POLYHYDRIC ALCOHOLS FROM WOOD

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POLYHYDRIC ALCOHOLS FROM WOOD

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Wood-sugar solutions produced in the laboratory-scale pilot plant at the U. S. Forest Products Laboratory have been proven to be satisfactory for the production of industrial alcohol, feeding yeast, and wood molasses for stock feed (14, 15, 16, 17). As a continuation of the program of the Laboratory for developing chemical utilization processes for the wood residues resulting from normal logging operations and lumber, veneer, and the other forest products manufacture, investigations are in progress to convert wood sugar into merchantable products.

Because of the versatility and greatly increased demand for polyhydric alcohols, a study of the production of these materials has been chosen. The alkyd resin industry in the United States has increased tenfold in the past few years and no evidence of decline has been noted. Recently sorbitol has been made available commercially by the catalytic hydrogenation of corn sugar (2). The annual capacity now is 75 million pounds. Sorbitol is widely used as a humectant and conditioner in tobacco, cellophane, and other products (3). However, one of its fast growing uses is for alkyd resins, where it may replace up to 50 percent glycerine and 25 percent pentaerythritol. This is fortunate since the production of glycerine in the United States as a byproduct of the soap manufacturing process.


2 The author gratefully acknowledges the assistance of Ira T. Clark, chemist, George J. Hajny, chemist, Elwin E. Harris, chemist specialist, and Edward G. Locke, chief, Division of Derived Products, in the preparation of this report.

3 Maintained at Madison, Wis., in cooperation with the University of Wisconsin.

4 Underlined numbers in parentheses refer to the literature cited at the end of this report.

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and various fat-splitting industries decreased about 35 percent from 1947 to 1951 because of the expanding use of synthetic detergents. Only part of this loss of glycerine production has been absorbed by synthetic glycerol from propylene, while the demands for glycerine for resins, explosives, and food products have increased. For example, the consumption of glycerine in the United States in March 1953 was almost 25 percent above the same month in 1952.

Ethylene glycol likewise has shown a greatly increased demand. From 1950 to 1962, it is estimated that the demand will increase by 50 percent. While a large part of this increase is for automotive antifreeze, the greatest percentage increase will be in synthetic fibers and in miscellaneous uses.

Recently a new synthetic polyester rubber with superior properties was announced. Its basic ingredients are ethylene glycol and propylene glycol, along with adipic acid. All of these materials can be produced from wood. With these growing demands for polyhydric alcohols it is important that unlimited sources of raw material be available for new processes. Wood is a renewable resource that is not dependent upon any one growing season and so fulfills the first requirement.

Two approaches are being taken in current projects at the Forest Products Laboratory. The first is the production of glycerine by the fermentation of wood sugars. The second is the hydrogenation of wood sugars followed by hydrogenolysis of the wood sugar polyhydric alcohols to produce sorbitol, xylitol, glycols, glycerol, and erythritol.

The raw material for both of these investigations is wood sugar produced from Douglas-fir logging and sawmill residues. The equipment for conversion is the laboratory-size pilot plant that has been used in research at the Forest Products Laboratory for the past 10 years. The sugar solution produced by the process described by Harris and Beglinger (15) is primarily a mixture of glucose, mannose, and xylose with small quantities of galactose and arabinose. A change in species would change the proportion of these sugars. The sugar solution also contains decomposition products of the sugars and fragments of lignin that tend to inhibit fermentation and inactivate the catalyst used in hydrogenation. A pretreatment of a 25 percent wood sugar solution by anion exchange resins or activated carbon has been used to remove these inhibiting substances.
Fermentation

Only a few polyhydric alcohols can be produced by fermentation. Among these are propylene glycol, mannitol, 2, 3-butylene glycol, and glycerine. As far as is known, only two of these have been prepared by the fermentation of wood-sugar solutions. They are 2, 3-butylene glycol and glycerine.

Propylene glycol cannot be produced by wood-sugar fermentation, since the organism used, \textit{Bacterium rhamnosifermentans}, works best on the sugar rhamnose (19).

Mannitol is produced both by bacteria and molds. However, the bacteria produce mannitol only from fructose, so wood sugar could not be used.

Some of the molds known to produce mannitol from glucose are \textit{Aspergillus elegans}, \textit{A. nidulans}, \textit{A. fischeri}, \textit{A. oryzae}, and \textit{Penicillium chrysogenum}. Yields of mannitol of 35 percent based on the sugar utilized have been obtained on media consisting of glucose, mannnose, or galactose and nutrient salts (1, 6). Careful control of aeration was found to be necessary for high yields. Yields from xylose and arabinose were less. No mannitol was produced from fructose.

Although no work has been done on the production of mannitol from wood sugars, the process appears feasible, especially since pentoses can be converted to mannitol.

2, 3-Butylene glycol is known to be produced by a number of bacteria, including \textit{Aerobacter aerogenes}, \textit{Bacillus polymyxa}, \textit{Aeromonas hydrophilia}, \textit{Bacillus subtilis}, and \textit{Serratia marcescens}. Much work has been done on this fermentation during the last decade, especially by Canadian workers of the National Research Council and the Canadian Department of Agriculture. The work was stimulated by the fact that 2, 3-butylene glycol can be converted to 1, 3 butadiene, one of the raw materials used in the production of synthetic rubber of the Buna type.

Most of the work done on the 2, 3-butylene glycol fermentation was on pure sugars, saccharified starch, or ground whole grains, such as wheat or corn. However, Perlman (29) at the University of Wisconsin worked with the acid hydrolyzates of both hardwoods and softwoods.
The culture used by Perlman was *Aerobacter aerogenes* NRRL #199. Because this organism will ferment both hexoses and pentoses, it is especially suitable for wood hydrolyzates. The fermentation products include 2, 3-butylene glycol, acetoin, ethyl alcohol, lactic acid, and succinic acid. The acetoin was determined with the 2, 3-butylene glycol, but never amounted to more than 2 percent of the sugar fermented.

The fermentation medium consisted of about 5 percent wood sugars, 0.2 percent urea, 0.1 percent monobasic potassium phosphate, and 0.3 percent calcium carbonate. Inoculum size varied between 3 and 5 percent of the fermentation volume. The fermentations were run at 30° C. at pH 6 with aeration. At higher sugar concentrations the fermentations were erratic, and it was necessary to add yeast extract or malt sprout extract for successful fermentations. However, by treating the wood-sugar solution with a lime slurry until a pH of 10 or 11 was reached, filtering the solution, adjusting the pH to 6 with sulfuric acid, and filtering again, it was fermented successfully without additional additives at a reducing sugar concentration of 17.8 percent.

If cultures acclimated to wood-sugar hydrolyzates were used, alkaline pretreatment and the use of auxiliary substances were unnecessary for the fermentation of concentrated wood-sugar solutions.

Yields of 2, 3-butylene glycol were about 35 percent, referred to the original sugar, and about 90 percent of the reducing substances from both hardwoods and softwoods were used.

The fact that glycerine is produced by yeast during alcoholic fermentation had been shown by Pasteur, who found that glycerine was produced to the extent of 2.5 to 3 percent of the sugar fermented.

Neuberg and coworkers (27) early in this century studied the mechanism of the alcoholic fermentation. In attempting to fix the intermediate product, acetaldehyde, with sodium sulfite, they obtained a large increase in the glycerine yield. Neuberg suggested the following reaction:

\[
C_6H_{12}O_6 + Na_2SO_3 + H_2O \rightarrow NaHCO_3 + CH_3CHO\cdot NaHSO_3 + C_3H_8O_3
\]

In this equation the ratio of acetaldehyde to glycerine is 1 to 2.09. Determinations of acetaldehyde and glycerine in fermentations of this type agree with this theoretical value.

The following is an outline of the mechanism of alcoholic fermentation. Glycerine fermentation is believed to go through the same intermediates, but is directed toward glycerine production by reagents that affect the acetaldehyde.

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The first step in the series of reactions for the production of alcohol is the phosphorylation of glucose by the coenzyme adenosine triphosphate. Adenosine triphosphate donates phosphate to glucose in two steps. First glucose 6-monophosphate appears and then fructose 1,6-diphosphate. With the loss of two phosphate groups, the adenosine triphosphate is converted to adenylic acid. Later in the reaction, phosphate is given up to adenylic acid, which then is converted back to adenosine triphosphate. Thus phosphate is not used up in the reaction but goes through a cyclic process.

Fructose 1,6-diphosphate is the compound found whether glucose, mannose, or fructose is the starting sugar. Fructose 1,6-diphosphate then is split into two triose units -- dihydroxyacetone phosphate and 3-glyceraldehyde phosphate.
The two triose units are in equilibrium with each other with a preponderance of dihydroxyacetone (25). In the presence of cozymase and water, glyceraldehyde is oxidized and the dihydroxyacetone is reduced.

\[
\text{Dihydroxyacetone} \quad \text{d-glyceraldehyde} \quad \text{a-glycerophosphate} \quad \text{3-phosphoglyceric acid}
\]

This reaction has been called the introductory phase of the fermentation. It accounts for the fact that a small amount of glycerine is found in a normal alcoholic fermentation. Thus

The 3-phosphoglyceric acid goes through a series of enzyme-catalyzed reactions to phosphopyruvic acid.

\[
\text{3-phosphoglyceric acid} \quad \text{2-phosphoglyceric acid} \quad \text{phosphopyruvic acid (enol form)}
\]

The enzyme enolase catalyzes these reversible reactions. The phosphopyruvic acid is dephosphorylated.
The enolic form of pyruvic acid is of course in equilibrium with the keto form. The enzyme carboxylase breaks down pyruvic acid to acetaldehyde and carbon dioxide.

\[
\text{Pyruvic acid} \quad \xrightarrow{\text{carboxylase}} \quad \text{Acetaldehyde}
\]

The acetaldehyde is reduced by the enzyme cozymase (coenzyme I) to ethyl alcohol. The cozymase is oxidized and then reacts with the 3-glyceraldehyde phosphate, oxidizing it to 3-phosphoglyceric acid. This product goes through the series of reactions outlined above to form more ethyl alcohol. Since this reaction bypasses what was called the introductory phase of the fermentation, only a small amount of glycerine is formed in a normal alcoholic fermentation.

To produce glycerine by fermentation, conditions must be changed to interfere with the enzyme-catalyzed series of reactions outlined above. When a bisulfite is added to the medium, for example, the acetaldehyde and the bisulfite form a complex that cannot be reduced by the cozymase. The cozymase then acts to reduce the dihydroxyacetone and to oxidize the glyceraldehyde. Thus the introductory phase of the fermentation becomes the main reaction and more glycerine is produced. Theoretical yields of glycerine have never been realized, since some of the acetaldehyde is reduced to ethyl alcohol.

If the medium is made alkaline, the following reaction takes place:

\[
\begin{align*}
\text{CHO} & + \text{CHO} \xrightarrow{H_2O} \text{HC-OH} & + & \text{COOH} \\
\text{CH}_3 & & \text{CH}_3 & \text{CH}_3 & \text{CH}_3
\end{align*}
\]

This likewise results in an increase of the glycerine yield.
The theoretical yield of glycerine, using either the sulfite or alkaline method of fermentation, is 51 percent based on the glucose. Yeast mutants appear to offer a fruitful line of inquiry for increasing yields of glycerine beyond this value. If a yeast mutant could be produced in which the alcohol dehydrogenase had been destroyed and the enzymes producing acetic acid and glycerine were intact, increased yields of glycerine would result. When ethyl alcohol is produced, hydrogen is not available for reduction of dihydroxyacetone to glycerine. If acetic acid production could be increased, additional hydrogen would be available for glycerine formation. If ethyl alcohol formation could be eliminated in favor of acetic acid, the following equation shows that the theoretical yield of glycerine from glucose would be 68 percent.

$$3 \text{C}_6\text{H}_12\text{O}_6 + 2 \text{H}_2\text{O} \rightarrow 4 \text{C}_3\text{H}_8\text{O}_3 + 2 \text{CH}_3\text{COOH} + 2 \text{CO}_2$$

Another advantage of a yeast mutant fermentation would be the elimination of the large quantities of steering chemicals that now must be added to the medium. These chemicals are an added cost, are costly to remove, and they cause difficulty in the recovery of glycerine, as will be described later.

Connstein and Lüdecke (5) developed a sulfite fermentation process that was used on a large scale in Germany during World War I. They found that many salts when added to the medium in large quantities (15 to 100 percent of the weight of the sugar) would cause increased yields of glycerine. Neutral salts, such as CaCl$_2$, NH$_4$Cl, NaCl, Na$_2$SO$_4$, and NaNO$_3$, caused yields of glycerine of from 6 to 16 percent. Alkaline salts, such as Na$_2$HPO$_4$, (NH$_4$)$_2$CO$_3$, NaOAc, and NaHCO$_3$, produced yields of glycerine of 10 to 15 percent. Caustic alkalis were found to injure the yeast cells. When sulfites, such as Na$_2$SO$_3$, were used, yields were increased to 36 percent of the sugar. Connstein and Lüdecke concluded that two factors played a role in the fermentation: one was a general salt effect leading to an increase in glycerine and the second was the specific action of the sulfite which, by forming a complex with the acetaldehyde, caused increased glycerine yields beyond that of the general salt effect.

The sulfite method of Connstein and Lüdecke was used to produce glycerine from beet sugar on an industrial scale in Germany during World War I (24). Production reached 1000 tons a month. The kind of sugar or variety of yeast apparently had very little influence on the fermentation.

Glycerine was obtained from the fermentation liquor after distilling off the alcohol and acetaldehyde (21). The sulfite was precipitated from the hot
liquor by means of lime and calcium chloride. Calcium and iron were removed by means of sodium carbonate. The solution was neutralized and concentrated in vacuum evaporators. This raw liquor then was distilled under vacuum. Schoenemann and Rinn (31) state that the total glycerine loss up to dynamite grade was about 40 percent of that contained in the fermentation liquor.

Cocking and Lilly (4) modified the sulfite method by using a mixture of sulfites and bisulfites and adding these in successive small quantities throughout the fermentation. The bisulfite is the reagent that combines with the acetaldehyde. In the sulfite process, the CO₂ formed by fermentations reacts with the sulfite to form bisulfite. Thus

\[ \text{Na}_2\text{SO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{NaHSO}_3 + \text{NaHCO}_3 \]

Cocking and Lilly claim increased yields of glycerine were due to the fact that acetaldehyde is fixed at an earlier stage in the fermentation, since the bisulfite is present at the start of the fermentation. Since bisulfites are antiseptic, no difficulty occurs through contamination, but high concentrations of free bisulfite must be avoided.

Eoff (8,9) developed an alkaline process for producing glycerine. Nutrient salts were added to the sugar solution, blackstrap molasses and corn sugar were used, a "trained" yeast was added, and the temperature was maintained at 30° to 32° C. Alkaline salts, usually sodium carbonate, were added according to a definite schedule until approximately 5 percent, referred to the solution, had been added. The yeasts had to be acclimated to the alkaline medium, and Eoff found that \textit{Saccharomyces ellipsoideus} (var. Steinberg) gave the best yields -- 20 to 25 percent of the sugar. Ethyl alcohol and acetic acid were also produced.

Fermented liquors often contain twice as much soluble salts as glycerine. These salts, as well as the residual unfermented sugars, lead to large losses in recovery of the glycerine. Fulmer, Underkofler, and Hickey (10, 11, 12) attempted to reduce the soluble salts in two ways. In one method, ammonium sulfite or bisulfite was used as the aldehyde fixing agent. The theory here was that after fermentation, lime could be added, the volatile ammonia driven off, and calcium sulfite precipitated, thus leaving a relatively salt-free liquor for glycerine recovery. This method was found to be impractical, since ammonium hydroxide is toxic to yeast at an alkaline pH, and at neutral or slightly acid pH the bisulfite ion is toxic to the yeast. Their second method consisted of using sulfite salts that are only slightly soluble, such as magnesium or calcium sulfite. These fermentations were successful when the pH was maintained at 6.5. Yields of glycerine of about 25 percent were obtained.
Work is now being carried on at the U. S. Forest Products Laboratory on the production of glycerine from wood sugars. Since pentoses are not used in the fermentation, all the work has been confined to softwood hydrolyzates, which contain less pentose than hardwood hydrolyzates. Softwood hydrolyzates are only about 80 percent fermentable, so yields of glycerine would be some 20 percent lower than from glucose.

The results both with the sulfite-bisulfite fermentation and the alkaline fermentation tend to confirm the results of other workers on this fermentation. Yields of glycerine on fermentable wood sugars are in the range of 30 to 35 percent.

At low sugar concentrations, that is, below 10 percent, the use of wood-sugar hydrolyzates offers no particular problem in the fermentations. At higher sugar concentrations, however, the fermentation becomes increasingly difficult on untreated wood sugars. Wood-sugar solutions treated with activated charcoal or ion-exchange resins can be fermented at 20 percent concentration. Sugar concentrations of 15 to 20 percent result in glycerine concentrations of 5 to 6 percent. Since it is difficult to recover glycerine from fermentation liquor, it is desirable to have the glycerine concentration as high as possible.

The stumbling block that has prohibited the use of fermentation to produce glycerine is not the fermentation itself, but the recovery of glycerine from the fermentation liquors. The chief reason for the difficulty of recovery is the large amount of soluble solids in the fermented liquor, consisting chiefly of salts and residual unfermented sugars. When the liquor is concentrated, these materials cause it to become very viscous. Sticky precipitates are formed that cause fouling of the heating surfaces and poor heat transfer. As yet no efficient means of recovering glycerine from fermentation liquors has been found.

**Hydrogenation and Hydrogenolysis**

The production of hexahydric alcohols from 6-carbon sugars began in early days of chemistry when sugar solutions were reduced with metallic sodium. This procedure was slow, dangerous, and expensive and was replaced by one involving reduction by electrolysis of an alkaline solution of the sugar. Commercial plants were built using this method, but interconversion of some of the sugar occurred in the alkaline solution giving impure products. During the past 40 years, the electrolysis process has been replaced by one using catalytic high-pressure hydrogenation.

Recently it was found that by increasing the temperature of the catalytic hydrogenation, sorbitol could be cleaved to a number of products of lower molecular weight, including glycols and glycerol. Sugars are converted by hydrogenation to sugar alcohols at relatively low temperatures. Sugar alcohols in the presence of hydrogen and a catalyst of the iron or platinum group at temperatures of 190° to 300° C. are converted to glycerol, propylene glycol, and other products (34).

Zartman and Adkins (37) hydrogenated glucose, sorbitol, mannitol, sucrose, and other sugar compounds under 300 atmospheres of hydrogen at 250° C.
in the presence of a copper-chromium oxide catalyst in ethyl alcohol solution. All sugar compounds underwent rapid cleavage and hydrogenation to a mixture of compounds of lower molecular weight. Propylene glycol was the principal product from all sugars and sugar derivatives. Sorbitol yielded 93 percent propylene glycol. Small amounts of products retaining the 6 carbons of the original sugar, but containing fewer hydroxyl groups, were obtained. Some of these boiled in the same range as glycerol. Otto Schmidt (32) had previously found that glycerol was converted to propylene glycol by catalytic hydrogenation at elevated temperatures. Glycerol therefore may have been an intermediate product that was converted to propylene glycol by further hydrogenation in the work of Zartman and Adkins.

Larchar (20) showed that sorbitol and dextrose in the presence of hydrogen at 2,000 pounds per square inch and at 200° C. over nickel-chromium catalyst gave propylene glycol and glycerol. Yoshikawa (36) found that a nickel-iron catalyst was better than nickel-chromium for the conversion of glucose to glycerol and propylene glycol. In the presence of nickel catalysts, calcium carbonate acted as a promoter for the cleavage of sorbitol to glycerol (30). When sucrose was used as a starting material (35) in the presence of hydrogen at 100 atmospheres with temperatures of 165° to 225° C. over nickel catalysts, d-mannitol, d-sorbitol, and propylene glycol were products.

Glycerol produced by the hydrogenolysis of sugars on an experimental scale by Commercial Solvents (33) was used to study methods of purification by Hass and Patterson (18).

A mechanism for the hydrogenation of sugars over nickel catalyst was proposed by Yoshikawa and Hanai as first producing hexitols that break down to give an intermediate glyceryl aldehyde, which is hydrogenated to glycerol and propylene glycol or cleaved to products that yield methanol and ethylene glycol. Such a proposal does not account for the formation of erythritol and 5-carbon polyhydric alcohols obtained in research reported in this paper.

DuPuis (7) studied a process to hydrogenate hydrol "80" or cane molasses after suitable purification to glycerol. Methanol was used as a solvent and copper-aluminum or copper barium-chromite as catalyst. Using similar conditions, Lenth and DuPuis (22) hydrogenated sucrose at 235° to 240° C. to obtain 39.5 percent propylene glycol and 25 percent of a fraction boiling in the range of glycerol. Glucose at 245° C. gave 36.8 percent propylene glycol and 25.4 percent glycerol fraction. Hydrogen absorption was 5.7 moles of hydrogen for a mole of sucrose and 2.72 for a mole of glucose.
Parodi-Delfino (28) and Lorand (23), believing that glycerol was lost by continuing the hydrogenation too long, proposed hydrogenation of sugars so that no more than half of the starting material had reacted in order to obtain a higher proportionate yield of glycerol. Low molecular weight products were removed and the residue recycled.

Natta, Rigamonti, and Beati (26) published the results of a study of the production of glycerol by catalytic hydrogenation of sugars. They found the first stage of the hydrogenation — conversion of the sugars to hexitols — to be quantitative, and therefore their study was concerned with the second stage, the conversion of hexitols to glycerol and glycols. Nickel catalysts were most suitable for water solutions and copper catalysts for alcohol solutions. Better yields of glycerol were obtained in water than in alcohol. At temperatures above 250° C. considerable glycerol was converted to low-boiling products. For best yields of glycerol, the temperature must be kept below 220° C. Some experiments gave 20 to 30 percent glycerol and 30 to 40 percent propylene glycol from glucose. Commercial corn sirup gave low yields and almost no glycerol. High temperatures gave polymerization or humic products that poisoned the catalyst. Some experiments indicated production of products in the ratio two moles of glycerol, one mole of ethylene glycol, and one of methyl glycerol. Low-boiling alcohols were produced in quantities representing about 1 percent of the sugars. Methanol, ethanol, and isopropanol were the principal alcohols present.

A plant was constructed and operated at Hoechst, Germany, during the period 1934 to 1944 by I. G. Farbinindustrie A. G. (13) to produce a product to be used without refining as a substitute for glycerol in tobacco, cellophane, cosmetics, commercial explosives, and other uses where a purified glycerol is not required. The product was called "glycerogen" and contained a mixture of about 35 percent glycerol, 35 percent glycols, and 25 to 28 percent higher boiling polyhydric alcohols. The monthly capacity of the plant was reported to be 250 tons. Sucrose, the starting material, was first hydrolyzed to simple sugars and then hydrogenated to hexitols and a mixture of glycerol and glycols in a series of 15 reactors operated at different temperatures ranging from 100° C. at the beginning and up to 230° for the final step of the reaction. Calcium carbonate was used as a promoter and to neutralize acids produced in the process. The catalyst was reduced nickel on pumice.

**Experimental Work**

Since wood sugar is a mixture of glucose, mannose, xylose, galactose, and arabinose, and all sugars may not react the same, the first hydrogenation tests were carried out on purified isolated sugars. Solutions of
commercial glucose and of crystalline xylose were used to establish conditions and to select the most suitable catalyst. All experiments were done in a rocking-type batch autoclave.

**Hydrogenation of Glucose and Xylose to Sugar Alcohols**

Solutions of commercial glucose in water solution were readily hydrogenated in the presence of several different supported nickel catalysts in 1 to 2 hours at 90° to 95° C. to yield a solution having less than 0.03 percent reducing sugar. Pure crystalline sorbitol was isolated from one batch in high yield. Hydrogen absorption was one mole of hydrogen for one mole of glucose. Higher temperatures at this stage produced discolored solutions and hydrogenation did not proceed to completion. Sorbitol was not isolated from the solutions that were to be used for hydrogenolysis to glycerol and glycols.

Water solutions of xylose were reduced to xylitol under conditions similar to those used with glucose. Hydrogen absorption averaged 0.94 moles per mole of sugar. Residual reducing material calculated as sugar was less than 0.1 percent. Xylitol was not isolated when it was used for study of the production of glycerol and glycols.

**Hydrogenolysis of Sugar Alcohols**

Solutions of sorbitol and xylitol were treated at higher temperatures and various conditions to determine the yield of glycerol and glycols that may be obtained. The reactions involve cleavage as well as hydrogenation of the various products to give compounds with fewer carbon atoms.

According to the products formed when compounds similar to sorbitol and xylitol are cleaved in the presence of hydrogen and active hydrogenation catalysts, the entire molecules may be reactive. However, some of the bonds are weaker than others and, by selecting conditions, the reactivity of some groups can be varied to obtain larger amounts of some primary cleavage products.

The probable weak bonds in sorbitol and xylitol are indicated by dots in the formulas shown in figure 1. Products representing many of the possibilities have been isolated and identified in the work of Zartman and Adkins (37) and Lenth and DuPuis (22). Glycerol and glycols are major products from both sorbitol and xylitol, indicating that the linkage between carbons 3 and 4 in the sorbitol molecule and between carbons 2 and 3 in the xylitol molecule are weaker than some of the other weak linkages.
Hydrogenolysis of Sorbitol

A study was made of the hydrogenolysis of sorbitol using an available commercial catalyst under a number of conditions to determine the effect of these variables on the yield of glycerol. No satisfactory method for the determination of glycerol in such hydrogenation mixtures was available, so initially the yields were reported as the products that distilled in the glycol and glycerol range. The fraction distilling in the glycerol range has been shown by recent tests to be 85 to 87 percent glycerol. As a result, it has been necessary to develop entirely new methods of analysis.

The principal primary products occurring when sorbitol is treated with hydrogen in the presence of an active catalyst are glycerol and propylene glycol, as shown in figure 2. Hydrogen absorption in all cases was about 2 moles of hydrogen for each mole of sorbitol reacted.

The Effect of Promoters on the Hydrogenolysis of Sorbitol

A few preliminary hydrogenation tests indicated that the addition of calcium hydroxide or calcium carbonate improved the rate of hydrogenation and the yield of products. If the promoter was not present, the solution became acidic. This led to the conclusion that the pH of the solution may alter the progress of the hydrogenolysis of sorbitol. Calcium, barium, and sodium hydroxides, calcium carbonate, and calcium sulfate, were tested for their ability to promote the hydrogenolysis. Calcium and barium hydroxide were about equally effective. The yield of glycerol was highest with calcium hydroxide. Excessive amounts of calcium hydroxide caused more of the sorbitol to react, but also caused glycerol to be converted to propylene glycol. The ratio of glycerol to glycols in the distillable products was higher when calcium carbonate was used as a promoter than when calcium hydroxide was used. Sodium hydroxide promoted hydrogenation of glycerol to propylene glycol. Calcium sulfate had no effect on the hydrogenation.

Effect of Temperature, Hydrogen Pressure, and Catalyst on the Hydrogenolysis of Sorbitol

The optimum temperature appeared to be from 215° to 220° C. Higher temperatures produced higher yields of glycol at the expense of glycerol yields.
The initial cold pressure of hydrogen was varied from 1,500 pounds per square inch to 3,100 at 220° C. The former amount of hydrogen provided only a slight excess, while the latter provided about twice the hydrogen absorbed in the reaction. The results showed that a slight excess of hydrogen is required for best results. A large excess increased the yield of glycols at the expense of the glycerol without much change in the amount of sorbitol reacting.

In addition to the effect of the promoter on the hydrogenolysis of sorbitol to glycols and glycerol, the activity of the catalyst is important. This activity depends on the amount of catalytic agent and, more important, the surface area of the agent.

Four commercially prepared catalysts containing 40 to 65 percent nickel were used in preliminary work. Studies on the amount of each required to convert sorbitol to glycols and glycerol in high yields indicated that 1 part of catalyst to about 7 parts of sorbitol was required. This high catalyst-to-reactant ratio would make it necessary to recover and reactivate the catalyst.

Search has been made for a catalyst that would contain more active surface and therefore require less nickel. Also, a catalyst was desired that would convert sorbitol to glycerol without converting glycerol to propylene glycol. After several trials, it was found that nickel-impregnated Kieselguhr produced a very active catalyst when activated by reduction with hydrogen. Yields of glycerol after 3 hours were about the same as those previously obtained in 5.5 hours, but the yield of glycols was less, indicating that this catalyst also favored higher glycerol production.

**Hydrogenolysis of Xylitol**

The hydrogenolysis of xylitol to glycerol was subjected to the same variables as the hydrogenolysis of sorbitol to glycerol, namely, the effect of promoters, time or reaction at temperature, and hydrogen pressure. Use of calcium hydroxide caused an increase in hydrogen absorption, the amount of xylitol reacted, and glycerol and glycols produced. An excess of calcium hydroxide as a promoter increased the amount of xylitol reacted and the amount of glycols produced with little change in the glycerol yield.

Increasing the temperature from 200° C. to 220° C. resulted in higher absorption of hydrogen and an increased amount of the xylitol reacted. The maximum yield of glycerol fraction was at 205° C. Higher temperature increased the amount of glycols.
Increasing the cold pressure of hydrogen from 1500 pounds per square inch to 3000 pounds per square inch resulted in greater absorption of hydrogen and increased amounts of xylitol reacted. The highest yield of glycerol resulted when the starting pressure of hydrogen was 3000 pounds per square inch.

These results indicated that the reaction of hydrogen with xylitol is a different type of reaction from that occurring when hydrogen reacts with sorbitol. The rate and amount of hydrogen absorption was lower for the sugar alcohol reacted. Increasing the pressure of hydrogen on the xylitol causes an increase in the yield of glycerol, while an increase of hydrogen pressure on sorbitol caused a decrease in the yield of glycerol.

**Hydrogenation of Wood Sugars and Hydrogenolysis of the Sugar Alcohols Produced**

Untreated crude wood-sugar solutions with the same amount and type of catalyst used for commercial glucose reacted slowly and incompletely with hydrogen, indicating the presence of inhibiting substances. When the catalyst was removed from the partially hydrogenated material and the material was rehydrogenated with fresh catalyst, the reaction was complete. Therefore wood-sugar solutions were treated by either anion exchange resins or activated carbon to remove these substances. The optimum conditions for commercial glucose gave comparable rates and yields of sugar alcohols with the treated wood-sugar solutions.

Samples of sugar alcohols obtained by the catalytic hydrogenation of wood sugars from the hydrolysis of Douglas-fir were subjected to the action of hydrogen under conditions that were found to give the maximum yield of glycerol by hydrogenolysis of sorbitol and xylitol. The rate of reaction using different quantities of two catalysts was as rapid and the yield of products as great as for sorbitol, showing that wood sugar is suitable for the production of glycols and glycerol by hydrogenation and hydrogenolysis.

**Recovery of Products**

Products from the hydrogenolysis of sorbitol, xylitol, and wood-sugar alcohols prepared from wood-sugar sirups purified by activated charcoal or ion-exchange resin treatment, have been recovered by the procedure used for refining glycerol obtained as a byproduct in soap production.

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Water and other low-boiling products were removed under conditions to avoid loss of glycols, which are easily steam distilled. Then glycols and glycerol were removed by distillation at low vacuum or by steam distillation under conditions to avoid decomposition of the glycerol and higher boiling products.

Conclusions

In general, wood sugars are suitable for any fermentation that requires glucose as a substrate. In some cases, however, wood-sugar solutions may require preliminary purifying treatments. Ion-exchange resins or activated charcoal gave readily fermentable solutions. Both 2,3-butylene glycol and glycerine can be produced from wood sugars, but satisfactory recovery methods remain to be developed.

The sugars resulting from the acid hydrolysis of wood have been given purifying treatments, then hydrogenated to their corresponding alcohols in high yields. The hydrogenolysis of these sugar alcohols produces glycols and glycerol in yields comparable to those obtained for glucose and xylose. Again, a satisfactory method of recovery from the hydrogenolysis step has not been developed.

The results reported here were determined in batch reactions at fixed reaction time. More recent work, not yet complete, has indicated that temperature, pressure, promoter, and reaction time are interdependent and selection of a suitable combination of conditions can result in improved glycerol yields.


26. Natta, G., Rigamonti, R., and Beati, E. Chemica e industria (Italy) 24: 419 (1942); Ber. 76B641 (1943).
Figure 1. -- Formulas of sorbitol and xylitol showing the probable weak bonds.

\[
\begin{align*}
\text{Sorbitol} & : & H (1) & \quad H (1) \\
 & & HC \ldots OH & \quad HC (1) \ldots OH \\
 & & HC (2) . OH & \quad HC (2) . OH \\
 & & HO \ldots C (3) - H & \quad HC (3) . OH \\
 & & HC (4) . OH & \quad HC (4) - OH \\
 & & HC (5) OH & \quad HC (5) - OH \\
 & & HC (6) - OH & \\
 & & H & \\
\text{Xylitol} & : & H & \quad H \\
 & & HC (1) \ldots OH & \quad HC (1) \ldots OH \\
 & & HC (2) . OH & \quad HC (2) . OH \\
 & & HO \ldots C (3) - H & \quad HC (3) . OH \\
 & & HC (4) . OH & \quad HC (4) - OH \\
 & & HC (5) OH & \quad HC (5) - OH \\
 & & HC (6) - OH & \\
 & & H & \\
\end{align*}
\]
Figure 2. -- Hydrogenolysis of sorbitol.

\[
\begin{align*}
\text{Sorbitol} & \quad \xrightarrow{4\text{H}} \quad \text{Glycerol} \\
\text{H} & \quad \text{HCOH} \\
\text{HCOH} & \quad \text{HC-OH} \\
\text{HOCH} & \quad \text{HC-OH} \\
\text{HCOH} & \quad \text{HC-OH} \\
\text{HCOH} & \quad \text{HC-OH} \\
\text{HC-OH} & \quad \text{HC-OH} \\
\text{H} & \quad \text{H}
\end{align*}
\]

\[
\begin{align*}
\text{Propylene glycol} & \quad + \text{H}_2\text{O} \\
\text{H} & \quad \text{HC-OH} \\
\text{HC-OH} & \quad \text{C}_2\text{H}_5 \\
\text{HC-OH} & \quad \text{ HC-OH} \\
\text{HC-OH} & \quad \text{HC-OH} \\
\text{H} & \quad \text{H}
\end{align*}
\]