



Co-catalysts for the hydrogenolysis of sorbitol  
by Jason E Ditsworth

A thesis submitted in partial fulfillment of the requirements for the degree Of Master of Science in  
Chemical Engineering  
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Abstract:

The production of polyols from agricultural products can be accomplished through hydrogenolysis. One such process is the production of sorbitol from corn starch with subsequent hydrogenolysis to form polyols such as glycerol, propylene glycol, and ethylene glycol. The amounts of these products produced and their market demand essentially determines whether the process may be economically feasible. Therefore, it was determined that an ideal hydrogenolysis process would allow for the alteration of product distribution depending on market demand.

The focus of this research was to determine the effects of various co-catalysts on product distribution for the hydrogenolysis of sorbitol while maintaining high to moderate conversion. Powdered forms of metal co-catalysts substantially soluble in aqueous solutions of sorbitol were tested. The desired products were glycerol, propylene glycol, and ethylene glycol. Other objectives were to determine gas production and lower alcohol yields for all runs. The effect of temperature on gas production, sorbitol conversion, product distribution, and product yields was also investigated.

The data collected provides evidence that maintaining high to moderate sorbitol conversion is probable with the hydrogenolysis conditions tested. Catalyst HC-1 was used for determining the co-catalysts that produced the best yields of the desired products. It was determined that co-catalyst CC-8 produced a significantly greater amount of glycerol while co-catalysts CC-1 and CC-2 produced the highest yields of propylene glycol. The greatest yields of ethylene glycol were achieved with co-catalyst CC-1 or CC-4. Co-catalyst CC-4 produced moderate yields of glycerol while CC-1 and CC-2 produced low glycerol yields.

Results show that gas production could be reduced with an alternate catalyst. Gas production was decreased by a factor of ten with the HC-2 catalyst when compared to catalyst HC-1. Glycerol yields were significantly increased with this catalyst, but conversion was decreased by a factor of 2.

Results also show that lower temperatures decreased gas production. Glycerol yields were increased at lower temperatures when HC-1 was used as the catalyst, but were decreased with the HC-2 catalyst. .

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**APPROVAL**

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## ABSTRACT

The production of polyols from agricultural products can be accomplished through hydrogenolysis. One such process is the production of sorbitol from corn starch with subsequent hydrogenolysis to form polyols such as glycerol, propylene glycol, and ethylene glycol. The amounts of these products produced and their market demand essentially determines whether the process may be economically feasible. Therefore, it was determined that an ideal hydrogenolysis process would allow for the alteration of product distribution depending on market demand.

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## CHAPTER 1

### INTRODUCTION

The majority of polyols are currently produced from petroleum fractions, but with the present concern that petroleum is a non-renewable resource there is an increasing desire for an alternate method of production. Hydrogenolysis of sugars is one alternative that may be of interest. Agricultural manufacturing industries are continuously burdened with by-products, such as starches, that have no immediate economical value. Several of these by-products can be converted into sugars and then be used in the production of polyols.

Sorbitol is easily produced from corn starch making it an excellent choice for use in the production of polyols. Some of the known products formed during the hydrogenolysis of sorbitol are glycerol, propylene glycol, ethylene glycol, and low molecular weight alcohols. Other products suspected to form include butanediols, propanediols, isosorbide, and a tetrahydrofuran derivative. Glycerol is used in pharmaceuticals, cosmetics, polymer resins, and as a humectant in the tobacco industry. Propylene glycol is used in nontoxic antifreeze, solvents, and as an emulsifying agent in foods. Ethylene glycol is used primarily in antifreeze and solvents. Low molecular weight alcohols are used in solvents and medical applications.

An economical overview is necessary to illustrate the relative value of the polyols and lower alcohols. Table 1 summarizes market values for the known products [1]. Glycerol is the most desired product based on the relative prices of the polyols. Propylene and ethylene glycol are also desirable based on their extensive use in antifreezes and their market values. The low molecular weight alcohols may be desirable products based on their market value, however the necessity of high purity levels could be too much of an opportunity cost.

**Table 1** Market values for known products.

<b>Known Product</b>	<b>Market Value (\$/lb)</b>
Glycerol	0.92 - 1.07
Propylene Glycol	0.48 - 0.56
Ethylene Glycol	0.30 - 0.35
Lower Alcohols	0.4

Several reaction mechanisms, including both parallel and series reactions, are possible for the formation of these products. Figure 1 illustrates some of the possible series and parallel reactions. An example of a series reaction is sorbitol and hydrogen reacting to form propylene glycol and glycerol with glycerol further reacting to form more propylene glycol. The propylene glycol could then further react to form lower alcohols. Many parallel reactions are possible such as propylene glycol and ethylene glycol being produced from two separate sorbitol molecules. Other possible reactions include the formation of gasses such as methane and ethane from methanol and ethanol.

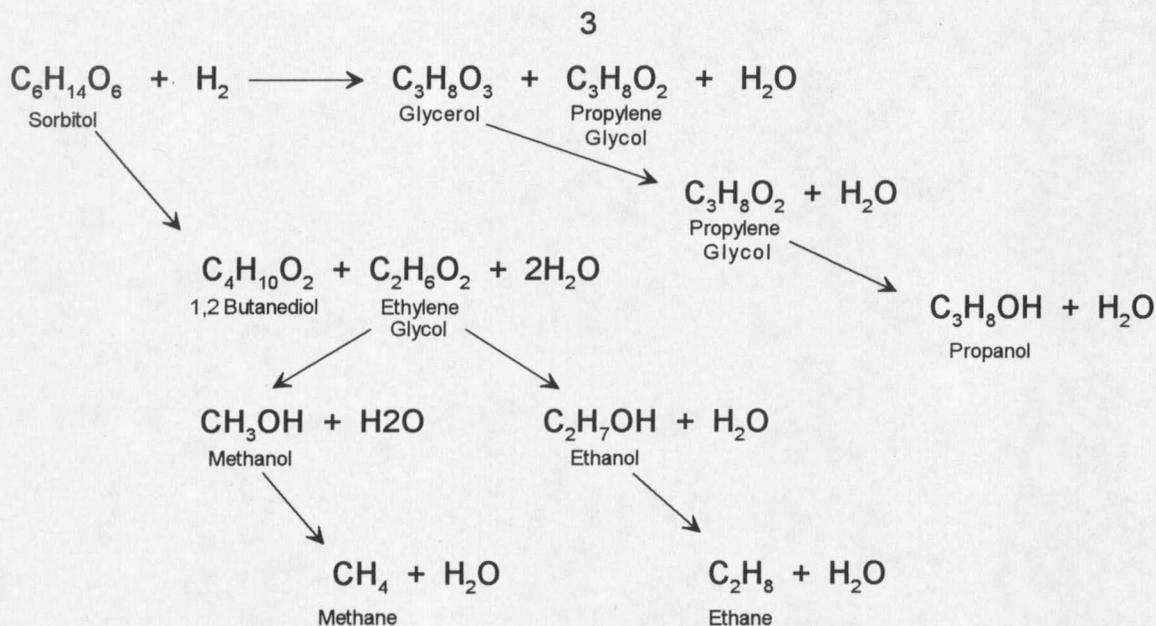


Figure 1 Possible series and parallel reactions.

Research relating to sorbitol hydrogenolysis began in the early 1900s with I. G. Farbenindustrie, A.-G., obtaining the first patent for the hydrogenation of sugar in 1927 [2]. The patent claimed the production of glycerol and propylene glycol from sugars, starches, cellulose, or other materials at temperatures above 150°C and pressure from 70 to 100 atm. In 1932 Lautenschläger et al., obtained a patent on the hydrogenation of polyhydroxy compounds at temperatures from about 200°C to about 300°C [3]. Zartmen and Adkins studied the hydrogenolysis of sugars to find the behavior of carbon-carbon and carbon-oxygen bonds when subjected to the action of hydrogen over a catalyst [4]. Larchar investigated catalytic hydrogenation and dehydration of polyhydroxy alcohols, over a nickel-chromium oxide catalyst, to

form glycols in 1934 [5]. Rothrock obtained a patent in 1935 for producing polyhydric alcohols such as glycerol, ethylene glycol, and propylene glycol by hydrogenation of polyhydric alcohols with more hydroxyl groups [6].

WW II brought a particular need for an alternate source of glycerol for the production of nitroglycerine. The I. G. Farbenindustrie, A.-G., started the first commercial plant in 1938 [2]. The plant was designed to produce 250 tons per month, but production only reached 2000 tons per year due to separation difficulties. The product was called "glycerogen" and was reported as no more than a substitute for glycerine. Lenth and Dupuis carried out a pilot plant study where a glycerol substitute was produced, but an economical source of pure glycerol was not achieved [7]. The process was carried out in a methanol suspension of sucrose or dextrose at a temperature of 240°C and a pressure of 1500 psig. A 60 to 65% yield of distillable polyhydric alcohols was obtained. The product contained 60% propylene glycol and 40% glycerol with other polyhydric alcohols of higher molecular weight.

In the early 1950s the USDA took an interest in the production of polyhydric alcohols from wood molasses [8]. This was due to a 35% decrease in the production of glycerol as a by-product of the soap manufacturing and various fat-splitting industries and a corresponding increase in demand for its use in resins, explosives, and food products. The hydrogenolysis process was conducted with a nickel catalyst impregnated on kieselguhr. Reactions were run at a temperature of 215°C to 220°C and pressures from 1500 psi to 3100 psi.

















































































































