. Figure 3.1 showed the reaction network of hydrogenolysis of sorbitol[69]. There are five possible cleavage positions of C-C, which are C1-C2, C2-C3, C3-C4, C4-C5 and C5-C6 to form C1 to C5 products.

Conradin et al.[70,71,72], Clack et al.[73] and Sirkar et al.[74] reported that hydrogen splitting of aqueous sorbitol solution to glycerol and propylene glycol can be carried out in the presence of a broad range of catalysts (e.g. Ni/Cu catalyst) provided sufficient alkali is added to ensure a pH of 11 to 12.5 as a promoter. The product distribution was about 43 % glycerol and 25 % propylene glycol with 83 % conversion at (80 to 140) bar and (200 to 260) °C.

Tanikella et al.[75] and Van Ling et al.[76] described the hydrolysis of sorbitol and xylitol in non-aqueous solvents containing at least 10 % (mole fraction) base. The catalyst used was nickel on silica/alumina. Distribution of ethylene glycol, propylene glycol and glycerol were reported.

Gubitosa et al.[77] discussed the hydrogenolysis of polyhydric alcohols, such as sorbitol, over a ruthenium-on-carbon catalyst. In the examples, it was reported that 100 % of the sorbitol was converted, with (41 to 51) % of the product carbon atoms in propylene glycol.

These batch hydrogenolysis reactions usually were carried out at (140 to 350) bar in the presence of hydrogen, temperatures of (200 to 250) °C, residence times in excess of 1.5 h and in the presence of slurry.

Liquid-phase packed-bed reactions were performed by Hellwig et al. [78] Hydrogenolysis reactions occurred in a single or multi-stage fixed bed catalytic reactor at (100 to 300) °C temperature and (50 to 240) bar hydrogen partial pressure, 1.2 liquid hourly space velocity (LHSV), and using nickel on alumina catalyst to produce 50 % (mass fraction) glycerol and 20 % (mass fraction) propylene glycol from sorbitol type feed.

To date, low selectivities, high pressure, and high catalyst recovery have limited the potential of these technologies. Thus, there is a need for new methods of converting sugars and sugar alcohols to value-added chemicals such as propylene glycol and 1,3-propanediol. Gas phase catalytic hydrogenolysis may be a way for sugar conversion in a continuous operation at reduced reaction conditions, using improved catalysts in packed bed reactors. To achieve this objective, copper-chromite, palladium and nickel beads catalysts were screened and gas phase conversion of sugar/sugar alcohol was investigated in this paper.

3.2 Experimental methods

3.2.1 Materials

Sorbitol (97.0 %), glucose (99.9 %), glycerol (99.9 %), acetol (90.0 %) were purchased from Sigma-Aldrich (Milwaukee, WI). High purity grade hydrogen, nitrogen and helium were obtained from Praxair (Dunbury, CT). Copper-chromite catalyst (45 % CuO, 47 % Cr_2O_3, 3.5 % MnO_2 and 2.7 % BaO) was supplied by Sud-Chemie Inc. (Louisville, KY). Palladium catalyst (5 % palladium/α-Al_2O_3) and nickel beads (100 % nickel, 1mm) catalyst were purchased from Alfa-Aesar (Ward Hill, MA).

3.2.2 Experimental setup

Figure 3.2 is a schematic of the reaction system: an evaporator, trap, packed bed reactor, air-cooled condenser and ice-water condenser. The temperatures of the evaporator, trap and reactor were controlled using Single Display Proportional-Integral-Derivative (PID) Controller (Winona, MN). The pressure of evaporation system was maintained using a GAST vacuum pump (Benton Harbor, MI).

For each run, a certain amount of catalyst was loaded into packed-bed reactor (ID =1 inch). Hydrogen was introduced at the entrance of the evaporator at a flow rate of 7-8 $L \cdot min^{-1}$ after the system was heated up. When the system reached the desired temperature and pressure, the aqueous sugar/sugar alcohol solution (sugar/sugar alcohol mass fraction in solution was 2.5 %) was pumped into the evaporator by a micro-pump at 150 g·h^{-1}. The samples were collected from ice-water condenser and analyzed by Hewlett-Packard high performance liquid chromatography (HPLC) and gas chromatography (GC) without further delay.

3.2.3 Chromatographic analysis

For sugar analysis, the samples were analyzed with a Hewlett-Packard 1100 high performance liquid chromatography with an Alltech ELSD 500 evaporative light-scattering detector (Alltech Associates Inc. Deerfield, IL). An Alltech HPLC silica based column (Apollo, 250 mm ×4.6 mm, 5 µm) was used for separation. The ELSD drift tube temperature was set at 75 °C. The nitrogen gas flow rate of the nebulizer was set 4.97 L·min^{-1} and the pressure was 0.56 bar. The injector was a Hewlett-Packard model 1100 with a 30 µL loop. The eluent flow rate was 1 mL·min^{-1} at room temperature. The eluent mixture was methanol:water with a 97:3 (v/v). The samples were placed in the oven at 80 °C for 24 h to remove water and dissolved in methanol prior to analysis. The calibration curves for sugar/sugar alcohol were prepared and the mass concentration of sugar/sugar alcohol was determined from these calibration curves.

The samples were also analyzed with a Hewlett-Packard 6890 (Wilmington, DE) gas chromatograph equipped with a flame ionization detector and mass specter detector. A J&W Scientific Inc. (Folsom, CA) DB-WAX 123-7033 GC column (30 m × 320 µm × 0.5 µm) was used for the separation. The detector and injector temperatures were 250 °C and 230 °C, respectively, and the oven temperature increase was programmed 10 ℃·min^{-1} from 45 ℃ to 200 ℃ and 15 ℃·min^{-1} to final temperature of 225 ℃, which was held for 10 min. Helium was used as carrier gas at a flow rate of 1.0 mL·min^{-1} and the split ratio was 1:120. Using the calibration curves that were prepared for all components, the integrated peak areas were converted to mass concentrations for each component in the sample. Figure 3.3 is a typical gas chromatograph of the sorbitol reaction products. The highest peak showed that acetol is the major product present in the samples.

For each data point, conversion of sugar/sugar alcohol, selectivity and yield of products and was calculated. Conversion is defined as the ratio of number of moles of sugar/sugar alcohol consumed to the total moles of sugar/sugar alcohol initially present. Selectivity is defined as the ratio of the number of moles of product to that of the sugar/sugar alcohol consumed in the reaction. Yield is defined as the ratio of the numbers of moles of each product to the theoretical number of moles of product.

3.3 Results and discussion

3.3.1 Catalyst selection

Heterogeneous catalysts, including copper-chromite, palladium and nickel beads were selected to carry out the reaction of sugar/sugar alcohol to C3 chemicals. To evaluate the catalytic effect, hydrogenolysis of glycerol was also performed to compare the conversion of sorbitol and glucose over the same catalysts. All reactions were performed in the temperature range of (200 to 280) ℃ and at 1 bar. For each case, 70 g of catalyst was loaded in the packed-bed reactor. The hydrogen flow rate was adjusted to 7-8 L·min^{-1}. When the system reached the desired temperature and pressure, the aqueous solution (mass fraction in solution was 2.5 %) was pumped into the evaporator at 150 g·h^{-1}.

The experimental results of glycerol, sorbitol and glucose over copper-chromite and palladium catalysts are shown in the Table 3.1 and Table 3.2. From the results, the nickel beads catalyst showed no catalytic effect, which might have been due to a low surface area.

Acetol was formed as the desired C3 product in glycerol, sorbitol and glucose conversion. Propylene glycol, 1-propanol, 1-hydroxy-2-butanone, 3-furaldehyde and furfural were produced in lower quantities, depending on the substrates, catalysts and reaction conditions. Propylene glycol was the desirable product from glycerol hydrogenolysis with copper-chromite catalyst in the temperature range of (200 to 240) °C. In glucose and sorbitol conversion, propylene glycol was not present at higher temperatures since high temperatures favored acetol over propylene glycol.

These data show that yields of major products from sugar/sugar alcohol are less than from glycerol. Since the yield of each product was calculated by quantifying the amount of the product in the effluent using a calibration curve for each component, any sugar/sugar alcohol that remained in the trap would show up as a decreased yield.

The low yields of the primary products in Table 3.2 are attributed to losses in the evaporator. As the temperature of the evaporator increased, the yields also increased for both sorbitol and glucose. The opposite is true for glycerol. Glycerol is known to evaporate at these temperatures in the presence of water and the yields decrease due to side reactions at higher temperature. Some yield reduction is also attributed to more by-product formation for both sorbitol and glucose as evident from the GC printouts.

3.3.2 Parametric study of sorbitol conversion

Comparison of Table 3.1 and Table 3.2 shows copper-chromite catalyst gave higher yield to desirable C3 products (acetol) than palladium catalyst. Copper-chromite catalyst was selected for further studies. The effect of reaction pressure, reaction temperature and initial sorbitol concentration were studied using copper-chromite catalyst. The results were discussed in the following sections.

3.3.2.1 Effect of reaction pressure

Reactions were carried out at 0.3, 0.6 and 1 bar and 280 ℃ to determine the effect of pressure on the overall reaction conversion. Table 3.3 showed the effect of pressure on the conversion of 2.5 % sorbitol solution at 280 ℃. The yield of acetol increased up to 20 % as the pressure decreased from 1 to 0.3 bar. There was no sorbitol detected in the product samples by HPLC analyses. By-products (e.g. acetone, 3-hydroxy-2-butanone and 1-hydroxy-2-butanone) were detected in the product samples.

Yield is defined as the ratio of the number of moles of product to the theoretical number of moles of product based on the amounts of feed to the evaporator.

Using the calibration curves that were prepared for all components, the integrated peak areas were transformed to the number of moles for each component in the sample.

In a separate study, the vapor pressure of sorbitol were calculated from the Clausius-Clapeyron equation[79,80]. Based on the data for pure sorbitol, the dew point curves for 2.5, 10 and 50 % sorbitol in water were calculated using the ChemCAD process simulation and shown in Figure 3.4.

Table 3.4 summarized the ChemCAD calculations with different sorbitol concentrations using various K-value models. These results were obtained with Wilson K-value model, NRTL K-value model and UNIQUAC K-value model. The UNIQUAC model was selected to represent the system for discussion purposes. The dew point trends based on the UNIQUAC model are shown in Figure 3.4.

From Table 3.4, 2.5 % sorbitol reagent should evaporate successfully at the temperature of 280 °C and the pressures of 0.3 to 1 bar. However, experimental evaporation results obtained by analyzing the evaporation samples with HPLC in an evaporation study at 280 °C, indicated that at 0.3, 0.6 and 1 bar evaporation percentages of sorbitol were 59 %, 38 % and 27 %, respectively.

3.3.2.2Effect of reaction temperature

There is the obvious difference between simulation results and experiment results. This difference could be that the temperature at the evaporator tube center is much lower than the measured temperature on the copper tube wall. There is some sorbitol in liquid phase accumulated in the evaporator and trap. Another reason may be that sorbitol could have side reactions at high temperature and cause charring in the evaporator. It was confirmed by the observation that some tiny black solids came out of the trap.

Reactions were performed at 270, 280 and 290 ℃ and at a pressure of 0.3 bar in presence of copper-chromite catalyst. As the temperature of the reaction increased from 270 to 290 ℃, there was an increase from 15 to 25 % in the yield of acetol.

As indicated in Figure 3.4, the calculated evaporated sorbitol percentages were 100% at the temperature of (270 to 290) ℃ and the pressure of 0.3 bar. But the experimental evaporated sorbitol percentages, by analyzing evaporation samples by HPLC in the evaporation study, were 43 %, 39 % and 33 % as indicated in Table 3.5. This indicated that at a pressure of 0.3 bar, higher temperatures could achieve better sorbitol evaporation and cause more reaction to acetol in the packed bed reactor, resulting in higher yield to acetol.

3.3.2.3 Effect of initial sorbitol concentraion

Reactions were performed with sorbitol reagent of different concentrations to study the effect of initial sorbitol concentration on the overall conversion. Figure 3.5 provided the effect of initial sorbitol concentraion on overall sorbitol conversion at 280 ℃ and 0.3 bar.

From experimental observation, more sorbitol accumulated in the trap with increasing sorbitol concentration in the feed. The accumulated sorbitol in the evaporator caused the further side reactions (charring) of sorbitol at high temperature and clogged the evaporator.

A critical step in the gas phase conversion of sorbitol is the evaporation process. Feed concentrations, evaporator temperature, evaporator pressure, designs to minimize plugging/fouling, and other components that may enhance evaporation (like hydrogen) must all be considered in designing such reactions.

3.3.2.4 Design-based Analysis

High conversions, low pressures, and use of packed bed reactors provide gas-phase conversion of sorbitol to higher-value chemicals with several competitive advantages. An optimal process will need to balance low pressures (to create vapor phase) with cost-effective means to maintain the low pressures. Commercial processes will need to balance higher temperatures (to create the vapor phases). Minimizing charring and selecting conditions to maximize selectivity are necessary for commercial success.

3.4 Conclusion

Gas phase heterogeneous catalytic hydrogenolysis can be applied to conversion of sugar/sugar alcohol to value-added C3 chemicals such as acetol. Copper-chromite catalyst was identified as one effective catalyst. The mild conditions in this study made gas phase hydrogenolysis more promising for industrial scale production than traditional liquid phase hydrogenolysis processes. High acetol yield (25 %) was achieved by hydrogenolysis of sorbitol at 290 ℃ and 0.3 bar with 2.5 % sorbitiol aqueous feed. The by-products (e.g. acetone, 1-hydroxy-2-butanone) were also produced in this process.

Table 3.1 The summary of conversion of three substrates at 1 bar over copper-chromite catalyst. t presents reaction temperature. C represents conversion of substrates. P1 represents main product 1. Y1 represents yield of main product 1. P 2 represents main product 2. Y 2 represents yield of main product 2.

Substrate	**t/℃**	**C/%**	**P 1**	**Y 1/%**	**P 2**	**Y 2/%**
Glycerol	200	67.1	acetol	16.6	Propylene glycol	23.5
	220	86.9		32.3		42.6
	240	88.4		27.1		22.3
	260	90.1		12.2		2.95
Sorbitol	240	100	acetol	1.91	1-hydroxy-2-butanone	2.42
	260	100		6.12		7.75
	280	100		11.8		3.69
Glucose	240	100	acetol	2.53	3-furaldehyde	5.68
	260	100		6.81		15.3
	280	100		8.99		8.85

Table 3.2 The summary of conversion of three substrates at 1bar over palladium catalyst. t presents reaction temperature. C represents conversion of substrates. P1 represents main product 1. Y1 represents yield of main product 1. P 2 represents main product 2. Y 2 represents yield of main product 2.

Substrate	**t/℃**	**C/%**	**P 1**	**Y 1%**	**P 2**	**Y 2%**
Glycerol	200	64.5	acetol	1.74	1-propanol	0.55
	220	88.7		9.33		2.94
	240	90.2		11.2		1.81
	260	91.7		4.69		1.08
Sorbitol	240	100	acetol	0.57	1-hydroxy-2-butanone	1.03
	260	100		1.36		1.49
	280	100		9.12		15.5
Glucose	240	100	acetol	0.88	furfural	5.34
	260	100		1.01		13.4
	280	100		1.13		54.8

Table 3.3 The effect of pressure on conversion of sorbitol to acetol. All reactions were performed at 280 °C. P represents reaction pressure. Cal-evap represents calculated sorbitol evaporation percentage. Exp-evap represents experimental sorbitol evaporation percentage. Y represents yield of acetol.

P/bar	Cal-evap/%	Exp-evap/%	Y/%
0.3	100	53	20
0.6	100	38	15
1	100	27	12

Table 3.4 Comparison of ChemCAD simulations with various K-value models.

Sorbitol concentration /%	Vapor fraction=1					
	Wilson K-value Model		NRTL K-value model		UNIQUAC K-value model	
	P/bar	T/℃	P/bar	T/℃	P/bar	T/℃
2.5	0.01	150.4	0.01	150.4	0.01	150.5
	0.34	200.0	0.34	200.0	0.33	200.0
	1	218.9	1	218.3	1	219.4
50	0.01	200.7	0.01	200.7	0.01	200.7
	0.15	250.0	0.151	250.0	0.15	250.0
	1	293.1	1	292.5	1	293.0
100	0.01	243.8	0.01	243.8	0.01	243.8
	0.12	300.0	0.12	300.0	0.12	300.0
	1	362.6	1	362.6	1	362.6

Table 3.5 The effect of temperature on conversion of sorbitol to acetol. All reactions were performed at 0.3 bar. t represents reaction temperature. Cal-evap represents calculated sorbitol evaporation percentage. Exp-evap represents experimental sorbitol evaporation percentage. Y represents yield of acetol.

t/℃	Cal-evap /%	Exp-evap/%	Y/%
270	100	33	15
280	100	39	20
290	100	43	25

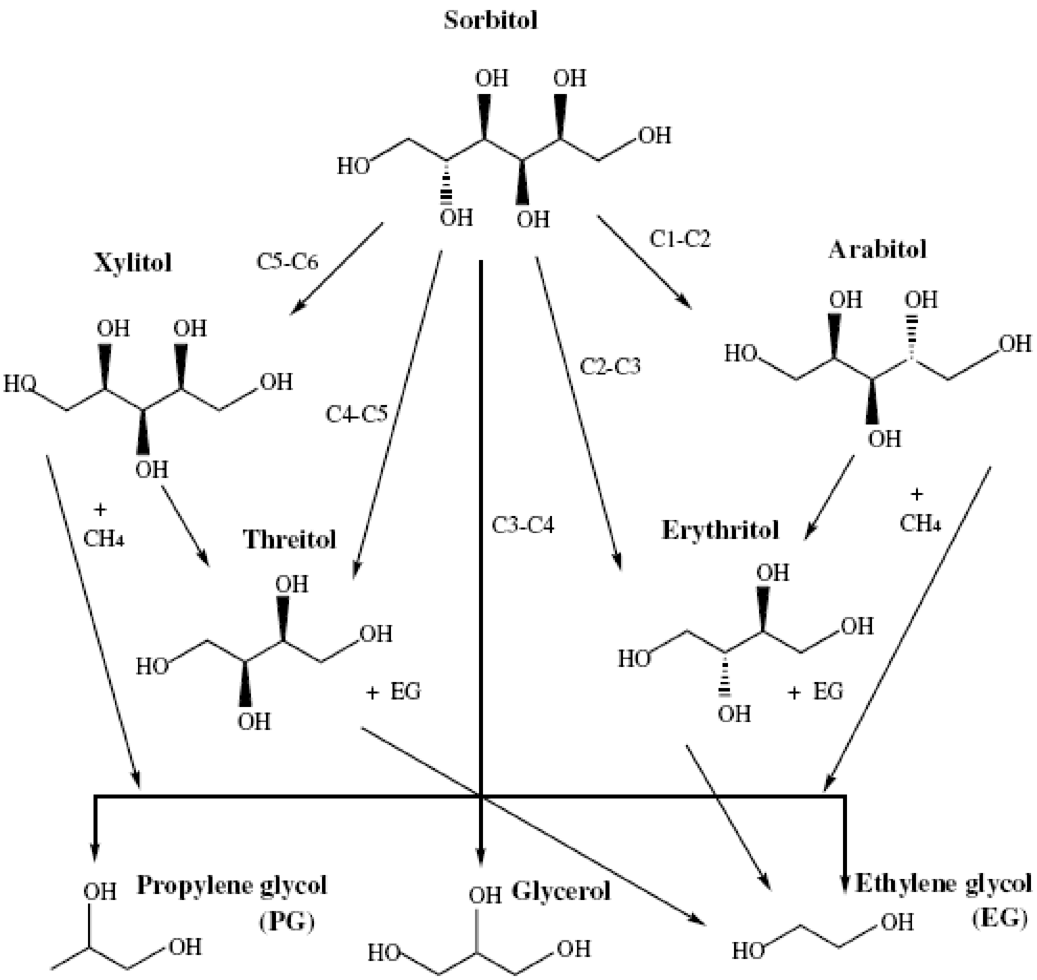


Figure 3.1 The reaction network of hydrogenolysis of sorbitol.

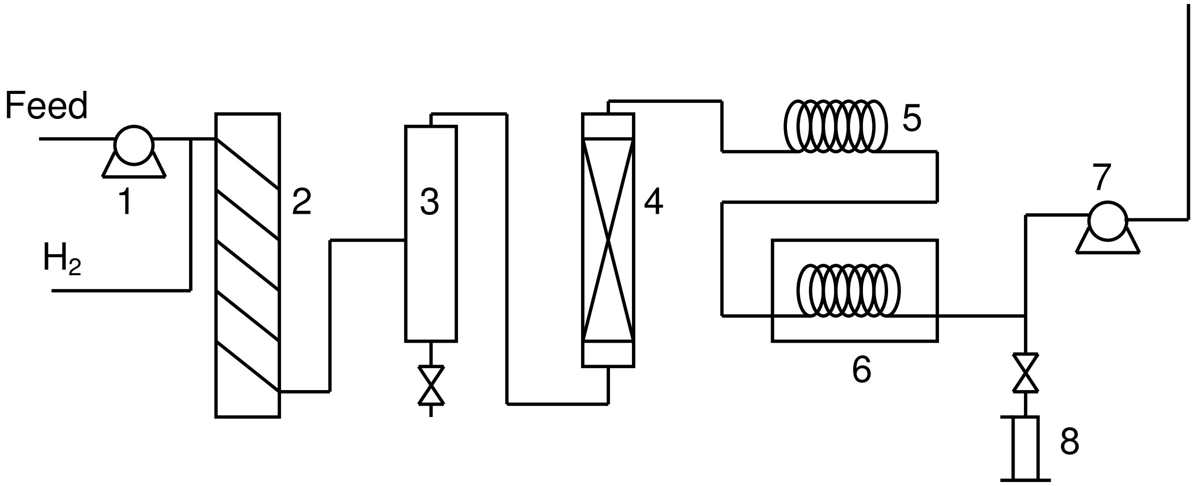


Figure 3.2 Experimental system for sugar/sugar alcohol conversions. The different components are: 1, Feed pump; 2, Evaporator; 3, Trap; 4, Packed-bed reactor; 5, Air-cooled condenser; 6, Ice-water condenser; 7, Vacuum pump; 8, Product collector.

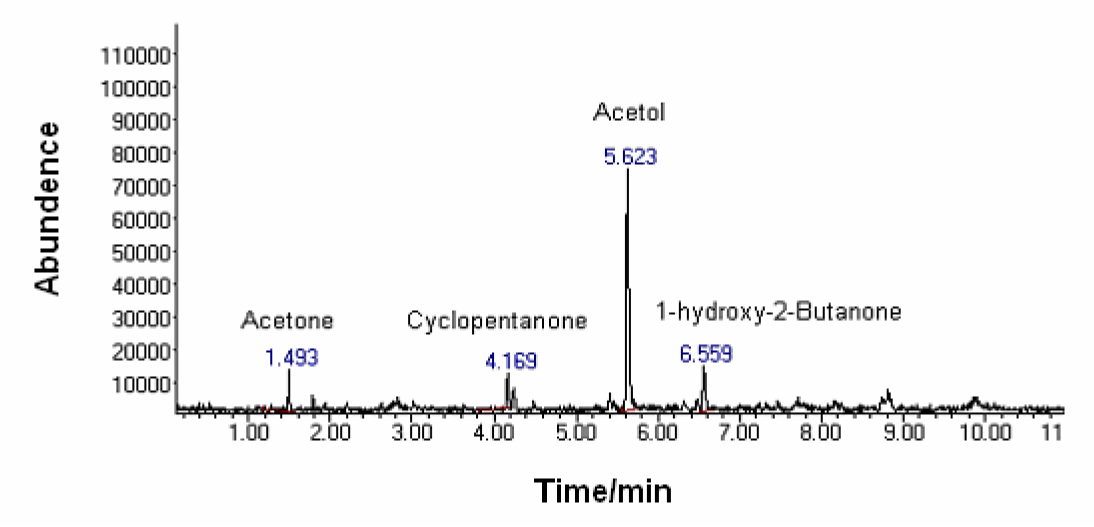


Figure 3.3 Gas chromatography of the sorbitol reaction products.

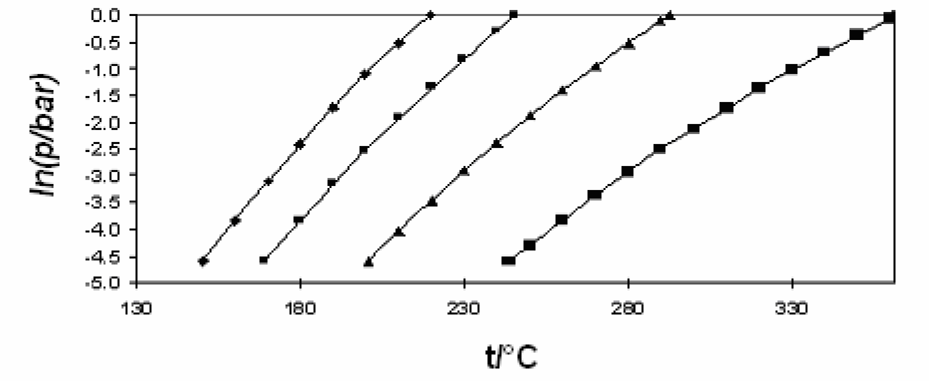


Figure 3.4 The dew point curves for 2.5, 10, 50 and 100 % sorbitol reagent. —♦— represent 2.5 % sorbitol feed; —▪— represents 10 % sorbitol feed; —▲— represents 50 % sorbitol feed; —■— represents 100 % sorbitol feed.

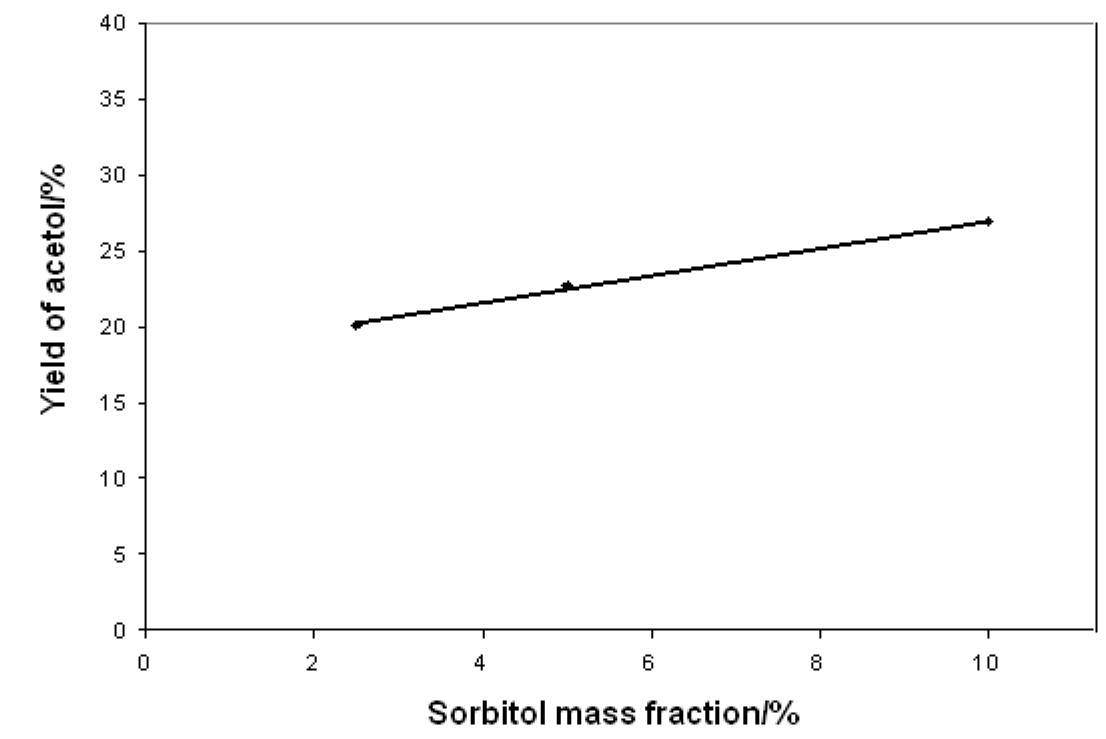


Figure 3.5 The effect of sorbitol content on formation of acetol from sorbitol. All the reactions were performed at 290 °C and 0.3 bar.

4 CHAPTER 4
GAS PHASE DEHYDRATION OF GLYCEROL TO ACROLEIN

Abstract

Recently, glycerol has become readily available from renewable energy sources. Its high functionality and low price make it a potential source chemical for value-added derivatives like acrolein. In his study, heterogeneously catalyzed gas-phase dehydration of glycerol using phosphoric acid supported on activated carbon was investigated. At mild condition of 260 ℃ and 0.85 bar, selectivity of glycerol to acrolein can be achieved up to 84 % while simultaneously maintaining long catalyst service life. The process based on phosphoric acid catalyst is an alternative process for industrial scale production of acrolein from crude glycerol.

Keywords: Catalytic dehydration; Acrolein; Glycerol; Solid acid

4.1 Introduction and background

Acrolein (i.e. acrylaldehyde) is the simplest unsaturated aldehyde. Acrolein can be used to synthesize a wide range of derivatives for use as building blocks in the pharmaceutical, aroma chemical, polymer, and agricultural industries. For example, acrolein is used as a chemical intermediate in the production of acrylic acid and its esters. Acrolein is also used as an aquatic herbicide and algicide in irrigation canals, as a microbiocide in oil wells, liquid hydrocarbon fuels, cooling-water towers and water treatment ponds, and as a slimicide in the manufacture of paper[81].

The commercial route to produce acrolein is the selective vapor oxidation of propylene with oxygen[82]. With the large scale production of bio-diesel derived from vegetable oil and animal fat[83,84,85,86], crude glycerol is being considered for production of value-added chemicals, such as acrolein. Over the past twenty years, several routes to acrolein from glycerol have been reported. The most common route[87,88,89] is dehydration of glycerol at high temperature in the presence of acidic substances. The acidic catalysts include salts of bibasic acid, tribasic acid, or mixture of such salts which may be held on the solid support. The drawbacks of the process involving such catalysts were the low yield of acrolein and the high weight ratio of dehydrating salts to glycerol. Several processes were performed at high temperatures from 350 to 500 °C. This process was unsuitable for the production of acrolein on an industrial scale.

Alternative processes[90,91,92] being proposed are dehydration of glycerol in critical water using sulfuric acid as the catalyst. The process could maintain conversion of glycerol of 39 % to 55 % and high selectivity to the main products: acrolein and acetaldehyde. This requires considerable technical costs of working in the supercritical range and recycling sulfuric acid, making this process unattractive for industrial scale production.

Our research focuses at developing a technology to perform the reaction at lower temperatures and in a vacuum environment while achieving high selectivity towards acrolein and minimum formation of acetol, allyl alcohol or other by-products.

It was necessary to understand the fundamental chemistry and mechanism behind the dehydration of crude glycerol to acrolein. The mechanism of hydrogenolysis of glycerol to propylene glycol, proposed by Dasari M. A. et al.[93,94] showed that acetol (hydroxyacetone) was formed as the main intermediate by dehydration of glycerol over various metallic catalysts, including nickel, alumina, magnesium, ruthenium, platinum, palladium, copper, copper chromite catalysts followed by hydrogenation of acetol to propylene glycol. Acetol is often in the product mix of acrolein production. So the question is whether acetol is an intermediate in reaction of glycerol to acrolein?

Hall R. H. et al.[95] and Pressman D. et al.[96] reported that acrolein can be hydrated into 3-hydroxypropanal at a lower temperature in the presence of acid catalyst. Then, 3-hydroxypropanal can be dehydrated into acrolein in an equilibrium-limited step. This provides a motivation to increase the temperature where more favorable equilibrium is attained for these exothermic dehydration reactions.

A reaction scheme that would account for the mechanism of Hall et al. and Pressman et al. is shown in Figure 4.1. This reaction mechanism will be evaluated in this study.

4.2 Experimental methods

4.2.1 Materials

Glycerol (99.9 %), acrolein (90 %), acetol (90 %), allyl alcohol (99.9 %), and o-phosphoric acid (85 %) were purchased from Sigma-Aldrich (Milwaukee, WI). High purity nitrogen and helium were obtained from Praxair (Dunbury, CT). Activated carbon (surface area>2000 $m^2 \cdot g^{-1}$) from biomass was obtained from the carbon group in our lab.

4.2.2 Experimental setup

The gas phase dehydration of glycerol was carried out at temperatures of (230 to 290) °C and pressures of (0.7 to 1) bar. Figure 4.2 is a schematic of the reaction system, including an evaporator, trap, packed bed reactor, air-cooled condenser and ice-water condenser. The temperatures of evaporator, trap and reactor were controlled using Single Display Proportional-Integral-Derivative (PID) Controller (Winona, MN). The pressure of reactor was maintained by GAST vacuum pump (Benton Harbor, MI). For each run, a known amount of catalyst (approximately 2.0 g) was loaded into copper packed bed reactor (ID =1 inch). When the system reached the desired temperature and pressure, the aqueous glycerol solution (mass ratio of glycerol to water = 0.2) was pumped into the reactor by a micro-pump at the flow rate of approximately 300 $g \cdot h^{-1}$. The reaction continued for 5 h and the reaction system was washed with distilled water for 1 h and dried for 0.5 h.

Phosphoric acid, zeolites and aluminum oxide were evaluated as acid catalysts. GC analysis of the dehydration products indicated that acetol was formed as one of main dehydration products. Acetol was also evaluated as the reagent to determine if acetol is the likely intermediate in this reaction. Five percent acetol aqueous solution was used as feed into packed-bed reactor, loaded with 5 g of solid acid catalysts. For acetol, dehydration reactions were carried out at temperatures in the range of (230 to 260) °C and ambient pressure.

The reaction samples were collected and analyzed by Hewlett-Packard gas chromatograph (GC) without delay. The carbon deposit for each run was also determined. The packed-bed reactor was weighed before and after the reaction. It was assumed that the carbon deposit was the increased weight of the packed-bed reactor.

4.2.3 Method of analysis

The samples were taken at selected time intervals and analyzed with a Hewlett-Packard 6890 (Wilmington, DE) gas chromatograph equipped with a flame ionization detector and mass specter detector. A J&W Scientific Inc. (Folsom, CA) DB-WAX 123-7033 GC column (30 m × 320 µm × 0.5 µm) was used for separation. The detector and injector temperatures were 250 ℃ and 230 ℃, respectively, and the oven temperature increase was programmed 10℃/min from 45 ℃ to 200 ℃ and 15 ℃·min^{-1} to final temperature of 225 ℃. The final temperature was held for 10 min. Helium was used as carrier gas at a flow rate of 1.0 mL·min^{-1}The split ratio was 1:120.

Figure 4.3 shows a typical gas chromatogram of the dehydration reaction product. Using the calibration curves prepared for all components, the integrated peak areas were transformed to weight percentages for each component in the sample. For each data point, the conversion of glycerol, the yield and the selectivity of the products were calculated. Conversion is defined as the ratio of number of moles of glycerol consumed to the total moles of glycerol initially fed. Yield is defined as the ratio of the numbers of moles of product to the theoretical number of moles of product. Selectivity is defined as the ratio of the number of moles of the product to that of the glycerol consumed.

4.3 Results and discussion

4.3.1 Catalyst selection

Heterogeneous catalysts were prepared either directly or impregnated on catalyst support as indicated in Table 4.1 and Table 4.2. Alpha-Al_2O_3 was directly purchased from market without any modification. Phosphoric acid/alpha-Al_2O_3 and phosphoric acid/BASF F-24 were prepared using the method described by Armin N. B. and Thomas H. F.[97]. Phosphoric acid/Carbon[1] was obtained by a procedure including acid soaking of corncobs and charring to form catalyst. Phosphoric acid/Carbon^2 was obtained by soaking of corncobs, charring, base treatment and catalyst formation. Phosphoric acid/Carbon^3 was obtained by a procedure including acid soaking of corncobs and charring.

The effect of temperature and pressure on the reaction over alpha-Al_2O_3, phosphoric acid/alpha-Al_2O_3 and phosphoric acid/BASF F-24 was shown in Table 4.2. The conversion, the yield and selectivity to acrolein are not strong functions of temperature and pressure. This indicates the reaction to acrolein depends on the catalyst. Alpha-Al_2O_3, phosphoric acid/alpha-Al_2O_3 and phosphoric acid/BASF F-24 showed low selectivity, less than 10 %, with higher concentrations of lower alcohols and aldehydes in the dehydration products. Phosphoric acid on activated carbon provided higher selectivity for acrolein and little selectivity for acetol, ally alcohol and other degradation by-products. The phosphoric acid supported on activated carbon was selected for further studies.

4.3.2 Reaction mechanism

Reactions were conducted with 5 % acetol in water as the reagent with a phosphoric acid on activated carbon catalyst. Table 4.3 summarizes the conversions at 230, 245, and 260 ℃. Figure 4.4 compares the gas chromatograph analyses for acetol versus glycerol reagents. No arolein formed from the acetol reagent, with about 93 % acetol remaining unreacted. These data suggest that acetol is not an intermediate for the acid dehydration of glycerol to acrolein.

4.3.3 Factional factorial experiment studies

Further studies were performed with the phosphoric acid on carbon catalyst in a factional factorial experiment design. The factional factorial experiment of $L_9(3^4)$ was designed to study the effect of three factors: reaction temperature, pressure and initial glycerol content. Three levels of each factor were investigated.

For these preliminary studies, reaction temperatures at 230, 260, and 290 ℃ were selected. In this range, the aqueous glycerol solution forms a gas phase with reduced tendencies to polymerize over the packed-bed reactor.

Pressures of 0.7, 0.85, and 1.0 bar were evaluated. The mild vacuum environment further removed the reaction mixture from dew point conditions. It is important to avoid dew point conditions because formation of liquids on the catalyst surface creates more-favorable conditions for oligomer and carbon deposit formation.

The initial glycerol content (mass ratio of glycerol to water) was evaluated at mass ratios of glycerol to water of 0.2, 0.4 and 0.6. The flow rate of aqueous glycerol solution was 300 $g \cdot h^{-1}$ and the catalyst loading was 2.0 g of catalyst. The results of the factional factorial experiment summarized in Table 4.4.

Statistical analysis (F-test) of the effect of reaction temperature, pressure and initial water content on carbon deposit, summarized in Table 4.5, pressure had a significant influence on the carbon deposit since p-value of pressure is lower than α (0.05). Lower carbon deposit at lower pressures is consistent with a mechanism where lower pressures are effective for rapidly removing the more-volatile products from the catalyst sites. A long catalyst service life could be achieved at lower pressures, which correspond to these conditions with greater potential for industrial scale production.

From statistical analysis (see Table 4.5), initial glycerol content in glycerol-water mixture significantly affected the selectivity of glycerol to acrolein. The catalyst could maintain high selectivity of glycerol to acrolein with low glycerol concentration in the feed. Dilution of glycerol with water lowers the partial pressure of glycerol in a manner similar to the way that lower static pressures lower partial pressure. This is consistent with a mechanism where lower "partial" pressures are effective for rapidly removing the more-volatile products from the catalyst sites and avoiding "coking" on the catalyst site.

In this study, reaction temperature was much lower than that reported in the literature[7]. Highest selectivity of acrolein (84 %) could be achieved at temperature of 260 ℃ and pressure of 0.85 bar with low glycerol concentration in the feed.

Water content directly affected the catalyst life since phosphoric acid can be "washed out" during the reaction. From experimental observation, pH value of samples at the beginning stage of the reaction was about 3.0-4.0. To achieve long catalyst life, the effect of feed flow rate was investigated.

Figure 4.5 shows the conversion of glycerol, selectivity and yield of acrolein all decreased dramatically with reaction time when flow rate of feed was 300 $g{\cdot}h^{-1}$. However, conversion, selectivity and yield for a lower flow rate (40 $g{\cdot}h^{-1}$)

maintained on the same level for 5 h, which indicated the catalyst might achieve a long life.

Addition of a low-concentration of phosphoric acid solution, mixed with glycerol vapor at the entrance of the reactor was investigated as a way to increase catalyst life. Although the catalyst life was longer than that without the acid feed, increase in carbon deposit was shown in Figure 4.6. More measurements are required to evaluate this way to continuously replenish the catalyst.

The solid acid catalyst was not effective for dehydrating glycerol to acetol since this catalyst with high-acidic sights favor the dehydration of glycerol to acrolein. This is confirmed in the work of Clacens J. M. et al.[98]. Based on this experimental observation and previous research[13-18], 3-hydroxypropanal was formed as an intermediate and continuous dehydration of 3-hydroxypropanal produces acrolein. Due to the relatively high temperature of the dehydration reaction, all 3-hdyrdoxpropanol was quickly reacted to form acrolein. No 3-hydroxyprapanol was detected in the product by GC analysis.

4.4 Conclusion

Mechanisms were investigated that acetol is not an intermediate for acrolein but 3-hydroxypropanaldehyde is probably the intermediate in the path of dehydration of glycerol to acrolein. Phosphoric acid supported on activated carbon was an effective catalyst for dehydration of glycerol to acrolein. The mild conditions used in these studies give the process advantages over traditional processes using other acidic catalysts. A higher selectivity (>84 %) can be achieved at 260 ℃ and 0.85 bar and this catalyst simultaneously shows a long catalyst service life.

Table 4.1 The summary of conversion of glycerol, yield and selectivity of acrolein from glycerol over various catalysts. Carbon [1,2,3]: Activated carbon from biomass with three different treatments. Reactions were carried out using 16.7 % mass fraction glycerol solution at 260 °C and 0.85 bar for 5 h. C represents conversion of glycerol. Y represents yield of acrolein. S represents selectivity of acrolein.

Catalyst	**Support**	**C/%**	**Y/%**	**S/%**
α-Al_2O_3	-	65.3	5.5	8.4
H_3PO_4	α-Al_2O_3	98.0	6.5	6.6
H_3PO_4	BASF F-24	73.1	6.2	8.5
H_3PO_4	Carbon[1]	79.5	66.8	84.0
H_3PO_4	Carbon[2]	79.2	36.2	45.7
H_3PO_4	Carbon[3]	87.4	21.9	25.1

Table 4.2 The effect of reaction conditions on conversion of glycerol, yield and selectivity of acrolein from glycerol over various catalysts. C represents conversion of glycerol. Y represents yield of acrolein. S represents selectivity of acrolein.

Catalyst	t/℃	P/bar	C/%	Y/%	S/%
α-Al_2O_3	230	1	62.9	4.4	7.0
	260	1	68.6	5.4	7.9
	290	1	72.1	5.0	6.9
	260	0.7	70.8	5.5	7.8
H_3PO_4 / α-Al_2O_3	230	1	82.3	4.3	5.2
	260	1	91.6	5.1	5.6
	290	1	96.0	4.5	4.7
	260	0.7	93.8	3.9	4.1
H_3PO_4 /BASF F-24	230	1	43.1	2.9	6.7
	260	1	63.9	5.1	7.9
	290	1	75.4	5.3	7.1
	260	0.7	68.7	4.3	6.2

Table 4.3 Conversion of 5 % acetol reagent at various temperatures. t represents temperature. P represents pressure. MC represents mass fraction of acetol in the effluent. R represents recovery of acetol.

t/℃	P/bar	MC/%	R/%
230	1	4.67	93.4
245	1	4. 71	94.2
260	1	4.63	92.6

Table 4.4 The summary of carbon deposit in the reactor and selectivity of acrolein. t represents temperature. P represents pressure. G/W represents the mass ratio of glycerol and water in the feed. CD represents carbon deposit in the reactor. S represents selectivity of each product.

t/℃	P/bar	G/W	CD/g	S/%		
				Acrolein	Acetol	Allyl alcohol
230	1.0	0.2	2.63	60.0	6.1	1.3
260	1.0	0.6	2.42	42.7	9.9	2.3
290	1.0	0.4	2.44	42.3	14.0	6.4
230	0.85	0.4	1.21	21.9	23.6	9.4
260	0.85	0.2	0.96	84.0	10.8	2.6
290	0.85	0.6	0.57	49.6	1.4	0.9
230	0.70	0.6	0.80	32.1	14.3	1.1
260	0.70	0.4	0.43	26.7	3.3	0.7
290	0.70	0.2	1.19	73.7	16.6	2.2

Table 4.5 Statistical analysis (F-test) of factorial experiment results.

	Carbon deposit			Selectivity		
	α	F	p-value	α	F	p-value
Temperature	0.05	0.48	0.678	0.05	4.75	0.174
Pressure	0.05	22.7	0.042	0.05	0.85	0.541
Glycerol/Water	0.05	0.72	0.583	0.05	28.5	0.034

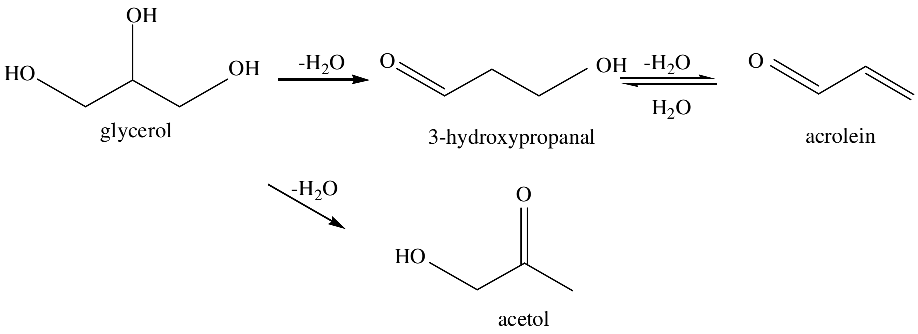


Figure 4.1 Reaction mechanism for dehydration of glycerol to acrolein.

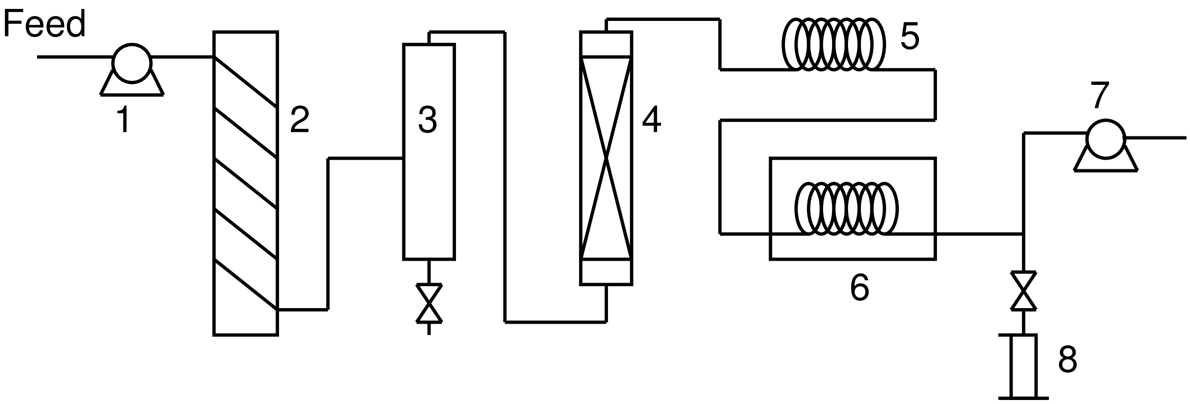


Figure 4.2 Experimental system for dehydration of glycerol to acrolein. The different components are: 1, Feed pump; 2, Evaporator; 3, Trap; 4, Packed-bed reactor; 5, Air-cooled condenser; 6, Ice-water condenser; 7, Vacuum pump; 8, Product collector.

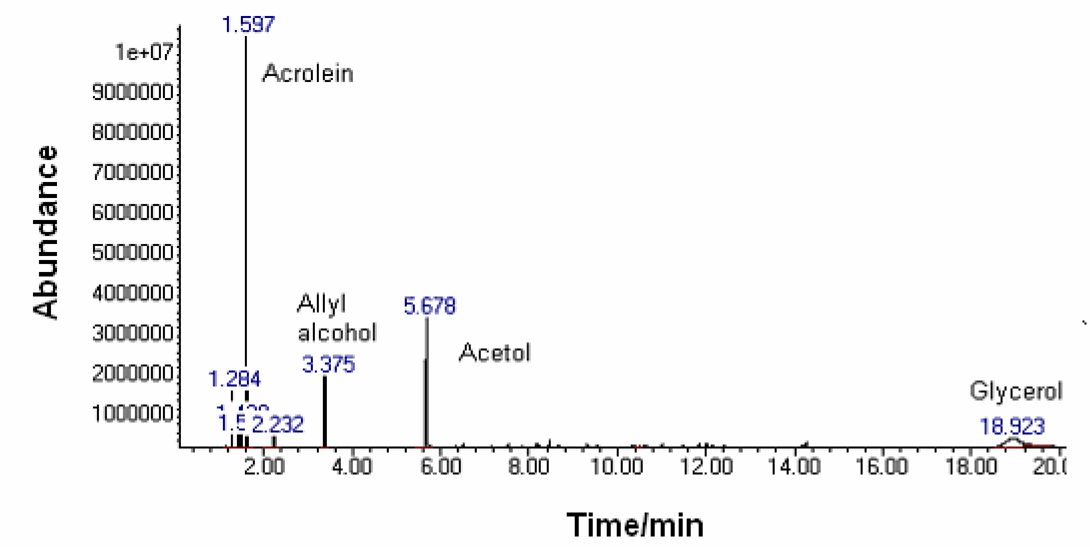


Figure 4.3 Gas chromatograph of the dehydration reaction product.

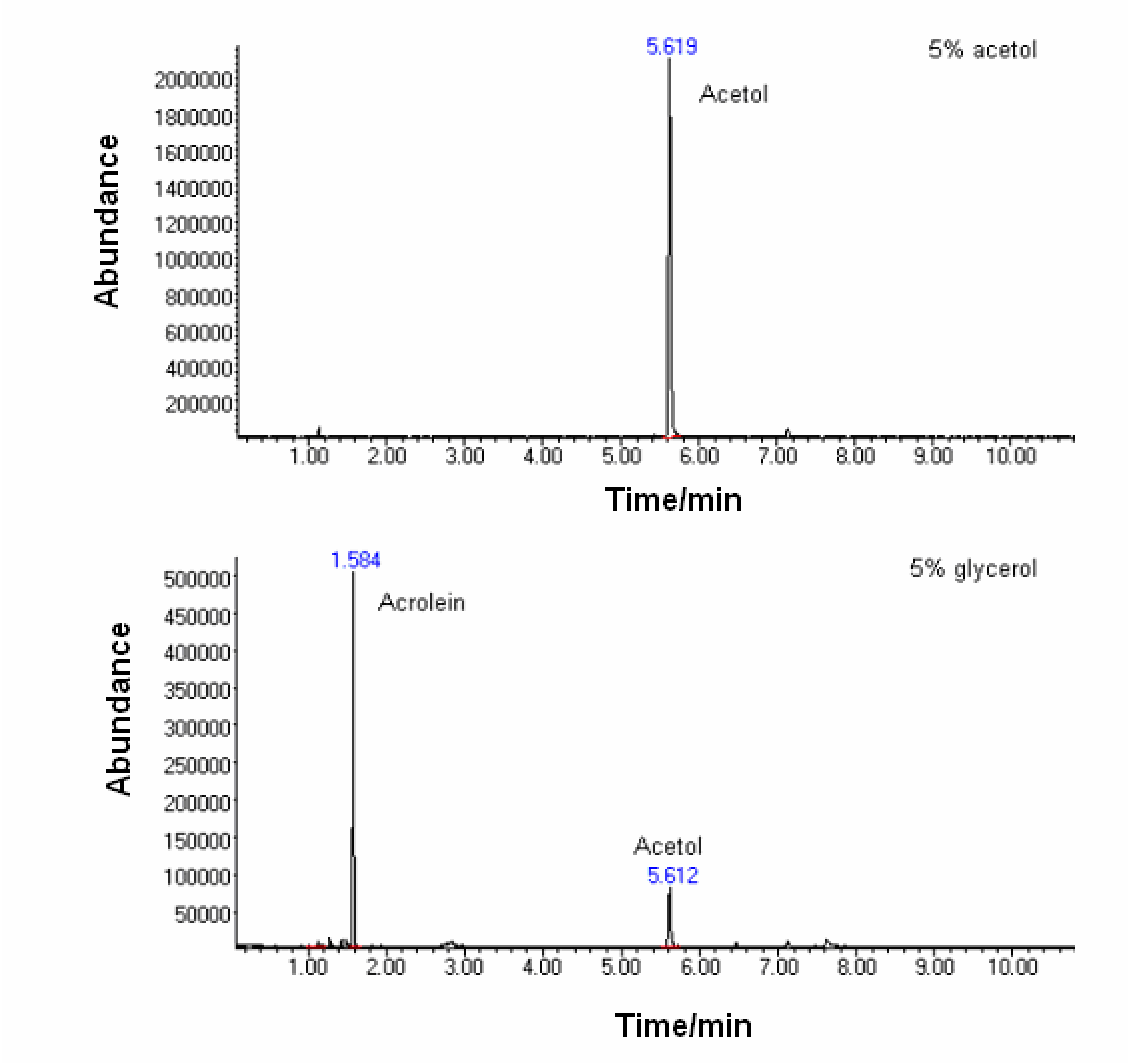


Figure 4.4 Comparison of gas chromatographs using 5 % acetol and 5 % glycerol solution as feed.

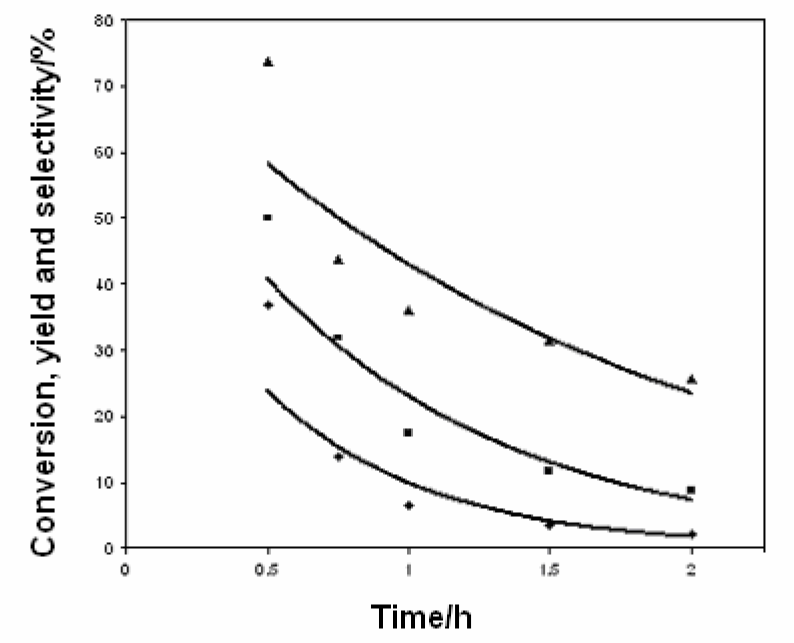


Figure 4.5 A time case study of conversion, selectivity and yield at high flow rate (300 g/h). Reactions were performed using 20 % mass fraction glycerol solution at 290 °C and 1 bar for 5 h. ▪ represents conversion of glycerol. ✦ represents yield of acrolein. ▲ represents selectivity of acrolein. Solid lines represent the trends of conversion of glycerol, yield and selectivity of acrolein.

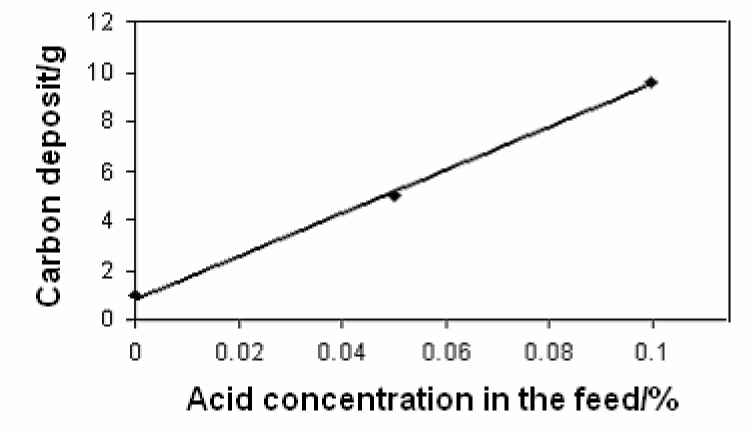


Figure 4.6 **The effect of phosphoric acid concentration in feed on carbon deposit in the reactor. Reactions were performed with 20 % mass fraction glycerol solution at 260 °C and 0.85 bar for 5 h.**

5 CHAPTER 5
SUMMARY

Clearly, fossil fuels are not going to be available in the coming future. Hence, scientists and researchers need to pay more attention to the renewable feed stocks (e.g. biomass). The discussion in Chapter 1 to Chapter 4 focused on the methods to convert biomass (sugars and sugar alcohols) into valuable chemicals.

High functionality and low price of sugar/sugar alcohol make them available platform chemicals to produce value-added chemicals. The method of heterogeneous catalysis has been widely studied in liquid-phase conversion. The significant drawbacks of this method are low selectivity to the desirable products, high costs of catalyst recovery and severe reaction conditions. Consequently, they greatly limited the commercialization of this technology for industry-scale production. Gas phase packed bed catalysis was proposed to achieve the conversion of sugars and sugar alcohols due to the success for the hydrogenolysis of glycerol to propylene glycol,

The vapor pressure estimation and evaporation of sugars and sugar alcohols was first discussed. The purpose of this study was to identify potential conditions for gas phase hydrogenolysis. A thermogravimetric analysis (TGA) method was used to estimate a boiling point of 362 °C for sorbitol with sorbitol's vapor pressure following a Clausius-Clapeyron model behavior. In addition, evaporation studies demonstrated sobitol evaporation and condensation on a practical level. The evaporation of sorbitol was experimentally validated with no decomposition at 0.1 bar and 294 ℃ and 2.5 % (mass fraction) in water. The evaporation of high-concentration sorbitol feed can be achieved by mixing with a high-temperature gas. Glucose evaporated with partial decomposition at temperatures as low as 220 ℃.

Based on the evaporation study, gas phase catalytic hydrogenolysis was secondly demonstrated to be a means to produce valuable chemicals from sugars and sugar alcohols. Copper-chromite, palladium, and nickel beads catalysts were investigated for gas phase hydrogenolysis of sorbitol. Complete conversion was attained at reaction pressures of 0.3 to 1 bars. The highest selectivities favored acetol. The advantages over liquid phase hydrogeonolysis are mild reaction conditions (low temperatures and pressures), high selectivity to acetol and continuous operation in packed bed reactor.

In addition, gas phase dehydration of glycerol was studied in the presence of solid acid catalyst. The reaction mechanism of producing acroelin from glycerol was proposed and validated. At mild condition of 260 ℃ and 0.85 bar, up to 84 % selectivity to acrolein can be achieved. Compared with other processes, this technology showed more advantages, e.g. higher selectivity, milder reaction conditions and long catalyst life. This process was considered as an alternative process for industry-scale production of acrolein.

Gas phase hydrogenolysis of sorbitol will be of great commercial interest for valuable lower-molecule chemicals when low cost and high-selectivity catalysts are available. Further work is required to prepare other hydrogeonolysis catalysts (e.g. nickel on granular activated carbon or ruthenium on granular activated carbon). The catalysts should have high mechanical resistance and a particle size that make it suitable for use in a packed-bed reactor.

Further work is also required to improve evaporating sugar/sugar alcohol at lower temperatures and perform the hydrogenolysis of sugars/sugar alcohols at ambient pressure. Technologies such as evaporation of sugars/sugar alcohols by direct contact with high-temperature steam have more advantages to prevent decomposing, side reaction or charring. The conversion at ambient pressure will greatly reduced the capital cost and operating cost, so this part of future work is worthwhile to be studied.

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